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Elucidation of the growth mechanism of sputtered 2D hexagonal boron nitride nanowalls

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ABSTRACT

Hexagonal boron nitride nanowall thin films were deposited on Si(100) substrates using a Ar(51%)/N₂(44%)/H₂(5%) gas mixture by unbalanced radio frequency sputtering. The effects of various target-to-substrate distances, substrate temperatures, and substrate tilting angles were investigated. When the substrate is close to the target, hydrogen etching plays a significant role in the film growth, while the effect is negligible for films deposited at a farther distance. The relative quantity of defects was measured by a non-destructive infrared spectroscopy technique that characterized the hydrogen incorporation at dangling nitrogen bonds at defect sites in the

deposited films. Despite the films deposited at different substrate tilting angles, the nanowalls of those films were found to consistently grow vertical to the substrate surface, independent of the tilting angle. This implies that chemical processes, rather than physical ones, govern the growth of the nanowalls. The results also reveal that the degree of nanowall crystallization is tunable by varying the growth parameters. Finally, evidence of hydrogen desorption during vacuum annealing is given based on measurements of infrared stretching (E_{1u}) and bending (A_{2u}) modes of the optical phonons, and the H-N vibration mode.

INTRODUCTION

Understanding the effect of various experimental parameters on the growth of hexagonal boron nitride (hBN) nanostructures is important for the realization of promising applications for hBN, including ultraviolet optical devices,¹ water cleaning,^{2,3} electron emission⁴ and other low-dimensional BN-based applications.⁵⁻⁸ A greater understanding of hBN nanostructure growth can also provide insight into the fundamental properties of BN, such as optical/microstructural properties,⁹⁻¹³ lattice dynamics,¹⁴⁻¹⁷ and correlations between defects and electronic/magnetic properties.¹⁸⁻²⁰ hBN has structural similarity to graphite, in which the boron and nitrogen atoms are alternatively placed in a hexagonal ring. In the hexagonal lattice plane, the atoms are connected by strong covalent bonds to form hBN sheets, while interaction between sheets is weak, and governed by van der Waals forces.^{5,6,9-11,21} Most reports in the literature focus on chemical vapor deposition of hBN, however there have been a few demonstrations using a physical vapor deposition (PVD) method.^{22,23} The CVD method is usually used at high temperature ($> 900\text{ }^{\circ}\text{C}$),³ which causes gas precursors to react chemically. The advantage of the PVD method is that it can be used at much lower temperatures ($< 500\text{ }^{\circ}\text{C}$),^{22,23} enabling film

deposition on temperature sensitive substrates. Moreover, PVD machines can be easily up-scaled and are used in industry to coat substrates of several square meters and more. We recently reported that hBN can be synthesized by PVD, leading to vertically oriented nanowalls on various unintentionally heated substrate materials when hydrogen (H) is added to the Ar/N₂ gas mixture.²³ H incorporation is critical to the formation of the nanowall structures, as only amorphous films are grown for gas chemistries without H addition.²⁴ It was also shown that there was no obvious effect on the growth orientation of the hBN nanowalls when different substrate materials, such as silicon, sapphire, quartz, or fused silica, were used. This work aims to further elucidate the mechanism that governs the nanowall growth.

EXPERIMENTAL DETAILS

Figure 1. Simplified schematic of the experimental setup in the home-built unbalanced 13.56 MHz RF sputtering system used in this work, showing the target-to-substrate distance (d) and substrate tilting angle (α).

hBN nanowalls were synthesized in a home-built, unbalanced, 13.56 MHz radio frequency (RF) sputtering system.²³ The optimal gas mixture leading to nanowall formation, determined in our previous work²³ was Ar(51%)/N₂(44%)/H₂(5%), with a cathode power of 75 W. A 3 inch, pyrolytic BN ceramic target (Kurt J. Lesker), with 99.99% purity and a density of 1.96×10³ kg.m⁻³ was used. The working pressure was 2.1×10⁻² mbar. As the properties of the plasma depend on the cathode power and gas composition,^{23,25-30} these parameters were fixed for all depositions of this work. The target-to-substrate distance (*d*) was varied from 3 cm to 6 cm, and the substrate tilting angle (*α*), as shown in Fig. 1, was set to 0° or 90°. The hBN thin films were deposited on 1×1 cm² Si(100) substrates. The substrate temperature (*T_{sub}*) can be controlled up to 500 °C during deposition, using a bench-top power supply (VOLTcraft VSP 1410 40 V/10 A). *T_{sub}* was monitored during depositions by a K-type thermocouple probe with a EUROTHERM 2408 readout. Morphological properties of the films in both plan-view and cross-section geometries were studied using a FEI Quanta 200F field emission gun scanning electron microscope (SEM).²³ High resolution transmission electron microscopy (HRTEM) measurements were carried out on a JEOL 3000F microscope, operated at 300 kV acceleration voltage. TEM cross-sections were prepared by a gentle milling technique,³¹ in which samples are cut by a diamond wire, and opposing top faces are stuck together. The resulting doubled cross-sections are milled down to 1 μm thickness by hand, then thinned to electron transparency by ion milling.³¹ The hBN wall feature distributions in SEM images were measured and performed with Digital Micrograph and ImageJ software packages.³² Optical properties of the films were characterized by Raman and Fourier transform infrared (FTIR) spectroscopy techniques.³³ FTIR spectra were taken on a Thermo Fisher NicoletTM 8700 FTIR instrument with a KBr beam splitter, in transmission mode with normal incidence to the film surface, in the frequency range

