Design of low-temperature thermal chemical vapor deposition processes

by D. B. Beach

The importance of an integrated approach involving synthetic chemistry, physical chemistry, and chemical engineering to the development of new thermal chemical vapor deposition (CVD) processes for the production of thin-film electronic materials is discussed. Particular emphasis is placed on choosing precursor molecules with facile thermal decomposition pathways that lead to pure films at low temperatures. Two examples from our laboratories, the deposition of copper from trialkylphosphine cyclopentadienyl copper complexes and the deposition of gallium nitride from diethylgallium azide, are used to illustrate the principles of precursor selection, the design factors for the construction of thermal CVD reactors, and the selection of processing conditions that optimize production of the desired material. In addition, new work on the thermal CVD of copper using an advanced reactor and examples of selective copper deposition and conformal copper deposition using the reactor are presented.

Introduction

As the dimensions of electronic devices decrease, the demands on the properties of the thin films used to produce these devices increase. Film purity, structure, stability, and interfacial properties become increasingly important with decreasing film thickness [1]. In addition, the demands made on the methods of deposition of these thin films become more stringent. Low-temperature (below 800°C) processes are required in device fabrication to prevent diffusion of previously deposited layers, and even lower temperatures (below 400°C) are required in the wiring of devices on chips and associated packages. Thinner films are also more susceptible to radiation and ion damage, so that physical methods of deposition (such as electron-beam evaporation or sputtering), which make use of a plasma or energetic particles, may not be as useful as previously.

Thermal chemical vapor deposition (CVD) can offer significant advantages over physical methods for the deposition of thin films. For example, an epitaxial silicon CVD reactor [2], because it can process many wafers at once, may have up to 100 times the wafer throughput of a molecular-beam epitaxy apparatus, and at substantially lower cost. For multilevel metallization, thermal CVD of tungsten interconnections between layers of wiring is being considered because thermal CVD is a highly conformal process; i.e., film growth at all surfaces proceeds at nearly the same rate [3]. The interconnections between levels of wiring, designated as vias, can thus be filled without the shadowing effects common to sputtering techniques and the poor sidewall coverage common to evaporation techniques. Another major advantage of thermal CVD over physical methods is selectivity, or the ability of the precursor molecule to chemically "recognize" the desired growth surface. An example of this is the selective filling of vias on patterned silicon/silicon dioxide wafers using tungsten hexafluoride (WF_6) as a precursor [4]. If an oxidized Si wafer is patterned and etched to expose the Si, direct ohmic contact may be made to silicon by the reaction of pure WF_6. After a layer of tungsten approximately 1000 Å thick has been deposited, the reaction ceases. By adding hydrogen to the gas mixture, tungsten continues to grow only on the previously deposited tungsten and eventually produces a planar surface with tungsten interconnections through the SiO_2 layer [3].

Perhaps the most significant advantage (and one that has only recently been appreciated) that CVD has over other methods of deposition is the production of metastable materials. Most CVD processes operate far from equilibrium conditions, so that kinetically rather than thermodynamically favored products are produced. An example of this can be seen in the heavily boron-doped epitaxial silicon films produced by Meyerson et al. [5]. When deposited at 550°C, the boron doping level exceeds the solid solubility of boron in silicon by at least an order of magnitude.

For all the possible benefits to be derived from CVD processing, relatively few new CVD processes have been introduced in the electronics industry in the last decade. One of the factors limiting progress in thermal CVD research and development has been the limited number of commercially available precursor compounds. Accordingly, in the last five years, a number of researchers in both academia and industry have initiated programs to identify new precursors [6].

In the remainder of this paper, attempts are made to show that the development of a new thermal CVD process requires an integrated approach involving synthetic chemistry, mechanistic studies, and chemical engineering. Synthetic chemistry studies are needed to produce precursors not available commercially and to synthesize unknown molecules with desirable decomposition characteristics. Mechanistic studies, including both gas-phase and surface reactions, are needed to define these desirable decomposition characteristics [7]. Since many of the new precursors have properties (volatility, reactivity) significantly different from those of precursors currently in use, chemical engineering studies are needed to determine CVD reactor design and processing conditions.

Choice of precursor

In the design of a new thermal CVD process, a very important factor is the selection of the precursor molecule. Film purity, growth rate, and transport phenomenon are unique to each precursor. The primary factors in deciding on a precursor are 1) facile decomposition to the desired product at an acceptable temperature, and 2) sufficient vapor pressure to allow transport of the precursor to the growth surface. The second factor dictates that the precursor have a relatively low molecular weight (below ~400 amu) and tend not to associate in either its gas or solid phase. Several methods for achieving facile decomposition are outlined in the following sections.

• *Molecules with adduct bonds*

There are relatively few examples of CVD precursors containing bonds with dissociation energies below 20 kcal/mol, because this is below the range of single-bond energies in molecules that are stable at room temperature. An exception to this is molecules containing adduct bonds. Such bonds are formed between molecules which donate and accept electron pairs. A simple example is the reaction product of the two stable molecules, trimethylamine and boron trifluoride:

$$(CH_3)_3N\!: + BF_3 \rightarrow (CH_3)_3N\!:\!BF_3\,. \qquad (1)$$

The trimethylamine molecule donates a lone pair of electrons to the vacant orbital of the boron trifluoride molecule.

