

NEW LIQUID PRECURSORS FOR CVD OF METAL-CONTAINING MATERIALS

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ABSTRACT

CVD processes are often limited by the available choice of chemical precursors. For many main-group metals, there have been no suitable compounds available to serve as CVD precursors. Only inconvenient solid sources have been known for the alkali and alkaline earth metals. Liquid sources for magnesium, aluminum, gallium and zinc have been dangerously pyrophoric. CVD precursors commonly used to supply transition metals such as titanium and tungsten contain corrosive halogens such as chlorine or fluorine. Many CVD precursors only react at temperatures too high for use with desired substrates. Recent advances in precursor design and synthesis have now removed these limitations. During the past several years, my research group has synthesized and tested new liquid precursors for more than 30 metals. The precursors have been used for low-temperature CVD of their nitrides and oxides, as well as some pure metals. This paper reviews the results of this work. Many of these new liquid precursors are now commercially available, and some are in widespread use for commercial production of coatings.

DESIRABLE PROPERTIES OF CVD PRECURSORS

The successful use of a CVD process depends on the availability of precursors having a variety of physical and chemical properties. Ideally, precursors should be gases at room temperature, or liquids that vaporize without decomposition at temperatures well below the temperatures of their CVD process. Solids are much less convenient as precursors, since their vaporization rate is hard to reproduce because of variations in particle size and contamination or decomposition byproducts on their surfaces. Thus almost all practical applications of CVD use gaseous or liquid precursors.

CVD precursors should also be inexpensive to manufacture and purify, and remain stable during storage and handling. Ideally they should not react with air or water, and should be non-pyrophoric, non-flammable, non-toxic and non-corrosive.

CVD reactions should take place at temperatures low enough not to damage substrates, but high enough to produce the desired phase. Plasma activation, which can damage substrates, should be avoided, if possible. If co-reactants are needed, the reactant vapors should not react with each other prematurely, in order to allow mixing to a uniform, reproducible vapor composition. Ligands should be cleanly eliminated to produce pure deposits with desirable properties, such as good step coverage. A high percentage of the precursor should be converted to product, at a sufficiently high growth

rate. Finally, the byproducts of a CVD reaction should be stable, non-reactive, non-corrosive, non-flammable and non-toxic.

Few, if any, CVD processes meet all these requirements. The following sections review the synthesis and use of new precursors that we designed to remove some of the limitations of precursors previously used for CVD. Convenient liquid precursors were found for some metals for which only solid precursors had been known. Non-pyrophoric liquids were found to replace known pyrophoric sources. Less corrosive precursors were synthesized to replace corrosive ones. Precursors were designed to react at lower substrate temperatures without the need for plasma activation.

GROUP 1: ALKALI METALS

No volatile, room-temperature liquid sources have been available for CVD of materials containing alkali metals. The first distillable liquid compounds of lithium, sodium and potassium were found among the alkylsilylamides of these alkali metals. For example, lithium bis(ethyltrimethylsilyl)amide, $\text{LiN}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_3]_2$, is a liquid at room temperature with viscosity 37 centipoise at 40 °C (1).

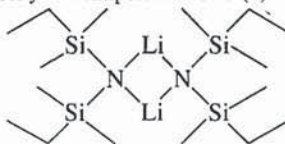


Figure 1. Lithium bis(ethyltrimethylsilyl)amide

It has a vapor pressure of 0.2 Torr at 122 °C. A similar sodium compound, sodium bis(*i*-butyltrimethylsilyl)amide, is the first distillable liquid sodium compound.

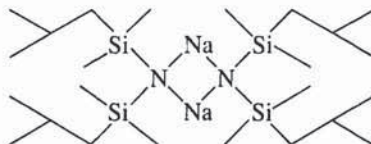


Figure 2. Sodium bis(*i*-butyltrimethylsilyl)amide

These compounds have been used for CVD of alkali metal hydroxides, and also mixed metal oxides such as lithium niobate (see below under niobium).

GROUP 2: ALKALINE EARTH METALS

The first non-pyrophoric, distillable liquid magnesium compounds were prepared. An example is the monomeric reaction product of magnesium bis(2,2,6,6-tetramethylheptane-3,5-dionate) ($\text{Mg}(\text{thd})_2$) with *N,N'*-dihexylethylenediamine. This liquid can be distilled at 72 °C under a pressure of 27 mTorr. Mixing this vapor with

oxygen allows CVD of magnesium oxide films on substrates at temperatures around 500 °C (2).