of 400-4000 cm^{-1} with a resolution of 2.0 cm^{-1} . Raman spectra were obtained using a Horiba Jobin Yvon T64000 Raman spectrometer equipped with a BXFM Olympus 9/128 microscope and a Horiba JY Symphony CCD detector, using a 488 nm Lexel SHG laser, in the backscattering configuration. The chemical composition of several films was examined by energy dispersive X-ray (EDX) measurements on an EDAX module of the FEI Quanta SEM. The EDX spectra of the films were compared with those obtained from the BN target used in the depositions to confirm the purity of the films.

RESULTS AND DISCUSSION

A. Nanowall growth rate and orientation: Influence of d and α

To evaluate the effect of d and α on the growth rate (R_G), hBN films at varying d were deposited, in two series, at $\alpha = 0^\circ$ and 90° . The substrates were not intentionally heated, and the plasma conditions resulted in T_{sub} varying from 78 $^\circ\text{C}$ at $d = 6$ cm to 125 $^\circ\text{C}$ at $d = 3$ cm. Cross-sectional SEM images of the films, like those shown in Fig. 2(b) and (c), were used to determine the film thicknesses. The R_G values were calculated by dividing the film thickness by the total deposition time. The R_G decreases linearly with increasing d for both $\alpha = 0^\circ$ and 90° , as shown in Fig. 2(a), however there is a difference in the slope of the R_G vs. d curve when the substrate was tilted from 0° to 90° . The decrease in the R_G for the 90° case is believed to be caused by a reduction of interactions with the plasma and/or scattering events at the substrate surface, which also reduce the total effect on the R_G as the d changes.²⁶⁻²⁸ Fig. 2(b) and (c) also show that the growth direction of the films is independent of the substrate tilting angle. The images show that hBN nanowalls grow vertically to the substrate surface in both films, despite the change in α from 0°

to 90° . This is in agreement with previous work²⁹ on the growth of hBN by RF PVD, in which nanowalls were also shown to grow preferentially in the vertical direction, such that the c -axis of the hBN covalent plane is parallel to the substrate surface.²⁹

Figure 2. (a) Growth rate (R_G) values as a function of target-to-substrate distance (d) for two substrate tilting angles (α). The lines serve as guides for the eye. Each point represents a single deposition experiment, with error bars computed independently for each film, as the standard deviation for the measurement of 10 different points in the cross-sectional SEM image. (b) and (c) Cross-sectional SEM images of two samples with same thickness ($\sim 2.9 \mu\text{m}$) deposited at $d = 3 \text{ cm}$ with a substrate tilting angle (α) of 0° and 90° , respectively. Three areas denoted as R_1 , R_2 and R_3 in (c) are defined by the imaging contrast and detailed in the text.

The size of the nanowalls can be determined based on the contrast in the SEM images in Fig. 2(b) and (c). The film with $\alpha = 0^\circ$ consists of large hBN nanowalls throughout the film thickness. The film with $\alpha = 90^\circ$ has smaller hBN nanowalls and three regions can be

distinguished, denoted as R_1 , R_2 and R_3 in Fig. 2(c). Nanowalls can be clearly seen in the middle area (R_2) of the film. The region R_3 , which corresponds to the top $\sim 1.3 \mu\text{m}$ of the film, shows reduced image contrast, which could be the result of nanowalls that were overlapped at wall branches in this region. The area located just above the Si surface, R_1 , which corresponds to the first stages of hBN growth, also shows a similar contrast.

The microstructure of the hBN nanowalls, as shown in Fig. 2(b) and (c), can be explained by a growth mechanism based on effects of the R_G . There seems to be a relatively constant lateral growth speed, which causes overlapping between neighboring nanowalls. When the growth proceeds more rapidly in the vertical direction, as is the case for samples with higher R_G , a reduction in the overlapping of neighboring hBN nanowalls is observed. This is because the lateral growth processes that cause overlapping have relatively less time to occur for films deposited with a higher R_G . In this case, large spaces form between the hBN nanowalls, as seen in the morphology in Fig. 2(b), as compared to the lower growth rate case of Fig. 2(c).

