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Control of Nanoplane Orientation in voBN for High Thermal Anisotropy in a Dielectric Thin Film: A New Solution for Thermal Hotspot Mitigation in Electronics

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ABSTRACT: High anisotropic thermal materials, which allow heat to dissipate in a preferential direction, are of interest as a prospective material for electronics as an effective thermal management solution for hot spots. However, due to their preferential heat propagation in the in-plane direction, the heat spreads laterally instead of vertically. This limitation makes these materials ineffective as the density of hot spots increases. Here, we produce a new dielectric thin film material at room temperature, named vertically ordered nanocrystalline h-BN (voBN). It is produced such that its preferential thermally conductive direction is aligned in the vertical axis, which facilitates direct thermal extraction, thereby addressing the increasing challenge of thermal crosstalk. The uniqueness of voBN comes from its h-BN nanocrystals where all their basal planes are aligned in the direction normal to the substrate plane. Using the 3ω method, we show that voBN exhibits high anisotropic thermal conductivity (TC) with a 16 times difference between through-film TC and in-plane TC (respectively $4.26 \text{ W.m}^{-1}.\text{K}^{-1}$ and $0.26 \text{ W.m}^{-1}.\text{K}^{-1}$). Molecular Dynamics simulations also concurred with the experimental data, showing that the origin of this anisotropic behavior is due to the nature of voBN's plane ordering. While the consistent vertical ordering provides an uninterrupted and preferred propagation path for phonons in the through-film direction, discontinuity in the lateral direction leads to a reduced in-plane TC. In addition, we also use COMSOL to simulate how the dielectric and thermal properties of voBN enable an increase in hot spot density up to 295% compared with SiO_2 , without any temperature increase.

Introduction

Currently, thermal management is the limiting factor for electronic devices. Indeed, denser electronic designs induce an increase in thermal crosstalk: neighboring hot spots are heating up each other, resulting in heat accumulation in their vicinity that can lead to a drop in performance or even device failure.¹⁻² As the hot spots are getting smaller and more densely packed (in the

submicron region), thermal management at the nanoscale is becoming necessary and the search for nanomaterials with interesting thermal properties, such as anisotropic thermal conductivity (TC), has become a subject of interest.³ So far, the focus on such materials has been essentially on highly anisotropic materials such as graphene⁴ and hexagonal BN⁵ or multilayered thin films⁶ where the many planar interfaces and boundaries are inducing thermal anisotropy in the material. Unfortunately, such anisotropy promotes heat extraction in the horizontal direction due to the material's greater thermal conductivity in the plane direction compared to the out-of-plane. As such, this may contribute to the thermal crosstalk issue. On the contrary, nanomaterials such as vertically aligned nanotube structures display preferential phonon transport along the tubes direction,⁷ which can be exploited in electronic devices to alleviate heat buildup by extracting it vertically.⁸ In particular, Boron Nitride Nanotubes, or BNNTs, exhibit excellent phonon transport along the tube direction while remaining electrically insulative,⁸⁻¹⁰ allowing them to be used directly on top of the active electronics. However, their synthesis remains complex, with processes involving high temperatures¹¹⁻¹³ and is limited to small areas which is unsuitable and incompatible with existing device fabrication methodology.

Previously, a particular carbon thin film structure made of nanocrystalline graphite (NCG) with vertical alignment was studied.¹⁴ Due to such peculiar structural formation, NCG's nanostructure can be considered a middle ground solution between vertically aligned superlattices at the nanoscale and extremely dense nanotube forests. It was demonstrated that due to NCG's crystalline vertical alignment, the through-film thermal conductivity would improve by a factor of up to 20 compared to amorphous carbon films.¹⁵ However, NCG remains electrically conductive which makes it unsuitable for heat extraction directly on top of the active device. On the other hand, Boron Nitride (BN) thin films, which are made of vertically ordered h-BN (voBN) nanocrystals

and have similar crystalline structure as NCG, exhibit similar thermal properties while being electrically insulative. The growth of voBN thin films was previously reported¹⁶ and even though it was found that their through-film thermal conductivity performance has improved, no analysis of the in-plane thermal conductivity was performed. It was suggested that the reason for this through plane thermal performance increase was due to the vertical ordering of h-BN nanocrystals in the film, thus improving the phonon transport along the vertical direction (through-film). Here we show that voBN has an anisotropic TC through experimental characterization as well as MD simulations. Both results show high TC anisotropy with the cross-plane direction an order of magnitude higher than its in-plane counterpart. Using the experimental thermal results, COMSOL simulations were performed to assess the impact of using voBN as a substrate in heat extraction for hot spot arrays. Its thermal performance was then compared to SiO₂'s to directly evaluate both materials' performance. While preserving identical heat crosstalk, the simulation showed that using voBN could enable a device density increase by almost 300% compared to SiO₂. Indeed, voBN could potentially be the next dielectric material of choice for electronic devices, which would also be capable of channeling heat away efficiently.

