

**What is claimed is:**

1. A Si-containing film forming composition comprising a catalyst and a N-H free, C-free, and Si-rich perhydropolysilazane having a molecular weight ranging from approximately 332 dalton to approximately 100,000 dalton and comprising N-H free repeating units having the formula  $[-N(SiH_3)_x(SiH_2-)_y]$ , wherein  $x=0, 1, \text{ or } 2$  and  $y=0, 1, \text{ or } 2$  with  $x+y=2$ ; and  $x=0, 1 \text{ or } 2$  and  $y=1, 2, \text{ or } 3$  with  $x+y=3$ .
2. The Si-containing film forming composition of claim 1, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has a Si:N ratio ranging from approximately 1.5:1 to approximately 2.5:1.
3. The Si-containing film forming composition of claim 1, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has an average molecular weight  $M_n$  ranging from approximately 500 to approximately 100,000, preferably from approximately 3,000 to approximately 80,000, more preferably from 5000 to 50,000.
4. The Si-containing film forming composition of claim 1, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has no  $-Si(-)(H)-$  and a  $SiH_2:SiH_3$  ratio ranging from approximately 1 to approximately 5, preferably from approximately 3.5 to approximately 4.5.
5. The Si-containing film forming composition of claim 1, wherein the N-H free, C-free, and Si-rich perhydropolysilazane is a liquid at standard temperature and pressure.
6. The Si-containing film forming composition of claim 1, wherein the catalyst is a desilylative coupling catalyst.
7. The Si-containing film forming composition of claim 1, wherein the catalyst is a dehydrocoupling catalyst.

8. The Si-containing film forming composition of claim 7, wherein the catalyst has the formula  $ML_4$ , with M being a Group IV or Group V element and each L independently being selected from the group consisting of  $NR_2$ , OR,  $R_5Cp$ ,  $N^{R,R'}$ ,  $R''$ -amd, beta-diketonate, iminoketonate, diiminate, and combinations thereof, with R, R' and R'' independently being H, a C1-C4 hydrocarbon, or a trialkylsilyl group.
9. The Si-containing film forming composition of claim 1, wherein the catalyst is both a desilylative coupling and dehydrocoupling catalyst.
10. The Si-containing film forming composition of claim 9, wherein the catalyst is a metal carbonyl or a metal carbonyl containing molecule, the metal being selected from Co, Ni, Ru, Fe, Rh, Os.
11. The Si-containing film forming composition of claim 10, wherein the catalyst is  $Co_2(CO)_8$ .
12. The Si-containing film forming composition of any one of claims 1 to 11, further comprising a polysilane.
13. The Si-containing film forming composition of claim 12, wherein the polysilane has the formula  $Si_xH_{(2x+2)}$ , wherein x ranges from approximately 4 to approximately 50, preferably from approximately 10 to approximately 40, and more preferably from approximately 15 to approximately 30.
14. The Si-containing film forming composition of claim 12, wherein the polysilane has the formula  $Si_nH_{2n+1-m}(NR_2)_m$ , with each R independently H or a C1-C4 hydrocarbon; m is 1 or 2; and n ranges from approximately 3 to approximately 50, preferably from approximately 10 to approximately 40, and more preferably from approximately 15 to approximately 30.
15. A Si-containing film forming composition comprising a polysilane and a N-H free, C-free, and Si-rich perhydropolysilazane having a molecular weight ranging from approximately 332 dalton to approximately 100,000 dalton and comprising N-

H free repeating units having the formula  $[-N(SiH_3)_x(SiH_2-)_y]$ , wherein  $x=0, 1, \text{ or } 2$  and  $y=0, 1, \text{ or } 2$  with  $x+y=2$ ; and  $x=0, 1 \text{ or } 2$  and  $y=1, 2, \text{ or } 3$  with  $x+y=3$ .

16. The Si-containing film forming composition of claim 15, wherein the N-H  
5 free, C-free, and Si-rich perhydropolysilazane has a Si:N ratio ranging from approximately 1.5:1 to approximately 2.5:1.

17. The Si-containing film forming composition of claim 15, wherein the N-H  
10 free, C-free, and Si-rich perhydropolysilazane has an average molecular weight Mn ranging from approximately 500 to approximately 100,000, preferably from approximately 3,000 to approximately 80,000, more preferably 5,000 to 50,000.

18. The Si-containing film forming composition of claim 15, wherein the N-H  
15 free, C-free, and Si-rich perhydropolysilazane has no  $-Si(-)(H)-$  and a  $SiH_2:SiH_3$  ratio ranging from approximately 1 to approximately 5, preferably from approximately 3.5 to approximately 4.5.

19. The Si-containing film forming composition of claim 15, wherein the N-H  
20 free, C-free, and Si-rich perhydropolysilazane is a liquid at standard temperature and pressure.

20. The Si-containing film forming composition of claim 15, wherein the  
25 polysilane has the formula  $Si_xH_{(2x+2)}$ , wherein  $x$  ranges from approximately 4 to approximately 50, preferably from approximately 10 to approximately 40, and more preferably from approximately 15 to approximately 30.