If the initial R_G in a deposition process is high, as is the case for the film shown in Fig. 2(b), then the nucleation density of hBN nanowalls is reduced, when compared to films grown with lower R_G . The higher nucleation density on the surface of the slower R_G film causes the formation of the near surface region of low contrast labeled R_1 in Fig. 2(c), but such a region is not visible for the higher R_G case shown in Fig. 2(b). For films with very low initial growth rates, as is especially the case as the d approaches 6 cm, the density of nucleated BN particles is very high, and the resulting deposited film morphology is therefore expected to be governed by the hBN granular phase,^{29,30} and/or mixed stacking types of different BN phases. However, the SEM image resolution shown in Fig. 2 is not enough to clearly determine the dominant growth phase.

Figure 3. (a) Low magnification cross-sectional TEM image of a 300 nm-thick hBN film deposited at $d = 3$ cm and $\alpha = 0^\circ$. (b) and (c) are high resolution TEM images recorded at typical areas near to ($\square$ -b) and far from ($\circ$ -c) the Si(100) substrate surface, respectively.

To further investigate the morphological evolution of the deposited BN film near the Si-interface, cross-sectional TEM images of a 300 nm-thick film deposited at $d = 3$ cm and $\alpha = 0^\circ$ were taken, as shown in Fig. 3. The TEM cross-section preparation method³¹ results in two head-on sample surfaces on top of each other in a single cross-section. A thickness of approximately 300 nm was selected for the deposition so that the entire film growth could be seen in the TEM image. The measured thickness of (300 ± 20) nm from the TEM measurement shown in Fig. 3(a) is in very good agreement with the intended growth thickness, which was controlled by a growth time computed from the estimated R_G , as shown in Fig. 2(a). The variation in the crystalline

grain structure observed in Fig. 3(a) indicates that the BN film is not homogeneous in the direction of film growth. Closer to the Si(100)/hBN interface, there is a region of lower contrast in the TEM image, which might indicate the presence of less crystalline structures at this interface, which would be consistent with the observations from Fig. 2. In order to clarify the structure at the Si-hBN interface, we performed high resolution TEM imaging. A typical HRTEM image of the Si/hBN interface is displayed in Fig. 3(b). The turbostratic phase of BN, in which there is poor alignment between imperfect BN planes, and the amorphous phase, in which there is no long range ordering in the atomic structure, are dominant in this region. Farther from the interface, regions of the well-aligned hexagonal phase of BN start to appear, as shown in Fig. 3(c). Once these hBN regions, which become the hBN nanowalls, begin to form, the turbostratic and amorphous BN phases still continue to grow, but are then limited to the spaces in between these wall regions. The hBN growth within the nanosheets, as shown in Fig. 3(c), is not perfectly ordered, and shows variation in the lattice spacing between hBN sheets. This implies that there is an existence of defects within hBN nanowalls. The nanowall shown in Fig. 3(c) appears to grow at an angle to the arbitrary orientation of the bottom of the image, as high magnification TEM imaging can result in a rotation of the imaging orientation. However, as can be seen in Fig. 3 (a), the dominant growth direction of the nanowalls is in the vertical direction with respect to the sample surface.

B. Nanowall optical and structural properties: Influence of film thicknesses

Figure 4. SEM images for a series of hBN films with different thicknesses which were deposited at $d = 3$ cm (a-d) and $d = 6$ cm (e-h).

As shown in Fig. 2, the growth behavior can change over the course of a growth process as a function of the film thickness. The relative lateral growth rate that results in overlapping growth processes of the walls, as compared to the vertical R_G that results in larger hBN nanowalls with greater spacing in between them, can vary throughout a single deposition process, as shown in Fig. 2(c). To better understand this effect, a series of hBN films were deposited at $d = 3$ cm and d

= 6 cm with different film thicknesses. The substrates were unintentionally heated, which results in sample temperatures of 78 °C at $d = 6$ cm and 125 °C at $d = 3$ cm. The resulting morphologies are shown in Fig. 4. As expected from the observations of Fig. 2, the hBN wall widths increase with increasing film thickness. The films deposited at $d = 6$ cm show smaller initial wall dimensions, however the pattern of the growth behavior, of increasing wall size with increasing thickness, is very similar to the films deposited at $d = 3$ cm.

