Measuring the dielectric and optical response of millimeter-scale amorphous and hexagonal boron nitride films grown on epitaxial graphene

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Abstract

Monolayer epitaxial graphene (EG), grown on the Si face of SiC, is an advantageous material for a variety of electronic and optical applications. EG forms as a single crystal over millimeter-scale areas and consequently, the large scale single crystal can be utilized as a template for growth of other materials. In this work, we present the use of EG as a template to form millimeter-scale amorphous and hexagonal boron nitride (*a*-BN and *h*-BN) films. The *a*-BN is formed with pulsed laser deposition and the *h*-BN is grown with triethylboron (TEB) and NH₃ precursors, making it the first metal organic chemical vapor deposition (MOCVD) process of this growth type performed on epitaxial graphene. A variety of optical and non-optical characterization methods are used to determine the optical absorption and dielectric functions of the EG, *a*-BN, and *h*-BN within the energy range of 1 eV to 8.5 eV. Furthermore, we report the first ellipsometric observation of high-energy resonant excitons in EG from the 4H polytype of SiC and an analysis on the interactions within the EG and *h*-BN heterostructure.

1. Introduction

Graphene is one of the leading constituents in the field of two-dimensional (2d) materials research partly due to its desirable electrical properties arising from the quantum confinement of electrons in the ultra-thin material.¹⁻³ When graphene is grown epitaxially (EG) on a 4H-SiC substrate, a single crystal can be formed over millimeter-scales which can then be fabricated into devices that are especially useful in the field of metrology.⁴⁻¹¹ Because of the large scale single-crystal growth of epitaxial graphene (EG), it can be utilized as a template for other 2d materials including transition metal dichalcogenides and insulators.¹²⁻¹⁶ The growth of 2d materials on EG presents a favorable mechanism to enable heterostructures of 2d materials in order to exploit the exciting properties and multifunctionalities that can arise from multi-material van der Waals structures.¹⁷ In particular, the synthesis and growth of 2d boron nitride films on graphene have been extensively studied.¹⁸⁻²⁰

To date, synthesis of *h*-BN by chemical vapor deposition (CVD) has been a versatile technique to create ultra-thin layers on various substrates.²¹⁻²³ Expanded CVD methods have emerged that increased the

flexibility in selecting the substrate, which can range from sapphire and metallic foils,²⁴⁻²⁶ and selecting the precursors, which can include trichloroborazine ($B_3N_3H_3Cl_3$), hexachloroborazine ($B_3N_3Cl_6$), and ammonia borane (NH_3 - BH_3).²⁷

In this work, EG is used as a template to form millimeter-scale amorphous and hexagonal boron nitride (*a*-BN and *h*-BN) films. Pulsed laser deposition is used to obtain the ultra-thin *a*-BN where the *h*-BN is grown with triethylboron (TEB) and NH₃ precursors, making it the first metal organic chemical vapor deposition (MOCVD) process performed on epitaxial graphene. The combination of measurements acquired by Mueller matrix ellipsometry (MME), atomic force microscopy (AFM), Raman spectroscopy, and differential reflectance contrast (DRC), as well as the added insights from Kramers-Kronig analyses, allow for the determination of the optical absorption and dielectric functions of the EG, *a*-BN, and *h*-BN within the energy range of 1 eV to 8.5 eV.

In general, one can use various optical methods to perform these large-area characterizations.²⁸⁻³² However, one of the major difficulties in analyzing these heterostructure systems was being able to precisely know the optical response of each layer in the system and to subsequently treat those responses with mathematical rigor. For instance, although the interfacial buffer layer (IBL) of EG/SiC was optically characterized in the recent past,³³ it was not done so with the level of accuracy (i.e., performed at smaller energy ranges) required for this study until earlier this year, when the IBL was carefully measured with a larger energy range, more accurate set of experimental techniques, and complimented with calculations from density functional theory.³⁴

In addition to being able to measure the dielectric responses of all the materials of interest, other fundamental observations are made which enhance the accuracy of those assessments. Specifically, the first ellipsometric observations of high-energy resonant exciton effects in EG on the 4H polytype of SiC are reported here, an observation that is vital to accurately characterize and successfully model the interactions

of light with these systems. The effects of dielectric screening within the EG and *h*-BN heterostructure, for the first time formed by this MOCVD method, are also discussed.

