Atomic layer deposition of wet-etch resistant silicon nitride using di(sec-butylamino) silane and N2 plasma on planar and 3D substrate topographies

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Atomic Layer Deposition of Wet-Etch Resistant Silicon Nitride Using Di(sec-butylamino)silane and N₂ Plasma on Planar and 3D Substrate Topographies

Tahsin Faraz,*†,‡,¹ Maarten van Drunen,†,‡,¹ Harm C. M. Knoops,†,‡,¹ Anupama Mallikarjunan,§ Iain Buchanan,§ Dennis M. Hausmann,† Jon Henri,† and Wilhelmus M. M. Kessels*§

¹Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
‡Oxford Instruments Plasma Technology, North End, Bristol BS49 4AP, U.K.
§Air Products and Chemicals Inc., 1969 Palomar Oaks Way, Carlsbad, California 92011, United States
†Lam Research Corporation, 11155 Southwest Leveton Drive, Tualatin, Oregon 97062, United States

ABSTRACT: The advent of three-dimensional (3D) finFET transistors and emergence of novel memory technologies place stringent requirements on the processing of silicon nitride (SiNₓ) films used for a variety of applications in device manufacturing. In many cases, a low temperature (<400 °C) deposition process is desired that yields high quality SiNₓ films that are etch resistant and also conformal when grown on 3D substrate topographies. In this work, we developed a novel plasma-enhanced atomic layer deposition (PEALD) process for SiNₓ using a mono-aminosilane precursor, di(sec-butylamino)silane (DSBAS, SiH₂(NHtBu)₂), and N₂ plasma. Material properties have been analyzed over a wide range of deposition parameters and compared with those obtained in our previous work for SiNₓ deposited using a bis-aminosilane precursor, bis(tert-butylamino)silane (BTBAS, SiH₂(NHtBu)₂), and N₂ plasma. Dense films (~3.1 g/cm³) with low C, O, and H contents at low substrate temperatures (<400 °C) were obtained on planar substrates for this process when compared to other processes reported in the literature. The developed process was also used for depositing SiNₓ films on high aspect ratio (4.5:1) 3D trench nanostructures to investigate film conformity and wet-etch resistance (in dilute hydrofluoric acid, HF/H₂O = 1:100) relevant for state-of-the-art device architectures. Film conformity was below the desired levels of >95% and attributed to the combined role played by nitrogen plasma soft saturation, radical species recombination, and ion directionality during SiNₓ deposition on 3D substrates. Yet, very low wet-etch rates (WER ≤ 2 nm/min) were observed at the top, sidewall, and bottom trench regions of the most conformal films deposited at low substrate temperature (<400 °C), which confirmed that the process is applicable for depositing high quality SiNₓ films on both planar and 3D substrate topographies.

KEYWORDS: silicon nitride, atomic layer deposition, ALD, plasma ALD, di(sec-butylamino)silane, DSBAS, thin film, wet etch

INTRODUCTION

Silicon nitride (SiNₓ) is a widely used material in both front and back end-of-the-line (FEOL/BEOL) processes of semiconductor device manufacturing.¹,² It regularly serves as hard masks and etch stop layers in critical processing techniques such as spacer defined patterning³–⁵ and self-aligned contacts.⁶,⁷ A key application of SiNₓ films is spacers⁸–¹⁰ for the high-k metal gate (HKMG) stack in both planar FET and state-of-the-art 3D finFET¹¹–¹³ architectures in CMOS nanoelectronics. These spacer films serve multiple purposes such as being a barrier against oxygen ingress and dopant out-diffusion while preventing any etch damage during subsequent processing steps.¹⁴,¹⁵ They also provide a constant spacing of the source and drain of the transistor, independent of transistor pitch.¹⁶ All these require the SiNₓ films to be highly conformal and etch resistant in dilute hydrofluoric (HF) acid (HF/H₂O = 1:100).¹⁷,¹⁴,¹⁵ However, the use of the HKMG stack requires a low temperature (~400 °C) processing environment to prevent interlayer diffusion or interfacial reactions from occurring at elevated temperatures.¹⁷ Processing of SiNₓ at even lower temperatures (~250 °C) is required for applications in emerging memory devices, such as encapsulation¹⁸ for magnetic tunnel junctions (MTJ) in MRAMs,¹⁹–²¹ where metal atom migration at high temperatures can lead to device degradation.²¹–²⁴ SiNₓ has been traditionally deposited using low-pressure chemical vapor deposition (LPCVD) or plasma-enhanced chemical vapor deposition (PECVD) processes.²⁵ LPCVD generally yields conformal SiNₓ films with low wet-

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etch rates (WERs < 1 nm/min)\(^\text{15}\) in dilute HF but only at high temperatures (\(>700 °C\)).\(^\text{14}\) Using PECVD can lower the process temperatures to \(\sim 400 °C\), but the SiN\(_x\) films exhibit a reduced conformality on 3D structures or imprecise film thickness control.\(^\text{25}\) Thermal and plasma-enhanced atomic layer deposition (ALD, PEALD) are well-known methods for depositing high quality thin films with excellent growth control.\(^\text{26-29}\) High quality SiN\(_x\) films when deposited on 3D substrates show a decrease in sidewall film thickness with depth inside the trench. Sidewall/top film thickness ratio was observed to be \(\sim 50\%\) (within 200 nm of the top of the trench), similar to that of \(40\%\) for SiN\(_x\) films deposited by PECVD.\(^\text{30}\) Sidewall/top film thickness ratio was observed to be \(\sim 50\%\) (within 200 nm of the top of the trench), similar to that of King.\(^\text{35}\) Exceptional wet etch resistance in dilute HF was observed (from 1 to 3 s) and plasma exposure (from 2 to 15 s).\(^\text{30}\) They also observed soft saturation of GPC as a function of N\(_2\) plasma exposure time, which indicates long cycle times similar to that of King.\(^\text{35}\) Exceptional wet etch resistance in dilute HF was observed (from 1 to 3 s) and plasma exposure (from 2 to 15 s).\(^\text{30}\) They also observed soft saturation of GPC as a function of N\(_2\) plasma exposure time, which indicates long cycle times similar to that of King.\(^\text{35}\) Exceptional wet etch resistance in dilute HF was observed (from 1 to 3 s) and plasma exposure (from 2 to 15 s).\(^\text{30}\) They also observed soft saturation of GPC as a function of N\(_2\) plasma exposure time, which indicates long cycle times similar to that of King.\(^\text{35}\)

Table 1 provides a brief summary of SiN\(_x\) ALD processes reported in the literature.

