Plasma Enhanced Atomic Layer Deposition of Silicon Nitride for Two Different Aminosilane Precursors Using Very High Frequency (162 MHz) Plasma Source

You Jin Ji, Hae In Kim, Seung Yup Choi, Ji Eun Kang, Albert Rogers Ellingboe, Haripin Chandra, Chang-Won Lee, and Geun Young Yeom

ABSTRACT: Plasma enhanced atomic layer deposition (PEALD) of silicon nitride (SiNₓ) using very high frequency (VHF, 162 MHz) plasma source was investigated at the process temperatures of 100, 200, and 300 °C. Two aminosilane precursors having different numbers of amino ligands, bis(tert-butylamino)silane (BTBAS) and di(sec-butylamino)silane (DSBAS), were used as Si precursors. A comparative study was also conducted to verify the effect of the number of amino ligands on the properties of SiNₓ film. At all process temperatures, DSBAS, having one amino ligand, performed better than BTBAS in various aspects. SiNₓ films deposited using DSBAS had lower surface roughness, higher film density, lower wet etch rate, improved electrical characteristics, and higher growth rate than those deposited using BTBAS. With the combination of a VHF plasma source and DSBAS with one amino ligand, the SiNₓ films grown at 300 °C exhibited low wet etch rates (<2 nm/min) in a dilute HF solution (100:1 of deionized water:HF) as well as low C content below the XPS detection limit. Also, excellent step coverage close to 100% on high aspect ratio (30:1) trench structures was obtained by using VHF plasma, which could provide sufficient flux of plasma species inside the trenches in conjunction with DSBAS having fewer amino ligands than BTBAS.

KEYWORDS: plasma enhanced atomic layer deposition, silicon nitride, bis(tert-butylamino)silane, di(sec-butylamino)silane, BTBAS, DSBAS, N₂ plasma, conformality

1. INTRODUCTION

Silicon nitride (SiNₓ) thin films are still actively investigated for next-generation semiconductor devices as a gate spacer for memory and logic devices and charge storage layer for nonvolatile memory devices.¹⁻⁹ The conventional deposition of SiNₓ thin films such as in low-pressure chemical vapor deposition (LPCVD) requires high temperatures (>600 °C), which is not compatible with the deposition of the metal layer of the semiconductor devices.¹⁰⁻¹³ Moreover, applications such as amorphous oxide semiconductor (AOS) low-temperature (<400 °C) SiNₓ deposition as a phase transition can occur at higher temperatures (400–500 °C).¹⁴⁻¹⁶ Besides the issues involved in lowering the process temperature, there are other process related requirements such as accurate thickness control, high conformality, and stability during the integration of semiconductor devices.¹⁷⁻²⁰ Therefore, the plasma-enhanced atomic layer deposition (PEALD) process that could lower the process temperature while maintaining the advantages of ALD is a promising technology among various SiNₓ thin film deposition methods.²¹⁻²⁴

Common SiNₓ PEALD processes using chlorosilane precursors (such as SiCl₄, SiH₂Cl₂, Si₂Cl₅, etc.) with NH₃ or N₂/H₂ plasmas have been reported.²⁵⁻³⁰ However, chlorosilane precursors require the use of a high temperature to obtain a high-quality film.²⁷,²⁸ Other drawbacks for chlorosilane are corrosive reactant (hydrochloric acid) and particle (ammonium chloride salts) by-products.¹⁸,¹⁹,³¹,³² In comparison, low-temperature high-quality SiNₓ depositions using nitrogen plasma and aminosilane precursors (such as bis(tert-buty lamino)silane (BTBAS), di(isopropylamino)silane (DIPAS), tris(dimethylamino)silane (3DMAS), bis(diethylamino) silane (BDEAS), di(sec-buty lamino)silane (DSBAS)), which have amine ligands with a high reactivity...
and low activation energy barrier compared to precursors that have chloro ligands, have been demonstrated.\textsuperscript{16,19,33,34} Also, aminosilane precursors are suitable for use in conjunction with \( \text{N}_2 \) plasma as coreactants instead of \( \text{NH}_3 \) plasma, which provides lower hydrogen contents in deposited films.\textsuperscript{25,35–37}

