Comparative study of thermal and radical-enhanced methods for growing boron nitride films from diborane and ammonia

Cite as: J. Vac. Sci. Technol. A 38, 033411 (2020); https://doi.org/10.1116/6.0000132
Submitted: 19 February 2020 . Accepted: 01 April 2020 . Published Online: 23 April 2020

Ramazan O. Apaydin, Arnoud J. Onnink, Xingyu Liu, Antonius A. I. Aarnink, Michel P. de Jong, Dirk J. Gravesteijn, and Alexey Y. Kovalgin

ARTICLES YOU MAY BE INTERESTED IN

Status and prospects of plasma-assisted atomic layer deposition
Journal of Vacuum Science & Technology A 37, 030902 (2019); https://doi.org/10.1116/1.5088582

Study of the phase nature of boron- and nitrogen-containing films by optical and photoelectron spectroscopy
Journal of Vacuum Science & Technology B 38, 044009 (2020); https://doi.org/10.1116/6.0000193

Plasma deposition—Impact of ions in plasma enhanced chemical vapor deposition, plasma enhanced atomic layer deposition, and applications to area selective deposition
Journal of Vacuum Science & Technology A 38, 033007 (2020); https://doi.org/10.1116/1.5140841

Advance your science and career as a member of AVS

LEARN MORE
Comparative study of thermal and radical-enhanced methods for growing boron nitride films from diborane and ammonia

Cite as: J. Vac. Sci. Technol. A 38, 033411 (2020); doi: 10.1116/6.0000132
Submitted: 19 February 2020 · Accepted: 1 April 2020 · Published Online: 23 April 2020

Ramazan O. Apaydin, Arnoud J. Onnink, Xingyu Liu, Antonius A. I. Aarnink, Michel P. de Jong, Dirk J. Gravesteijn, and Alexey Y. Kovalgin

AFFILIATIONS
MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

ABSTRACT
This work studies the deposition of boron/boron nitride (B/BN) composite films at low substrate temperature (275–375 °C) by alternating pulses of diborane (B\textsubscript{2}H\textsubscript{6}) and ammonia (NH\textsubscript{3}) with argon purging in between to avoid gas-phase reactions of the precursors. This process is similar to atomic layer deposition in which the dominance of surface reactions simplifies the growth mechanism. However, non-self-limiting decomposition of B\textsubscript{2}H\textsubscript{6} and incomplete nitridation lead to the incorporation of pure boron (pure-B), causing deviation from the desired 1:1 B:N stoichiometry. Using the pure-B fraction as a measure of incomplete nitridation, this article describes consecutive experiments to control this effect and ultimately understand it in the context of a surface reaction model. First, it is demonstrated that, in a purely thermal mode, the growth of the layers and their composition strongly depend on the total gas pressure. The pure-B content (not to be confused with the total boron content) could thus be varied in the range of \(~\sim\)6–70 vol. %. Next, enhancement of nitridation by the dissociation of NH\textsubscript{3} into reactive radicals using a hot-wire was found to be insufficient to produce stoichiometric BN. Finally, plasma-assisted deposition at 310 °C resulted in nearly stoichiometric polycrystalline BN with an interplane distance matching that of hexagonal BN; the material was stable in air for at least six months. The pressure dependence in the purely thermal mode is consistent with a growth model of BN from B\textsubscript{2}H\textsubscript{6} and NH\textsubscript{3} via the so-called surface-adduct mechanism. The effects of the radical-enhanced methods on nitridation are explained using this model.

I. INTRODUCTION
Boron nitride (BN), a wide-bandgap group III–V compound, has attracted attention because of its remarkable combination of properties.\textsuperscript{1–3} Among them, high thermal conductivity, wide-bandgap, high temperature stability and mechanical strength, low dielectric constant, and high chemical stability in air make BN an attractive material for scientific research and potential applications.\textsuperscript{1–10} BN can be synthesized in amorphous, rhombohedral, wurtzitic, cubic, and hexagonal phases, of which the cubic and hexagonal phases are the most studied.

Several methods have been used to deposit BN, including molecular beam epitaxy,\textsuperscript{7,11} ion beam assisted deposition,\textsuperscript{12,13} magnetron sputtering,\textsuperscript{14} RF sputtering,\textsuperscript{15} pulsed laser deposition,\textsuperscript{16} and chemical vapor deposition (CVD).\textsuperscript{17–19} Among these, CVD is the most intensively studied, commonly using diborane (B\textsubscript{2}H\textsubscript{6}) and ammonia (NH\textsubscript{3}) gas mixtures as precursors.\textsuperscript{20–22} However, the high growth temperatures (close to 1000 °C) required to form crystalline films limit many (potential) applications.\textsuperscript{20,24} In addition, different thermal expansion coefficients of the substrate and of the deposited film negatively affect processing at high temperatures. BN films deposited at temperatures below 800 °C are usually amorphous.\textsuperscript{20,25}