Results and discussion

Microstructure analysis of the BN film through TEM and FTIR

The preferential vertical alignment of the BN thin film used for thermal characterization was verified by HRTEM as shown in Figure 1a. The BN thin film thickness was measured by cross section TEM and was 1134 nm. The image in Figure 1a shows the vertical alignment of h-BN nanocrystals in the film, with the computed FFT (inset of Figure 1a) confirming the (0002) h-BN planes have a vertical alignment, with an average spacing of 0.35 nm which is slightly higher than crystalline bulk h-BN (0.33 nm). In addition to the HRTEM characterization, FTIR was performed

to confirm the presence of voBN by computing the peak ratio between the in-plane B-N stretch mode located at 1380 cm^{-1} and the out-of-plane B-N-B bending mode located at 800 cm^{-1} . The computation method is explained in details in a previous study¹⁶ and can be found in the Supporting Information. The ratio of those 2 peak responses gives a good idea of the alignment of the h-BN nanocrystals. A ratio above 0.5 would indicate the presence of vertically ordered BN whereas a ratio below 0.2 would be the typical response for in-plane h-BN.¹⁶⁻¹⁹ Any value in between indicates random ordering of the nanocrystals. Figure 1b displays the FTIR response from the vertically ordered BN thin film used for this study. The ratio between the out-of-plane and in-plane response is 0.613, indicating a high ordering of the h-BN crystals in the vertical direction. The absence of any peak at 1050 cm^{-1} shows there is no c-BN phase existing in the film, demonstrating it is only made of sp^2 nanoclusters of BN.

Figure 1. (a) High resolution cross section TEM image of a vertically ordered BN thin film. The top left image is a zoom-in showing in more detail the BN crystal lattice with vertical alignment. The vertical alignment is further confirmed by the computed FFT which displays the typical partial rings for the (0002) h-BN planes with alignment perpendicular to the substrate plane. The outer

ring corresponds to the (-2110) h-BN plane. (b) FTIR response for a typical BN film with h-BN planes vertically ordered with respect to the silicon substrate. The determining criteria is a value above 0.5 when computing the normalized ratio between the in-plane and out-of-plane IR active modes.

Thermal conductivity characterization via the 3ω method

The 3ω method was used on the prepared BN thin film to measure the experimental value for the thermal conductivity in both in-plane and cross-plane directions.²⁰⁻²¹ A slope method was applied to determine the cross-plane thermal conductivity by measuring the 40 μm wide wire temperature oscillation ΔT_{s+f} using equation (1):²²

$$\Delta T_{s+f} = \Delta T_s + \frac{pd_f}{2blk_f} \quad (1)$$

Where p/l is the power per unit length of the heater, b is the heater half width, d_f and k_f are respectively the thin film thickness and the thin film cross-plane thermal conductivity. ΔT_s is the temperature oscillation of the bare substrate and ΔT_s is computed using equation 2:²²

$$\Delta T_s = \frac{p}{\pi l k_s} f_l(\ln \omega) \quad (2)$$

f_l is a linear function of $\ln \omega$ while k_s is the thermal conductivity of the bare silicon wafer and p/l is the same as above. Figure 2a shows the experimental temperature oscillation of the 40 μm wide wire on the BN film and the calculated temperature oscillation for the reference sample (bare Si substrate). By measuring the temperature difference between the reference sample and the BN sample, the thin film cross-plane thermal conductivity was computed to be $4.26 \pm 0.4 \text{ W.m}^{-1}.\text{K}^{-1}$. The in-plane thermal conductivity and $R_{\text{BN-Si}}$ require the use of the 4 μm wide wire. An exact solution of the temperature oscillation for a heater deposited on a thin film with anisotropic thermal

properties is given by the equations 3-5 below. The complex temperature oscillation of the heater, with the thermal boundary resistance contribution, can be expressed as:²²⁻²³

$$\Delta T = \frac{-p}{\pi l k_{y1}} \int_0^\infty \frac{1}{A_1 B_1} \frac{\sin^2(bx)}{(bx)^2} dx \quad (3)$$

