Direct, Transfer-Free Growth of Large-Area Hexagonal Boron Nitride Films by Plasma-Enhanced Chemical Film Conversion (PECFC) of Printable, Solution-Processed Ammonia Borane

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Supporting Information

ABSTRACT: Synthesis of large-area hexagonal boron nitride (h-BN) films for two-dimensional (2D) electronic applications typically requires high temperatures (~1000 °C) and catalytic metal substrates which necessitate transfer. Here, analogous to plasma-enhanced chemical vapor deposition, a nonthermal plasma is employed to create energetic and chemically reactive states such as atomic hydrogen and convert a molecular precursor film to h-BN at temperatures as low as 500 °C directly on metal-free substrates—a process we term plasma-enhanced chemical film conversion (PECFC). Films containing ammonia borane as a precursor are prepared by a variety of solution processing methods including spray deposition, spin coating, and inkjet printing and reacted in a cold-wall reactor with a planar dielectric barrier discharge operated at atmospheric pressure in a background of argon or a mixture of argon and hydrogen. Systematic characterization of the converted h-BN films by micro-Raman spectroscopy shows that the minimum temperature for nucleation on silicon-based substrates can be decreased from 800 to 500 °C by the addition of a plasma. Furthermore, the crystalline domain size, as reflected by the full width at half-maximum, increased by more than 3 times. To demonstrate the potential of the h-BN films as a gate dielectric in 2D electronic devices, molybdenum disulfide field effect transistors were fabricated, and the field effect mobility was found to be improved by up to 4 times over silicon dioxide. Overall, PECFC allows h-BN films to be grown at lower temperatures and with improved crystallinity than CVD, directly on substrates suitable for electronic device fabrication.

KEYWORDS: boron nitride (BN), two-dimensional (2D) material, plasma, chemical vapor deposition (CVD)

INTRODUCTION

Hexagonal boron nitride (h-BN) is an insulating material with excellent chemical, mechanical, and thermal properties. Combined with its layered structure and potential to be produced as an atomically flat and thin film, h-BN is ideal for integration with two-dimensional metallic and semiconducting materials in electronic devices.1 Encapsulation by h-BN allows devices to be isolated from the environment, and has been shown to provide excellent protection to thermal and photodegradation.3 In addition, because of its close lattice match (sometimes termed “white graphene”), h-BN has been employed as a substrate to epitaxially grow high-quality graphene.4,5

Thin films of h-BN have been typically produced by two approaches: exfoliation from a bulk crystal via mechanical cleavage6 or sonication in liquid7,8 and chemical vapor deposition (CVD).5,10 Exfoliation is capable of producing high quality single crystals of layered materials, but the size of material produced is relatively small (<10 mm), the yield is poor, and the process is not controllable with respect to the thickness or number of layers. While methods such as pulsed laser deposition,11 reactive magnetron sputtering,12 and ion beam sputtering have been reported for large-area and thickness-controlled growth,13 CVD remains the most desirable scalable synthesis technique.14 Initial reports of CVD of h-BN employed metals as a catalytic substrate including nickel (Ni),1 copper (Cu),10,15 platinum (Pt),16 and iron (Fe).17 For electronic applications, this necessitates transfer to a suitable substrate that introduces mechanical deformation18 and chemical impurities19 on the h-BN surface.
A smaller number of studies have demonstrated metal-free growth of h-BN films directly on Si-based substrates. However, adsorption of the vapor precursor, nucleation, and growth rate are sensitive to the substrate, leading to poor crystallinity. Here, we report the metal-free growth of large-area, continuous, highly crystalline h-BN films by a plasma-assisted, precursor-film conversion process which we term plasma-enhanced chemical film conversion (PECFC). In contrast to CVD, a molecular precursor for h-BN, ammonia borane, is initially deposited on a substrate from solution and then converted which circumvents barriers associated with adsorption and nucleation. A similar strategy was reported by Park et al. using borazine oligomer as a precursor film and thermally converting at 1026 °C but required a metal (Ni) substrate. Our approach is highly versatile, and we show that films can be prepared by a range of solution processing methods including spray deposition, spin coating, and inkjet printing to control the film thickness and geometry. Following deposition, the films are converted by plasma-assisted heating in a home-built, cold-wall reactor equipped with a planar, atmospheric-pressure dielectric barrier discharge (DBD). Analogous to plasma-enhanced CVD, plasma-enhanced atomic layer deposition, and plasma-enhanced molecular beam epitaxy, the nonthermal plasma excites and dissociates the gas to create energetic and reactive species that interact with the film and lower the growth temperature. Systematic comparison of films synthesized by PECFC and by thermal conversion alone using Raman spectroscopy show that the minimum temperature for h-BN nucleation is decreased from 800 to 650 °C in a background of argon (Ar) and to 500 °C in a mixture of Ar and hydrogen (H₂). Moreover, the plasma increases the crystallinity of the synthesized h-BN, as assessed by the full width at half-maximum (FWHM) of the E₂g Raman scattering peak which decreases from >40 cm⁻¹ to as low as 13 cm⁻¹ and atomic resolution scanning transmission electron microscopy (STEM). We suggest that a key role of the plasma is the generation of atomic hydrogen (H), confirmed by optical emission spectroscopy, which through surface reactions such as hydrogen abstraction and strain relief enables nucleation at lower temperatures and growth of high crystalline quality h-BN. The average dielectric constant of the h-BN films was measured using metal–insulator–metal devices to be 3.8, comparable to bulk values. Molybdenum disulfide (MoS₂) field effect transistors (FET) fabricated with PECFC h-BN films exhibited carrier mobilities 4 times higher than silicon dioxide as the gate dielectric. These properties are comparable to h-BN grown on metal substrates and the best reported to date for metal-free substrates.