The utility of adduct compounds as CVD precursors arises from their ability to prevent oligomerization of coordinatively unsaturated molecules, and to stabilize electron-deficient species by the donation of electron density. Examples demonstrating both of these properties are the adducts of borane, BH_3. Borane dimerizes spontaneously and is extremely reactive but can be isolated as a monomeric adduct with a variety of bases, some of which are stable in air. Accordingly, we have used the analogous adduct of trimethylamine and alane, $(CH_3)_3N\!:\!AlH_3$, to deposit aluminum films of very high purity [8]. Alane, AlH_3, is a polymeric substance with no appreciable vapor pressure that decomposes to aluminum and hydrogen at temperatures above 100°C. On the other hand, the trimethylamine–alane complex has a vapor

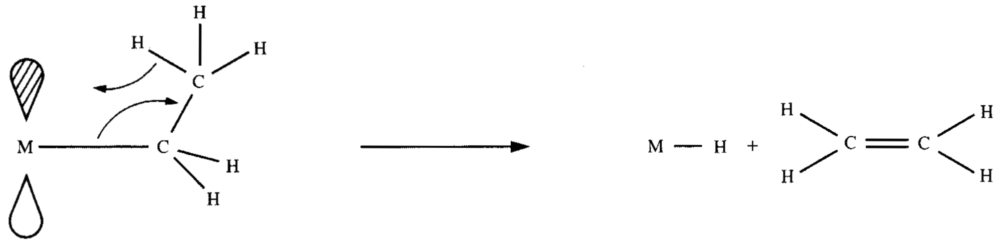


Figure 1

Mechanism of β-hydride elimination of ethylene from an organometallic compound containing an ethyl ligand.

pressure of 2 torr at room temperature [9] and transports readily at reduced pressures. This complex dissociates at higher temperatures, leaving the unstable alane on the growth surface; the trimethylamine is pumped away without being incorporated in the film.

- *Molecules with "pre-formed" bonds*

Films containing two elements, such as the III–V semiconductors and the binary insulators (e.g., Si_3N_4, SiO_2, AlN, BN), have usually been deposited by the reaction of two gases, each containing one of the elements. An example of this is the preparation of epitaxial GaAs films from trimethylgallium and arsine:

$$Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + CH_4 . \tag{2}$$

While this approach is quite successful for the synthesis of some materials, there are numerous examples where it has been difficult to control the film stoichiometry. For example, in order to avoid formation of silicon-rich silicon nitride films when using silane/ammonia mixtures, a large excess of ammonia must be used [10]; and in the growth of boron nitride films from boron hydride/ammonia mixtures, the films are invariably boron-rich [11]. In both of these cases, the source of the problem is the lower stability and higher reactivity of the metal hydrides relative to ammonia.

One method of controlling film stoichiometry is to control the precursor stoichiometry by "pre-forming" a strong bond between the two atoms to be incorporated in the film. For example, if use is made of the aluminum nitride precursor synthesized via the reaction of trimethylaluminum and ammonia by Interrante et al. [12],

$$3(CH_3)_3Al + 3NH_3 \rightarrow [(CH_3)_2AlNH_2]_3 + 3CH_4 , \tag{3}$$

the strong aluminum–nitrogen bond formed during the synthesis of the precursor molecule is unlikely to cleave during film deposition. Other examples are the III–V precursors developed by Cowley et al. [13], the synthesis of one of which is shown below:

$$2GaCl_3 + 2(C_4H_9)_2AsLi + 4C_2H_5Li \rightarrow [(C_2H_5)_2GaAs(C_4H_9)_2]_2 + 6LiCl. \tag{4}$$

These compounds may permit the achievement of CVD of Group III arsenides at conditions of extremely low pressure and temperature because the relatively high pressure (>80 torr) of arsine or arsenic used in conventional thermal CVD would not be required. Thus, better deposition control and the use of more economical batch reactors might be possible.

- *Molecules that undergo elimination reactions*

Ideally, a low-temperature precursor should decompose on the growth surface without incorporating unwanted atoms from the precursor. This is best accomplished by having the unwanted atoms of the precursor eliminated as a stable molecule. A simple example of this is the elimination on decomposition of carbon monoxide from a metal carbonyl such as in the purification of nickel by decomposition of nickel tetracarbonyl (the Mond process). A more complicated but more useful example is the loss of ethylene from a molecule containing an ethyl group attached to an atom with a vacant and accessible orbital. Under this condition, a process known as β-hydride elimination can occur, as shown in **Figure 1**. This mechanism may be responsible for the observed reduction in carbon incorporation when triethylgallium instead of trimethylgallium is used to deposit gallium arsenide [14],

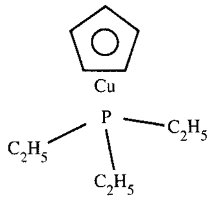


Figure 2

Structure of triethylphosphine(cyclopentadienyl)copper(I).

