Atomic layer deposition of silicon nitride from Bis(tert-butylamino)silane and N2 plasma

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Atomic Layer Deposition of Silicon Nitride from Bis(tert-butylamino)silane and N₂ Plasma

Harm C. M. Knoops, Eline M. J. Braeken, Koen de Peuter, Stephen E. Potts, Suvi Haukka, Viljami Pore, and Wilhelmus M. M. Kessels

INTRODUCTION

Silicon nitride (SiNₓ) is one of the most widely used thin-film materials, with a very extensive range of applications. However, the requirements on the material properties and on the growth control of these films are becoming ever more stringent. One method for the deposition of high-quality thin films with excellent growth control is atomic layer deposition (ALD). However, there are currently few reports on the ALD of silicon nitride. One application that could benefit greatly from a silicon nitride ALD process is gate spacers for high-k metal gate transistors. These spacer films should serve as oxygen barrier and barrier to processing conditions and also provide a constant spacing of the source and the drain of the transistor, independent of transistor pitch. The films should therefore have a good etch resistance and have a high conformality.\(^1\)\(^,\)\(^2\)

Because of shrinking device features and the adaption of new materials, the associated allowed thermal budget during processing is also decreasing and the spacers have to be deposited at low temperatures (e.g., below 500 °C), while the film quality has to remain high.\(^3\) For the ALD of SiNₓ chlorosilanes (e.g., SiClₓ, SiHₓClₓ, Si₂Cl₆, and Si₃Cl₈) have generally been used as the silicon precursor in combination with coreactants such as NHₓ, NHₓ plasma, or NₓHₓ.\(^4\)\(^–\)\(^9\)

However, processes using chlorosilanes require relatively high deposition temperatures and can be undesirable because of detrimental effects caused by the chlorine in these precursors.\(^10\) Therefore, a chlorine-free process is highly desired. As with other nitride ALD processes, plasmas can be employed as coreactant to increase the coreactant’s reactivity.\(^11\) Nonetheless, even with the high reactivity afforded by the plasma exposure, long plasma times are typically required to avoid high impurity contents. Recently, plasma ALD processes using chlorine-free precursors (i.e., SiHₓ and N(SiHₓ)y) have been reported using N₂ plasma or NHₓ plasma as coreactant, respectively.\(^12\)\(^,\)\(^13\)

In this work, a novel ALD process using bis(tert-butylamino)silane (BTBAS) and N₂ plasma was developed and studied. High-quality SiNₓ was obtained at >700 °C and higher, similar to that achieved in the literature using low-pressure chemical vapor deposition of SiNₓ at >700 °C. For novel applications requiring significantly lower temperatures, the temperature window from room temperature to 200 °C can be a solution, where relatively high material quality was obtained when operating at low plasma pressures or long plasma exposure times.

KEYWORDS: ALD, SiₓNₓ plasma, thin film, wet etch, atomic layer deposition, plasma-assisted ALD, silicon nitride

ABSTRACT: Atomic layer deposition (ALD) of silicon nitride (SiNₓ) is deemed essential for a variety of applications in nanoelectronics, such as gate spacer layers in transistors. In this work an ALD process using bis(tert-butylamino)silane (BTBAS) and N₂ plasma was developed and studied. The process exhibited a wide temperature window starting from room temperature up to 500 °C. The material properties and wet-etch rates were investigated as a function of plasma exposure time, plasma pressure, and substrate table temperature. Table temperatures of 300–500 °C yielded a high material quality and a composition close to Si₃N₄ was obtained at 500 °C (N/Si = 1.4 ± 0.1, mass density = 2.9 ± 0.1 g/cm³, refractive index = 1.96 ± 0.03). Low wet-etch rates of ~1 nm/min were obtained for films deposited at table temperatures of 400 °C and higher, similar to that achieved in the literature using low-pressure chemical vapor deposition of SiNₓ at >700 °C. For novel applications requiring significantly lower temperatures, the temperature window from room temperature to 200 °C can be a solution, where relatively high material quality was obtained when operating at low plasma pressures or long plasma exposure times.

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composition and wet-etch rates are addressed, and a comparison is made with SiNₓ ALD processes reported in the literature.