To further investigate the crystalline quality as a function of grown thickness, Raman spectra were taken, as shown in Fig. 5(a) and (b). The reciprocal of crystallite size has been shown to be proportional to the full width at half maximum ($\Gamma_{1/2}$) value of the Raman high-frequency (E_{2g}) mode.¹⁰ Therefore, a decrease in the $\Gamma_{1/2}$ value at this frequency indicates an improvement in the crystallization. The $\Gamma_{1/2}$ values of the spectra at the E_{2g} mode were calculated for the spectra shown in Fig. 5(a) and (b), and are given in Fig. 5(c). A lower value of the $\Gamma_{1/2}$ again corresponds to higher crystalline hBN phase, and therefore improved crystalline quality of the films. As shown in Fig. 5(c), the hBN crystallization does not change significantly with increasing film thickness for films grown at $d = 3$ cm. For the films grown at $d = 6$ cm however, the degree of hBN crystallization improves with increasing film thicknesses until the film thickness reaches approximately 1 μm . The poor crystalline quality for the thin films is potentially due to a high density of the turbostratic and amorphous BN phase in between the hBN nanowalls near the growth interface, consistent with the previous observations from Fig. 3. These overlap growth processes are enhanced for thinner films by the existence of multiple stacking types during the first stage of film growth.^{11,20,23,29} After 1 μm , the measured degree of hBN crystallization for $d = 6$ cm does not change significantly, and the $\Gamma_{1/2}$ values are very similar to those measured for the films deposited at $d = 3$ cm. These results are in agreement with the SEM results shown in Fig. 4.

Figure 5. Raman spectra of the hBN films deposited at $d = 3$ cm (a) and $d = 6$ cm (b) with different film thicknesses. The mean values of $\Gamma_{1/2}$ of E_{2g} peak were evaluated from Raman spectra measured over five different locations on each film (c). The error bars represent the standard deviation of the mean value.

C. Nanowall growth rate: Influence of T_{sub}

Figure 6. (a) Growth rates (R_G) and (b) etching rates (R_E) of hBN films deposited at different d , as a function of substrate temperature (T_{sub}). Each point represents a single deposition or etching experiment, with error bars computed independently for each film, as the standard deviation for the measurement of 10 different points in the cross-sectional SEM image used for thickness determination.

The SEM investigations of hBN nanowalls grown with different d indicate that there is an influence of this parameter on the growth process. However, since the d has an effect on T_{sub} , the observed changes in the growth process might be due only indirectly to the d . To determine the effects of T_{sub} on the R_G , hBN films were deposited with $\alpha = 0^\circ$ in two series, at $d = 3$ cm and 6 cm. T_{sub} was varied by intentionally heating a substrate to a specified temperature, which was held constant during the deposition. The resulting R_G as a function of substrate temperature are plotted in Fig. 6(a).

One can see that at $d = 3$ cm, R_G values significantly reduce with increasing T_{sub} for $T_{sub} > 250$ °C. Previous reports in the literature have found that a hydrogen etching effect becomes prominent at higher T_{sub} (~350 °C).¹² The presence of hydrogen within the gas mixture is also necessary to form the nanowall structures, and it is therefore expected that hydrogen plays a key role in the plasma chemistry that determines the sample morphology. In order to investigate this effect in the absence of other deposition processes, a series of hBN films were grown and then exposed to hydrogen plasmas for 5 hours at various T_{sub} to determine the hydrogen etching rates (R_E). The exposed films used for etching were first deposited to a thickness of 700 nm on unintentionally heated substrates at the same d used for the etching, either 3 cm or 6 cm. As argon and nitrogen gases were not used during etching, the hydrogen gas flow rate was increased to maintain the working pressure of 2.1×10^{-2} mbar. The resulting hydrogen R_E as a function of T_{sub} are given in Fig. 6(b). The hydrogen etching effect is clearly significant at $d = 3$ cm, especially at high T_{sub} (> 250 °C). As etching is a competitive process with growth, etching is clearly a significant effect in the growth of the films deposited at $d = 3$ cm. The effect is much smaller for $d = 6$ cm, even at high T_{sub} (> 250 °C). Little variation in either the R_G or R_E values was observed for the films deposited at $d = 6$ cm at low T_{sub} (< 250 °C). We therefore attribute the drop in growth rate observed for samples grown at high T_{sub} (> 250 °C) and $d = 3$ cm to an increase in the hydrogen etching rate under these conditions.

Figure 7. SEM images of 1.2 μm -thick films which were deposited at untilted ($\alpha = 0^\circ$) $d = 3$ cm (a-c) and $d = 6$ cm (d-f) at different substrate temperatures (T_{sub}).

In addition to the differences in R_G observed for changes in both d and T_{sub} in Fig. 6, the d was also seen to have an impact on the grown sample morphology, as shown in Fig. 4. To determine if the morphological changes observed were merely a function of the d , or if changes in T_{sub} also affect the morphology of the grown hBN nanowalls, the effect of T_{sub} was also independently investigated. This investigation is shown Fig. 7, in which SEM images of 1.2 μm -thick films that were deposited on untilted substrates at $d = 3$ cm (Fig. 7(a-c)) and $d = 6$ cm (Fig. 7(d-f)) at different T_{sub} are presented for comparison. 1.2 μm thickness was selected so as to improve the signal in the subsequent FTIR investigation. As shown in Fig. 7(a), the hBN phase forms

nanowalls that branch out into wall branches or subwalls. The size of these walls varies with the deposition temperature.