2. Experimental Section

2.1 Material Preparation

1. Growth of EG on SiC.

Sixteen EG samples were prepared by first performing a growth on square SiC chips that were diced from 100 mm 4H-SiC(0001) semi-insulating wafers (CREE^[see notes]), where the wafer miscut angle was measured to be about 0.10°. SiC chips were placed in a 5:1 diluted solution of hydrofluoric acid (< 10 %) and deionized water. A bath in only deionized water followed. The SiC chips were oriented such that the silicon face rested on a polished pyrolytic graphite substrate (SPI Glas 22^[see notes]). To promote homogeneous growth conditions, a diffusion barrier for escaping Si vapor must be provided. This barrier was sufficient when the chips were in close contact with the substrate, where the closeness was defined as the observation of Newton's rings. The annealing process was performed in ambient argon with a graphite-lined resistive-element furnace (Materials Research Furnaces Inc.^[see notes]). Heating and cooling rates were approximately 1.5 °C/s and the process involved: (1) Chamber evacuation and flush with 100 kPa Ar from a 99.999 % liquid Ar source, and (2) a final growth stage performed at 1900 °C.^{4,35}

2. Growth of *a*-BN on EG samples.

Seven EG samples were placed in a home-built vacuum chamber with residual base pressure of 10⁻⁶ Pa, and the *a*-BN thin films were deposited at optimized growth conditions onto the whole chip in the same manner as described in the references.^{366,37} The deposition involves the ablation of a high purity amorphous BN target with a KrF laser in 6.66 Pa of ultrahigh pressure nitrogen gas. The ablated plasma and nitrogen background gas facilitate collisional gas phase reactions to allow for stoichiometric BN film formation on the surface of the heated substrate.³⁸ The growth rate of the BN film was approximately 1 nm growth per 10 laser pulses, with the substrate stage during growth set to 200 °C. Four depositions were 50 nm thick and three were 100 nm thick.

3. Growth of *h*-BN on EG samples.

BN films were deposited in a vertical, cold-walled, RF-heated MOCVD system using TEB and NH₃ as precursors. The four EG samples were ramped to the BN deposition temperature under 6.66 kPa of flowing N₂. All depositions were conducted at 1600 °C and at 6.66 kPa total pressure using N₂ as the balance, carrier, and diluent gas with a total flow of 16.2 *standard* L/min. The term '*standard*' is defined as a flow unit in which the reference temperature is 0 °C. TEB flow was 12 µmol/min and NH₃ flow was either 10 *standard* cm³/min or 2000 *standard* cm³/min. These conditions were transferred from experiments of BN deposition on c-sapphire substrates where they yielded a BN deposition rate of 5 nm/min with 10 *standard* cm³/min of NH₃ flow or yielded self-limiting deposition of 1 to 2 monolayers of BN with 2000 *standard* cm³/min of NH₃ flow. Deposition was ended by halting TEB and NH₃ flows and cooling the samples under flowing N₂.

4. Preparation of samples for experiments.

For all samples, the back surface was roughened by a diamond-tipped scribe tool to allow for more accurate MME measurements by greatly reducing backside reflections from the SiC for photon energies below its band gap. More details on the gradual removal of layers will be presented in the main text.

2.2 Experimental Methods

1. Raman spectroscopy, atomic force microscopy, and X-ray photoelectron spectroscopy.

Raman spectroscopy was used to verify the type of material being measured and spectra were collected with a Renishaw InVia micro-Raman spectrometer^[see notes] using a 633 nm wavelength excitation laser source. A backscattering configuration was used along with a 1 μ m spot size, 300 s acquisition time, 1.7 mW power, 50 × objective, and 1200 mm⁻¹ grating. Rectangular Raman maps were collected with step sizes of 20 μ m in a 5 by 3 raster-style grid. An Asylum Cypher^[see notes] atomic force microscope in non-contact mode was used at a scan rate of 1 Hz to collect images of varying sizes under 30 μ m. X-ray photoelectron spectroscopy (XPS) measurements were performed in a commercial instrument equipped with a hemispherical electron analyzer and a monochromatic Al K α excitation as the photon source. All XPS

measurements were performed at a base pressure of 2.7×10^{-7} Pa or less, electron take-off angle of 0° with respect to the surface normal, and an energy resolution of 0.1 eV.

2. Differential reflectance contrast.

For DRC measurements, samples were probed by a combined broadband emission from a halogen and deuterium lamp with a 10 μ m spot size. DRC spectra are labelled as Δ R/R, where Δ R/R = (R_{sample} – R_{substrate})/R_{substrate}, where R_{sample} is the reflectance of the layer of interest while on the substrate, and R_{substrate} denotes the reflectance of the substrate beneath the layer of interest. The reflected light was collected by a Filmetrics F20 spectrometer.^[see notes] Measurements were performed in air at room temperature from 1.13 eV to 6.22 eV photon energies with 4 meV resolution. All presented DRC data is smoothed with ten-point adjacent averaging.

