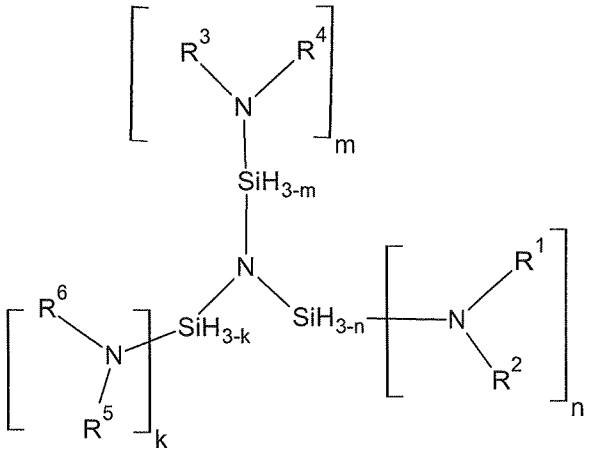
[0003] At present the standard method for producing silicon nitride films by CVD involves inducing a reaction between ammonia gas or other amine (the amino compound) and a halosilane such as chlorosilane (the silane compound); however, ammonium chloride or amine hydrochloride is produced as a by-product by this reaction. Ammonium chloride is a white solid and as such accumulates in and clogs the exhaust lines of the CVD reaction apparatus. Amine hydrochloride salts are highly undesirable contaminants in aminosilanes used for electrical applications because they can react with metals in the CVD chamber and degrade the electrical properties of the semiconductor material or lead the creation of other types of defects. More than that, these salts are known to sublimate by a dissociation-recombination process generating HCl. Hydrogen chloride is a corrosive gas that can damage any process taking place in the CVD chamber as well as the chamber itself. Reactive chlorine from these an any other sources may cause these deleterious effects.

[0004] In CVD methods, it is therefore desired to have a starting material that is halogen-free.

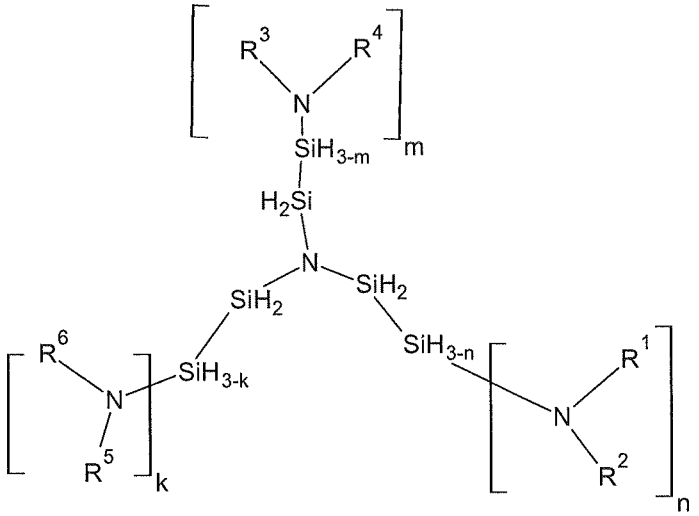
SUMMARY

In one aspect, there is provided a formula;



where n = 1 to 3; m = 0 to 3; k = 0 to 3; $R^1$, $R^3$, and $R^5$ are independently selected from the group of H, linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^2$, $R^4$, and $R^6$ are independently selected from the group of linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^1R^2N$, $R^3R^4N$ and $R^5R^6N$ can be cyclic saturated or unsaturated cyclic secondary amines independently selected from the group aziridine, azetidine, piperidine, pyrrolidine, pyrrole, imidazole, pyrazole, indole or any C-substituted derivatives of the cyclic secondary amine; and excluding compounds having the formula $C_{18}H_{48}N_4Si_3$; $C_{15}H_{41}N_3Si_3$; $C_6H_{21}NSi_3$ and $C_7H_{23}NSi_3$ or $[(SiH_3)_2N]_2SiH_2$.

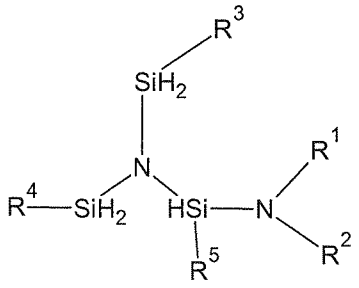
In another aspect, there is provided a compound having the formula:




where n = 1 to 3; m = 0 to 3; k = 0 to 3; $R^1$, $R^3$, and $R^5$ are independently selected from the group of H, linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-

substituted silyl; $R^2$, $R^4$, and $R^6$ are independently selected from the group of linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^1R^2N$, $R^3R^4N$ and $R^5R^6N$ can be cyclic saturated or unsaturated cyclic secondary amines independently selected from the group aziridine, azetidine, piperidine, pyrrolidine, pyrrole, imidazole, pyrazole, indole or any C-substituted derivatives of the cyclic secondary amine.