The effect of T_{sub} on the growth morphology is significant, as shown in Fig. 7. When T_{sub} is held at 125 °C at either $d = 3$ cm or 6 cm, the resulting morphologies of those films are very similar, as shown in Fig. 7(b) and (e). The nanowalls grown in both cases look similar in shape and width, with a similar number of sub-branches grown from the main walls. This means that the growth morphology is largely dependent on a thermal effect at low T_{sub} (< 250 °C). In particular, the sizes of the hBN nanowalls are clearly enlarged for the film deposited at $d = 6$ cm with $T_{sub} = 125$ °C shown in Fig. 7(e), as compared to the unintentionally heated $T_{sub} = 78$ °C case shown in Fig. 7(d). The increase in temperature also results in an increase in the R_G , as shown in Fig. 6 (a). This observation is consistent with the growth mechanism proposed based on the observations from Fig. 2, where a higher R_G results in larger nanowalls. When T_{sub} is further increased up to 500 °C, the hBN nanowall phase incrementally degenerates, due to the increasing hydrogen etching at higher temperatures, consistent with the results shown in Fig. 6. As can be seen from the changes observed in the morphologies at higher T_{sub} in Fig. 7, the effect of the hydrogen etching appears to be to remove material from wall branches and also to truncate the heights of main walls. These effects reduce the R_G as well as the fraction of the film composed of the hBN nanowall phase.

The nanowall morphologies observed for $d = 3$ cm for the unintentionally heated and 500 °C-heated samples are significantly different, as seen in Fig. 7(a) and (c). As the hydrogen etching effect is less significant for $d = 6$ cm, as previously shown in Fig. 6, the effect on the hBN

nanowall phase is much less significant than for the case of $d = 3$ cm. A similar nanowall morphology is retained, even at $T_{sub} = 500$ °C, for $d = 6$ cm, as shown in Fig. 7(f). However, the hBN nanowalls deposited at this stage are thinner than that of the films deposited at lower T_{sub} .

The samples grown for all the R_E measurements shown in Fig. 6 were unintentionally heated samples, such as those shown in Fig. 7(a) and (d), which show different size nanowalls. To quantify the difference in the wall size feature distributions, the images of the hBN nanowalls from Fig. 7(a) and Fig. 7(d) were projected onto the plane of the substrate surface and fitted as ellipses in image processing software.^{32,34} The averaged widths of the walls in the given films were determined to be (95 ± 11) nm ($d = 3$ cm) and (51 ± 9) nm ($d = 6$ cm). The two unintentionally heated samples therefore show differences in morphologies, which may affect the degree of hydrogen etching, which will be addressed later in this work.

A further effect that appears for $d = 3$ cm at high temperatures, *e.g.* at $T_{sub} = 500$ °C, is that the increasing hydrogen etching appears to have a significant effect on the nucleation process. There is a decrease in the amount of hBN, and the growth of other phases of BN increases, forming BN clusters like those denoted as dashed domains in Fig. 7(c). These clusters, with sizes ranging from 500 nm to 1000 nm, form small partitions spread over the substrate surface. The formation of these BN cluster boundaries follows the growth model of diffusion-limited aggregation.³⁵⁻³⁸

Figure 8. Etching rates (R_E) of hBN films deposited at $d = 3$ cm and 6 cm are plotted against the substrate temperature (T_{sub}). The trends of the results from Fig. 6(b) are also shown for comparison. The d was switched in between growth and etching, such that the $d = 3$ cm and 6 cm films were hydrogen etched at $d = 6$ cm and 3 cm, respectively. Each data point represents a single deposition or etching experiment, with error bars were computed as the standard deviation of the film thickness as measured at 10 different points in the SEM image.

The results of Fig. 7(a), (d) indicate that there are significant morphological differences between unintentionally heated films grown at $d = 3$ cm and $d = 6$ cm. To determine if the differences in the observed R_E behavior shown in Fig. 6 were due to differences primarily with the difference in the d , or if the differences in the grown sample morphology prior to etching also had an effect, additional unintentionally heated samples of approximately 700 nm thickness were grown, at $d = 3$ cm and $d = 6$ cm, and then were switched for the subsequent hydrogen etching, such that the samples grown at $d = 3$ cm were hydrogen etched at $d = 6$ cm, and the samples grown at $d = 6$ cm were etched at $d = 3$ cm. Two etching experiments for each case were performed, at each $T_{sub} = 125$ °C and 500 °C. The results of this investigation are plotted in Fig. 8 and show that the

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3 samples etched at $d = 3$ cm had R_E of 24 and 18 nm/h (solid-circle symbols), while the samples
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5 etched at $d = 6$ cm had R_E of approximately 2 and 10 nm/h (open-circle symbols) in the case of
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7 T_{sub} were 125 and 500 °C, respectively. This clearly indicates that the hydrogen etching rate
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9 depends not only on the d , but also on the grown sample morphology, which may be due to faster
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11 etching of the thinner walls of the samples grown at $d = 3$ cm.
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16 17 **D. Nanowall defects** 18 19