3. Mueller matrix ellipsometry.

MME measurements were performed in a Woollam-302^[see notes] vacuum-ultraviolet spectroscopic ellipsometer equipped with a nitrogen gas chamber at room temperature. The light is emitted from a xenon and deuterium lamp covering the wavelengths from 145 nm to 1240 nm and has an elliptical spot size measuring approximately 2 mm by 4 mm. Data was acquired at 65°, 70°, and 75° with the photon energy ranging from 1 eV to 8.5 eV in 0.02 eV steps.

3. Results and Discussion

To effectively elucidate optical properties for any heterostructure or thin-film system, analyzing each of the constituents is required. For that reason, we begin by evaluating the EG on 4H-SiC, which serves as the substrate for later BN growth. Figure 1 show a series of measurements taken on EG to evaluate its optical behavior. In figure 1 (a), the DRC data is presented for two cases. The first case is when the EG is pristine and unaltered, as shown by the red curve. This data, when using the SiC as the reference substrate, includes the responses from both EG and the IBL. The DRC measurements were repeated on regions where the EG, along with any small strips of bilayer epitaxial graphene which may form on the terrace edges, was peeled

away with a deposited layer of nickel.³⁹ This peel left the fully-formed IBL experimentally accessible, and upon subtracting the response exclusively from the IBL, the EG response is obtained.



Figure 1. (a) The DRC data is shown for the combination of EG and IBL (red curve). Upon removal of the EG, an IBL spectrum was acquired (violet curve) and subtracted from the total ensemble signal, yielding the response exclusively from the EG (cyan curve). The shading for all curves indicates a 1 σ uncertainty. (b) Atomic force microscopy is performed to verify the thickness of the EG, yielding 0.342 nm ± 0.088 nm and taken from an average (shown in cyan/blue triangles) of 20 profiles, some of which are shown in transparent solid colors. (c) Raman spectra are shown in the top graph for the EG/IBL/SiC areas, the IBL/SiC areas, and the SiC areas. All three spectra are averages of maps taken over 120 µm by 80 µm areas of the samples. The bottom two graphs show subtracted spectra for clarity and to verify existence of the layers of interest. (d) An example scatterplot from a Raman map shows the position versus full width at half maximum (FWHM) of the 2D (G²) peak in the spectra that are averaged above. The points are within the spread expected of homogeneous EG as reported in Ref. 4.

In figure 1 (b), EG thickness was verified by AFM and measured to be 0.342 nm \pm 0.088 nm, which is well within the expected value for EG thickness on SiC.⁴⁰ Lastly, Raman spectroscopy is used to verify the

layers that are being measured by DRC and MME, and the Raman data are shown in figure 1 (c). The response for EG shows the D, G, and G' (2D) peak and the IBL response shows the expected contribution to the Raman due to the vibrational density of states.⁴¹

The DRC measurements are useful for providing information on the absorption of the material and can be transformed in the limit of weak reflectance contrast, as for the case of a transparent substrate.⁴² Although SiC is transparent in the visible range, the optical behavior of the SiC outside of the visible range needed to be accounted for by using a generalized version of the DRC-to-absorption transformation:^{34,42}

$$\frac{\Delta R}{R} = \frac{4}{n_{SiC}^2 + k_{SiC}^2 - 1} * A \tag{1}$$

In Equation 1, *A* is the absorption and *n* and *k* are the varying optical constants of SiC over the energy range of the DRC data, about 1.12 to 6.22 eV. To maintain the highest accuracy for our analysis, optical constants for SiC were directly measured via MME for each of the samples. The approximate absorption of the EG is shown in figure 2 (a) in terms of $\pi\alpha$, along with three example absorption curves. Example 1, 2, and 3 are respectively from an exfoliated graphene sample,⁴³ a reported ellipsometric measurement of EG on 4H-SiC,³² and a tight-binding band structure model for graphene.⁴⁴



Figure 2. (a) The DRC-based absorption of EG is shown in cyan and compared to the MME-based absorption of EG in dark blue as well as three other works. (b) A schematic is presented here depicting MME measurements taken on an EG sample. (c) The MME-based dielectric function of EG is extracted in its most accurate form after accounting for the IBL and 4H-SiC beneath. The real and imaginary portions are shown in green and purple, respectively. The DRC-based dielectric function is calculated with Kramers-Kronig relations as described in the text, and its real and imaginary portions are shown in dotted orange and dotted blue, respectively. The shading for all curves indicates a 1 σ uncertainty.

