Nanoscale

PAPER



Cite this: Nanoscale, 2015, 7, 18984

Vertically self-ordered orientation of nanocrystalline hexagonal boron nitride thin films for enhanced thermal characteristics†

Olivier Cometto,^{a,b} Bo Sun,^c Siu Hon Tsang,^d Xi Huang,^c Yee Kan Koh^c and Edwin Hang Tong Teo*^{a,e}

Vertically self-ordered hexagonal boron nitride (ordered h-BN) is a highly ordered turbostratic BN (t-BN) material similar to hexagonal BN, with its planar structure perpendicularly oriented to the substrate. The ordered h-BN thin films were grown using a High Power Impulse Magnetron Sputtering (HiPIMS) system with a lanthanum hexaboride (LaB₆) target reactively sputtered in nitrogen gas. The best vertical alignment was obtained at room temperature, with a grounded bias and a HiPIMS peak power density of 60 W cm⁻². Even though the film contains up to 7.5 at% lanthanum, it retains its highly insulative properties and it was observed that an increase in compressive stress is correlated to an increase in film ordering quality. Importantly, the thermal conductivity of vertically ordered h-BN is considerably high at 5.1 W m⁻¹ K⁻¹. The favourable thermal conductivity coupled with the dielectric properties of this novel material and the low temperature growth could outperform SiO₂ in high power density electronic applications.

Received 27th July 2015, Accepted 12th October 2015 DOI: 10.1039/c5nr05009j

www.rsc.org/nanoscale

Introduction

Textured carbon, a nanostructured carbon film with its basal plane oriented vertically, has been studied in the past for its remarkable properties.^{1,2} Studies have shown that it has an excellent through plane thermal conductivity³ (*i.e.* perpendicular to its substrate) of up to 16 W m⁻¹ K⁻¹ as compared to amorphous carbon (less than 5 W m⁻¹ K⁻¹). The simplicity to obtain it under low temperature growth conditions (*i.e.* below 200 °C) and by post-deposition phase transformation treatments on amorphous carbon film (*i.e.* laser annealing⁴ and stress induction⁵) have unveiled its potential for thermal dissipation applications in electronics. However, textured carbon is electrically conductive⁶ and less applicable for devices where an insulative material is necessary. Conversely, Boron Nitride (BN) compounds, which are isostructural to the polymorphs of

carbon, are however highly electrically insulative and a material of choice for use as a dielectric. BN exists in many phases analogous to carbon, the most common being the sp^2 bonded hexagonal phase (h-BN) comparable to graphite, the sp³-bonded cubic phase (c-BN) similar to cubic diamond as well as the turbostratic BN (t-BN) phase analogous to turbostratic carbon. This similarity in structure suggests that a BN equivalent of textured carbon phase could exist and a similar thermal improvement is expected while preserving its intrinsic insulative properties. Importantly, although turbostratic BN possesses out-of-alignment basal planes, the intrinsic random orientation of the planes hampers the phonon transport due to the disordered planar orientation and the lack of a continuous crystalline structure. Also, despite the fact that t-BN was first discovered in the 1960s,⁷ the primary research was conducted mainly for the suppression of its formation, in an attempt to obtain high quality c-BN or h-BN.8-11 Here, we introduce a controlled growth of a vertically self-ordered hexagonal BN structure with High Power Impulse Magnetron Sputtering (HiPIMS).¹² Since BN is electrically insulative, a Lanthanum Hexaboride (LaB₆) target was used instead and reactively sputtered in nitrogen gas to grow BN. It is shown that the lanthanum content in the film remains low and does not affect the electrical properties of the BN films. The vertically oriented arrangement of boron and nitrogen sp² clusters in our BN film is structurally equivalent to h-BN and retains similar characteristics. In addition, this oriented structure



View Article Online

^aSchool of Electrical and Electronics Engineering, Nanyang Technological University, Block S1, 50 Nanyang Avenue, Singapore 639798. E-mail: htteo@ntu.edu.sg

^bCINTRA CNRS/NTU/THALES, UMI 3288, Research Techno Plaza, 50 Nanyang Drive, Border X Block, Level 6, Singapore 637553

^cDepartment of Mechanical Engineering, National University of Singapore, Singapore 117576

^dTemasek Laboratories@NTU, 50 Nanyang Avenue, Singapore 639798, Singapore ^eSchool of Materials Science and Engineering, Nanyang Technological University, Block N4.1, Nanyang Avenue, Singapore 639798

