then form Si-OH groups and NH_3. The Si-OH groups would then condense to form Si-O-Si bridges. However, no shrinkage data were reported. The fact that the film has a low dielectric constant is also an indication of the low film density, and/or the remain of large quantities on Si-H bonds and N-H in the film. Such films are typically etched very rapidly in dilute HF solution and are not suitable for gapfill spin on applications like shallow trench isolation or pre-metal dielectrics in advanced semiconductor device, where high quality silicon oxide having a wet etch rate as close as possible to a thermal oxide (i.e. SiO2 formed by the thermal oxidation of Si under O2/H2O vapor at elevated temperature, typically > 800°C) film are sought.

Bae et al. Proc. of SPIE, 2014, p. 90511 reported using proprietary amines as an additive for promoting the oxidation of PHPS at low temperature (400-600°C) to silicon oxide films. However, it is expected that the amines will interact and react with the PHPS during the curing process and chemically bind to the polymer, yielding C contaminated films. For semiconductor applications, the absence of C contamination is strongly desired (typically <5 at.%, and more preferably <1 at.%).

US Pat App Pub No 2010/0184268 A1 claims a method for producing a semiconductor device comprising: coating the coating composition for forming an oxide film comprising: a polysilazane and a polysilane on a substrate and forming the oxide film inside the groove by heat treatment in an oxidizing atmosphere. The formulas of polysilazane $(SiH_2NH)_n$ (n – positive integer) and polysilane Si_nR_{2n+2} and Si_nR_{2n} (n ≥ 3, R - hydrogen) are mentioned only in embodiment.

A silicon-based coating composition, comprising: of a) polysilazane $[H_2Si\text{-}NH]_n$, b) polysiloxane, c) polysilane of a formula $(R^1R^2Si)_n$, wherein n is greater than 1, R^1, R^2 – organic group and d) organic solvent is claimed in US Pat No 9,567,488 B2. The cured coatings have a thickness between 0.1 μm and 3 μm, and having hardness between about 4H and about 9H for superior mold release characteristics.

A need remains to develop new compositions, formulations, and methods to further reduce PHPS film shrinkage, and equally important, to establish the understanding between additive chemistry and shrinkage.

Summary

In one aspect, there is provided a Si-containing film forming composition comprising a) a dehydrocoupling catalyst, wherein the dehydrocoupling catalyst having 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 C_1-C_4 hydrocarbon, or a trialkylsilyl group; and b) a N-H free, C-free, and Si-rich perhydropolysilazane having a molecular weight ranging from ~~approximately~~ 500 dalton to ~~approximately~~ 1,000,000 dalton and comprising 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 terminal groups having x= 0, 1 or 2 and y=1, 2, or 3 with x+y=3.

In another aspect, there is provided a method of forming a Si-containing film on a substrate, the method comprising contacting the 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.

What is claimed is:

1. A Si-containing film forming composition comprising

a) a dehydrocoupling catalyst, the dehydrocoupling catalyst having 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 C_1-C_4 hydrocarbon, or a trialkylsilyl group; and

b) a N-H free, C-free, and Si-rich perhydropolysilazane having a molecular weight ranging from ~~approximately~~ 500 dalton to ~~approximately~~ 1,000,000 dalton and comprising 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 terminal groups having x= 0, 1 or 2 and y=1, 2, 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 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.

4. The Si-containing film forming composition of claim 1, further comprising a desilylative coupling catalyst.

5. The Si-containing film forming composition of any one of claims 1 to 4,wherein the N-H free, C-free, and Si-rich perhydropolysilazane has a molecular weight ranging from ~~approximately~~ 1000 dalton to ~~approximately~~ 200,000 dalton.

6. The Si-containing film forming composition of any one of claims 1 to 4, wherein the N-H free, C-free, and Si-rich perhydropolysilazane has a molecular weight ranging from ~~approximately~~ 3000 dalton to ~~approximately~~ 100,000 dalton.

7. The Si-containing film forming composition of any one of claims 1 to 4, further comprising a polysilane.

8. The Si-containing film forming composition of claim 7, wherein the polysilane has a 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, or a formula

$$Si_nH_{2n+1-m}(NR_2)_m,$$

where each R independently H or a C_1-C_4 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.

9. 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 4 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 ~~approximately~~ 1:1 to ~~approximately~~ 1:100.

11. The method of claim 9, further comprising exposing the Si-containing 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.

12. The method of claim 11, further comprising exposing the Si-containing film to an oxidizing atmosphere comprising at least one of O_2, O_3, H_2O_2, H_2O, N_2O, or NO at a temperature ranging from 200°C to 1000°C, preferably from 300°C to 600°C.