CVD PRECURSORS CONTAINING HYDROPYRIDINE LIGANDS

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ABSTRACT

Hydropyridine is introduced as a new ligand for use in constructing precursors for chemical vapor deposition. Detachment of hydropyridine occurs by a low-temperature reaction leaving hydrogen in place of the hydropyridine, and a very stable byproduct, pyridine vapor. Hydropyridine ligands can be attached to a variety of elements, including main group metals, such as aluminum and antimony, transition metals, such as titanium and tantalum, semiconductors such as silicon, and non-metals such as phosphorus and arsenic.

PROPERTIES OF IDEAL CVD PRECURSORS

An ideal CVD precursor should have a number of properties:

1) Its vapor pressure should be sufficiently high (e.g. 1 Torr) at a relatively low temperature (e. g. less than 200 C).

2) It should be thermally stable at its vaporization temperature.

3) Its vaporization kinetics should be rapid and reproducible, which is usually the case if it is a non-associated liquid (not a solid) at its vaporization temperature.

4) It should react at temperatures above its vaporization temperature according to a single, well-defined reaction mechanism, to produce a pure product material.

5) The byproducts of its CVD reaction should be stable and non-reactive.

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6) The reactants and byproducts should be non-flammable, non-toxic and non-corrosive.

7) The precursor should be inexpensive to manufacture and to purify.

8) It should remain stable during storage.

PROPERTIES OF CVD REAL PRECURSORS

Few, if any, CVD precursors satisfy all of these criteria. For example, silicon, a widely used semiconductor, is deposited from a variety of CVD sources, particularly silane, disilane and dichlorosilane, which are hazardous spontaneously flammable gases. It would be advantageous to have CVD sources for silicon which are not as hazardous as these gases.

Boron and phosphorus are added to silicon as impurities (dopants) to increase its electrical conductivity. Diborane and phosphine are extremely poisonous gases which are used to provide dopants during CVD of silicon or silicon dioxide. It would be advantageous to have less toxic boron and phosphorus sources which also have lower vapor pressures, so that they could not be spread as easily by gas leaks.

Gallium arsenide is another useful semiconductor, which is often made by a CVD process starting from arsine, an extremely toxic gas, and trimethylgallium, which is spontaneously flammable. It would be desirable to have less toxic arsenic sources with lower vapor pressures, and gallium sources which are not spontaneously flammable.

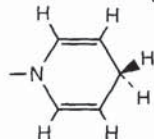
Aluminum is a metal that is useful in making interconnections in microcircuits. Currently known CVD aluminum sources include aluminum alkyls, which are spontaneously flammable and also leave carbon impurities in the aluminum, and aluminum hydride complexes, which are unstable when stored at room temperature. Because of these disadvantages, aluminum is not usually made by CVD. It would be desirable to have aluminum CVD sources which make pure metal, are not spontaneously flammable, and are stable during storage.

Titanium sources, such as cyclopentadienyl-cycloheptatrienyl titanium and tetrakis(dimethylamido)titanium, do not decompose cleanly to produce the metal, but rather produce a film that is mainly composed of carbon. Addition of ammonia cleanly removes the carbon, but the deposited film is titanium nitride, rather than the free metal. No satisfactory CVD source is known for titanium metal. The present work was initiated as a search for

such a titanium precursor. Although we have not yet identified a completely satisfactory CVD source for pure titanium metal, the novel ligand design which we have explored appears to have considerable promise for producing improved CVD precursors for many materials.

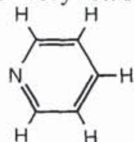
SOME NEW CVD PRECURSORS

As potential new CVD precursors, we have synthesized some new compounds containing dihydropyridinato ligands

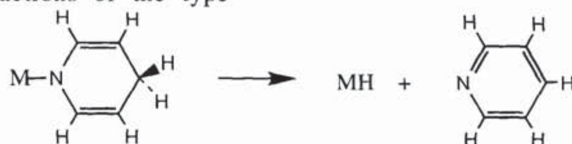


1,4-dihydropyridinato

which may be considered to be derived formally by adding a hydrogen atom to the very stable aromatic heterocycle, pyridine:



During a CVD reaction, these ligands should be removed from a molecule by reactions of the type



in which M stands for the remainder of the molecule to which the dihydropyridine ligand is attached.

