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ARTICLE

Dielectric dispersion and superior thermal characteristics in isotope-enriched hexagonal boron nitride thin films: evaluation as thermally self-dissipating dielectrics for GaN transistor

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High performance tuneable dielectrics at millimetre-wave frequencies are crucial constituents for emerging adaptive and reconfigurable electronic applications in automotive, artificial intelligence, and telecommunication. Hexagonal boron nitride (h-BN), an ideal candidate for gate-insulating dielectrics, has been attractive for integrated circuits and photonic devices. However, advanced applications to electronic and optoelectronic devices are often limited by synthesis technique and flake size, as well as dielectric reliability. Herein, we have studied the isotope engineering of h-BN thin films directly grown on wafer-scale Si and GaN substrates with pure boron isotope (B^{10} and B^{11}) in comparison with controlled isotopic compositions. The dielectric characteristics of isotope-enriched h-BN films at frequency ranging up to 10^7 Hz were investigated, exhibiting a broad dielectrics dispersion with the low dielectric loss, below 1.3%. Furthermore, their optical band gap energies indicate a strong dependence on isotopic composition, ranging from 5.54 to 5.79 eV. Thermal conductivity of pure $B^{10}N$ and $B^{11}N$ over a broad temperature range are superior to those of other compositions, with an enhancement of around 231%. Therefore, great thermal response combined with excellent dielectrics properties and wide bandgap make h-BN a promising dielectric material for heat self-dissipation GaN and AlGaN/GaN transistor. Hall mobility, sheet resistivity and sheet concentration of GaN with $B^{10}N$ films were analyzed, ascertaining that h-BN does function well as both a dielectric layer and a passivating layer on electronic devices. Our findings could lead to microelectronics thermal management and integrated optoelectronics applications at these frequencies.

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Introduction

Hexagonal boron nitride (h-BN) is amongst the many layered materials which hold great promises in revolutionizing the fields of electronics and nanophotonics.^{1–3} It has many unique properties such as large bandgap (~ 6 eV), high anisotropic thermal conductivity, optical anisotropy (as a hyperbolic material), strong chemical inertness, high thermal neutron cross-section and a low dielectric constant. Due to these properties, it is used as a dielectric layer on graphene-based field-effect transistors, thermal management, single-photon emitter and neutron-sensitive layer in neutron detectors. Amongst these applications, thermal management in nanoscale devices is known to be one of important problems due to the high energy densities in these devices. Consequently, h-BN with

its various unique and excellent thermal and dielectric properties is touted as a plausible mitigation solution.^{4,5}

Monoisotopic variants of semiconductors have shown a marked enhancement in their thermal conductivities, making it a viable strategy for improved thermal management and device performances. For instance, as compared to their variant in isotopic natural abundance, the reported percentage enhancement in thermal conductivities at room temperature for these materials are: $\sim 5\%$ for GaAs,⁶ 10% for BP,⁷ 7% for Si,^{8,9} 30% for Ge¹⁰, $\sim 58\%$ for graphene¹¹ and $\sim 50\%$ for diamond.¹² For h-BN, the remarkable increment in thermal conductivity of isotope-enriched single-layer h-BN is reported theoretically and experimentally.^{13,14} Moreover, isotope engineering is beneficial in thermal neutron detection as B^{10} isotope has a high thermal neutron cross-section (~ 3840 barns).¹⁵ Similarly, isotopic substitution is also useful for reducing propagation losses in phononic devices as lifetimes of the optical phonons are reduced in isotopically-modified h-BN.¹⁶ However, studies on understanding and manipulating thermal performances of isotopically-enriched h-BN have mostly been focused on few-layers h-BN synthesized by chemical vapour deposition (CVD) or bulks by conventional high pressure and high temperature processes.^{17,18} Few studies on direct deposition of isotopically-enriched h-BN on Si or GaN wafers for mass-production and actualized applications were done. Moreover, the effect of boron isotopic composition on bandgap and dielectric

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Electronic Supplementary Information (ESI) available: deposition conditions of thin films deposited, Raman and FTIR spectra of h-BN^{ATN}, Raman spectra of h-BN thin films on GaN and percent changes of electron properties pre- and post-depositions. See DOI: 10.1039/x0xx00000x

performances remains unclear. In particular, the dielectric dispersion in isotopically tailored h-BN at high frequency, such as dielectric constant, loss, and breakdown field, is in general highly desired for multifunctional nanoelectronic and optoelectronic devices.

