[0010] US20070160774 or JP 2005213633 patent application to Tsukada *et al*. discloses SiN films formed by an aminosilane gas represented by $(H)_n$-Si-$[N(R^1)_2]_{4-n}$ (R^1 = H, C_{1-4} alkyl, trimethylsilyl; n = 0-3; all of R are not H) and a hydrazine gas represented by $N_2(H)_{4-x}(R^2)_x$ (R^2= Me, Et, Ph; x = 0-4) in a CVD chamber at low temperature without generation of ammonium chloride.

[0011] Discovery of new and novel ALD precursors that are applicable to the ALD processes at high temperatures, typically > 500°C, and preferably around 700°C or higher, is challenging, since their applications to ALD processes achievable at higher temperatures require high step coverage (SC) and low wet etch rate (WER). Thus, there are needs to provide such precursors to meet these requirements.

Summary

[0012] Disclosed are methods to form a Si-containing film on a substrate. The method comprises the steps of heating the substrate in a reactor to a temperature of 550°C or higher, exposing the substrate to a vapor including a Si-containing film forming composition that contains a Si-containing precursor having the formula:

$$SiR^1_yR^2_{4-x-y}(NH\text{-}SiR'_3)_x,$$

wherein x=2, 3, 4; y=0, 1, 2, R^1 and R^2 each are independently selected from H, a halogen (Cl, Br, I), an C_1-C_4 alkyl, an isocyanate, a C_1-C_4 alkoxide, or an $–NR^3R^4$ group in which R^3 and R^4 each are independently selected from H, a C_1-C_4 alkyl, provided that if R^3 = H, R^4 > C_1; each R' is independently selected from H, a halogen (Cl, Br, I), or a C_1-C_4 alkyl, and depositing at least part of the Si-containing precursor onto the substrate to form the Si-containing film on the substrate through an ALD process.

[0012a] In one aspect, there is provided a method for forming a Si-containing film on a substrate, the method comprising the steps of heating the substrate in a reactor to a temperature of higher than 550°C; exposing the substrate to a vapor including a Si-containing film forming composition that contains a Si-containing precursor having the formula:

$$SiR^1_yR^2_{4-x-y}(NH\text{-}SiR'_3)_x,$$

wherein x=2, 3, 4; y=0, 1, 2, R^1 and R^2 each are independently selected from H, Cl, Br, I, an C_1-C_4 alkyl, an isocyanate, a C_1-C_4 alkoxide, or an $–NR^3R^4$ group in which R^3 and R^4 each are independently selected from H, a C_1-C_4 alkyl, provided that if R^3=H, R^4> C_1; each R' is independently selected from H, Cl, Br, I, or a C_1-C_4 alkyl; and

depositing at least part of the Si-containing precursor onto the substrate to form the Si-containing film on the substrate through an atomic layer deposition (ALD) process.

[0013] Also, the method comprises the steps of heating a substrate in a reactor to a temperature of higher than 550°C, and forming a chemisorbed and/or physisorbed film, on the surface of the substrate, of a Si-containing precursor having the formula:

$$SiR^1_yR^2_{4-x-y}(NH\text{-}SiR'_3)_x,$$

wherein x=2, 3, 4; y=0, 1, 2, R^1 and R^2 each are independently selected from H, a halogen (Cl, Br, I), an C_1-C_4 alkyl, an isocyanate, a C_1-C_4 alkoxide, or an $–NR^3R^4$ group in which R^3 and R^4 each are independently selected from H, a C_1-C_4 alkyl, provided that if R^3 = H, R^4 > C_1; each R' is independently selected from H, a halogen (Cl, Br, I), or a C_1-C_4 alkyl.