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/ c5nr05009j

Nanoscale

facilitates phonon transport in the vertical direction, and thus a relatively high thermal conductivity of 5.1 W m⁻¹ K⁻¹ is achieved in the vertical direction. Here, we propose that the controlled growth of highly ordered h-BN is due to the ioninduced compressive stress during growth, where the Gibbs energy would be minimal when the basal plane orientates itself parallel to the stress plane,^{13,14} similar to the previous observation in carbon.^{1,6}

Experimental setup

Film growth

BN films have been deposited using a HiPIMS system from Mantis Deposition Ltd combined with a Hipster 1 pulsed power supply from Ionautics. The pulse rate was set to 4000 Hz, with a pulse width of 25 μ S, achieving a duty cycle of 10%. The base pressure used in the chamber is 10^{-6} mbar, and goes up to 8×10^{-3} mbar during deposition. Pure boron is electrically insulative at room temperature and requires to be heated up to 500 °C before it starts being conductive, which complicates the sputtering setup.¹⁵ Instead, a 3" diameter lanthanum hexaboride (LaB₆) target was used as it does not require high temperature and is also able to produce plasma with very high boron content and high ionization rate.^{16,17} The LaB₆ target was reactively sputtered by a mixture of nitrogen (20%) and argon (80%). The pulse voltage was 350 V with a pulse intensity of 25-30 A and an average power of 270 W. With a duty cycle of 10%, the peak power density is $\sim 60 \text{ W cm}^{-2}$. Several BN thin films were deposited with various bias voltage ranges from 0 V (substrate grounded), -47 V (floating substrate), -75 V and -100 V, and substrate temperatures of room temperature (RT), 50 °C, 600 °C and 1000 °C. All the samples were deposited on double sided polished silicon substrates (100) with a thickness of about 700 µm.

Film characterization

High resolution transmission electron microscopy (HRTEM) was performed to study the film crystalline structure, and electron energy loss spectroscopy (EELS) was used to deduce the B: N ratio as well as the amount of La in the film. In addition, the sample smoothness (RMS average) was measured via atomic force microscopy (AFM) on a square surface where each side is 25 µm in length. X-ray diffraction (XRD) patterns and rocking curves were obtained using a Shimadzu XRD-6000 X-ray diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm), using the Bragg Brentano geometry. The film resistivity was measured using a 4-point probe system (Keithley 4200-SCS). Fourier Transform Infrared Spectroscopy (FTIR) was performed to analyse the presence of h-BN and c-BN. The stress data were gathered using a Bruker DektakXT surface profiler with the Vision64 software to compute the stress from the film profiling. The thickness and profile of the substrates were measured before the film deposition at a specific location (profile length of 10 000 µm). After the film was grown, the sample was profiled again and the software compared both profiles to

compute the stress. The film thickness was measured at 4 different locations on each sample in order to obtain an average film thickness and confirm the uniformity of the film across the substrate. The average stress was then computed using the stress analysis component of the software.

The thermal conductivity was measured using time domain thermoreflectance (TDTR),¹⁸ a pump-probe technique that has been widely used for thermal properties of thin films^{19,20} and interfaces.²¹ To prepare the samples for TDTR measurements, a \sim 90 nm thick Al film was deposited on the samples to be the transducer for the measurements. In TDTR measurements, a train of ultrashort laser pulses is split into a pump beam and a probe beam using a polarizing beam splitter. The pump beam, modulated by an electro-optic modulator, is absorbed by the Al transducer and thus heats the sample periodically. The synchronized but time-delayed probe beam measures the temperature oscillation on the surface of the samples via the change in reflectance with temperature (i.e. thermoreflectance). The thermal conductivity of BN and the thermal conductance of Al/ BN interfaces are then derived by comparing the TDTR measurements to the calculations of a thermal model for heat flow in layered structures.²² In the measurements, we used a modulation frequency of 1–10 MHz, a $1/e^2$ laser radius of 6–30 µm and a total laser power of 25-130 mW; the total power was chosen according to the laser spot size to limit the steady state temperature rise to only <10 K. Similar values of thermal conductivity were derived when different modulation frequencies and laser spot sizes were used.