EXPERIMENTAL SECTION

Deposition of Ammonia Borane Precursor Film. Three approaches to preparing ammonia borane films from solution were utilized: spray coating, spin coating, and inkjet printing. In all cases, ammonia borane, which is a molecular precursor and a solid powder at room temperature, was completely dissolved in polar solvents at concentrations well below its solubility limit of >5 M. For spray coating, ammonia borane (Sigma-Aldrich, 97% purity) was dissolved in ethanol (Fisher Scientific, 200 proof) at 0.1 M. The spray coating setup consisted of a simple commercial airbrush (Master Model G233) powered by compressed Ar gas at 12 psi and a substrate placed on a hot plate heated to 60 °C, separated by a distance of 15 cm. For spin coating, ammonia borane was dissolved in dimethylformamide (Fisher Scientific) at various concentrations from 0.075 to 0.25 M with average M₃, 5000 linear poly(ethyleneimine) (Sigma-Aldrich) and sonicated at 50 °C for 1 h to completely dissolve the polymer. The spin coater was typically operated at 2000 rpm for 10 s and then 3000 rpm for 50 s, and following spin coating, films were dried in air overnight. For inkjet printing, 0.031 g of ammonia borane was dissolved in a mixture of 10 mL of ethanol and 3 mL of ethylene glycol (Fisher Scientific). The ethylene glycol was needed to adjust the viscosity and measured to be 10–12 cp (Brookfield DV-E). Before printing, the solution was filtered through a 0.5 μm syringe filter to remove any precipitate. Printing was performed with an piezoelectric inkjet printer (DMP 3000, Fujifilm Dimatix) equipped with 16 nozzles. Requisite patterns were preprogrammed, and the drop size, drop spacing, nozzle driving waveform, and number of print layers could be tailored from the computer. The typical substrate for all deposition approaches was Si which was pretreated in an O₂ plasma at 150 W for 90 s to remove organic residue and improve the surface wettabiliy.

Synthesis of h-BN by PECFC. PECFC was performed in a homemade atmospheric-pressure reactor consisting of a DBD and cold-wall substrate heater. The DBD was formed in a planar electrode geometry between a 2 in. diameter powered aluminum electrode covered by a ceramic and a grounded aluminum electrode, separated by a gap of 3 mm. The reactor was backfilled with either Ar or an 80:20 mixture of Ar and H₂ by continuously flowing gas at a flow rate of 100 sccm, controlled by digital mass flow controllers, beginning at least 1 h before each experiment to purge and remove background air. The plasma was ignited and sustained by high-voltage alternative current (Model PVM500, Information Unlimited) typically at 20–30 kHz and 8.5 kV peak-to-peak voltage (Figure S1, Supporting Information). To heat the substrate, a 1 in. diameter microheater (MHI, Inc.) served as the bottom electrode, and the temperature was controlled by a variable ac voltage regulator and measured by a high temperature infrared thermometer (Model 42545, Extech). In this study, all films were converted with or without plasma for 1 h.