<table>
<thead>
<tr>
<th>precursor</th>
<th>coreactant</th>
<th>mass density (g/cm(^3))</th>
<th>3D substrate aspect ratio</th>
<th>conformality (side/top ratio in %)</th>
<th>wet-etch rate (nm/min)</th>
<th>planar surface</th>
<th>3D sidewall surface</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl(_4)</td>
<td>NH(_4)Cl, NH(_3), NH(_4)Cl, NH(_3), N(_2)H(_4)</td>
<td>2.7</td>
<td>≥3.5:1</td>
<td>&lt;50</td>
<td>&gt;10</td>
<td>-</td>
<td>-</td>
<td>15, 31, 37</td>
</tr>
<tr>
<td>SiH(_4)</td>
<td>N(_2)</td>
<td>2.8</td>
<td>≤2:1</td>
<td>&gt;80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>N(silHN(CH(_3))(_2)CH(_3))Si(CH(_3))(_3)</td>
<td>H(_2)/N(_2)</td>
<td>2.9</td>
<td>≤6:1</td>
<td>&lt;50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>Si(silHN(CH(_3))(_2)CH(_3))</td>
<td>N(_2)</td>
<td>3.1</td>
<td>≤5:1</td>
<td>&lt;50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>39</td>
</tr>
<tr>
<td>SiH(_4)(N(_2)Bu(_3))</td>
<td>N(_2)</td>
<td>4.5:1</td>
<td>-</td>
<td>&gt;80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>SiH(_3)(N(_2)Bu(_3))</td>
<td>N(_2)</td>
<td>-</td>
<td>-</td>
<td>&gt;80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16</td>
</tr>
</tbody>
</table>

\(^\text{1}\)The selected reports are chosen based on data available for film conformality on 3D substrate topographies and wet-etch resistance (in dilute hydrofluoric acid, HF/H\(_2\)O = 1:100) of SiN\(_x\) at planar and 3D surfaces when deposited at temperatures \(<400 °C\). A *" indicates data not reported.

\(^\text{2}\)Data available only for refs 31, 33, and 37. Data available only for refs 15, 36, and 37. Data available only for refs 15 and 36. *Wet-etch rate reported using dilute HF solution with HF/H\(_2\)O = 1:500. For substrate temperatures <400 °C.

In previous work conducted within our group, Knoops et al.\(^\text{16}\) developed a SiN\(_x\) process employing a bis(tert-butylamino)silane (BTBAS, SiH\(_3\)(N\(_2\)Bu\(_3\))) precursor, depicted in Figure 1a, in combination with a remote N\(_2\) gas. High quality SiN\(_x\) films were deposited having reasonable impurity contents ([C] < 10 at. % and [O] < 5 at. %). Moreover, the H content was relatively low ([H] < 11 at. %), and a low WER (\(\sim 0.2 \pm 0.5 \text{ nm/min at } 400 °C\)) was obtained in dilute HF solution.\(^\text{16}\) Insights provided by Ande et al.\(^\text{41}\) later demonstrated that the growth rate of SiN\(_x\) using BTBAS is strongly reduced when NH\(_3\), N\(_2\), or H\(_2\) plasmas were used. This explained the choice of using an N\(_2\) plasma over other H-containing plasmas as the coreactant during PEALD with BTBAS. In other studies related to this work, Knoops et al.\(^\text{42}\) identified parameters governing the quality of SiN\(_x\) films deposited using BTBAS and N\(_2\) plasma, while Bosch et al.\(^\text{43}\) investigated the surface chemistry of that process with in situ infrared spectroscopy. They demonstrated that tert-butylamine
Research Article

Mono-aminosilane precursor di(2-butoxymethyl)aminosilane (DBAS, SiH3N(sBu)2)38,44 was synthesized and provided by Air Products and Chemicals Inc., was used as the precursor and held at a bubbler temperature of 40°C. During precursor dosage, DBAS was vapor drawn into the reaction chamber using Ar (25 sccm, purity 99.9999%) as a carrier gas in the delivery line, with the APC valve completely closed. A reaction step was employed immediately after precursor dosage with the APC valve set to 10° to reduce the effective pumping speed and maximize precursor usage by confining it within the chamber. Setting the APC valve to 10° (i.e., almost closed) was necessary because a continuous flow of inert N2 gas (50 sccm, purity 99.9999%) was passed through the alumina plasma tube during all process steps to reduce precursor adsorption on the inner surfaces of the tube during precursor dose and reaction steps. For both purge steps, the APC valve was fixed to a 90° valve position (i.e., fully open) for maximum pumping while 50 sccm of N2 gas flowed through the alumina tube. The precursor delivery lines were heated to 70°C to prevent precursor condensation and were purged with 100 sccm of Ar to remove any residual gas from previous ALD cycles.

**PEALD Process Conditions.** On the basis of the saturation curves for precursor dosage and plasma exposure obtained during process development using DBAS and N2 plasma (see ALD film growth section), the following step sequence was chosen as a standard PEALD recipe for SiNₓ: 1 s delivery line purge, 100 ms DBAS dose time, 3 s reaction time, 1 s precursor purge time, 2 s preplasma time (gas stabilization prior to plasma ignition), 10 s plasma exposure time, and 1 s plasma purge time. The 100 sccm N2 gas flow and 12 mTorr pressure conditions were used for the plasma exposure step. These are outlined in Table 2. The standard PEALD recipe used for the previously reported PEALD process using BTBAS and N2 plasma16 is also outlined in Table 2 for comparison. For investigating conformality, additional runs using extended precursor dose times of 500, 1000, and 2000 ms and plasma exposure times of 20, 40, and 80 s were performed. These additional runs were initially based on previous Monte Carlo simulations on conformality by Knoops et al.48 and then further extended based on the results observed. Extended precursor purge time of 3 s and plasma purge time of 2 s were also implemented.

