containing films is the formation of solid electrolyte materials used in solid-state batteries. Solid-state batteries are solvent-free systems having longer lifetime, faster charger time and higher energy density than conventional lithium-ion batteries. They are considered as the next technology step in battery development. Lithium-containing film solid electrolytes such as lithium phosphate, lithium borate and lithium borophosphate are deposited by ALD/CVD techniques. Uniform and conformal Li-containing films may even be obtained on complex architecture like 3D batteries.

[0004] With the raising energy storage needs, higher capacity retention together with improved safety performances is demanded. Li-containing films may effectively prevent or reduce the formation of Solid Electrolyte Interphase (SEI), such as lithium phosphate, lithium phosphorus oxynitride (LiPON), and different lithium metal oxides such lithium titanates, lithium zirconates and lithium niobates. These materials are expected to improve the interfaces between electrodes and electrolyte, either in current lithium ion batteries or solid state batteries. Li-containing films such as lithium niobate may also be used for high frequency electronic devices, for example, mobile applications. Lithium fluoride is also an interesting material for optical or as a potential gate dielectric owing to high band-gap and high dielectric constant.

[0005] WO 00/67300 A1 to Gordon, et al. discloses synthesis of alkali lithium amides precursors with the general formula: $MN(E^1R^1R^2R^3)(E^2R^4R^5R^6)$, wherein M is an alkali metal:Li, Na, K; E^1 and E^2 = C, Si, Ge or Sn; R^1, R^2, R^3, R^4, R^5, R^6 are H, alkyl groups or fluoroalkyl groups. All the compounds are liquid at 20°C. Formation of films containing alkali metals by CVD is disclosed.

[0006] WO 02/27063 A2 to Gordon, et al. discloses CVD and ALD of lithium phosphate using $LiN(SiMe_3)_2$, $LiN(SiEtMe_2)_2$ and Li(TMPD) as lithium precursor. Diisopropylphosphate was used as phosphate precursor. TMPD stands for 2,2,6,6-tetramethylpiperidide.

[0007] WO 2011/002920 A2 to Pallem, et al. discloses silicon-free Lithium-containing precursors, that is lithium alkyl amidinate and lithium alkylcyclopentadienyl compounds having a general formulas: $Li(R^1R^2R^3R^4R^5Cp).D$, Li(NR-amd).D and Li(NR-fmd).D, where D = monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system; R, R^1, R^2, R^3, R^4, R^5, R^6 are H or alkyl groups.

[0008] US 2012/0276305 to Hamalainen, et al. discloses the syntheses of $LiN(SiMe_3)_2$, LiOtBu, Li(thd) and Li(hfac) from commercial sources. They are used as lithium sources for the formation of lithium phosphate films by ALD. Phosphorus sources disclosed are phosphate reagents with the formula $O=P(OR)_3$ where R is an alkyl group. In the examples, $LiN(SiMe_3)_2$ and LiOtBu are used in combination with trimethylphosphate (TMPO) for ALD

branched or cyclic C_1-C_8 alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

R^2 is independent and selected from the group consisting of hydrogen, linear, branched or cyclic C_1-C_8 alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

L^2 is of the form (C_pH_q)-ER^3R^4 or (C_pH_q)-$E'R^3$, wherein

C_pH_q is an alkyl chain and may be linear, branched or cyclic alkyl groups;

E represents B, N;

E′ represents a divalent element such as O, S;

p and q are independent integers ranging from 1 to 16, preferably p is comprised from 1 to 8 and q is comprised from 2 to 16, most preferably p is different from m;

R^3 and R^4 are independent and selected from the group consisting of hydrogen, linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system, preferably a monodentate or a bidentate;

x is an integer comprised between 0 and 4;

y represents the degree of association of the molecule and is comprised between 1 and 6;

- the lithium precursor being silicon-free;
- the lithium precursor being selected from $LiNMe(CH_2CH_2NMe_2)$, $LiNMe(CH_2CH_2NMe_2)$(1,2-diethoxyethane), $LiNMe(CH_2CH_2NMe_2)$(1,2-dimethoxyethane), $LiNEt(CH_2CH_2NMe_2)$, $LiNiPr(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NEtMe)$, $LiNtBu(CHMeCH_2NMe_2)$, $LiNtBu(CH_2CHMeNMe_2)$, $LiN(CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2NEt_2)_2$, $LiN(CH_2CH_2NiPr_2)_2$, $LiN(CH_2CH_2NEtMe)_2$, $LiN(CH_2CH_2CH_2NMe_2)_2$, $LiN(CHMeCH_2NMe_2)_2$, $LiN(CHMeCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHMeNMe_2)_2$, $LiN(CH_2CHMeNMe_2)(CH_2CH_2NMe_2)$, $LiN(CHEtCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHEtNMe_2)(CH_2CH_2NMe_2)$, $LiN(CMe_2CH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CMe_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2CH_2NMe_2)$, $LiNMe(CH_2CH_2OMe)$, $LiNMe(CH_2CH_2OEt)$, $LiNMe(CH_2CH_2OiPr)$ $LiNMe(CH_2CH_2OtBu)$, $LiNEt(CH_2CH_2OMe)$, $LiNEt(CH_2CH_2OEt)$, $LiNiPr(CH_2CH_2OMe)$,