As one specific example of this type of precursor, we have prepared a silicon-containing compound tris(1,4-dihydropyridinato)silane, which should decompose to silane according to the reaction

The thermodynamic driving force for this reaction should be favorable because these ligands become much more stable aromatic molecules after they give up their "extra" hydrogen to the remainder of the molecule. We may make a rough estimate of the likely enthalpy change in these reactions, by assuming additive bond energies. The heat of dissociating one dihydropyridine ligand may be estimated in terms of typical bond energies (BE) and the resonance stabilization energy (RE) of pyridine, as follows

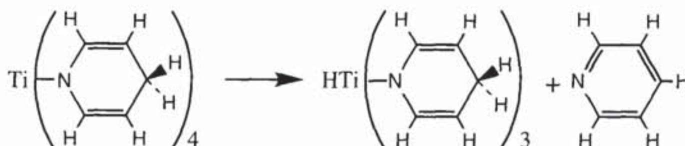
$$\Delta H = BE(Si\text{-}N) + BE(C\text{-}H) + BE(C\text{-}N) - BE(Si\text{-}H) - BE(C{=}N) - RE(pyridine)$$

$$= BE(Si\text{-}N) + 415 + 273 - 250 - 615 - 134 \text{ kJ/mol}$$

$$= BE(Si\text{-}N) - 311 \text{ kJ/mol}$$

This estimate predicts that the dissociation reaction with hydrogen transfer is much less endothermic than simple bond homolysis of the Si-N bond. Although the quantitative accuracy of this estimate may not be too great, the qualitative conclusion should be reliable, that thermal decomposition should occur by hydrogen transfer rather than by simple bond homolysis.

A similar estimate may be made for the heat dissociating each hydropyridine ligand from tetrakis(1,4-dihydropyridinato)titanium by hydrogen transfer reactions, the first of which is the following:



$$\Delta H = BE(Ti\text{-}N) + BE(C\text{-}H) + BE(C\text{-}N) - BE(Ti\text{-}H) - BE(C{=}N) - RE(pyridine)$$

$$= BE(Ti\text{-}N) + 415 + 273 - 159 - 615 - 134 \text{ kJ/mol}$$

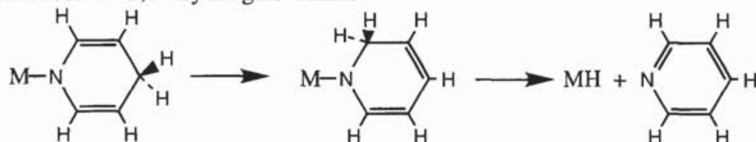
$$= BE(Ti\text{-}N) - 220 \text{ kJ/mol}$$

Thus for this titanium compound, dissociation accompanied by hydrogen transfer also costs less energy than simply breaking the bond.

The activation energies for these reactions are harder to estimate quantitatively. However, this reaction should have a fairly low activation energy because this hydrogen motion is a process allowed by the Woodward-Hoffmann rules of organic chemistry. (It is called a 1,5-

sigmatropic hydrogen shift.) Thus this ligand dissociation should be rapid even at relatively low temperatures.

It is also possible that dissociation may take place by a sequence of two successive 1,3 hydrogen shifts:

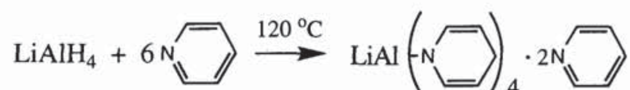


This second hydrogen shift, together with the MN bond cleavage, constitute a beta-hydride elimination reaction. Because 1,3 hydrogen shifts are "forbidden" by the Woodward-Hoffmann rules, this two-step pathway is expected to have a slightly higher activation energy than a single allowed 1,5 hydrogen shift. The products from either pathway are identical.