Thin Film Characterization. The synthesized h-BN films were characterized by atomic force microscopy (AFM) (Dimension 3100, Veeco), micro-Raman spectroscopy (LabRam HR800, Horiba), John-Yvon, 633 nm laser excitation), scanning electron microscopy (SEM) (Helios Nanolab 650, FEI), optical profilometry (NewView7300, Zygo), X-ray diffraction (XRD) (Discover D8, Bruker, Co source), transmission electron microscopy (TEM) (Tecnai F30, FEI, 300 kV), STEM (Themis Z advanced probe aberration corrected analytical STEM, Thermo, 300 kV), and electron energy loss spectroscopy (EELS) (Tecnai F30, FEI, 300 kV). Wide-field Raman imaging of a patterned h-BN film was performed by a custom-made system that filtered photons specific to the E₂g peak of h-BN at 1372 cm⁻¹ using a kinematically tunable band-pass filter. The field of view was illuminated by a 532 nm laser (GSLR-S52-2.5W, Lasermate Group, Inc.) that provided a near flat-top profile and an image was captured by a high quantum efficiency 2D CCD (iKon-M 934, Andor). The difference between this peak image and a baseline image, which was obtained with a band-pass filter at 1248 cm⁻¹ chosen near the valley of the E₂g peak, resulted in a final Raman image of the E₂g intensity. Each image was averaged from 15 scans with a 10 s integration time for a total acquisition time of 150 s.

For XRD and micro-Raman characterization, h-BN films were synthesized by converting drop-coated films of 0.1 M ammonia borane in ethanol on Si and quartz substrates, respectively. For TEM, h-BN films were synthesized by converting spin-coated ammonia borane films on Si substrates and transferred to a carbon-coated Cu TEM grid by etching away the Si substrate in 30 wt % KOH solution for 3 h and picking up the floating, free-standing films.

Metal–insulator–metal (MIM) Capacitor Device Fabrication and Analysis. Metal–insulator–metal (MIM) capacitor devices to measure the relative dielectric constant (εr) were fabricated as follows: First, h-BN films were synthesized by PECFC or thermal conversion from ammonia borane films spin coated onto gold-coated Si substrates. A second metal electrode (50 nm Al) was then evaporated on top of the h-BN films by physical vapor deposition (PVD) through a mask with 50 × 50 μm² openings. The capacitances were measured.
from multiple devices across the film by a LCR meter (Model E4980A, Keysight Technologies).

**MoS$_2$ FET Device Fabrication and Characterization.** MoS$_2$ FET devices were fabricated on h-BN films synthesized by PECFC directly on nm p-doped Si substrates with 300 nm thick SiO$_2$. Few-layer MoS$_2$ flakes were obtained by mechanical exfoliation using Scotch tape. After transferring to the h-BN surface, metal contacts (Ni/Ti 60/25 nm) were deposited by electron beam evaporation (Angstrom Engineering Evovac) through glider TEM grids (Ted Pella G200HS) which served as stencil masks.

Electrical measurements were performed at ambient conditions with a Lakeshore probe station, a Keithley 228A voltage/current preamplifier with a Lakeshore probe station, a Keithley 228A voltage/current preamplifier, and a Stanford Research Systems SR570 low-noise current preamplifier. Standard dc techniques were used to obtain current–voltage and gate transfer curves.

### RESULTS AND DISCUSSION

**Figure 1**a schematically illustrates the process flow that was developed for PECFC of h-BN. Ammonia borane was chosen as the precursor because it is nontoxic and nonflammable and, thus, a safe compound, and serves as a single molecule precursor for h-BN having the prerequisite 1:1 B:N stoichiometry. Previously, h-BN thin films have been synthesized using ammonia borane by CVD, with ammonia borane heated and brought into the reactor as a vapor.$^{10,22,29}$ The ability to pyrolytically decompose ammonia borane to h-BN has also been known for some time, but as a powder.$^{30}$ Here, we prepared the ammonia borane as a thin film by solution processing methods and then converted it by a combination of plasma treatment and heating. Three different approaches to film deposition were explored: (1) spray deposition, (2) spin coating, and (3) inkjet printing. The solution containing ammonia borane was slightly altered in each of these cases to enable deposition. Spray deposition was the simplest with ammonia borane dissolved in pure ethanol. In the case of spin coating, a polymer, linear polyethylenimine (L-PEI), was critical to act as a binder and obtain a continuous film; the polymer was in situ removed by the conversion process as long as the temperature was $>400$ °C.$^{31}$ Inkjet printing using a piezoelectric head required ethylene glycol to sufficiently increase the viscosity. Other approaches to deposition from solution should also be possible with very little restriction on the solvent, other than solubility, and substrate, other than temperature, reflecting the versatility of this general methodology. Following preparation of the ammonia borane film, the conversion to h-BN was performed by treating with a planar atmospheric-pressure dielectric barrier discharge (DBD) while heating the substrate in a home-built, cold-wall reactor. The size of the substrates was only limited by our DBD, which is an easily scalable plasma with commercial applications in large-area and roll-to-roll surface treatment.$^{32}$

