

Reviews

Selective Metallization by Chemical Vapor Deposition

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The selective growth of metal films by chemical vapor deposition processes is reviewed. A working definition of selectivity, based on the relative rates of nucleation on the growth and nongrowth surfaces, is proposed. After consideration of the factors that effect nucleation and a brief description of the methods used to measure selectivity, a review of the selective depositions of tungsten, copper, and aluminum will be presented.

1. Introduction

Many vapor-deposited metal films for commercial applications are grown by evaporation or sputtering techniques. Because of the potential advantages of chemical vapor deposition (CVD), including conformal coverage of irregularly shaped surfaces and higher throughput, there is continuing interest in developing such methods for depositing metal films.¹ An extensive literature exists describing the CVD of aluminum² and tungsten,³⁻⁹ and there is rapid growth in the number of studies on the CVD of other metals, especially copper.^{10,11} In current technology, the thickness of a film is controlled by chemical reaction rates and/or physical parameters of a given growth process. Subsequent patterning of the film is accomplished by multistep lithographic procedures. The minimum size of the features that can be etched into a film is dependent on the lithographic procedure; the current limit for large-scale production of devices is approximately 0.3 μm .

One of the most challenging goals in the area of CVD is to control the chemistry of a deposition in such a way that the process becomes selective and film growth occurs only on one surface in the presence of others. This produces what is termed a self-aligned structure using fewer lithographic steps. Laser chemical vapor deposition and other means of exciting molecules or heating small areas of a surface offer additional methods leading to selective deposition.^{12,13} These methods are not described further. This review will cover metallizations in which selectivity is mediated by differences in the surfaces exposed to the same precursor flux.

Selective chemical vapor deposition of silicon,^{14,15} various compound semiconductor,¹⁵⁻¹⁸ and tungsten has been used to grow device-quality structures for commercial applications. The specific applications in microelectronics for selective metallization include contact and diffusion barrier formation as well as contact and via filling.

The goals of this review are to develop a definition of selectivity, briefly outline details pertinent to its measurement, and then describe the selective deposition of tungsten, copper, and aluminum. In each case the mechanism of deposition on the growth surface is contrasted to the interactions that take place on the nongrowth surface. It should be recognized that many connections exist between parameters that effect the nucleation and growth processes in CVD reactors. For instance, the partial pressure of the precursor at the growth surface is dependent upon the inlet and outlet flow rates, temperature, surface area, and fundamental constants of the process. In many studies, all of these details are not available.

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2. Defining Selectivity

Currently, depositions are described as being either selective or nonselective, and few reports define the criteria that would differentiate between the two results. What follows is an attempt to develop a more useful, at least somewhat quantitative, *empirical* procedure to describe selective depositions. In addition to the empirical description, under certain conditions more fundamental information on selectivity can be described for a given materials system.

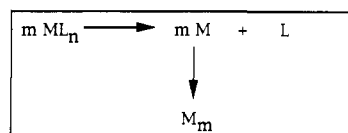
Selectivity is defined as a comparison of the rate of two or more processes that usually share a common starting material, in this case the relative rates of deposition on different surfaces. An important question is what rate should be used to evaluate selective growth. The formation of a new phase as a thin film on top of a different material usually occurs by a nucleation and growth process. From the most general perspective nucleation refers to the formation of a specific quantity of the new phase that, once formed, will continue to accrue mass of the new phase at a steady state rate. It is unclear whether the quantitative models developed for homogeneous and heterogeneous nucleation apply to the chemical vapor deposition of thin films at relatively low temperatures. As discussed below, the activation barrier to nucleation in these situations may be due to specific chemical reactions, such as the shedding of the ligands, rather than to the instability of nuclei of subcritical radii. In chemical systems, the term "initiation" may at times reflect more accurately the events that lead to growth.

Under similar conditions, achieving nucleation is more difficult than maintaining the subsequent steady state growth. As a result, once the nucleus is formed, growth will continue regardless of the substrate material. *Selectivity is achieved by control of the nucleation stage of thin-film growth.*

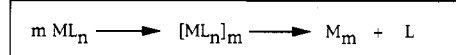
2.1. Causes of Nucleation Involving Molecular Precursors. Nucleation events involving molecular precursors can be divided into three categories. The events described below may occur in the gas phase or on the surface or at both locations. First, there is a finite probability that nucleation will occur entirely on its own as long as the free energy change for the overall deposition is negative for the conditions under consideration. Little is known about the intrinsic nucleation of thin films using molecular precursors. At one extreme the growth species, such as a metal atom, could be required for nucleation to occur. The nucleation rate could depend either on the rate of formation of the metal atom or on its subsequent condensation (Figure 1A). The other extreme (Figure 1B) would involve initial coalescence of the molecular precursor, which could then begin to lose its ligands to form the metal. Perhaps the most likely scenario is one of the numerous situations that lie between the extremes. For example, the precursor could lose one of its ligands and begin to coalesce with other precursor molecules (Figure 1C). The formation of numerous molecular metal clusters occurs by just such a mechanism.¹⁹ If these paths occur on the surface, the surface itself is likely to exhibit a strong influence on the reactions shown in Figure 1.

