

Boron Nitride–Graphene Nanocapacitor and the Origins of Anomalous Size-Dependent Increase of Capacitance

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Supporting Information

ABSTRACT: Conventional wisdom suggests that decreasing dimensions of dielectric materials (e.g., thickness of a film) should yield increasing capacitance. However, the quantum capacitance and the so-called "dead-layer" effect often conspire to decrease the capacitance of extremely small nanostructures, which is in sharp contrast to what is expected from classical electrostatics. Very recently, first-principles studies have predicted that a nanocapacitor made of graphene and hexagonal boron nitride (h-BN) films can achieve superior capacitor properties. In this work, we fabricate the thinnest possible nanocapacitor system, essentially consisting of only monolayer



materials: h-BN with graphene electrodes. We experimentally demonstrate an increase of the h-BN films' permittivity in different stack structures combined with graphene. We find a significant increase in capacitance below a thickness of \sim 5 nm, more than 100% of what is predicted by classical electrostatics. Detailed quantum mechanical calculations suggest that this anomalous increase in capacitance is due to the negative quantum capacitance that this particular materials system exhibits.

KEYWORDS: Hexagon boron nitride, graphene, nanocapacitor, quantum capacitance, h-BN/graphene stacking heterostructure

E xtensive efforts have been directed at reducing the sizes of insulators and identifying novel material systems with high permittivities (and hence capacitances).^{1,2} Unfortunately, experiments and computations have shown that in many thin and high permittivity insulators (such as $SrTiO_3$) their capacitance values actually decrease with decreasing size.^{3,4} In the case of thin-film configurations, this counters the conventional wisdom from electrostatic theory that the geometric capacitance density, C_{geo} , is related to the applied voltage, ΔV , as

$$C_{\text{geo}} = \frac{\sigma}{\Delta V} = \frac{\varepsilon_{\text{r}} \varepsilon_{\text{o}}}{d} \tag{1}$$

where σ is the surface charge density, ε_o is the permittivity of free space ~8.85 × 10⁻¹² F m⁻¹, and *d* is the thickness of the dielectric material. Using *ab inito* studies, this perplexing observation has been explained in part by the existence of an atomically thin charge interface between the insulator and the metallic gate, sometimes referred to the "dead layer".³ The dramatic capacitance reduction at small sizes is theorized to

originate from positive quantum capacitance, C_{Q2} of this accumulated two-dimensional electron gas.

Despite being identified as a key ingredient in engineering nanoscale devices over four decades,⁵ the quantum capacitance of the interface two-dimensional electron gas, arising from many-body interactions, has only gained much interest in recent years.^{2,6,7} The quantum capacitance is related to the net capacitance, *C*, through the relation

$$\frac{1}{C} = \frac{1}{C_{\text{geo}}} + \frac{2}{C_{\text{Q}}}$$
(2)

The value of C_Q is many orders of magnitude greater than C_{geo} , and hence its effect usually appears only in very small systems. However, in some cases, the quantum capacitance can dramatically enhance the overall capacitance, rather than

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Figure 1. Optical images, AFM, Raman spectra and TEM of graphene, and h-BN thin films. (a) Optical images of graphene films on SiO_2 substrates with different thicknesses. (b-f) Optical images of h-BN thin films with different thicknesses. (g-l) AFM height profile of (a-f). (m,n) Raman spectra of graphene and h-BN films. (o) Filtered HRTEM images of h-BN.

decrease it. A few materials systems have already been identified as plausible platforms for utilization of this opposite quantumcapacitance phenomenon, including C–CuO₂–Cu coaxial nanowires and LaAlO₃/SrTiO₃ films for which about 100 and 40% enhancements of capacitance, respectively, have been reported.^{2,6,8–10}

In this work, we successfully fabricated arguably the thinnest possible nanocapacitor system via the use of atomically thin monolayer materials such as graphene and hexagonal boron nitride (h-BN). We observed the unusual size dependence substantially enhanced the graphene-h-BN-graphene system. We also performed quantum transport calculations to elucidate the mechanism underpinning the unusual size-dependence of capacitance in this particular materials system. Furthermore, we experimentally demonstrated that insertion of graphene into h-BN stacks may also lead to possible intriguing applications.

