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 and oxygen containing film formation process, the process comprising the steps of: depositing a silicon and oxygen containing film on a substrate by sequentially introducing a vapor of a mono-substituted TSA precursor and an oxygen-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; a C_1-C_6 hydrocarbyl group; or a silyl group [SiR'_3] with each R' being independently selected from H or a C_1-C_6 hydrocarbyl group.

[0005b] In another aspect, there is provided an ALD silicon oxide film formation process, the process comprising the steps of: depositing a silicon oxide film on a substrate at a rate ranging from approximately 2.1 Å/cycle to approximately 3.1 Å/cycle by sequentially introducing a vapor of a mono-substituted TSA precursor and an oxygen-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 $(SiH_3)_2NSiH_2\text{-}X$, 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 embodiments:

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

[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:

	$SiH_2(NEt_2)_2$	$(SiH_3)_2N\text{-}SiH_2\text{-}NiPr_2$
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
Wet Etch Rate 150°C[2]	7.2 Ang/sec	6.7 Ang/sec
Wet Etch Rate 300°C[2]	6.6 Ang/sec	6.7 Ang/sec
Refractive Index 70°C[3]	1.432	1.460
Atomic % Carbon 70°C[4]	0.05%	TBD
Atomic % Carbon 150°C[4]	0.045%	0,015-0,03%
Atomic % Hydrogen 150°C[4]	~10%	~10%
Atomic % Nitrogen 150°C[4]	0.015%	0,1%
Within Wafer Non Uniformity[5]	2.84%	2.90%

[1] Growth rate for films deposited at the stated temperatures

[2] Wet Etch Rate using 0.1% v/v HF (determined by ellipsometry) of films deposited at the stated temperatures

[3] Refractive index for film deposited at 70°C

[4] Atomic percentage in a film deposited at the stated temperature as determined by Secondary Ion Mass Spectrometry (SIMS). Hydrogen content is subject to uncertainty when measured by SIMS, as one skilled in the art would

Depositions were performed with the substrate heated to 150°C. A self limited ALD growth behavior was found as shown in **FIG 7** by increasing the number of precursor pulses to reach a cumulative opening time higher than 0.4 second per cycle.

[00132] As in Example 4, the approximately 3.0 Å/cycle growth rate for films produced by $(SiH_3)_2N\text{-}SiH_2\text{-}NEt_2$ at 150°C is much better than the 1.42 Å/cycle and 0.98 Å/cycle produced by $SiH_2(NEt_2)_2$ at 70°C and 300°C, respectively.

Example 8

[00133] ALD tests were performed using $(SiH_3)_2N\text{-}SiH_2\text{-}Cl$ as the silicon-containing film forming composition **10**, which was placed in an ampoule heated to 30°C and O_2 plasma as oxidizing reactant. $(SiH_3)_2N\text{-}SiH_2\text{-}Cl$ gas a molecular weight of 141.78, is liquid at room temperature and standard pressure, and has a boiling point at standard pressure between approximately 83°C and approximately 85°C.

[00134] 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 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 (%)