Where:

$$A_1 = ((A_2 + k_{y2} B_2 R_{th}) \frac{k_{y2} B_2}{k_{y1} B_1} - \tanh(\varphi_1)) / (1 - (A_2 + k_{y2} B_2 R_{th}) \frac{k_{y2} B_2}{k_{y1} B_1} \tanh(\varphi_1)) \quad (4)$$

And:

$$B_i = (k_{xi}/k_{yi} x^2 + 2i\omega/\alpha_{yi})^{1/2}, \varphi_i = B_i d_i, i = 1, 2, \quad A_2 = -\tanh^{-1}(B_2 d_2) \quad (5)$$

In equation 3, b and p/l are the same as in equations 1 and 2. In equations 4 and 5, k corresponds to the thermal conductivity and α is the layer thermal diffusivity. The x and y subscripts correspond to in-plane and cross-plane respectively. The experimental temperature oscillation was fitted using equation 3 to obtain the in-plane thermal conductivity and R_{BN-Si} using the previously computed cross-plane thermal conductivity. The in-plane thermal conductivity and R_{BN-Si} are found to be $0.26 \pm 0.05 \text{ W.m}^{-1}.\text{K}^{-1}$ and $(5.9 \pm 1.2) \times 10^{-8} \text{ m}^2.\text{K}.\text{W}^{-1}$ respectively. Figure 2b shows the experimental temperature oscillation and fitting curve of the $4 \mu\text{m}$ wide wire, and the experimental temperature oscillation and calculated theoretical curve of the $10 \mu\text{m}$ wide wire, for the best fitting values obtained from the 40 and $4 \mu\text{m}$ wire. Indeed, it can be observed that there is good agreement between both experimental and calculated temperature oscillations values. Finally, the thermal conductivity anisotropy of voBN could be experimentally observed with a cross-plane TC of $4.26 \pm 0.4 \text{ W.m}^{-1}.\text{K}^{-1}$ and an in-plane TC of $0.26 \pm 0.05 \text{ W.m}^{-1}.\text{K}^{-1}$, which yields a ratio of 16 between both directions. This could be explained by the preferential phonon transport along the h-BN nanocrystals, which are aligned in the vertical direction in voBN.

Figure 2. (a) The experimental and the calculated temperature oscillation for the 40 μm wide wire deposited on BN/Si and reference (bare Si), respectively. The temperature difference between the Si substrate and the BN/Si is used to calculate the cross-plane thermal conductivity of BN film on Si substrate. (b) (i) The experimental temperature oscillation for the 4 μm wide deposited wire on BN/Si and corresponding fitting curve from the two-dimensional heat conduction model and calculated curve for $\pm 20\%$ change in the best fitted value for K_x . (ii) The experimental temperature oscillation for 10 μm wide deposited wire on BN/Si and corresponding calculated curve from the two-dimensional heat conduction model based on the K_y , and the fitted K_x and $R_{\text{BN-Si}}$ values determined by fitting the 4 μm wide heater.

Molecular Dynamics simulation of the anisotropic thermal property

To verify the hypothesis that this increase in TC in the h-BN plane direction is induced by the preferential vertical alignment of h-BN crystals, we performed Molecular Dynamics simulations. Figure 3a and 3c show the stable temperature distribution between 2 planes – inter-plane (Figure 3a) and within the same plane – intra-plane (Figure 3c) directions of the crystalline h-BN layers, respectively.

Figure 3. Temperature distribution and the accumulative energy changes with the simulation time between 2 planes (a, b) and within the same plane (c, d) directions for the crystalline h-BN.