The first flash-vaporizable liquid compounds of calcium, strontium and barium were formed from certain polyamine complexes of β -diketonates of these alkaline earth metals. An example is the monomeric reaction product of barium bis(2,2,6-trimethylheptane-3,5-dionate) with N,N',N'',N'''-tetrahexyltriethylenetetramine. This compound is similar to the crystalline strontium compound whose molecular structure is shown in Figure 2. This liquid has a viscosity of 246 centipoise at 40 °C, and can be flash-vaporized with negligible residue at temperatures around 240 °C. Mixtures of its vapor with that of tetrakis(dimethylaminoethoxy)titanium, oxygen and nitrous oxide deposited barium titanate films at substrate temperatures of 400 to 500 °C (3).

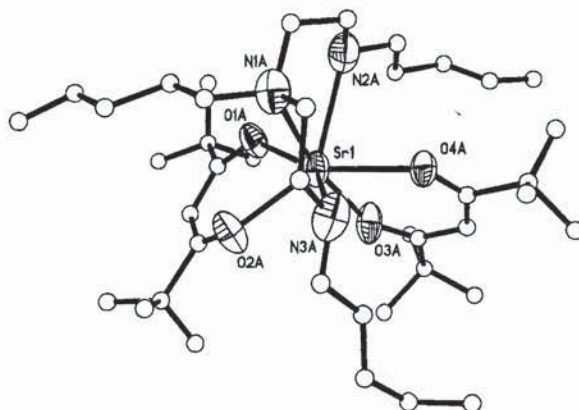


Figure 2. Molecular structure of strontium bis(2,2,6,6-tetramethylheptane-3,5-dionate) N,N',N''-tripentyltriethylenetriamine

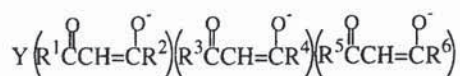
Similar liquid compounds were prepared for strontium and calcium (2).

GROUP 3: YTTRIUM AND LANTHANUM

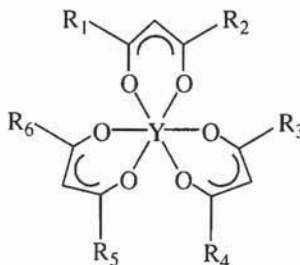
Liquid yttrium oxide CVD precursors

Yttrium 2,2,6,6-tetramethyl-3,5-heptanedionate, Y(thd)₃, is the precursor most commonly used for CVD of yttrium-containing high temperature superconductors (4) and of electroluminescent yttrium oxide (5). Y(thd)₃ is a solid at room temperature, so it is not very convenient to measure into a flash-vaporization system. Y(thd)₃ is not very stable in a heated bubbler, and thus it is difficult to form a reproducible concentration of its vapors.

A liquid yttrium precursor can be formed by mixing beta-diketonate compounds having the general formula



and structure



in which R_1, R_2, \dots, R_6 are chosen randomly from the groups

isopropyl	$-\text{CH}(\text{CH}_3)_2$
isobutyl	$-\text{CH}_2\text{CH}(\text{CH}_3)_2$
sec-butyl	$-\text{CH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$
tert-butyl	$-\text{C}(\text{CH}_3)_3$

This mixed beta-diketonate yttrium precursor is a liquid at room temperature and is miscible with most organic solvents. It is stable to air and water during storage. Direct liquid injection of this liquid mixture into nitrogen carrier gas at 220 °C produced a vapor mixture that was mixed with oxygen and used to deposit carbon-free yttrium oxide, Y_2O_3 , at substrate temperatures of 420 to 520 °C (6).

A similar liquid CVD precursor for lanthanum was made using these mixed beta-diketone ligands. Under the same CVD conditions as the yttrium precursor, the product film contained carbon, having composition $LaC_{2.5}O_{2.5}$.

GROUP 4: TITANIUM, ZIRCONIUM AND HAFNIUM

Titanium nitride

Titanium nitride combines high electrical conductivity, high thermodynamic stability, high melting point, high hardness and reflectivity to infrared radiation. It is also a good barrier to diffusion of aluminum and copper. Because of these remarkable properties, titanium nitride has many applications, including energy-conserving coatings for

windows, wear-resistant coatings on machine tools, corrosion-resistant and decorative coatings on jewelry, and barrier layers in microelectronics.