[0014] The disclosed methods may include one or more of the following aspects:

include one or more of the following aspects:

- the Si-containing precursor being selected from $SiH_2(NH\text{-}Si(CH_3)_3)_2$, $SiH(NH\text{-}Si(CH_3)_3)_3$, $SiHCl(NH\text{-}Si(CH_3)_3)_2$, $SiCl_2(NH\text{-}Si(CH_3)_3)_2$, $SiCl(NH\text{-}Si(CH_3)_3)_3$, or $Si(NH\text{-}Si(CH_3)_3)_4$;
- the Si-containing precursor being $SiH_2(NH\text{-}Si(CH_3)_3)_2$;
- the Si-containing precursor being $SiH(NH\text{-}Si(CH_3)_3)_3$;
- the Si-containing precursor being $SiHCl(NH\text{-}Si(CH_3)_3)_2$;
- the Si-containing precursor being $SiCl_2(NH\text{-}Si(CH_3)_3)_2$,;
- the Si-containing precursor being $SiCl(NH\text{-}Si(CH_3)_3)_3$;
- the Si-containing precursor being $Si(NH\text{-}Si(CH_3)_3)_4$;
- the Si-containing precursor having a purity ranging from approximately 93% w/w to approximately 100% w/w; and
- the Si-containing precursor having a purity ranging from approximately 99% w/w to approximately 99.999% w/w.

[0015a] In another aspect, there is provided a composition for deposition of a film comprising a Si-containing precursor having the formula:

$$SiR^1_yR^2_{4-x-y}(NH\text{-}SiR'_3)_x,$$

wherein x= 3, 4; y=0, 1, 2, R^1 and R^2 each are independently selected from H, a halogen (Cl, Br, I), an C_1-C_4 alkyl, an isocyanate, a C_1-C_4 alkoxide, or an $–NR^3R^4$ group in which R^3 and R^4 each are independently selected from H, a C_1-C_4 alkyl, provided that if R^3=H, R^4> C_1; each R' is independently selected from H, a halogen (Cl, Br, I), or a C_1-C_4 alkyl, provided that if x=3 and y=1, $R_1 \neq H$.

Notation and Nomenclature

[0016] The following detailed description and claims utilize a number of abbreviations, symbols, and terms, which are generally well known in the art, and include:

[0017] As used herein, the indefinite article “a” or “an” means one or more.

[0018] As used herein, “about” or “around” or “approximately” in the text or in a claim means ±10% of the value stated.

[0019] As used herein, “room temperature” in the text or in a claim means from approximately 20°C to approximately 25°C.

[0020] The term “ambient temperature” refers to an environment temperature

approximately 20°C to approximately 25°C.

[0021] As used in the disclosed embodiments, the term “independently” when used in the context of describing R groups should be understood to denote that the subject R group is not only independently selected relative to other R groups bearing the same or different subscripts or superscripts, but is also independently selected relative to any additional species of that same R group. For example in the formula $MR^1_x(NR^2R^3)_{(4-x)}$, where x is 2 or 3, the two or three R^1 groups may, but need not be identical to each other or to R^2 or to R^3. Further, it should be understood that unless

What is claimed is

1. A method for forming a Si-containing film on a substrate, the method comprising the steps of:

heating the substrate in a reactor to a temperature of higher than 550°C ~~or higher~~;

exposing the substrate to a vapor including a Si-containing film forming composition that contains a Si-containing precursor having the formula:

$$SiR^1_yR^2_{4-x-y}(NH\text{-}SiR'_3)_x,$$

wherein x=2, 3, 4; y=0, 1, 2, R^1 and R^2 each are independently selected from H, ~~a halogen (~~Cl, Br, I~~)~~, an C_1-C_4 alkyl, an isocyanate, a C_1-C_4 alkoxide, or an $–NR^3R^4$ group in which R^3 and R^4 each are independently selected from H, a C_1-C_4 alkyl, provided that if R^3=H, R^4> C_1; each R' is independently selected from H, ~~a halogen (~~Cl, Br, I~~)~~, or a C_1-C_4 alkyl; and

depositing at least part of the Si-containing precursor onto the substrate to form the Si-containing film on the substrate through an atomic layer deposition (ALD) process.

2. The method of claim 1, further comprising the step of exposing the substrate to a co-reactant.

3. The method of claim 2, wherein the co-reactant is selected from O_3, O_2, H_2O, NO, N_2O, NO_2, H_2O_2, O radicals and combinations thereof.

4. The method of claim 2, wherein the co-reactant is selected from NH_3, NO, N_2O, hydrazines, N_2 plasma, N_2/H_2 plasma, NH_3 plasma, amines and combinations thereof.

5. The method of any of claims 1 to 4, further comprising the step of heating the substrate to a temperature greater than 550°C to no more than 650°C.

6. The method of any of claims 1 to 4, further comprising the step of heating the substrate to a temperature greater than 550°C to no more than 750°C.

