Dielectric Dispersion and High Field Response of Multilayer Hexagonal Boron Nitride

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The dielectric dispersion of a material holds significant importance for the understanding of basic material characteristics and the design parameters of a functional device. Here, the dielectric dispersion characteristics of multilayer hexagonal boron nitride (hBN) using time domain reflectometry under an extended device operating frequency range up to 100 MHz are studied. Contrary to what is previously reported, the capacitance, hence the effective dielectric constant, of hBN decreases with the increase of frequency above the MHz range, indicating heat dissipation in lossy hBN dielectric. Furthermore, hBN shows stubborn dielectric characteristics with temperature changes that confirm its thermal stability in extreme operating conditions. The charge carriers in hBN are transported by Fowler–Nordheim tunneling with increasing the electrical field. Lastly, hBN endures electrical field of 7.8 MV cm\(^{-1}\) that implies its potential use as a promising dielectric material. These results will benefit the research and development of hBN supported high-speed electronics operated at high-frequency conditions for energy-efficient device applications.

1. Introduction
The dielectric properties of a material are of great significance both for understanding basic material characteristics as well as for its integration in novel device applications. With the growing interest in high-speed electronics, the demand of the hour is to study the dielectric characteristics of materials under ultrafast and high frequency operating conditions, since the dielectric dispersion (dielectric constant as a function of frequency) and its corresponding losses influence the overall device performance. For example, a high dielectric constant material is required to reduce the operating voltage of devices, which enables a thinner gate dielectric and, therefore, a high electric field and high current. Meanwhile, a high dielectric constant of an intermetallic dielectric material in the backend metallization of electronic devices results in an increased time delay and degraded device performance. Therefore, a low dielectric constant material is required for low power device applications such as interconnects to reduce the intrametal capacitance and propagation delay of signals.

Although the low dielectric constant materials are highly important, little is known about the dielectric dispersion of the emerging low dielectric constant two-dimensional (2D) insulting materials, such as hexagonal boron nitride (hBN). hBN is a wide-bandgap (5.8 eV), layered insulating material, in which, boron and nitrogen atoms are strongly held together by sp\(^2\)-hybridized covalent bonds in a honey-comb lattice structure to form atomically thin sheets, similar to those of graphene. hBN exhibits a naturally pristine surface that is free of dangling bonds and charge traps, even in its monolayer form. Conversely, its bulk counterpart materials, such as SiO\(_2\), Al\(_2\)O\(_3\), HfO\(_2\), exhibit surface roughness, oxide traps, and active defects, particularly when scaled to the sub-nm node. Moreover, hBN possesses a reasonable dielectric constant \((k = 3.5)\) and two times higher optical phonon energies (150–200 meV) than conventionally used SiO\(_2\) (60–80 meV). Furthermore, unlike conventional dielectric materials, the layered structure of hBN provides mechanical flexibility, optical transparency, and chemical stability down to its monolayer.
thickness. These qualities make hBN a potential candidate for ultrathin gate dielectric material to fabricate future flexible and transparent miniaturized devices.\(^{[17]}\) Generally, the basic dielectric characteristics of insulating materials are studied by a typical capacitance measurements method. However, the dielectric properties of layered hBN are difficult to compute by these measurements because of its low dielectric constant (3.5), atomically thin physique\(^{[8,9]}\) and small-size (area) stochastic test samples prepared by a mechanical cleavage technique. These factors lead to smaller capacitance (\(C = kA\varepsilon_0/\ell\), where \(C\), \(\ell\), and \(A\) are capacitance, thickness and area of hBN capacitor, while \(\varepsilon_0 = 8.85 \times 10^{-12}\) F m\(^{-1}\) is the permittivity of free space) and higher impedance (\(z = 1/\omega C\), where \(z\) is impedance and \(\omega\) is angular frequency) in hBN capacitors that are hard to detect by typical capacitance measurement systems operating within their nominal frequency range. Meanwhile, we understand that the dielectric dispersion of hBN was studied at a very high frequency range from optical measurements,\(^{[10,11]}\) where it exhibits a strong peak around 215 nm due to its wide bandgap (5.8 eV).