550°C for a plasma deposition process;

- the deposition temperature ranging from approximately 100°C to approximately 500°C for ALD and CVD;
- the deposition temperature ranging from approximately 250°C to approximately 350°C for ALD and CVD;
- the deposition temperature ranging from approximately 200°C to approximately 800°C for a thermal process;
- the deposition temperature ranging from approximately 400°C to approximately 600°C for a thermal process;
- the deposition temperature being 100°C for ALD;
- the deposition temperature being 125°C for ALD;
- the deposition temperature being 135°C for ALD;
- the deposition temperature being 150°C for ALD;
- the deposition temperature being 175°C for ALD;
- the deposition temperature being 200°C for ALD;
- the deposition temperature being 250°C for ALD;
- the deposition temperature being 500°C for ALD;
- the deposition temperature being 200°C for CVD;
- the deposition temperature being 300°C for CVD;
- the deposition temperature being 400°C for CVD;
- the deposition temperature being 500°C for CVD;
- the temperature of the substrate ranging from room temperature to approximately 600°C;
- the lithium precursor being a silicon-free lithium precursor;
- the lithium precursor being a monomer, a dimer, a trimer, or combinations thereof;
- further comprising the step of delivering into the reactor a co-reactant;
- the co-reactant being selected from O_3, O_2, H_2O, trimethylphosphate, an alkylphosphate, an alkylphosphimine, NO, N_2O, H_2O_2, O radicals, or combinations thereof;
- the co-reactant being selected from N_2, NH_3, N_2H_4, or an alkylhydrazine;
- the co-reactant being O_3;
- the lithium precursor being liquid below 150°C;
- the lithium precursor being liquid at 50°C;
- the lithium precursor being liquid at 25°C;

- the Li-containing film, islet or cluster being a film, islet or cluster of Li_2O, LiOH, Li_2S, Li_3N, LiF, lithium carbonate, lithium aluminum fluoride, lithium aluminum oxide, lithium aluminum, lithium cobalt oxide, lithium titanate, lithium zirconate, lithium niobate, LiPON, lithium phosphate, lithium borate, lithium borophosphate, lithium niobate, lithium zirconium oxides, or the like.

[0013] Also, disclosed is a composition comprising a lithium precursor having a general formula:

$$[Li\text{-}NL^1L^2\text{-}D_x]_y \qquad (I)$$

wherein

L^1 has a general formula: C_mH_n, (C_mH_n)-ER^1R^2) or (C_mH_n)-$E'R^1$), wherein

- C_mH_n is a linear, branched or cyclic alkyl groups;
- m and n are independent integers, 1≤m≤16, 1≤n≤16;
- E is B, N;
- E′ is a divalent element;
- R^1 and R^2 each are independently selected from the group consisting of hydrogenlinear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

L^2 has a general formula: (C_pH_q)-ER^3R^4 or (C_pH_q)-$E'R^3$, wherein

- C_pH_q is a linear, branched or cyclic alkyl groups;
- p and q are independent integers, 1≤p≤16, 1≤q≤16;
- E is B, N;
- E′ is a divalent element;
- R^3 and R^4 each are independently selected from the group consisting of linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system;

x is an integer, 0≤x≤4; and

y is the degree of association of the molecule, 1≤y≤6.

The disclosed compositions include one or more of the following aspects:

- L^1 being a C_1-C_{16} linear, branched or cyclic carbon chains, or of the form (C_mH_n)-ER^1R^2 or (C_mH_n)-$E'R^1$, wherein

  C_mH_n is an alkyl chain and may be linear, branched or cyclic alkyl groups;

  E represents B, N;

  E′ represents a divalent element such as O, S;

alkyl groups substituted by other atoms or groups;