Results and discussion

Microstructure analysis of the BN film through TEM

Oriented BN films with thicknesses beyond 1.5 µm have been achieved without any film dislocation at the interface between the silicon substrate and the film. Fig. 1 shows two HRTEM images of a film deposited with a power density of 60 W $\rm cm^{-2}$ at room temperature and a floating bias of -47 V. From Fig. 1a, it can be seen that the film consists of a thin buffer zone at the interface between the BN film and the substrate that is made of amorphous BN, with a thickness of approximately 6 nm, before the ordered layer starts. This transition layer, induced by the different lattice constants between silicon and the oriented BN film, acts as a lattice mismatch buffer, preventing film dislocations. The Fast Fourier Transform (FFT) of the oriented BN film exhibits the characteristic pattern of normal orientation along the (0002) plane, with an inter-planar distance of 0.35 nm. In addition, the FFT of the silicon substrate also shows a highly crystalline structure, which is evidence that no damage was made to the substrate during the deposition process. Fig. 1b shows another HRTEM image taken a few hundred nanometers away from the substrate. From the distinct observation of the basal planes and the diffraction arcs seen in the FFT image (inset), the formation of the planes is highly oriented and homogeneous across the entire film.



Fig. 1 (a) HRTEM of a BN film grown at room temperature with floating bias showing the interface between the film and the silicon substrate. A transition layer of ~6 nm is located at the interface before the vertically ordered structure starts. The smooth interface implies a good film adhesion and no damage to the substrate. The top FFT shows a normal orientation along the (0002) plane, with an interplanar distance of 0.35 nm. (b) HRTEM of the same film taken in the middle region with its FFT displaying compact partial circles, which indicates normal orientation.

Quantifying the film ordering and its dependence to film stress

The quality of the film structure was measured using FTIR. It is a technique that has been widely used for BN thin film characterization^{9,23,24} and can provide information about the vibrational modes in the BN crystalline structure to detect the presence of either the hexagonal or cubic crystal structure. In addition, it can also differentiate between vertical and horizontal ordering of the hexagonal phase by comparing the degree of ordering between the films. An enhanced response peak at 800 cm⁻¹ (out-of-plane B-N-B bending mode absorption peak) relative to the main 1380 cm^{-1} peak (in-plane B-N stretch mode), as well as the emergence of a 2-phonon peak or "derivative-like" response^{25,26} at 1600 cm⁻¹, is evidence of h-BN with vertical plane orientation. Indeed, h-BN planes exhibit an IR active mode at 800 cm⁻¹ which is forbidden in the case of an IR beam with normal incidence. In the case of non-normal incidence, the 800 cm⁻¹ mode starts being active and is maximum when the basal planes are aligned perpendicular to the substrate.²⁵⁻²⁷ In this study, we computed the ratio of the in-plane and outof-plane IR responses to quantify the extent of plane orientation in the films. Fig. 2 compares the FTIR response of an ordered h-BN film, a BN film containing both cubic and turbostratic phases as well as h-BN powder. For the c-BN/t-BN film, the cubic content a_{cBN} is directly computed from the ratio of the cubic peak intensity as per the following formula:^{23,28}

$$a_{\rm cBN} = \frac{I_{\rm c}}{I_{\rm c} + I_{\rm h}}$$

where I_c and I_h are respectively the c-BN (1080 cm⁻¹) and inplane h-BN (1380 cm⁻¹) maximum absorption peaks, and it is found to be 20%. For the oriented BN thin film, the



Fig. 2 FTIR spectra of BN samples. The h-BN powder is a high purity powder made of 10 μ m particles. The c-BN/t-BN film was grown with HiPIMS at 500 °C, a 0 V substrate, and a peak power density of 200 W cm⁻². The ordered h-BN sample was grown with HiPIMS at room temperature and 60 W cm⁻² peak power density. The computed $R_{770/1380}$ peak ratios for ordered h-BN, c-BN/t-BN and h-BN powder are respectively 0.51, 0.19 and 0.29.

absence of any peak around 1080 cm^{-1} confirms the absence of the cubic phase in the film. It is also characterized by its broader peak around 1400 cm^{-1} and a significant response at around 800 cm^{-1} whereas the other spectra in Fig. 2 exhibit a sharper response around 1400 cm^{-1} and a much weaker peak around 800 cm^{-1} . Each spectrum was normalized between 0 and 1 for all values in between 650 cm^{-1} and 2000 cm⁻¹ after subtracting a baseline (see ESI† for more details of the spectrum processing). The maximum of the absorption peak seen in Fig. 2 reaches 0 for the in-plane vibration at 1380 cm^{-1} and the ratio $R_{770/1380}$ can be written as follows:

$$R_{770/1380} = \frac{1 - I_{770}}{1 - I_{1380}} = \frac{1 - I_{770}}{1}$$

Using this peak ratio definition, we computed the values for the 3 samples in Fig. 2 (as shown in the caption).