Experimental Section. Hexagonal BN, a novel twodimensional material with a wide band gap, has received considerable attention in the past decade. The unique honeycomb lattice structures made by boron and nitrogen atoms exhibit several promising physical properties, including high mechanical strength, high thermal conductivity, and good high-temperature stability. Moreover, the similarity between graphene and h-BN in terms of lattice structure enables heterostructures without dangling bonds and charge traps; accordingly, they are an ideal substrate material for each other. It has been reported that mobilities of graphene devices on h-BN substrates can be dramatically increased compared to those deposited on Si/SiO₂ surfaces.^{11–13} Some other appealing properties of graphene-h-BN stacking structures have also been reported, such as intrinsic doping, chemical reactivity, tailored band gaps and electron effective masses, and so forth.^{13,14}

In this paper, we specifically studied the dielectric properties of different h-BN/graphene heterostructures, including Au/h-BN/Au (BN) stacks, Au/graphene/h-BN/Au (GBN) stacks, Au/h-BN/graphene/Au (BNG) stacks, and Au/graphene/h-BN/graphene/Au (GBNG) stacks. Our experimental and theoretical results show that the relative permittivity of a h-BN thin film can be almost twice higher than that of bulk boron nitride (at 20 kHz). An atomic force microscopy system (Agilent PicoScan 5500) was used to measure the thicknesses of the films. A JEOL-2100 field-emission HRTEM was used for high-resolution transmission electron microscopy (HRTEM). Raman spectroscopy was performed at 514.5 nm laser excitation using a Renishaw inVia system. Electrical measurements were performed in a probe station with a high vacuum chamber. An Agilent E4980A Precision LCR Meter was used to perform the capacitance measurements. An Agilent B1500A Semiconductor Device Analyzer was used to measure all other electrical properties (I-V and C-V curves) in this work.

By controlling growth conditions, we deliberately prepared single-layer graphene as well as multilayer h-BN thin films for device fabrication. The methodology for material synthesis has been reported in detail elsewhere.^{15,16} Figure 1a is an optical image of a graphene thin film on a silica substrate while its AFM image and Raman spectrum are shown in panels g and m,

respectively. The height-profile acquired by AFM demonstrate that this is a single-layer graphene sample. The single-layer property is further verified by the typical signatures of a 2D/Gpeak integral intensity ratio of around 5 and a 2D peak width (fwhm) of 29.0 ± 0.8 cm^{-1.17} Figure 1b-f shows optical images of five different h-BN thin films on silica. The color variation from green to light purple implies a change in the number of atomic layers from one film to another. A further verification of the actual thicknesses by AFM is shown in panels h-l. The heights read from AFM data for the five different h-BN thin films are 14.5, 5.9, 2.8, 1.5, and 0.8 nm, respectively, which can be reasonably considered as a bulk material, a thin film with 16 atomic layers, 8 layers, 4 layers, and 2 layers, respectively. These numbers are further confirmed by the unique Raman spectra of these films shown in panel n. A filtered HRTEM image of the bilayer h-BN film is shown in panel o, which clearly exhibits the distinctive hexagonal atomic structures with a decent degree of crystallization.

h-BN in nature is an ideal electrical insulator that can be polarized by applying an external electric field. A slight shift of electrical charges on the surface of h-BN from their average equilibrium positions induces a dielectric polarization, which can be quantified as a nonunit value of the relative permittivity, ε_{rr} appearing in eq 1.

In order to measure the dielectric changes induced by an electric field, we fabricated a thin parallel capacitor based on this model. Figure 2 shows the general design and major steps



Figure 2. Fabrication process and the optical/SEM images of the testing capacitors. (a–f) The six major steps to make the Au/G/h-BN/G/Au stack device on SiO₂ wafer. The first step (a) is to deposit the bottom layer electrode onto SiO₂ wafer with a dumbbell shape. Steps (b–d) are layer-by-layer transfer of the CVD grown films onto the bottom electrode by acid lift-off methods. The fifth step (e) is to etch away all other unnecessary areas except a 10 μ m × 10 μ m square in the middle of each device. The last step (f) is to deposit the top layer electrode on top of the film, perpendicular to the bottom electrodes. (g,h) These panels show optical and SEM images of a device after etching. The inset scale bar in (h) is 10 μ m. (i) This panel indicates the measuring methods and connections from the device to the probe station.