### Table 2. Standard Parameters for the Previously Developed BTBAS Process and the DSBAS Process Developed in This Work

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BTBAS</th>
<th>DBAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubbler temperature</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Precursor dose time</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Plasma (N2) exposure</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Precursor reaction</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Precursor purge time</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Plasma purge time</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Plasma (N2) pressure</td>
<td>40</td>
<td>12</td>
</tr>
<tr>
<td>Plasma (N2) gas flow</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

**Experimental Details**

**PEALD of SiNₓ.** PEALD of SiNₓ was performed using an Oxford Instruments FlexAL reactor. It is equipped with a remote inductively coupled (ICP) plasma source, which was operated at 600 W of radio frequency power at 13.56 MHz and controlled by an automated matching network. The source consists of a water-cooled copper coil wrapped around a cylindrical alumina plasma tube. A base pressure in the reactor chamber of ~10⁻⁵ Torr was obtained using a turbo pump. A butterfly valve in front of the turbo pump controlled the effective pumping speed and functioned as an automated pressure controller (APC). The chamber wall temperature was set to 150°C, except for instances where the deposition temperatures were below 150°C, during which the wall was set to the deposition temperature. Due to poor thermal contact in vacuum, the actual temperatures of the substrates (wafer, coupon, see ALD film growth section) were lower than the set temperature of the substrate stage/table. This set temperature (henceforth referred to as stage temperature) can be fixed to a value between 25 and 500°C. An estimation of the actual substrate temperature as a function of stage temperature is given in the Supporting Information. All substrates underwent a 30 min heating step prior to commencing deposition to ensure substrate temperature stabilization. DBSAS (assay ≥99.9%, see Supporting Information), synthesized and provided by Air Products and Chemicals Inc., was used as the precursor and held at a bubbler temperature of 40°C.
for the additional conformality runs to account for any CVD component that could arise in the extended PEALD recipes.

**Material Analysis and Characterization.** SiN$_x$ films were deposited on planar c-Si substrates with a thin native oxide layer (∼1.5 nm) for developing the PEALD process. The optical properties and film thickness of the deposited layers on c-Si substrates were measured using spectroscopic ellipsometry (SE). Ex situ SE measurements were conducted using a J.A. Woollam Variable Angle SE with a VB-400 Control Module and an HS-190 Monochromator (1.2−6.5 eV). In situ SE measurements were performed in vacuum at an incidence angle of 70° (1.2−5 eV). The optical model used consisted of a silicon substrate, ∼1.5 nm native oxide, and a silicon nitride layer fitted with a Cauchy dispersion relation in the optically transparent region for SiN$_x$ (1.2−4 eV). The surface roughness was assumed negligible for these PEALD films. Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) measurements were used to determine the film composition (stoichiometry) and mass density of SiN$_x$ deposited on planar c-Si substrates. The RBS and ERD measurements with subsequent data simulations were performed by AccTec B.V. and Detect 99 using a 1.8−2 MeV helium-ion beam. The areal densities of the elements were determined from raw data simulations. SiN$_x$ film composition on the planar c-Si substrates was also investigated with X-ray photoelectron spectroscopy (XPS) measurements using a Thermo Scientific K-Alpha spectrometer equipped with a Al Kα X-ray source (hν = 1486.6 eV). Note that the sensitivity factors, which are required for obtaining elemental concentrations, were previously determined for the XPS system used. Depth profiles were measured by sputtering with Ar$^+$ ions.

For investigating film conformality and wet-etch resistance on 3D substrate topographies, SiN$_x$ layers were deposited using PEALD on coupons containing high aspect ratio trench nanostructures (width ∼100 nm, height ∼450 nm, AR = 4.5:1) and analyzed with cross-sectional TEM. These 3D nanostructures were created by first depositing a thick SiO$_2$ film on a Si wafer using PECVD, which was subsequently etched into trench structures. The SiO$_2$ trench structures were then coated with a SiN$_x$ layer using high-temperature CVD, on which a SiO$_2$ layer was deposited using ALD. Coupons containing these trench based HARS were prepared and provided by Lam Research. A JEOL 2010F ultrahigh-resolution scanning TEM at 200 kV was employed to obtain cross-sectional images of the SiN$_x$ films deposited on the 3D trench nanostructures. The films were coated with a layer of spin-on epoxy to protect them from damage during sample preparation for TEM cross-sectional imaging. The samples were then placed on a Cu TEM grid, after which an energetic ion beam was used to mill and polish the samples at 30 kV, 100 pA and 5 kV, 40 pA, respectively. SiN$_x$ film thickness was measured at three regions of several trench nanostructures in the sample, namely at the planar top and bottom regions together with the vertical bottom-side region (Conformality section, Figure 6A) by counting pixels in the TEM image. Conformality was determined by taking the ratio of SiN$_x$ film thicknesses at the bottom-side and top of the trench to that at the top of the trench. The conformality values reported are the averages of the results obtained across several trench nanostructures with the same aspect ratio. Uncertainties reported for the values were based on both the accuracy of the measurement and the variation between measurements conducted across several trench nanostructures of the same sample.

For obtaining wet-etch rates (WER) of films at planar and vertical surfaces of the 3D substrates, coupons containing the trench nanostructures with SiN$_x$ films deposited using PEALD were dipped in a dilute HF solution (HF/H$_2$O = 1:100) for 30 s. Two samples for TEM cross-sectional imaging were prepared from the same coupon, one before and one after the chemical wet-etch treatments. TEM measurements were conducted at the three aforementioned regions across several trench nanostructures of the same as-deposited and post wet-etch samples. The WERs at the aforementioned trench regions were determined by comparing the as-deposited and post wet-etch film thicknesses at those regions. The WER values reported are the average of the results obtained across several trench nanostructures with the same aspect ratio. Uncertainties reported for the values were based on both the accuracy of the measurement and the variation between measurements conducted across several trench nanostructures of the same sample. The WER and conformality values obtained using TEM for SiN$_x$ deposited on trench nanostructures were used as a basis for determining film quality and thickness uniformity at planar and vertical surfaces of the 3D substrates. Potential depletion of the etchant inside the trench was not taken into account in these experiments.

