- The SAM precursor containing less than 0.1% v/v of any of its undesired congeneric species, reactants, or other reaction products;
- The SAM precursor containing less than 0.01% v/v of any of its undesired congeneric species, reactants, or other reaction products;
- The SAM precursor containing between 5% v/v and 50% v/v of one or more of congeneric monomers, or other reaction products, particularly when the mixture provides improved process parameters or isolation of the target compound is too difficult or expensive;
- The SAM precursor containing between approximately 0 ppbw and approximately 500 ppbw metal impurities;
- the concentration of trace metals and metalloids in the SAM precursors each ranging from approximately 0ppb to approximately 100ppb; and
- the concentration of trace metals and metalloids in the SAM precursors each ranging from approximately 0ppb to approximately 10ppb.

[0016a] In one aspect, there is provided a film-forming process, the process comprising the steps of

placing a surface on a substrate into a reactor for exposure of the surface to a self-assembling monolayer (SAM) forming composition, the composition comprising a SAM precursor having a silicon-based tail or backbone with a surface reactive group X that bonds to a tail silicon,

wherein the silicon-based tail or backbone contains no Si-C bonds and is selected from the group consisting of a Si-C free polysilane and a trisilylamine,

wherein the surface reactive group X is selected from:

- a halide selected from Cl, Br, I;
- a cyanate, an isocyanate or a thiocyanate group;
- an amino group $-NR^1R^2$, wherein R^1 is selected from H, a linear, branched or cyclic C_1-C_{10} alkyl or alkenyl group or an alkyl silyl group; R^2 is selected from a linear, branched or cyclic C_2-C_{10} alkyl or alkenyl group, provided that $R^1 = R^2 \neq Et$; or an alkyl silyl group; or R^1 and R^2 are bridged so that NR^1R^2 forms a cyclic ligand, provided that the cyclic ligand includes heteroatoms S, N or O;
- an amidinate group $-R^3-N-C(R^4)=N-R^5$, wherein R^3 and R^5 are each independently selected from a C_1 to C_{10} linear or branched alkyl or a trialkylsilyl; and R^4 is selected from H, a C_1 to C_{10} linear or branched alkyl;

- wherein, when the surface to be covered is a metal, the surface reactive group X is selected from –SH, a phosphonic acid or a carboxylic acid

exposing the surface to the SAM forming composition;

forming a SAM on the surface through a liquid or gas phase exposure of the SAM forming composition; and

growing a film on top of the SAM through a wet or dry deposition process using a film-forming precursor selected from a main group element, or a transition metal element selected from Ti, Ta, W, Mo, Nb, or V, a fluoride, a chloride, a bromide, an iodide, an oxychloride, an oxybromide, an oxyfluoride or combinations thereof,

wherein the tail silicon of the SAM precursor acts as a reducing agent to the film-forming precursor.

[0017] Also disclosed are processes of forming a self-assembling monolayer (SAM) on a surface, the processes comprising the steps of

preparing the surface for exposure of the surface to a SAM forming composition, the composition comprising a SAM precursor having a backbone with a surface reactive group X,

wherein the backbone contains no Si-C bonds and is selected from the group consisting of a Si-C-free polysilane and a trisilylamine,

wherein the surface reactive group X is selected from:

- a halide (Cl, Br, I);
- a cyanate, an isocyanate or a thiocyanate group;
- an amino group $-NR^1R^2$, wherein R^1 is selected from H, a linear, branched or cyclic C_1-C_{10} alkyl or alkenyl group or an alkyl silyl group; R^2 is selected from a linear, branched or cyclic C_2-C_{10} alkyl or alkenyl group, or an alkyl silyl group; or R^1 and R^2 are bridged so that NR^1R^2 forms a cyclic ligand, provided that the cyclic ligand includes heteroatoms S, N or O;
- an amidinate group $-R^3$-N-C(R^4)=N-R^5, wherein R^3 and R^5 are each independently selected from a C_1 to C_{10} linear or branched alkyl or a trialkylsilyl; and R^4 is selected from H, a C_1 to C_{10} linear or branched alkyl; or
- a thiol –SH group, a phosphonic acid or a carboxylic acid;

exposing of the surface to the SAM forming composition; and

What is claimed is:

1. A film-forming process, the process comprising the steps of:

placing a surface on a substrate into a reactor for exposure of the surface to a self-assembling monolayer (SAM) forming composition, the composition comprising a SAM precursor having a silicon-based tail or backbone and a surface reactive group X that bonds to the silicon-based tail or backbone,

wherein the silicon-based tail or backbone contains no Si-C bonds and is selected from the group consisting of a Si-C free polysilane and a trisilylamine,

wherein the surface reactive group X is selected from:

- a halide selected from Cl, Br, I;
- a cyanate, an isocyanate or a thiocyanate group;
- an amino group $-NR^1R^2$, wherein R^1 is selected from H, a linear, branched or cyclic C_1-C_{10} alkyl or alkenyl group or an alkyl silyl group; R^2 is selected from a linear, branched or cyclic C_2-C_{10} alkyl or alkenyl group, provided that $R^1 = R^2 \neq Et$; or an alkyl silyl group; or R^1 and R^2 are bridged so that NR^1R^2 forms a cyclic ligand, provided that the cyclic ligand includes heteroatoms S, N or O; or
- an amidinate group $-R^3$-N-C(R^4)=N-R^5, wherein R^3 and R^5 are each independently selected from a C_1 to C_{10} linear or branched alkyl or a trialkylsilyl; and R^4 is selected from H, a C_1 to C_{10} linear or branched alkyl; wherein, when the surface to be covered is a metal, the surface reactive group X is selected from –SH, a phosphonic acid or a carboxylic acid;

exposing the surface to the SAM forming composition;

forming a SAM on the surface through a liquid or gas phase exposure of the SAM forming composition; and

growing a film on top of the SAM through a wet or dry deposition process using a film-forming precursor selected from a main group element, or a transition metal element selected from Ti, Ta, W, Mo, Nb, or V, a fluoride, a chloride, a bromide, an iodide, an oxychloride, an oxybromide, an oxyfluoride or combinations thereof,

wherein the tail silicon of the SAM precursor acts as a reducing agent to the film-forming precursor.

2. The process of claim 1, wherein the film-forming precursor is selected from WF_6, WOF_4, $WOCl_4$, WCl_6, WCl_5, $MoCl_5$, $MoOCl_4$, MoO_2Cl_2, $TiCl_4$, $TiBr_4$, TiI_4, $TaCl_5$, $AlCl_3$, VCl_4, $NbCl_5$, BCl_3, BBr_3, $GeCl_4$, $GeBr_4$ or $GeCl_2$, $GeBr_2$ and combinations thereof.

3. The process of claim 1, wherein the dry deposition process is an ALD or CVD process.

4. The process of claim 1, wherein X is a dialkylamino group $–NR^1R^2$, wherein R^1 is H, a C_2 to C_5 alkyl, and R^2 is a C_1 to C_5 alkyl, provided that if R^1=H, R^2 is a C_3 to C_5 alkyl, and if R^1 not H, R^1 and R^2 are identical.

5. The process of claim 1, wherein X is an amidinate group $-NR^3-C(R^4)=N-R^5$ wherein R^3 and R^5 are each independently selected from Et, *n*Pr, *i*Pr, *n*Bu, *t*Bu, *s*Bu, *i*Bu; and R^4 is H or Me.

6. The process of claim 1, wherein the silicon-based tail or backbone of the SAM precursor is selected from $–SiH_2-SiH_3$ or $–SiH_2-SiH_2-SiH_3$.

7. The process of any one of claims 1-6, wherein the SAM precursor having the silicon-based tail or backbone is selected from

$X-(SiH_2)_n-SiH_3$, wherein n=1 to 3,

$X-(Si_nH_{2n-1})$, wherein Si_nH_{2n-1} refers to a cyclic hydridosilane backbone with n=5, 6, 7,

$X-(SiH(SiH_3)_2)$, or

$X-SiH_2-Si(SiH_3)_3$.