In this work, we have investigated isotope engineering of h-BN thin films by high power impulse magnetron sputtering (HIPIMS) which can be scaled to an industrial level. h-BN thin films synthesized using pure boron isotopes (B^{10} and B^{11}) were studied systematically in comparison with controlled boron isotopic compositions of the as-deposited h-BN thin films (80% B^{10} , 60% B^{10} , 50% B^{10}). Our results reveal that their dielectric constants, dielectric loss and optical band gap are strongly dependent on the isotope component of B^{10} . In addition, the dielectric dispersion characteristics of isotopically enriched h-BN films at frequencies ranging up to 10^7 Hz exhibited excellent stability and low dielectric loss, below 1.3%. Besides, thermal conductivity of pure $B^{10}N$ and $B^{11}N$ over a broad temperature range is superior to those of other isotopic compositions, achieving an enhancement of around 231%. Therefore, high thermal response combined with excellent dielectrics properties and large bandgap make h-BN a promising dielectric material suitable for heat self-dissipation GaN and AlGaIn/GaN transistors. Our study sheds insights on high performance adaptive and reconfigurable electronics at these frequencies.

Experimental Procedure

Preparation of h-BN thin films

HIPIMS equipped with a dual magnetron sputtering system was used to synthesize these h-BN films. It is known for the high target power densities and ion densities during the deposition in creating films with better adhesion, higher hardness, lower surface roughness and denser films.^{19–21} Furthermore, direct deposition of h-BN on Si wafer is entirely possible with HIPIMS and this enables the integration with the current industrial semiconductor processes.^{22,23} A schematic of the system is provided in FIG. S1(a). In the schematic, both magnetrons are shown to be sputtering. The targets are isotopically pure boron targets (purity: 99.99%, for both B^{10} and B^{11} targets) that are 3-inch in diameter. For characterization of the h-BN films deposited, double-sided polished silicon wafers of <100> orientation, 350 μm thick, were diced and used as substrates. Similarly, GaN wafers and AlGaIn/GaN heterostructure were also used as the substrate in one of the depositions. Prior to each deposition, the chamber is first pumped down to a base pressure of $\sim 3 \times 10^{-6}$ Torr. Afterwards, all the procedures were conducted under a mixed Ar and N_2 atmosphere (total gas flow rate of 100 sccm) with a gas flow rate ratio of 25% at a process pressure of $\sim 1.0 - 1.5 \times 10^{-2}$ Torr. The temperature of the substrate during depositions is around 800 $^{\circ}\text{C}$, measured using a thermocouple located above the graphite heater which is supplying the heat. The two magnetrons are powered by a HIPIMS power supply, which can deliver up to negative 1000 V to the target for reactive sputtering as depicted in FIG. S1(b). The pulses were supplied at a frequency of 8000 Hz and a length

of 10 μs . The detailed deposition procedures and experimental plans can be found in our previous work.³ A total of 5 samples deposited on Si, labelled according to the ratios of Boron-10 and Boron-11 isotopic compositions, were deposited for material characterizations. Concurrently, h- $B^{\text{nat}}N$ thin film (19.9% B^{10} and 80.1% B^{11}) was also synthesized at the same condition for comparison. The exact deposition conditions and associated parametric values are summarized in Table S1 (Supporting Information). As for BN-encapsulated GaN transistor, the Van der Pauw-Hall contacts were made using corner Ohmic contacts consisting of Ti/Al/Ni/Au (thickness of each layer: 20/120/40/50 nm, respectively) via e-beam deposition. Subsequently, further thermal-annealing at 775 $^{\circ}\text{C}$ for 30 s in a nitrogen environment was carried out to improve the electrode contact. The AlGaIn/GaN heterostructures were synthesized using metalorganic chemical vapor deposition (MOCVD) on 4" Si substrates with <111> orientation, followed by BN coating, electrode deposition and electronic measurements.