■ EXPERIMENTAL DETAILS

Figure 1 shows a simplified schematic representation of the Oxford Instruments FlexAL reactor in which the depositions were carried out. The reactor is equipped with a remote inductively coupled (ICP) plasma generator, which was operated at 60 W at 13.56 MHz. The depositions were performed on c-Si substrates with a thin native oxide layer. No additional cleaning steps were used. Due to poor thermal contact in vacuum, actual wafer temperatures were lower than the set table temperature. See the Supporting Information for a table with the determined wafer temperature for each set-point table temperature. In the remainder of this work the set-point table temperatures are reported. The chamber wall temperature was set to 150 °C, except for deposition temperatures below 150 °C for which the wall temperature was set to the deposition temperature. A base pressure in the reactor chamber of ~10⁻⁶ Torr was reached by a turbo pump. A butterfly valve in front of the turbo pump controlled the effective pumping speed and functions as an automated pressure controller (APC). SiH₂(NH₂Bu)₂ (BTBAS, purity ≥98.5%, Air Products Inc.) was used as the precursor and held at a bubbler temperature of 50 °C. The precursor was vapor drawn, where Ar (25 sccm, purity 99.999%) was used as a carrier gas in the line during precursor dosing and during the subsequent reaction step. For both steps the APC valve was set to 10° to reduce the effective pumping speed and maximize precursor usage. During the purging step after precursor dosing the Ar flow was 100 sccm. For both purging steps the APC valve was set to 90° valve position for maximum pumping. The delivery lines were heated to 70 °C to prevent precursor condensation. Based on the saturation curves for precursor dose and plasma exposure, the following recipe was chosen as a standard: 1 s delivery line purge, 150 ms BTBAS dose time, 3 s reaction time, 1 s precursor purge time, 2 s preplasma time, 10 s plasma exposure time, 100 sccm N₂ flow plasma gas (purity 99.9999%), 40 mTorr set plasma pressure, and 1 s plasma purge time. These settings were used unless mentioned otherwise.

The film thickness and optical properties of the layers were measured by spectroscopic ellipsometry (SE), using a J.A. Woollam Co. M-2000F ellipsometer over a wavelength range of 243–1000 nm. The optical model consisted of a silicon substrate, ~1.5 nm native oxide, and a silicon nitride layer modeled with a Tauc-Lorentz dispersion relation. The chemical composition and stoichiometry of the SiNₓ films were investigated with X-ray photoelectron spectroscopy (XPS), using a Thermo Scientific K-Alpha spectrometer with a monochromatic Al Kα X-ray source (hv = 1486.6 eV). Depth profiles were measured by sputtering with Ar⁺ ions. Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) measurements were also used to determine the composition and mass density of the films. The RBS and ERD experiments and the simulations were performed by AccTec B.V using a 1.85 MeV helium-ion beam. Simulations were used to determine the areal densities of the elements.

For determining the wet-etch rates of the silicon nitride films, two types of HF solution were used: (1) a buffered HF solution composed of a 7:1 volume ratio of 40% NH₄F in water and 49% HF in water, referred to as 7:1 BHF, and (2) a nonbuffered 0.5% (0.25 mol/L) HF solution, referred to as 100:1 HF. The procedure for etching the films was as follows. First, the samples were placed in a holder that could hold multiple samples at once so no influence of different incubation or rinse times had to be taken into account. Second, the holder was immersed in the HF solution for a set time and subsequently rinsed in deionized water with resistance R > 10 MΩcm. After rinsing, the samples were blown dry with nitrogen gas and then characterized by SE. The steady-state etch rates were determined from linear regression of thickness measurements on at least three separate samples each with a different etch time.