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21 The investigation of the effect of the deposition parameters on the nanowall morphology of hBN
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23 films has revealed the presence of defects within the grown nanowalls, such as in Fig. 3(c),
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25 where the distance between atomic planes within the hBN nanowalls varies within a nanowall
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27 crystal. The degree of defects existing in those films may be indirectly related to H-N, and/or H-
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29 B bonds, where H radicals can become incorporated in the crystal by bonding to dangling bonds
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31 on the B- or N-termination edges during growth.^{16,18-20} We attempted to measure B-H vibrations
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33 (~ 2400 cm⁻¹) however, we were not able to get a high enough signal-to-noise ratio for this
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35 absorption feature, even with longer acquisition times. There have also been reports in the
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37 literature^{16,20} that B vacancies are preferably formed, and we have therefore assumed that the
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39 defects in our films are mostly N-H bonds. It is possible that the stoichiometry could be altered
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41 from a 50/50 ratio of B and N by the preferential formation of B vacancies. However we assume
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43 the effect is very small, since in our previous work the stoichiometric properties of samples
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45 deposited with 5% H₂ were reported, which were very consistent with a simulation based on a
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47 50/50 ratio of B and N.²³ The presence of H atoms within the lattice indicates the existence of
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49 these kinds of defects within the nanowalls. FTIR spectroscopy was used to quantify the strength
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of the H-N-bond vibration modes, as a measure of the relative concentrations of H within the various films.

Figure 9. FTIR transmission spectra from 3.5 μm -thick films deposited at different T_{sub} , recorded around the H-N vibration mode (3436.6 cm^{-1}), for (a) $d = 3 \text{ cm}$ and (b) $d = 6 \text{ cm}$. (c)

Illustration of absorption band area calculation method. The data shown is from for the FTIR spectrum of the film deposited at $d = 6$ cm and $T_{sub} = 375$ °C. (d) Absorption band area of the peaks shown in (a) and (b), as a function of T_{sub} .

A series of 3.5 μm -thick hBN films were deposited at $d = 3$ cm and 6 cm with different T_{sub} . FTIR transmission spectra of those films were recorded at the H-N vibration mode ($\sim 3450 \text{ cm}^{-1}$),^{39,40} and the resulting transmission spectra are given in Fig. 9(a) and (b). The measurement was taken normal to the substrate surface, i.e. parallel to the vertical standing nanowalls. The relative strength of the H-N vibration modes were characterized by calculating the area of the infrared absorption band,⁴⁰ as is illustrated in Fig. 9(c) and the results are given in Fig. 9(d). The position of the H-N peak can vary due to differences in H-N bond environment, which can be explained by defects, impurities, or the presence of different phases throughout the complete film thickness. The absorption area for the samples deposited at $d = 3$ cm decreases when T_{sub} increases from 125 °C to 250 °C. This indicates that the amount of hydrogen in the sample deposited at 125 °C is higher than in the sample deposited at 250 °C, though following this decrease, the quantity of H in the films remains relatively constant with increasing temperature for $d = 3$ cm. This change at $T_{sub} \geq 250$ °C could be due to an increase in hydrogen desorption processes during growth at higher temperatures.⁴¹ A decrease in the number of H atoms attaching to dangling bonds at N-terminated edges that are subsequently incorporated into hBN nanowalls may also lower the probability for branch or sub-nanowall formation. The break in the symmetry of the crystal caused by the H-defect could provide a location for the nucleation of a new wall branch. This would indicate that wall branches have a higher chance to form in the samples deposited at lower T_{sub} (≤ 250 °C) in comparison with the samples deposited at high T_{sub} . For films deposited at $d = 6$ cm, a significant reduction is seen when T_{sub} increases from 78 °C to 125

°C. The measured absorption then remains at this absorption level as T_{sub} increases to 250 °C. This is perhaps an analogous mechanism to the reduction in absorption seen in the $d = 3$ cm case, though the decrease was noted there at a higher temperature, between 125 °C and 250 °C. This effect is therefore potentially due to the change in the H desorption rate during growth between unintentionally heating and heating the substrates from below during deposition. Further increasing T_{sub} at $d = 6$ cm shows a continual decrease in the measured absorption as T_{sub} increases to 500 °C. In this range of T_{sub} , the role of hydrogen desorption is mostly similar for the samples deposited at both d . This is the expected result, since hydrogen desorbs much faster at higher growth temperatures, leading to less H-N bonds in those samples.⁴¹

E. Nanowall optical and structural properties: Influence of T_{sub}

As shown in Fig. 7, T_{sub} can have a significant effect on the grown nanowall morphology, and the results of the FTIR investigation shown in Fig. 9 indicate that T_{sub} can also affect the amount of hydrogen incorporated in the films during growth. To determine if the differences in the growth morphology and hydrogen defect concentration in the films affect the crystalline quality of the hBN phase, films grown at different T_{sub} were investigated by Raman spectroscopy. Raman spectra of two series of 700 nm-thick hBN films, deposited at $d = 3$ cm and 6 cm, were measured, as shown in Fig. 10(a) and (b). The $\Gamma_{1/2}$ values of the spectra at the E_{2g} mode were calculated as was done in Fig. 5(c), and are given in Fig. 10(c). The observed fluctuations in the degree of hBN crystallization correspond approximately to the relative levels of hydrogen in those films, as measured by FTIR and given in Fig. 9.