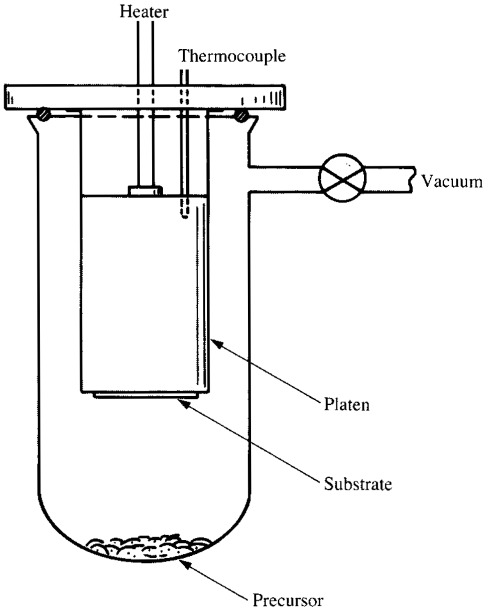


Figure 3

Thermal CVD reactor for deposition of Cu. From [22], reproduced with permission.

and for the low carbon content of aluminum films deposited from tri-isobutyl aluminum [15]. Many other elimination reactions are known in organic chemistry, including decarbonylation (loss of CO_2 from an ester or carboxylic acid), dehydration (such as occurs following the condensation of a primary amine with a carbonyl group), and loss of nitrogen from azide and azo compounds, but these reactions have not been widely used or studied for CVD purposes.

Thermal chemical vapor deposition of copper

In addition to numerous packaging applications such as chip carriers and circuit boards using pure copper films, small additions of copper are used to improve the electromigration performance of aluminum interconnections on chips [16]. A thermal CVD process that could conformally deposit Al/Cu into vias would certainly be of potential interest. Previously, the CVD of copper for electronic applications had been accomplished using acetyl acetonate [17] and alkoxide [18] complexes of copper. However, these compounds contain oxygen, and they cannot be used with compounds that deposit aluminum (typically aluminum alkyls and hydrides). Organocopper compounds (which would be compatible with aluminum precursors) are known, but tend to be unstable. For example, ethyl copper decomposes if the solution in which it is prepared is warmed to room temperature [19].

One class of organocopper compounds that are stable are the trialkylphosphine(cyclopentadienyl)copper(I) complexes [20]. The structure of the triethylphosphine derivative [21] is shown in **Figure 2**. These compounds are prepared by the reaction of thallium cyclopentadienide and the copper halide complex of the appropriate phosphine:

$$\mathrm{Tl(C_5H_5)} + [\mathrm{P}R_3\mathrm{Cu}X]_4 \rightarrow \mathrm{C_5H_5CuP}R_3 + \mathrm{Tl}X, \qquad (5)$$

where $R = CH_3$, C_2H_5, or C_4H_9 and X = Cl, Br, or I. They are purified by vacuum sublimation at 60–70°C to give colorless solids that have room-temperature vapor pressures of ~1 millitorr and remain stable in air for several minutes.

- *Initial deposition studies*

In order to rapidly evaluate possible copper precursors and to establish deposition conditions, initial deposition studies were performed in a standard vacuum flash pyrolysis apparatus in which the precursor was allowed to flow at reduced pressure from a sample reservoir through a glass tube heated by a tube furnace into a liquid nitrogen cold trap to collect the volatile products of decomposition. In the case of the trialkylphosphine cyclopentadienyl copper compounds, the hot zone was maintained at a temperature of 220°C, and the sample reservoir and tubing leading from the reservoir to the hot zone were maintained at 60°C to increase the vapor pressure of the precursor. A mirror-like film of copper was deposited in the hot zone. The film was scraped from the walls of the tube, weighed, dissolved in nitric acid, and analyzed by atomic absorption spectroscopy. It was found to contain at least 99% copper. The contents of the cold trap were separated by fractional condensation into three components: unreacted precursor, trialkylphosphine, and a hydrocarbon product that spontaneously polymerized to form a waxy, nonvolatile substance upon warming to room temperature. The identity of this hydrocarbon compound is discussed in a subsequent section.

• *Reactor design*

The first successful Cu thermal CVD reactor using these trialkylphosphine cyclopentadienyl copper complexes has been described by Beach et al. [22] and is depicted in **Figure 3**. The reactor is basically a vacuum-sublimation apparatus with its cold finger replaced by a heated platen. Although it is primitive, it has provided essential information for the construction of the more elaborate reactor diagrammed in **Figure 4**. In the first reactor, substrate heating was accomplished by heat-sinking the substrate to the platen with gallium, while in the second reactor the platen was replaced by a gas-conduction wafer chuck. Because the room-temperature vapor pressures of these compounds are only 1–2 millitorr, it was necessary to have large conductances between the source and the substrate and to heat the source and the reactor walls. In the first reactor, the glass vacuum envelope surrounding the substrate and platen was placed in a 60°C bath. In the second reactor, the entire apparatus was placed in an oven 10–20°C warmer than the precursor reservoir (which again was held between 60 and 80°C). The first reactor was pumped by a cold-trapped diffusion pump, while the second reactor was pumped by a throttled turbomolecular pump. The second reactor was also fitted with an argon-ion sputter gun for cleaning wafers prior to deposition and with a residual gas analyzer to identify reaction products.