Characterization

The Bruker DektakXT surface profiler complemented by the Vision64 software was utilized to determine the thickness of each deposited film. Optical spectrometry involving Raman spectrometry (Raman spectra were obtained at 532 nm excitation.) and Fourier-Transform Infrared Spectrometry (FTIR) was employed to characterize the optical responses of the samples. Likewise, Transmission Electron Microscope (TEM, FEI Tecnai™ G2 F20) and its associated techniques were employed to study the microstructure of the as-deposited films. Both electron energy loss spectrometry (EELS) and energy dispersive spectrometry (EDS) were used to study their elemental composition. To better understand the bonding characteristics of the films, X-ray photoelectron spectrometry (XPS), powered by an energetic Al K α source of 1486.6 eV, was also performed. Ultraviolet-visible (UV-vis) spectroscopy (Shimadzu UV-2450) was utilized to investigate the absorbance spectrum and the optical bandgap energies of h-BN films. The dielectric properties of the h-BN films deposited were measured using an impedance parameter analyzer, with a two-point probe. The NanoTR technique was performed to study the thermal conductivity of all samples. Thermo-reflectance is the phenomenon in which the reflectivity of light is altered by temperature variations. The characterization of the DC performances was done on the device, under standard laboratory conditions, using Agilent B1505A semiconductor parameter analyzer.

Results and Discussions

FIG. 1(a) gives the Raman spectra for all the five samples, the E_{2g} phonon has different energies for different isotopic (B^{10} and B^{11}) compositions in the h-BN thin films as its $\sim 1/\mu^{1/2}$ dependence is inherited from the harmonic oscillator,^{13,14} hence showing that isotope substitution changes the frequency of the phonon. The E_{2g} phonon occurs as the vibration of the N and B atoms in the hexagonal ring in opposite directions. Interestingly, there is not TO-LO splitting for this phonon mode

FIG. 1 Optical characterizations of isotope-enriched h-BN. (a) Raman spectra of the samples with different isotopic compositions. (b) The frequency of the E_{2g} phonon mode with respect to the reduced mass, μ , of h-BN samples. (c) FTIR spectra of the films with different isotopic compositions. (d) Frequency dependency on reduced mass of the E_{1u} and A_{2u} phonon modes in the films.

as the contributions from the two adjacent planes cancel out each other.²⁴ FIG. 1(b) depicts the frequency of the E_{2g} phonon mode of h-BN thin films, indicating a strong dependence on the reduced mass (μ). In particular, the linear relation of the wavenumber of the E_{2g} phonon mode is proportional to the reciprocal of square root of μ , as predicted by virtual crystal approximation (VCA), from h-B¹¹N (1362.5 cm⁻¹) to h-B¹⁰N (1399.1 cm⁻¹).¹³ C. Yuan et al. and S. Liu et al. reported similar results on the frequencies of the phonon of h-BN crystals with various isotopic compositions using the melt flux method (presented as green and red data points in FIG. 1(b)).^{25,26} The frequencies of the phonon modes of h-B¹⁰N and h-B¹¹N crystals are lower in magnitude as compared to the frequencies of the corresponding samples in this work. The higher phonon frequencies, especially for the samples corresponding to h-B¹⁰N and h-B¹¹N, can be ascribed to the compressive stress subjected to these thin films, a result of the highly energetic ion bombardment on the substrate during the HIPIMS sputtering process.²⁷ Another factor is the nanocrystalline structure of the film, which is known to increase the frequency of the phonon mode.²⁸ To understand the nanocrystalline nature of the samples, the FWHM of the samples, which range from 40 cm⁻¹ to 60 cm⁻¹, was used to calculate the size of these nanocrystals. The values of the FWHM are within the range of FWHM values measured from the h-BN deposited using other methods, such as chemical method,²⁹ RF sputtering,³⁰ atomic layer deposition (ALD)³¹ and chemical vapour deposition.^{32,33} The FWHM of the h-BN crystals with various isotopic compositions grown using the metal flux method are around 1 order of magnitude smaller, as smaller crystallite size leads to the broadening of the Raman peak and using the equation $L_a = [1417/(\text{FWHM})] - 8.7$,²⁸ the samples in this work are estimated to have crystallite sizes ranging from 14.8 nm to 23.8 nm, these values are compiled in

Table 1, together with the values of dielectric constant, its associated dielectric loss and optical bandgaps, which are discussed in subsequent sections.