**Figures 1b and 1c** show optical images of two $2 \times 1$ cm$^2$ Si substrates with ammonia borane films deposited by spin coating before and after PECFC, respectively. The slightly white appearance of the film after PECFC is indicative of h-BN formation. Optical images of spray-coated films show similar continuous, large-area coverage and color change following PECFC (Figure S2). By adjusting the concentration of ammonia borane in the spin-coating solution, we could control the converted film thickness from $\sim 3$ to 100 nm (Figure S3). SEM images of spray-coated and spin-coated films converted by PECFC are shown in Figures S4 and S5. Figure 1d shows an AFM image of a converted spin-coated film that has a thickness of 2.8 nm. We note that spin coating produced the thinnest and smoothest films, followed by spray deposition ($>100$ nm) and inkjet printing ($>10$ μm). To confirm the conversion of ammonia borane to h-BN and assess the crystallinity, the films were characterized by XRD. The XRD spectra in Figure 1e of the films before and after PECFC show that the as-deposited ammonia borane, which exhibits its characteristic (110), (101), and (211) peaks, is completely converted to h-BN, which exhibits its characteristic (002) and (004) peaks. The strong presence of only these peaks corresponding to h-BN indicates that the multilayers in the plasma-converted film are well-aligned.$^{37}$ Figure 1f shows an optical image of a patterned film in the shape of the letter “C” standing for Case Western Reserve University produced by
PECFC of inkjet-printed ammonia borane. The corresponding Raman mapping image of the $E_{2g}$ peak characteristic of h-BN in Figure 1g (see Figure S6 for details) confirms that controlled patterns of h-BN can be directly (nonlithographically) obtained.

To more carefully assess the crystalline quality of the PECFC-grown h-BN, we performed micro-Raman spectroscopy and systematically compared plasma-assisted heating and heating alone. Raman spectroscopy provides clear evidence of ammonia borane from its prominent scattering peaks at 782, 2281, 2378, and 3254 cm$^{-1}$ and h-BN from its scattering peak at 1366 cm$^{-1}$ corresponding to the in-plane optical phonon mode with $E_{2g}$ symmetry (Figure S7). Figure 2a shows a series of representative micro-Raman spectra of ammonia borane films deposited by drop casting on Si substrates after conversion in an Ar background at different temperatures with and without plasma treatment. Additional spectra collected from multiple spots on each sample are shown in Figure S8. We note that in agreement with XRD the Raman spectra did not show any peaks corresponding to ammonia borane. In addition, the presence of the Raman scattering peak corresponding to the underlying Si substrate indicated that the entire film was probed (see, for example, Figure S6), confirming that the ammonia borane was converted throughout the film depth in all of our processed samples. In the absence of a plasma, the $E_{2g}$ peak appears at temperatures $>800 \degree$C. Previous reports for CVD-grown h-BN have shown that nucleation required $>900 \degree$C on Si-based substrates, which is moderately higher than metal substrates, which can nucleate at $\sim750 \degree$C because of the lower catalytic activity of nonmetals. We suggest that the slightly lower minimum temperature achieved here is because there is no adsorption barrier by beginning with ammonia borane on the substrate. Based on the peak intensity which is proportional to the film thickness, the conversion of ammonia borane to h-BN also exhibits thicker film growth than CVD of h-BN from ammonia borane on Si-based substrates. Further lowering of the minimum temperature for h-BN nucleation to 650 $\degree$C and increase in the peak intensity at a given temperature (800 $\degree$C) are observed for PECFC. The peak also appears to be narrower in films grown by PECFC than thermal conversion, which is related to the film crystallinity and will be discussed in additional detail. The conversion of ammonia borane films to h-BN was also performed in a background mixture of Ar and $H_2$ (20%) (Figure 2b and Figure S9). Adding $H_2$ did not change the minimum temperature for h-BN nucleation by thermal conversion but, in the case of PECFC, decreased even more to 500 $\degree$C. Moreover, the peak intensity was found to increase at comparable temperatures (650 $\degree$C) (compare Figure 2b to Figure 2a).