Although the researches on Si\( \text{N}_x \) PEALD using aminosilane precursors were heavily carried out, problems still remain to be studied and the biggest challenge in the PEALD process using aminosilane with \( \text{N}_2 \) plasma is known to be film conformality.\textsuperscript{38,39} In addition, in the research studies on the Si\( \text{N}_x \) PEALD process using aminosilane precursors and capacitively coupled plasma (CCP) for nitrogen reactant at high operating pressures, the radio frequency of 13.56 MHz has generally been used for the operation of plasma.\textsuperscript{23,25,35,38–40}

However, for CCP, with increasing the operating frequency, the plasma density increases, whereas the ion bombardment energy to substrate decreases, which can improve the physical and electrical properties of PEALD thin films with reduced plasma damage.\textsuperscript{34} Especially, very high frequency (VHF) plasma that can dissociate \( \text{N}_2 \) molecule effectively than conventional high frequency (HF) plasma is useful for the Si\( \text{N}_x \) PEALD process requiring low hydrogen contamination by using \( \text{N}_2 \) plasma.\textsuperscript{43–45} We previously found that high quality Si\( \text{N}_x \) thin films can be deposited effectively by VHF (162 MHz)-CCP PEALD using di(isopropylamino) -silane (DIPAS) and \( \text{N}_2 \) plasma at a low process temperature (100 °C).\textsuperscript{44,45}

In this study, we investigated the PEALD of Si\( \text{N}_x \) using the VHF (162 MHz)-CCP \( \text{N}_2 \) plasma at the process temperature range of 100–300 °C. Two different aminosilane precursors, BTBAS and DSBAS, were used as Si precursor, and the effect of the number of ligands of precursors on the resulting Si\( \text{N}_x \) film properties was also discussed. The VHF-CCP has a high nitrogen gas dissociation rate and allows for a high operating pressure range of 0.05–5 Torr required for the PEALD process. We demonstrate that these combinations of VHF-CCP plasma source and an appropriate choice of Si precursors allow for a high growth rate, high quality of films, and excellent conformality.

2. EXPERIMENTAL METHODS

In the deposition of PEALD Si\( \text{N}_x \) films, \( \text{N}_2 \) plasma was generated by a VHF (162 MHz) CCP system. This system has multiple electrodes (inductively power divided floating multitile electrodes), which enables uniform and stable plasma generation at a high operating pressure ranging from tens of mTorr to Torr. A schematic drawing of the VHF (162 MHz)-CCP PEALD system used for the deposition of Si\( \text{N}_x \) films is show in Figure 1. More detailed descriptions of the VHF (162 MHz) CCP with the multitile electrode have been published previously.\textsuperscript{41–44}

The aminosilane precursors studied are di(sec-butylamino)silane (DSBAS) and bis(tert-butylamino)silane (BTBAS), which have one and two amino-ligands, respectively. The property details of the two precursors are available in Table S1. During deposition, both the chemical canister and the delivery line were heated to 50 °C, while the chamber wall temperature was set to 100 °C. The PEALD Si\( \text{N}_x \) films...
using BTBAS and DSBAS were grown on Si wafers and trench patterns with an aspect ratio (AR) of 30:1 (AR = 30:1). The deposition temperatures of 100, 200, and 300 °C were used. Film thickness was measured by spectroscopic ellipsometry (SEMG-1000UV, Nano-view), while surface roughness was analyzed using atomic force microscopy (AFM, nx-10) with a scanning area of 5 μm × 5 μm. Also, the film density was determined by X-ray reflectivity (XRR) measurement using X-ray diffractometry (SmartLab, Rigaku). The film etch rate was evaluated by dipping in a dilute HF solution (1:100 or 1:500 49% HF and DI water). The elemental compositions of the SiN_x films were evaluated using X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo VG, Mg Ka source) after the calibration with a C 1s peak (284.5 eV). The XPS measurement was conducted after in situ Ar^+ ion sputtering of the surface to remove the surface contamination and oxide layer. The conformality of the film deposited on high aspect ratio trench samples (AR = 30:1) was evaluated through transmission electron microscopy (TEM, HD-2300A, Hitachi). Furthermore, the film property in the trench was determined by comparing the film thickness of the as-deposited and post-wet-etched SiN_x films on high aspect ratio trench patterns (AR = 30:1). The breakdown field and capacitance of the metal–insulator–semiconductor (MIS) capacitor were obtained from current–voltage (I–V) and capacitance–voltage (C–V) curves, respectively, using the Keithley semiconductor characterization system (4200-SCS/F). To fabricate the MIS capacitors, PEALD SiN_x layers were grown on p-type silicon wafer. After the SiN_x deposition, e-beam evaporated Al metal contact (30 nm thick, 100 μm diameter) was formed on the SiN_x layer by a lift-off method after photolithographic patterning with an AZ5214E photoresist and AZ MIF 300 developer.