Similarly, other 2D materials such as graphene and topological insulator exhibit absorption at microwave and optical frequency regime due to their unique Dirac band nature.\(^{[12,13]}\) Therefore, hBN is suitable for ultraviolet lasing, whereas graphene and topological insulator can be incorporated for broadband microwave and optical devices. However, these frequency ranges \(>100\) GHz are not directly related to the operating frequency of semiconductor devices. Therefore, a frequency range wider than impedance analyzer limits (over MHz frequency range) is required to counter leakage problems by reducing the impedance of capacitor,\(^{[14]}\) within the operating frequency range of transistors. In addition to this, there is currently a fresh impetus to explore hBN usage in association with other 2D materials to form van der Waals heterostructures.\(^{[15,16]}\) hBN encapsulated 2D layered materials like graphene, MoS\(_2\) and black phosphorus exhibit very high field effect mobility (over thousands of cm\(^2\) V\(^{-1}\) s\(^{-1}\)), such that mobility values approached their corresponding theoretically predicted phonon-limited numbers.\(^{[7,17,18]}\) Besides this, hBN serves as an encapsulating layer,\(^{[19]}\) tunnel barrier,\(^{[8,9]}\) charge trapping layer,\(^{[20]}\) charge separating layer,\(^{[10]}\) and a heat sink\(^{[21]}\) for other 2D materials. Because of its huge potential for future miniaturized ultrafast devices, it is more likely that hBN-based devices might be subjected to extreme operating conditions, such as high electric field, high frequency, and different temperature values. To the best of our knowledge, hBN has rarely been studied at high frequency and aggressive operating conditions, mainly due to small sample size and system limitations.\(^{[22–24]}\)

From the perspective of a measurement system, the typical impedance analyzer can be operated in the frequency range of a few MHz, while a network analyzer could cover up to 100 GHz, though it requires complex techniques and large test samples, which is a bottleneck, considering the small size of hBN samples. Herein, we employed a time domain reflectometry (TDR) technique to carry out capacitance–voltage (C–V) and capacitance–frequency (C–f) measurements over 100 MHz frequency range without regard to sample size and structure. TDR does not require additional test structures to compensate for parasitic components; therefore, it is highly useful in calculating the capacitance of ultrathin, leaky gate dielectrics over an extended frequency regime. Interestingly, our measurements on a multilayer hBN capacitor show an unusual decrease in capacitance, hence effective dielectric constant, when applying high frequency (up to 100 MHz) by TDR. This is different from the previously reported constant trends observed at relatively smaller frequency values.\(^{[22–24]}\) Moreover, the dielectric dispersion of hBN does not show any significant change to the applied temperature range (223–373 K). In addition to these, the field dependent carrier transport mechanisms are also studied. Lastly, electrical breakdown of hBN is studied to elaborate its electrical endurance, which shows dielectric strength of 7.8 MV cm\(^{-1}\).

For the experiment, we fabricated an hBN based metal–insulator–metal (MIM) capacitor, as shown in Figure 1a,b. We began the fabrication process by patterning and depositing a bottom electrode of 5/30 nm thick Cr/Au over p-Si substrate capped with thermally grown 285 nm SiO\(_2\). A few layered hBN flakes were exfoliated on a polydimethylsiloxane, which acts as a sacrificial stamp to transfer candidate flakes to the Cr/Au electrode. Note that we avoided using polymer assisted transfer techniques, such as polyvinyl alcohol and/or polymethyl methacrylate, so that we could ensure residue-free and sharp metal–hBN interface, as shown in transmission electron microscopy (TEM) image in Figure 1c. Lastly, 5/100 nm thick Cr/Au metals were deposited in a similar fashion to fabricate the top electrode. Further details about fabrication processing and hBN–metal interface are given in Figures S1 and S2 of the Supporting Information. Thickness of the candidate hBN flakes was confirmed by atomic force microscopy, see Figure S3 of the Supporting Information. We compiled Raman spectra of one of the exfoliated multilayer hBN flakes, as shown in Figure 1d. hBN exhibits just one characteristic Raman peak depicting \(E_{2g}\) vibration mode at 1366 cm\(^{-1}\), which is analogous to the G mode in graphene. However, the absence of the D peak corresponds to the lack of the Kohn anomaly in hBN.\(^{[25]}\)

After physical characterization and device fabrication of the multilayer (32 nm thick) hBN capacitor, we carried out typical capacitance measurements. For this, we first employed an impedance analyzer (Agilent 4294A) operating in a frequency range of 1 kHz to 10 MHz. Initially, we swept the applied voltage from \(-2\) to 2 V at a fixed frequency value to obtain the device capacitance, as shown in Figure 2a. The measured capacitance values do not show a significant change as a function of applied voltage at 1 MHz frequency value, as is normally observed in MIM capacitors. For further information, see Figure S4 of the Supporting Information. Furthermore, we swept the frequency from 1 kHz to 10 MHz and computed capacitance as shown in Figure 2b, and thereby we extracted the dielectric constant as \(k = C/\ell C_{0}\). By using a 32 nm thickness of hBN and a \(47 \times 43 \mu m^2\) effective capacitor area, the extracted \(k\) value ranges around 3.5–3.8, close to that previously reported.\(^{[7]}\) At low frequency, the plot shows significant noise, probably due to the high impedance of the hBN capacitor, while at frequency values in the range of 10 kHz to 0.2 MHz, the trend is almost linear. After that, a rise in capacitance was observed. At that point, the system followed the equivalent series resistance and parasitic components.\(^{[26]}\) The overall capacitance, hence the effective \(k\) value, does not show any noticeable change across the moderate measured frequency range. This kind of behavior
has been observed in most of the previous studies.\cite{22-24} In fact, under the measured frequency range, all the dipole charges in hBN dielectric follow the oscillating electric field, therefore we did not observe any appreciable change in the effective $k$ of hBN. Therefore, it is imperative to apply high frequency to realize the dielectric dispersion of hBN.