of device fabrication. (a) First, Au/Cr (30/1.5 nm) is deposited on SiO₂ as the bottom electrode by electron-beam evaporation. The bottom electrode is dumbbell shaped. On both sides there are two square pads with 100 μ m width and length. The ribbon that bridges the pads is of 500 μ m in length and 10 μ m in width. (b) Second, a large piece of single-layer graphene is transferred onto the bottom electrodes by a standard acid liftoff method.^{16,18,19} In our experiments, as the area of the film is much larger than the size of electrodes, one piece of graphene or h-BN film can fully cover 20-40 electrodes simultaneously on the same wafer. (c,d) are the steps in which we stack graphene and h-BN onto the bottom electrode and let them tightly bond to each other by van der Waal forces. (e) illustrates the step of making a square mask on top of the stacked layers of 10 μ m length and 10 μ m width by reactive ion etching (RIE) with photolithographic masks. This process ensures isolation of different devices on the same substrate. (f) shows the step that the top electrode is deposited on top of the transferred stacked layers. The geometry of the top electrode is identical to the bottom electrode but rotated by 90°. As a result, the top and bottom electrodes together form cross-shaped electrodes with a small overlapping parallel plate in between. Figure 2g,h shows optical and SEM images, respectively, of one such capacitor. Figure 2i shows how the two measuring probes contact the top and bottom electrodes and perform the following measurements.

On the basis of the aforementioned procedure, we fabricated 10 groups of devices, as shown in Table 1. Groups BN-1 to BN-7 have the Au/h-BN/Au stack structure. The thicknesses of the h-BN films of these seven batches were 26.7 nm (bulk), 20.2 nm (bulk), 14.5 nm (bulk), 5.9 nm (~16 layers), 2.8 nm (~8 layers), 1.5 nm (~4 layers), and 0.8 nm (~2 layers), respectively. In addition, in order to demonstrate unique properties of different stacking sequences, we made three other groups: GBN-8, BNG-9, and GBNG-10. In Group GBN-8, the Au/graphene/h-BN/Au stacking structure was made in which a laver of graphene was inserted in between the bottom electrode and the h-BN film. Group BNG-9 reverses the stacking sequences of h-BN and graphene, as compared to Group GBN-8. The last batch, Group GBNG-10, is a full stacking structure of graphene/h-BN/graphene. The graphene and h-BN used in the latter three groups are single and double-layers, respectively. By comparing BN-7, GBN-8, BNG-9, and GBNG-10 we can infer the effect of stacking sequence on the electrical properties as well as the impact of graphene on h-BN's physical behaviors.

We first measured the capacitance of batches BN-1 to BN-7 at 20 kHz. The Precision LCR Meter Agilent E4980A was set to work in Cp/D function mode with a level voltage of 0.01 V. Two probes were contacted to the top and bottom electrodes, respectively. In order to minimize the impact from the cable capacitance and other noises, we followed a two-step process to calibrate the setup: (1) calibrate the open-circuit capacitance and (2) calibrate the short-circuit capacitance with the top and bottom electrodes. We then apply eq 1 to calculate the relative permittivity, whose values are plotted in Figure 3. The data were obtained based on the statistical average of at least 40 identical devices of each group. We can clearly observe a significant increase of the relative permittivity with decreasing film thickness. Not so surprisingly, the measured relative permittivity of devices in Groups BN-1, BN-2, and BN-3 are 4.2 \pm 0.1, which is almost the same as the reported value for bulk BN.²⁰ However, an anomalous size dependence appears when the thickness becomes <~5 nm, or less than 16 atomic layers, that is, the relative permittivity systematically increases with decreasing h-BN thickness. The relative permittivity values of BN-4, BN-5, and BN-6 are 4.9 ± 0.4 , 5.6 ± 0.6 , and 6.8 ± 0.9 , respectively. For BN-7, which is made by bilayer h-BN, the permittivity is measured to be 7.9 \pm 1.1, which is almost twice as large as the bulk value. The measured values for all devices

Table	1. 8	Sample	Code	es and	the	Correspond	ing S	Stackin	g Structures
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sample code	staking structures (from bottom to top)	thickness of h-BN thin films	layers of h-BN films	over-lap area (μm^2)	capacitance (pf)	relative permittivity [mean value] ± [max diff]
BN-1	Au/h-BN/Au stack	26.7 nm	bulk	100	0.139	4.2 ± 0.1
BN-2	Au/h-BN/Au stack	20.2 nm	bulk	100	0.184	4.2 ± 0.1
BN-3	Au/h-BN/Au stack	14.5 nm	bulk	100	0.256	4.2 ± 0.1
BN-4	Au/h-BN/Au stack	8.1 nm	16	100	0.735	4.9 ± 0.4
BN-5	Au/h-BN/Au stack	2.8 nm	8	100	1.770	5.6 ± 0.6
BN-6	Au/h-BN/Au stack	1.5 nm	4	100	4.012	6.8 ± 0.9
BN-7	Au/h-BN/Au stack	0.8 nm	2	100	8.739	7.9 ± 1.1
GBN-8	Au/G/h-BN/Au	0.8 nm	2	100	10.952	9.9 ± 1.9
BNG-9	Au/h-BN/G/Au	0.8 nm	2	100	11.394	10.3 ± 2.5
GBNG-10	Au/G/h-BN/G/Au	0.8 nm	2	100	11.948	10.8 ± 2.3