**RESULTS**

**PEALD of SiN$_x$ on Planar Substrates. ALD Film Growth.** Growth per cycle (GPC) values as a function of precursor dose time and plasma exposure time measured using in situ SE are shown in Figure 2a and b, respectively. GPC as a function of precursor purge and plasma purge times are also shown in Figure 2c and d, respectively. An apparent saturation for the GPC (∼0.08 Å) can be observed in Figure 2a for the precursor dose time. The GPC using DSBAS is relatively low (<0.1 Å), and its rapid stagnation as a function of dose time suggests that the precursor quickly occupies the available reactive surface sites. Contrary to this apparent saturation behavior, the GPC as a function of N$_2$ plasma exposure time shows a soft saturation behavior (Figure 2b). This differs from the corresponding trend of GPC for the SiN$_x$ PEALD process developed by Knoops et al. using BTBAS. The GPC in that process peaked for short N$_2$ plasma exposure times and then gradually decreased to a constant value as the plasma exposure times were increased. Despite the nonideal soft saturation observed using DSBAS, SiN$_x$ film growth was linearly dependent on the number of ALD cycles, while showing almost no nucleation delay, depicted in Figure 3. The slope of the plots is observed to decrease with temperature indicating a lower GPC at higher temperatures (see Effect of Substrate Temperature section).

On the basis of these exploratory saturation experiments, a standard process was defined whose parameters were outlined in Table 2. Ideally, all process parameters are chosen assuming that the GPC saturates at a particular value. From Figure 2, it can be observed how a precursor dose time of 100 ms and purge times of 1 s can be expected to yield saturated film growth. The observed soft saturation of the GPC as a function of the plasma exposure time implies that very long exposures (≥20 s) would result in film growth closer to saturation. This would result in long cycle times (≥30 s), which, considering the
already low GPC, would eventually lead to a long deposition time (~20 h) to grow SiNₓ films of ~30 nm (roughly the target thickness required for accurate material characterization via RBS, see Table 3). As a result, a plasma exposure time of 10 s was chosen for the standard process to obtain a feasibly productive cycle time (~20 s).

**Effect of Substrate Temperature.** SiNₓ film growth using DSBAS and N₂ plasma has been confirmed over a wide range of stage temperatures between 100 and 500 °C. This approximately corresponds to lower actual substrate temperatures ranging between 100 and 360 °C (see Table 3 and Supporting Information). Film growth and material properties have been characterized at several temperatures in this range. The results are outlined in Table 3 and graphically depicted in Figure 4. The growth properties are presented in terms of both the thickness deposited per cycle (Figure 4a) and the number of silicon atoms deposited per nm² per cycle (Figure 4b). The material properties are shown in terms of the N/Si ratio (Figure 4c), mass density (Figure 4d), and impurity content (Figure 4e and f). Note that the results obtained using DSBAS in this work are presented in Figure 4 with the results obtained in previous work for SiNₓ deposited using BTBAS and N₂ plasma to facilitate comparison between the material properties of films grown using the two processes.

Figure 4a shows how DSBAS yielded a fairly low, but constant film GPC (~0.1 Å) at various stage temperatures, with the exception of 100 °C where the GPC was higher (~0.2 Å). This increase in GPC is partly attributed to an increased impurity content ([C], [O], and [H]) at lower stage temperatures, as observed in Figure 4e and f.

Figure 4b shows the number of deposited Si atoms per nm² per cycle, denoted as GPC [Si] (Si at./nm²). Since the only source of silicon is the one Si-atom present in both precursor molecules, GPC [Si] can be considered as a more quantitative measure of precursor adsorption. Like GPC, the values for GPC [Si] using DSBAS remain fairly unchanged at ~0.4 Si at./nm² with an increasing stage temperature. Both GPC and GPC [Si] are observed to be higher using BTBAS compared to those obtained using DSBAS at the standard conditions investigated for the two precursors. The differences are more pronounced at lower stage temperatures, while at 500 °C, they have been greatly reduced. The fairly unchanging trend in GPC and GPC [Si] exhibited by DSBAS differs from the trend observed for films grown using BTBAS where GPC and GPC [Si] monotonically decrease as a function of increasing stage temperature.

From Figure 4c, it can be observed that the N/Si ratio for films deposited using DSBAS is very close to that of stoichiometric Si₃N₄ (1.33), especially at 300 and 400 °C (1.3 and 1.4, respectively). At both low (<200 °C) and high (500 °C) stage temperatures, more nitrogen-rich SiNₓ films were deposited. The highest mass density of 3.1 g/cm³ was obtained at a stage temperature of 500 °C, as seen in Figure 4d, even though the film was more nitrogen-rich in composition at that temperature. The highest obtained density is very close to the mass density of bulk Si₃N₄ (~3.2 g/cm³). The high refractive indices, close to 2.0, measured using ex-situ SE at stage temperatures >300 °C (shown in Table 3) also indicate high film quality.

The high quality is further corroborated by the low impurity content ([C], [O], and [H]) of the DSBAS grown films, especially at stage temperatures >200 °C. At 500 °C, both [C] and [O] levels have decreased to values below the detection limit of 2% and 1%, respectively. However, at 100 °C, the [C] and [H] levels were significantly higher (11% for both) compared to those at higher temperatures (>200 °C), as observed in Figure 4e and f, respectively. The film density at 100 °C is quite low (~2.3 g/cm³), which is most likely due to the aforementioned high [C] and [H] levels together with postdeposition oxidation (see Supporting Information). Values below detection limit (d.l.) of 2% for [C] and 1% for [O].