Based on an initial assessment of these curves, it becomes evident that the DRC energy range (below 3 eV and above 5.5 eV) is inadequate to make a rigorous basis for comparison. To measure a more accurate set of optical constants, MME measurements are made on each of the samples. An illustration of this technique is shown in figure 2 (b). The recorded polarization data is converted by equipment software from Fresnel reflection coefficients, representing the *p* and *s* polarized light (R_p and R_s , respectively), to the quantities psi (Ψ) and delta (Δ), where $\frac{R_p}{R_s} = e^{i\Delta} \tan \Psi$. Psi and delta are further converted into optical constants of a measured material when an accurate optical model is implemented during data analysis.

Because data was analyzed by the instrument with Mueller matrix formalism, effects from depolarization and minor sample inhomogeneity are accounted for. MME measurements are more accurate than the DRC measurements because of two main factors: (1) water vapor and other potential unaccounted gases that absorb light outside the visible range are not present during the measurement, and (2) a ratio of intensities is measured as opposed to DRC where absolute intensities are measured and subtracted. Furthermore, the specialized modeling program WVASE32^[see notes] allows for careful and rigorous treatment of all layers in an optical model. Despite the advantages of MME, DRC measurements were still required for two reasons: (1) to provide a basis for self-consistent comparison of the materials' optical responses and (2) to provide a reasonable initial estimate for the dielectric function of EG, IBL, SiC, and eventually *a*-BN and *h*-BN. The latter reason significantly reduces the parameter space in the WVASE32 program for a converging fit, and this will be revisited after the next paragraph.

Following the MME measurements, a procedure was needed to properly interpret and analyze the data. As mentioned, optical constants from MME can only be extracted accurately for a specific layer if every other layer's thickness and dielectric function is experimentally well-known. The MME measurements were made on each layer of each sample to ensure the highest possible accuracy in how materials are treated in the modeling program. For instance, an EG sample would be measured with MME and DRC, then the EG itself would be peeled away.³⁹ The next MME and DRC measurements were then performed on what was just the IBL on SiC. After a 7 s argon dry etch to remove the IBL,³⁴ MME and DRC measurements were repeated once again. Even though the measurements were taken in a reasonable order, the analysis had to be done starting with the most recent measurement. The SiC optical constants were accurately determined directly by MME measurements. To analyze the MME data from the IBL on SiC, the SiC had to be well-known. The thickness of the IBL is known from recent work,⁴⁵ and thus one could accurately extract the optical constants of the IBL. And finally, to analyze the EG MME data, both the IBL and SiC needed to be well-known. The thickness of the EG was determined by AFM, and so the accurate optical constants were extracted and labelled as the real (ϵ_1) and imaginary (ϵ_2) portions of the dielectric function of EG in figure

2 (c), where $\varepsilon = \varepsilon_1 - i\varepsilon_2$. For details regarding the Bruggeman effective medium approximation (EMA),⁴⁶ please see the Supporting Information.

The general method for analyzing MME data is straightforward, but an estimate for each layer's dielectric function was required to reduce the parameter space in the modeling program. With the use of the Kramers-Kronig relations, one can reasonably estimate a material's dielectric function for a given range of photon energies, which has been done before for other two-dimensional materials' DRC spectra.^{47,48} The approximate absorption spectrum for EG shown in figure 2 (a) was found with this relation: $\frac{\varepsilon_2}{A(E)} = \frac{hc}{EL}$, where \hbar is the reduced Planck constant, *c* is the speed of light, *E* is the energy, and L is the layer thickness.⁴⁹ With an approximate imaginary portion of the dielectric function as the input, the Kramers-Kronig relation shown below yielded the real portion:

$$\varepsilon_1(E) = 1 + \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\varepsilon_2(E')}{E' - E} dE'$$
⁽²⁾

After the estimated dielectric function is extracted from DRC data, a thin film analysis procedure was implemented on this dielectric function to generate a DRC curve comparable to the in curve in figure 1 (a).⁵⁰ By using Equation 1, the same general estimation of the dielectric function was done for the IBL. The resulting DRC-based dielectric function is also shown in figure 2 (c) as dotted curves for comparison to the MME-based dielectric function. One should note that although backside reflections in SiC were drastically reduced by scattering from a roughened back surface, some oscillations indicating internal reflections remain below 3 eV. The MME-based dielectric function for EG was also used to calculate the absorption, which was added to figure 2 (a), and now allows us to return to the discussion relevant to the latter figure.