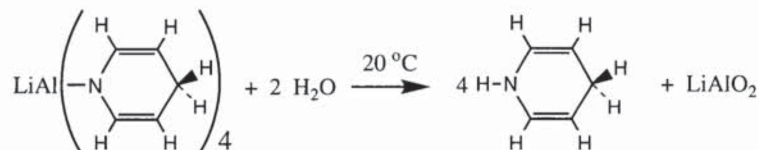
The bis(dihydropyridinato) derivatives of magnesium and zinc have been prepared, and were observed to decompose at temperatures around 125 C, to form magnesium hydride and zinc metal, respectively.[1] (Zinc hydride, the presumed initial product of this decomposition reaction, decomposes at 125 C.) Tris(dihydropyridinato)aluminum has also been prepared[2], but no data have been obtained about its thermal stability.

SYNTHESIS OF SOME NEW CVD PRECURSORS

The syntheses may be started from 1,4-dihydropyridine, which is not commercially available. The 1,4-dihydropyridine may be synthesized conveniently by the lithium aluminum hydride reduction of pyridine[3] to form lithium tetrakis(1,4-dihydropyridyl)aluminate:



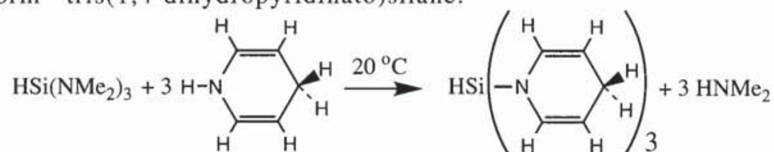
Carrying out this reaction at elevated temperatures (up to 120 °C) results in nearly pure 4H isomer, with less than one per cent of the less stable 2H isomer. Hydrolysis by water of its pyridine solution results in a mixture of pyridine and the desired 1,4-dihydropyridine, which are vacuum distilled together from the hydrolysis byproducts, because the boiling points of dihydropyridine and pyridine are very close together.



In some cases, the remaining pyridine does not cause problems with the further processing, and may be retained as the solvent. In other cases, it may be desirable to form pure dihydropyridine, free from pyridine impurity. In such cases, a higher-boiling solvent is added to the pyridine solution of lithium tetrakis(1,4-dihydropyridyl)aluminate, and the unreacted pyridine is removed by distillation at reduced pressure, before the hydrolysis step. A suitable higher-boiling solvent is 1-methylimidazole, which has a boiling point (198 °C) much higher than that of pyridine (115 °C).

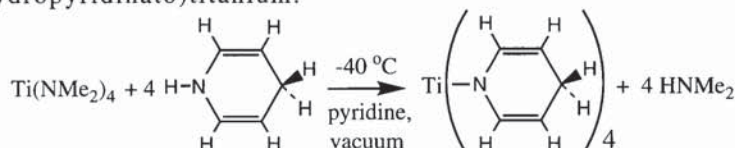
It should be noted that 1,4-dihydropyridine is very sensitive to oxygen, heat and acids, which appear to cause it to polymerize or decompose. Inhibitors, such as diphenylamine or phenothiazine, should be added to stabilize the material during vacuum distillation or storage. Without an inhibitor, dihydropyridine polymerizes within a few days of storage at room temperature in an inert-atmosphere glove box. With the addition of only 0.04% diphenylamine, no polymerization has been observed over a period of two months. Most of the other compounds are also very reactive to water and oxygen. Therefore, these syntheses must exclude the ambient atmosphere by careful use of Schlenk techniques and an inert-atmosphere glove box.

After preparing the 1,4-dihydropyridine, the CVD source material may be synthesized by transamination reactions, in which partially hydrogenated aromatic nitrogen-containing heterocyclic ligands replace dimethylamido ligands. This procedure is illustrated below for the case of transamination of tris(dimethylamido)silane by 1,4-dihydropyridine to form tris(1,4-dihydropyridinato)silane:



In order to carry out this reaction, the tris(dimethylamido)silane is mixed with a 1,4-dihydropyridine solution and stirred in a fractional distillation apparatus so that the volatile dimethylamine gas byproduct distills out of the mixture. This reaction appears to be complete in about two days at room temperature.