Table 3. GPC, Refractive Index at 2 eV, Mass Density, and Elemental Composition of ~30 nm Thick SiNₓ Films Deposited Using Standard 100 ms DSBAS Precursor Dose and 10 s N₂ Plasma Exposure Times at 12 mTorr N₂ Plasma Pressure and Various Stage Temperatures (100–500 °C)

<table>
<thead>
<tr>
<th>stage temp. (°C)</th>
<th>estimated actual substrate temp. (°C)</th>
<th>GPC (Å)</th>
<th>refractive index</th>
<th>mass density (g/cm³)</th>
<th>#Si at. per nm² per cycle</th>
<th>N/Si at. %</th>
<th>[C] at. %</th>
<th>[O] at. %</th>
<th>[H] at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100 ± 20</td>
<td>0.19 ± 0.02</td>
<td>1.86 ± 0.05</td>
<td>2.3 ± 0.1</td>
<td>0.43 ± 0.02</td>
<td>1.9 ± 0.1</td>
<td>11 ± 2</td>
<td>2 ± 1 b</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>200</td>
<td>180</td>
<td>0.12</td>
<td>1.93</td>
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<tr>
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<td>360</td>
<td>0.10</td>
<td>1.97</td>
<td>3.1</td>
<td>0.37</td>
<td>1.5</td>
<td>&lt;d.l. b</td>
<td>&lt;d.l. b</td>
<td>5</td>
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</tbody>
</table>

Typical uncertainties are given in the first row. Bulk Si₃N₄ has a refractive index of 2.02 and a mass density of 3.2 g/cm³. XPS measurements showed this film had a high level of oxygen at the surface, which is likely due to the low mass density of the film that leads to significant postdeposition oxidation (see Supporting Information). Values below detection limit (d.l.) of 2% for [C] and 1% for [O].
postdeposition oxidation that the films may have undergone upon exposure to the atmosphere.

With respect to the high quality of films obtained previously using the BTBAS process, it can be concluded that the film quality yielded by the DSBAS process is generally very high. The density, N/Si ratio, and refractive index values of the DSBAS grown films tend to be closer to those of bulk Si₃N₄ compared to BTBAS grown films, with an exception for the higher N/Si ratio at 500 °C. The N/Si ratio trend for DSBAS differs from that for BTBAS, which shows a monotonic decrease in N/Si as a function of increasing stage temperature, as observed in Figure 4c. For the conditions investigated, it can be concluded that using DSBAS as a precursor for PEALD of Si₃N₄ yields denser films with lower impurities, and hence higher quality films at all stage temperatures compared to using BTBAS as the precursor.

To verify whether Si₃N₄ film composition remained uniform throughout the entire layer of the deposited films, depth profiles were measured using alternating XPS measurements and Ar⁺ ion sputter steps. The constant N and Si atomic contents, as observed in Figure 5, indicate a uniform film stoichiometry (i.e., constant N/Si ratio) throughout the entire film thickness. Elevated [C] and [O] levels can be observed near the film surface, which indicate that some surface contamination takes place after the deposited films are exposed to the atmosphere.

Effect of Plasma Pressure. As mentioned before, the residence time is a key parameter that can influence the redeposition effect and hence govern growth properties and material quality during PEALD. Since the residence time was shown to depend on plasma pressure, which was not the same for the two processes compared, the effect of similar plasma pressures on material properties of both BTBAS and DSBAS grown Si₃N₄ films was investigated (at stage temperature of 200 °C). These results are outlined in Table 4. The films deposited using DSBAS show higher refractive indices and lower impurity contents at both 12 and 40 mTorr compared to the films deposited using BTBAS at similar pressures. Furthermore, the GPC using BTBAS increased significantly when the plasma pressure was increased from 13 to 40 mTorr, whereas the GPC using DSBAS remained unaffected. The [C] of the films deposited using both precursors increased with pressure, indicating elevated impurity content at higher plasma pressure.

PEALD of Si₃N₄ on 3D Substrates. Conformality. TEM images of as-deposited Si₃N₄ layers grown on 3D trench
nanostructures (AR = 4.5:1) using DSBAS and N₂ plasma are shown in Figure 6, and their corresponding deposition conditions are outlined in Table 5. SiNₓ film thicknesses measured at the top, bottom-side, and bottom regions of the trench together with film conformality (as % of film thickness at the top) are also depicted in Figure 6 and Table 5. In the first experiment, the film was deposited on 3D trench nanostructures using the standard recipe of 100 ms DSBAS dose and 10 s N₂ plasma exposure at 500 °C stage temperature and 12 mTorr plasma pressure. These standard conditions yielded bottom-side and bottom conformalities of 30% and 51%, respectively, as shown in Figure 6A.

Using Monte Carlo simulations, Knoops et al. showed that to reach 100% conformality in HARS, generally higher precursor doses and longer plasma exposures are needed compared to those used for obtaining saturation on planar substrates. On the basis of this and the low film conformalities exhibited by the standard recipe, extended precursor dose and plasma exposure times were used to deposit SiNₓ films on the 3D trench nanostructures (Figure 6B–F). The conformalities

Table 4. GPC, Refractive Index at 2 eV, Mass Density and Elemental Composition of ~30 nm Thick SiNₓ Films Deposited at a Stage Temperature of 200 °C Using Standard Dose Times of 100 or 150 ms for the DSBAS or BTBAS Precursor Steps, Respectively

<table>
<thead>
<tr>
<th>precursor</th>
<th>N₂ plasma pressure (mTorr)</th>
<th>GPC (Å)</th>
<th>refractive index</th>
<th>N/Si [C] at. %</th>
<th>[O] at. %</th>
<th>mass density (g/cm³)</th>
<th>Si at. per nm² per cycle</th>
<th>N/Si</th>
<th>[C] at. %</th>
<th>[O] at. %</th>
<th>[H] at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTBAS</td>
<td>13</td>
<td>0.24 ± 0.02</td>
<td>1.91 ± 0.05</td>
<td>1.6 ± 0.2</td>
<td>6 ± 2</td>
<td>5 ± 2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>BTBAS</td>
<td>40</td>
<td>0.32</td>
<td>1.83</td>
<td>1.7</td>
<td>9</td>
<td>5</td>
<td>2.2 ± 0.1</td>
<td>0.66 ± 0.02</td>
<td>2.0 ± 0.1</td>
<td>12 ± 1</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>DSBAS</td>
<td>12</td>
<td>0.12</td>
<td>1.93</td>
<td>1.2</td>
<td>4</td>
<td>4</td>
<td>2.7</td>
<td>0.37</td>
<td>1.4</td>
<td>3 ± 2</td>
<td>3</td>
</tr>
<tr>
<td>DSBAS</td>
<td>40</td>
<td>0.12</td>
<td>1.89</td>
<td>1.2</td>
<td>5</td>
<td>7</td>
<td>2.7</td>
<td>0.37</td>
<td>1.5</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>

“All films were deposited using 10 s N₂ plasma exposure times but at different pressures in the reactor during plasma exposure. Typical uncertainties are given in the first and second rows, unless otherwise noted. A ‘-’ means not measured.