■ RESULTS

Film Growth and Effect of Table Temperature. Initial experiments showed that the use of H-containing plasmas (e.g., H₂/N₂ plasmas or NH₃ plasmas) led to very low growth-per-cycle (GPC) values of 0.05 ± 0.02 Å at both 200 and 500 °C, and therefore only results from pure N₂ plasmas will be reported in the remainder of this article. Note that termination by -H and -NH species of surface groups limiting BTBAS precursor adsorption is believed to be the main mechanism for this suppressed growth. The SiNₓ process with N₂ plasma showed linear growth with no growth delay at all table temperatures (shown for 100, 200, and 500 °C in Figure 2). The thickness nonuniformity on an 8 in. wafer was typically less than 5%. In Table 1 the GPC and material properties are shown for films deposited at different table temperatures. Figure 3 shows the saturation curves for the precursor step for 100 °C, 200 °C, and 500 °C. Interestingly, over this entire temperature range the precursor showed saturating behavior with possibly a
Table 1. Growth per Cycle (GPC), Refractive Index, Mass Density, and Elemental Composition of SiN$_x$ Films Deposited Using 10 s Plasma Exposure Time at 40 mTorr N$_2$ Pressure and Various Table Temperatures$^{a}$

<table>
<thead>
<tr>
<th>Table temp (°C)</th>
<th>GPC (Å)</th>
<th>Refractive index</th>
<th>Mass density (g/cm$^3$)</th>
<th>N/Si ratio</th>
<th>RBS</th>
<th>N/Si ratio</th>
<th>[C] at. %</th>
<th>[O] at. %</th>
<th>[H] at. %</th>
<th>ERD</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.93 ± 0.02</td>
<td>1.63 ± 0.03</td>
<td>-</td>
<td>-</td>
<td>2.7 ± 0.1</td>
<td>25 ± 1</td>
<td>3 ± 1</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.32</td>
<td>1.83</td>
<td>2.2 ± 0.1</td>
<td>2.0 ± 0.1</td>
<td>1.7</td>
<td>9</td>
<td>5</td>
<td>10.9 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.21</td>
<td>1.92</td>
<td>2.8</td>
<td>1.6</td>
<td>1.6</td>
<td>4</td>
<td>5</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.16</td>
<td>1.96</td>
<td>2.8</td>
<td>1.5</td>
<td>1.5</td>
<td>2</td>
<td>4</td>
<td>5.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.15</td>
<td>1.96</td>
<td>2.9</td>
<td>1.4</td>
<td>1.5</td>
<td>2</td>
<td>5</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk Si$_3$N$_4$</td>
<td>-</td>
<td>2.02</td>
<td>3.2</td>
<td>1.33</td>
<td>1.33</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$Typical error margins are indicated for the first value in each column. A dash indicates "not measured". The last row indicates the properties of bulk Si$_3$N$_4$.22,23

Effect of Plasma Exposure. Figure 4 and Table 2 show the effect of the plasma exposure time on the GPC and the material properties. Figure 4 shows that there was initially a rapid increase in the GPC followed by a slow decrease toward a constant value. Furthermore, there was a continuous decrease in C content with plasma exposure time. Table 2 shows that with longer plasma exposure time there was also an increase in refractive index and a slight increase in O content, which was likely incorporated from background species in the reactor (i.e., a longer plasma exposure leads to a longer exposure of the surface to species present in the background such as oxygen and water). The mass density data for 10 and 15 s plasma exposure time, 2.2 ± 0.1 g/cm$^3$ and 2.4 ± 0.1 g/cm$^3$, respectively, shows an increase of mass density for longer plasma exposure times. The deposition at a lower pressure of 13 mTorr instead of 40 mTorr demonstrated that a decrease in plasma pressure can improve the material properties, i.e., a higher refractive index, a lower N/Si ratio, and low C and O contents were obtained.

Figure 5a shows the refractive index as a function of plasma exposure time, measured directly after deposition and after 1 and 2 months. Films deposited using 7.5 s plasma or longer were stable to oxygen incorporation over this period of time. For shorter plasma times there was a decrease in refractive index over time. Figure 5b and 5c show the XPS depth profiles for films deposited using 3 and 15 s plasma exposure times, respectively. The profiles directly after deposition and 1 month later are shown. Directly after deposition, both films showed a low O content over the film thickness. After 1 month, the film deposited using 3 s plasma exposure showed a much higher O content (~50 at. %) and a relative decrease in N and C content. SE showed that this change was accompanied by a thickness increase from 63.9 to 84.3 ± 0.5 nm and a decrease in refractive index from 1.75 to 1.53 ± 0.03. The change in material properties and thickness indicates oxidation of the film. The low gradient in O content can be explained by the oxidation having proceeded down to the interface, with no oxidation further occurring. Figure 5c shows that the film deposited using 15 s plasma exposure underwent no observable change in composition. Note that both films were deposited on Si substrates with a native oxide layer, which accounts for the higher O content at the interface between film and substrate. Experiments on HF-dipped Si substrates did not show this higher O content at the interface.