For both cases, the temperature decreases almost linearly from the heat source to the heat sink, except for the significant temperature drop occurring near both heat sources and sinks for the distribution along the inter-plane direction due to the weak non-covalent interaction between the adjacent h-BN layers. Figure 3b and 3d show the accumulative energy changes in the heat sources and sinks for both the inter-plane and intra-plane directions. For both directions, the accumulative energy changes increase linearly with the simulation time. Likewise for amorphous BN, similar results have been computed as they will be required later. Linear fittings are conducted to obtain the temperature gradient and the heat flux. The average is taken on the fitting results from both sides of the heat source. According to Fourier's law of thermal conduction $J = -\lambda \nabla T$, the thermal conductivity for the crystalline h-BN layers along the inter-plane and intra-plane directions are obtained as 26.97 and 1.39 W.m⁻¹.K⁻¹ respectively, and the thermal conductivity for the amorphous BN is obtained as 6.61 W.m⁻¹.K⁻¹. Figure 4 shows the temperature distribution along the heat flux direction for the hybrid system of the crystalline h-BN and amorphous BN with covalently bonded interface (refer to the Supporting Information for more details). It is observed that there is a sharp

temperature drop ΔT_{In} of ~ 17 K at the interface. The heat flux is obtained at 8.245 eV/ps. Based on the relationship $G = J / \Delta T_{\text{In}}$, the covalent-bonded interface thermal conductance is obtained as $4.08 \times 10^9 \text{ W.m}^{-2}.\text{K}^{-1}$. A similar temperature distribution has been obtained for the non-covalent bonded interface and the interface thermal conductance is obtained as $0.514 \times 10^9 \text{ W.m}^{-2}.\text{K}^{-1}$.

Figure 4. Temperature distribution along the heat flux direction for the hybrid system of the crystalline h-BN and amorphous BN with covalent-bonded interface shown in Figure S1a. The red lines are drawn to guide the eye.

To predict the overall thermal conductivity of the voBN thin films, the simple series chain model as shown in **Figure 5** is used. In this model, multiple cubic crystalline h-BN grains are arranged into arrays and embedded into the matrix of amorphous BN which serves as the grain boundaries. In each grain, the h-BN layers are aligned parallel to the y-direction. The rule of mixtures is applied to the series chain for the calculation of the thermal conductivity k with equation 6 as:^{24 25}

$$k^{-1} = \sum_i f_i k_i^{-1} + nG^{-1} \quad (6)$$

where f_i and k_i are the length fraction and thermal conductivity of component i , and G is the interface thermal conductance with n being the number of interfaces per unit length.

Figure 5. Series chain model for the calculation of thermal conductivity along the (a) out-of-plane and (b) in-plane directions.

A side length of 5 nm for the cubic h-BN crystal and a thickness of 1 nm of the grain boundaries was used after estimating the grain size from high resolution TEM images. The length fractions of the crystalline h-BN and amorphous BN are obtained as 0.833 and 0.167 respectively, and the number of interfaces per unit length is 0.33 nm^{-1} . The intra-plane thermal conductivity $26.97 \text{ W.m}^{-1}.\text{K}^{-1}$ of the crystalline h-BN is used for the calculation of the out-of-plane thermal conductivity of the voBN thin film and it is obtained as $7.30 \text{ W.m}^{-1}.\text{K}^{-1}$. The inter-plane thermal conductivity $1.39 \text{ W.m}^{-1}.\text{K}^{-1}$ of the crystalline h-BN is used to calculate the in-plane thermal conductivity of the voBN film which is obtained as $0.79 \text{ W.m}^{-1}.\text{K}^{-1}$. The thermal conductivities along both the in-plane and out-of-plane directions are close to but higher than those measured by experiments. It is important to point out that the higher thermal conductivity values from the molecular dynamics simulation compared to the experimental values are most likely due to the series chain model. Indeed, the h-BN crystals are ideally arranged to be perfectly aligned with each other and all the h-BN layers have the same parallel orientation as the y-direction. Hence, the simple series chain model may not exactly reflect the practical arrangement of the grains and the network of their boundaries. Moreover, the h-BN layers are modelled as defect-free. However, both experimental and simulation results agree on the extent of the thermal conductivity anisotropy, with an out-of-plane TC which is approximately an order of magnitude higher than the in-plane TC. Such