To measure the dielectric characteristics at higher frequency, we used the $C$-$f$ measurement method using a TDR scope (Lecroy Wave Expert 100H) which can measure the $C$-$f$ characteristics over 100 MHz frequency range.\cite{26} Further details about the TDR setup are shown in Figure 3a. The test sample was connected to the TDR scope through a ground-signal probe, transmission lines, and a bias tee. We used a parameter analyzer (Keithley 4200) to apply a DC bias to the sample with the help of a bias tee. The incident signal, that is a step pulse with a 20 ps rise time and 250 mV step voltage, is generated by the TDR scope. When the incident signal was applied to the sample, it was reflected back toward TDR scope due to the impedance mismatch between the transmission line and the sample. The TDR scope captured only the change in the ac component. When the sample was charged by step pulse, the reflected pulse was affected by the concurrent change in the

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**Figure 1.** a,b) Schematic and optical image of 32 nm thick hBN-based MIM capacitor, respectively, with scale bar of 20 µm in optical microscope image. c) TEM image indicating abrupt and clean interface along hBN and metal electrode (bottom). d) Raman spectra of few layer hBN flake depicting characteristic peak at 1366 cm$^{-1}$.

**Figure 2.** a) $C$-$V$ plot of hBN MIM capacitor obtained by impedance analyzer at given frequency value. b) $C$ and effective $k$ as a function of frequency.
the impedance of the sample. Finally, the difference between the curves reflected from an open circuit and the sample was integrated and analyzed to obtain capacitance. Further details about TDR setup, data acquisition and analysis can be found elsewhere.\cite{26,27}

The extracted capacitance as a function of applied frequency from TDR is compiled in Figure 3b. The readers should note that at relatively lower frequency range (≤3 MHz), the capacitance values obtained from the impedance analyzer and the TDR are very close, and this testifies to the accuracy and reliability of our measurements and extracted results. For further comparison see Figures S5 and S6 of the Supporting Information. Besides experimental results, we also generated C–f plot by Cole-Cole model (open blue circles),\cite{26,28} which fits with the great confidence with the TDR results (solid red line), as shown in Figure 3b. The measured capacitance values by the TDR scope were translated to k by a parallel plate model and plotted in Figure 3c as a function of applied frequency. To better understand the results, we distributed Figure 3c into two regions, I and II. From 120 Hz–3 MHz (region I), k shows no change with frequency, as observed in the impedance analyzer data. After that, it shows a sharp decrease up to 0.5 GHz frequency (region II). We carried out these measurements to eight different thickness hBN capacitors, all the measured devices showed a similar k–f trend, as shown in inset of Figure 3c and Figures S5 and S6 (Supporting Information). It is important to note that, the onset of decreasing trend of dispersion curves is at the similar frequency value (4–5 MHz) for all the measured thickness of hBN. Additionally, the measured dispersion characteristics were repeatable even after half year, and this confirms the long-term stability of hBN under ambient conditions, see Figure S8 of the Supporting Information. The stubborn behavior of the frequency dispersion plot in region I is mainly due to the fact that the boron and the nitrogen atoms are held together in the hBN lattice by very strong sp²-hybridized covalent bonds. For the stronger covalent interactions, the charge relaxation occurs at relatively higher frequency values.

As mentioned earlier, when an alternating field is applied to a dielectric material, the charges orient themselves in the direction of the alternating field. In this way, the applied electrical energy is compensated to polarize the charges. However, with the enhancement in applied frequency, the charges could not align with the very fast oscillating field; therefore slower polarization mechanisms were left behind. As a result, the applied electrical energy is partially dissipated in the form of thermal energy. Therefore, a decreasing capacitance, hence, effective k is realized.
energy due to inner atomic friction. The net heat loss mainly depends on the applied frequency and nature of the dielectric material. Under such conditions, the effective dielectric constant appears to be smaller to that observed at the lower frequency range, as realized in Figure 3c. This explains that the dielectric response depends not only on the dielectric properties of a material (permittivity, permeability) but on the applied frequency value. Few bulk dielectric materials exhibit dielectric dispersion at relatively lower frequency range than that of hBN, as they exhibit interface polarization due to the charged surface, grain boundaries, and interphase boundaries, which can be relaxed at relatively smaller frequency range.

