to DNF Co., Ltd., discloses Amino-silyl Amine Compounds, Methods for Preparing the Same and Silicon-containing Thin-Film Using the Same. US5413813 to Cruse et al. disclose CVD of silicon-based ceramic materials on internal surfaces of a reactor using, among others, $R_3Si\text{-}N(X)\text{-}SiR_3$, wherein each R is H, $C_{1\text{-}20}$ alkyl, halogen (preferably Cl) or NR_2 and X is H, Li, or SiR_3. US2014/0158580A to Air Products and Chemicals, Inc., describes Alkoxysilylamine Compounds and Applications Thereof. US 7,122,222, also to Air Products and Chemicals, Inc., discloses Precursors for Depositing Silicon Containing Films and Processes Thereof. Silazane compounds $N\text{-}(SiR^1R^2R^3)_mR^4_{3\text{-}m}$ disclosed in WO2013/058061 are used as a coating gas. $(RR^1R^2M^a)_yA(R^3)_x$ disclosed in US 5,332,853 is used as a catalytic compound to produce a functionalized alkylalkali metal compound. Similar patents include US 5663398A, US 5332853A, US 5340507A, and EP 525881 A1.

[0005] Industries using vapor-based deposition processes such as CVD or ALD (in all possible meanings, such as LPCVD, SACVD, PECVD, PEALD, *etc.*) are still looking for precursors that are ideal for their applications, *i.e.* having the highest possible deposition rates within the constraints of their processes, substrates and film targets.

Summary

[0005a] In one aspect, there is provided an ALD silicon nitride film formation process, the process comprising the steps of: depositing on a substrate a silicon nitride film having an etch rate from 0.1% w/w HF normalized to thermally grown silicon dioxide in a range from approximately 0.7 to approximately 3.5 by sequentially introducing a vapor of a mono-substituted TSA precursor and a nitrogen-containing reactant into a reactor containing the substrate, the mono-substituted TSA precursor having a formula $(SiH_3)_2N\text{-}SiH_2\text{-}X$, wherein X is a halogen atom or an amino group [$-NR_2$] and each R is independently selected from the group consisting of H or a C_1-C_6 hydrocarbyl group.

[0006] Disclosed are Si-containing film forming compositions comprising a mono-substituted TSA precursor having the formula $(SiH_3)_2NSiH_2$-X, wherein X is a halogen atom selected from Cl, Br or I; an isocyanato group [–NCO]; an amino group [$–NR^1R^2$]; a N-containing C_4-C_{10} saturated or unsaturated heterocycle; or an alkoxy group [–O–R]; R^1, R^2 and R is independently selected from H; a silyl group [$-SiR'_3$]; or a C_1-C_6 linear or branched, saturated or unsaturated hydrocarbyl group; with each R' being independently selected from H; a halogen atom selected from Cl, Br, or I; a C_1-C_4 saturated or unsaturated hydrocarbyl group; a C_1-C_4 saturated or unsaturated alkoxy group; or an amino group [$–NR^3R^4$] with each R^3 and R^4 being independently selected from H and a C_1-C_6 linear or branched, saturated or unsaturated hydrocarbyl group, provided that if R^1 = H, then $R^2 \neq$ H, Me or Et. The disclosed Si-containing film forming compositions may include one or more of the following aspects:

- the mono-substituted TSA precursor wherein X is a halogen atom;
- the mono-substituted TSA precursor being $(SiH_3)_2N$-SiH_2-Cl;
- the mono-substituted TSA precursor being $(SiH_3)_2N$-SiH_2-Br;

[00123] The following PEALD testing was performed using a Picosun R200 PEALD 8" deposition tool with a 4" wafer. The vapor of the mono-substituted TSA precursor was delivered to the Picosun tool as shown in **FIG 3**.

[00124] ALD tests were performed using $(SiH_3)_2N$-SiH_2-$NiPr_2$ as the silicon-containing film forming composition **10**, which was placed in an ampoule heated to 70°C and O_2 plasma as oxidizing reactant. Typical ALD conditions were used with the reactor **50** pressure fixed at ~9 hPa (1 hPa=100 Pa=1mbar). Two 0.1-second pulses of the precursor vapor were introduced into the deposition chamber via overpressure in the ampoule using the 3-way pneumatic valve **51**. The 0.1-second pulses were separated by a 0.5 second pause. A 4-second N_2 purge removed any excess precursor. A 16-second plasma O_2 pulse was followed by a 3-second N_2 purge. The process was repeated until a minimum thickness of 300 Angstrom was obtained. Depositions were performed with the substrate heated to 70°C, 150°C, and 300°C. Real self limited ALD growth behavior was validated as shown in **FIG 4** by increasing the number of precursor pulses within a given cycle.