3. RESULTS AND DISCUSSION

Figure 2 shows the ALD saturation behaviors of SiN_x PEALD films for two different precursors of DSBAS and BTBAS at 300 °C. Figure 2a depicts ALD saturation growth with precursor dose time while the N_2 plasma exposure time was set to 60 s. Figure 2b shows film growth with increasing N_2 plasma exposure time while the precursor dose time was set to 3 s. In both cases, the purge times after the precursor adsorption and plasma generation were kept at 30 and 10 s, respectively, with 100 mTorr N_2. As shown in Figure 2a, DSBAS showed a saturated GPC of 0.8 Å/cycle after ∼1 s of precursor dose time, whereas BTBAS showed a saturated GPC of 0.6 Å/cycle after ∼3 s of precursor dose time. For N_2 plasma exposure time, as shown in Figure 2 (b), the GPC was initially high and it decreased with the increase of N_2 plasma exposure time and, finally, at 60 s of N_2 exposure time, both BTBAS and DSBAS were saturated at the GPCs of 0.8 Å/cycle and 0.6 Å/cycle, respectively. Therefore, it is found that 3 s of precursor exposure and 60 s of N_2 plasma exposure were sufficient to achieve saturated GPC for both BTBAS and DSBAS processes. The initial high GPCs at low N_2 plasma exposure time for both BTBAS and DSBAS are believed to be related to the densification effect by continuously bombarding nitrogen ions or to the remaining ligand materials in the growing SiN_x film due to the low reaction time of nitrogen with the precursors.

The effects of substrate temperature (100–300 °C) on the PEALD SiN_x film properties deposited on blank silicon wafers

![Figure 2](https://doi.org/10.1021/acsami.3c02950)
using BTBAS and DSBAS were investigated, and the results are shown in Figure 3 for (a) GPC, (b) wet etch rate, (c) film density, and (d) RMS surface roughness. The wet etch rate was conducted at room temperature using a HF solution (HF:deionized water = 1:100, thermal SiO₂ etch rate was ∼2.57 nm/min). For both precursors of BTBAS and DSBAS, SiNₓ films were deposited using at the same cyclic process sequence shown in Figure S1. As shown in Figure 3a, with increasing substrate temperature, the GPC of DSBAS remained similar at ∼0.8 Å/cycle, which was potentially due to the high reactivity even at low temperature while that of BTBAS decreased from ∼0.8 to ∼0.6 Å/cycle with increasing substrate temperature from 100 to 300 °C due to the low reactivity at lower substrate temperature and the additional elimination of precursor fragments at higher temperature. In the case of wet etch rates, as shown in Figure 3b, those of PEALD SiNₓ films deposited using BTBAS and DSBAS were decreased with increasing substrate temperature, but at all substrate temperatures, SiNₓ films by DSBAS showed lower wet etch rates than those by BTBAS. Also, the PEALD SiNₓ deposited at 300 °C by using DSBAS showed the lowest wet etch rate (∼1.5 nm/min) among the PEALD SiNₓ described by various researchers, as shown in Figure S2. The wet etch rate of PEALD SiNₓ film using BTBAS was also comparable to other results in the literature. Film density was also increased with increasing substrate temperature at (a, d) 100 °C, (b, e) 200 °C, and (c, f) 300 °C. To obtain the wet etch rates, the SiNₓ films were dipped in a dilute HF solution (HF/H₂O = 1:100) for 60 s. The SiNₓ films deposited at a substrate temperature of 100 °C were only dipped for 30 s due to the high wet etch rate.