Titanium tetrachloride is a suitable liquid precursor for deposition of TiN for infrared-reflective solar control coatings on glass windows (7). However, the high deposition temperatures (typically over 600 °C) and the corrosive chloride byproducts preclude the use of TiCl₄ for deposition of TiN barriers between metals in microelectronics. The corrosive solids TiBr₄ and TiI₄ have been used to reduce the deposition temperature to around 400 °C, but halogen contamination remains a problem(8). The non-halogen-containing liquid precursor tetrakis(diethylamido) titanium (TDEAT), Ti(NEt₂)₄, reacts with ammonia to produce TiN films at substrate temperatures of only 200 to 400 °C (9). This reaction is now being applied in microelectronics to produce barriers to diffusion of aluminum and copper, and "glue" layers between tungsten and silicon dioxide. The conformality of these layers has been improved by reversible co-adsorption of trimethylamine during the CVD process (10).

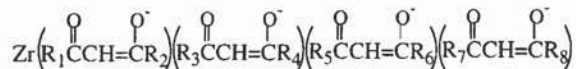
Zirconium and hafnium nitrides

Zr₃N₄ and Hf₃N₄ combine high dielectric constants, high electrical resistance, high stability in contact with silicon, high melting point and high chemical stability. Their possible applications in microelectronics include gate insulators and capacitors.

The known CVD precursors to Zr₃N₄ and Hf₃N₄ include the solids Zr(NMe₂)₄ and Hf(NMe₂)₄ and the liquids Zr(NEt₂)₄ and Hf(NEt₂)₄ (11). The new precursors zirconium tetrakis(ethylmethylamide), Zr(NEtMe)₄, and hafnium tetrakis(ethylmethylamide), Hf(NEtMe)₄, are more volatile liquids (12). CVD from these precursors and ammonia produces Zr₃N₄ or Hf₃N₄ at substrate temperatures of 200 to 400 °C.

Zirconium and hafnium oxides

Zirconium tert-butoxide, Zr(O^tBu)₄, is a liquid source that has been used for the CVD of zirconium oxide (13). However, this material is prone to decomposition during storage, and is very susceptible to catalytic decomposition by traces of moisture. A more stable liquid source can be made using the mixed beta-diketonate ligands described above for yttrium.



Direct liquid injection into nitrogen preheated to 185 °C and mixing the vapors with oxygen allows CVD of zirconium oxide at substrate temperatures of 420 to 460 °C (6).

GROUP 5: VANADIUM, NIOBIUM AND TANTALUM

Niobium nitride

Niobium nitride, NbN_x , has high electrical conductivity, high melting point, high stability to copper and silicon dioxide, and is a good barrier to diffusion of copper. It has suitable properties to be a diffusion barrier for copper in microelectronics. The CVD precursors known for NbN_x include the solids NbF_5 , $NbCl_5$, and $Nb(NMe_2)_5$ (14). The liquid precursor ethylimidotris(diethylimido)niobium, $(NEt_2)_3Nb=NEt$,

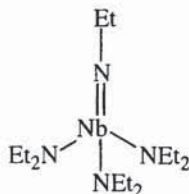


Figure 3. Structural formula of Ethylimidotris(diethylimido)niobium

combined with ammonia, deposits niobium nitride at substrate temperatures of 200 to 400 °C (15). The high step coverage of this deposit makes it a good candidate as a barrier and adhesion layer for copper in future microelectronics.

Lithium Niobate

Ethylimido tris-diethylamido niobium vapors combined with those of lithium bis(ethylmethylsilyl)amide and oxygen deposit lithium niobate, a non-linear optical material, on substrates heated to 300 °C (16).

GROUP 6: CHROMIUM, MOLYBDENUM AND TUNGSTEN

Tungsten Metal

Tungsten has a high melting point, high electrical conductivity, and high stability to copper and silicon dioxide. It has a work function that is mid-gap in silicon. Currently, tungsten is widely used in microelectronics as a metallic connector to silicon transistors. Tungsten hexafluoride, WF_6 , is currently used as the precursor for CVD tungsten.