Figure 3. The extended measurements of relative permittivity from 2 kHz to 2 MHz. (a) Measured relative permittivity of the Au-h-BN-Au stacking groups from 2 kHz to 2 MHz. (b) Comparison between different stacking structures in the same range.

are summarized in the format of [mean value] \pm [max diff], as shown in Table 1.

There are a variety of device-related issues, which we can exclude as the reason for the observed size-dependent relative permittivity: (1) the surface residues of resists or water, (2) different bonds between films and electrodes, (3) the inhomogeneity and defects of the h-BN films, and (4) roughness of the gold (metal)- BN (dielectric) interfaces. We took a few precautions to eliminate the impacts of (1-3), including annealing the whole chip under vacuum at 300 °C for 2 h in order to vaporize possible residues of polymers, waters, or resists. AFM mapping after each of the fabrication steps indicated that the surface height inhomogeneity of the surfaces was about 2%. For (4), in order to ensure formation of tight bonds between electrodes and thin films after device fabrication we baked the whole devices under vacuum at 105 °C for 2 h. In Supporting Information, we provide a detailed discussion on the impacts of roughness of the gold-BN interfaces on the capacitance. It shows that the roughness of the gold electrodes, in our case a \sim 1.9 nm height variation, would cause a \sim 2% capacitance variation, which is not significant enough to explain the anomaly large capacitance values of the devices with the thinnest h-BN films.

We extended the test from 2 kHz to 2 MHz for batches of BN-3, BN-4, BN-5, BN-6, and BN-7, as Figure 3a shows. As can be seen, the relative permittivity is increased at all frequencies as the thickness of h-BN gets smaller. For BN-3, the relative permittivity is stable as the frequency changes, whereas that of those films thinner than 5 nm becomes lower as the frequency becomes higher. Atomistic calculations, discussed in the next section, demonstrate a similar trend to this experimental observation and provide a mechanistic explanation for some of the anomalous size-effects.

Furthermore, we measured the capacitances of three other types of devices with differing stacking sequences: BN-7, GBN-8, BNG-9, and GBNG-10. The results are shown in Figure 3b. The relative permittivity values of h-BN at 20 kHz in GBN-8, BNG-9, and GBNG-10 are 9.9 \pm 1.9, 10.3 \pm 2.5, and 10.8 \pm 2.3, respectively, which are more than double of the value of bulk BN. Figure 3b also shows the frequency dependence of the relative permittivity of these different stacking structures from 2 kHz to 2 MHz. As the design of GBN-8 and BNG-9 is geometrically symmetric, their electrical properties are equivalent but notably different from BN-7. Therefore, we infer that the bonding sequence does not really affect the graphene/h-BN bonds. GBNG-10 exhibited stable responses though all testing bands, which could potentially be a clue for designing next generation two-dimensional capacitors and electronics. Discussions about breakdown voltages and leakage currents are included in Supporting Information.

Computational Study. Models for a nanoscale dielectric capacitor consisting of two metallic graphene layers separated by an insulating h-BN thin layers have been successfully used to simulate stacking structures of graphene/h-BN/graphene, that is, groups GBN-8, BNG-9 and GBNG-10.²¹ Here, we further investigated the roles of negative quantum effects in the interaction between the gold electrodes and h-BN films in these structures. We determined the dielectric permittivity as a function of dielectric size via *ab inito* calculations using the SIESTA atomistic simulation package. We employed density



Figure 4. The computational study of Au-(h-BN)-Au Stacks. (a) Adsorption surface geometry of h-BN on (111)-Au surface. Three layers of Au atoms (brown) are displayed. The boron and nitrogen atoms are in green and blue, respectively. (b,c) A macroscopic averaged charge density profile under an applied bias of 0.2 V. The color representation is the same as in Figure 1. (d) Comparisons between experimental and calculated relative permittivity.

functional theory with the van der Waals density functional (vdW-DF) to model the exchange-correlation energies of Au and h-BN.²² We took into account relativistic effects for Au via a relativistic pseudopotential, whose validity has been proven in a previous study.^{23,24}

