Dielectrics



# High-Performance Polymers Sandwiched with Chemical Vapor Deposited Hexagonal Boron Nitrides as Scalable High-Temperature Dielectric Materials

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Polymer dielectrics are the preferred materials of choice for power electronics and pulsed power applications. However, their relatively low operating temperatures significantly limit their uses in harsh-environment energy storage devices, e.g., automobile and aerospace power systems. Herein, hexagonal boron nitride (h-BN) films are prepared from chemical vapor deposition (CVD) and readily transferred onto polyetherimide (PEI) films. Greatly improved performance in terms of discharged energy density and chargedischarge efficiency is achieved in the PEI sandwiched with CVD-grown h-BN films at elevated temperatures when compared to neat PEI films and other high-temperature polymer and nanocomposite dielectrics. Notably, the h-BN-coated PEI films are capable of operating with >90% charge-discharge efficiencies and delivering high energy densities, i.e., 1.2 J cm<sup>-3</sup>, even at a temperature close to the glass transition temperature of polymer (i.e., 217 °C) where pristine PEI almost fails. Outstanding cyclability and dielectric stability over a straight 55 000 charge-discharge cycles are demonstrated in the h-BNcoated PEI at high temperatures. The work demonstrates a general and scalable pathway to enable the high-temperature capacitive energy applications of a wide range of engineering polymers and also offers an efficient method for the synthesis and transfer of 2D nanomaterials at the scale demanded for applications.

Dielectrics are commonly used as electrical energy storage materials in advanced electronics and electric power systems because of their superior power density (on the order of million watt) and excellent rate capability (on the order of micro-second).<sup>[1]</sup> Polymer dielectrics are the materials of choice compared to their ceramic counterparts owing to their lightweight,

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mechanical flexibility, low cost, scalability, as well as high breakdown strength and great reliability.<sup>[2-10]</sup> Yet, their comparatively low working temperatures limit their usage in a wide range of applications under harsh environments, e.g., electric vehicles and aerospace systems, which require an operating temperature of at least 140 °C.<sup>[11]</sup> The maximum operating temperature of biaxially oriented polypropylene (BOPP) films, the state-of-the-art commercially available dielectric polymer, is limited to about 105 °C.<sup>[12]</sup> When the working temperature exceeds 80 °C, the voltage applied to BOPP must be significantly derated due to sharp rise in dielectric loss and corresponding decrease in the charge-discharge efficiency under high applied fields. Hence, a secondary cooling system with a coolant temperature of 60-80 °C is required when BOPP film capacitors operate at elevated temperatures and high electric fields. This undesirably increases the weight and volume of the integrated power system and decreases the fuel efficiency.

It is believed that electrical conduction is the dominant energy loss mechanism of dielectric materials at high fields and elevated temperatures.<sup>[13,14]</sup> In addition to reduced charge-discharge efficiency and increased dielectric loss, the exponentially increased tunneling current with electric field and temperature generates Joule heating and thus causes thermal runaway in dielectric polymers. Therefore, under high fields and elevated temperatures, dielectric polymers are always broken down at a temperature that is well below their thermal transition temperatures, such as glass transition temperatures  $(T_{g})$ .<sup>[15]</sup> Several approaches have been explored to enhance the temperature stability of polymer dielectrics. A cross-linking method is utilized in polyethylenes for high voltage wire and cable insulation with enhanced heat resistance<sup>[16]</sup> and has also been demonstrated to improve elevated-temperature capacitive properties of ferroelectric poly(vinylidene fluoride-co-chlorotrifluoroethylene)s.<sup>[17,18]</sup> Hexagonal boron nitride (*h*-BN) is the structural analog of graphite, where alternating boron and nitrogen atoms replace carbon atoms in the sp<sup>2</sup> lattice structure and result in a large band gap of  $\approx 5.97 \text{ eV}$ .<sup>[19]</sup> The incorporation

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Figure 1. Low-magnification SEM (top), higher magnification SEM (middle), and high-resolution TEM (bottom) images of the *h*-BN films grown for a) 10, b) 20, and c) 45 min.