Figure 6. (A–F) TEM images of as-deposited SiNₓ layers grown on 3D trench nanostructures (AR = 4.5:1) using DSBAS and N₂ plasma at 500 °C stage temperature and 12 mTorr plasma pressure. The deposition conditions for each image are outlined in Table 5. SiNₓ film thicknesses for all depositions are measured at three regions of the trench, top, bottom-side, and bottom, as indicated in panel A. SiNₓ film conformality at the bottom-side and bottom regions of the trench are indicated as a percentage of film thickness at the top in all panels.
improved slightly to 37% and 56% at the bottom-side and bottom, respectively, in accordance with the simulations, when either the precursor dose was extended to 500 ms (Figure 6C), or the plasma exposure to 20 s (Figure 6B), or both simultaneously (Figure 6D). Doubling both the precursor dose to 1000 ms and plasma exposure to 40 s (Figure 6E) significantly improved bottom-side and bottom film conformalities to 50% and 65%, respectively. This trend of continued improvement in film conformity by extending the durations of both PEALD half cycles was the reason to further double the precursor dose and plasma exposure times to 2000 ms and 80 s, respectively (Figure 6F). However, no further improvements were observed as film conformalities of 50% and 69% were obtained at the bottom-side and bottom regions of the trench, respectively, which was also the most conformal film obtained in this work.

**Wet-Etch Rate.** WERs for SiNₓ films deposited on 3D trench nanostructures using DSBAS and N₂ plasma at 500 °C stage temperature (<400 °C actual substrate temperature) and 12 mTorr plasma pressure are outlined in Table 5. The WER values were determined by comparing the as-deposited and post wet-etch film thicknesses at the three trench regions depicted in Figure 6A. The deposited SiNₓ films seem to be highly etch resistant at the planar top and bottom regions of the trench, as indicated by small or insignificant WER values (≤2 ± 1 nm/min) observed at those regions (Table 5). These low WERs indicate the deposition of high quality SiNₓ films on planar or horizontal surfaces of the 3D trench nanostructures, as observed in Figure 6. This is also corroborated by the high mass density (3.1 g/cm³) exhibited by the film deposited on a planar c-Si substrate using the standard deposition condition (100 ms DSBAS, 10 s N₂ plasma), as outlined in Table 3. Additional RBS measurements were conducted for two SiNₓ films deposited on planar c-Si substrates using extended conditions (500 and 1000 ms DSBAS, 20 and 40 s N₂ plasma, respectively), which also showed high mass densities (~3.1 g/cm³) and near-stoichiometric N/Si ratios (~1.4) for both films. This corroborates the low WERs that were also observed for SiNₓ films deposited on 3D trench nanostructures using the extended deposition conditions. It is noted that the mass densities of the two SiNₓ films deposited on planar c-Si substrates using extended precursor dose and plasma exposure conditions remained high even though slightly elevated [C] and [O] levels (~4% for both) were observed for the films at those conditions.

The WERs observed at the bottom-side region of the trench are somewhat higher than those at the two planar trench regions for all SiNₓ films, indicating a reduced HF-etch resistance at the vertical trench surfaces. However, they are small in absolute magnitude (≤3 nm/min) indicating a high HF-etch resistance for all SiNₓ films for both planar and vertical surfaces. Only the film deposited using 500 ms DSBAS dose and 10 s N₂ plasma exposure (Table 5, TEM image C) is an exception. The bottom-side WER for this particular film is significantly high (~6 nm/min), and the film was deposited after only the precursor dose time was extended from 100 to 500 ms in the standard recipe, without extension of the plasma exposure time. When the plasma exposure time was also extended from 10 to 20 s for the extended 500 ms precursor dose (Table 5, TEM image D), the WER was seen to decrease (~3 nm/min). This indicates that an increased precursor dose requires a corresponding increase in plasma exposure in order for the SiNₓ films to retain their etch resistance at the vertical surfaces within a 3D structure. A high film quality was observed in general with the lowest WERs (≤2 nm/min) exhibited by the standard (100 ms DSBAS, 10 s N₂ plasma) and the most extended (2000 ms DSBAS, 80 s N₂ plasma) deposition conditions, as seen in Figure 7. The most extended deposition condition resulted in optimum SiNₓ, having both low WERs and the highest conformity on 3D trench nanostructures in this work. WERs at the regions inside a trench nanostructure (bottom-side and bottom) were always higher than the region at the trench entrance (top). Although any potential depletion of etchant inside the trench was not taken into account, the comparatively higher WERs at the regions inside the trench ensured etchant penetration to the bottom of the trench nanostructures. Furthermore, nonexistence of lower WERs at the regions inside the trench indicated the absence of any delay in wetting of the etchant on the film surfaces within the trench. Therefore, the wetting of the etchant was assumed to occur instantaneously relative to the large time scale (30 s) of the etch treatment.

**DISCUSSION**

**PEALD of SiNₓ on Planar Substrates.** The results on planar substrates indicate that high quality SiNₓ films with properties relatively close to that of bulk SiNₓ can be obtained using DSBAS as the precursor for PEALD of SiNₓ. This is demonstrated by stoichiometric N/Si ratios (between 1.3 and 1.5), high mass densities (>2.9 g/cm³), and low impurity contents ([C] < 2%, [O] < 3%, and [H] ≈ 5%) exhibited by the SiNₓ films deposited at stage temperatures between 300 and 500 °C.