Films were also prepared at room temperature, and for this temperature saturating behavior was also found (Figure S1).15 The best material properties were obtained for a plasma exposure of 20 s N$_2$ at 13 mTorr. For this sample, the GPC was 1.17 ± 0.02 Å, and the refractive index was 1.76 ± 0.03.

Figure 3. Growth cycle (GPC) as a function of the precursor dosing time for a table temperature of 100 °C, 200 °C, and 500 °C. The GPC was determined using a 3 s plasma exposure time. The lines serve as a guide to the eye.

Figure 4. GPC and carbon content of the SiN$_x$ films as a function of plasma exposure time for a table temperature of 200 °C. The lines serve as a guide to the eye.
Table 2. GPC, Refractive Index, and Composition of SiNₓ Films Deposited Using Different Plasma Exposure Times in the Cycle at 40 mTorr N₂ Pressure and a Table Temperature of 200 °C

<table>
<thead>
<tr>
<th>plasma exposure time (s)</th>
<th>GPC (Å)</th>
<th>refractive index</th>
<th>XPS</th>
<th>ERD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N/Si ratio</td>
<td>[C] at. %</td>
</tr>
<tr>
<td>1</td>
<td>0.39 ± 0.02</td>
<td>1.56 ± 0.03</td>
<td>2.1 ± 0.1</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>3</td>
<td>0.46</td>
<td>1.75</td>
<td>2.1</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>0.42</td>
<td>1.78</td>
<td>1.9</td>
<td>14</td>
</tr>
<tr>
<td>7.5</td>
<td>0.36</td>
<td>1.82</td>
<td>1.8</td>
<td>11</td>
</tr>
<tr>
<td>10</td>
<td>0.32</td>
<td>1.83</td>
<td>1.7</td>
<td>9</td>
</tr>
<tr>
<td>15</td>
<td>0.28</td>
<td>1.86</td>
<td>1.7</td>
<td>8</td>
</tr>
<tr>
<td>10²</td>
<td>0.24</td>
<td>1.91</td>
<td>1.6</td>
<td>6</td>
</tr>
</tbody>
</table>

“`The N₂ plasma pressure was set at 13 mTorr instead of 40 mTorr. Typical error margins are indicated for the first value in each column. A dash indicates "not measured".

Figure 5. (a) The refractive index as a function of plasma exposure time for films analyzed directly after deposition and compared to those of the same films analyzed 1 month and 2 months after deposition. The X-ray photoelectron spectroscopy (XPS) depth profiles measured directly after deposition and 1 month after deposition for a film deposited with a plasma exposure time of 3 s (b) and 15 s (c) are shown. The substrate table temperature was 200 °C.

(determined in situ). XPS measurements showed a N/Si ratio of 2.3 ± 0.1, a C content of 20 ± 1%, and an O content of 2 ± 1%. Note that the longer plasma exposure and lower pressure used for this film deposited at room temperature led to a higher refractive index, a lower N/Si ratio, and a lower C content than for films prepared at 100 °C under standard conditions. Nevertheless, these films were prone to immediate oxidation on removal from the reactor. An Al₂O₃ capping layer was deposited in situ by ALD onto the SiNₓ film, which prevented this oxidation to the extent that the film composition was the same after 2 months in air as it was directly after deposition.