The FTIR spectrometry is widely used in understanding the bonding characteristics of thin films, especially in the case of h-BN.^{3,34} The different infrared active phonon modes can typically be used to distinguish between h-BN and cubic boron nitride (c-BN). The FTIR spectra of all the h-BN samples with various isotopic compositions are plotted in FIG. 1(c). From the plot, both the characteristic infrared active E_{1u} and A_{2u} phonon modes of h-BN are present, accompanied by a significant shift towards the smaller wavenumber. The A_{2u} phonon mode corresponds to the out-of-plane B-N-B bending vibration (in the range of 800 cm⁻¹ – 820 cm⁻¹) whereas the E_{1u} phonon mode corresponds to the in-plane B-N stretching mode (in the range of 1380 cm⁻¹ – 1410 cm⁻¹).³ Similar to the frequency of the E_{2g} Raman active phonon mode, both the frequencies of A_{2u} and E_{1u} infrared active phonon modes are expected to have a reciprocal relationship with the reduced mass, μ , of the h-BN films, in the form of $\omega \propto \mu^{-1/2}$, as predicted by VCA.¹³ This dependency is illustrated in FIG. 1(d) in blue dotted lines. There is comparable agreement between the observed frequencies of the phonon modes and the $\sim \mu^{-1/2}$ mass dependence giving strong confidence that the samples deposited are indeed varied on their isotopic compositions.

HRTEM was further employed to study the microstructure and crystallinity of the as-deposited h-BN films. FIG. 2(a) provides a cross-section HRTEM image of the interface between h-BN film and Si wafer. FIG. 2(b) gives a highly magnified HRTEM image of the sample. From the image, nanoclusters within the h-BN films are oriented randomly with respect to other clusters. Each cluster contains multiple layers of h-BN and are delineated by dotted white lines on the image.

Table 1 Reduced mass, crystalline size and relative properties of isotopic h-BN thin films.

	Reduced mass	Crystalline size (nm)	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	Bandgap (eV)	Dielectric constant	Dielectric loss
B^{10}	5.833	22.740	3.901	5.56	5.061	0.016
80% B^{10}	6.000	20.529	1.902	5.72	5.462	0.0198
60% B^{10}	5.967	14.821	1.361	5.79	6.392	0.0270
50% B^{10}	5.901	16.107	1.802	5.71	7.112	0.0189
B^{11}	6.160	26.797	3.541	5.54	5.741	0.0137

FIG. 2 Microstructural characterizations and chemical bonding of h-BN. HRTEM images of (a) the interface between h-BN layer and silicon substrate and (b) the h-BN thin film. (c) A FFT of the image in (b), showing the two diffraction arcs, corresponding to the (002) planes of h-BN and a diffraction ring, corresponding to the (010) planes of h-BN. (d) EDS and (e) EELS spectra of the h-BN sample. (f) XPS full survey, (g) B 1s and (h) N 1s spectra of the h-BN sample.

Using the FFT shown in FIG. 2(c), the inter-planar distance between the h-BN planes is 0.366 nm, comparable to the characteristic inter-planar distance of h-BN.³⁴ In addition, the diffraction arcs are assigned to (002) planes, whereas the diffraction ring is assigned to the (010) planes of h-BN. The EDS spectrum shown in FIG. 2(d) ascertains the presence of the various elements, namely, boron, nitrogen, carbon and oxygen. The carbon present may be due to the inevitable contamination

resulted from the mechanical handling of the sample placed on a copper grid during TEM observation, this is supported by the absence of the well-known 'D' and 'G' peaks of carbon and B-N-C samples in the Raman spectra of these h-BN thin films.³⁵ Furthermore, the existence of the typical π^* and σ^* peaks located near the Boron and Nitrogen K-shells indicates the presence of sp^2 hybridization bonds in h-BN films (FIG. 2(e)). The sharp π^* absorption edge in close vicinity of the boron-K edge

FIG. 3 Thermal performances and bandgap energies of isotopic h-BN. (a) Experimental and fitting curves for thermal conductivity measurement. The inset is an illustration on the measurement technique. (b) Measured thermal conductivities (TC) of the h-BN samples with different isotopic compositions at room temperature. (c) Temperature dependence of thermal conductivity (TC) across a range of temperatures from room temperature to 300 °C of the h-BN samples with different isotopic compositions. (d) Absorption coefficients of isotopic h-BN films. (e) Optical bandgaps of the h-BN samples with different isotopic compositions. (f) Bandgap of isotopic h-BN in comparison with those of common dielectric materials. (g)–(j) Tauc plots of the samples with 100%, 80%, 60%, and 0% B^{10} , respectively.