The position and shape of the $E_{2g}$ Raman peak are related to the h-BN film structure (i.e., crystallinity) and thickness. As the thickness decreases, the peak shifts upward ($>1366$ cm$^{-1}$). We note that our films were all significantly thicker than where this shift would occur ($<3$–4 layers). As previously stated, the peak intensity is also related to the film thickness but is affected by crystallinity as well. Alternatively, the FWHM has been found to show minimal correlation with film thickness, but again only for very thin films, and can be used to obtain information about film crystallinity. In support, we compared Raman spectra for films prepared by drop casting with spin coating which are significantly thinner ($\sim80$ nm) and found that while the peak intensity decreased as expected, the FWHM was unchanged (Figure S10). The relationship between crystallinity and FWHM is attributed to the domain size of the crystallites and for h-BN is given by $L_a = 1417/\Gamma_{1/2} - 8.7$ where $L_a$ is the domain size and $\Gamma_{1/2}$ is FWHM of the $E_{2g}$ Raman peak. Therefore, larger crystalline domains lead to narrower peaks or smaller FWHM. Figure 2c summarizes our analysis of the $E_{2g}$ peak FWHM for all of the h-BN films converted by PECFC and heating alone at different temperatures in Ar and in Ar/$H_2$. The FWHM for thermally converted films are found to fall between $\sim26$ and 61 cm$^{-1}$, while PECFC films are significantly reduced to between $\sim13$ and 19 cm$^{-1}$, indicating that the addition of a plasma increases...
the average crystallite size (Table S1). For both thermal conversion and PECFC, increasing the temperature and adding H₂ are found to enhance film crystallinity. The lowest achieved FWHM of 13 cm⁻¹ for PECFC at 800 °C in Ar/H₂ compares favorably with the best literature values reported to date for CVD-grown h-BN on metal substrates (≈7−21 cm⁻¹) and is remarkably lower than CVD-grown h-BN on Si substrates (32−44 cm⁻¹).

The role of a nonthermal plasma in the conversion process is to create energetic and reactive species in the gas phase that interact with the ammonia borane film. The energy of the species can be much higher than the background temperature and thus enhance h-BN nucleation and growth at lower temperatures than required by heating alone, supporting our observations by Raman characterization. To characterize the species produced by the plasma, we implemented optical emission spectroscopy (OES), which is a nonintrusive technique that relies on radiative transitions. Figure 3a shows emission spectra collected from the DBD formed at the two process conditions studied: in Ar and a mixture of Ar and H₂. We note that the light was collected near the center of the discharge and is representative of the plasma volume without any spatial significance. The intense lines observed in Ar between ≈700 and 800 nm correspond to Ar neutrals (metastables). No lines corresponding to Ar ions which are typically between ≈400 and 500 nm were detected. This is not surprising because of the high operating pressure of 1 atm, which leads to quenching of the more energetic Ar ions. Additionally, the DBD is inhomogeneous, made up of filamentary microdischarges ≈100 μm in diameter that are random in space and time. The Ar ions are most probably contained in these bursts which were not captured by our steady-state optical system. The spectrum for Ar/H₂ shows one key difference: the appearance of a line at 654 nm corresponding to Hα, the most intense of the emission spectrum of atomic hydrogen in the visible known as the Balmer series.