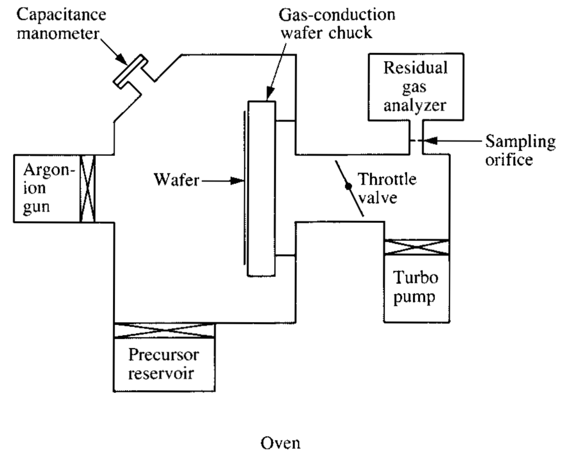


Figure 4

More elaborate thermal CVD reactor for copper deposition, utilizing a gas-conduction wafer chuck.

• *Processing conditions*

With the construction of the second reactor, it was possible to accurately measure and control reactor pressure and precursor flow. Typical deposition pressures were between 5 and 50 millitorr at a precursor flow rate of 75 sccm. (The flow rate was calculated from the rate of transport of the precursor material, and was controlled by varying the temperature of the precursor reservoir.) At that flow rate, and at substrate temperatures below 220°C, the rate of deposition of Cu was not limited by mass transport and depended only on substrate temperature. No carrier gas was used with the Cu precursors.

It was determined that copper films containing less than 1% carbon could be deposited only over the temperature range from 150–210°C. Above 220°C, carbon was incorporated in the films, and below 150°C the reaction was too slow to give growth rates greater than 100 Å/min. It was also found that there was a significant barrier to nucleation in this temperature range for growth on surfaces other than clean transition metals. For this reason, most of the growth studies were carried out using insulators coated with a thin adhesion layer of chromium followed by a thin seed layer of copper.

Previous studies [22] of growth rate as a function of temperature using the first reactor with triethylphosphine(cyclopentadienyl)copper(I) gave a linear Arrhenius plot with an activation energy of 18 kcal/mole. This activation energy is considerably below the weakest bond dissociation energy in the precursor molecule, and is consistent with the occurrence of a surface-catalyzed reaction. A maximum growth rate of 2200 Å/min was obtained at a substrate temperature of 210°C. Films as thin as 200 Å and as thick as 4.4 μm were grown under appropriate combinations of substrate temperature and deposition time. Using the second reactor, growth rates identical to those provided by the first reactor were obtained only if the reactor surfaces were thoroughly cleaned prior to deposition and the precursor reservoir was freshly charged with precursor. If the reactor was used for consecutive depositions without cleaning and recharging, the growth rate fell by as much as 95% in subsequent depositions. (We believe that this was probably due to surface poisoning caused by the reaction byproducts, probably the organophosphine.)

• *Reaction products*

The residual gas analyzer attached to the second reactor gave more information about the volatile products of the deposition reaction. The m/e values for the principal ions that appear upon decomposition of triethylphosphine(cyclopentadienyl)copper(I) at 180°C in the region of 110–130 amu are listed in **Table 1**. The peaks at 117 and 118 amu correspond to the molecular ion of triethylphosphine. The cluster of peaks between 126 and 131 amu is due to a $C_{10}H_{10}$ hydrocarbon. We believe that this hydrocarbon is 9,10-dihydrofulvalene **(Figure 5)**, the unrearranged product of the coupling of two cyclopentadienyl radicals. This compound has also been observed as the product of the thermal decomposition of nickelocene, $(C_5H_5)_2Ni$ [23]. The analysis of the reaction products is consistent with the following overall reaction:

$$2C_5H_5CuP(C_2H_5)_3 \rightarrow 2Cu + 2P(C_2H_5)_3 + C_{10}H_{10} . \tag{6}$$

The coupling of the cyclopentadienyl radicals is analogous to the Ullmann reaction [24], in which aryl halides are coupled to form biphenyl compounds using copper metal. Although well known in solution chemistry, this type of reaction has not been reported in thermal CVD chemistry.

- *Film properties*

Analysis by Auger electron spectroscopy (AES) of the depth profile of a CVD Cu film (**Figure 6**) indicated that the film consisted of pure Cu with no detectable carbon or phosphorus contamination. Resistivity measurements gave a resistivity of 2.0 $\mu\Omega$-cm, a value just 10% greater than that of OFHC copper. Transmission electron microscopy revealed that the copper grains of the film were tightly packed and that its grain boundaries were free of precipitates [22].