The second category of nucleation events are caused by contaminants and/or surface defects on the substrate.

A. Molecules to Atoms to Metal Clusters



B. Molecules to Molecular Clusters to Metal Clusters



C. Molecules to Molecular Clusters (with Intermediate Ligand Loss) to Metal Clusters

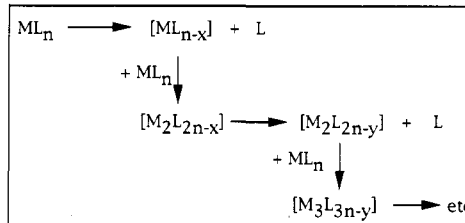


Figure 1. Possible nucleation paths (category 1, intrinsic) involving molecular precursors without the involvement of impurities or surface defects. These paths can occur in the gas phase or on the surface or at both locations. In this scheme of generic events, no attempt has been made to balance the equations.

These include molecular contaminants such as water or oxygen present both in the gas phase and on the substrate surface as well as larger particulates. Once again little is known about these, but it can be anticipated that nucleation caused by them will have a different and often highly irreproducible rate than found for the intrinsic process. An example of this phenomena in a thermal CVD process was recently reported. Trace quantities of water induced gas-phase nucleation of crystalline aluminum particles during the CVD of aluminum using dimethyl-ethylamine alane.^{20,21}

The third category of nucleation includes reactions between fresh precursor and volatile intermediates or products of the process either formed on the wafer or on hot surfaces in the reactor. There is strong evidence that this is important in the selective tungsten system.²²⁻²⁴ Although the last two causes of nucleation share some common features from a mechanistic perspective, they can cause the appearance of unwanted metal deposits in different sections of the reactor. This will be discussed in more detail in the section on selective tungsten deposition.

2.2. Relationship between Nucleation, Coverage, and Selectivity. Ideally, selectivity is defined, eq 1, as the rate of nucleation on the growth surface (GS) divided

$$\text{selectivity on GS} = k_{\text{nuc}}(\text{GS}) / [k_{\text{nuc}}(\text{NS}) + k_{\text{nuc}}(\text{GS})] \quad (1)$$

$$\text{selectivity on NS} = k_{\text{nuc}}(\text{NS}) / [k_{\text{nuc}}(\text{NS}) + k_{\text{nuc}}(\text{GS})] \quad (2)$$

(20) Simmonds, M. G.; Gladfelter, W. L.; Nagaraja, R.; Szymanski, W. W.; Ahn, K.-H.; McMurry, P. H. *J. Vac. Sci. Technol.* **1991**, *A9*, 2782.

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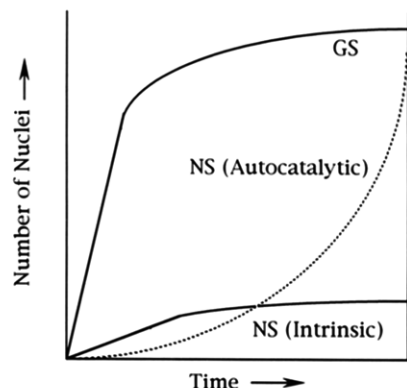


Figure 2. Conceptual diagram of the saturation behavior of the number of nuclei during earliest stage of growth. Note the important difference in behavior on the nongrowth surface between the intrinsic (cause 1) and autocatalytic (cause 3) behavior. The behavior of impurity-induced nucleation (cause 2) would depend on whether or not the impurity is continuously present in the gas phase. The representation of nucleation on both growth and nongrowth surfaces assumes a stronger interaction of the monomer on the like surface than on the unlike surface.

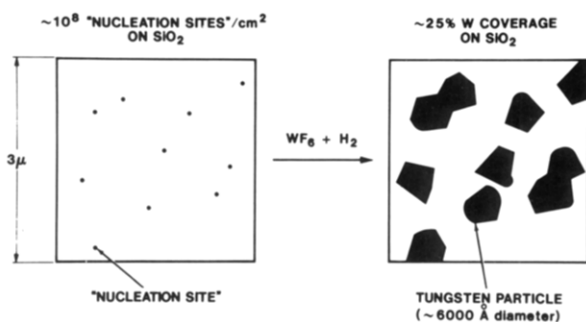


Figure 3. Coverage is proportional to the number of nuclei prior to the point of coalescence.²² [Reprinted by permission of the publisher, The Electrochemical Society, Inc.]

by the sum of the rates of nucleation on the growth and the nongrowth surfaces (NS). The rate of nucleation is defined as the rate formation of new particles on the surface. The proportion of material deposited on the nongrowth surface is similarly defined (eq 2).