D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system, preferably a monodentate or a bidentate;

x is an integer comprised between 0 and 4; and

y represents the degree of association of the molecule and is comprised between 1 and 6,

provided that x=0, p=2, q=4, E=N and all L^2, R^3 and R^4 are methyl is excluded;

provided that x=0, p=2 or 3, q=4 or 6, E=N, L^2= tertiary butyl, R^3 and R^4 are methyl is excluded;

provided that x=0, m=p=2, n=q=4, E=N, all R^1, R^2, R^3, R^4 are methyl is excluded;

provided that x=0, m=p=2, n=q=4, E′=O, both R^1 and R^3 are methyl is excluded;

provided that x=0, m=2, n=4, E′=O and R^1 is methyl is excluded;

provided that L^1 = Me, L^2 = {C_pH_q = CH_2CH_2, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = Et, L^2 = {C_pH_q = CH_2CH_2, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = iPr, L^2 = {C_pH_q = CH_2CH_2, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = tBu, L^2 = {C_pH_q = CH_2CH_2, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = tBu, L^2 = {C_pH_q = $CMeHCH_2$, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = tBu, L^2 = {C_pH_q = CH_2CHMe, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = {C_mH_n = CH_2CH_2, E = N, both R^1 and R^2 are Me}, L^2 = {C_pH_q = CH_2CH_2, E = N, both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = {C_mH_n = CH_2CH_2, E = N, both R^1 and R^2 are Et}, L^2 = {C_pH_q = CH_2CH_2, E = N, both R^3 and R^4 are Et}, x = 0 is excluded; and

provided that L^1 = Me, L^2 = {C_pH_q = CH_2CH_2, E' = O, R^3 is Me}, x = 0 is excluded.

[0040] Exemplary examples of the disclosed silicon-free lithium precursors shown in the general formula (I) include $LiN^tBu(CH_2CH_2NMe_2)$, $LiN^tBu(CH_2CH_2NEtMe)$, $LiN^tBu(CHMeCH_2NMe_2)$, $LiN^tBu(CH_2CHMeNMe_2)$, $LiN(CH_2CH_2NEtMe)_2$, $LiN(CH_2CH_2OEt)_2$, $LiN(CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2NMeEt)_2$, $LiN(CHMeCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHMeNMe_2)(CH_2CH_2NMe_2)$, $LiN(CHEtCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHEtNMe_2)(CH_2CH_2NMe_2)$,

to form Li-containing films or islets such as Li_2O, LiOH, Li_2S, Li_3N, LiF, lithium carbonate, lithium aluminum fluoride, lithium aluminum oxide, lithium aluminum, lithium cobalt oxide, lithium titanate, lithium zirconate, lithium niobate, LiPON, lithium phosphate, lithium borate, lithium borophosphate, lithium niobate, lithium zirconium oxides, etc.

[0059] Preferably, the disclosed silicon-free lithium precursors have suitable properties for vapor deposition methods, such as vapor pressure ranging from approximately 0.1 Torr at 23°C to approximately 1,000 Torr at 23°C, a melting point below 20°C (preferably being in liquid form at room temperature) and more preferably below -20°C to prevent freeze/thaw issues, and exhibiting 0% by volume or v/v to 1% v/v decomposition per week at the temperature required to obtain a usable vapor pressure (1-100 Torr).

[0060] While the disclosed silicon-free lithium precursors are ideally liquids and vaporized in bubblers or direct liquid injection systems, the use of solid precursors for ALD/CVD precursor vaporization is also possible using sublimators such as ones disclosed in PCT Publication WO 2009/087609 to Xu *et al*. Alternatively, solid precursors may be mixed or dissolved in a solvent to reach a usable melting point and viscosity for usage by Direct Liquid Injection systems. While the disclosed silicon-free lithium precursors are ideally liquids, solid precursors for liquid phase deposition techniques such as spray coating, slit coating and spin on deposition, may be mixed or dissolved in a solvent to reach a usable melting point and viscosity for flowing the precursor solutions into the reactor.

[0061] To ensure process reliability, the disclosed silicon-free lithium precursors may be purified by continuous or fractional batch distillation or sublimation prior to use to a purity ranging from approximately 93% by weight or w/w to approximately 100% w/w, preferably ranging from approximately 99% w/w to approximately 99.999% w/w, more preferably, ranging from approximately 99% w/w to approximately 100% w/w. One of ordinary skill in the art will recognize that the purity may be determined by ^1H NMR or gas or liquid chromatography with mass spectrometry. The Li-containing film, islet or cluster forming compositions may contain any of the following impurities: ammonium salts; alkylamines, dialkylamines, alkylimines, THF, ether, pentane, cyclohexane, heptanes, toluene, halogenated metal compounds. Preferably, the total quantity of these impurities is below 0.1% w/w. The purified composition may be produced by recrystallization, sublimation, distillation, and/or passing the gas or liquid through a suitable adsorbent, such as 4Å molecular sieves.

[0062] The disclosed Li-containing film, islet or cluster forming composition contains less than 5% v/v, preferably less than 1% v/v, more preferably less than 0.1% v/v, and even more preferably less than 0.01% v/v of any of its analogs or other reaction products. This

includes approximately 500°C or higher. When a plasma deposition process is utilized, the deposition temperature may range from approximately 20°C to approximately 550°C, preferably from approximately 125°C to approximately 250°C. Alternatively, when a thermal process is performed, the deposition temperature may range from approximately 300°C to approximately 800°C, preferably from approximately 400°C to approximately 600°C.