anisotropy is believed to originate from the anisotropic thermal conduction for the crystalline h-BN along the intra- and inter-plane directions, and the anisotropic atomic structure and thermal conductance of the interfaces between the crystalline h-BN and amorphous BN. To characterize the role of the interface in the overall thermal conduction of the thin film, a ratio $R = nG^{-1} / k^{-1}$ is defined. This ratio demonstrates the contribution of the interface thermal resistance to the overall thermal resistance. For thermal conduction along the out-of-plane and in-plane directions of the thin film, R is obtained as 59% and 51%, respectively, indicating that the interfaces between the crystalline h-BN and amorphous BN are the main barrier for thermal conduction inside the self-ordered BN thin films. This is consistent with our previous studies about the interface in a hybrid system²⁶⁻²⁷. Based on equation 6, it can be induced that the thin film thermal conductivity increases with the decrease of the interface density, namely, with the increase of the grain size. Figure 6a and 6b show the dependence of the thin film thermal conductivity on the grain size with a fixed thickness of the grain boundary along both the out-of-plane and in-plane directions, respectively. As the grain size increases, the thin film thermal conductivity increases for both the out-of-plane and in-plane directions. Such increase is more prominent for the former. Figure 6c shows the anisotropic ratio between the out-of-plane and in-plane thermal conductivity and indicates that the ratio increases as the grain size increases. It should be noted that in Figure 6, the intra-plane and inter-plane thermal conductivities of the crystalline h-BN with the grain size of 5 nm are used to estimate the thermal conductivity of the thin film with different grain size. In practice, the intra-plane thermal conductivity of the crystalline h-BN increases with the grain size, while the inter-plane thermal conductivity does not. Hence, the out-of-plane thermal conductivity of the thin film would be higher than those presented in Figure 6a. As a result, the anisotropic ratio shown in Figure 6c would be even higher in practice. Finally, it is important to note that previous studies

have demonstrated that the thermal resistance at the interface of a hybrid system mainly stems from the mismatch of the phonon spectra of the materials at both sides of the interface. Indeed, there is a significant mismatch between the phonon spectra of amorphous BN and crystalline hexagonal BN, especially in the low-frequency range of 0-10 THz and the high-frequency range of 45-55 THz. Due to the spectrum mismatch, intensive phonon scattering occurs at the interface and leads to the large interface thermal resistance which significantly affects the overall thermal conductivity of the voBN thin films. Both spectra can be found in the Supporting Information in Figure S3.

Figure 6. The dependences of (a) the out-of-plane, (b) the in-plane thermal conductivities and (c) the anisotropic ratio between them on the grain size of the crystalline h-BN.

Performance of voBN at preventing thermal crosstalk

Having demonstrated that voBN has high thermal conductivity anisotropy, COMSOL simulations were used to demonstrate how such property in voBN can be used as a channel for heat extraction thanks to its preferential thermal conductivity in the vertical direction. Instead of simulating a whole array of hotspots, the simulated system consists solely of a unit cell containing one hotspot due to the symmetrical boundary conditions between two hotspots (the full description of the simulation model is given in the Methods section below).²⁸ When performing the simulation

to solve the system for a stationary solution (once the whole device temperature has reached equilibrium), we obtain the results as depicted in Figure 7.

Figure 7. Cross section image (as per the inset image) of the isothermal contours for the temperature response of a hot spot (0.1 W heat source) heating up from the bottom a 100 μm cubic structure. The diagram on the left is for the case of a device made of SiO_2 while the one on the right is a device made of voBN. The anisotropy of voBN induces an elongated temperature response in height, while keeping the in-plane temperature spread more compact compared to SiO_2 .

The schematic shows the plane view from which the isothermal contours are extracted. The contours are the simulation results with SiO_2 used as the device material (left), while the other is based on voBN (right). The effect of a thermal conductivity anisotropy is clearly apparent when comparing both hot spot shapes. While SiO_2 generates spherical shaped response temperature contours, voBN displays a stretched response in the out-of-plane direction, with a thinner temperature spread in the xy plane direction. In addition, the temperature profile along the hotspots

is displaying a temperature oscillation along the x axis direction where the maximum in temperature is located at the hotspot itself, while the coolest region is at the unit cell edges exactly in between two hotspots, which is in good agreement with other simulation models.²⁸⁻²⁹ Figure 8a illustrates the temperature plot along the line plot located as shown in the small diagram. That particular line is used to represent the temperature variation as it is equidistant to a neighboring hot spot (in the case of an infinite array of hot spots) and the temperature response along that line is directly affected by the thermal crosstalk between two hot spots. The temperature is the highest at the bottom of the device as it is the closest to the hot spots and tends towards 20 degC at 100 μm as it reaches the top surface where the boundary condition has been set to that temperature. It can be observed that voBN prevents thermal crosstalk much more efficiently than SiO_2 for the same hot spot distance due to its preferential thermal transport in the z direction as displayed by the isothermal contours stretched in the vertical direction in Figure 8b.