Fig. 3a is a plot of the compressive stress and the FTIR peak ratio versus substrate negative bias. It can be observed that the compressive stress decreases with an increase of bias. Furthermore, the FTIR peak ratio shows a downward trend when the bias voltage increases, indicating that a higher compressive stress induces an increased vertical alignment of the basal planes in the film. The FTIR peak ratio at 75 V negative bias shows a slightly higher value compared to the floating bias point (47 V) due to the fitting of the baseline, introducing small errors (± 0.02) into the peak heights. Fig. 3b shows that the compressive stress in the film decreases with increasing negative bias and/or increasing temperature, with a maximum of 4 GPa for a grounded substrate at room temperature. The decrease in compressive stress in the film on increasing the energies during film growth is explained further below.

The growth mechanism of the film could be explained by two competing effects that are contributing to the film structure formation: temperature and ion energy (controlled by the bias voltage). A higher temperature increases the ion mobility but also moves the h-BN/c-BN phase equilibrium to a higher pressure.²⁹ In the case of PVD processes in a vacuum, compressive film stress accounts for the high pressure zone localized at the growth region. In the case of HiPIMS with LaB₆, no in-plane hexagonal BN structure could be obtained even at 1000 °C as the stress build-up in the film during deposition remains too high, promoting the vertical orientation instead. Following the trend seen in Fig. 3a, increasing the ion energy will lower the stress, which means that increasing the bias further could potentially lower the stress enough to allow the formation of in-plane h-BN. Unfortunately, no successful growth beyond -100 V bias was achieved due to the occurrence of electrical breakdowns at the substrate. This is because the deposited BN is electrically insulative and acted as an immediate dielectric layer inbetween the substrate (negatively charged) and the plasma B^+ , La^+ and N^+ ions (positively charged). As the deposition continues, it reaches a critical charge build-up on both sides



Fig. 3 (a) Film stress as a function of the applied bias voltage and the FTIR peak intensity ratio between the in-plane response located at 1380 cm⁻¹ and the out-of-plane response located at 770 cm⁻¹. (b) Compressive stress value for films grown at different temperatures and biases. The lowest bias is 0 when the substrate holder is connected to the ground. The value of -47 V is the floating bias.

of the film, leading to an electrical breakdown and damages to the surface.

Impact of stress on the film structure

From the above results, a direct relationship between compressive stress, ion energy and film ordering is established. As observed in Fig. 3, increasing the bias would decrease the stress, unlike carbon where it would reach a maximum stress before decreasing.³⁰ McKenzie *et al.* suggested that the stress σ could be written as follows:¹³

$$\sigma \propto \frac{\sqrt{E}}{\frac{R}{j} + kE^{5/3}}$$

where $k = 0.016\rho E_0^{-5/3}$, *E* is the ion energy, *j* is the ion flux, and ρ , E_0 and *R* are material related parameters. This formula describes 3 different behaviours depending on the incident ion energy *E*. For low values of *E*, the ions will bounce off the film and will not disturb the film structure much, meaning that the stress will remain low. For intermediate values of *E*,

Paper

the ions will penetrate the surface of the film and contribute to the stress increase by forcing themselves in the film and create a denser and more compact structure. For higher *E* values, the ions will go deeper into the film and start displacing atoms in the structure, creating defects in the crystals and thus reducing the film stress. When correlating the stress curve experimentally obtained for the case of HiPIMS with LaB₆, the trend observed in Fig. 3a is located in the later portion of the stress *versus* ion energy curve as per Fig. 4. For high values of *E* the stress can be approximated as:

$$\sigma \propto \frac{1}{kE^{7/6}}$$

When computing a curve fitting of the experimental data, a good match was obtained for $k = 3.73 \times 10^{-4}$ and E = 259 eV. A value of 259 eV as an average ion energy distribution of B⁺ is higher than expected but is still within a reasonable range. By comparison, a carbon film obtained from filtered cathodic vacuum arc deposition usually produces a plasma made of C⁺ ions with an average energy of 20 eV.³¹ The lower energy for carbon allows the tuning of the ion energy to reach the peak of the stress curve, permitting the growth of ta-C for instance.