[0074] Alternatively, the substrate may be heated to a sufficient temperature to obtain the desired Li-containing film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the substrate may be heated includes from room temperature to approximately 600°C. Preferably, the temperature of the substrate remains less than or equal to 500°C.

[0075] The reactor contains one or more substrates onto which the films or islets will be deposited. A substrate is generally defined as the material on which a process is conducted. The substrates may be any suitable substrate used in semiconductor or lithium battery industry. Examples of suitable substrates include wafers or supports, such as silicon, silica, glass substrates. The support may have one or more layers of differing materials deposited on it from a previous manufacturing step. For example, the supports may include silicon layers (crystalline, amorphous, porous, *etc*.), silicon oxide layers, silicon nitride layers, silicon oxy nitride layers, carbon doped silicon oxide (SiCOH) layers, or combinations thereof. The disclosed silicon-free Li-containing precursors used in the lithium battery industry may be deposited on powders made of graphite, doped graphite, especially Si-doped graphite, silicon and silicon alloys, or powders made of metallic oxides (especially lithium nickel oxide, lithium nickel manganese oxide, lithium nickel cobalt oxide, lithium nickel cobalt manganese oxide, lithium nickel cobalt aluminum oxide, lithium iron phosphate, and the corresponding materials with dopants, or combinations thereof. Additionally, the wafers may include copper layers or noble metal layers (*e.g.* platinum, palladium, rhodium, or gold). The layers may include oxides which are used as dielectric materials in MEMS, MIM, DRAM, RF front end modules, or FeRam technologies. The underlying materials may include such as a nickel oxide, a manganese oxide, a cobalt oxide, a graphitic or amorphous carbon, *etc*. Plastic layers, such as poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) [PEDOT:PSS] may also be used. The layers may be planar, spherical, rounded or patterned, or may not have regular structures (see above). For example, the layer may be underlying materials made of hydrogenated carbon, for example CH_x, wherein x is greater than zero. The preferred underlying materials are a graphitic or amorphous carbon, a lithium nickel manganese oxide, a lithium nickel manganese cobalt oxide, a lithium nickel cobalt aluminum oxide.

may provide the desired film thickness or may be repeated until a film having the necessary thickness has been obtained.

[0098] The Li-containing films or islets formed by the disclosed silicon free Li-containing precursors through vapor deposition process include Li_2O, LiOH, Li_2S, Li_3N, LiF, lithium carbonate, lithium aluminum fluoride, lithium aluminum oxide, lithium aluminum, lithium cobalt oxide, lithium titanate, lithium zirconate, lithium niobate, LiPON, lithium phosphate, lithium borate, lithium borophosphate, etc.

[0099] The disclosed silicon-free lithium precursors have the following advantages. The disclosed silicon-free lithium precursors do not contain silicon. Although silicon-containing lithium precursors, such as the most common precursor LiHMDS, e.g., $Li(SIMe_3)_2$, is quite stable and sufficiently volatile, silicon would remain in part in the deposited film. The presence of silicon may be a problem when forming materials such as $LiTiO_3$, $LiNbO_3$ or LiZrOx where silicon may lead to adverse electrochemical features, linked to the induced disorder of the material, and hence lower ionic conductivity.

[0100] The disclosed silicon-free lithium precursors are high melting point and low volatility lithium sources. Lithium compounds exist as various aggregates in solution and in the solid state. These molecules have commonly multimeric structures, typically trimeric or tetrameric, leading to high molecular weight, high melting point and low volatility. For example, n-BuLi is tetrameric in diethyl ether and hexameric in cyclohexane. $Li(SiMe_3)_2$ is reported as a trimer in solid state, LiOtBu is said to evolve as a hexamer. The use of liquid or low melting point solid precursors is well known in the industry, especially semiconductor industry. In addition, these precursors are convenient, so that the flow rate may be measured and/or controlled accurately. When precursors are not very volatile and thus need to be heated, the way to deliver the precursor is to heat only a portion of the precursor in a tank so that it will be delivered quickly, and the rest of the precursor is kept in ambient conditions in the tank called a “mother tank”. It is then important to feed the heated tank in a practical way. Liquids or low melting point solids may be transfilled with simple valve opening. The melting point should be thus significantly lower than Li(OtBu) or $Li(SiMe_3)_2$, e.g. below 150°C, preferably lower 80°C, most preferably lower than 25°C. Furthermore, the delivery of stable feed rates of high melting point solid is a challenge, considering their changes of morphology: small particles, typically with a higher surface to bulk ratio, are consumed faster than bigger particles. On the contrary, particles may merge, making the feed rate potentially unstable. The disclosed silicon-free lithium precursors having low melting point could overcome these issues.