Combining the OES and Raman results, we present the following picture for conversion of ammonia borane films to h-BN. Figure 3b shows the thermal decomposition mechanism that has been previously reported for ammonia borane. For both the thermally converted and PECFC films, the temperatures are higher than 500 °C, and the films should decompose similar to the first two steps, first forming polyiminoborane and second forming polymerminoborane, evolving H₂ in both steps. The key difference lies in the third step to form semicrystalline h-BN that was previously found to require 1150−1500 °C. Here, we find that h-BN nucleation by heating alone occurs at
a lower temperature of 800 °C. We note that our conversion was performed on thin films whereas the previous study was for a bulk powder of ammonia borane. Similar to metals in CVD of h-BN, there may be a small catalytic effect of the substrate. Nucleation is further enhanced by the addition of plasma which lowers the temperature to 650 °C in Ar and 500 °C in Ar/H2. In Ar alone, we suggest that Ar ions and metastables are involved in bond breaking and forming, particularly in the third step to dissociate polyaminoborane and evolve hydrogen. Low-energy ions (<20 eV) have been previously shown to be capable of displacing lattice atoms and transferring energy to aid in crystallization of thin films while avoiding undesirable sputtering. When H2 is added, H may play a critical role in nucleating and growing h-BN. The importance of H in thin film growth is general and well-known. Two examples that we refer to in this context are CVD of silicon and diamond. In the case of Si, H has been shown to facilitate crystallization at lower temperatures by abstraction of hydrogen, either from the surface or from silicon hydrides with overcoordinated Si atoms, and insertion into strained Si–Si bonds. In the case of diamond, the growth is more complicated because the formation of diamond competes with the formation of non-diamond (graphitic) carbon. Nonetheless, H is similarly involved in abstraction of hydrogen to create surface radical sites that nucleate diamond as well as stabilize the diamond nuclei by suppressing surface reconstruction and removing non-diamond nuclei.

The above description can be summarized by the following proposed mechanism which is illustrated in Figure 3c: (i) nucleation of h-BN nanoparticles via decomposition of polyaminoborane and, importantly, hydrogen abstraction by either heating alone for thermal conversion, or Ar ions, metastables, and/or H for PECFC; (ii) growth of the h-BN nuclei into larger crystals aided by heating alone for thermal conversion, or Ar ions, metastables, and/or H for plasma conversion. The role of H is of particular importance since it leads to the lowest minimum temperature for h-BN nucleation and the largest crystallite size. In (i), hydrogen abstraction by H could allow the removal of hydrogen at lower temperatures and the creation of free radicals that promote nucleation of h-BN. In (ii), H could interact with the already formed h-BN crystal nuclei through a combination of abstraction and insertion reactions. Analogous to CVD of Si and diamond, these reaction pathways could promote amorphous to crystalline transitions and the growth of larger crystallite sizes in the films grown by PECFC. We note that H2 could also have other effects on film conversion such as reducing oxidation which could explain its impact on the size of the grown crystals for thermal conversion (see Figure 2c). However, the highly reactive H has a stronger effect which may explain why there is no change in the minimum temperature for h-BN nucleation with the addition of H2 in thermal conversion. This also suggests that H is more important for nucleation (i) than growth (ii), which is corroborated by the stronger effect it has on temperature as compared to crystallite size (see Figure 2c). A similar argument has been made in the growth of Si where nucleation has an activation energy of 5 eV while growth has an activation energy of 2.7 eV, and thus, plasma treatment and the generation of H are more important to creation of seed nuclei than the growth of the larger crystal from the seeds.

To assess the surface flatness of our films, our smoothest films prepared by converting spin-coated solutions were characterized by AFM. Figure 4 shows representative AFM images of h-BN synthesized by PECFC in Ar/H2 at 500 °C (Figure 4a), PECFC in Ar/H2 at 800 °C (Figure 4b,c), and thermal conversion in Ar/H2 at 800 °C (Figure 4d). The surface morphologies of the two PECFC films are comparable, with the surface roughness slightly reduced from a RMS value of ~1 to 0.5 nm by increasing the growth temperature from 500 to 800 °C. Additionally, we synthesized films on a masked Si substrate and measured the thickness at multiple locations along the film edge. The thicknesses were found to vary by 0.06 nm (Figure S11). The flatness confirms the high quality of the PECFC films and are similar to the lowest report for CVD-grown h-BN films which is important for electronic device applications. In comparison, the thermally converted h-BN films were found to be much rougher characterized by a RMS roughness value of ~20 nm.