of highly insulating h-BN nanosheets into the cross-linked bisbenzocyclobutene (c-BCB) yields the polymer nanocomposites (c-BCB/BNNS) with great improvements in the energy storage and discharge capacity at high temperatures.<sup>[15,20]</sup> Such enhancement in the energy storage also stems from high intrinsic thermal conductivity of *h*-BN, which facilitates heat dissipation to avoid thermal runaway. h-BN nanosheets, however, are mostly prepared from solution-phase exfoliation of h-BN powders under sonication.<sup>[21-25]</sup> Although liquid exfoliation has been widely used to produce h-BN nanosheets, it is a time-consuming process that suffers from low yield (e.g., less than 1 g) and the use of a large amount of chemical reagents. Moreover, the high-performance engineering polymers currently explored as high-temperature dielectric materials,<sup>[26-31]</sup> such as polycarbonates, poly(ether ether ketone) s and polyimides, have poor solution solubility, especially in the solvents, e.g., dimethylformamide, used in the exfoliation of *h*-BN powders. Therefore, the preparation of the *h*-BN/engineering polymer nanocomposites using the solution mixing and casting methods is not feasible. It is thus highly desirable to develop scalable and cost-effective approaches to high-temperature polymer dielectrics while taking advantage of unique features of *h*-BN nanosheets.

Chemical vapor deposition (CVD) is, in contrast, a reproducible and scalable method for the synthesis of 2D materials, such as graphene, BN, and transition metal dichalcogenides.[32-34] Here, we demonstrate, for the first time, successful transfer of the large-scale high-quality h-BN films prepared from CVD onto polyetherimide (PEI) films. PEI has been one of the leading hightemperature polymer dielectrics. For example, PEI can discharge an energy density of 1.57 J cm<sup>-3</sup> with an efficiency of 73.8% at 400 MV m<sup>-2</sup> and 150 °C, surpassing all the commercially available polymer dielectrics.<sup>[15]</sup> By surface-coating PEI with CVDgrown h-BN films, superior high-temperature energy storage properties have been achieved when compared to original PEI films and other high-temperature polymer and nanocomposite dielectrics. The h-BN-coated PEI can operate with more than 90% charge-discharge efficiencies under high electric fields even at the temperature very close to its  $T_{\rm g}$  (i.e., 217 °C), where pristine PEI films nearly fail. The scalability and processability of the method presented here are expected to enable the continuous production of 2D nanomaterial-functionalized polymers at large scales for advanced electronics and energy devices.

*h*-BN films with different thicknesses were grown on copper (Cu) foils using low-pressure CVD at 1050 °C (see Supporting Information for details). **Figure 1** displays low-magnification





Figure 2. Schematics of the transfer process of the CVD-grown *h*-BN films onto the polymer films.

scanning electron microscopy (SEM) (top), higher magnification SEM (middle), and high-resolution transmission electron microscopy (HRTEM) (bottom) images of the synthesized h-BN films. The wrinkles observed in Figure 1a-c (top and middle) are characteristic of *h*-BN, which form during cooling after the growth as a result of the negative thermal expansion coefficient of *h*-BN.<sup>[35]</sup> As can be seen in the SEM micrographs, the wrinkles become thicker with increasing growth time and eventually are not discernible for the thickest sample (i.e., 45 min growth). This might be attributed to the redeposition of nanocrystalline BN from the CVD reactor walls onto the film surface after a prolonged growth<sup>[36]</sup> or the nucleation of 3D structures at defect sites on the surface owing to crystallinity degradation with growing thickness.<sup>[37]</sup> The structure of the *h*-BN films with different thicknesses has been examined using transmission electron microscopy (TEM) imaging and spectroscopy. The h-BN films with various thicknesses were directly transferred from the Cu substrates to Quantifoil TEM grids using a poly(methyl methacrylate) (PMMA)-assisted technique (see Supporting Information for details). The number of lines at a folding edge or a wrinkle shown in the HRTEM images (Figure 1, bottom) of the *h*-BN films was counted to determine the thickness (i.e., number of layers). An almost a linear relationship is observed between thickness of *h*-BN films and the growth time, which is consistent with previous reports.<sup>[35,38]</sup> In addition, the thickness of the *h*-BN films was measured using atomic force microscopy (AFM), after the films were transferred onto a silicon substrate using PMMA. The AFM images and corresponding height profiles of the synthesized h-BN films are presented in Supporting Information. Figure S1 in the Supporting Information demonstrates their characteristic thickness, which is in good agreement with the TEM observations.