Figure 8. Temperature line plot (inset a) along the temperature line as shown by the vertical dotted arrow located at a distance of $d/2$ from the hot spot in the unit cell schematic (inset c). The distance

d is the square dimensions in the xy plane, which can be seen as the distance between two adjacent hot spots. Each line represents the temperature variation across the 100 μm thick layer, for various hot spot distances. The temperature response of SiO_2 is sandwiched between two voBN responses with closer hot spot distances: 50.3 and 54.1 μm . Inset b shows the stretched isothermal contours in the vicinity of a hot spot due to the anisotropic nature of voBN.

This enables a structure redesign where the distance between two hot spots can be decreased. Thus, the solid line which is the SiO_2 temperature response for $d = 100 \mu\text{m}$ can be sandwiched between two different temperature responses using voBN, where the distance d between two hot spots was changed in order to get either a maximum temperature equivalent to SiO_2 ($d = 50.3 \mu\text{m}$) or a lower boundary where the voBN temperature response is below the SiO_2 response along the whole line ($d = 54.1 \mu\text{m}$). A shrinking of the space between two neighboring hot spots using voBN allows a more compact device design. In other words, the simulated cell with SiO_2 containing one hot spot spreads on a surface of $100 \mu\text{m} \times 100 \mu\text{m}$ which is $10000 \mu\text{m}^2$. When replacing SiO_2 with voBN, a new design, enabling improved temperature crosstalk along the whole device's borders, can be used with two neighboring hot spots only 54.1 μm from each other. In this way, the cell occupies now a surface of $2927 \mu\text{m}^2$, which is an improvement of approximately 242% in the surface area for the same amount of heat dissipation. In the best case scenario, where only the maximum temperature has to be solely considered at the cell boundaries, a design with a distance of 50.3 μm between hot spots can be achieved and thus represents an improvement of 295% in surface area.

Conclusion

A complete study of the thermal conductivity of voBN was performed and its anisotropic property was evaluated and analyzed. Thanks to the 3ω characterization, the through-plane thermal

conductivity was computed to be $4.26 \text{ W.m}^{-1}.\text{K}^{-1}$ which is 16 times greater than its in-plane thermal conductivity ($0.26 \text{ W.m}^{-1}.\text{K}^{-1}$). In addition, the thermal boundary conductance with silicon was found to be $0.17 \times 10^8 \text{ W.m}^{-2}.\text{K}^{-1}$ which is similar to the thermal boundary conductance between Si and SiO_2 .³⁰ Molecular Dynamics simulations successfully verified the thermal conductivity anisotropy observed experimentally and the anisotropic behavior was found to be due to the interfacing of the crystalline nanostructure of the film with the surrounding amorphous regions. Indeed, in voBN, the h-BN planes are consistently ordered along the vertical direction, facilitating the phonon transport in that direction. In addition, the increase of thermal conductivity was correlated with the increase of crystal size and therefore suggests the possibility of getting voBN with improved thermal performances by enhancing the growth process. Finally, the anisotropic thermal conductivity of voBN was computed in COMSOL simulations and it was observed that voBN is preventing the heat from spreading compared to an isotropic material like SiO_2 . In addition, the improved thermal performance obtained when replacing SiO_2 with voBN enables an increase in hot spot density of up to 295% while keeping the overall device temperature the same due to a decrease in heat cross over between hot spots. The anisotropy in thermal conductivity combined with the dielectric property (with a dielectric constant computed to be approximately 8.9 – refer to Supporting Information for more details) makes vertically ordered BN a unique material with the potential of protecting densely packed electronic devices from neighboring hot spots by preventing heat spread. When combining that unique anisotropic property with the capability of producing such material on wafer scale at room temperature, voBN provides a readily available solution to existing thermal design issues. Indeed, voBN can encapsulate devices to provide electrical insulation while allowing thermal dissipation from the top, with a preferential heat channel directed towards the heat sink.