7. The method of claim 1, wherein the silicon-containing film is a silicon oxide layer.

8. The method of claim 7, wherein a WER of the silicon oxide film as deposited, normalized with thermal SiO_2, is from 2 to 4.

9. The method of any of claims 1 to 4, wherein the Si-containing precursor is selected from $SiH_2(NH\text{-}Si(CH_3)_3)_2$, $SiH(NH\text{-}Si(CH_3)_3)_3$, $SiHCl(NH\text{-}Si(CH_3)_3)_2$, $SiCl_2(NH\text{-}Si(CH_3)_3)_2$, $SiCl(NH\text{-}Si(CH_3)_3)_3$, or $Si(NH\text{-}Si(CH_3)_3)_4$.

10. The method of any of claims 1 to 4, wherein the precursor is $H_2Si(NH\text{-}SiMe_3)_2$.

11. The method of any of claims 1 to 4, wherein the precursor is $HSi(NH\text{-}SiMe_3)_3$.

12. The method of any of claims 1 to 4, wherein the precursor is $Si(NH\text{-}SiMe_3)_4$.

13. The method of any of claims 1 to 4, wherein the ALD process is a thermal ALD.

14. A composition for deposition of a film comprising a Si-containing precursor having the formula:

$$SiR^1_yR^2_{4-x-y}(NH\text{-}SiR'_3)_x,$$

wherein x=~~2,~~ 3, 4; y=0, 1, 2, R^1 and R^2 each are independently selected from H, a halogen (Cl, Br, I), an C_1-C_4 alkyl, an isocyanate, a C_1-C_4 alkoxide, or an $–NR^3R^4$ group in which R^3 and R^4 each are independently selected from H, a C_1-C_4 alkyl, provided that if R^3=H, R^4> C_1; each R' is independently selected from H, a halogen (Cl, Br, I), or a C_1-C_4 alkyl, provided that ~~if x=2 and y=1, R_1=H, R_2≠H or R_2=H, R_1≠H; or~~ if x=3 and y=1, R_1≠H.

15. The composition of claim 14, wherein the Si-containing precursor is selected from ~~$SiH_2(NH\text{-}Si(CH_3)_3)_2$,~~ $SiH(NH\text{-}Si(CH_3)_3)_3$, ~~$SiHCl(NH\text{-}Si(CH_3)_3)_2$, $SiCl_2(NH\text{-}Si(CH_3)_3)_2$~~, $SiCl(NH\text{-}Si(CH_3)_3)_3$, or $Si(NH\text{-}Si(CH_3)_3)_4$.

16. A method for forming a Si-containing film on a substrate, the method comprising the steps of:

heating a substrate in a reactor to a temperature of higher than 550°C; and

forming a chemisorbed and/or physisorbed film, on the surface of the substrate, of a Si-containing precursor having the formula:

$$SiR^1_yR^2_{4-x-y}(NH\text{-}SiR'_3)_x,$$

wherein x=2, 3, 4; y=0, 1, 2, R^1 and R^2 each are independently selected from H, a halogen (Cl, Br, I), an C_1-C_4 alkyl, an isocyanate, a C_1-C_4 alkoxide, or an $–NR^3R^4$ group in which R^3 and R^4 each are independently selected from H, a C_1-C_4 alkyl, provided that if R^3=H, R^4> C_1; each R' is independently selected from H, a halogen (Cl, Br, I), or a C_1-C_4 alkyl.

17. The method of claim 16, further comprising the step of chemically reacting the chemisorbed and/or physisorbed film comprising the Si-containing precursor with a co-reactant.

18. The method of ~~either~~ claim ~~16 or~~ 17, wherein the co-reactant reacting with the Si-containing precursor in the chemisorbed and/or physisorbed film produces a reaction product that forms a second film on the surface of the substrate.

19. The method of ~~either~~ claim ~~16 or~~ 17, wherein the co-reactant is selected from O_3, O_2, H_2O, NO, N_2O, NO_2, H_2O_2, O radicals and combinations thereof.

20. The method of ~~either~~ claim ~~16 or~~ 17, wherein the co-reactant is selected from NH_3, NO, N_2O, hydrazines, N_2 plasma, N_2/H_2 plasma, NH_3 plasma, amines and combinations thereof.