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**Table 5. Conformality and Wet-Etch Rates of SiNₓ Films Grown on Coupons Containing 3D Trench Nanostructures (AR = 4.5:1) Using DSBAS and N₂ Plasma at 500 °C Stage Temperature and 12 mTorr Plasma Pressure**

<table>
<thead>
<tr>
<th>TEM image</th>
<th>precursor dose time (ms)</th>
<th>plasma exposure time (s)</th>
<th>TEM thickness at the top (nm)</th>
<th>as-deposited conformality (% of top)</th>
<th>wet-etch rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>10</td>
<td>24 ± 1</td>
<td>30 ± 5</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>20</td>
<td>24</td>
<td>37 ± 5</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>C</td>
<td>500</td>
<td>10</td>
<td>23</td>
<td>37 ± 5</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>D</td>
<td>500</td>
<td>20</td>
<td>26</td>
<td>37 ± 5</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>E</td>
<td>1000</td>
<td>40</td>
<td>50</td>
<td>50 ± 6</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>F</td>
<td>2000</td>
<td>80</td>
<td>50</td>
<td>50 ± 6</td>
<td>0 ± 1</td>
</tr>
</tbody>
</table>

*The wet-etch rates are reported for SiNₓ films located at planar (top, bottom) and vertical (bottom-side) regions of the 3D substrate topographies after 30 s dip in an etchant solution of dilute hydrofluoric acid (HF/H₂O = 1:100). Typical uncertainties, which are based on both the accuracy of the measurement and the variation between measurements conducted across different trenches of the same coupon, are given in the first row.*
consists of a silyl group (and one amino (N('Bu)2) ligand, as shown in Figure 1b) in addition to exhibiting a similar soft saturation behavior during N2 plasma exposure. On the basis of these similarities, it could be speculated that DSBAS precursor adsorption following an N2 plasma step results in a surface closely resembling a Si−Hx terminated surface, which is generated by the two aforementioned SiH4 terminated precursors. Such a surface could be generated by the one-step elimination of the sole amino ligand during DSBAS adsorption that has been reported to occur for ALD processes employing this precursor.38,50

On the other hand, when BTBAS was used as the precursor for depositing SiNx in previous work,16 the GPC as a function of N2 plasma exposure time exhibited a different behavior from soft saturation. The GPC was reported to undergo an initial rapid overshoot followed by a gradual decrease to a constant (or saturated) value as the N2 plasma exposure time was increased.16 Unlike the DSBAS molecule, which has one amino ligand and a silyl group, the bis-aminosilane BTBAS molecule consists of two amino (NH'Bu) ligands and a silanediyl (SiH4) group, as shown in Figure 1a. DFT studies on the surface chemistry of BTBAS during ALD have shown that it involves the sequential elimination of primary and secondary NH'Bu ligands,31,52 while DSBAS undergoes the elimination of just one N('Bu)2 ligand.38,50 Experimental studies on the surface chemistry of the SiNx ALD process employing BTBAS and N2 plasma43 confirmed that a part of the amino ligands are liberated as gas-phase NH2'Bu species during BTBAS adsorption, while a part remains on the surface as NH'Bu. Consequently, BTBAS precursor adsorption can be considered to generate a more amino ligand terminated surface compared to a more Si−Hx (or conversely, amino ligand deficient) surface hypothesized earlier for DSBAS. Previous work by Knoops et al.42 and recent investigation by Bosch et al.15 demonstrate that the amino ligands remaining on the surface after a BTBAS precursor step get dissociated into reactive fragments (e.g., C2N2, C3H8, HCN, etc.) during the subsequent N2 plasma step. These fragmented ligand species can then be redeposited as impurities on the growing film surface, which is manifested as the initial rapid overshoot in GPC reported for BTBAS,16 but not observed in this work for DSBAS. As a result, the NH'Bu terminated surface after BTBAS adsorption could undergo a more prominent redeposition effect during N2 plasma exposure compared to the more amino ligand deficient surface speculated for DSBAS. This may explain the lower total GPC (Figure 4a), smaller impurity content ([C] and [H], Figure 4e,f), and consequently higher film density (Figure 4d) observed for SiNx films deposited using DSBAS compared to previous results obtained using BTBAS.

The one-step ligand elimination process for DSBAS38,50 entails overcoming a single energy barrier compared to the two-step counterpart process for BTBAS31,52 where two energy barriers need to be overcome. The sequential two-step ligand elimination for BTBAS may be incomplete at low temperatures causing more NH'Bu ligands to remain on the surface after BTBAS dosage. Conversely, fewer amino ligands may be left on the surface after a precursor dose step using DSBAS instead of BTBAS, with the difference becoming more prominent on decreasing the stage temperature. The more amino ligands remaining on the surface after precursor adsorption, the greater the extent of ligand fragmentation during plasma exposure and the larger the effect of redeposition. Species that redeposit on the surface can be again removed by the plasma, and these
redeposition and removal processes occur continuously until the fragmented species are flushed out of the reaction chamber.\(^\text{23}\) High temperatures could be speculated to enhance the removal process by facilitating thermal desorption of redeposited species, while low temperatures could have the opposite effect and lead to more impurity redeposition. This may account for the significantly higher impurity contents (\([C]\) and \([H]\), Figure 4e,f) observed at low stage temperatures (<300 °C) using BTBAS that results in a much lower film density (Figure 4d) and a more elevated total GPC (Figure 4a) compared to DSBAS. Conversely, thermally enhanced desorption of redeposited species or a more complete two-step ligand elimination process may occur for BTBAS at high temperatures (>300 °C), which lowers redeposition and leads to \(\text{SiN}_x\) film properties approaching those observed for DSBAS.

**PEALD of Si\(_x\text{N}_y\) on 3D Substrates.** \(\text{SiN}_x\) films deposited on 3D trench nanostructures \((\text{AR} = 4.5:1)\) using standard DSBAS and \(\text{N}_2\) plasma conditions \((\text{Table } S, \text{ TEM image } A)\) yielded suboptimal bottom-side and bottom conformalities \((30\%\) and \(51\%, \text{respectively, Figure } 6\text{A})\). This indicates that the film GPCs at the bottom-side and bottom regions of the 3D trench nanostructures were significantly lower than the GPC at the top. Increases in precursor dose and plasma exposure times were subsequently implemented with the aim of ensuring film GPC, and consequently film thickness, were the same at all regions of the trench nanostructures. Simultaneously extending both precursor dose and plasma exposure conditions \((\text{Table } S, \text{ TEM images } D \text{ and } E)\) seemed to offer a route toward improving bottom-side and bottom film conformalities \((\text{Figure } 6\text{D,E})\). However, this trend did not continue at a certain point when further extension in both precursor dose and plasma exposure times \((\text{from 1000 to 2000 ms and 40 to 80 s, respectively})\) no longer improved bottom-side and bottom conformalities \((\text{Figure } 6\text{E,F})\). This observation can potentially be explained by the combined role played by three factors during \(\text{SiN}_x\) deposition on such 3D substrates.