The extremely high plasma energies are a result of the use of the LaB₆ target combined with the high current pulses of HiPIMS, which facilitates the phase change from amorphous BN to a crystalline structure. The B⁺ energy distribution comprises two areas: a peak at 1–5 eV, followed by a long tail an order of magnitude lower in density, but extending to several tens of eV.^{16,17} Such an energetic plasma has the effect of increasing the impact energy between the ions and the substrate, contributing to the nanostructural formation of the



Fig. 4 Curve plotted from the stress curve formula given by McKenzie *et al.* showing the compressive stress depending on the ion energy for carbon. Assuming a similar curve distribution for boron nitride, the current results are located at the high ion energy portion as shown in the inset, displaying the computed compressive stress for ordered h-BN films grown at room temperature.

oriented planes by inducing sufficient compressive stress in the film.

Impact of c-BN nanocrystals on the vertically oriented BN growth

When the power density is increased beyond $\sim 200 \text{ W cm}^{-2}$, with a temperature of 500 °C and a bias voltage of -200 V, the growth condition is more favourable for the formation of c-BN and the presence of c-BN nanocrystals of $\sim 5 \text{ nm}$ in the film was observed, embedded in a mixture of turbostratic and amorphous phases (Fig. 5).

The cubic nanocrystals disrupt the formation of any vertical ordering structure by introducing directional seeds along the (111) direction, enabling the epitaxial growth of (001) sp² planes in all directions. By preventing c-BN formation, the sp² layers formed by the high ion energies simply follow the direction minimizing the Gibbs free energy, which is driven by the biaxial compressive stress across the substrate. Ultimately, the t-BN phase can be seen as a defective ordered h-BN phase where its linear vertical growth is disrupted by c-BN nanocrystal formation.

We confirm the presence of c-BN and h-BN nanocrystals through an XRD 2θ detector scan at a fixed $\omega = 3.71^{\circ}$, as seen in Fig. 6. Diffraction peaks corresponding to c-BN [111] and h-BN [101] are detected. The peaks are fitted with two Gaussian curves and we obtain a rough estimation of grain size of the order of ≈ 10 nm, in agreement with the TEM images. More discussions of our XRD scans are presented in the ESI.†



Fig. 5 HRTEM of a BN film deposited with a bias of -200 V at 600 °C and a HiPIMS maximum power density of 200 W cm⁻². The film is highly disordered, with c-BN nanocrystals of ~5 nm, embedded in a matrix of turbostratic sp² BN made of hexagonal and/or rhombohedral structures. (a) is the FFT of the whole image, displaying the characteristic rings for turbostratic BN: the inner (0.36 nm per cycle) and outer (0.21 nm per cycle) rings are induced respectively by the random orientation of the h-BN (0002) and c-BN (111) configurations. (b) and (c) are respectively the FFT of the green (top) zone containing c-BN and the blue (bottom) zone made of h-BN/r-BN. More HRTEM images displaying c-BN nanocrystals can be found in the ESI.†

Nanoscale



Fig. 6 2θ scan of the c-BN/t-BN sample with ω fixed at 3.712°. Two Gaussian curves are used to fit the graph, which is contributed by c-BN (111) and h-BN (101) respectively. The fixed ω is determined by rocking curve scan on the c-BN/t-BN sample at various phi angles to detect the (111) plane of c-BN at the 2θ of 43.314°. A weak peak is detected at the ω of 3.712° for the rocking curve scan.

Lanthanum presence in the film

As the films were produced using an LaB_6 target, it is important to quantify the content of La in the film. The EELS spectra in Fig. 7a-c are typical responses respectively from boron, nitrogen and lanthanum. The boron response exhibits a higher π^* electron transition response relative to the σ^* one, indicating a full sp² hybridization. The EELS measurement in Fig. 7d shows a constant B:N:La ratio (0.4:0.5:0.1), measured from the top of the BN film to the bottom (substrate), as indicated in Fig. 7e. The nitrogen ratio remains at around 50 at% which is slightly higher than that of boron (~42 at%), giving a B:N ratio of 1.15. The La content is stable between 5 and 10 at% and no aggregates of La could be observed in HRTEM images or *via* EELS mapping, indicating an even spread across the whole film. The extra La atoms in the structure could be accounted for by the occupation of some B vacancies in the film as the ratio between N and La + B is 1.

The film resistivity was measured using a 4-point probe system but no accurate results could be obtained. This is due to the film resistance being comparable to the instrument's input impedance of $10^{16} \Omega$ cm, which is of the same order of magnitude as a pure BN film. This observation suggests that the film remains insulative, as per a pure BN film, despite the presence of La. Also, the ratio of La : B measured in the film (1 in 12, *i.e.* ~8 at% as per the EELS measurements) is also found to be different from the target (1 in 6). The change in stoichiometry from the target to the film is due to the difference in ionization energy between B and La, leading to a higher content of boron as the peak power increases. This has been shown to be directly correlated to the nominal peak power density.¹⁶ Indeed, an increase of peak power density would



Fig. 7 Measurement of the relative atomic % composition of the film using EELS. (a), (b) and (c) Respectively show the EELS spectra of B, N and La. (d) Computed atomic concentration of boron (blue), nitrogen (red) and lanthanum (green). The ratio of B and N indicates a BN film stoichiometry of 1.15. The lanthanum content is constant at around 7.5 at%. The measurement is made along the whole film as shown in (e).