The CVD-grown *h*-BN films were transferred onto PEI films ( $\approx$ 12.5 µm, General Electric) using a novel approach as illustrated in **Figure 2**. First, two pieces of *h*-BN films on the growth substrate (i.e., Cu) with the same dimensions were cut

and flattened. The topside of the Cu substrate with continuous h-BN films was marked. The PEI was then sandwiched between two *h*-BN/Cu films with PEI in direct contact with *h*-BN on both sides. The whole assembly was hot-pressed under  $\approx$ 26 000 Torr at 230 °C, a temperature that is slightly above the  $T_g$  of PEI, for 30 min. We then etched the Cu substrates from both sides of the assembly using iron trichloride solution (0.5  $\times$  FeCl<sub>3</sub>). Chemical etching of the Cu layer was done at 50 °C for faster etching. Samples were left floating on the etchant solution for about 20 min (each side) at 50 °C until all of Cu were dissolved into the solution. Next, the samples were rinsed with deionized water for 15 min on each side to remove residual etchant. The sample was finally removed from the water bath and left in air for few minutes to dry. It is worth noting that this etching and transfer process can be alternatively accomplished using a costand time-effective roll-to-roll production method.<sup>[39]</sup>

The optical image of Cu/h-BN/PEI/h-BN/Cu assembly after hot-compressing is given in Figure 3a, while the sandwichstructured *h*-BN/PEI/*h*-BN films after etching the Cu foil can be seen in Figure 3b. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) was performed on the h-BN/PEI/h-BN film to determine the success of the transfer process. We carried out the measurements on both sides of the sample and at the interface of the region coated with *h*-BN and pristine PEI film (marked with a blue-dashed rectangle on Figure 3b). It is evident from Figure 3c,d that boron is uniformly distributed on the right side of the film (i.e., the area coated with h-BN) while no boron signal was found on the left side (i.e., pristine PEI films). Thin slices of h-BN/PEI/h-BN films were also prepared using microtomy for cross-sectional TEM imaging (see Supporting Information for details). HRTEM imaging (Figure 3e) combined with electron energy-loss spectroscopy (EELS) analysis (Figure 3f) further confirms the successful transfer of the *h*-BN film onto PEI. Figure 3e shows the cross-sectional HRTEM image of the sandwich-structured films at the interface of h-BN and PEI, providing a strong evidence of the existence of h-BN







**Figure 3.** a) The Cu/*h*-BN/PEI/*h*-BN/Cu assembly after hot-pressing. b) The *h*-BN/PEI/*h*-BN film after etching the Cu substrates. Tof-SIMS maps of boron obtained from c) side 1 and d) side 2 of the sandwiched film, verifying the homogeneous distributions of boron in the region with *h*-BN. e) Cross-sectional HRTEM image of the microtomed slice of the sandwich-structured film, confirming the presence of the *h*-BN film on the surface of PEI. f) EELS spectrum of the *h*-BN/PEI/*h*-BN film observed at the PEI surface.

on the PEI surface. Moreover, the EELS spectrum (Figure 3f) uncovers the chemical compositions of the layer-structured film at the interface, displaying three evident edges starting at 183, 275, and 399 eV attributable to the characteristic *K*-shell ionization edges of boron, carbon, and nitrogen, respectively.<sup>[40]</sup> The carbon signal may come from the PEI region and/or potential carbon redeposition during imaging.