Figure 4. (a) N/Si ratio and (b) C & O contents in PEALD SiNₓ films deposited using BTBAS and DSBAS as a function of deposition temperature.

Figure 5. Cross-sectional TEM images of (a–c) as-deposited and (d–f) post wet etched PEALD SiNₓ films on high aspect ratio trenches (AR ≈ 30:1) deposited using DSBAS as a function of substrate temperature at (a, d) 100 °C, (b, e) 200 °C, and (c, f) 300 °C. To obtain the wet etch rates, the SiNₓ films were dipped in a dilute HF solution (HF/H₂O = 1:100) for 60 s. The SiNₓ films deposited at a substrate temperature of 100 °C were only dipped for 30 s due to the high wet etch rate.
compared to those of film deposited with BTBAS. In addition, as shown in Figure 3d, higher substrate temperature showed lower RMS surface roughness of deposited SiN$_x$ films, and the PEALD SiN$_x$ films deposited with DSBAS showed lower RMS surface roughness than those deposited with BTBAS at all substrate temperatures (measured RMS surface roughness data are shown in Figure S3).

The chemical composition of PEALD SiN$_x$ films deposited using BTBAS and DSBAS was determined by XPS analysis according to deposition temperature for the process conditions presented in Figure 3, and the results are shown in Figure 4. Figure 4a shows the N/Si ratio of the films deposited at different temperatures. The N/Si ratio of SiN$_x$ films deposited using DSBAS ranged from 0.8 at 100 °C to 0.97 at 300 °C, while films deposited using BTBAS showed similar N/Si ratios of ≤0.8 at all temperatures. As shown in Figure 4b, the carbon percentages in the deposited SiN$_x$ were decreased with increasing substrate temperature for both precursors, but the carbon content of SiN$_x$ films by DSBAS was markedly lower than that by BTBAS at all deposition temperatures, and it was ~0% at 300 °C. The C content lower than 4% of DSBAS grown SiN$_x$ films might be related to the lowest wet etch rates obtained among the reported wet etch rate results of PEALD SiN$_x$ films, as shown in Figure S2. The oxygen contents of all films were approximately 5–6% for both precursors. The detailed elemental compositions (N, Si, C, and O) of SiN$_x$ films deposited by BTBAS and DSBAS according to substrate temperature can be found in Table S2.

The differences in physical properties such as GPC, wet etch rate, film properties, composition, etc., between PEALD SiN$_x$ films deposited using BTBAS and DSBAS are believed to be caused by the differences in the molecular structures of two precursors. After the chemisorption of DSBAS with one amino ligand, no residue may remain on the surface. However, in the case of BTBAS with two amine ligands, only one amino ligand can be removed after precursor adsorption, and the other amino ligand can remain on the surface and reduces the ability to react with N$_2$ plasma by the steric hindrance effect. Moreover, the residual amino ligand of BTBAS on the surface may participate during the reactant N$_2$ plasma step, resulting in impurities of the films. Because of this phenomenon, more carbon can be included in the deposited SiN$_x$ films as an impurity when using the BTBAS. As a result, due to the increased impurities contained in SiN$_x$ films using BTBAS, the wet etch rates appear to be higher than those of SiN$_x$ films deposited with DSBAS having relatively higher purity. However, for clear understanding of the reaction mechanism, more investigation appears to be required.