8. The process of any one of claims 1-6, wherein the SAM precursor having the silicon-based tail or backbone is selected from N*i*Pr_2-(SiH_2)-SiH_3, N*n*Bu_2-(SiH_2)-SiH_3, N*t*Bu_2-(SiH_2)-SiH_3, N*s*Bu_2-(SiH_2)-SiH_3, N*i*Bu_2-(SiH_2)-SiH_3, NPen_2-(SiH_2)-SiH_3, N*n*Pr_2-$(SiH_2)_2$-SiH_3, N*i*Pr_2-$(SiH_2)_2$-SiH_3, N*n*Bu_2-$(SiH_2)_2$-SiH_3, N*t*Bu_2-$(SiH_2)_2$-SiH_3, N*s*Bu_2-$(SiH_2)_2$-SiH_3, N*i*Bu_2-$(SiH_2)_2$-SiH_3, N*s*Pen_2-$(SiH_2)_2$-SiH_3, NHtBu-$(SiH_2)_2$-SiH_3, NHPen-$(SiH_2)_2$-SiH_3, NHsBu-$(SiH_2)_2$-SiH_3, NHiBu-$(SiH_2)_2$-SiH_3, N*n*Pr_2-$(SiH_2)_3$-SiH_3, N*i*Pr_2-$(SiH_2)_3$-SiH_3, N*n*Bu_2-$(SiH_2)_3$-SiH_3, N*t*Bu_2-$(SiH_2)_3$-SiH_3, N*s*Bu_2-$(SiH_2)_3$-SiH_3, N*i*Bu_2-$(SiH_2)_3$-SiH_3, N*s*Pen_2-$(SiH_2)_3$-SiH_3, NEt_2-$(SiH(SiH_3)_2)$, N*i*Pr_2-$(SiH(SiH_3)_2)$, N*n*Pr_2-$(SiH(SiH_3)_2)$, N*i*Bu_2-$(SiH(SiH_3)_2)$, N*t*Bu_2-$(SiH(SiH_3)_2)$, N*n*Bu_2-$(SiH(SiH_3)_2)$, N*s*Bu_2-$(SiH(SiH_3)_2)$, N*s*Pen_2-$(SiH(SiH_3)_2)$, NH*t*Bu-$(SiH(SiH_3)_2)$, NH*n*Bu-$(SiH(SiH_3)_2)$, NH*i*Bu-$(SiH(SiH_3)_2)$, or NHPen-$(SiH(SiH_3)_2)$.

9. The process of any one of claims 1-6, wherein the SAM precursor having the silicon-based tail or backbone has a general formula

$$XR_2Si\text{-}N(SiR_3)_n(SiX'R_2)_{2-n},$$

wherein n=1 or 2; R is H; X′ has the same definition as X and is independent from X.

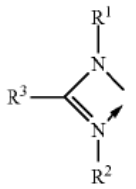
10. The process of any one of claims 1-6, wherein the SAM precursor having the silicon-based tail or backbone is $XH_2Si\text{-}N(SiH_3)_n(SiX'H_2)_{2-n}$,
wherein X' has the same definition as X and is independent from X.

11. The process of any one of claims 1-6, wherein the SAM precursor having the silicon-based tail or backbone contains more than one $N(–Si)_3$ units and has backbones of $(Si)_2N–Si–N(Si)(Si–X)$ or X–Si–N(Si)–Si–N(Si)(Si–X).

12. The process of any one of claims 1-6, wherein the SAM precursor is (Diisopropylamine)trisilylamine ($(CHMe_2)_2$-N-SiH_2-N-$(SiH_3)_2$, TSA-N$(CHMe_2)_2$).

13. The process of any one of claims 1-6, wherein the SAM precursor is Chlorotrisilylamine $(SiH_3)_2$-N-SiH_2Cl, TSA-Cl).

14. The process of any one of claims 1-6, wherein the SAM precursor is

AMD, -$R^1HN(CR^3)$═NR^2, 

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15. The process of any one of claims 1-6, wherein the SAM precursor is bi-disilylaminohalogensilane (BDSASi-X), wherein X = F, Cl, Br or I.

16. The process of any one of claims 1-6, wherein the SAM precursor is Diisobutylamine)trisilane (DIBATS, (*i*Bu)$_2$-N-SiH_2-SiH_2-SiH_3).