As revealed in dielectric spectra shown in Figure S2 in the Supporting Information, the *h*-BN/PEI/*h*-BN films retain the distinct weak-field dielectric properties of PEI, e.g., stable dielectric constant up to 200 °C. The capacitive energy storage properties of the films were analyzed by high-field polarization–electric field (*P*–*E*) loops at elevated temperatures.<sup>[41]</sup> The widening (or opening) of *P*–*E* loops depicts a deviation from the linear behavior of the electrical polarization versus the applied field and corresponds to the dielectric loss (space-charge, conduction, etc.). As exemplified in

Figure S3 in the Supporting Information, it is evident that the introduction of h-BN onto PEI drastically narrows the *P*–*E* loops. While the thickness of *h*-BN layer has a marginal effect on the weak-field dielectric constant and loss of the h-BN/PEI/h-BN films (Figure S2, Supporting Information), the *P*–*E* loops of the sandwiched films become slimmer with the increase of h-BN film thickness, indicative of reduced high-field loss with thicker coatings of h-BN. For instance, the dielectric loss decreases continuously from 74.2% of PEI to 24.3%, 22.1%, and 10.8% of the *h*-BN/PEI/*h*-BN films coated with 6-, 11-, and 19-layered h-BN, respectively, measured at 400 MV m<sup>-1</sup> and 150 °C. Figure S4 in the Supporting Information summarizes the dielectric loss of the h-BNcoated PEI with varied h-BN layer thicknesses and pristine PEI films measured at different temperatures and applied electric fields. Apparently, the h-BN/PEI/h-BN-sandwiched films possess much decreased high-field high-temperature







**Figure 4.** Charge–discharge efficiency of the dielectrics as a function of temperatures measured at an applied field of a) 200, b) 300, and c) 400 MV m<sup>-1</sup>. d) Discharged energy density achieved at above 90% charge–discharge efficiency at varied temperatures.

dielectric loss in comparison to pristine PEI. For example, at 200 °C and an applied field of 300 MV m<sup>-1</sup>, pristine PEI exhibits a dielectric loss of 71%, whereas the losses of the PEI films coated with 11- and 19-layer *h*-BN are only 9% and 7%, respectively. It is understood that substantial reductions in dielectric loss arise from the introduction of *h*-BN, which effectively blocks the charge injection from electrodes.<sup>[15,20]</sup> In particular, as demonstrated in our simulations,<sup>[20]</sup> the sandwiched structures are known to display much smaller leakage current than the uniformly mixed nanocomposites. The basic mechanism of the injection of carriers from metal electrode into dielectric films includes Schottky emission and tunneling, in which the injection current is critically dependent on the interfacial barrier height. As illustrated in Figure S7 in the Supporting Information, the introduction of h-BN layer causes the band alignment at the PEI/h-BN interfaces and builds a potential barrier due to their differences in bandgap and electron affinity. PEI has a bandgap of 3.16 eV assessed from our first-principles calculations (see Supporting Information for details), whereas a bandgap of 5.97 eV is experimentally determined for h-BN.<sup>[42]</sup> The electron affinity for PEI is estimated to have a positive value around 2.17 eV from the first-principles calculations, while it is a negative value for h-BN.<sup>[42]</sup> As a result, an electron barrier larger than 5.1 eV is established at the interface of PEI/h-BN/Au, which is significantly larger than the barrier height of typical metal electrode-dielectric polymer contacts, e.g., 3.2 eV of BOPP/Au and 2.93 eV of PEI/Au, indicating that charges are more difficult to be injected from electrode into the h-BN-coated PEI films. Consistent with the calculations of the energy barrier, as presented in Figure S8 in the Supporting Information, it is found experimentally that h-BN-coated PEI has an electrical resistivity that is more than one order of magnitude higher than pristine PEI films, e.g.,  $3.69\times 10^{13}$  versus  $2.34\times 10^{12}~\Omega$  m measured at 150 °C and 200 MV m<sup>-1</sup>, which is even greater than the newly developed high-temperature polymer nanocomposite c-BCB/BNNS with an electrical resistivity of  $8.48\times 10^{12}~\Omega$  m.  $^{[15]}$ 

The improvement in electrical resistivity and corresponding decrease in dielectric loss results in substantial enhancements in discharged energy density and charge–discharge efficiency of the h-BN/PEI/h-BN sandwiched films.