This work studies low-temperature (275–375 °C) CVD of BN films by alternating pulses of B\textsubscript{2}H\textsubscript{6} and NH\textsubscript{3} interspersed with argon (Ar) purging. Similar to atomic layer deposition (ALD) and in contrast to continuous CVD, the pulsed approach suppresses gas-phase reactions to yield a simplified and more easily modeled mechanism of layer growth, governed by only surface reactions. However, the low substrate temperature and non-self-limiting...
decomposition of B₂H₆ present a challenge to the production of stoichiometric BN by this approach, as the NH₃ step may fail to nitridize all of the growth from the preceding B₂H₆ step. Such an incomplete nitridation results in the incorporation of pure boron (pure-B) in the layers, as shown in Sec. III C. The present work addresses this issue by experimentally studying the degree of nitridation in pulsed low-temperature CVD of BN, both with and without methods to enhance nitridation (see below), and incorporating the results in a model of layer growth by surface reactions. The fraction of pure-B in the layers is used as the measure of incomplete nitridation to be minimized.

Several radical-enhanced deposition methods have been employed to increase the degree of nitridation. In plasma-enhanced CVD or PECVD, NH₃ is dissociated in a plasma discharge to produce a variety of nitrogen-containing (NHₓ, where x = 0–2) radicals that react more readily with the low-temperature layer surface than NH₃ itself. Surface bombardment with energetic plasma species can additionally enhance the crystallization of the growing film. For instance, several groups have observed an improvement in the crystallinity by PECVD of aluminum nitride (AlN), zinc oxide (ZnO), hafnium oxide (HfO₂), and vanadium oxide (V₂O₅) films.²⁶

Another approach to generate radicals is by utilizing a hot-wire (HW). In this method, a hot tungsten (W) filament heated up to ≈2700 K can be used to dissociate gas molecules such as molecular hydrogen (H₂) and ammonia (NH₃) into atomic hydrogen (at-H) and NH₃ radicals.³¹⁻³⁷ Compared to plasmas, this method is purely chemical as it excludes the presence of energetic charged species and (UV) photons, reducing poorly controlled chemical reactions, surface bombardment effects, and photoactivation.³⁸⁻⁴⁴ Differentiating between the contributions of the chemical (both heterogeneous and homogeneous) reactions by radicals (chemical process) and of the bombardment effects (physical process) can clarify the film growth mechanism. In our previous work,⁴⁶ we had already started exploring the effects of using HW for the deposition of BN films, thereby enabling a pure-chemical but still radical-enhanced process.

The novelty of this work is in making consecutive efforts to optimize and model the film growth mechanism, with specific focus on the nitridation of the growing surface by NH₃ at low temperatures. The study was carried out in steps, with every next step increasing the degree of nitridation by various means. First, the deposition was performed in a purely thermal mode, meaning no other (except by temperature) enhancement of nitridation. This expectedly gave the lowest share of nitrogen in the films. It, however, appeared that the gas pressure remarkably played a crucial role in the nitridation process. For a particular precursor system, this finding was considered to be practically important and scientifically interesting, since, combined with the previous literature findings, it allowed to hypothesize the film deposition mechanism via the surface-adduction formation. Furthermore, we gradually increased the efficiency of the nitridation reaction by dissociating NH₃ into reactive species, from soft by HW to hard by plasma. The corresponding observations were in line with the proposed mechanism. Finally, the crystalline and stable-in-air BN films were obtained with plasma at a temperature of just 310 °C. The latter was an important practical outcome.

II. EXPERIMENT

A. Reactor design

Thin film growth experiments were carried out using two different reactor systems. The purely thermal and HW-assisted deposition experiments were performed using a home-built ALD/CVD cluster system equipped with three single wafer reactors connected via a loadlock, allowing to keep the reactors under high vacuum continuously. This enabled wafer transfer without vacuum break, thus preventing surface/interface deterioration. The reactor for BN consisted of a 32 cm² inner chamber and a path of 25–30 cm between the radical generation region (i.e., the HW position) and the wafer. The HW was installed in a small tool above the chamber, allowing to place the HW both in and out of the line-of-sight with the substrate. More detailed information on the reactor design can be found in our previous publication.⁴⁵ In this study, HW-assisted experiments were performed with the HW position in the line-of-sight with the substrate, in order to minimize the recombination of generated radicals upon their delivery to the substrate. A resistively heated W filament was used as the hot-wire.

To perform plasma-assisted film deposition experiments, a Picosun Plasma ALD/CVD R-200 reactor was used. The precursors (B₂H₆ and NH₃) were carried by Ar gas and introduced through the gas inlet on the top of the reactor. During the deposition process, the plasma was switched on only during the ammonia pulses.

B. Substrate preparation

Prior to deposition, silicon (Si) (100) wafers were cleaned in an ultraclean environment using a standard procedure: (i) a 1-min dip into 1% HF to strip the native oxide, (ii) rinsing in de-ionized water, and (iii) ozone-steam cleaning, followed by another HF dip and rinsing.

After the cleaning process, wafers were placed in the home-built ALD/CVD reactor for thermally and HW-assisted experiments. For the experiments performed in the Picosun reactor, the as-cleaned wafers were first oxidized with oxygen gas at 1050 °C to grow 100 nm silicon dioxide (SiO₂) layers.