is evident of the K-shell electrons being excited into the anti-bonding π^* states,³⁶ ascertaining the sp^2 hybridized-bonding characteristic of hexagonal BN.³⁷ Meanwhile, a broader unoccupied σ^* absorption edge occurs owing to the K-shell electrons being excited into the anti-bonding σ^* states.³⁶ Moreover, the π^* and σ^* states in the as-grown films are located at 198.3 and 206.2 eV, which are also comparable with the values reported for h-BN.³⁸

The study on bonding characteristics of the h-BN thin films was conducted using XPS technique. The sample corresponds to the natural abundance in its isotopic composition was chosen for this XPS survey as it represents the sample that would be least influenced by the effects of variations in isotopic compositions and would allow the study of the chemical composition of the film under the deposition conditions. FIG. 2(f) reveals the full XPS survey of the sample, all the B 1s, N 1s and O 1s peaks were observed, also evidenced by EDS analysis (FIG. 2(d)). Presence of oxygen in the sample can be due to imperfect stoichiometry between B and N within the film, leading to excess boron interacting with oxygen. FIG. 2(g) and 2(h) exhibit the high resolution XPS analysis of B 1s and N 1s located at 189.9 eV and 396.9 eV, which agree well with the values reported in the literature.^{18,34} Apparently, highly symmetric single peak was observed in both B 1s and N 1s spectra, clearly suggesting the presence of typical sp^2 -hybridized B-N bonding in hexagonal BN. Absence of an

asymmetric B 1s XPS peak, whose presence may have indicated the existence of boron oxide, shows the interaction between boron and atmospheric oxygen is not of a chemical nature. The XPS gave an estimated B/N stoichiometric ratio of 1.04:1, indicating a good 1:1 stoichiometry for the h-BN film deposited.

As explained in the previous sections, thermal conductivity of isotopically pure h-BN is of primary concern. As thermal conductivity in insulators and semiconductors mainly originated from the transport of acoustic phonons, the crucial factor affecting the thermal conductivity of such materials is the mean free path of the acoustic phonons, which is again,³⁹ directly dependent on the phonon relaxation time. Of the factors influencing it, the scattering of the acoustic phonons by isotopic mass fluctuations can be manipulated. The equation describing the scattering rate for phonons with frequency ω is given by:³⁹

$$\tau_{ph}^{-1} = \frac{g_2 V}{4\pi \langle V_{ph} \rangle^3} \omega^4 \quad (1)$$

where V is the volume occupied by the isotopically mixed atom and the mass fluctuation parameter, g_2 , is given by:

$$g_2 = \frac{\langle M^2 \rangle - \langle M \rangle^2}{\langle M \rangle^2} \quad (2)$$

where M is the isotopic mass of the atom and angular brackets represent average for the quantity. As g_2 is maximised in isotopically pure semiconductors, we expect the scattering rate for the phonons to be minimum and hence, the phonon transport would be enhanced. Therefore, isotopic enrichment of semiconductors will lead to an enhancement in its thermal conductivity.

The raw signal derived from the NanoTR technique,⁴⁰ was used to measure the thermal conductivity of h-BN films with different isotopic compositions, is plotted in FIG. 3(a). The fitting for the raw signal is superimposed onto the plot. Prior to each measurement, one Al layer with 100-nm thickness was grown on h-BN films, which acts as a transducer for the thermal signal during the measurement process, this is illustrated as an inset in FIG. 3(a). The thermal conductivities for all the samples are summarized on FIG. 3(b). The enhancement in thermal conductivity of h-B¹⁰N is nearly 231.0% as compared to the isotopically mixed samples whereas the thermal conductivity of h-B¹¹N is 210.0% greater than that of the isotopically mixed samples. The thermal conductivities of the isotopically mixed samples are within a margin of 4.68% from their average value. These enhancements in thermal conductivities for the isotopically pure samples are well within expectations.^{21,41} As it is often the case that electronic devices may have to function reasonably well under elevated temperatures, the thermal conductivities of the h-BN samples were measured within a temperature range from room temperature to 300 °C (FIG. 3(c)). For each of these samples, an enhancement in the measured thermal conductivity was observed. The enhancement at 300 °C is in the range of 8.5% (FIG. S3, Supporting Information), this may be explained by the annealing effect whereby the increased thermal energy caused the nanoclusters of h-BN to congregate and reduced the phonon scattering effects from the boundaries of clusters. This result highlights the stability of the thermal heat-spreading effect of h-BN layers, with its ability to

function at elevated temperatures and possibly on electronic devices as a mitigation to the thermal hotspots problem.