Wet-Etch Rates. Table 3 shows wet-etch rates, from high to low, for a selection of SiNₓ films. The results for a thermal oxide film (400 nm SiO₂) are given for comparison. The 100:1 HF etch rates of thermal oxide have the same order of magnitude but have a lower value than reported in the literature (e.g., 0.6 nm/min versus 2.3 nm/min).17 Thermal oxide etch rates for 7:1 BHF were in the range reported in the literature which is between 50 and 100 nm/min.17 Note that BHF solutions are considered to be more reliable for controlled etching since etching is affected by the acidity of the solution which is more constant in buffered solutions such as BHF.17

Table 3. Wet-Etch Rates for SiNₓ Films Deposited at Various Table Temperatures and with Different Plasma Times at 40 mTorr N₂ Pressure

<table>
<thead>
<tr>
<th>table temp (°C)</th>
<th>plasma time (s)</th>
<th>100:1 HF</th>
<th>7:1 BHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>7.5</td>
<td>71 ± 15</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>10</td>
<td>28 ± 8</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>15</td>
<td>11 ± 4</td>
<td>38 ± 4</td>
</tr>
<tr>
<td>200</td>
<td>10²</td>
<td>2.7 ± 0.7</td>
<td>14 ± 2</td>
</tr>
<tr>
<td>300</td>
<td>10</td>
<td>1.3 ± 0.7</td>
<td>5.6 ± 0.2</td>
</tr>
<tr>
<td>400</td>
<td>10</td>
<td>0.2 ± 0.5</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>0.0 ± 0.1</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>thermal oxide</td>
<td>0.6 ± 0.1</td>
<td>82.8 ± 0.7</td>
<td></td>
</tr>
</tbody>
</table>

“`The N₂ plasma pressure was set at 13 mTorr instead of 40 mTorr. Wet-etch rates for thermal oxide are shown in the last row as a reference. A dash indicates "not measured".

**DISCUSSION**

To obtain SiNₓ films with a composition close to stoichiometric Si₃N₄ and with low wet-etch rates, the most important parameters were table temperature, plasma exposure time, and plasma pressure. For high table temperatures, properties relatively close to those of bulk Si₃N₄ were obtained. At 200 °C,
a long plasma exposure time of 15 s or a low plasma pressure of 13 mTorr gave the best material properties and most stable films. The benefit of using lower pressure could be related to ion bombardment (ion energy $\approx 15$ eV$^\text{11,18}$). However, as was shown in a recent publication,$^\text{19}$ the effect of faster removal of reaction products from the chamber was more important as it limits the chance of these products to be dissociated and redeposit on the surface. At short plasma exposure times and low table temperatures, impurity levels were high and the films were unstable in air. This could again be related to redeposited species that are not completely removed from the surface or alternatively that ligands were not completely removed during the plasma step. Both these processes would result in a higher carbon content and lower mass density of the films, which would lead to a higher GPC. Incorporation of N from the N$_2$ plasma on the impurity-containing surface could explain the high N/Si ratio of 2.7 at 100 °C.

When comparing the main results from this work with those from SiN$_x$ ALD processes reported in the literature, several observations can be made. The first observation is that ALD behavior was investigated over a wider temperature window in this work (even at room temperature), while for instance for chlorosilanes the lowest reported temperature is 225 °C.$^\text{4}$ On the other hand, fairly low GPC values were observed in this work compared to the other processes in the literature, e.g., 0.32–0.15 Å at 200–500 °C compared to 0.65 Å for growth using N(SiH$_3$)$_3$ (TSA) and NH$_3$ plasma or compared to 2.3 Å for growth using Si$_2$Cl$_6$ and N$_2$H$_4$.$^\text{3,13}$ This difference could be related to the larger size of the BTBAS precursor. Furthermore, the used precursors have often more than one Si atom per precursor molecule (e.g., TSA has three Si atoms), which can lead to more Si atoms deposited per precursor molecule. The fairly short precursor dosing time of 150 ms might suggest that the reactivity of BTBAS with the surface after N$_2$ plasma is higher than for other SiN$_x$ ALD processes. This would be supported by the fact that the required exposure for saturated growth was much lower than that reported for SiH$_2$Cl$_2$ on an NH$_3$ plasma exposed surface (i.e., < 0.1 Torr·s compared to 1–10 Torr·s).$^\text{10}$ The material quality was remarkably high, taking into account that at a 500 °C table temperature the actual wafer temperature is expected to be more than 100 °C lower.$^\text{15}$ For instance the process from Morishita et al. using SiCl$_4$ and N$_2$H$_4$ required a temperature of $>525$ °C to obtain the same refractive index. The refractive index was also higher than the refractive index obtained for other chlorine-free processes reported, i.e., $\leq 1.96$ versus $\leq 1.85$, while the films were also nitrogen-rich.$^\text{12,13}$ The latter could be related to the N/Si ratio in the precursor, 2:1 for BTBAS compared to 1:3 for TSA, and it could also be related to the usage of a pure N$_2$ plasma as the coreactant instead of H-containing coreactants such as NH$_3$ plasma used by others.$^\text{3,5,6,13}$ Also, a relatively low H content was observed, which is important for the wet-etch rate as will be discussed in the next paragraph.