C. Compositional and crystallinity analysis

The deposited films were characterized by x-ray photoelectron spectroscopy (XPS) to obtain the elemental composition and type of chemical bonding. In situ spectroscopic ellipsometry (SE) was used to monitor the actual surface temperature,⁴⁶ film thickness, and optical functions in real time. Additionally, ex situ SE was employed to determine the uniformity of the thickness and optical functions across the wafer. Films deposited with plasma were further characterized by high resolution transmission electron microscopy (HRTEM), energy filtered TEM (EFTEM), grazing incidence angle x-ray diffraction (GIXRD), and x-ray reflectivity (XRR) techniques. XPS spectra were acquired with a Quantera SXM (scanning XPS microprobe, from Physical Electronics) machine using monochromatic Al Kα radiation at 1486.6 eV. The binding energies of the photoelectron lines of the samples, as received, are referenced to the C1s line of adventitious hydrocarbons at 284.8 eV. For compositional analysis, XPS sputter depth profiling was performed using Ar ions (1–3 keV). SE measurements were carried out with a
Woollam M2000UI spectroscopic ellipsometer, operating in the wavelength ($\lambda$) range between 0.72 and 5.05 eV, in combination with COMPLETEEASE 5.19 modeling software. A brief explanation of the procedure used to interpret the SE data is given in Sec. II D.

TEM measurements were performed with a CM300ST-FEG TEM from Philips, while GIXRD and XRR analyses were carried out with an X’pert Powder XRD system from Malvern Panalytical.

D. Spectroscopic ellipsometry analysis

SE measures the change in the polarization of a beam of light reflected from the substrate, as a function of the wavelength.\textsuperscript{32–49} The change in the polarization can be related to the parameters of interest (i.e., refractive index $n$ and extinction coefficient $k$) by a least-square fitting to an optical model.\textsuperscript{46,50} Thus, to interpret the measured data, a reliable optical model is required. For our studies, the optical model comprised of an Si or SiO$_2$ substrate with a deposited layer on top.

The initial fits of the SE data were performed via Kramers–Kronig consistent B-Spline parameterization with a node spacing (control points) of 0.3 eV to determine the optical functions of any experimental and shown in the supplementary material.\textsuperscript{130} The change in the polarization can be related to the parameters of interest (i.e., refractive index $n$ and extinction coefficient $k$) by a least-square fitting to an optical model.\textsuperscript{46,50} Thus, to interpret the measured data, a reliable optical model is required. For our studies, the optical model comprised of an Si or SiO$_2$ substrate with a deposited layer on top.

The initial fits of the SE data were performed via Kramers–Kronig consistent B-Spline parameterization with a node spacing (control points) of 0.3 eV to determine the optical functions of any layer without assuming a certain spectral shape.\textsuperscript{51} The Sellmeier model was used to describe ($n$($\lambda$)-dependencies of stoichiometric BN films,\textsuperscript{46,52} while the Tauc–Lorentz oscillator model was used to describe the optical functions of amorphous boron (a-B). For layers thinner than 5 nm, an additional feature was observed and described by the Lorentz oscillator model.\textsuperscript{46} This feature does not match any electronic transitions of BN in the theoretical and experimental works that have been surveyed,\textsuperscript{46–55} suggesting the presence of a second compound. Based on SE, this compound was attributed to the pure boron (B) phase (later on also mentioned as excess-B), which was then confirmed by XPS; the latter indicated boron rich B/BN composites. The parameter correlation in the SE fits was minimized by following the approach explained elsewhere.\textsuperscript{46,56} Sensitivity tests following Ref. 61 were performed to confirm the SE fits represented the unique global solutions.

In our study, the Bruggeman effective medium approximation (EMA) \textsuperscript{46,48,54} model was employed to describe the optical functions of a composite layer (i.e., B and BN), by using the optical functions of the two components. For this, we used the dielectric functions of a pure boron layer deposited by CVD and a stoichiometric BN layer deposited by pulsed PECVD. The validity of the composite assumption is the subject of another publication\textsuperscript{64} and is not discussed in this paper.

III. RESULTS AND DISCUSSION

A. Purely thermal deposition

Thermal decomposition of B$_2$H$_6$ is not expected to be self-limiting in the studied temperature ($T$) range. This was confirmed experimentally and shown in the supplementary material.\textsuperscript{130} The non-self-limiting nature of B$_2$H$_6$ chemisorption implies two coexisting processes in the BN formation mechanism. First, (dissociative) chemisorption of B$_2$H$_6$ should occur during a B$_2$H$_6$ pulse, presumably leading to the formation of the pure boron (pure-B) phase. The growth surface can be BH$_x$ ($x = 0$–3) terminated after this step. This step is not self-limiting since the pure-B layer will keep growing with time (Fig. S1).\textsuperscript{130} Second, during the subsequent exposure to NH$_3$, the as-formed surface is expected to react with NH$_3$, thereby incorporating nitrogen into the layers. This step is self-limiting in the sense that the nitrogen content in BN can hardly exceed a certain share.