The atomic-scale morphology and structure of h-BN films synthesized by PECFC and thermal conversion were examined by TEM and STEM. In agreement with AFM analysis, the films were highly continuous, stable to transfer, and free-standing, permitting suspension on TEM grids (Figure S12a). Low-magnification STEM images of the PECFC films showed crystals as large as ~50 nm (Figure S12b). The interlayer distance was measured to be 0.34 nm from a cross-sectional TEM image, close to the expected value of bulk h-BN (Figure S12c). High-magnification STEM images in Figures 5a and 5b of PECFC films grown at 500 and 800 °C, respectively, reveal regions containing lattice fringes with hexagonal arrangement that are relatively disorder-free and continuous, confirming the high quality of our h-BN films and supporting Raman analysis. The selected area electron diffraction (SAED) in the inset of Figure 5b for the PECFC film grown at 800 °C displays a single hexagonal pattern, indicating that the films are highly ordered. The (~1100) and (01–10) lattice planes could be identified in the (0001) zone axis from the SAED. In comparison, the STEM image of a thermally converted film in Figure 5c reveals poor crystallinity, characterized by nanometer-sized grains (~5 nm) surrounded by amorphous regions, similar to previous reports of metal-free h-BN growth. The SAED pattern shown in the inset is consistent with a polycrystalline film. The trend in the crystal sizes between PECFC and thermally converted films is generally consistent with the FWHM analysis of the Raman spectra (Table S1). However, the sizes of the crystalline regions observed in TEM
edges consisting of thermal conversion, both grown in Ar/H2 gas at 800 °C. Insets in (b) and (c) show the corresponding selected area electron diffraction (SAED) patterns. (d) EELS showing B and N K-shell ionization edges at ∼190 and ∼400 eV, respectively. We estimated the stoichiometry of boron and nitrogen from the integrated areas of the corresponding peaks to be 0.93, which is reasonably close to the expected 1:1 ratio. The distinct π* and σ* energy-loss peaks confirm that the film contains sp3-hybridized bonds, and the sp3:sp2 ratio was evaluated by the “two-window intensity ratio” method⁴⁹ to be 98% sp3, confirming the h-BN phase.

The dielectric properties of the PECFC films were evaluated by fabricating metal–insulator–metal (MIM) capacitor structures to obtain the relative dielectric constant, εr. Figure 5a shows a schematic diagram of the MIM device which consisted of gold-coated Si as one metal electrode, and an Al layer evaporated on top of the h-BN film by physical vapor deposition (PVD). Devices with varying thicknesses of h-BN were synthesized by adjusting the ammonia borane concentration in the spin-coating solution (Figure S3), and the film thickness was measured after conversion by either profilometry (Figure S13) or AFM. The averages of the capacitances measured from multiple devices as a function of h-BN thickness for PECFC and thermal conversion, both grown in Ar/H2 at 800 °C, are shown in Figure 6b. Two sets of error bars are shown: the horizontal error bars correspond to differences in the film thickness at different locations and the vertical error bars correspond to differences in the capacitance measurements from multiple devices. By fitting the data in Figure 6b (see the Supporting Information for details), we can extract an average dielectric constant, εr, of 3.8 for h-BN synthesized by PECFC and 2.8 for thermally converted h-BN. The significantly higher relative dielectric constant with the addition of a plasma is consistent with the improved crystalline structure of the h-BN films found by Raman analysis. These values are comparable to those previously reported for bulk single-crystals of h-BN of ∼3–4⁵⁰ and CVD h-BN of 2–5.¹⁷,⁵¹