[0101] The disclosed silicon-free lithium precursors are highly moisture sensitive and

What is claimed is:

1. A method for forming a Li-containing film, islet or cluster on a substrate, the method comprising the steps of:

introducing a silicon-free lithium precursor having a general formula

$$[Li\text{-}NL^1L^2\text{-}D_x]_y (I)$$

into a reactor containing the substrate disposed therein, wherein

L^1 has a general formula: C_mH_n, (C_mH_n)-ER^1R^2) or (C_mH_n)-$E'R^1$), wherein

- C_mH_n is a linear, branched or cyclic alkyl groups;
- m and n are independent integers, $1 \leq m \leq 16$, $1 \leq n \leq 16$;
- E is B, N;
- E′ is a divalent element;
- R^1 and R^2 each are independently selected from the group consisting of linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

L^2 has a general formula: (C_pH_q)-ER^3R^4 or (C_pH_q)-$E'R^3$, wherein

- C_pH_q is a linear, branched or cyclic alkyl groups;
- p and q are independent integers, $1 \leq p \leq 16$, $1 \leq q \leq 16$;
- E is B, N;
- E′ is a divalent element;
- R^3 and R^4 each are independently selected from the group consisting of linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system;

x is an integer, $0 \leq x \leq 4$; and

y is the degree of association of the molecule, $1 \leq y \leq 6$; and

depositing at least part of the silicon-free lithium precursor onto the substrate to form the Li-containing film, islet or cluster using a vapor deposition method.

2. The method of claim 1, wherein

L^1 is a C_1-C_{16} linear, branched or cyclic carbon chains, or of the form (C_mH_n)-ER^1R^2 or (C_mH_n)-$E'R^1$, wherein

- C_mH_n is an alkyl chain and may be linear, branched or cyclic alkyl groups;

- E represents B, N;
- E′ represents a divalent element such as O, S;
- m is an integer which value is 1 or an integer ranging from 1 to 8;
- n is an independent integer ranging from 2 to 16;
- R^1 is independent and selected from the group consisting of hydrogen, linear, branched or cyclic C_1-C_8 alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;
- R^2 is independent and selected from the group consisting of hydrogen, linear, branched or cyclic C_1-C_8 alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

L^2 is of the form (C_pH_q)-ER^3R^4 or (C_pH_q)-$E'R^3$, wherein

- C_pH_q is an alkyl chain and may be linear, branched or cyclic alkyl groups;
- E represents B, N;
- E′ represents a divalent element such as O, S;
- p and q are independent integers ranging from 1 to 16, preferably p is comprised from 1 to 8 and q is comprised from 2 to 16, most preferably p is different from m;
- R^3 and R^4 are independent and selected from the group consisting of hydrogen, linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;
- D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system, preferably a monodentate or a bidentate;
- x is an integer comprised between 0 and 4; and
- y represents the degree of association of the molecule and is comprised between 1 and 6.

3. The method of claim 1, wherein the silicon-free lithium precursor is selected from $LiNMe(CH_2CH_2NMe_2)$, $LiNMe(CH_2CH_2NMe_2)$(1,2-diethoxyethane), $LiNMe(CH_2CH_2NMe_2)$(1,2-dimethoxyethane), $LiNEt(CH_2CH_2NMe_2)$, $LiNiPr(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NEtMe)$, $LiNtBu(CHMeCH_2NMe_2)$, $LiNtBu(CH_2CHMeNMe_2)$, $LiN(CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2NEt_2)_2$, $LiN(CH_2CH_2NiPr_2)_2$, $LiN(CH_2CH_2NEtMe)_2$, $LiN(CH_2CH_2CH_2NMe_2)_2$, $LiN(CHMeCH_2NMe_2)_2$, $LiN(CHMeCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHMeNMe_2)_2$, $LiN(CH_2CHMeNMe_2)(CH_2CH_2NMe_2)$, $LiN(CHEtCH_2NMe_2)(CH_2CH_2NMe_2)$,

$LiN(CH_2CHEtNMe_2)(CH_2CH_2NMe_2)$, $LiN(CMe_2CH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CMe_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2CH_2NMe_2)$, $LiNMe(CH_2CH_2OMe)$, $LiNMe(CH_2CH_2OEt)$, $LiNMe(CH_2CH_2OiPr)$ $LiNMe(CH_2CH_2OtBu)$, $LiNEt(CH_2CH_2OMe)$, $LiNEt(CH_2CH_2OEt)$, $LiNiPr(CH_2CH_2OMe)$, $LiNtBu(CH_2CH_2OMe)$, $LiN(CH_2CH_2OMe)_2$, $LiN(CH_2CH_2OEt)_2$, $LiN(CH_2CH_2OiPr)_2$, $LiN(CH_2CH_2OtBu)_2$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OMe)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OEt)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OiPr)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OtBu)$, or $LiNMe(CH_2CH(OMe)_2)$.