In the subsequent experiments, the effects of substrate temperature, diborane dose, and total pressure (ranging from 5 × 10$^{-3}$ to 12 mbar) on the growth rate (growth per cycle, GPC) of the films and on the amount of excess-B were investigated. The experimental conditions can be found in Table S1 in the supplementary material.\textsuperscript{130} It was observed that the nitrogen content was hardly affected by lowering the substrate temperature from 375 to 290 °C, whereas the GPC decreased from 0.045 to 0.021 nm/cycle. These results suggest that the temperature rather affects the B$_x$H$_y$ (dissociative) chemisorption than the pure-B nitridation. Strong enhancement of the GPC with increasing B$_2$H$_6$ pulse time, as shown in Fig. 1(a), implies that the GPC is limited by the B$_x$H$_y$ dose. The B$_2$H$_6$ pulse time also crucially determines the excess-B in the layers [Fig. 1(b)].

Importantly, increasing the total pressure ($P_{tot}$) leads to higher nitrogen content and a correspondingly lower amount of excess-B [Fig. 2(a)]. However, a gradual decrease in the GPC ($P_{tot} < 1$ mbar) was observed with increasing the pressure [Fig. 2(b)]. This rather unusual result can be explained by a decreased delivery of B$_2$H$_6$ to the wafer at a higher pressure (i.e., lower diffusion rate of B$_2$H$_6$) or a suppressed (dissociative) chemisorption of B$_2$H$_6$ (the rate limiting step) on the as-nitridized NH$_3$-terminated ($x = 1$, 2) surface compared to the BH$_x$ terminated surface. Since increasing $P_{tot}$ has a remarkably large impact on both GPC and excess-B, we have expanded the pressure range up to 12 mbar (see Fig. 2).

Although all data were obtained at somewhat different B$_2$H$_6$-pulse, Ar-purge, and NH$_3$-pulse durations [see Table S1 for details (Ref. 130)], the data given in Fig. 2(a) exhibit a clear trend of GPC versus $P_{tot}$. Particularly, the GPC slightly decreases with increasing the pressure for $P_{tot} < 1$ mbar and starts to increase rapidly for $P_{tot}$ exceeding 1 mbar. The excess-boron share (as obtained by SE) gradually decreases with increasing the $P_{tot}$, being as high as ~70 vol. % in the low-pressure range and as low as ~6 vol. % in the high-pressure range [Fig. 2(b)]. In spite of showing the cumulative data of different reactors (experiments at $P_{tot} ≥ 1$ mbar were carried out in the Picosun reactor, in the purely thermal mode, whereas the low-pressure data were obtained using the home-built cluster system) and substrates (Si and SiO$_2$), Fig. 2 indicates a consistent and clear effect of $P_{tot}$. We consider these findings to be a strong point, indicating a general trend, weakly dependent on the actual reactor geometry and the type of substrate used.

Obviously, changing $P_{tot}$ affects the partial pressures of both diborane ($P_{B_2H_6}$) and ammonia ($P_{NH_3}$). However, it should be noted that $P_{NH_3}$ was one order of magnitude higher than $P_{B_2H_6}$. Particularly, for $P_{tot} ≥ 1$ mbar, $P_{B_2H_6}$ was in the range of 0.01–0.1 mbar, whereas $P_{NH_3}$ ranged from 0.1–2 mbar. Likewise, for $P_{tot} < 1$ mbar, the partial pressures were of the orders 10$^{-4}$–10$^{-5}$ mbar (B$_2$H$_6$) and 10$^{-2}$–10$^{-3}$ mbar (NH$_3$). Considering the large difference in the partial pressures, in combination with the significant decay of excess-B with increasing $P_{tot}$, a dominant role of $P_{NH_3}$ in the growth process might be suggested. Section IV B.
provides a quantitative description of the relation between pressure and excess-B.

As stated above, the film growth occurs via the sequential steps of (i) growing pure-B during each B₂H₆ pulse and (ii) nitridation of the as-formed B during the subsequent NH₃ pulse. The rather strong increase of the GPC at \( P_{\text{tot}} \geq 1 \text{ mbar} \), which coexists with the gradually decreasing amount of excess-B in the films, suggests nitridation to control the growth at \( P_{\text{tot}} \geq 1 \text{ mbar} \). The nitrification may in turn enhance the B formation by changing the termination toward getting more NHₓ (\( x = 1, 2 \)) surface groups.

Summarizing, thermal depositions performed at \( P_{\text{tot}} < 0.1 \text{ mbar} \) indicate a crucial role of \( P_{\text{B₂H₆}} \) in the growth rate and film composition, whereas the impact of \( P_{\text{NH₃}} \) dominates at \( P_{\text{tot}} \geq 1 \text{ mbar} \) (see Fig. 2), increasing the GPC and lowering the excess-B. Decreasing the excess-B below 6 vol. % is, however, challenging in purely thermal mode and at low temperatures. We, therefore, continued the study to explore two radical-enhanced approaches. To explore the effects of radicals on both the film growth rate and composition, and thereby to indirectly confirm the proposed deposition mechanism, we gradually changed the degree of dissociation of NH₃ from soft by HW to hard by plasma.
B. Radical-enhanced deposition