21. The Si-containing film forming composition of claim 15, wherein the  
30 polysilane has the formula  $Si_nH_{2n+1-m}(NR_2)_m$ , with each R independently H or a C1-C4 hydrocarbon;  $m$  is 1 or 2; and  $n$  ranges from approximately 3 to approximately 50, preferably from approximately 10 to approximately 40, and more preferably from approximately 15 to approximately 30.

22. The Si-containing film forming composition of any one of claims 15 or 21, further comprising a catalyst.
23. The Si-containing film forming composition of claim 22, wherein the catalyst  
5 is a desilylative coupling catalyst.
24. The Si-containing film forming composition of claim 22, wherein the catalyst is a dehydrocoupling catalyst.
- 10 25. The Si-containing film forming composition of claim 24, wherein the catalyst has the formula  $ML_4$ , with M being a Group IV or Group V element and each L independently being selected from is selected from the group consisting of  $NR_2$ , OR,  $R_5Cp$ ,  $N^{R,R'}R''$ -amd, beta-diketonate, iminoketonate, diiminate, and combinations thereof, with R, R' and R'' independently being H, a C1-C4  
15 hydrocarbon, or a trialkylsilyl group.
26. The Si-containing film forming composition of claim 22, wherein the catalyst is both a desilylative coupling and dehydrocoupling catalyst.
- 20 27. The Si-containing film forming composition of claim 26, wherein the catalyst is a metal carbonyl or a metal carbonyl containing molecule, the metal being selected from Co, Ni, Ru, Fe, Rh, Os.
28. The Si-containing film forming composition of claim 27, wherein the catalyst  
25 is  $Co_2(CO)_8$ .
29. A Si oxide film forming composition comprising a catalyst and a N-H free, C-free, and Si-rich perhydropolysilazane having a molecular weight ranging from approximately 332 dalton to approximately 100,000 dalton and comprising N-H  
30 free repeating units having the formula  $[-N(SiH_3)_x(SiH_2-)_y]$ , wherein  $x=0, 1, \text{ or } 2$  and  $y=0, 1, \text{ or } 2$  with  $x+y=2$ ; and  $x=0, 1 \text{ or } 2$  and  $y=1, 2, \text{ or } 3$  with  $x+y=3$ .

30. The Si oxide film forming composition of claim 29, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has a Si:N ratio ranging from approximately 1.5:1 to approximately 2.5:1.
- 5 31. The Si oxide film forming composition of claim 29, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has an average molecular weight  $M_n$  ranging from approximately 500 to approximately 100,000, preferably from approximately 3,000 to approximately 80,000, more preferably 5,000 to 50,000.
- 10 32. The Si oxide film forming composition of claim 29, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has no  $-\text{Si}(-)(\text{H})-$  and a  $\text{SiH}_2:\text{SiH}_3$  ratio ranging from approximately 1 to approximately 5, preferably from approximately 3.5 to approximately 4.5.
- 15 33. The Si oxide film forming composition of claim 29, wherein the N-H free, C-free, and Si-rich perhydropolysilazane is a liquid at standard temperature and pressure.
- 20 34. The Si oxide film forming composition of claim 29, wherein the catalyst is a desilylative coupling catalyst.
35. The Si oxide film forming composition of claim 29, wherein the catalyst is a dehydrocoupling catalyst.
- 25 36. The Si oxide film forming composition of claim 35, wherein the catalyst has the formula  $\text{ML}_4$ , with M being a Group IV or Group V element and each L independently being selected from is selected from the group consisting of  $\text{NR}_2$ , OR,  $\text{R}_5\text{Cp}$ ,  $\text{N}^{\text{R}}, \text{R}'$  R''-amd, beta-diketonate, iminoketonate, diiminate, and combinations thereof, with R, R' and R'' independently being H, a C1-C4 hydrocarbon, or a trialkylsilyl group.
- 30 37. The Si oxide film forming composition of claim 29, wherein the catalyst is both a desilylative coupling and dehydrocoupling catalyst.

38. The Si oxide film forming composition of claim 37, wherein the catalyst is a metal carbonyl or a metal carbonyl containing molecule, the metal being selected from Co, Ni, Ru, Fe, Rh, Os.
- 5 39. The Si oxide film forming composition of claim 38, wherein the catalyst is  $\text{Co}_2(\text{CO})_8$ .
40. The Si oxide film forming composition of any one of claims 29 to 39, further comprising a polysilane.
- 10 41. The Si oxide film forming composition of claim 40, wherein the polysilane has the formula  $\text{Si}_x\text{H}_{(2x+2)}$ , wherein x ranges from approximately 4 to approximately 50, preferably from approximately 10 to approximately 40, and more preferably from approximately 15 to approximately 30.
- 15 42. The Si oxide film forming composition of claim 40, wherein the polysilane has the formula  $\text{Si}_n\text{H}_{2n+1-m}(\text{NR}_2)_m$ , with each R independently H or a C1-C4 hydrocarbon; m is 1 or 2; and n ranges from approximately 3 to approximately 50, preferably from approximately 10 to approximately 40, and more preferably from approximately 15 to approximately 30.
- 20 43. A Si oxide film forming composition comprising a polysilane and a N-H free, C-free, and Si-rich perhydropolysilazane having a molecular weight ranging from approximately 332 dalton to approximately 100,000 dalton and comprising N-H free repeating units having the formula  $[-\text{N}(\text{SiH}_3)_x(\text{SiH}_2)_y]$ , wherein  $x=0, 1, \text{ or } 2$  and  $y=0, 1, \text{ or } 2$  with  $x+y=2$ ; and  $x=0, 1 \text{ or } 2$  and  $y=1, 2, \text{ or } 3$  with  $x+y=3$ .
- 25 44. The Si oxide film forming composition of claim 43, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has a Si:N ratio ranging from approximately 1.5:1 to approximately 2.5:1.
- 30 45. The Si oxide film forming composition of claim 43, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has an average molecular weight  $M_n$