4. The method of claim 1, wherein the silicon-free lithium precursor is selected from $LiNtBu(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NEtMe)$, $LiNtBu(CHMeCH_2NMe_2)$, $LiNtBu(CH_2CHMeNMe_2)$, $LiN(CH_2CH_2NEtMe)_2$, $LiN(CH_2CH_2OEt)_2$, $LiN(CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2NMeEt)_2$, $LiN(CHMeCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHMeNMe_2)(CH_2CH_2NMe_2)$, $LiN(CHEtCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHEtNMe_2)(CH_2CH_2NMe_2)$, $LiN(CMe_2CH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CMe_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CH_2NiPr_2)_2$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2CH_2NMe_2)$, $LiN(CH_2CH_2OEt)_2$, $LiNMe(CH_2CH_2OEt)$, or $LiNMe(CH_2CH(OMe)_2)$.

5. The method of claim 1, wherein the silicon-free lithium precursor is $LiN(CH_2CH_2NMe_2)_2$.

6. The method of claim 1, wherein the silicon-free lithium precursor is a monomer, a dimer, a trimer, or combinations thereof.

7. The method of claim 1, wherein the silicon-free lithium precursor is liquid below 150°C.

8. The method of claim 1, wherein the vapor deposition method is ALD, CVD, spray coating, dip coating, slit coating, spin-on deposition or a combination thereof.

9. The method of any one of claims 1 to 8, further comprising the step of delivering into the reactor a co-reactant selected from O_3, O_2, H_2O, trimethylphosphate, an alkylphosphate, an alkylphosphimine, NO, N_2O, H_2O_2, O radicals, or combinations thereof.

10. The method of claim 9, wherein the co-reactant is O_3.

11. The method of any one of claims 1 to 8, wherein the Li-containing film, islet or cluster is a film, islet or cluster of Li_2O, LiOH, Li_2S, Li_3N, LiF, lithium carbonate, lithium aluminum fluoride, lithium aluminum oxide, lithium aluminum, lithium cobalt oxide, lithium titanate, lithium zirconate, lithium niobate, LiPON, lithium phosphate, lithium borate, lithium borophosphate, lithium niobate, lithium zirconium oxides, or the like.

12. The method of any one of claims 1 to 8, wherein the temperature within the reactor ranges from about 0°C to about 600°C.

13. A composition comprising a lithium precursor having a general formula:

$$[Li\text{-}NL^1L^2\text{-}D_x]_y \qquad (I)$$

wherein

L^1 has a general formula: C_mH_n, (C_mH_n)-ER^1R^2) or (C_mH_n)-$E'R^1$), wherein

- C_mH_n is a linear, branched or cyclic alkyl groups;
- m and n are independent integers, $1 \le m \le 16$, $1 \le n \le 16$;
- E is B, N;
- E′ is a divalent element;
- R^1 and R^2 each are independently selected from the group consisting of hydrogenlinear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

L^2 has a general formula: (C_pH_q)-ER^3R^4 or (C_pH_q)-$E'R^3$, wherein

- C_pH_q is a linear, branched or cyclic alkyl groups;
- p and q are independent integers, $1 \le p \le 16$, $1 \le q \le 16$;
- E is B, N;
- E′ is a divalent element;
- R^3 and R^4 each are independently selected from the group consisting of linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system;

x is an integer, $0 \le x \le 4$; and

y is the degree of association of the molecule, $1 \le y \le 6$.

14. The composition of claim 13, wherein

L^1 is a C_1-C_{16} linear, branched or cyclic carbon chains, or of the form (C_mH_n)-ER^1R^2 or (C_mH_n)-$E'R^1$, wherein

- C_mH_n is an alkyl chain and may be linear, branched or cyclic alkyl groups;
- E represents B, N;
- E′ represents a divalent element such as O, S;
- m is an integer which value is 1 or an integer ranging from 1 to 8;
- n is an independent integer ranging from 2 to 16;
- R^1 is independent and selected from the group consisting of hydrogen, linear, branched or cyclic C_1-C_8 alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;
- R^2 is independent and selected from the group consisting of hydrogen, linear, branched or cyclic C_1-C_8 alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