Now that the absorption spectra reported for graphene can be adequately compared, we note two features (see figure 2 (a), MME in blue). We can observe both the 4.6 eV absorption peak due to excitonic effects,^{29,43,51} and more notably, the high energy absorption peak around 6.1 eV, which can be attributed to

resonant excitons between the σ -to- σ^* transition at the Brillouin zone Γ point.⁵² Measurements of EG on the 4H polytype of SiC appeared to be discrepant with ours in the absorption above 4 eV (see example curve 2 in figure 2 (a)).³² Upon further inspection, we find that the discrepancy arises because of the IBL not being fully accounted for in example curve 2. The IBL has a stronger absorption above 4 eV, as shown by Hill *et al.*, and so should provide a substantial increase to the measured absorption of Ref. 32. With the analysis thus far, an accurate dielectric function of EG on 4H-SiC was experimentally determined and can now be used for analyzing other relevant systems.

One such system is a-BN on EG. The thin film system was developed to encapsulate, and thereby preserve, certain electrical properties of EG.⁵ The systems were also analyzed here for their optical properties, and while the EG DRC and absorption fell within the uncertainty of the set of previouslymeasured EG samples, we are also able to measure the DRC, calculate the absorption, and extract the dielectric function of the 50 nm thick a-BN film in figure 3 (e). Figure 3 (a) and (b) are a set of XPS measurements taken on these samples to demonstrate successful deposition of the *a*-BN film by measuring the B 1s and N 1s photoelectrons. The main B 1s feature in figure 3 (a) is deconvoluted with two Voigt functions and indicates two boron-containing chemical species are present at the surface. The low binding energy feature centered at 189.4 eV and in green is assigned to BN, and the high binding energy feature centered at 190.9 eV in blue is assigned to a boron oxynitride (BN_xO_y). The majority of the B atoms detected on the surface are as BN. At higher binding energies of the B 1s spectrum (196 eV to 201 eV), a broad, low intensity feature is detected and assigned to π to π^* which is present in *h*-BN and indicates that the electronic properties of these films are similar to that of *h*-BN.⁵³ The same analysis is applied to the nitrogen atoms in figure 3 (b), which are mostly present at the surface as BN, consistent with the B 1s XPS results. The low binding energy feature centered at 396.9 eV and in green is assigned to BN, and the high binding energy feature centered at 398.5 eV in blue is assigned to a boron oxynitride (BN_xO_y). A broad, low intensity feature is also present between 404 eV and 408 eV and is assigned as a π to π^* and in agreement with our assessment that these films have h-BN-like electronic properties.⁵³ When the layers beneath the a-BN

needed to be exposed for MME and DRC measurements, aqua regia (three parts hydrochloric acid to one part nitric acid) was used to remove the BN film. Figure 3 (c) shows the Raman spectra before and after this treatment to verify that the EG was not damaged. In figure 3 (e), our resulting dielectric function is compared to that of a calculation of the dielectric function of *a*-BN under strong negative bias using a Tauc-Lorentz model for amorphous semiconductors.⁵⁴ Our DRC measurements allow us to make a very good estimate of the dielectric function of the film, and this is also shown in figure 3 (e) as green and brown dotted curves. Although the absolute values of the dielectric function are different between our study and Lousinian *et al.*,⁵⁴ the general trend of the real and imaginary portions of the function are identical. Moreover, in the limit of small energies, the dielectric function agrees with the measured value of the dielectric constant at 1 kHz.³⁹



Figure 3. Both (a) and (b) show XPS data for B 1s and N 1s, respectively, verifying the existence of boron and nitrogen on *a*-BN-coated EG samples. The XPS B 1s and the N 1s peaks are centered around 190 eV and 397 eV, respectively. The π to π^* is a signature of electronic structure similar to that of *h*-BN, but much subtler in the case of *a*-BN. (c) After using aqua regia to remove *a*-BN films, Raman spectra are collected on multiple spots to verify that the BN films are successfully removed while also showing that the EG remains intact. The inset of this graph shows the difference of the two curves normalized to the *a*-BN/EG spectrum. (d) DRC data is shown for the *a*-BN films in the top half of the graph (orange) while the absorption, obtained with Equation 1, is shown in the bottom half of the graph (pink). (e) The *a*-BN dielectric function is extracted for both DRC-based (dotted green and brown dotted curves) and MME-based (magenta and blue curves) data. The dielectric function from a similar study by Lousinian *et al.* is shown for comparison (shaded yellow and light blue regions).