- *Conformality and selectivity*

Conformality and selectivity are especially important in the deposition of low-resistivity metals for forming interconnections for microelectronic chips. Conformality facilitates the multilevel interconnection of the devices and circuits of the chips; selective growth may potentially reduce the number of interconnection processing steps required. As a test of conformality, a 1.5-μm-thick Cu film was deposited at a substrate temperature of 175°C onto an oxidized silicon substrate containing a trench that was 2 μm deep and 0.7 μm wide. The substrate was then cleaved to expose a cross section of the trench, and the conformality was determined using scanning electron microscopy. **Figure 7** shows that such a trench can be completely filled without shadowing effects, voiding, or poor sidewall coverage. Figure 7 also shows the 2000–3000-Å surface roughness of the Cu film. All of the films grown under conditions in which the growth rate was not limited by mass transport exhibited a surface roughness of 10–20% of their thickness. Thus, films less than 1 μm thick had a specular appearance, while films thicker than 1 μm appeared matte. By limiting the rate of mass transport of the precursor and increasing the substrate temperature, smoother films could be grown, but with a significant loss in conformality.

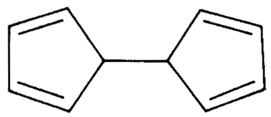


Figure 5

Structure of 9,10-dihydrofulvalene.

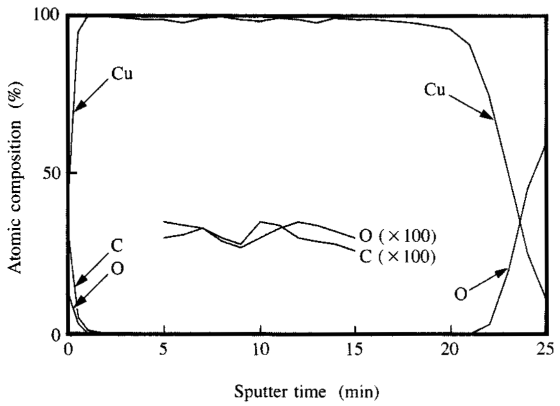


Figure 6

Compositional depth profile of a 1.5-μm-thick Cu film deposited by thermal CVD, as determined by Auger electron spectroscopy.

Table 1 Principal m/e peaks associated with the decomposition of $(C_5H_5)CuP(C_2H_5)_3$ in the 115–135-amu range.

m/e	*Relative abundance*
117	40.9
118	100
119	7.0
126	4.3
127	17.4
128	44.3
129	74.8
130	67.8
131	6.6

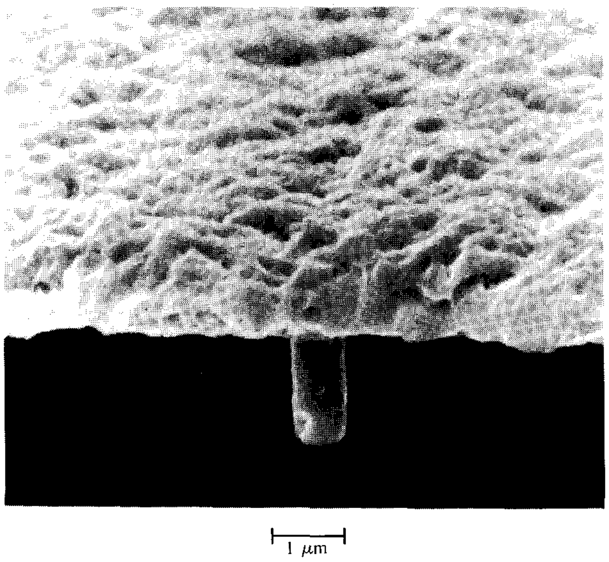


Figure 7

SEM image of a cleaved sample, illustrating the filling of a trench 0.7 μm wide and 2.0 μm deep by a 1.5-μm-thick Cu film, deposited by thermal CVD.

As mentioned earlier, the first experiments on these precursors indicated a significant barrier to nucleation on surfaces other than clean transition metals. We have taken advantage of this to deposit copper selectively on a tungsten surface. This was carried out using an oxidized Si wafer patterned with trenches that were 1 μm wide and 0.5 μm deep; Si was exposed at the bottom of the trenches. Use was then made of WF_6 to deposit a 1000-Å seed of selective tungsten. The seeded wafers were exposed to $C_5H_5CuP(CH_3)_3$ at 175°C to grow a 3000-Å-thick layer of copper. The results are shown in **Figure 8**. Although the selectivity was not perfect (there was some growth on the oxide field), the growth occurred predominantly in the trench. Interestingly, the copper film growth seemed to be significantly faster along the sidewalls and in the trench corners. At present, we have no satisfactory explanation for this phenomenon, although it may indicate high surface mobility of the adsorbed precursor molecules prior to decomposition.