Table 3 shows that both 0.5% HF and 7:1 BHF wet-etch rates show the same trend for the SiN$_x$ films, where low etch rates were obtained for films deposited at high table temperatures and for films with lower impurity and hydrogen levels. This is, for instance, revealed by the films deposited at longer plasma time (15 s compared to 10 s) and at lower plasma pressure (13 mTorr versus 40 mTorr). Chow et al. reported etch rates with similar BHF etchant (i.e., 13:2 BHF compared to 7:1 BHF) for SiN$_x$ films deposited using plasma-enhanced chemical vapor deposition (PECVD) and low-pressure chemical vapor deposition (LPCVD) and observed that films with low H content had the lowest etch rates. The lowest values were around 1 nm/min for LPCVD Si$_3$N$_4$ films deposited at $>700$ °C,$^\text{20}$ which is similar to those of the best films in this work (prepared at 400 and 500 °C) with a comparable H content ($\sim 5\%$). Note also that the H content was lower than the 15% reported for LPCVD BTBAS at 550–600 °C.$^\text{21}$ Hence, in comparison to wet-etch rates for other SiN$_x$ ALD processes, good results were already achieved at relatively low temperatures. Koehler et al. achieved $\sim 1$ nm/min at 500 °C using a similar etchant (1:100 HF), which were achieved at table temperatures between 300 and 400 °C in this work. The fact that the coreactant was a pure N$_2$ plasma (i.e., without any H) suggests that H-free plasmas are beneficial for obtaining films with low H content and low wet etch rates.

**CONCLUSIONS**

A new ALD process for silicon nitride was developed using bis(tert-butylamino)silane (BTBAS) and N$_2$ plasma. The process exhibited a wide temperature window stretching from room temperature up to 500 °C. The material properties depended strongly on plasma exposure time, plasma pressure, and substrate table temperature. For applications where LPCVD and high-temperature thermal ALD have to be replaced to reduce the thermal budget, table temperatures of 300 to 500 °C would be best for this process. Under these conditions a composition close to Si$_3$N$_4$ was obtained at a table temperature of 500 °C, i.e., a N/Si ratio of 1.4 ± 0.1, a mass density of 2.9 ± 0.1 g/cm$^3$, and a refractive index of 1.96 ± 0.03. Low buffered HF wet-etch rates of $\sim 1$ nm/min were obtained for films deposited at table temperatures of 400 and 500 °C, similar to that achieved in the literature using LPCVD Si$_3$N$_4$ at $>700$ °C. The low H content (i.e., $\sim 5\%$) of the films is expected to be an important factor for this result.

For applications demanding ALD SiN$_x$ at lower temperatures, the temperature window from room temperature to 200 °C could be a solution. For these temperatures fairly high material quality was obtained for low plasma pressure or long plasma exposure time (e.g., for deposition at 200 °C using 13 mTorr plasma pressure, the N/Si ratio was 1.6 ± 0.1, and the refractive index was 1.91 ± 0.03). The relatively low precursor doses needed for the presented process could indicate a highly reactive surface after the N$_2$ plasma that could be beneficial to minimize precursor consumption and facilitate growth at low temperatures. Future work will focus on studying the conformity of the ALD SiN$_x$ process and understanding the growth mechanisms.

**ASSOCIATED CONTENT**

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06833.

Table S1 and Figure S1 (PDF)

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Author Contributions

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Notes
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REFERENCES
(15) See the Supporting Information for actual wafer temperatures and saturation curve for growth at room temperature.

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