Methods

Sample preparation

All samples in this study were produced using a High Power Impulse Magnetron Sputtering (HiPIMS) system from Mantis Deposition Ltd with a Hipster 1 pulsed power supply from Ionautics. The vertically ordered BN (voBN) films were obtained using a Lanthanum Hexaboride (LaB_6) target reactively sputtered in nitrogen gas, as described in a previous study.¹⁶ The chamber base pressure was 10^{-6} mbars and would increase to a partial pressure of 2.5×10^{-3} mbars during film growth. The BN thin films were produced at room temperature, with a repetition rate of 4 kHz and pulses of 25 μs , yielding an on/off ratio of 10%. The peak current for each pulse was 30 A at 700 V, with an average power of 350 W and current of 500 mA, which is equivalent to a peak power density of 115 W.cm^{-2} . The thin films were characterized using High Resolution Transmission Electron Microscopy (HRTEM) as well as Fourier Transform Infrared Spectroscopy (FTIR) to study the film microstructure and confirm the presence or absence of voBN in the films.

Thermal characterization

The 3ω method^{22, 31-32} was employed to measure the in-plane and cross-plane thermal conductivity (referred respectively as K_x and K_y) of the voBN film and the thermal boundary conductance between the BN thin film and the Si substrate ($R_{\text{BN-Si}}$). In this technique, a metal wire is micro-fabricated onto the sample surface to act as both a heater and a thermometer. To carry out the thermal characterization, an AC current with angular frequency ω is passed through the metal wire and the third harmonic voltage across the metal wire is measured to determine the temperature oscillation of the wire. A two-dimensional heat conduction model can be utilized to model the temperature oscillation of the metal wire to measure in-plane and cross-plane thermal conductivity as well as $R_{\text{BN-Si}}$ ^{22-23, 33}. To perform the measurement, metal lines of Au/Cr with thickness of 200/5

nm, 1 mm long and with different widths of 4, 10, 40 μm were deposited on a BN/300 μm thick Si sample by using lithography. The 40 μm wide wire and 4 μm wide wire are used to measure cross-plane and in-plane thermal conductivity respectively, and the wire with 10 μm width is used to evaluate the results. The metal lines are finally bonded onto a chip carrier using gold wire bonding and was placed in a vacuum chamber to perform the measurement.

Thermal simulation

Molecular Dynamics (MD) simulations were performed to assess the role and impact of the crystalline ordering on the thermal conductivity. To simulate the thermal conductivity of the synthesized voBN thin films, the thermal conductivities of multilayered h-BN nanosheets along the intra-plane and inter-plane directions, as well as the thermal conductivity of the amorphous BN are first calculated. The schematics of the simulation models as well as the in-depth explanation of the model parameters for the thermal conductivity calculations are shown in the Supporting Information (**Figure S1**).

Thermal crosstalk simulation

A simple simulation has been set up for the purpose of understanding how the thermal anisotropy of vertically ordered BN would affect the design of a device generating heat through multiple hot spots. The simulation uses COMSOL Multiphysics 5.2 with the Heat Transfer module and the device geometry consists of a 100 μm by 100 μm square with a thickness of 100 μm and is made of either SiO_2 or voBN. The thermal conductivity values used for both materials are $1.4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for SiO_2 (the value was directly taken from the COMSOL library for bulk SiO_2) and the experimental results obtained in this study (i.e. $0.26 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the in-plane direction and $4.26 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the out-of-plane direction) were used for voBN. In order to generate heat across the square, one hot spot represented as a small 1 μm by 1 μm square and generating 0.1 mW of heat

across its surface was placed at the bottom of the device. As simulating an array would imply having the same cube patterns and hot spots repeated in the same plane, it is easy to notice that their thermal response would be identical, implying that a simple element (one cube plus a hot spot) can be considered as an adiabatic system where the cube sides in contact with their neighbor are playing the role of a perfect thermal isolator. In addition, the bottom surface was also considered thermally insulating. This is in order to prevent heat from escaping from the bottom and to redirect the hot spot thermal energy towards the top of the device where a boundary condition of temperature set to 20 degC was chosen. For more information about the simulation setup, please refer to the supporting information.

Supporting Information Available

The supporting information is available and contains the following information:

- Detailed method for Molecular Dynamics simulation of the thermal conductivity
- The FTIR peak ratio computation method
- Detailed method for hot spot crosstalk simulation with COMSOL
- Method for dielectric constant computation

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡ The following authors contributed equally this work: O. Cometto, M. K. Samani and L. Bo

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