The absorbance spectra of these h-BN thin films can be found in FIG 3(d). The h-BN films were observed to have a sharp peak around 200 nm, which is a typical strong indication of the as-deposited h-BN thin films. To extract the optical band gap of the film, a Tauc's plot is derived from each of the absorbance spectrum for each of the samples, using a derived formula for an indirect band gap (E_g) semiconductor and using the absorption coefficient which is written as:^{42,43}

$$\alpha = C(E - E_g)^{\frac{1}{2}} \quad (3)$$

Where the absorption coefficient $\alpha = A/d$ (A is the absorbance and d is the film thickness), C is a constant, and E is the phonon energy. Thus, to calculate the optical bandgap for h-BN films, one would need to plot $(\alpha E)^2$ against E and extrapolate a linear line to the x-axis where the x-intercept would give the calculated optical band gap (E_g). Interestingly, the optical band gap for the isotopically pure h-BN films (h-B¹⁰N and h-B¹¹N) is lower than the isotopically mixed h-BN samples, as shown in FIG. 3(e). In particular, band gaps of the two isotopically pure samples are within 0.18% of their average value. The average optical band gap value of the isotopically mixed samples is 3.27% higher than the average value of the isotopically pure counterparts. The difference in the optical band gap values are more likely to be accounted by variations in deposition conditions and the microstructures of the films, which in turn alter the bonding characteristics and therefore, the band structure of the film. It is also reported that the isotopic compositions of thin films are known to have miniscule effects on its optical band gap at 0 K.¹⁶ The bandgap of the h-BN samples are plotted with the bandgap values measured for other materials and is shown in FIG. 3(f). The Tauc's plots and

FIG. 4 Dielectric dispersions and high field response of h-BN. (a) Dielectric constant and dielectric loss of h-BN thin films as functions of frequency. (b) The influence of isotope B¹⁰ on dielectric constant and loss of h-BN thin films at 40 kHz. (c) Thickness-dependent dielectric constant and dielectric loss of h-B¹⁰N thin films. (d) The breakdown field of h-BN in comparison with common dielectric materials.

its corresponding optical band gap for these samples are plotted in FIG. 3(g) - 3(j). The calculated optical band gap ranges from 5.54 eV to 5.79 eV, comparable to the theoretical value of 6.0 eV.³⁵ Although the bandgap of h-BN is less than those of Al₂O₃ (8.8 eV) and SiO₂ (9.0 eV) and also comparable to those of HfO₂ (6.0 eV), Si₃N₄ (5.3 eV), and ZrO₂ (5.8 eV),⁴⁴ it possesses excellent thermal performance while maintaining its dielectric characteristics, thereby suggesting the viability of heat self-dissipation as a gate material for electronic devices.

FIG. 4(a) shows the measured dielectric constant and corresponding loss of h-BN thin films, with different isotopic compositions, as functions of the applied frequency in the MHz range. Within this range, the dielectric constant is around 5 to 7, these values are comparable to the values reported.^{45,46} The dielectric constant remains relatively constant in the MHz range, demonstrating its suitability in electronic applications which involve high power density. Besides, the dielectric losses of pure hexagonal B¹⁰N and B¹¹N samples are lower than those of mixed compounds, indicating a minimal value of 1.3%. FIG. 4(b) depicts both the dielectric constant and loss of the h-BN thin films at 40 kHz as a function of the isotopic composition. Similar to the measured values at frequencies in the range of MHz, the dielectric constant falls within the expected value of h-BN as reported in the literature.^{45,46} This is to be expected as the h-BN thin films have a polycrystalline structure. Noting that the dielectric constant of h-BN is anisotropic, $\epsilon_r = 3.38$ in-plane and $\epsilon_r = 6.61$ out-of-plane,⁴⁷ h-BN thin film with a polycrystalline structure should have dielectric constant in the same order of magnitude. The measured values for the dielectric constant are relatively stable across the h-BN films with different isotopic compositions, the values are within a 19.6% margin. The measured dielectric loss has a peak for the film with an isotopic composition of 60% B¹⁰. FIG. 4(c) demonstrates the trend of dielectric constant of the h-B¹⁰N thin film and its dependence

