- the N-H free, C-free, and Si-rich perhydropolysilazane composition having an average molecular weight Mn ranging from approximately 17,000 to approximately 80,000;
- the N-H free, C-free, and Si-rich perhydropolysilazane composition having an average molecular weight Mn ranging from approximately 20,000 to approximately 50,000;
- the N-H free, C-free, and Si-rich perhydropolysilazane composition having no –Si(-)(H)-;
- the N-H free, C-free, and Si-rich perhydropolysilazane composition having a SiH_2:SiH_3 ratio ranging from approximately 1 to approximately 5; or
- the N-H free, C-free, and Si-rich perhydropolysilazane composition having an average molecular weight Mn preferably from approximately 3.5 to approximately 4.5.

In one aspect, there is provided a N-H free, C-free, and Si-rich perhydropolysilazane composition comprising perhydropolysilazane molecules having N-H free repeating units having the formula $[-N(SiH_3)_x(SiH_2-)_y]$, wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3; the N-H free, C-free, and Si-rich perhydropolysilazane composition being a liquid at standard temperature and pressure, wherein less than 1% of the Nitrogen atoms in the perhydropolysilazane molecules of the composition have an N-H bond and wherein the molecular weight of the perhydropolysilazane molecules of the composition are greater than 332 Dalton.

Si-containing film forming compositions comprising the N-H free, C-free, and Si-rich perhydropolysilazane compositions produced by any of the methods above are also disclosed. The Si-containing film forming compositions may have one or more of the following embodiments:

- the Si-containing film forming composition being a spin-on film forming composition;
- the Si-containing film forming composition being a vapor deposition film forming composition;
- the Si-containing film forming composition consisting essentially of the N-H free, C-free, and Si-rich perhydropolysilazane;

- the Si-containing film forming composition consisting of the N-H free, C-free, and Si-rich perhydropolysilazane;
- the N-H free, C-free, and Si-rich perhydropolysilazane composition comprising N-H free repeating units having the following formula $[-N(SiH_3)_x(SiH_2-)_y]$, wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3;
- the N-H free, C-free, and Si-rich perhydropolysilazane composition consisting essentially of N-H free repeating units having the following formula $[-N(SiH_3)_x(SiH_2-)_y]$, wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3;

- the solvent being methylethylketone, cyclohexanone, 2-heptanone, or combinations thereof;
- the solvent being ethyl ether, tetrahydrofuran, or combinations thereof;
- the solvent being pyridine, xylene, methyl pyridine, or combinations thereof;
- the solvent being 2-hydroxy ethyl propionate, hydroxyl ethyl acetate, or combinations thereof;
- the solvent being the N-H free, C-free, and Si-rich perhydropolysilazane composition comprising N-H free repeating units having the following formula $[-N(SiH_3)_x(SiH_2-)_y]$, wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3;
- the solvent being the N-H free, C-free, and Si-rich perhydropolysilazane composition consisting essentially of the N-H free repeating units having the following formula $[-N(SiH_3)_x(SiH_2-)_y]$, wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3;
- the solvent being the N-H free, C-free, and Si-rich perhydropolysilazane composition consisting of the N-H free repeating units having the following formula $[-N(SiH_3)_x(SiH_2-)_y]$, wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3;
- the Si-containing film forming composition comprising a solid N-H free, C-free, and Si-rich perhydropolysilazane composition dissolved or dispersed in a liquid N-H free and Si-rich perhydropolysilazane composition;
- the Si-containing film forming composition consisting essentially of a solid N-H free, C-free, and Si-rich perhydropolysilazane composition dissolved or dispersed in a liquid N-H free, C-free, and Si-rich perhydropolysilazane composition;
- the Si-containing film forming composition consisting of a solid N-H free, C-free, and Si-rich perhydropolysilazane composition dissolved or dispersed in a liquid N-H free, C-free, and Si-rich perhydropolysilazane composition.

In another aspect, there is provided a spin-on Si-containing film forming composition comprising a N-H free, C-free, and Si-rich perhydropolysilazane having N-H free repeating units having the formula $[-N(SiH_3)_x(SiH_2-)_y]$, wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3, the spin-on Si-containing film forming composition being a liquid at standard temperature and

pressure; and wherein the N-H free, C-free, and Si-rich perhydropolysilazane has no –Si(-)(H)- and a SiH_2:SiH_3 ratio ranging from 1 to 5, preferably from 3.5 to 4.5, wherein less than 1% of the Nitrogen atoms in the perhydropolysilazane molecules of the composition have an N-H bond and wherein the molecular weight of the perhydropolysilazane molecules of the composition are greater than 332 Dalton.

Also disclosed are processes for the deposition of silicon-containing films on substrates. The Si-containing film forming compositions disclosed above are introduced into a reactor having a substrate disposed therein. At least part of the N-H free, C-free, and Si-rich perhydropolysilazane composition is deposited onto the

- the silicon oxide film having a thickness between approximately 15 nm and approximately 30 nm;
- the silicon-containing film being a silicon nitride (Si_uN_v, wherein each of u and v is an integer which inclusively range from 1 to 6); or
- the silicon nitride being Si_3N_4.