A more conductive replacement for polycrystalline silicon is needed for future gate electrodes in silicon microelectronics. WF_6 cannot be used as a precursor for this application, because the byproduct hydrogen fluoride destroys the thin gate oxide insulators. Tungsten hexacarbonyl, $W(CO)_6$, is currently being investigated as a non-corrosive precursor for tungsten gate electrodes (17), diffusion barriers and trench capacitors (18). $W(CO)_6$ is a solid, so it is not so convenient to meter into the process, and it is a hazardous substance, since it has sufficient volatility to emit toxic vapors at room temperature. These limitations of $W(CO)_6$ have been overcome by a new liquid precursor, tungsten alkylisonitrile pentacarbonyl, $RNCW(CO)_5$, where R is a

hydrocarbon with 5 or more carbons (19). These liquids are stable to air and water, and have low hazard potential because of their low vapor pressure at room temperature. They have monomeric molecular structures similar to that of the low-melting solid compound pictured below:

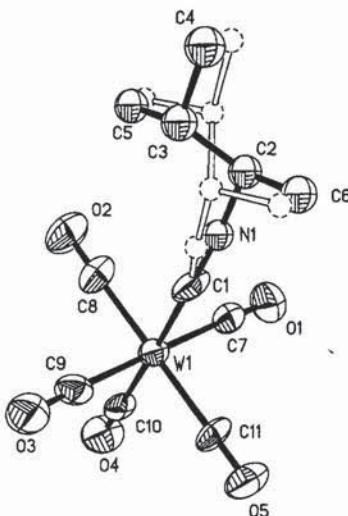


Figure 4. Molecular structure of tungsten(0) pentacarbonyl 1,2-dimethylpropylisonitrile.

The strength of the bond between tungsten and the isonitrile is identical to that of the W-CO bond in $W(CO)_6$, so their CVD properties are similar. Liquid chromium and molybdenum precursors have also been made by alkylisonitrile substitution of the analogous solid hexacarbonyls.

The same new liquid tungsten precursors can be reacted with ammonia to deposit tungsten nitride on substrates at temperatures from about 250 to 400 °C. Tungsten nitride is also an excellent barrier to diffusion of copper and other metals.

Tungsten oxide can be formed by oxidation of the vapors of these liquid precursors on substrates at temperatures from 200 to 300 °C. These tungsten oxide films are electrochromic, and could be used in displays or in "smart" windows or mirrors with electrically controllable optical properties.

LATER TRANSITION METAL OXIDES: Mn, Fe, Ru, Co, Ni, Cu

The mixed beta-diketonate ligands described under Group 3 (Y and La) were used to make precursors for a number of transition metals. Fe(III) and Ru(III) formed liquid

precursors, while Mn(II), Co(III), Ni(II) and Cu(II) formed high-viscosity glasses at room temperature. These glasses were easily flash vaporized from solutions in organic solvents such as mesitylene or N,N,N',N''-pentamethyldiethylenetriamine. The mixed beta-diketonates are much more soluble than individual pure beta-diketonate compounds of the same metals. Some vaporization and CVD conditions are given in Table I, along with analyses of the composition of the deposited films by Rutherford backscattering (RBS) (20).

Table I. CVD of some transition metal oxides from mixed beta-diketonate precursors

Metal	Vaporization Temp. °C	Deposition Temp. °C	Composition by RBS
Mn	180	300-400	MnO ₂
Fe	165	360-420	Fe ₂ O ₃
Ru	180	200-400	RuO to RuO ₂
Co	180	360	Co ₂ O ₃
Ni	220	440-460	NiO _{1.2}
Cu	180	340-460	Cu to CuO

GROUP 12: FLUORINE-DOPED ZINC OXIDE ZnO:F

Zinc oxide is a transparent semiconductor. When doped with impurities such as boron, aluminum, gallium, indium or fluorine, it can become a good electrical conductor. Fluorine gives the best performance as a transparent conductor (21). Its high resistance to hydrogen plasmas is helpful in making amorphous silicon solar cells. Its ready etchability facilitates its use in displays.

Common CVD precursors for ZnO include diethylzinc, Et₂Zn, a dangerously pyrophoric liquid, and Zn(acac)₂ (acac = acetylacetonate = 2,4-pentanedionate), a solid. These disadvantages can be avoided by the use of a new precursor, the N,N,N',N''-tetraethylethylenediamine adduct of diethylzinc, whose structural formula follows:

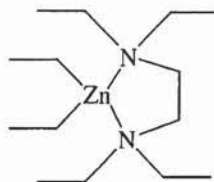


Figure 5. Structural formula of diethylzinc N,N,N',N''-tetraethylethylenediamine

Et₂Zn(Et₂NCH₂CH₂NEt₂) is a non-pyrophoric liquid whose vapors react with ethanol vapor to deposit ZnO at substrate temperatures of 400 to 500 °C. Addition of benzoyl fluoride to the liquid precursor provides fluorine doping to the films (22).