1. Hot-wire assisted deposition

The impact of an HW on the dissociation of NH₃ has been investigated by several groups, confirming the formation of mainly NH₂ radicals. This also means providing a corresponding flux of atomic hydrogen (at-H) to the substrate. For NH₃ dissociation, the at-H flux is expected to be larger than that of NH₂, due to a higher recombination probability of the latter. The generation, recombination, and delivery of radicals to the growth surface were previously studied in our experiments on tellurium etching (for at-H) and silicon nitridation (for NH₃). The HW-assisted deposition led to a dramatic decrease in the GPC with increasing HW temperature \( T_{HW} \). In particular, being \( \sim 0.01 \) nm/cycle in the HW-off mode, the GPC decreased to \( \sim 0.001 \) nm/cycle at \( T_{HW} = 2100 \) K. The efficient dissociation of NH₃ was already observed at \( T_{HW} > 1600 \) K (Ref. 45).

In spite of the lower GPC, more nitrogen was incorporated into the layers with increasing \( T_{HW} \). Under specific conditions, the excess-B decreased from \( \sim 50 \) vol. % at \( T_{HW} = 300 \) K to \( \sim 37 \) vol. % at \( T_{HW} = 1800 \) K, as determined by SE and later confirmed by XPS. Furthermore, a clear shift in the XPS B1s peak position toward that of BN was observed with increasing \( T_{HW} \) (see Sec. III C).

Although utilizing an HW has a clear effect on both GPC and stoichiometry, the concentration of N-containing radicals seems to be insufficient to nitridize the growing film to the extent required for the production of stoichiometric BN. Additionally, the competing interaction of at-H with the surface was hypothesized to decrease the GPC, as schematically illustrated in Fig. 5(b).

We must bear in mind that the gas pressure crucially affects both the film growth rate and the film composition in a purely thermal mode at low temperatures (Sec. III A). Further decreasing the excess-B to below 6 vol. %, as shown in Fig. 2(b), to approach stoichiometric BN, is however problematic. The soft dissociation of NH₃ by HW does not sufficiently enhance the film nitridation. To obtain stoichiometric and crystalline BN at only 310 °C, we therefore proceed with a plasma radical source to ensure a higher degree of NH₃ dissociation.

2. Plasma-assisted deposition

The depositions were performed on thermal SiO₂ (100 nm), with the Picosun reactor at a substrate temperature of 310 °C. We must bear in mind that the previously described experiments were performed at comparable substrate temperatures of 290 ± 20 °C. The total gas pressure was kept at 1 mbar for all the plasma experiments, corresponding to the excess-boron share of \( \sim 6 \) vol. % obtained in a purely thermal mode [Fig. 2(b)]. The other process conditions were kept identical to the thermal counterpart. Remarkably, the GPC in plasma (0.017 nm/cycle) was hardly changed compared to that in the thermal mode (0.02 nm/cycle), meaning that the plasma merely enhanced the nitridation process. To obtain stoichiometric and crystalline BN at only 310 °C, we therefore proceed with a plasma radical source to ensure a higher degree of NH₃ dissociation.

C. Comparative analysis of the film properties

1. XPS analysis

A comparison of B1s and N1s spectra showed a significant influence of the growth methods. As mentioned, the amount of excess-B, as estimated by SE and confirmed by XPS, decreased from \( \sim 50 \) to \( \sim 37 \) vol. % for the thermally and HW-deposited films. The plasma enhancement resulted in 46 at. % of N, 50 at. % of B, and 4 at. % of oxygen.

The B1s spectra were obtained after sputtering the initial 0.5–1 nm of the film surface to prevent the contribution of various surface contaminants. A comparison of the B1s spectra of pure-B as well as thermally, HW-, and plasma-deposited B/BN films is shown in Fig. 3.

Going from thermal through HW- to plasma-assisted deposition, one can clearly see that the B1s peak broadens toward higher binding energies and that the binding energy of the main peak gradually shifts from 188.4 eV (i.e., B–B bonding) to 190.6 eV (i.e., B–N bonding). This confirms that effective nitridation is enabled by external energy sources. In addition to the B1s spectra, we analyzed the N1s binding energies [Fig. 3(b)]. For all the samples, the N1s peak positions corresponded to...
stoichiometric BN; no shift toward higher or lower binding energies was observed.

To support the increase in the BN share in the B1s peak with an increasing degree of nitridation, B1s peak fitting was performed (Fig. S4).130 It was concluded that the broad features seen in the thermally and HW-deposited films could adequately be described by two Gaussian peaks fixed at the binding energies of pure-B and stoichiometric BN. On the other hand, the B1s peak of the plasma-deposited film was solely fitted by a single Gaussian peak at the B−N binding energy. These results are consistent with the formation of mixed pure-B and stoichiometric BN phases in the thermally and HW-deposited films, whereas plasma assistance leads to growing nearly stoichiometric BN.