For capacitive energy storage, the amount of stored electrical energy that can be released from dielectrics, i.e., discharged energy density, is a central parameter as improvements in energy density enable compactization and modernization of electrical power systems. An equally critical attribute for the evaluation of dielectric materials is the charge-discharge efficiency calculated from the ratio of discharged energy density versus total stored energy density. A low value of the chargedischarge efficiency denotes the presence of large dielectric loss, which causes Ohmic heating to induce thermal runaway and degrade dielectric materials during continuous operations.<sup>[15]</sup> Therefore, it is more meaningful to improve the energy density of dielectrics with a prerequisite of a high charge-discharge efficiency. Figure 4 compares the chargedischarge efficiency of 19-layer h-BN-coated PEI with other high-performance dielectric polymers and nanocomposites, including pristine PEI, BOPP, c-BCB/BNNS, fluoropolyester (FPE), and polvimides (PI, Kapton), as a function of temperature measured under applied fields ranging from 200 to 400 MV m<sup>-1</sup>. Evidently, *h*-BN-coated PEI outperforms all the currently available polymer dielectrics, e.g., at 200 MV m<sup>-1</sup> and 200 °C, h-BN-coated PEI has a charge-discharge efficiency of 96% in comparison to 90% of c-BCB/BNNS, 59% of PEI, 37% of PI, and 29% of FPE. Even at 300 MV m<sup>-1</sup> and 200 °C, h-BN-coated PEI still retains an efficiency of 91%, while the efficiencies drop to 83% and 29% for c-BCB/BNNS and PEI, respectively, and none of the other dielectric polymers are able to survive. The discharged energy densities achieved at above 90% charge-discharge efficiency are summarized in Figure 4d, in which marked improvements are manifest with the PEI coated with the *h*-BN surface layers. For instance, at 100 °C, the discharged energy densities of h-BN-coated PEI, c-BCB/BNNS, PEI, FPE, BOPP, and PI are 2.93, 2.38, 2.35, 0.82, 0.56, and 0.45 J cm<sup>-3</sup>, respectively, with their charge-discharge efficiencies >90%. The advantages of coating the h-BN surface layers onto PEI are more distinct with increasing operating temperatures. At 200 °C, the *h*-BNcoated PEI film delivers an energy density of 1.19 J cm<sup>-3</sup>, more than double that of *c*-BCB/BNNS nanocomposite which is the next best dielectrics under investigation. To examine the stability of the h-BN/PEI/h-BN sandwiched films under electric fields and elevated temperatures, the cyclic fast discharge experiments have been carried out at 150 °C and 200 MV m<sup>-1</sup>. Remarkably, as shown in Figure 5, no sign of degradation in the discharged energy density and the charge-discharge efficiency has been detected in the h-BN/ PEI/h-BN films coated with 19-layered h-BN over a straight 55 000 cycles of charge-discharge. Comparatively, pristine PEI film begins to display noticeable variations in the discharged energy density and the charge-discharge efficiency starting from the 1000th cycle.

In summary, we have presented a facile and versatile approach to the PEI films sandwiched with *h*-BN, in which the CVD-grown *h*-BN films are directly transferred onto both sides of the polymer films. The fidelity of synthesis and transfer has been confirmed by electron microscopy imaging and electron energy loss spectroscopy as well as TOF-SIMS. The elevated-temperature capacitive energy storage performance, e.g., the discharged energy density and the



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**Figure 5.** a) Discharged energy density and b) charge–discharge efficiency of the PEI coated with *h*-BN and pristine PEI as a function of cycle numbers.

charge-discharge efficiency, of the *h*-BN-coated engineering polymer films is significantly improved in comparison to the pristine polymer, and even more noteworthy, exceeds those reported for high-temperature polymer and nanocomposite dielectrics. Impressively, the h-BN/PEI/h-BN films are capable of operating efficiently and delivering high energy densities even at a temperature that is close to the  $T_{\alpha}$  of polymers where pristine polymers normally fails. Outstanding cyclability and dielectric stability have also been demonstrated in the *h*-BN-coated PEI at elevated temperatures. This work paves the way for the applicability of a wide range of engineering polymers as high-performance dielectric materials in high-temperature electronic and energy devices. Moreover, we anticipate that the reported method of transfer of *h*-BN nanosheets to polymer thin films can be extrapolated to realize a variety of 2D nanomaterial-based heterostructures for scalable, flexible devices.

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## **Supporting Information**

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

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# **Conflict of Interest**

The authors declare no conflict of interest.

### Keywords

2D materials, chemical vapor deposition, dielectrics, electrical energy storage, high temperature

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