Thermal chemical vapor deposition of gallium nitride

Gallium nitride is a large-bandgap (3.4 eV) direct semiconductor that crystallizes in both cubic and hexagonal forms [25]. It has been used as an optoelectronic material, and as an insulator and passivation layer for gallium arsenide. The traditional method for producing gallium nitride films by thermal CVD involves the reaction of gallium trichloride and ammonia at 800°C [26]. We were interested in developing a single-molecule source that would produce high-purity films below 600°C. The molecule we chose was diethylgallium azide [27], which has the trimeric structure [28] shown in **Figure 9**. This molecule is particularly attractive as a thermal CVD precursor for gallium nitride because the azide group should eliminate nitrogen, and the ethyl groups should eliminate ethylene by β-hydride elimination. The desired overall reaction is

$$[(C_2H_5)_2GaN_3]_3 \rightarrow 3GaN + 3N_2 + 6C_2H_4 + 3H_2 . \qquad (7)$$

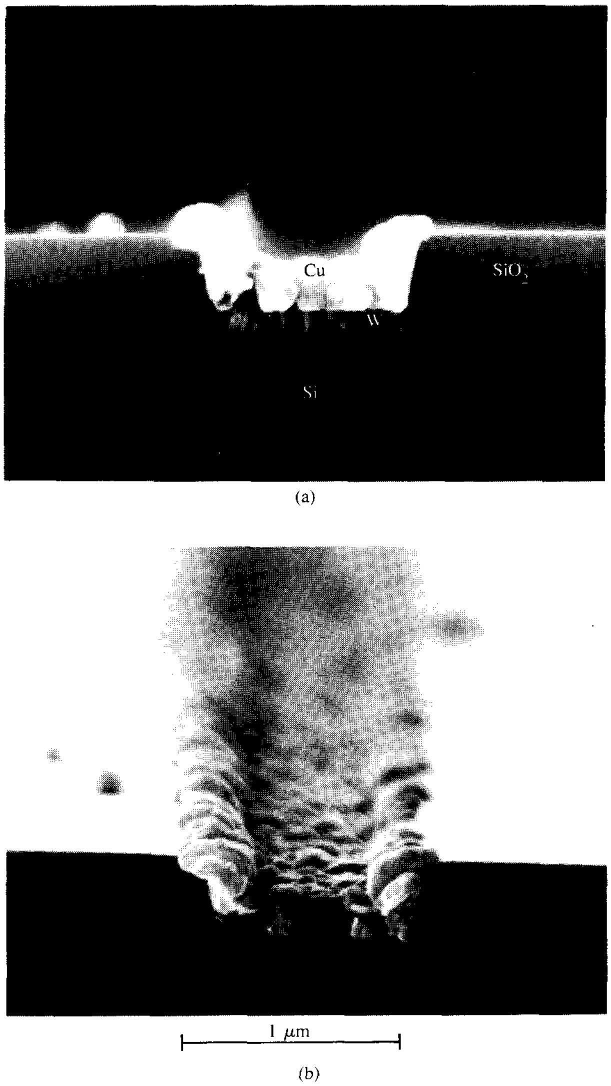


Figure 8

SEM image of a cleaved sample, illustrating selective deposition of copper in a trench seeded with tungsten. View (b) is tilted 60° from view (a).

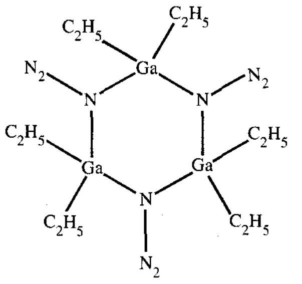


Figure 9

Structure of diethylgallium azide.

The analogous aluminum compound, diethylaluminum azide, has previously been used to deposit aluminum nitride [29].

By using a synthetic procedure similar to that of the aluminum compound, diethylgallium azide was prepared by the reaction of diethylgallium chloride and sodium azide in benzene [30], viz.,

$$(C_2H_5)_2GaCl + NaN_3 \rightarrow (C_2H_5)_2GaN_3 + NaCl, \qquad (8)$$

or, more conveniently, by the reaction of diethylgallium chloride and trimethylsilyl azide:

$$(C_2H_5)_2GaCl + (CH_3)_3SiN_3 \rightarrow (C_2H_5)_2GaN_3 + (CH_3)_3SiCl. \qquad (9)$$

The compound was purified by reduced-pressure distillation (bp 130°C, 3 torr) to give a colorless liquid that decomposes rapidly on exposure to air but does not spontaneously inflame.

- *Reactor design*

In contrast to copper deposition, for which the rate of oxidation is very much slower than that of film growth, a film containing gallium is likely to incorporate oxygen at rates comparable to the growth rate. For this reason, the primary consideration in design of the gallium nitride reactor was the achievement of very low concentrations of residual water and oxygen. The reactor used has been described by Kouvetakis and Beach [27], and is depicted in **Figure 10**. It is equipped with a load-lock to avoid venting between deposition runs. A turbomolecular pump is used both to establish the base pressure of the reactor (2×10^{-9} torr) and to serve as the process pump. (The pump is protected by a liquid-nitrogen trap, which is allowed to warm after deposition so that the contents can be pumped through a high-temperature burn-off furnace to destroy any unreacted precursor.) High-purity helium was used as the carrier gas, and flow through both the bubbler and the reactor was controlled by electronic mass flow controllers. The total pressure in the reactor was regulated independently of flow by using a throttle control valve in the pumping line. Typical deposition conditions for gallium nitride CVD are 2 torr total pressure, 35 sccm flow rate of helium, 1.5 sccm flow rate of diethylgallium azide, and a bubbler temperature of 80°C. By using these conditions, a film growth rate of 25 Å/min could be achieved at a reactor temperature of 350°C.