Similar transamination reactions may be used to form other compounds having dihydropyridine ligands, such as tetrakis(1,4-dihydropyridinato)titanium:



This transamination reaction is complete within a few minutes even at low temperatures(-40 °C), and is accompanied by a color change to a deep red-purple solution. Attempts to run this transamination reaction at room temperature resulted in polymerization of the product.

Preparation of 1,4-dihydropyridine

1,4-dihydropyridine was made by reaction of lithium aluminum hydride with excess pyridine. The pyridine was dried by storage over molecular sieves. 250 cubic centimeters of dry pyridine was added to 5.04 g lithium aluminum hydride and stirred until most of it dissolved. The undissolved material was mostly lithium hydride impurity in the lithium aluminum hydride. The undissolved material was filtered out and the clear solution was stirred at room temperature for one hour, and then heated to reflux temperature (about 120 °C) for 12 hours. The resulting pyridine solution of lithium tetrakis(4H-pyridin-1-yl)aluminate was cooled to 20 °C, 0.1 gram of diphenylamine was dissolved in it, and then 4.75 g of degassed water was added slowly while stirring and maintaining the solution at 20 °C. The stirring was continued for 15 minutes. Trap to trap vacuum distillation was then used to remove the dihydropyridine and excess pyridine from the non-volatile hydrolysis byproducts. The resulting mixture was analyzed by proton NMR to be a 10% solution of 1,4-dihydropyridine in pyridine. The NMR shifts in pyridine-d_5 are in agreement with the literature.[3]

Preparation of tris(1,4-dihydropyridinato)silane

Ten grams of a 19% dihydropyridine solution in 1-methylimidazole was placed in a three-necked flask which was purged through one neck with dry nitrogen containing less than one ppm of oxygen or water vapor. Another neck held an addition funnel containing 1.038 g of tris(dimethylamido)silane (from Strem Chemicals) which was added to the

magnetically-stirred solution. The light yellow mixture was stirred at room temperature and atmospheric pressure for two days, during which time it gave off dimethylamine gas (basic to litmus test) through an oil bubbler attached to the third neck of the flask.

NMR of the resulting solution confirmed that the reaction had occurred, because the majority of the methyl resonance of the reactant had been removed. The resonances of the carbon-bound hydrogens in 1,4-dihydropyridine were only shifted slightly by the reaction, while line from the nitrogen-bound hydrogen disappeared. The proton NMR shifts in pyridine-d_5 are (in ppm) 6.15 (H on C2), 4.35 (H on C3) and 3.12 (H on C4), insignificantly changed from the free dihydropyridine.

Preparation of tetrakis(1,4-dihydropyridinato)titanium

Five cubic centimeters of a 10% dihydropyridine solution in pyridine was cooled to -40 ^{o}C and 0.23 g of tetrakis(dimethylamido)titanium was added to the stirred flask. The dark red mixture was stirred under vacuum for one hour, during which time it gave off dimethylamine gas. NMR analysis of the solution indicated the presence of 1,4-dihydropyridine ligands bound to titanium(IV) in a non magnetic compound. If this solution is warmed to room temperature, it polymerizes within about an hour. Addition of 0.1% diphenylamine retarded, but did not eliminate, this polymerization. Therefore the solution was made, stored and used at -40 ^{o}C. NMR analysis of the solution indicated the presence of 1,4-dihydropyridine ligands bound to titanium(IV) in a non magnetic compound. The proton NMR shifts for this product in benzene-d_6 are (in ppm) 7.16 (H on C2), 4.29 (H on C3) and 3.10 (H on C4).

CHEMICAL VAPOR DEPOSITION EXPERIMENTS

A funnel-shaped stainless steel reaction chamber, having inside dimensions 20 cm tall and 15 cm diameter, was heated from above. A silicon wafer substrate, with its polished surface facing down, was positioned on the top of the chamber. Pure nitrogen gas, containing less than 0.2 ppm water or oxygen, was flowed into the bottom of the chamber, and out through a washer-shaped screen placed between the top of the funnel and the silicon wafer, as shown in Figure 1.