Using high aspect ratio trenches having the aspect ratio (AR ≈ 30:1), PEALD SiN$_x$ films using BTBAS and DSBAS were deposited for 200 cycles at substrate temperatures of 100–300 °C, and the step coverage of the deposited PEALD SiN$_x$ was observed by cross-sectional TEM. The results for DSBAS and BTBAS are shown in Figures 5a–c and 6a–c, respectively, and the measured step coverage values are presented in Table S4. As shown in Figure 5a–c and 6a–c, the step coverage was improved with increasing substrate temperature, with values ≥85% at 100 °C and ≥95% at 300 °C, and SiN$_x$ deposited using DSBAS generally showed higher step coverage than that deposited using BTBAS. Especially, at 300 °C, SiN$_x$ deposited using DSBAS showed ~100% step coverage for AR ≈ 30. The differences in conformality between the SiN$_x$ films using BTBAS and DSBAS are believed to be caused by the structural properties of the precursors. Due to the larger size and lower surface packing density of BTBAS, penetration and adsorption into deeper inside the trench pattern are expected to be more
difficult for BTBAS than DSBAS. To investigate the differences in step coverage between SiN$_x$ films deposited by BTBAS and DSBAS, using a simple lateral gap structure shown in Figure S4, the thickness profile along the penetration depth of lateral gap was measured for the PEALD SiN$_x$ deposited at 300 °C; similar to the TEM results, BTBAS showed a higher slope in the thickness profiles, which means a shorter penetration depth along the gap compared to DSBAS as shown in Figure S4. The use of the VHF (162 MHz) plasma source also seems to be a key factor in the excellent conformality in Figure 5c. In the case of VHF (162 MHz) plasma, where N$_2$ plasma can be effectively dissociate, sufficient radical fluxes are supplied to deeper inside the trench pattern, which appears to result in good conformality. A comparative study examining the differences in film conformality between the SiN$_x$ films deposited using 13.56 and 162 MHz was conducted to prove the effect of VHF plasma, and the results are shown in Figure S5 and Table S3.

In Figures 5d−f and 6d−f, the cross-sectional TEM images after the wet etching of as-deposited SiN$_x$ in Figures 5a−c and 6a−f with a dilute HF solution (HF/H$_2$O = 1:100) are shown, respectively, and the measured wet etch data are shown in Table S4. To obtain the wet etch rates, the SiN$_x$ films deposited at 200–300 °C were dipped for 60 s while the SiN$_x$ films deposited at 100 °C were dipped for only 30 s, due to the high wet etch rate. As shown in Figures 5d−f and 6d−f and Table S4, the wet etch rates of BTBAS grown SiN$_x$ at the trench top region were faster than those of DSBAS grown SiN$_x$ films and the wet etch rates at the top trench regions were similar to those of SiN$_x$ on blank silicon, as shown in Figure 3d. The wet etch rates at the trench sidewall and trench bottom regions were generally faster than those at the trench top regions, and at the sidewall and bottom regions, SiN$_x$ films using BTBAS were also etched much faster than the films using DSBAS, and they were etched away completely within 60 s in a dilute HF solution (HF/H$_2$O = 1:100). The reason for the very low wet etch rate (WER ≤ 2 nm/min) of 1.5 nm/min observed at the top surface and the better wet etch resistance at the sidewall and bottom of DSBAS grown films compared to those seen in the BTBAS case is believed to involve the difference in film impurities stemming from the structural difference between the two precursors. To see the differences in wet etch rates of both SiN$_x$ films more clearly, cross-sectional TEM images measured after the wet etching of SiN$_x$ films deposited at 300 °C using a more dilute HF solution (HF/H$_2$O = 1:500) for 30 s are shown in Figure S6.