As can be seen in Figure 10, wafer loading and pumping are located at the same end. While this introduces some complexity into the design, it allows greater flexibility in the manner in which precursors are introduced. For example, very low-vapor-pressure solids can be placed in a tube in front of the reactor and sublimed into it by using an auxiliary furnace. (In the case of diethylgallium azide, the compound was held in a bubbler at 100°C mounted directly on the reactor to prevent condensation of the precursor.) Substrate heating can be changed from a hot-wall to a cold-wall configuration by replacing the tube-furnace with the working coil of an rf generator. In the hot-wall configuration shown in Figure 10, as many as ten substrates can be accommodated per run. In the cold-wall configuration (not shown), the wafer boat is replaced by a single-wafer graphite susceptor, and the substrate temperature is measured through a salt window in front of the reactor using an infrared pyrometer.

- *Film properties*

Initial deposition experiments using diethylgallium azide indicated that decomposition occurs at temperatures as low as 275°C, although the achievement of growth rates higher than 5 Å/min required the use of higher temperatures. Composition analysis of the films produced by Auger electron spectroscopy indicated that films deposited at a temperature above 375°C contained significant (more than 1%) amounts of carbon, and that films deposited at a temperature between 300 and 400°C reacted rapidly with atmospheric moisture to produce a gallium oxide surface layer several hundred Å thick. The sensitivity of the films to moisture indicated that an as-deposited film contained hydrogen attached to its gallium. This was confirmed by using transmission infrared spectroscopy. A 3000-Å-thick film was deposited at 350°C on a Si wedge and transferred under nitrogen to an infrared spectrometer. The resulting spectrum, obtained in the region from 1750–2250 cm^{-1}, is shown in **Figure 11** (solid line). Two overlapping bands at 2070 and 1930 cm^{-1} correspond respectively to Ga–H and Ga–H_2 stretches. For comparison, the infrared spectrum of a film deposited under identical conditions but annealed in the reactor at 600°C is also shown in Figure 11 (dotted line). The gallium–hydrogen stretches completely

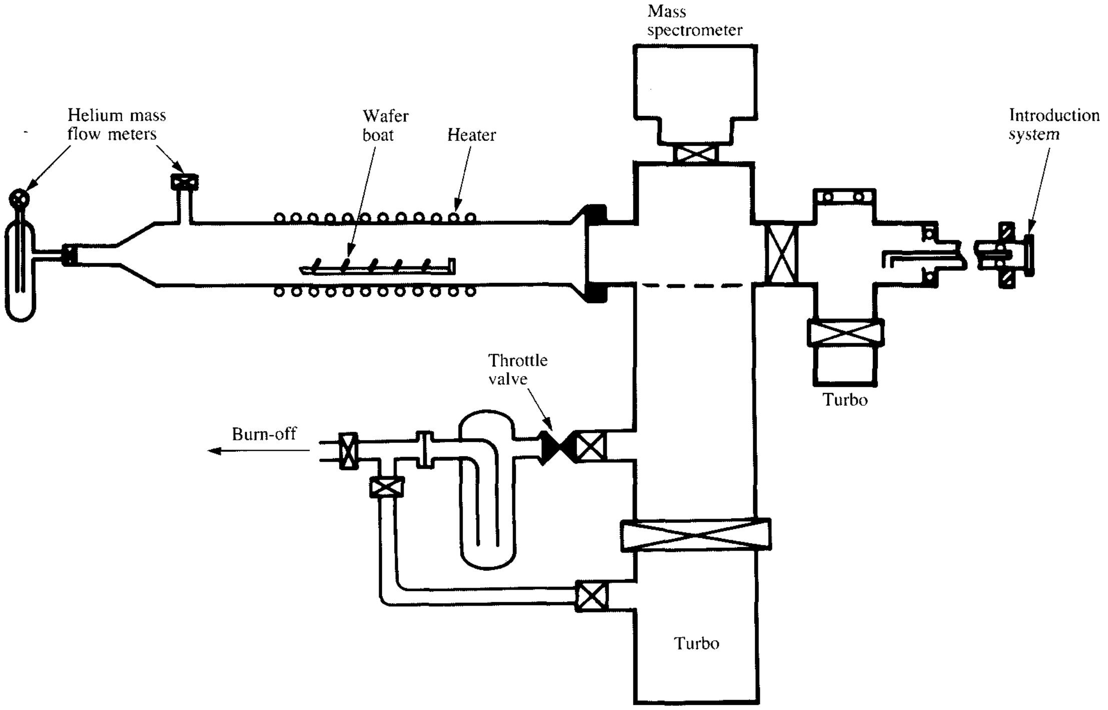


Figure 10

Load-locked thermal CVD reactor for deposition of gallium nitride. From [27], reproduced with permission.

disappeared and the film no longer reacted with moisture. Thus, it appears that low-temperature deposition to reduce carbon impurity levels followed by annealing at higher temperatures to reduce hydrogen content is essential for obtaining stable gallium nitride films of high chemical purity.