A part of the reason could be due to the previously mentioned aspect of soft saturation observed for the GPC as a function of \(\text{N}_2\) plasma exposure time. A continued increase in \(\text{SiN}_x\) film growth rate was observed when the \(\text{N}_2\) plasma exposure time was increased to 40 and 80 s. This may cause the GPC at the top to exceed those at the bottom-side and bottom regions of the trench nanostructures and thereby yield nonconformal films. Another reason could be due to the recombination of growth species at the vertical surfaces near the top of the trench. The ALD process developed in this work for depositing \(\text{SiN}_x\) is an \(\text{N}_2\) plasma based process, whereby atomic N radicals generated in the plasma are deemed as important contributors toward film growth.\(^\text{25}\) These charge-free N radical species are isotropic or nondirectional in nature, which means that they can collide and recombine at the vertical surfaces of the trench nanostructures before they reach the bottom regions of the trench. Kessels et al.\(^\text{35,54}\) estimated the recombination loss probability of N radicals on \(\text{SiN}_x\) surfaces to be of the order of \(\sim10^{-2}\). Knoops et al.\(^\text{38}\) identified that recombination losses of plasma radicals at the surfaces within a HARS during PEALD can lower the radical flux at the bottom regions of the HARS. This means that the flux of growth species composed of N radicals is reduced at the bottom regions of the 3D trench nanostructures, which causes film GPC in those regions to be lower than that at the top. This GPC discrepancy between the top and bottom regions of the trench lowers film conformity. Finally, anisotropic ion bombardment, which is a distinct feature of plasma ALD processes at such low pressures,\(^\text{27}\) can also play a role behind the low conformalities. \(\text{N}_2^+\) ion bombardment can preferentially generate more reactive sites on the planar or horizontal surfaces of 3D trench nanostructures than on the vertical sidewalls. Therefore, the GPCs at the planar surfaces exceed those at the vertical ones which subsequently lowers film conformity within the 3D trench nanostructures. Similar low conformalities were also observed by King\(^\text{25}\) and Weeks et al.\(^\text{56}\) who also used \(\text{N}_2\) plasma for PEALD of Si\(_x\text{N}_y\) on 3D trench nanostructures. Both works also attributed the low conformalities to the anisotropic nature of \(\text{N}_2^+\) ion bombardment.

Despite the low conformalities, high quality \(\text{SiN}_x\) films were obtained, which were demonstrated by the low WERs exhibited by nearly all the films deposited on 3D trench nanostructures. The WERs at the vertical trench sidewalls are slightly higher than those at the planar or horizontal trench surfaces. This could be due to the anisotropic nature of \(\text{N}_2^+\) ion bombardment, which preferentially improves film properties at horizontal surfaces more than those at vertical ones. The trade-off between high conformity and high quality \((i.e., \text{low WERs, high density})\) observed for \(\text{SiN}_x\) films deposited on 3D substrate topography in this work seems to be a generally observed phenomenon for ALD processes of \(\text{SiN}_x\).\(^\text{55,56}\) Processes employing chlorosilane precursors and \(\text{NH}_2\) gas or \(\text{NH}_3\) plasma report films having high conformity but low film quality \((i.e., \text{high WERs, low density})\), whereas those using an organosilane precursor and \(\text{N}_2\) plasma report films with the properties reversed.\(^\text{25,46}\) The latter is consistent with the results obtained in this work.

### CONCLUSIONS

A new PEALD process for \(\text{SiN}_x\) was developed using DSBAS and \(\text{N}_2\) plasma. Material properties were analyzed over a wide stage temperature range \((100–500 °C)\) and compared with those obtained in our previous work for \(\text{SiN}_x\) deposited using BTBAS and \(\text{N}_2\) plasma. High-quality films were obtained on planar substrates using DSBAS and \(\text{N}_2\) plasma, with the best films showing high density \((\sim3.1 \text{~g/cm}^3)\) approaching that of bulk \(\text{Si}_3\text{N}_4\) and low \([\text{C}], [\text{O}], \text{and } [\text{H}]\) impurity levels at low substrate temperature \((<400 °C)\). DSBAS, having one amino ligand and a silyl group, is hypothesized to leave a more amino ligand deficient surface after precursor adsorption compared to BTBAS that has two amino ligands and a silanediyl group. As a result, a lower redeposition effect during the subsequent \(\text{N}_2\) plasma step could take place for DSBAS, which could account for the denser \(\text{SiN}_x\) films having lower impurity contents compared to those obtained previously using BTBAS. The process developed using DSBAS was also used for depositing \(\text{SiN}_x\) films on high aspect ratio \((4.5:1)\) 3D trench nanostructures. Film conformity is not yet at desired levels of >95% and is attributed to the combined role played by nitrogen plasma soft saturation, radical species recombination, or ion directionality during \(\text{SiN}_x\) deposition on 3D substrates. However, high-quality films were obtained on the 3D substrates as demonstrated by the low or insignificant wet-etch rates \((\text{WER} \leq 2 \text{ nm/min})\) observed at the top, sidewall, and bottom trench regions of the most conformal film deposited at low substrate temperature \((<400 °C)\). These observations are in line with similar results reported in the literature employing...
organosilane precursors and N₂ plasma for ALD of SiN on 3D substrates.

## Supporting Information

### ABBREVIATIONS

DSBAS, di(tert-butyaminosilane); BTBAS, bis(tert-butyaminosilane); WER, wet-etch rate; HARS, high aspect ratio structure

### REFERENCES