The breakdown fields of MIS capacitors (~30 nm Al/∼20 nm SiN$_x$/p-type Si) fabricated with PEALD SiN$_x$ deposited using BTBAS and DSBAS at substrate temperatures of 100–300 °C are shown in Figure 7a. As shown in Figure 7a, the breakdown fields did not exhibit significant variation with substrate temperature for both precursors. However, the MIS fabricated with BTBAS shows a lower breakdown field of 14–14.75 MV/cm compared to the MIS fabricated with DSBAS, which has a breakdown field of 16–16.75 MV/cm. This might be due to higher quality SiN$_x$ film using DSBAS that has a lower wet etch rate, higher film density, lower surface roughness, and lower impurities than BTBAS grown SiN$_x$ films. However, when the breakdown fields of PEALD SiN$_x$ in this work, which were fabricated using BTBAS and DSBAS, were compared with those reported in other studies that were fabricated using comparable deposition conditions, as shown in Figure 7b, the breakdown fields of the MIS capacitor with both DSBAS and BTBAS were sufficiently high and comparable to other results reported in the literature. The dielectric constants of MIS capacitors with PEALD SiN$_x$ films deposited at different substrate temperatures (100, 200, and 300 °C) are also found in Table S5.

4. CONCLUSIONS

We studied the PEALD of SiN$_x$ using VHF (162 MHz)-CCP N$_2$ plasma and also discussed the effects of the number of amino ligands on the properties of SiN$_x$ films by using two different Si precursors, BTBAS and DSBAS, at the substrate temperature range of 100–300 °C. In comparison to the PEALD SiN$_x$ films deposited using BTBAS, SiN$_x$ films deposited using DSBAS showed higher GPC, higher film density, lower impurity, lower wet etch rate, lower surface roughness, and improved electrical property (e.g., breakdown field of MIS capacitor) at all deposition temperatures. High qualities of DSBAS grown films can be attributed to the structural feature of DSBAS, having one amino ligand and a smaller molecular size than BTBAS. The two amino ligands of BTBAS have a higher probability of fragment redeposition relative to DSBAS, which leads to higher carbon content in films and low conformity at high aspect ratio trenches. By using DSBAS having one amino ligand as the precursor along
with VHF CCP N₂ plasma for the reaction, at a substrate temperature of 300 °C, the following results could be obtained: the highest breakdown field of 16.75 MV/cm, lowest carbon impurity percentage of ~0%, and excellent conformality close to ~100% on high aspect ratio trenches (AR ≈ 30:1). It is believed that, by using other silicon precursors with one amino ligand and smaller molecular size in addition to the VHF-CCP N₂ plasmas, similar or better PEALD SiNₓ deposition characteristics can be generally obtained.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsami.3c02950.

One cycle of SiNₓ PEALD, comparison of wet etch rate, AFM images, thickness profiles, TEM images of PEALD SiNₓ using 13.56 MHz, TEM images, properties of precursors, elemental composition, step coverage and wet etch rate of PEALD SiNₓ, using 13.56 MHz step coverage, wet etch rate, and electrical properties of SiNₓ films (PDF).

■ AUTHOR INFORMATION

Corresponding Author
Geun Young Yeom — School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon-si, Gyeonggi-do 16419, Republic of Korea; SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, Suwon-si, Gyeonggi-do 16419, Republic of Korea; orcid.org/0000-0002-1176-7448; Email: gyyeom@skku.edu

Authors
You Jin Ji — School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon-si, Gyeonggi-do 16419, Republic of Korea
Hae In Kim — School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon-si, Gyeonggi-do 16419, Republic of Korea
Seung Yup Choi — School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon-si, Gyeonggi-do 16419, Republic of Korea
Ji Eun Kang — School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon-si, Gyeonggi-do 16419, Republic of Korea
Albert Rogers Ellingboe — School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon-si, Gyeonggi-do 16419, Republic of Korea; Plasma Research Laboratory, School of Physical Sciences and NCPST, Dublin City University, Dublin D9, Ireland
Haripin Chandra — EMD Electronics, Carlsbad, California 92011, United States
Chang-Won Lee — Merck Korea, Ansan-si, Gyeonggi-do 15601, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.3c02950

Author Contributions
*Y.J.J. and H.L.K. contributed equally.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Versum Materials, EDM Electronics and by the Technology Innovation Program (20014639, Development of high density inorganic thin film deposition system without micro defects) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

■ REFERENCES

(13) Yang, C.; Pham, J. Characteristic study of silicon nitride films deposited by LPCVD and PECVD. Silicon 2018, 10, 2561–2567.