Figure 10. Raman spectra of the 700 nm-thick hBN films deposited at $d = 3$ cm (a) and $d = 6$ cm (b) at different T_{sub} . (c) $\Gamma_{1/2}$ values calculated from the above spectra as a function of T_{sub} . A decrease in the $\Gamma_{1/2}$ indicates an increase in crystalline quality.

F. Nanowall thermal stability: Influence of annealing temperature

We have shown in Fig. 9 that the amount of H grown into the hBN nanowall structures varies with temperature, and also have shown in Fig. 10 that the crystalline quality varies in a similar way. To separate the effect of growth parameters from the role of hydrogen, annealing on grown

films can be performed, to allow the H to diffuse out of the hBN nanowall structures. Characterization of annealed films can therefore determine the thermal stability of H-N bonds, and also the resulting changes in the crystalline quality, as measured by the strength of the phonon modes in the hBN films. The phonon modes can also be investigated by FTIR, similar to the H-N vibration mode (3436.6 cm^{-1}) analysis as shown in Fig. 9. The optical phonon modes of the hBN can be observed by the B-N bending (A_{2u} (LO) at 817 cm^{-1}) and B-N stretching (E_{1u} (TO) at 1376 cm^{-1}) absorption features.^{7-10,39-41}

Figure 11. FTIR transmission spectra of (a) as-deposited, (b) 750 °C- and (c) 1000 °C-annealed films with the thickness of $1.2\text{ }\mu\text{m}$.

Three $1.2\text{ }\mu\text{m}$ -thick films were deposited with the same deposition conditions, at $d = 3\text{ cm}$ on unintentionally heated substrates. $1.2\text{ }\mu\text{m}$ thicknesses were selected to improve the FTIR signal for the subsequent analysis. Two films were annealed at $750\text{ }^{\circ}\text{C}$ and $1000\text{ }^{\circ}\text{C}$ in a high vacuum ($\sim 10^{-6}\text{ mbar}$) for 5.5 hours. The FTIR transmission spectra for the films are given in Fig. 11. The optical phonon modes of the hBN can be observed by the B-N bending (A_{2u} (LO) at 817 cm^{-1})

and B-N stretching (E_{1u} (TO) at 1376 cm^{-1}) as shown in Fig. 11 (a) and (b). The measured phonon modes are mostly unchanged for the $750\text{ }^{\circ}\text{C}$ -annealed film, as compared to the as-deposited film. After annealing to $1000\text{ }^{\circ}\text{C}$, the A_{2u} (LO) and E_{1u} (TO) phonon modes are annihilated, indicating that the crystalline structure is significantly damaged. The crystalline quality can also be observed in the SEM images of the as-deposited film and annealed films, shown in Fig. 12. The as-deposited film and the film annealed to $750\text{ }^{\circ}\text{C}$ both show good crystalline quality. The film annealed to $1000\text{ }^{\circ}\text{C}$ however shows the appearance of more defects. This is consistent with the observations of the crystalline structure in Fig. 11.

Figure 12. SEM images showing the morphologies of the three films analyzed in Fig. 11. (a) as-deposited, (b) $750\text{ }^{\circ}\text{C}$ - and (c) $1000\text{ }^{\circ}\text{C}$ -annealed films the thicknesses of $1.2\text{ }\mu\text{m}$.

The H-N vibration mode (3436.6 cm^{-1}), measured by FTIR transmission spectroscopy, for the three samples is shown in Fig. 11(c). The H-N vibration gradually decreased with increasing annealing temperature, indicating that hydrogen desorption occurs during annealing, and that this desorption is a temperature dependent process, with greater desorption at the higher temperature. The loss of crystal quality at $1000\text{ }^{\circ}\text{C}$, as noted by the annihilation of the phonon modes in Fig. 11(a) and (b), may be caused by this H-desorption process. It has been shown in literature that desorption of H is nearly complete for BN annealed to $1000\text{ }^{\circ}\text{C}$.^{16,42,43} As the H leaves the

crystalline lattice, a number of vacancies appear within the structure. As a result, the hBN nanowalls and wall-branches appear significantly more defective in the 1000 °C-annealed film, as shown in Fig. 12(c). These observations are consistent with theoretical predictions and experimental results observed by other authors.^{16,42-44}

The loss of the phonon modes in the 1000 °C-annealed film can also be explained by the formation of non-crystalline phases within the nanowall structures. At such high annealing temperature the migration of single B and N vacancies can be thermally activated allowing the formation of more stable BN di-vacancies. As a result, the hBN lattice could become distorted and/or rippled¹⁶ and hBN is possibly converted to aBN and/or tBN. Even though most of the microscale nanowalls remain, the presence of other phases within the structures could break the long range crystalline order which allows LO and TO phonon mode propagation.