Another system of interest was the *h*-BN/EG system, which was produced for the first time with the TEB and NH₃ MOCVD precursor method described in the experimental section. The intent of optically probing this system was to learn about the possible interactions between the few-layer thick *h*-BN and EG, which is used here as a growth template.

In figure 4 (a), the DRC, absorption, and Raman spectra are shown for the *h*-BN film, along with a quick comparison of the DRC measurement made by Hoffman *et al.*⁵⁵ The AFM profile yields a thickness of 1.096 nm \pm 0.137 nm in figure 4 (b) which includes both the *h*-BN and the EG. The measured thickness of the film is 0.754 nm \pm 0.225 nm, which equates to between two and three layers of *h*-BN.⁵⁶ To successfully perform DRC and MME measurements, the *h*-BN needed to be removed in such a way as to leave the EG unharmed. Unlike a-BN, h-BN is chemically resistant to aqua regia and so the nickel peel method was implemented instead. For a Ni/*h*-BN bilayer/Graphene/IBL/SiC structure, the various interface energies per atom have been calculated and measured in other works, and take on the following values: > 140 meV for nickel-*h*-BN (140 meV reported for nickel-EG),^{39,57} about 86 meV for *h*-BN-*h*-BN,⁵⁸ about 55 meV - 75 meV for *h*-BN-graphene,^{59,60} and about 106 meV for EG-IBL.³⁹ An illustration is provided in Figure 4 (d) for visual clarity.



Figure 4. (a) DRC data, both a solid curve for the average (orange) and a set of example measurements (slightly transparent curves), are shown for the *h*-BN films in the top panel of the graph (orange vertical axis). The absorption of the average DRC curve for *h*-BN, obtained with Equation 1, is shown in central panel of the graph (pink vertical axis with identical horizontal axis as top panel). In the bottom panel (red axes), the Raman data for the *h*-BN on EG is shown in dark cyan, while the post-*h*-BN-removal Raman data is shown in dashed cyan. (b) AFM profiles were obtained and averaged to yield the approximate thickness of the *h*-BN/EG heterostructure: 1.096 nm \pm 0.137 nm. (c) The absorption for EG is found while in the heterostructure (Case 2, red curve) and after *h*-BN is removed (Case 1, dark blue curve), with all curves shown in the top panel of the graph. In the bottom panel, a difference between cases 1 and 2 is shown, indicating that a phenomenon is observed beyond experimental uncertainty (shaded cyan region). (d) The illustration depicts the rationale for why one would expect a nickel deposition to successfully peel the *h*-BN from the EG while leaving the EG intact. The weakest point is between the *h*-BN and EG.

After successfully removing the *h*-BN with a nickel peel, all measurements were repeated on the EG surface, whose existence was still verified with Raman (figure 4 (a)), filtered optical microscopy,⁶¹ and DRC measurements (figure 4 (c)). When comparing EG's DRC data before and after *h*-BN removal,

absorption appears to be lower by $0.5\pi\alpha$ and is redshifted by approximately 60 meV. In the bottom panel of figure 4 (a), observed Raman changes from lone EG to the heterostructure include a 3 cm⁻¹ blueshift and 25 cm⁻¹ broadening of the G' (2D) mode, both of which are associated with a change in the dielectric environment.⁶² These observations are also signatures of enhanced electron-electron scattering with the increased level of doping,⁶³ which we calculate to be approximately 5×10^{12} cm⁻² additional carriers.⁶⁴ The additional doping is expected to cause a redshift in the observed exciton absorption peak of similar shift in energy to what we observe.⁶⁵ The absorption being reduced can be attributed to the reduction of overall *sp*² order in the carbon atoms,⁶⁶ likely due to the presence of *h*-BN. Such reductions have also been observed with increases in *sp*² disorder caused by oxygen plasma exposure.^{66,67}

Based on these effects on EG, we modified the optical model accordingly and used it to obtain the dielectric function of the grown *h*-BN, shown in figure 5 (a). As with the *a*-BN, we compare our result to the DRC-based dielectric functions (shown as green and brown dotted lines) as well as an independent measurement of the in-plane imaginary portion of the dielectric function from Mamy *et al.* (shown as a dotted yellow curve).⁶⁸ Our MME-based ε_2 is in excellent agreement with Mamy *et al.* and, furthermore, our measurement is an expansion of their original measurement. The corresponding ellipsometric data is shown in figure 5 (b) to justify the optical model we used. The optical model used experimentally obtained data from the SiC, IBL, and EG, thereby leaving the dielectric function of the *h*-BN as the only fit parameter.