The double ζ -basis set with polarization orbitals (DZP) were used for Au atoms while single ζ -basis sets with polarization orbitals (SZP) were employed for the h-BN layers and Au atoms, respectively. All calculated equilibrium configurations were fully relaxed with residual forces smaller than 0.04 eV/Å. The calculated lattice constant of Au is 4.217 Å. For h-BN, the lattice constant is 2.536 Å, and the c/a ratio is 2.78; thus, the interlayer distance in h-BN is 3.524 Å, which is in reasonable agreement with the corresponding experimental value (3.306 $Å^{25}$) and the theoretical value (3.54 Å) calculated using the plane-wave basis set with the vdW-DF method.²⁶ The adsorption geometry of h-BN on a (111) surface of Au is shown in Figure 4a. For the calculations of bonding between h-BN and Au surfaces, a supercell of three Au layers and two h-BN layers was employed with a grid of $12 \times 12 \times 2$ and an energy cutoff of 300 Ry. The calculated equilibrium adsorption distance is 3.296 Å.

We investigated electrical properties of our nanocapacitors under a finite bias voltage using the nonequilibrium Green's functions (NEGF) approach within the TranSIESTA package.²⁷ The contact leads were composed of semifinite Au-(111) surfaces, with the top and bottom electrodes containing seven and six Au layers, respectively. The number of h-BN layers was varied to examine size-dependent electrical properties. The three layers of the top (bottom) Au electrodes next to the h-BN layers and all h-BN layers were fully relaxed until the force was reduced to less than 0.06 eV/A, prior to performing the NEGF calculations. The contact geometry is shown in Figure 4b.

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The static dielectric constant is related to the capacitance density per unit area through eq 1. We extracted charge density profiles from first-principles calculation through an averaging process described in ref 28. An example profile is shown in Figure 4c whereas the corresponding slap geometry is shown in Figure 4b. The calculated relative permittivity is displayed along with the experimental results in Figure 4d. Because of computational limitations on the sizes that can be explored by first-principles calculations, only three calculated permittivity values are shown, but the trend is in good agreement with the experimental observations.

According to eq 2, the observed anomalous increase in capacitance with decreasing size suggests that for this particular system the quantum capacitance is negative. This effect arises from many-body interactions because the chemical potential of the electrons decreases with the electron density.² Near the thin interface layers, the accumulated electron density overscreens the external fields, thus causing an effect opposite to those of the dead layers. For a given material system, the sign determination of the quantum capacitance from first principles is still ongoing research, and the current material system presents a unique example of its ramifications and possibly unprecedented potential in electronic applications.

Summary. In conclusion, we experimentally studied dielectric property changes of CVD grown h-BN thin films in four kinds of stack structures with CVD grown graphene. Two major factors, the thickness of h-BN and the stack sequence of h-BN and graphene, significantly affect the electrical properties h-BN. In the Au/h-BN/Au structure, we found the capacitance to be similar to that of bulk BN for thicknesses larger than 20

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nm; when the thickness was between 20 and 3 nm, the capacitance was found to be as large as two times the bulk value (at 20 kHz). By adding graphene layers to the stacking structure, the dielectric constant of h-BN was further enhanced. Our results reveal that the capacitors containing graphene/h-BN/graphene stacks exhibit excellent capacitance stability and quality factors. *Ab inito* calculation results are in qualitative agreement with the experiments and suggest that a negative quantum capacitance is responsible for the rather unexpected and large size-dependent increase of capacitance for these atomically thin nanocapacitors. These results indicate that stacking structures of graphene and h-BN have controlable properties that are potentially useful for diverse future electronic applications.

ASSOCIATED CONTENT

Supporting Information

The material provides an in-depth discussion of the impacts of roughness of the gold (metal)—boron nitride (dielectric) interfaces to the variety of capacitance, the breakdown voltages, and leakage currents of different device configurations. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Author Contributions

G.S. and Y.H. contributed equally to this work. G.S. and Z.L. designed and carried out most of the experiments (growth, SEM, Raman, XPS, UV, device fabrications, and characterization) and analyzed the data. Y.H. conducted the theoretical calculations. Y.G. and B.L, worked on the CVD growth of graphene and boron nitride. W.G. worked on the device fabrications. G.S., Y.H., Z.L., Y.G., J.L., R.V., P.S., and P.M.A. cowrote the paper. All the authors discussed the results.

Notes

The authors declare no competing financial interest.

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