On the other hand, hBN, being a layered material, possesses an ultraclean surface compared to SiO$_2$, see Figure S9 of the Supporting Information. We observed a significant change with temperature mainly due to impact of defects in the dielectric. As hBN is well-known for its structural, chemical and thermal stability due to the strong covalent bonds between its boron and nitrogen atoms, Li et al. reported that few layer hBN flakes can sustain around temperature of 1100 K without any significant structural and chemical degradation. This explains the stubborn dielectric characteristics of hBN observed here.

In order to elucidate the high field response of hBN, we electrically stressed the hBN capacitor. To do this, we gradually ramped up the applied field ($F = V/t$) until electrical breakdown occurred. Figure 5a shows the field dependent results of 32 nm thick hBN capacitor, where, a non-monotonic behavior of current density was very high impedance, which masked the device capacitance, but as the frequency increases, the capacitor is charged, leading to a decrease in its impedance, and as a result, we realize the dielectric dispersion in the hBN capacitor.

Next, we studied the effect of temperature on the dielectric characteristics of hBN. For this, we increased the temperature from 223 to 373 K to observe the possible response of hBN to the change. We assembled the $C$-$f$ and $z$-$f$ plots of the hBN capacitor at given temperature points, as shown in Figure 4a,b. At all the measured temperature points, both plots showed similar trends as explained in the previous paragraph. This further explains the reliability and reproducibility of our data. Surprisingly, even with the 150° change in temperature, we could not observe any significant change in the capacitance (effective $k$) and impedance of the hBN at all the measured points. As a reference, we also measured the dispersion characteristics of a bulk high-$k$ dielectric material, as shown in Figure S10 of the Supporting Information. We observed a significant change with temperature mainly due to impact of defects in the dielectric. As hBN is well-known for its structural, chemical and thermal stability due to the strong covalent bonds between its boron and nitrogen atoms, Li et al. reported that few layer hBN flakes can sustain around temperature of 1100 K without any significant structural and chemical degradation.

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Fowler–Nordheim tunneling

\[ I \propto V^2 \exp \left( -\frac{8\pi d \sqrt{2m^*\phi_B}}{3hqV} \right) \]  

(1)

\[ \ln \left( \frac{I}{V^2} \right) \propto -\frac{1}{V} \left( \frac{8\pi d \sqrt{2m^*\phi_B}}{3hq} \right) \]  

(2)

where \( d \) and \( \Phi_B \) are separation between electrodes and barrier height respectively. While \( m^* \), \( h \), and \( q \) are effective electron mass (0.26 m for hBN), Plank’s constant and elementary charge of electron, respectively. At low field, up to 4 MV cm\(^{-1}\) (13 V), the applied field value was not strong enough to significantly affect the metal–hBN interfacial barrier and therefore, smaller current density is realized. However, the charge carriers in hBN followed FNT model for the field values in the range of 4–7.8 MV cm\(^{-1}\) (13–25 V) as shown in Figure 5b. As the applied field was increased, the interfacial barrier became relatively narrower and triangular in shape due to band bending, as shown in Figure 5c. That facilitated carrier injection into hBN and increased the current density. Beyond 7.8 MV cm\(^{-1}\) (25 V) field value, hBN suffered a permanent hard breakdown, and thereby, increasing current density vertically.

We obtained 7.8 MV cm\(^{-1}\) field strength of hBN that is similar to the previously reported value by Lee et al.,\(^{[9]}\) and it is smaller than that of SiO\(_2\) (10–15 MV cm\(^{-1}\)).\(^{[36]}\) We rule out any such possibility in our measured hBN flakes since that reported field value is beyond the breakdown strength of hBN observed here. The smaller leakage current density, gradual breakdown and sufficient electrical field endurance of hBN strongly support the possibility of its use as an alternative gate dielectric material for future miniaturized device applications.

The unusual dielectric dispersion of hBN was studied by the TDR technique, by which the effective dielectric constant shows a decreasing trend with the applied frequency. At measured

Figure 5. a) Electrical breakdown of hBN capacitor, where red color indicates FNT region. b) \( \ln(I/V^2) \) versus \( I/V \) plot to fit according to FNT model. c) Schematic diagram of FNT through hBN.
temperature range, hBN does not show any appreciable changes on dispersion characteristics. The electric breakdown shows unique gradual degradation in hBN dielectric. These findings will help integrate hBN into future devices based on 2D materials.

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.

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