2. SE analysis

Applying the EMA model (see Sec. II D for details) confirmed the presence of excess-B in the samples shown in Fig. 2. The plasma samples showed no detectable amount of excess-B, which was further confirmed by EFTEM elemental mapping, indicating the presence of only nitrogen and boron with some trace amounts of oxygen (see Fig. S5).130

3. Stability in air

The environmental stability of BN is of prime importance for practical applications and occurs for films with a sufficient degree of crystallinity. It is known that (partially) amorphous and low-crystal-order BN films can quickly degrade in air due to their interaction with oxidizing species,20 whereas h-BN layers are chemically inert in many environments.68 Degradation in air is, therefore, a measure of the film crystallinity and nonstoichiometry.

The degradation can be investigated by ex situ SE. The measurements were performed for the as-deposited (i.e., measured within 20 min) samples and after their exposure to air for more than 6 months. To draw conclusions regarding the degradation of films, a comparison of the delta values was carried out, since delta is rather sensitive to changes in their thickness and optical functions.46 It can be concluded from Fig. S6130 that the thermally and HW-deposited samples significantly changed their optical responses after the 6-month exposure, presumably due to their oxidation, whereas the plasma-deposited samples showed no changes. The latter might be the first indication of having a crystalline structure.20,24

4. HRTEM, GIXRD, and XRR analyses

The crystalline structure of the plasma-deposited films is confirmed by HRTEM. Figure 4(a) shows a lamellar-type structure with the crystal planes perpendicular to the substrate surface. A line profile analysis (the inset) reveals that the interplane distance (d-spacing) ranges between 3.4 and 3.8 Å. These values fall in the range previously reported for hexagonal BN (3.3–3.7 Å).6,10,19,25,69–71

Further confirmation of the interplane distance was carried out by fast Fourier transform (FFT) analysis of the three selected sections (FFT1, FFT2, and FFT3), using radial profile analysis with IMAGEJ 1.52i (Ref. 72) and RADIAL PROFILE EXTENDED (Ref. 73) software. The three boxed areas shown in Fig. 4(a) revealed an average interplane distance of 3.57 Å, with a second periodicity at 2.16 Å, as shown in Fig. 4(b). The former matches with the (002) d-spacing of h-BN (3.3–3.7 Å), while the latter corresponds to the (100) d-spacing of h-BN (2.17 Å). This is close to the values of sphalerite β-BN (2.09 Å)74 and wurtzite γ-BN (2.20 and 2.10 Å).75 These two structures, however, do not have any d-spacing above
2.2 Å, and so cannot cause the broad peak centered at 3.57 Å. In the 3.3–3.7 Å range reported for BN, larger d-spacings have been attributed to curved\(^7\) and turbostratic\(^7\) BN. The d-spacing may increase due to the presence of \(\text{NH}_x\) (\(x = 1, 2\)) groups in BN, similar to the effect of the hydroxyl or carboxyl groups reported for graphite\(^8\).\(^9\)

The GIXRD analysis of the plasma-deposited film shown in Fig. 4 confirmed the occurrence of the h-BN phase. The diffraction peak positions coincide well with the values reported for h-BN (Ref. 80) (Fig. S7).\(^{130}\) XRR revealed a thickness of 14.3 nm, which is in accordance with the TEM and SE results. Fitting the mass density revealed 1.82 g/cm\(^3\), which is close to 1.89 g/cm\(^3\) reported for h-BN films.\(^{31}\)

IV. THE MECHANISM OF GROWTH AND NITRIDATION

A model of the layer growth and nitridation by surface reactions is required to understand the demonstrated dependence of both GPC and excess-B share on \(P_{\text{NH}_3}\) (recall Fig. 2). Section IV A hypothesizes such a model based on the literature. Section IV B applies the model specifically to incomplete nitridation described in Sec. III A. Section IV C details how the model can incorporate the observed effects of hot-wire and plasma enhancement on nitridation. The agreement with these observations identifies the proposed model as a candidate to be confirmed by more direct methods, such as in situ vibrational spectroscopy of surface groups.

A. Surface-adduct pathway for purely thermal deposition

It is well known that the so-called Lewis-acid and Lewis-base compounds can react with each other, resulting in the formation of a gas-phase adduct.\(^8\) The formation of adducts on the surface was confirmed for ALD of AlN\(^{86,88}\) and suggested to play a role for ALD of gallium nitride (GaN).\(^{86,88}\) Details can be found in the supplementary material.\(^{130}\)

Since \(\text{B}_2\text{H}_6\) is also a known Lewis acid that forms adducts,\(^8\)\(^9\)\(^96\) in this study, we attempt to adopt the adduct-assisted pathway for growing BN from \(\text{B}_2\text{H}_6\) and \(\text{NH}_3\). The dependence of both the GPC and the composition (degree of nitridation) on the total pressure, as demonstrated in Fig. 2, may also be interpreted as the dependence on \(P_{\text{NH}_3}\), indeed suggesting the adduct-assisted mechanism. To the best of our knowledge, hypothesizing the role of the surface-adduct for growing BN from \(\text{B}_2\text{H}_6\) and \(\text{NH}_3\) at low temperatures has not been done so far.