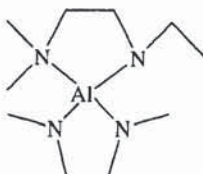
GROUP 13: ALUMINUM AND GALLIUM

Aluminum and Gallium Nitride

Aluminum nitride, AlN, has high transparency to ultraviolet, visible and infrared light, high electrical resistance, a high melting point and good mechanical stability. Films of AlN are outstanding barriers to diffusion of oxygen and water. Exposure of AlN films to air or moisture creates a self-limiting, thin layer of an oxygen-containing material on the surface, but oxygen does not penetrate into the interior of the film, even during heating to 250 °C in humid air. AlN has applications as a protective layer for moisture and oxygen-sensitive electroluminescent powders, microelectronics, displays and solar cells.

Known CVD precursors for aluminum nitride include the pyrophoric liquid aluminum alkyls such as trimethylaluminum, which react with ammonia at high temperatures (typically over 600 °C) to form AlN. Use of hexakis(dimethylamido)dialuminum, Al₂(NMe₂)₆, brought the CVD reaction temperature down to below 200 °C (23). However, this precursor is still a solid at room temperature (melting point 90 °C).

A new precursor, aluminum bis(dimethylamide)-N-ethyl-N',N'-dimethylethylenediamide, Al(NMe₂)₂(NEtCH₂CH₂NMe₂),



is a non-pyrophoric liquid at room temperature with viscosity 6 centipoise at 40 °C, and vapor pressure of 0.3 Torr at 65 °C. Its vapors react with ammonia at temperatures between about 150 and 400 °C to deposit films of amorphous aluminum nitride (24). Gallium nitride was made under similar mild conditions by CVD from the analogous gallium compounds (25).

Aluminum Oxide

A number of precursors have been used for the CVD of aluminum oxide, including the pyrophoric liquid aluminum alkyls, and solid aluminum isopropoxide and aluminum acetylacetonate. A safer and more convenient source is the non-pyrophoric liquid triethyl-tri(isopropoxy)dialuminum, which can be distilled at a temperature of 190 °C and 30 Torr. Its vapors react with oxygen at temperatures around 400 °C to deposit films of amorphous aluminum oxide that are excellent barriers to diffusion of sodium out of soda-lime glass (26).

GROUP 14: TIN AND LEAD

Tin Nitride

Films of tin nitride, Sn_3N_4 , were deposited from vapors of the liquid precursor tetrakis(diethylamido)tin and ammonia at substrate temperatures of 200 °C to 400 °C (27).

Tin Oxide

The electrical and optical properties of tin oxide are very similar to those of zinc oxide. As in the case of ZnO, fluorine is the dopant that produces the most transparent and electrically conductive films of tin oxide. CVD of fluorine-doped tin oxide was first obtained using the vapors of liquid tetramethyltin (28). In commercial CVD of $\text{SnO}_2\text{:F}$, tetramethyltin has now been largely replaced by the less toxic and less expensive liquid precursors butyltin trichloride and tin tetrachloride.

Lead Oxide

Using the same beta-diketonate ligand mixture described for Group 3, lead forms a high-viscosity glass at room temperature. This $\text{Pb}(\beta\text{-diketonate})_2$ is highly soluble in organic solvents, such as mesitylene. These solutions were flash vaporized at about 250 °C, mixed with oxygen and flowed over substrates at temperatures of 280 to 420 °C to form PbO_2 (6).

GROUP 15: BISMUTH OXIDE

Bismuth behaves similarly to lead. A mesitylene solution of bismuth beta-diketonate mixture, $\text{Bi}(\beta\text{-diketonate})_3$, was flash vaporized at about 175 °C and mixed with oxygen. This vapor mixture deposited Bi_2O_3 at substrate temperatures from 300 to 360 °C (6).

CONCLUSIONS

Limitations of available precursors have made CVD of many materials difficult. Only inconvenient solid sources were known for some metals, and available liquid sources for others were dangerously pyrophoric. The first vaporizable liquid precursors were synthesized for the alkali metals lithium, sodium and potassium and the alkaline earth metals calcium, strontium and barium. The first non-pyrophoric liquid precursors were made for magnesium, aluminum, gallium and zinc. Convenient, non-corrosive liquid CVD precursors were also found for many transition metals. Commercial sources are now available for many of these new liquid precursors. Some are being used in large-scale commercial CVD processes.

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