Table 1 Thermal conductivity of various amorphous materials such as BN, as well as textured carbon which is similar in structure to ordered h-BN

Material	Thermal conductivity at 300 K (W m ^{-1} K ^{-1})	Resistivity (Ω cm)	Growth parameters
Random tr-BN/c-BN Ordered h-BN (along the <i>c</i> -axis) Textured carbon (along the <i>c</i> -axis – deposited at 300 °C) ² Textured carbon (along the <i>c</i> -axis – deposited at 400 °C) ² SiO ₂ for electronic devices	$ \begin{array}{r} 1.7^{a} \\ 5.1^{a} \\ 5.32^{3} \\ 16.72^{3} \\ 1.27^{36} \end{array} $		HiPIMS, 500 °C, a few hundred nm thick HiPIMS, <50 °C, 400 nm thick FCVA, 300 °C, max. thickness <500 nm FCVA, 400 °C, max. thickness <500 nm Dry/wet oxidation, 600–1200 °C
^{<i>a</i>} Measured in this work.			

further increase the B:La ratio of the film. However, we also noted the start of c-BN nucleation as the peak power density reaches 150 W cm⁻². This phenomenon disrupts the film structure and will be explained later.

Thermal conductivity improvement with vertical orientation structure

We measured the thermal conductivity of two BN thin films deposited by HiPIMS using the LaB_6 target. The first sample is an ordered h-BN nanocrystalline film, and the TEM image of the sample is shown in Fig. 1. The second sample is a randomly oriented BN nanocrystalline film with a mixture of c-BN and t-BN phases. The TEM image of the second sample is shown in Fig. 5 and the composition is estimated to be 20% cubic and 80% turbostratic phases, estimated from the FTIR spectrum in Fig. 2. Both samples have a thickness of around 400 nm.

We measured the thermal conductivity of both samples by TDTR. We found that the cross-plane thermal conductivity (along the *c*-axis) of the ordered h-BN thin film is 5.1 W m⁻¹ K⁻¹ at room temperature, while the thermal conductivity of the random turbostratic/cubic BN sample is 1.7 W m⁻¹ K⁻¹. We note that the thermal conductivity of the ordered h-BN sample is ~80 times smaller than the thermal conductivity of bulk BN along the [0001] direction of 390 W m⁻¹ K⁻¹.^{32,33} Considering that the grain size of the sample is ~10 nm in the [0001] direction as estimated from the TEM image and XRD scans, this reduction in the thermal conductivity is comparable to the reduction observed in Si nanotubes of similar thicknesses.³⁴ We thus attribute the reduction in the thermal conductivity of the ordered h-BN sample mainly to the additional scattering of phonons by grain boundaries. As for the random t-BN/c-BN sample, the thermal conductivity approaches the minimum thermal conductivity³⁵ of amorphous materials, suggesting that the sample is highly defective.

Table 1 summarizes the thermal conductivity of the ordered and random BN and carbon thin films. The ordered h-BN thin film has a considerably high thermal conductivity, comparable to that of nanocrystalline graphite grown at 300 °C³ and four times higher than the thermal conductivity of amorphous SiO₂. This favourable thermal conductivity is useful for heat dissipation from active regions of electronic devices if ordered h-BN is used to replace SiO₂ as the gate dielectrics.

Conclusion

Vertically oriented BN films were successfully grown and their structure was characterized. The film was obtained using a new growth process based on HiPIMS with a lanthanum hexaboride target and nitrogen gas, and would structure itself with vertical orientation when the peak power density is between 20 and 100 W cm⁻². This new BN growth method is capable of producing large area BN thin films stoichiometrically balanced with a low lanthanum content (~7.5 at%), yielding excellent interface with the substrate and a growth rate in excess of 10 nm min⁻¹. The surface roughness of the film was below 1 nm (RMS), which makes it functional for electronic applications and the introduction of lanthanum into the film does not change the insulative properties of the material. In addition, the effect of preferential vertical ordering on the thermal conductivity of BN films was studied. Unlike any other high thermally conductive dielectric materials such as diamond and c-BN,37 the new h-BN film reported here can be deposited in a room temperature environment. The recurrent heat dissipation issue which affects the performance of electronic devices^{38,39} could be addressed by using vertically ordered h-BN. For instance, it could be an alternative to SiO₂ in high power electronics (i.e. GaN based HEMT on h-BN40) where the dielectric layer is always the thermal bottleneck due to its poor thermal conductivity.41,42 The advantage of employing vertically ordered h-BN in power electronics as a dielectric layer enables the extraction of heat from hot spots directly through the dielectric layer and minimize the heat from spreading in the lateral directions that would heat up the neighbouring components.