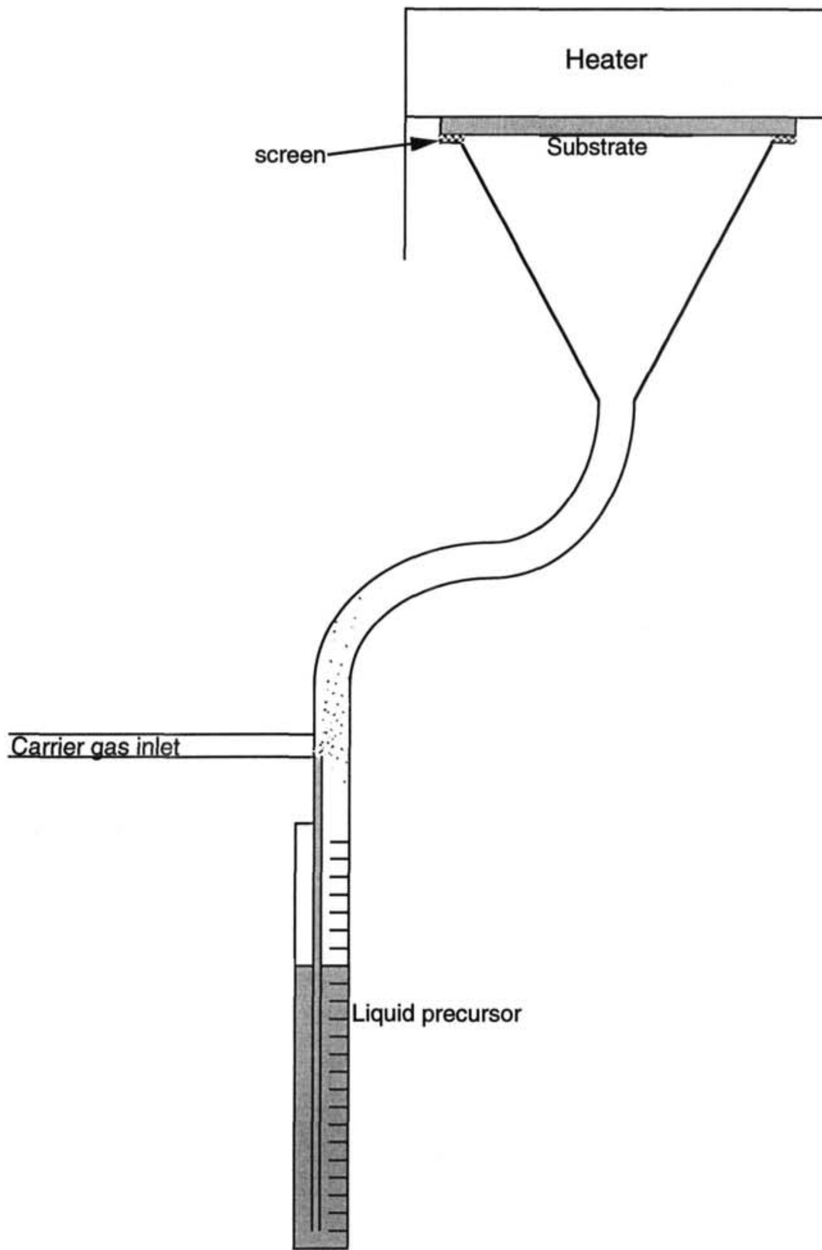


Figure 1. Aerosol CVD System

CVD of Silicon

A 1-methylimidazole solution of tris(1,4-dihydropyridinato)silane was placed in the reservoir of a pneumatic atomizer (TSI, Inc.) held at 20 ^{o}C while a stream of pure nitrogen passed through the atomizer at a rate of 4 liters per minute. This created an aerosol of submicron droplets which was then passed directly into the reaction chamber. Flow of the aerosol was maintained for a period of ten minutes, while the substrate was held at a temperature of about 625 ^{o}C. Then the substrate was cooled in a flow of pure nitrogen.