L^2 is of the form (C_pH_q)-ER^3R^4 or (C_pH_q)-$E'R^3$, wherein

- C_pH_q is an alkyl chain and may be linear, branched or cyclic alkyl groups;
- E represents B, N;
- E′ represents a divalent element such as O, S;
- p and q are independent integers ranging from 1 to 16, preferably p is comprised from 1 to 8 and q is comprised from 2 to 16, most preferably p is different from m;
- R^3 and R^4 are independent and selected from the group consisting of hydrogen, linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system, preferably a monodentate or a bidentate;

x is an integer comprised between 0 and 4; and

y represents the degree of association of the molecule and is comprised between 1 and 6,

provided that L^1 = Me, L^2 = {C_pH_q = CH_2CH_2, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = Et, L^2 = {C_pH_q = CH_2CH_2, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = iPr, L^2 = {C_pH_q = CH_2CH_2, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = tBu, L^2 = {C_pH_q = CH_2CH_2, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = tBu, L^2 = {C_pH_q = $CMeHCH_2$, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = tBu, L^2 = {C_pH_q = CH_2CHMe, E = N, and both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = {C_mH_n = CH_2CH_2, E = N, both R^1 and R^2 are Me}, L^2 = {C_pH_q = CH_2CH_2, E = N, both R^3 and R^4 are Me}, x = 0 is excluded;

provided that L^1 = {C_mH_n = CH_2CH_2, E = N, both R^1 and R^2 are Et}, L^2 = {C_pH_q = CH_2CH_2, E = N, both R^3 and R^4 are Et}, x = 0 is excluded; and

provided that L^1 = Me, L^2 = {C_pH_q = CH_2CH_2, E' = O, R^3 is Me}, x = 0 is excluded.

15. The composition of any one of claims 13 and 14, wherein the lithium precursor is selected from $LiNMe(CH_2CH_2NMe_2)$, $LiNMe(CH_2CH_2NMe_2)$(1,2-diethoxyethane), $LiNMe(CH_2CH_2NMe_2)$(1,2-dimethoxyethane), $LiNEt(CH_2CH_2NMe_2)$, $LiNiPr(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NEtMe)$, $LiNtBu(CHMeCH_2NMe_2)$, $LiNtBu(CH_2CHMeNMe_2)$, $LiN(CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2NEt_2)_2$, $LiN(CH_2CH_2NiPr_2)_2$, $LiN(CH_2CH_2NEtMe)_2$, $LiN(CH_2CH_2CH_2NMe_2)_2$, $LiN(CHMeCH_2NMe_2)_2$, $LiN(CHMeCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHMeNMe_2)_2$, $LiN(CH_2CHMeNMe_2)(CH_2CH_2NMe_2)$, $LiN(CHEtCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHEtNMe_2)(CH_2CH_2NMe_2)$, $LiN(CMe_2CH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CMe_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2CH_2NMe_2)$, $LiNMe(CH_2CH_2OMe)$, $LiNMe(CH_2CH_2OEt)$, $LiNMe(CH_2CH_2OiPr)$ $LiNMe(CH_2CH_2OtBu)$, $LiNEt(CH_2CH_2OMe)$, $LiNEt(CH_2CH_2OEt)$, $LiNiPr(CH_2CH_2OMe)$, $LiNtBu(CH_2CH_2OMe)$, $LiN(CH_2CH_2OMe)_2$, $LiN(CH_2CH_2OEt)_2$, $LiN(CH_2CH_2OiPr)_2$, $LiN(CH_2CH_2OtBu)_2$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OMe)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OEt)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OiPr)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OtBu)$, or $LiNMe(CH_2CH(OMe)_2)$.

16. The composition of any one of claims 13 and 14, wherein the lithium precursor is selected from $LiNtBu(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NEtMe)$, $LiNtBu(CHMeCH_2NMe_2)$, $LiNtBu(CH_2CHMeNMe_2)$, $LiN(CH_2CH_2NEtMe)_2$, $LiN(CH_2CH_2OEt)_2$, $LiN(CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2NMeEt)_2$, $LiN(CHMeCH_2NMe_2)(CH_2CH_2NMe_2)$,

$LiN(CH_2CHMeNMe_2)(CH_2CH_2NMe_2)$, $LiN(CHEtCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHEtNMe_2)(CH_2CH_2NMe_2)$, $LiN(CMe_2CH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CMe_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CH_2NiPr_2)_2$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2CH_2NMe_2)$, $LiN(CH_2CH_2OEt)_2$, $LiNMe(CH_2CH_2OEt)$, or $LiNMe(CH_2CH(OMe)_2)$.