Acknowledgements

The authors would like to acknowledge support from CNRS-International-NTU-THALES Research Alliance (CINTRA). The authors would like to acknowledge the funding support from NTU-A*STAR Silicon Technologies Centre of Excellence under Grant No. 1123510003 and the Singapore Ministry of Education's Academic Research Fund Tier 2 under award no. MOE2013-T2-2-050 and no. MOE2013-T2-2-147.

Notes and references

- 1 E. H. T. Teo, J. Kulik, Y. Kauffmann, R. Kalish and Y. Lifshitz, *Appl. Phys. Lett.*, 2011, 98.
- 2 M. Shakerzadeh, G. C. Loh, N. Xu, W. L. Chow, C. W. Tan, C. Lu, R. C. C. Yap, D. Tan, S. H. Tsang, E. H. T. Teo and B. K. Tay, *Adv. Mater.*, 2012, 24, 4112–4123.
- M. Shakerzadeh, M. K. Samani, N. Khosravian, E. H. T. Teo,
 M. Bosman and B. K. Tay, *Carbon*, 2012, 50, 1428–1431.
- 4 M. Shakerzadeh, N. Xu, M. Bosman, B. K. Tay, X. Wang,
 E. H. T. Teo, H. Zheng and H. Yu, *Carbon*, 2011, 49, 1018– 1024.
- 5 D. W. M. Lau, A. Moafi, M. B. Taylor, J. G. Partridge, D. G. McCulloch, R. C. Powles and D. R. McKenzie, *Carbon*, 2009, 47, 3263–3270.
- 6 D. W. M. Lau, D. G. McCulloch, M. B. Taylor, J. G. Partridge, D. R. McKenzie, N. A. Marks, E. H. T. Teo and B. K. Tay, *Phys. Rev. Lett.*, 2008, **100**, 176101.
- 7 J. Thomas, N. E. Weston and T. E. O'Connor, J. Am. Chem. Soc., 1962, 84, 4619–4622.
- 8 I. S. Gladkaya, G. N. Kremkova and V. N. Slesarev, *J. Less-Common Met.*, 1986, **117**, 241–245.
- 9 X. W. Zhang, H. G. Boyen, H. Yin, P. Ziemann and F. Banhart, *Diamond Relat. Mater.*, 2005, **14**, 1474–1481.
- 10 E. J. M. Hamilton, S. E. Dolan, C. M. Mann, H. O. Colijn, C. A. McDonald and S. G. Shore, *Science*, 1993, 260, 659– 661.
- 11 S. Alkoy, C. Toy, T. Gönül and A. Tekin, *J. Eur. Ceram. Soc.*, 1997, **17**, 1415–1422.
- 12 V. Kouznetsov, K. Macák, J. M. Schneider, U. Helmersson and I. Petrov, *Surf. Coat. Technol.*, 1999, **122**, 290–293.
- 13 D. R. McKenzie, W. D. McFall, W. G. Sainty, C. A. Davis and R. E. Collins, *Diamond Relat. Mater.*, 1993, 2, 970–976.
- 14 D. R. McKenzie, J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct. – Process., Meas., Phenom., 1993, 11, 1928.
- J. Hahn, M. Friedrich, R. Pintaske, M. Schaller, N. Kahl, D. R. T. Zahn and F. Richter, *Diamond Relat. Mater.*, 1996, 5, 1103–1112.
- 16 E. M. Oks and A. Anders, J. Appl. Phys., 2012, 112, 086103.
- 17 F. Robert, C. César, B. Rustem, M. Rueben and A. André, *Plasma Sources Sci. Technol.*, 2014, 23, 035001.
- 18 K. Kang, Y. K. Koh, C. Chiritescu, X. Zheng and D. G. Cahill, *Rev. Sci. Instrum.*, 2008, **79**, 114901.
- C. Chiritescu, D. G. Cahill, N. Nguyen, D. Johnson,
 A. Bodapati, P. Keblinski and P. Zschack, *Science*, 2007, 315, 351–353.
- 20 Y. K. Koh, Y. Cao, D. G. Cahill and D. Jena, Adv. Funct. Mater., 2009, 19, 610–615.
- 21 Y. K. Koh, M. H. Bae, D. G. Cahill and E. Pop, *Nano Lett.*, 2010, **10**, 4363–4368.