[00125] ALD tests were also performed using the prior art $SiH_2(NEt_2)_2$ precursor as the Si-containing film forming composition **10**, which was placed in an ampoule heated to 60°C and O_2 plasma as oxidizing reactant. Applicants believe that $SiH_2(NEt_2)_2$ is currently used to deposit SiO_2 in several commercial processes. Typical ALD conditions were used with the reactor pressure fixed at ~9 hPa (1 hPa=100 Pa=1mbar). Two 0.1-second pulses of the precursor vapor were introduced into the deposition chamber via overpressure in the ampoule using the 3-way pneumatic valve. The 0.1-second pulses were separated by a 0.5 second pause. A 4-second N_2 purge removed any excess precursor. A 16-second plasma O_2 pulse was followed by a 3-second N_2 purge. The process was repeated until a minimum thickness of 300 Ang was reached. Depositions were performed at 70°C, 150°C, 200°C, and 300°C. As shown in **FIG 5**, the growth per cycle decreased with increasing temperature.

Table 2 summarizes the results:

	$SiH_2(NEt_2)_2$	$(SiH_3)_2N$-SiH_2-$NiPr_2$
Growth rate 70°C[1]	1.42 Ang/cycle	3.10 Ang/cycle
Growth rate 300°C[1]	0.98 Ang/cycle	2.05 Ang/cycle
Wet Etch Rate 70°C[2]	9.4 Ang/sec	8.8 Ang/sec

O_2 pulse was followed by a 3-second N_2 purge. The process was repeated until a minimum thickness of 300 Angstrom was obtained. Depositions were performed with the substrate heated to 100°C, 150°C, 200°C, 250°C, and 300°C. As shown in **FIG 8**, the growth per cycle remained steady (i.e., approximately 2 Å/cycle) with increasing deposition temperatures from 100°C to 300°C.

[00135] The resulting silicon oxide films were deposited at a high deposition rate (approximately 2Å/cycle) at multiple temperatures. These results are beneficial when temperature uniformity is difficult to maintain across the substrate (*i.e.*, for large substrates) or from one substrate to another due to temperature gradients in the reactor.

[00136] The average thickness of the film was also uniform across the wafer. Table 3 summarizes the film uniformity obtained. These results demonstrate extremely good film uniformity.

Experiment Number (Process Conditions)	Deposition Temp. (°C)	Average Thickness (Å)	Non Uniformity[1] (%)	σ^2	3 σ/Average (%)
1272 (1 x 0.1 s)	100	321	1.04	1.66	1.56
1256 (2 x. 0.1 s)	100	329	1.07	1.59	1.45
1271 (3 x 0.1 s)	100	323	0.93	1.34	1.24
1252 (1 x 0.1 s)	150	590	1.30	4.45	2.26
1253 (2 x 0.1 s)	150	585	1.96	6.61	3.39
1267 (1 x 0.1 s)	200	319	0.66	1.09	1.03
1273 (2 x 0.1 s)	200	325	1.15	1.94	1.79
1268 (3 x 0.1 s)	200	324	1.15	2.01	1.87
1263 (1 x 0.1 s)	250	362	0.74	1.37	1.13
1265 (2 x 0.1 s)	250	317	0.88	1.27	1.20

[1] % non-uniformity = [(maximum thickness – minimum thickness)/(2x average)] x 100

[2] σ = standard deviation

Example 9

[00137] Thermal, low pressure CVD tests were performed using $(SiH_3)_2N\text{-}SiH_2\text{-}Cl$ and NH_3 at 1 torr, 550°C, and a precursor to NH_3 ratio of 1:20. **FIG 9** is a X-ray Photoelectron Spectroscopy (XPS) graph showing the resulting film composition. Cl was below the detection limit of the analyser (< ~ 1 atomic %). The deposition rate

What is claimed is:

1. An ALD silicon nitride film formation process, the process comprising the steps of:

depositing on a substrate a silicon nitride film having an etch rate from 0.1% w/w HF normalized to thermally grown silicon dioxide in a range from approximately 0.7 to approximately 3.5 by sequentially introducing a vapor of a mono-substituted TSA precursor and a nitrogen-containing reactant into a reactor containing the substrate, the mono-substituted TSA precursor having a formula $(SiH_3)_2N\text{-}SiH_2\text{-}X$, wherein X is a halogen atom or an amino group [$–NR_2$] and each R is independently selected from the group consisting of H or a C_1-C_6 hydrocarbyl group.

2. The ALD silicon nitride film formation process of claim 1, wherein the nitrogen-containing reactant is selected from the group consisting of ammonia, N_2, N atoms, N radicals, N ions, saturated or unsaturated hydrazine, amines, diamines, ethanolamine, and combinations thereof.

3. The ALD silicon nitride film formation process of claim 2, wherein the nitrogen-containing reactant is plasma N_2.

4. The ALD silicon nitride film formation process of any one of claims 1 to 3, wherein X is Cl, Br, or I.

5. The ALD silicon nitride film formation process of any one of claims 1 to 3, wherein X is Cl.

6. The ALD silicon nitride film formation process of any one of claims 1 to 3, wherein X is $NiPr_2$.

7. The ALD silicon nitride film formation process of any one of claims 1 to 3, wherein X is NEt_2.

8. The ALD silicon nitride film formation process of any one of claims 1 to 3, wherein X is $N(SiH_3)_2$.