ranging from approximately 500 to approximately 100,000, preferably from approximately 3,000 to approximately 80,000, more preferably 5,000 to 50,000.

46. The Si oxide film forming composition of claim 43, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has no  $-\text{Si}(-)(\text{H})-$  and a  $\text{SiH}_2:\text{SiH}_3$  ratio ranging from approximately 1 to approximately 5, preferably from approximately 3.5 to approximately 4.5.

47. The Si oxide film forming composition of claim 43, wherein the N-H free, C-free, and Si-rich perhydropolysilazane is a liquid at standard temperature and pressure.

48. The Si oxide film forming composition of claim 43, wherein the polysilane has the formula  $\text{Si}_x\text{H}_{(2x+2)}$ , wherein x ranges from approximately 4 to approximately 50, preferably from approximately 10 to approximately 40, and more preferably from approximately 15 to approximately 30.

49. The Si oxide film forming composition of claim 43, wherein the polysilane has the formula  $\text{Si}_n\text{H}_{2n+1-m}(\text{NR}_2)_m$ , with each R independently H or a C1-C4 hydrocarbon; m is 1 or 2; and n ranges from approximately 3 to approximately 50, preferably from approximately 10 to approximately 40, and more preferably from approximately 15 to approximately 30.

50. The Si oxide film forming composition of any one of claims 43 or 49, further comprising a catalyst.

51. The Si oxide film forming composition of claim 50, wherein the catalyst is a desilylative coupling catalyst.

52. The Si oxide film forming composition of claim 50, wherein the catalyst is a dehydrocoupling catalyst.

53. The Si oxide film forming composition of claim 52, wherein the catalyst has the formula  $ML_4$ , with M being a Group IV or Group V element and each L independently being selected from is selected from the group consisting of  $NR_2$ , OR,  $R_5Cp$ ,  $N^{R,R'}$ -amd, beta-diketonate, iminoketonate, diiminate, and combinations thereof, with R, R' and R'' independently being H, a C1-C4 hydrocarbon, or a trialkylsilyl group.

54. The Si oxide film forming composition of claim 50, wherein the catalyst is both a desilylative coupling and dehydrocoupling catalyst.

55. The Si oxide film forming composition of claim 54, wherein the catalyst is a metal carbonyl or a metal carbonyl containing molecule, the metal being selected from Co, Ni, Ru, Fe, Rh, Os

56. The Si oxide film forming composition of claim 55, wherein the catalyst is  $Co_2(CO)_8$ .

57. A method of forming a Si-containing film on a substrate, the method comprising contacting the Si-containing film forming composition of any one of claims 1 to 11, 15 to 21, 29-39, or 43-49 with the substrate via a spin coating, spray coating, dip coating, or slit coating technique to form the Si-containing film.

58. The method of claim 57, wherein the substrate comprises trenches having an aspect ratio ranging from approximately 1:1 to approximately 1:100.

59. The method of claim 58, wherein the trenches have a critical dimension ranging from approximately 10 nm to approximately 1 micron.

60. The method of claim 57, additionally comprising exposing the film at a temperature ranging from approximately 30°C to 200°C, preferably from approximately 80°C to approximately 150°C under an inert atmosphere.

61. The method of claim 57, wherein the Si-containing film is SiO<sub>2</sub>, further comprising exposing the film to an oxidizing atmosphere comprising at least one of O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>O, or NO at a temperature ranging from 200°C to 1000°C, preferably from 300°C to 600°C.

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62. The method of claim 60, wherein the film is exposed to an oxidizing atmosphere at a temperature of approximately 400°C.

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63. The method of claim 60 or 61, wherein the Si-containing film is SiO<sub>2</sub> having a wet etch rate ranging from approximately 1 to approximately 5 as compared to thermal oxide grown at 1100°C, preferably ranging from approximately 1 to approximately 3.

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64. The method of any one of claims 57 to 61, wherein the Si-containing film is SiO<sub>2</sub> having a shrinkage ranging from approximately -5% to approximately 15%, preferably 0-10%, and more preferably 0-5% thickness.