The formation of the gas-phase \(\text{H}_4\text{B}_2\text{NH}_3\) compound from \(\text{B}_2\text{H}_6\) and \(\text{NH}_3\) has been suggested to be the most energetically favorable reaction, based on the calculations performed by Nguyen et al.\(^{93}\) Furthermore, through a subsequent release of \(\text{H}_2\), first \(\text{H}_2\) to \(\text{NH}_3\) and then \(\text{HB}\) to \(\text{NH}\) species can be produced. As the reaction temperature increases, the gas-adduct complex progressively loses hydrogen, and at temperatures above 500 °C, BN can finally be obtained.\(^{21,22,92,97-100}\) Gómez-Aleixandre et al.\(^{21}\) and Rodriguez et al.\(^{181}\) showed that, as a result of the limited (partial) dissociation of ammonia at temperatures below 850 °C, the interaction between diborane and ammonia is strongly temperature dependent.

The gas-phase decomposition of \(\text{B}_2\text{H}_6\) was studied by many researchers.\(^{102-109}\) On the surface, \(\text{B}_2\text{H}_6\) is known to cause a non-self-limiting formation of solid boron.\(^{109-112}\) The studies of Fehlner,\(^{113-116}\) Baylis et al.\(^{117}\) and Söderlund et al.\(^{118}\) suggested that \(\text{BH}_3\) species dominate in the gas phase. (Since \(\text{BH}_3\) is also a known Lewis acid,\(^{119}\) it readily forms the gas-phase \(\text{H}_3\text{B}:\text{NH}_3\) adduct\(^{91}\) by reacting with \(\text{NH}_3\).) Mohammadi et al.\(^{111}\) proposed a growth model based on the chemisorption of \(\text{BH}_3\) and the subsequent elimination of \(\text{H}_2\). A similar mechanism for the interaction of \(\text{B}_2\text{H}_6\) with silicon oxide surfaces has been proposed by Gillis-D’Hamers et al.\(^{120,121}\) The authors showed that, upon chemisorption, diborane forms BH- or BH\(_2\)-terminated surface sites. To simplify the reaction schematic diagram, we have only drawn BH-terminations here.

B. Excess B fraction described by the surface-adduct model

Applying the model to our work, the initial step is likely the decomposition of \(\text{B}_2\text{H}_6\) (in the gas phase or on the surface), forming \(\text{BH}_3\)-terminations (\(x \geq 1\) and/or 2) accompanied by the release of \(\text{H}_2\). Because this decomposition is not self-limited, additional species of \(\text{B}_2\text{H}_6\) and/or \(\text{BH}_3\) may already react with \(\text{BH}_3\)-terminated sites, encapsulating the underlying B and releasing its hydrogen termination as \(\text{H}_2\). These B atoms can then no longer be nitridized in the subsequent \(\text{NH}_3\) step, since the latter requires an accessible BH\(_3\) group at the surface (see below). Let \(F\) denote the fraction of B atoms bonded to hydrogen at the surface of the growing layer when the \(\text{NH}_3\) pulse begins.
In the next step, we hypothesize the chemisorption of NH₃ to BH₂-terminated surface sites yielding a surface-adduct, analogous to the known gas-phase H₂B:NH₃ adduct. Modeling the chemisorption with a Langmuir isotherm, Eq. (1) gives the fraction \( \theta \) of the available BH₂ sites that are covered with NH₃ in equilibrium,

\[
\theta = \frac{K_{eq} P_{NH_3}}{1 + K_{eq} P_{NH_3}},
\]

where \( K_{eq} \) is an equilibrium constant with dimensions of inverse pressure, related but not equal to the dimensionless equilibrium constant. As also in the thermal ALD of GaN, the adsorption of NH₃ is expected to reach equilibrium much faster than the duration of the pulse. Taking into consideration that the chemisorption of NH₃ leads to nitridation (see below) and the partial pressure \( P_{NH_3} \) scales up with the throttle-regulated total pressure \( P_{tot} \), Eq. (2) provides an expression for the atomic fraction of excess B, \( f_B \),

\[
f_B = 1 - F\theta = 1 - F + \frac{K P_{tot}}{1 + K P_{tot}},
\]

where \( K \) is the product of \( K_{eq} \) and the pressure scaling factor (0.182 in this work). We show elsewhere that \( f_B \) may be approximated by the volume fraction of pure-B determined by SE. The model of Eq. (2) describes the trend of Fig. 2(b), using \( K = 200 \) mbar⁻¹ and \( F = 0.92 \). The Langmuir isotherm (and thus \( K \)) dominates the trend at low pressures, whereas \( F \) determines the lowest pure-B fraction possible without the radical enhancement of nitridation (see Sec. IV C). The model may be improved by including the dependency of \( F \) on the duration of the B₂H₆ pulse.

After the adsorption of NH₃, the reaction of the adduct-NH₃ with hydrogen of a neighboring –BH₂-termination occurs, releasing H₂ [Fig. 5(a)]. This forms –NH₂- bridges between the neighboring B atoms (i.e., B−NH₂−B linkages), analogous to Al−NH₂−Al linkages in AlN ALD. Such B−NH₂−B linkages laterally expand over the entire growth surface in a self-limiting fashion. Exposure to B₂H₆ during the subsequent precursor pulse restores the required BH-terminations (not a self-limiting process), once again releasing H₂. It should be noted that direct thermal nitridation of pure-B is thermodynamically inhibited at temperatures below 900 °C. However, via the proposed adduct-assisted pathway, nitrogen can still be effectively incorporated at much lower temperatures.