To demonstrate the potential of PECFC h-BN films for electronic device applications with 2D materials, MoS2 devices were fabricated. Figure 7a shows a schematic diagram of the FET device structure (bottom) and a corresponding representative AFM image (top). A 2.8 nm thick h-BN film was first synthesized by PECFC in Ar/H2 at 800 °C from a spin-coated solution of ammonia borane on a 300 nm SiO2/p+ + Si substrate. A few layered MoS2 flake was then mechanically exfoliated and transferred onto the h-BN film. Ni/Ti contacts were then lithographically deposited by electron beam evaporation. We also fabricated MoS2 FETs without h-BN on the SiO2/Si substrate for comparison. MoS2 FETs with thermally converted h-BN films could not be fabricated because of their large roughness (Figure S14).
The linear output curves (I\textsubscript{ds} vs V\textsubscript{ds}) in Figure 7b confirm that Ohmic contacts were formed between the Ti metal layer underlying Ni and the MoS\textsubscript{2} films in devices with h-BN. The application of a gate voltage is found to change the conductance as expected and is consistent with n-type semiconductor behavior, which has been linked in MoS\textsubscript{2} to trapped charge in the form of adsorbates or defects at the gate insulator interface.\textsuperscript{52,53} Figure 7c shows a comparison of representative transfer curves (I\textsubscript{ds} vs V\textsubscript{g}) for MoS\textsubscript{2} FETs on h-BN and on only SiO\textsubscript{2}. The inclusion of h-BN is found to increase both the conductance and transconductance by more than an order of magnitude because of reduced Coulomb scattering from the charge traps in SiO\textsubscript{2} as has been previously reported.\textsuperscript{54,55} Field-effect mobilities of 4–5 devices (Figure S15a,b) were extracted from the transfer curves (see the Supporting Information for details), and a histogram is shown in Figure 7d. We used an average dielectric constant, \( \varepsilon_r \), of 3.8 obtained from our capacitance measurements for h-BN and 3.9 for SiO\textsubscript{2}. It should be noted that as the thickness of h-BN increases, however, for the multilayer films with a thickness of 2.8 nm used here, the dielectric constant would increase by only \( \sim \)30% and change the mobility by only \( \sim \)0.2%. The average mobility for devices with h-BN was estimated to be 14.4 ± 1.2 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, more than 4 times higher than the average mobility of 3.2 ± 0.4 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} for devices with only SiO\textsubscript{2}. The mobility improvement of MoS\textsubscript{2} FETs on the PECFC h-BN films over only SiO\textsubscript{2} is comparable to previously reported devices with CVD-grown h-BN.\textsuperscript{56} We also note that the devices with h-BN qualitatively exhibited better reproducibility. Because the thickness of the h-BN film is only 2.8 nm, the gate capacitance, \( C_{\text{gate}} \) for the h-BN-covered SiO\textsubscript{2} is only \( \sim \)1% lower than that of the bare 300 nm SiO\textsubscript{2} (note that \( C_{\text{gate}} = 1/(C_{\text{SiO}_2}^{-1} + C_{\text{hBN}}^{-1}) \)). Therefore, the improvement does not come from a change in gate capacitance and confirms an improved interface as compared to that between MoS\textsubscript{2} and SiO\textsubscript{2}. We note that an important distinction from previous work is that here the h-BN is grown directly (no transfer) on the SiO\textsubscript{2}, which reduces the number of device processing steps.

### CONCLUSIONS

In summary, the combination of plasma-assisted heating and conversion of a precursor film has been demonstrated to produce large-area, continuous, high crystalline quality h-BN films directly on metal-free substrates. The approach is fundamentally different from traditional CVD and circumvents substrate interactions that can influence nucleation, growth, and adsorption, allowing the film thickness or geometry to be controlled by a variety of deposition methods including spray coating, spin coating, and inkjet printing. The generation of energetic species such as Ar ions and metastables and H in a nonthermal plasma lowers the minimum growth temperature to as low as 500 °C and increases the film crystallinity. The method is generic and could be applicable to other layered materials as well such as MoS\textsubscript{2} to similarly enable low-temperature, large-scale growth of 2D materials on arbitrary substrates.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b17152.
Charge–voltage waveforms for dielectric barrier discharge (DBD), optical images of spray-coated films before and after PECFC, spin-coated film thickness before and after PECFC as a function of solution precursor concentration, SEM images of spray-coated and spin-coated films, micro-Raman spectra of inkjet printed films, micro-Raman spectra of ammonia borane precursor and bulk h-BN reference, micro-Raman spectra from different spots on films processed in Ar and Ar and H2 by PECFC and thermal conversion, micro-Raman spectra of droplet vs spin-coated films, FWHM analysis of micro-Raman spectra, AFM analysis of film thickness, TEM analysis of films, optical profilometry of films, dielectric constant calculation from capacitor measurements, optical micrographs of MoS2, FET devices, transfer curves of MoS2 FET devices, and FET mobility calculation (PDF).

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Department of Energy Basic Energy Sciences (DOE-BES) Grant DE-AC02-09CH11466. K.P. and X.G acknowledge support by the National Science Foundation (NSF) under Grant DMR-1151534. H.A.B.M. and K.P and X.G acknowledge support by the National Science Foundation (NSF) under Grant DMR-1151534. H.A.B.M. and O.A. acknowledge support by NSF under Grant MRI-1531035. We thank J. Toth for help with setup and electrical characterization of the DBD, J. Cole and H. Ishida for help with micro-Raman spectroscopy, and S. Bhattacharya for help with AFM characterization. STEM imaging was carried out in the Frederick Seitz Materials Research Laboratory at the University of Illinois.

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