- 22 D. G. Cahill, Rev. Sci. Instrum., 2004, 75, 5119-5122.
- 23 P. B. Mirkarimi, K. F. McCarty and D. L. Medlin, *J. Mater. Sci. Eng. B*, 1997, **21**, 47–100.
- 24 Y. Shi, C. Hamsen, X. Jia, K. K. Kim, A. Reina, M. Hofmann, A. L. Hsu, K. Zhang, H. Li, Z.-Y. Juang, M. S. Dresselhaus, L.-J. Li and J. Kong, *Nano Lett.*, 2010, 10, 4134–4139.
- 25 T. A. Friedmann, K. F. McCarty, E. J. Klaus, J. C. Barbour, W. M. Clift, H. A. Johnsen, D. L. Medlin, M. J. Mills and D. K. Ottesen, *Thin Solid Films*, 1994, 237, 48–56.
- 26 R. Geick, C. H. Perry and G. Rupprecht, *Phys. Rev.*, 1966, 146, 543–547.
- 27 W. Dworschak, K. Jung and H. Ehrhardt, *Thin Solid Films*, 1995, **254**, 65–74.
- 28 A. Schütze, K. Bewilogua, H. Lüthje, S. Kouptsidis and S. Jäger, Surf. Coat. Technol., 1995, 74–75, 717–722.
- 29 V. L. Solozhenko, V. Z. Turkevich and W. B. Holzapfel, J. Phys. Chem. B, 1999, 103, 2903–2905.
- 30 D. R. McKenzie, D. Muller and B. A. Pailthorpe, *Phys. Rev. Lett.*, 1991, 67, 773–776.
- 31 M. Shakerzadeh, E. H. T. Teo, A. Sorkin, M. Bosman,
 B. K. Tay and H. Su, *Carbon*, 2011, 49, 1733–1744.
- 32 E. K. Sichel, R. E. Miller, M. S. Abrahams and C. J. Buiocchi, *Phys. Rev. B: Solid State*, 1976, **13**, 4607– 4611.
- 33 I. Jo, M. T. Pettes, J. Kim, K. Watanabe, T. Taniguchi, Z. Yao and L. Shi, *Nano Lett.*, 2013, **13**, 550–554.
- 34 M. C. Wingert, S. Kwon, M. Hu, D. Poulikakos, J. Xiang and R. K. Chen, *Nano Lett.*, 2015, **15**, 2605–2611.
- 35 D. G. Cahill, S. K. Watson and R. O. Pohl, *Phys. Rev. B: Condens. Matter*, 1992, **46**, 6131–6140.
- 36 M. G. Burzo, P. L. Komarov and P. E. Raad, *IEEE Trans.* Compon. Packag. Technol., 2003, 26, 80–88.
- 37 A. Soltani, A. Talbi, V. Mortet, A. BenMoussa, W. J. Zhang, J. C. Gerbedoen, J. C. De Jaeger, A. Gokarna, K. Haenen and P. Wagner, *AIP Conf. Proc.*, 2010, **1292**, 191–196.
- 38 C. Sukwon, E. R. Heller, D. Dorsey, R. Vetury and S. Graham, *IEEE Trans. Electron Devices*, 2013, 60, 159– 162.
- 39 A. Pérez-Tomás, A. Fontserè, M. Placidi, N. Baron, S. Chenot, J. C. Moreno and Y. Cordier, *Semicond. Sci. Technol.*, 2012, 27, 125010.
- 40 M. Hiroki, K. Kumakura, Y. Kobayashi, T. Akasaka, T. Makimoto and H. Yamamoto, *Appl. Phys. Lett.*, 2014, 105, 193509.
- 41 J. G. Felbinger, M. V. S. Chandra, Y. Sun, L. F. Eastman, J. Wasserbauer, F. Faili, D. Babic, D. Francis and F. Ejeckam, *IEEE Electron Device Lett.*, 2007, 28, 948–950.
- 42 D. Cheney, E. Douglas, L. Liu, C.-F. Lo, B. Gila, F. Ren and S. Pearton, *Materials*, 2012, **5**, 2498–2520.