Figure 5. (a) The *h*-BN dielectric function is extracted for both DRC-based (dotted green and brown dotted curves) and MME-based (magenta and blue curves) data. The imaginary portion of the dielectric function from a study by Mamy *et al.* is shown for comparison (yellow dotted curve).⁶⁸ (b) The ellipsometric data for the *h*-BN is shown here, with the psi data in the top panel and the delta data in the bottom panel. The red curves are the experimental results while the teal curves are the best-fit, model-generated data based on the experimentally known properties of the SiC, IBL, and EG.

4. Conclusion

In conclusion, EG was used as a template to form amorphous and hexagonal boron nitride (*a*-BN and *h*-BN) heterostructures whose properties could be examined on the millimeter-scale. Using Mueller matrix ellipsometry (MME), atomic force microscopy (AFM), Raman spectroscopy, and differential reflectance contrast (DRC), the optical absorption and dielectric functions of the EG, *a*-BN, and *h*-BN are extracted within the energy range of 1 eV to 8.5 eV. Moreover, the first ellipsometric observations of high-energy resonant exciton effects in EG on the 4H polytype of SiC are reported, as well as the effects of dielectric screening within the EG and *h*-BN heterostructure. The understanding gained in the interfacial contributions to dielectric properties of EG heterostructures in this study will be vital as 2d material-based devices become commonplace for future electronic systems.

Supporting Information

Supporting Information is available from the IOP Online Library or from the author.

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Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information: Measuring the dielectric and optical response of millimeter-scale amorphous and hexagonal boron nitride films grown on epitaxial graphene

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1. X-ray photoelectron spectroscopy - additional details



Figure S1. XPS measurements from survey spectra are shown here along with the labels in (a) and (b), respectively representing the sample prior to and following the removal of the *a*-BN film. The expected differences are present, with the boron and nitrogen atoms disappearing after the removal. (c) and (d) show the same regions with a lack of signal, indicating a successful removal of *a*-BN with aqua regia.

XPS measurements were primarily taken to verify the existence of *a*-BN both before and after its removal from EG samples. The removal of BN is confirmed afterwards by the survey XPS spectra in figure S1 (a) and (b), showing the absence of any B 1s feature between 193 eV and 188 eV and N 1s feature between 400 eV and 395 eV. In the B 1s energy window seen in figure S1 (c), there is a broad feature between 195 eV and 200 eV detected, and this is due to the Si 2s plasmons from the SiC substrate. As a secondary note, figure S1 (b) shows trace amounts of F on the surface of the EG after the *a*-BN removal, and this atom is likely a remnant from when the chip is processed prior to the EG growth (the chips are washed in an HF solution, see main text for more details).

2. Variation in EG DRC measurements



Figure S2. DRC measurements for several EG samples are shown here to give insight into the variation from sample to sample. These curves constitute the set which determines the uncertainty presented in the main text. The solid cyan curve is the average of the five transparent curves which represent the five samples used as the control group (no material was grown on them).

EG samples have some level of variation in their DRC measurements, and so we compare them above in figure S2 to give the reader the origin of the 1 σ uncertainty, which is shown in the main text by shading the region surrounding the average DRC curve.

3. Ellipsometric data for EG



Figure S3. Raw ellipsometric data is shown above to include another metric for indicating changes introduced by the various layers of the EG samples. The top panels show psi data and the bottom panels show delta data, and all graphs are marked with the angle of incidence. The MME data curves taken on bare SiC are green, while the curves for IBL on SiC are purple, and the curves for EG on IBL on SiC are cyan. There is a notable change for all three scenarios, but the interpretation is not as straightforward without an optical model.

EG samples were measured on all three types of surface configurations to ensure the highest possible accuracy with regards to how each material is treated in the MME analysis. For instance, it would be insufficient to build an optical model for an EG/IBL/SiC system while assuming that the SiC material file provided by the WVASE32^[see notes] program was an exact representation of the SiC we actually measure. This is the reason for directly measuring the optical constants of each sample's SiC and creating customized material files for each constituent of each sample.