Also disclosed are coating methods of forming Si-containing films on substrates. The Si-containing film forming compositions disclosed above are contacted with the substrate and the Si-containing film formed via a spin coating, spray coating, dip coating, or slit coating technique. The disclosed methods may include the following aspects:

- forming the Si-containing film via a spin coating technique;
- forming the Si-containing film via a spray coating technique;
- forming the Si-containing film via a dip coating technique;
- forming the Si-containing film via a slit coating technique;
- thermal curing the Si-containing film;
- photon curing the Si-containing film;
- annealing the Si-containing film;
- laser treating the Si-containing film;
- the Si-containing film being SiO_2;
- the SiO_2 film having a wet etch rate ranging from approximately 1 to approximately 5 as compared to thermal oxide grown at 1100°C;
- the SiO_2 film having a wet etch rate ranging from approximately 1 to approximately 3 as compared to thermal oxide grown at 1100°C;
- the Si-containing film being SiN;
- the Si-containing film being SiON;
- the substrate comprising trenches having an aspect ratio ranging from approximately 1:1 to approximately 1:100; or
- the trenches having a critical dimension ranging from approximately 10nm to approximately 1 micron.

In another aspect, there is provided a method of forming a Si-containing film on a substrate, the method comprising contacting the spin-on Si-containing film forming composition as described herein with the substrate via a spin coating, spray coating, dip coating, or slit coating technique to form the Si-containing film.

Notation and Nomenclature

Certain abbreviations, symbols, and terms are used throughout the following description and claims, and include:

We claim:

1. A N-H free, C-free, and Si-rich perhydropolysilazane composition comprising perhydropolysilazane molecules having N-H free repeating units having the formula [-N(SiH_3)$_x$(SiH_2-)$_y$], wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3; the N-H free, C-free, and Si-rich perhydropolysilazane composition being a liquid at standard temperature and pressure~~.~~, wherein less than 1% of the Nitrogen atoms in the perhydropolysilazane molecules of the composition have an N-H bond and wherein the molecular weight of the perhydropolysilazane molecules of the composition are greater than 332 Dalton.

2. The N-H free, C-free, and Si-rich perhydropolysilazane composition of claim 1, the composition having a Si:N ratio ranging from 1.5:1 to 2.5:1.

3. The N-H free, C-free, and Si-rich perhydropolysilazane composition of claim 1, the composition having no –Si(-)(H)- and a SiH_2:SiH_3 ratio ranging from 1 to 5, preferably from 3.5 to 4.5.

4. A spin-on Si-containing film forming composition comprising a N-H free, C-free, and Si-rich perhydropolysilazane having N-H free repeating units having the formula [-N(SiH_3)$_x$(SiH_2-)$_y$], wherein x=0, 1, or 2 and y= 0, 1, or 2 with x+y=2 ; and x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3, the spin-on Si-containing film forming composition being a liquid at standard temperature and pressure; and wherein the N-H free, C-free, and Si-rich perhydropolysilazane has no –Si(-)(H)- and a SiH_2:SiH_3 ratio ranging from 1 to 5, preferably from 3.5 to 4.5, wherein less than 1% of the Nitrogen atoms in the perhydropolysilazane molecules of the composition have an N-H bond and wherein the molecular weight of the perhydropolysilazane molecules of the composition are greater than 332 Dalton.

5. The spin-on Si-containing film forming composition of claim 4, the N-H free, C-free, and Si-rich perhydropolysilazane composition having a Si:N ratio ranging from 1.5:1 to 2.5:1.

6. The spin-on Si-containing film forming composition of claim 5 further comprising a solvent or a solvent system.

7. The spin-on Si-containing film forming composition of claim 6, wherein the solvent or the solvent system comprises hydrocarbons, ketones, ethers, amines, esters, or combinations thereof.

8. The spin-on Si-containing film forming composition of claim 6, wherein the solvent or the solvent system comprises benzene, toluene, xylene, n-hexane, mesitylene, methylethylketone, cyclohexanone, 2-heptanone, ethyl ether, tetrahydrofuran, pyridine, xylene, methyl pyridine, 2-hydroxy ethyl propionate, hydroxyl ethyl acetate, or combinations thereof.

9. A method of forming a Si-containing film on a substrate, the method comprising contacting the spin-on Si-containing film forming composition of any one of claims 4 to 8 with the substrate via a spin coating, spray coating, dip coating, or slit coating technique to form the Si-containing film.

10. The method of claim 9, wherein the substrate comprises trenches having an aspect ratio ranging from 1:1 to 1:100.

11. The method of claim 10, wherein the trenches have a critical dimension ranging from 10 nm to 1 micron.

12. The method of any one of claims 9 to 11, wherein the Si-containing film is SiO_2 having a wet etch rate ranging from 1 to 5 as compared to thermal oxide grown at 1100°C, preferably ranging from 1 to 3.