Gallium nitride films deposited from diethylgallium azide at 350°C and then annealed *in situ* at 600°C were found to be stoichiometric, with carbon and oxygen levels below the limits of detection of AES (~1%). The films were found to adhere well to silicon, and were smooth and featureless upon examination by optical microscopy. X-ray and electron diffraction data indicated that they were polycrystalline, with the hexagonal wurtzite structure.

- *Reaction products*

At temperatures between 275°C (the onset of decomposition) and 350°C, the only gaseous by-products of decomposition detectable by mass spectrometry were ethylene, nitrogen, and a small amount of hydrogen. As

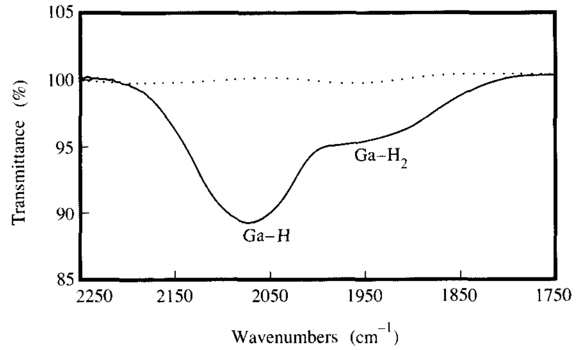
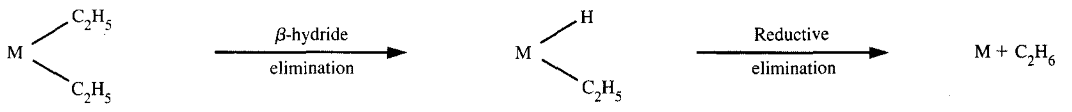


Figure 11

Solid line is the infrared transmittance of a GaN film that was deposited at 350°C. Dotted line is that of a film deposited at 350°C and annealed *in situ* at 600°C. From [27], reproduced with permission.



$$M\begin{matrix} \nearrow C_2H_5 \\ \searrow C_2H_5 \end{matrix} \xrightarrow[\text{elimination}]{\beta\text{-hydride}} M\begin{matrix} \nearrow H \\ \searrow C_2H_5 \end{matrix} \xrightarrow[\text{elimination}]{\text{Reductive}} M + C_2H_6$$

Figure 12

Mechanism of β-hydride elimination, followed by reductive elimination.

the temperature was increased, significant amounts of ethane and traces of methane were observed. At 450°C, the ratio of ethane to ethylene was found to be ~1–2. This implies that the mechanism of hydrocarbon elimination changed with increasing temperature, from β-hydride elimination to reductive elimination or loss of an ethyl radical. Reductive elimination could occur following the loss of one ethylene molecule to produce a gallium atom with a hydride and an ethyl group attached, which then could couple to form ethane, as shown in **Figure 12**. Dissociation of a carbon–gallium bond to form an ethyl radical is another possibility. The ethyl radical could then abstract hydrogen from the growth surface to produce ethane. This ethyl radical could also migrate to a nitrogen atom, forming a relatively strong nitrogen–carbon bond, subsequently decomposing to produce species such as methyl radical, methane, and hydrogen, with some of the carbon bonded to the nitrogen remaining in the film. We speculate that this ethyl radical mechanism may be responsible for the observed high carbon contamination of films deposited above 350°C.

Concluding remarks

The thermal chemical vapor deposition of copper from trialkylphosphine cyclopentadienyl copper complexes and gallium nitride from diethylgallium azide illustrates many of the principles delineated earlier. The copper precursors have an adduct bond between the phosphine ligand and the cyclopentadienyl copper that cleaves readily. The cyclopentadienyl ligands are eliminated via a facile coupling reaction characteristic of organocopper chemistry. The gallium nitride precursor eliminates nitrogen from an azide group and eliminates ethylene by successive β-hydride eliminations. In both cases, film purity is found to be strongly dependent on temperature, with higher temperatures leading to carbon incorporation. This implies that at higher temperatures, reaction pathways other than the low-energy elimination reactions become energetically possible, and points out the advantage of control that thermal processes have over high-energy processes such as laser CVD and plasma CVD.

In conclusion, it should be kept in mind that in designing thermal CVD processes for commercial applications, aspects relating to film purity, deposition rate, precursor and equipment cost, and safety considerations must all be acceptable. In the two examples cited, although the initial results are quite promising, several concerns would need to be addressed before the technological advantages offered by these processes could be exploited. In the case of copper, the major concern is that the organophosphine ligand possesses several undesirable properties. As mentioned earlier, all of the phosphines adsorb strongly to the reactor walls and persist in the reactor, interfering with subsequent depositions. The phosphines are also toxic and pyrophoric. Hence, efforts should be aimed at the synthesis of new copper precursors that retain the low-temperature decomposition pathway afforded by an organometallic ligand while doing away with the organophosphine ligand. In the case of diethylgallium azide, the limited temperature range for the deposition of carbon-free films makes it difficult to combine this process with standard III–V semiconductor growth processes that operate at temperatures at least 200°C higher. Further work in our laboratory on gallium and aluminum nitride precursors will concentrate on attempting to replace the organic ligands with hydride ligands.

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