In another aspect, there is provided a compound having the formula:




where $R^1$, $R^2$ are independently selected from the group of H, linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^3$, $R^4$, and $R^5$ are independently selected from H and the group of linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, linear or branched $C_1$ to $C_6$ alkyl ether, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; and $R^1R^2N$ can be a cyclic saturated or unsaturated cyclic secondary amine selected from the group of aziridine, azetidine, piperidine, pyrrolidine, pyrrole, imidazole, pyrazole, indole or any C-substituted derivatives of the cyclic secondary amine.

In another aspect, there is provided a method of preparing the compounds described herein, comprising:

a) contacting the reactants TSA and n $R^1R^2NH$ and m $R^3R^4NH$ and k $R^5R^6NH$ in the presence of a transition metal catalyst forming a reaction mixture;

b) optionally adding a solvent to the reaction mixture;

c) maintaining the reaction mixture at a temperature between about 0 °C to about 250 °C;

d) allowing the reaction to proceed to form $(R^1R^2N)_n$ and $(R^3R^4N)_m$ $(R^5R^6N)_k$ $(NSi_3H_{(9-n-m-k)})$ + (n+m+k) $H_2$ ;

e) separating the $(R^1R^2N)_n$ and $(R^3R^4N)_m$ $(R^5R^6N)_k$ $(NSi_3H_{(9-n-m-k)})$ from the reaction mixture;

wherein the reaction mixture temperature may vary during the synthesis and is maintained such that the temperature of the reaction mixture is not allowed to drop below about 0°C and not exceed about 250 °C.

In another aspect, there is provided a method of depositing a Si containing thin film by a vapor deposition wherein the precursor compound is selected from the group of compounds described herein.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a typical reactor apparatus wherein the reaction vessel is an autoclave reactor fitted with a stirrer and connected to a manifold capable of providing vacuum and reactants.

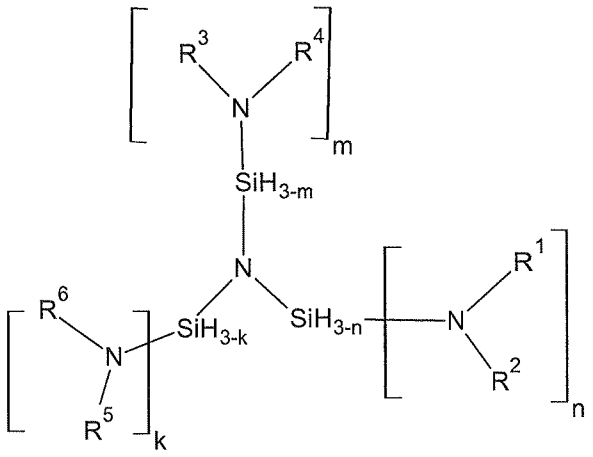
Figure 2 is a typical reactor apparatus wherein the reactor vessel is attached to a condenser allowing for hydrogen venting and a Dip-tube with filter for removal of the product.

## DETAILED DESCRIPTION OF THE INVENTION

[0005] A method for the synthesis of compounds having silicon-nitrogen bonds without the formation of halogen salt byproducts has been developed. All of the compounds produced by

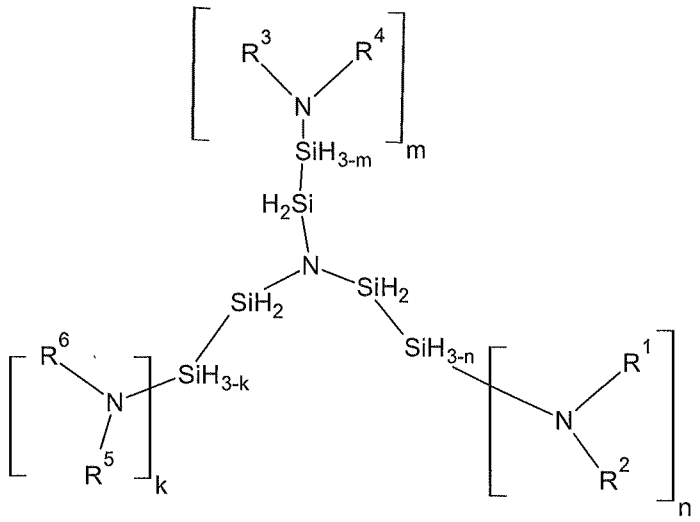
We Claim:

1. A compound having the formula;



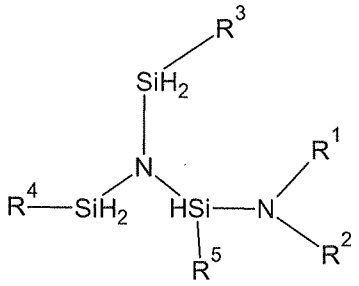
where n = 1 to 3; m = 0 to 3; k = 0 to 3; $R^1$, $R^3$, and $R^5$ are independently selected from the group of H, linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^2$, $R^4$, and $R^6$ are independently selected from the group of linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^1R^2N$, $R^3R^4N$ and $R^5R^6N$ can be cyclic saturated or unsaturated cyclic secondary amines independently selected from the group aziridine, azetidine, piperidine, pyrrolidine, pyrrole, imidazole, pyrazole, indole or any C-substituted derivatives of the cyclic secondary amine; and excluding compounds having the formula $C_{18}H_{48}N_4Si_3$; $C_{15}H_{41}N_3Si_3$; $C_6H_{21}NSi_3$ and $C_7H_{23}NSi_3$ or $[(SiH_3)_2N]_2SiH_2$.

2. A compound having the formula:



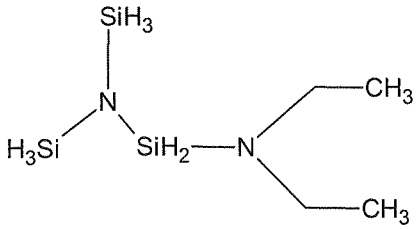
where n = 1 to 3; m = 0 to 3; k = 0 to 3; $R^1$, $R^3$, and $R^5$ are independently selected from the group of H, linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^2$, $R^4$, and $R^6$ are independently selected from the group of linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^1R^2N$, $R^3R^4N$ and $R^5R^6N$ can be cyclic saturated or unsaturated cyclic secondary amines independently selected from the group aziridine, azetidine, piperidine, pyrrolidine, pyrrole, imidazole, pyrazole, indole or any C-substituted derivatives of the cyclic secondary amine.

3. A compound having the formula:



where $R^1$, $R^2$ are independently selected from the group of H, linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; $R^3$, $R^4$, and $R^5$ are independently selected from H and the group of linear or branched $C_1$ to $C_6$ alkyl, linear or branched $C_1$ to $C_8$ alkenyl, linear or branched $C_1$ to $C_8$ alkynyl, $C_6$ to $C_{10}$ aryl, linear or branched $C_1$ to $C_6$ alkyl ether, silyl, trimethyl silyl, or linear or branched $C_1$ to $C_6$ alkyl-substituted silyl; and $R^1R^2N$ can be a cyclic saturated or unsaturated cyclic secondary amine selected from the group of aziridine, azetidine, piperidine, pyrrolidine, pyrrole, imidazole, pyrazole, indole or any C-substituted derivatives of the cyclic secondary amine.

4. The compound of claim 3 having the formula:



5. The compound of claim 3 wherein $R^1$, $R^2$ are independently selected from the group consisting of H, methyl, ethyl, iso-propyl, and t-butyl; and $NR^1R^2$ are a cyclic saturated or unsaturated cyclic amine with 3 to 8 carbon atoms selected from the group of azetidine, piperidine, pyrrolidine, pyrrole, imidazole, pyrazole, indole or any C-substituted derivatives of the cyclic secondary amine, when $R^1$ is H then $R^2$ cannot be methyl or ethyl.

6. The compound of claim 3 wherein $R^1$, $R^2$ are iso-propyl.

7. The compound of claim 3 wherein $R^1$, $R^2$ are ethyl.

8. A method of preparing the compounds according to claim 1, comprising:

a) contacting the reactants TSA and n $R^1R^2NH$ and m $R^3R^4NH$ and k $R^5R^6NH$ in the presence of a transition metal catalyst forming a reaction mixture;

b) optionally adding a solvent to the reaction mixture;

c) maintaining the reaction mixture at a temperature between about 0 °C to about 250 °C;

d) allowing the reaction to proceed to form $(R^1R^2N)_n$ and $(R^3R^4N)_m$ $(R^5R^6N)_k$ $(NSi_3H_{(9-n-m-k)})$ + $(n+m+k)$ $H_2$ ;

e) separating the $(R^1R^2N)_n$ and $(R^3R^4N)_m$ $(R^5R^6N)_k$ $(NSi_3H_{(9-n-m-k)})$ from the reaction mixture;

wherein the reaction mixture temperature may vary during the synthesis and is maintained such that the temperature of the reaction mixture is not allowed to drop below about 0°C and not exceed about 250 °C.

9. The method of claim 8 wherein the transition metal catalyst is selected from the group consisting of Ru, Pd, Rh, Ir, Fe, Ni, Pt, Cr, Cu and Au.