C. A comparison of purely thermal and radical-enhanced modes

Applying HW or plasma is expected to alter the growth mechanism and, therefore, can be considered to be an indirect confirmation of the proposed model. In particular, the dissociation of NH₃ into NH₂ (x = 0−2) radicals and at-H may facilitate alternative chemical routes and thus suppress the adduct-assisted pathway. Furthermore, plasma enhancement of nitridation includes surface bombardment by energetic particles that may enable the nitridation of subsurface boron (effectively increasing \( F \) in Eq. (2)), whereas hot-wire enhancement lacks this effect.

The effect of radicals from a hot-wire or plasma on nitridation greatly depends on the efficiency with which various radical species are generated and transported to the growing layer. First, the generated at-H can remove hydrogen of the BH-terminations (the so-called hydrogen abstraction), thereby eliminating the B-H surface sites which are essential to nitridation by the adduct-assisted mechanism [Fig. 5(b)]. If reactive NH₂ radicals are present in sufficient quantities, they can still support the formation of B−NH₂−B and/or B−NH−B linkages. Atomic nitrogen can further directly nitridize elemental boron. Therefore, for optimized process conditions, radical-enhanced methods increase the nitrogen share, still having diborane chemisorption as the rate limiting step.

On the other hand, nonoptimized conditions (i.e., not enough NH₂ radicals but too much at-H) may lead to lower GPC (see Sec. III B) and nonstoichiometric B share. The latter is due to a decreased efficiency of nitrogen incorporation via the thermally assisted surface-adduct mechanism, as schematically shown in Fig. 5(b). A deficiency of NH₂ radicals at the growth surface and an excess of at-H, for example, due to a low-power radical source or because of recombination on the way to the substrate, may result in B-rich samples.

Our experiments show that the highest degree of nitrogen incorporation is provided by the plasma-assisted growth; this gives nearly stoichiometric, crystalline, and air-stable BN films at a substrate temperature of 310 °C. Enhancement of nitridation by using a hot-wire was much less effective, presumably due to a suboptimal flux of radicals (e.g., too much at-H) and/or a lack of surface bombardment to nitridize subsurface B.

V. CONCLUSIONS

This work studied the formation of B/BN composites using purely thermal, hot-wire, and plasma-assisted deposition methods by sequentially pulsing B₂H₆ and NH₃ precursors. It has been demonstrated that, in the purely thermal mode, increasing the total gas pressure considerably enhances the GPC, incorporating a bigger share of nitrogen in the layers and thereby reducing the pure-B content from ~70 to 6−7 vol. %. However, a further decrease in the excess-B share, to obtain a stoichiometric BN in thermal mode, is challenging. To improve both stoichiometry and crystallinity, HW- and plasma-assisted methods have been explored. Utilizing the HW had a clear effect on both the GPC and the film composition, although the concentration of NH₂ radicals was not sufficiently high enough to effectively decrease the excess-B share. Therefore, switching to plasma provided nearly stoichiometric, crystalline, and air-stable BN films at just 310 °C.

Concerning the growth mechanism in the purely thermal mode, we hypothesized a surface-adduct-assisted reaction pathway, analogous to the earlier suggested surface-adduct mechanisms for growing AlN and GaN by thermal ALD at low temperatures. In particular, BH-terminated surface sites react with NH₃, forming surface adducts. The adduct-NH₃ consequently reacts with hydrogen of a neighboring BH₄-termination \( (x = 1, 2) \), forming B−NH₂−B linkages and releasing H₂. A subsequent B₂H₆ pulse restores the original BH₄-terminations, once again eliminating H₂.

The experimentally measured excess-B share was modeled based on the surface-adduct mechanism, describing the adsorption...
of NH₃ that leads to nitridation with a Langmuir isotherm. Both the model and the data show that the adduct-assisted pathway enables effective incorporation of nitrogen into BN films at low temperatures and sufficiently high partial pressures of NH₃. However, subsurface B is not nitridized as it lacks the BH₂ group required for the formation of the adduct. Applying HW or plasma provides additional reaction pathways and alters the growth mechanism, further enhancing nitridation under optimal conditions.

ACKNOWLEDGMENTS

This work was financially supported by The Netherlands Organization for Scientific Research (NWO), Domain Applied and Engineering Sciences (TTW), Project No. 13929. The authors thank G. A. M. Kip and E. G. Keim of the MESA+ Institute for performing XPS and (EF)TEM examination, respectively. We further thank Seda Kizir (XUV group, University of Twente) and Sourish Banerjee (IDS group) for their help with XRR and GIXRD measurements, respectively. Jurriaan Schmitz (IDS) is acknowledged for their fruitful discussions. Toyota Europe and ASM International are acknowledged for their partial financial support of this project.

REFERENCES