on the film thickness. It is noted that its dielectric constant slightly increases with the increasing of thickness while its loss significantly reduces, to even below 1.0%. Such low dielectric loss is favourable for electronic performances, especially at the high frequency range. FIG. 4(d) presents the breakdown field in relation to its dielectric constant of h-BN, alongside other common dielectric materials. It can be seen that h-BN has high breakdown field and a low dielectric constant, making it suitable as a passivating or encapsulating layer. Another advantage is its excellent thermal performance, revealing the possibility of heat self-dissipation in devices. However, the trade-off between the high breakdown field and a low dielectric constant is apparent, as an insulating layer, the high breakdown field presents an advantage over other materials but would require a thicker layer due to its low dielectric constant. Consequently, h-BN films deposited using the HIPIMS deposition technique may offer an alternative to depositing h-BN thin films with high thickness, consequently, avoiding a high dielectric loss while preserving its high breakdown field advantage.

To study the electronic properties of isotopically pure h-BN films, these thin films were deposited on GaN substrates. A schematic of BN-GaN heterostructure is shown in FIG. 5(a). Correspondingly, the HRTEM of the GaN substrate is provided in FIG. 5(b) with its inset being the FFT of FIG. 5(b). The FFT of FIG. 5(b) clearly illustrates the diffraction pattern of GaN substrate. The value of d is around 0.512 nm, corresponds to the (100) plane of GaN.⁴⁸ FIG. 5(c) gives the Raman spectra of the three h-BN thin films deposited on GaN substrates, there are clear differences between the frequencies of the E_{2g} phonon modes as to be expected, h-B¹⁰N has the highest phonon energy while h-B¹¹N has the lowest phonon energy. The associated FTIR spectra are presented in FIG. S4 (Supporting Information). The h-BN thin films were deposited on the GaN substrates. The Hall mobility, sheet resistivity and sheet concentration were

FIG. 5 Structure characterization and electronic performances of isotopic h-BN-coated GaN wafers. (a) Schematic of BN/GaN heterostructure. (b) HRTEM image of the GaN substrate. Inset shows the corresponding FFT. (c) Raman spectra of the h-BN with different isotopic compositions grown on GaN substrate. (d) Hall mobility, (e) sheet resistivity and (f) sheet concentration of BN-encapsulated GaN wafer.

measured for each of these samples prior and after each deposition (FIG. 5(d) - FIG. 5(g)). In general, post-deposition Hall mobility decreases, sheet resistivity increases, and sheet concentration decreases for all the samples, except for the sheet concentration of h-B¹⁰N which increased slightly. The post-deposition percentage changes of these electronic properties are tabulated in Table S2 (Supporting Information). The enhancement in the Hall mobility may be due to effectiveness of the h-BN layers as dielectric layer between the GaN substrate and the electrodes.⁴⁵ The low dielectric constant of h-BN, coupled with its high resistivity, making it a good dielectric layer between the interface of the Ohmic electrodes and the GaN substrate and achieving a better electric field penetration from the voltage applied to the gate, this is also achieved in other transistors.^{49,50} The sheet resistivity and sheet concentration also showed significant improvement post-deposition, illustrating the utility of h-BN as a passivation layer.

Based on the experimental observations that h-B¹⁰N has the largest Hall mobility, a moderate drop in sheet resistivity and a modest increment in sheet concentration post-deposition, the h-B¹⁰N film was chosen to be deposited onto a high electron mobility transistor (HEMT) device based on AlGaN/GaN

heterostructure. Investigations on the DC performances of a h-B¹⁰N as a passivation layer on an AlGaN/GaN HEMT device were done to ascertain the suitability of isotopically pure h-BN film functionality, as both a dielectric layer and a heat dissipative layer, thereby mitigating the self-heating problem in high power HEMT devices. FIG. 6(a) gives a schematic on the HEMT device, at the top is the h-B¹⁰N layer and followed by GaN and AlGaN/GaN heterostructure on a Si substrate. FIG. 6(b) gives a cross-section HRTEM image showing the different layers as illustrated in FIG. 6(a). To ascertain the elemental composition of these layers, an EDS line scan was done. The EDS line scan gives the elemental composition of Ga, B, N, Al and Si throughout the entire depth of the device (FIG. 6(c)). The different notable layers are demarcated with the different shaded regions, it begins with the h-BN layer, then the GaN layer and the AlGaN/GaN heterostructure and finally with a thin buffer layer of AlN on the Si substrate. FIG. 6(d) gives an atomic schematic on the lattice of the AlGaN/GaN heterostructure, showing how AlGaN and GaN forms two-dimensional electron gas (2DEG) layer by forming a bandgap-induced potential well. FIG. 6(e) gives the high-magnification HRTEM image at the AlGaN/GaN interface and FIG. 6(f) is the EDS line scan