A shiny, smooth film adhered strongly to the substrate, as well as to the adjacent portions of the stainless steel funnel. Analysis of the deposited film by Rutherford Backscattering Spectroscopy (RBS) showed that it consisted mainly of silicon.

CVD of Titanium-containing Films

A pyridine solution of tetrakis(1,4-dihydropyridinato)titanium was placed in the reservoir of a pneumatic atomizer (TSI, Inc.) held at -40 ^{o}C while a stream of pure nitrogen precooled to -40 ^{o}C passed through the atomizer at a rate of 4 liters per minute. This created an aerosol of submicron droplets which was then passed directly into the reaction chamber. Flow of the aerosol was maintained for a period of thirty minutes, during which time the substrate was held at a temperature of about 450 ^{o}C. Then the substrate was cooled in a flow of pure nitrogen.

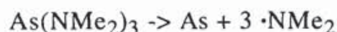
A shiny, smooth, dark-colored film was deposited on the silicon, as well as on the hottest parts of the funnel's inner surface. The absence of any spots indicates that complete vaporization of the solution droplets occurred. Analysis of the deposited film by RBS showed that it consisted of titanium metal, along with carbon, nitrogen, oxygen and hydrogen. Simulations of the spectrum suggest that more than 90% of the ligands have been cleaved under these conditions, but that still leaves more carbon atoms than titanium atoms in the film. The carbon-to nitrogen ratio remains similar to that of the precursor, about 5:1. X-ray Photoelectron Spectroscopy indicated that the carbon is organic, rather than bound to the titanium as a carbide. The oxygen is presumably acquired during exposure to air between deposition and analysis. The electrical resistance of the films increases during exposure to the air, indicating that the film probably has a porous structure.

DISCUSSION

Similar decomposition pathways are expected for a wide variety of elements attached to hydropyridine ligands. Main group metals, such as aluminum, gallium, indium, tin and antimony should be deliverable into CVD reactions by hydropyridine-containing precursors. Semiconductors, such as silicon, germanium, arsenic and selenium may be transported similarly. Even non-metals, such as phosphorus and sulfur may form suitable compounds. Early transition metals may also be transported using hydropyridine ligands, but further work will be needed to stabilize them against polymerization, and to find deposition conditions under which the ligands cleave completely.

A comparison can be made between CVD using the dihydropyridine ligand introduced in this paper, and the dimethylamido ligands which have recently received much attention for the CVD of nitrides of the transition metals titanium[4], zirconium and hafnium[5], vanadium, niobium and tantalum[6],; the nitrides of the main-group elements aluminum[7] , gallium[8], silicon[9] and tin[10], as well as oxides[11], and gallium arsenide.[12,13] The dimethylamido ligands generally yield precursors with higher vapor pressure and higher stability than the hydropyridine ligands. Thus for those reactions, such as the reactions with ammonia[4-10], in which the dialkylamido ligands provide satisfactory reactivity, they will be preferred over hydropyridine. However, in cases where a pure element, such as silicon or a metal, is to be deposited, the lower energy decomposition pathway of the hydropyridine may provide a lower deposition temperature.

Another advantage of the hydropyridine ligand may appear in cases such as gallium arsenide, for which high purity is important. The thermal removal of dimethylamido ligands from arsenic leads[12] to highly reactive byproducts, including radicals, such as the dimethylamine radical, from bond homolysis:



$$As(NMe_2)_3 \text{ -> } As + 3\ {\cdot}NMe_2$$

These radical byproducts can bind strongly to surfaces and contaminate them. Beta-hydride elimination reactions lead to highly reactive Schiff bases, such as N-methylmethyleneimine:

$$As(NMe_2)_3 \text{ -> } AsH_3 + 3\ H_3CN{=}H_2$$

These Schiff bases readily polymerize, and such polymeric byproducts can adhere to the surface of the growing film, or to the reactor walls.

In contrast, the decomposition byproduct of a hydropyridine ligand is the very stable and relatively non-reactive molecule pyridine, which is much less likely to lead to contamination of the product or the reactor.

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