4. The Bruggeman effective medium approximation (EMA)

To successfully model the optical constants for the IBL, the Bruggeman effective medium approximation (EMA) was implemented to account for the surface roughness. The relevant layers of the model for the EG

system are, starting from the bottom up: (1) A 0.5 mm thick SiC layer. (2) An IBL of thickness 0.25 nm.¹ (3) The EG layer of thickness 0.342 nm (AFM). (4) An EMA layer, limited to three constituents, had equal percentages of SiC and void (where no material is present) as well as a smaller percentage of an EG/IBL blend. The SiC and void are only approximately equal, as seen in figure S4 (a) and (b). The EG/IBL, required for the model in figure S4 (b), is a blend of the two dielectric functions in proportion to their thicknesses. The surface roughness was estimated to be around 1 nm based on AFM measurements, and the resulting model, calculated with WVASE32, $^{\circ}$ yielded the dielectric function of EG.

In the cases of *a*-BN and *h*-BN, the EMA layer was 50 % of the relevant BN form and 50 % void since the thickness of the layers were large enough to dominate the cross-sectional areas, as seen in figure S4 (c) and (d).



Figure S4. EMA layer construction is depicted in the illustration above. These are cross-sections of the sample where *x* is the length of a terrace that forms during EG growth and is typically on the order of $10 \square m$ (a) We use surface roughness values based on AFM measurements. For this example, the surface roughness of the example *h*-BN sample is 1 nm. When modeling for the IBL, the void and SiC are roughly equal to 42 % and the IBL is 16 % of the total EMA layer. (b) When modeling for the EG/IBL case, the void and

SiC are roughly 32 % each and the EG/IBL blend is 36 %. (c) When *h*-BN is on top, and since its thickness is roughly 0.75 nm, it can be approximately to have equal contribution to the EMA layer as the void, both being 50 %. (d) The *a*-BN system is shown having a clear 50 % composition in the EMA layer.

5. Additional comments and discussion about homogeneity

The intended electrical application of the *h*-BN/EG heterostructure, whereby this system could be made into a protected Hall bar for metrological measurements of the quantum Hall effect (QHE), was unsuccessful. Hall bar devices were fabricated with dimensions of 0.4 mm and 2.2 mm and are usually done so to accurately measure the QHE within 1 part in 10^8 . The largest difficulty with the *h*-BN/EG heterostructures were leaky top gates. The additional layer of Al₂O₃ deposited by atomic layer deposition was also insufficient to prevent leakage current.

The same phenomenon was found with *a*-BN/EG heterostructures, where the apparent existence of pinholes prevented electrical measurements for millimeter-sized devices.

On the matter of graphene homogeneity, we use confocal laser scanning microscopy to examine the quality of the grown graphene, and an example acquisition is shown in figure S5. The determination of homogeneity based on these images is more clearly elaborated on in a recent work.² Once the EG is determined to be suitable, it is used as a template for the *h*-BN growth. Examples of the millimeter-scale coverage of the material is shown in figure S6 as a device that was also used for AFM measurements in the main text.



 $-----= 50 \,\mu m$

Figure S5. Confocal laser scanning microscopy (CLSM) is a technique which combines the breadth of image acquisition coverage of a traditional optical microscope with the resolution of a wide-field atomic force microscope image. (a) To determine the homogeneity, we scan chips with grown EG using CLSM. In this image, an example of a poorly grown sample shows very obvious markers for the boundaries between

the EG and the interfacial buffer layer (and SiC). (b) and (c) shows a pair of images taken from the same chip with excellent EG growth, where no visible terraces or voids can be seen. The characteristics of the image filtering is what contributes to the appearance of interference patterns on the surface. The scale bar is set to $50 \square m$.



Figure S6. The optical image above shows an example region of *h*-BN on EG, with the heterostructure already fabricated into the shape of a Hall bar. The width of the figure is about 700 \Box m and the height is about 450 \Box m. The total device measures 0.4 mm wide by 2.2 mm long. The shaded region on the right side is the *h*-BN/EG heterostructure.

NOTES

^{*ô*} Commercial equipment, instruments, and materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology or the United States government, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

¹ Nair M N, Palacio I, Celis A, Zobelli A, Gloter A, Kubsky S, Turmaud J P, Conrad M, Berger C, de Heer W, Conrad E H, Taleb-Ibrahimi A and Tejada A 2017 Band Gap Opening Induced by the Structural Periodicity in Epitaxial Graphene Buffer Layer *Nano Lett.* **17** 2681

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