FIG. 6 Fabrication and electronic performances of h-B¹⁰N-encapsulated GaN HEMT devices. (a) Schematics of GaN/AlGaN HEMT with h-B¹⁰N as the insulating-gate layer. (b) Cross-section TEM image of the HEMT device. (c) Line EDS mapping of the cross-section of HEMT device, showing the different elemental compositions of each layer. (d) Schematic illustration of GaN / AlGaN interface. (e) HRTEM image of GaN-AlGaN/GaN zone. (f) Line EDS mapping of this region showing the periodical distribution of Ga, N and Al in these layers. (g) The I-V characteristics of the HEMT at room temperature, illustrating that the device is Ohmic. (h) The DC output performance curve of the HEMT device made with h-BN as a passivation layer. (i) The transfer characteristics of the HEMT device.

confirming the highly layered structure of the AlGaIn/GaN 2DEG heterostructure. FIG. 6(g) gives the linear I-V characteristics of the HEMT device under normal operating conditions, indicating that the HEMT device behaves as an ohmic conductor. FIG. 6(h) shows the DC performance, I_D - V_D characteristic of GaN/h-B¹⁰N HEMT which was measured up to $V_D = 20$ V at different V_G ranging from 1 V to 5 V to avoid dielectric breakdown. The GaN/h-B¹⁰N HEMT exhibited maximum drain current density (I_{Dmax}) of 150.2 mA mm⁻¹. As shown in FIG. 6(h), the I_D in GaN/h-B¹⁰N HEMT was reduced beyond the maximum current density (I_{Dmax}) due to the self-heating effect. However, the effect of this is weak in extent, as the drop is only around 5.3%, as opposed to GaN/Diamond and GaN/SiC HEMTs, ~ 10% and ~ 27%, respectively.^{51,52} Beyond the reduction of I_D , maximum transconductance (g_{mmax}) and maximum drain current density (at $V_G = 0$ V), I_{DRM} , were analyzed from the measured transfer characteristics (FIG. 6(i)). The GaN/h-B¹⁰N HEMT was observed to attain a peak extrinsic transconductance (g_{mmax}) of 33.82 mS mm⁻¹ and a maximum I_{DRM} of 171.1 mA mm⁻¹. It is again, observed that the change in g_{mmax} at different values of V_D is small, in the range of 2.3% maximally whereas I_{DRM} increases with increase in V_D . Lower g_{mmax} reduction of GaN/h-B¹⁰N HEMT may indicate a negligible reduction in effective mobility of the device and further confirms the low self-heating effect of the HEMT due to the heat dissipation effect through the h-BN passivation layer. Consequently, the GaN/h-B¹⁰N HEMT configuration can operate at a high V_D with a low power output and without a significant trade-off of current density and transconductance, which are key requirements for GaN-based HEMT devices.

Conclusions

To sum, h-BN thin films with different isotopic compositions have been deposited directly on Si and GaN wafers by reactive-HIPIMS under a mixed argon and nitrogen environment. The as-grown BN thin films are hexagonal and exhibits the remarkable isotope-induced characteristics in Raman and FTIR analysis. A 231% enhancement in thermal conductivity was measured for isotopically pure h-B¹⁰N film and 210% enhancement for pure h-B¹¹N film compared to mixed composites. Besides the excellent thermal response, the dielectric dispersion and optical bandgap energy of the films exhibit a strong dependence on the isotopic composition of boron. The dielectric constant varies in the range from 5 to 7, while the dielectric loss can be less than 1.3%. Therefore, strong thermal performance combined with excellent dielectrics properties and wide bandgap make h-BN a promising dielectric material for heat self-dissipation GaN transistor. Hall mobility, sheet resistivity and sheet concentration of the as-deposited films on GaN substrates were analyzed, indicating that h-BN does function well as both a dielectric layer and a passivating layer on electronic devices. These result shows the primary results of the actualization of applying isotopically pure thin film with superior material properties on electronic devices and paves the way for future optical, thermal and electronic applications.

Conflicts of interest

There are no conflicts to declare

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