G. Nanowall growth mechanism

The analysis of the hBN nanowall growth performed in this work has given significant insight into the growth mechanism and nanowall formation. This greater understanding of the growth mechanism now allows us to propose an overall growth scheme for the hBN nanowall formation, as shown in Fig. 13, in which the formation of five imperfect nanosheets is illustrated schematically. The results of the cross-sectional SEM investigation shown in Fig. 2 suggested that there is an interfacial layer that forms before the crystalline hBN nanosheets begin to grow, and the HRTEM investigation of Fig. 3 showed that this interfacial layer is composed of turbostratic and amorphous BN phases. This phase is shown just above the substrate surface in Fig. 13. After the turbostratic and amorphous layer forms at the surface, regions of hBN phase

begin to nucleate, as seen in Fig. 3(c). The turbostratic and amorphous layers still form, but become limited to the spaces in between the hBN nanowalls.

Figure 13. Schematic diagram showing the growth mechanism of an imperfect hBN nanowall

The hBN phase that forms is not perfect, as also shown in Fig. 3(c), where the spacing between adjacent nanosheets varies slightly, indicating the presence of defects. This is shown in the inset of Fig. 13, where a side-on view of a defective hBN nanosheet is shown schematically. The defects arise from displaced boron or nitrogen atoms during growth, which leave vacancies in the grown hBN structure. Both boron and nitrogen atoms can be displaced during a deposition, however boron vacancies have previously been shown to be preferentially formed.^{20,43} The boron vacancies leave N-terminated edges in the hBN lattice, and atomic hydrogen in the growth plasma is subsequently able to be incorporated into the hBN nanosheets through the dangling bonds at those N-terminated edges. The presence of these H-N bonds within the hBN structure was confirmed by the FTIR results, as shown in Fig. 9. The unsaturated N atoms within the

nanowalls can also interact with the terminated edges of other adjacent hBN nanosheets, and also can act as nucleation sites for nanosheets that expand outward in a different direction. Thus, the dangling bonds of N can act as agents for nucleation of the growth of branches or subwalls from main nanowalls.

CONCLUSIONS

The growth behavior of hBN nanowall films deposited by unbalanced RF sputtering were investigated by means of variations of target-to-substrate distance (d), substrate temperature (T_{sub}) and substrate tilting angle (α). Our results demonstrate that the structural and optical properties of deposited hBN nanowall films are dependent on these parameters. Thin films deposited at shorter d showed higher R_G , higher porosity and more well-defined crystallization of the hBN nanowall phase, as compared to the results obtained for farther d . Depositing at $\alpha = 90^\circ$ was found to decrease the R_G , and alter the structural properties of the deposited films. However, even at $\alpha = 90^\circ$ the orientation of the main hBN nanowalls remained vertical with respect to the substrate surface, *i.e.* independent of the degree of substrate tilting. This implies that the growth behavior is governed by chemical processes rather than physical ones. Thin films deposited at higher R_G showed larger hBN nanowalls, however the turbostratic and amorphous phase of BN was not completely suppressed in the deposited samples. Thus, the growth mechanism of hBN nanowalls is a competitive process between different phases of BN that form during a deposition.

We also found that the hydrogen etching, hydrogen incorporation during growth, and thermal effects also play important roles in determining the properties of the hBN films. The relative quantity of defects in the deposited hBN nanowalls were characterized by FTIR by measuring

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the H-N bonds at N-terminated points of hBN nanosheets. Finally, based on the results of this work, a growth mechanism illustrating the formation of a hBN nanowall was presented.

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Author Contributions:

The manuscript was realized through contributions of all authors. DQH, PP and SDJ designed experiments and carried out the hBN nanowall depositions, FTIR and Raman measurements. ST and JD performed TEM and SEM imaging characterization. KH coordinated the study and wrote the manuscript together with DQH, SSN, and MKVB. All authors discussed the obtained results and have given approval to the final version of the manuscript.

Notes:

The authors declare no competing financial interest

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Elucidation of the growth mechanism of sputtered 2D hexagonal boron nitride nanowalls

D.Q. Hoang, P. Pobedinskas, S.S. Nicley, S. Turner, S.D. Janssens, M.K. Van Bael, J. D’Haen, K. Haenen

We present hexagonal boron nitride nanowall synthesis using the unbalanced RF sputtering technique. By varying several deposition parameters and analyzing the grown samples with a wide range of advanced characterization techniques, we are able to propose a model based on chemical rather than physical processes governing the growth. The results provide insight the role of temperature for defect and wall formation.