17. The composition of any one of claims 13 and 14, wherein the lithium precursor is $LiN(CH_2CH_2NMe_2)_2$.

18. A film, islet or cluster forming precursor having a general formula:

$$[Li\text{-}NL^1L^2\text{-}D_x]_y \qquad (I)$$

wherein

L^1 has a general formula: C_mH_n, $(C_mH_n)\text{-}ER^1R^2)$ or $(C_mH_n)\text{-}E'R^1)$, wherein

- (C_mH_n) is a linear, branched or cyclic alkyl groups;
- m and n are independent integers, $1 \le m \le 16$, $1 \le n \le 16$;
- E is B, N;
- E′ is a divalent element;
- R^1 and R^2 each are independently selected from the group consisting of hydrogen, linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

L^2 has a general formula: $(C_pH_q)\text{-}ER^3R^4$ or $(C_pH_q)\text{-}E'R^3$, wherein

- C_pH_q is a linear, branched or cyclic alkyl groups;
- p and q are independent integers, $1 \le p \le 16$, $1 \le q \le 16$;
- E is B, N;
- E′ is a divalent element;
- R^3 and R^4 each are independently selected from the group consisting of hydrogen, linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system;

x is an integer, $0 \le x \le 4$; and

y is the degree of association of the molecule, $1 \le y \le 6$.

19. The film, islet or cluster forming precursor of claim 18, wherein

L^1 is a C_1-C_{16} linear, branched or cyclic carbon chains, or of the form (C_mH_n)-ER^1R^2 or (C_mH_n)-$E'R^1$, wherein

- C_mH_n is an alkyl chain and may be linear, branched or cyclic alkyl groups;
- E represents B, N;
- E′ represents a divalent element such as O, S;
- m is an integer which value is 1 or an integer ranging from 1 to 8;
- n is an independent integer ranging from 2 to 16;
- R^1 is independent and selected from the group consisting of hydrogen, linear, branched or cyclic C_1-C_8 alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;
- R^2 is independent and selected from the group consisting of hydrogen, linear, branched or cyclic C_1-C_8 alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

L^2 is of the form (C_pH_q)-ER^3R^4 or (C_pH_q)-$E'R^3$, wherein

- C_pH_q is an alkyl chain and may be linear, branched or cyclic alkyl groups;
- E represents B, N;
- E′ represents a divalent element such as O, S;
- p and q are independent integers ranging from 1 to 16, preferably p is comprised from 1 to 8 and q is comprised from 2 to 16, most preferably p is different from m;
- R^3 and R^4 are independent and selected from the group consisting of hydrogen, linear, branched or cyclic alkyl groups, or linear, branched or cyclic alkyl groups substituted by other atoms or groups;

D is independently selected from monodentate, bidentate, tridentate, or polydentate neutral coordinating ligand system, preferably a monodentate or a bidentate;

x is an integer comprised between 0 and 4; and

y represents the degree of association of the molecule and is comprised between 1 and 6.

20. The film, islet or cluster forming precursor of any one of claims 18 and 19, being selected from $LiNMe(CH_2CH_2NMe_2)$, $LiNMe(CH_2CH_2NMe_2)$(1,2-diethoxyethane), $LiNMe(CH_2CH_2NMe_2)$(1,2-dimethoxyethane), $LiNEt(CH_2CH_2NMe_2)$, $LiNiPr(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NMe_2)$, $LiNtBu(CH_2CH_2NEtMe)$, $LiNtBu(CHMeCH_2NMe_2)$, $LiNtBu(CH_2CHMeNMe_2)$, $LiN(CH_2CH_2NMe_2)_2$, $LiN(CH_2CH_2NEt_2)_2$, $LiN(CH_2CH_2NiPr_2)_2$, $LiN(CH_2CH_2NEtMe)_2$, $LiN(CH_2CH_2CH_2NMe_2)_2$, $LiN(CHMeCH_2NMe_2)_2$,

$LiN(CHMeCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHMeNMe_2)_2$, $LiN(CH_2CHMeNMe_2)(CH_2CH_2NMe_2)$, $LiN(CHEtCH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CHEtNMe_2)(CH_2CH_2NMe_2)$, $LiN(CMe_2CH_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CMe_2NMe_2)(CH_2CH_2NMe_2)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2CH_2NMe_2)$, $LiNMe(CH_2CH_2OMe)$, $LiNMe(CH_2CH_2OEt)$, $LiNMe(CH_2CH_2OiPr)$ $LiNMe(CH_2CH_2OtBu)$, $LiNEt(CH_2CH_2OMe)$, $LiNEt(CH_2CH_2OEt)$, $LiNiPr(CH_2CH_2OMe)$, $LiNtBu(CH_2CH_2OMe)$, $LiN(CH_2CH_2OMe)_2$, $LiN(CH_2CH_2OEt)_2$, $LiN(CH_2CH_2OiPr)_2$, $LiN(CH_2CH_2OtBu)_2$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OMe)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OEt)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OiPr)$, $LiN(CH_2CH_2NMe_2)(CH_2CH_2OtBu)$, or $LiNMe(CH_2CH(OMe)_2)$.