Identifying the correct value of the nucleation rate is complicated by its time dependence.²⁵ In studies of the nucleation of films in evaporative processes a nearly constant nucleation rate is often observed during the earliest stage of deposition, but as it proceeds the additional monomers added to the surface are captured by existing particles rather than combining to form new ones.²⁵ The line labeled "NS (intrinsic)" in Figure 2 displays a representative saturation behavior of the number of nuclei as a function of time for this type of nucleation. If the nucleation rate is dependent on the surface area, as is observed for the nucleation of tungsten on dielectrics, the process becomes autocatalytic leading to an exponential increase in the number of nuclei.

The relationship between the number of nuclei initially present on a surface and the coverage of the surface after a period of growth has been discussed²² and is represented in Figure 3. The initial coverages of the growth and nongrowth surfaces evaluated at the same point in time (i.e., after the same amount of particle growth) is directly

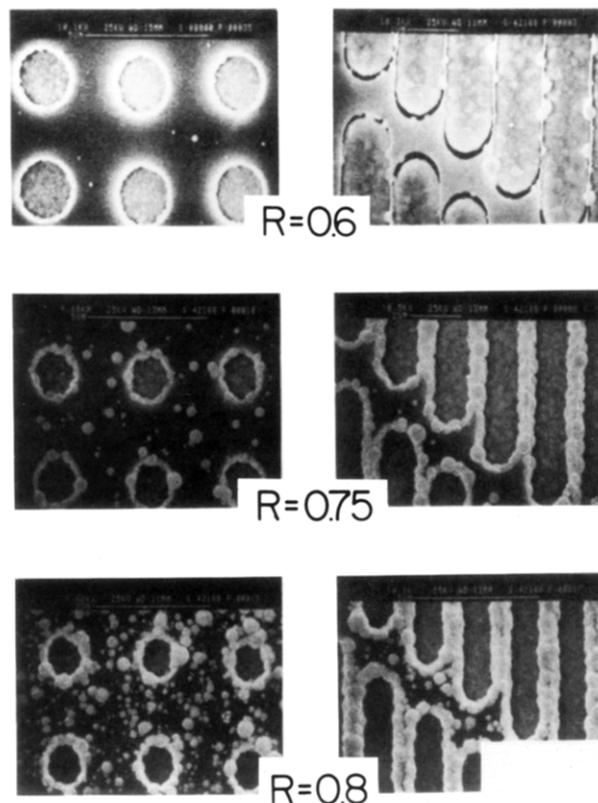


Figure 4. Selective tungsten depositions conducted at 285 °C at the indicated gas flow ratios, $R = \text{SiH}_4/\text{WF}_6$.²⁶ The values of Si_{SiO_2} for the films grown at $R = 0.6$ and 0.75 are 0.995 and 0.919, respectively. [Reprinted with permission from the Materials Research Society.]

proportional to the number of nuclei. This assumes that the shapes and orientations of all the metal particles are similar, and it will remain true until the point where coalescence of the particles begins. It further assumes that the entire flux of additional monomer to the surface is consumed by particle growth rather than by the formation of additional nuclei and that the growth rates of the particles on the growth and nongrowth surfaces are similar. Although these assumptions are somewhat limiting, the useful result is that eqs 1 and 2 can be recast in terms of the coverage of the respective surfaces. One of the advantages of expressing these ratios in terms of coverage is that various surface spectroscopic and microscopic methods can give direct values of surface coverage:

$$\text{selectivity on GS} = \theta_{\text{GS}} / [\theta_{\text{NS}} + \theta_{\text{GS}}] \quad (3)$$

$$\text{selectivity on NS} = \theta_{\text{NS}} / [\theta_{\text{NS}} + \theta_{\text{GS}}] \quad (4)$$

We propose that the selectivity of a process be defined by the expression (eq 5) obtained by subtracting eq 4 from eq 3. Although derived for a limiting case, the

$${}^{\text{gs}}S_{\text{ns}} = (\theta_{\text{gs}} - \theta_{\text{ns}}) / (\theta_{\text{gs}} + \theta_{\text{ns}}) \quad (5)$$

comparison of coverages as an empirical measure of selectivity can be generalized. As an example, consider Figure 4, which shows scanning electron micrographs of three depositions of tungsten at varying reactant flow rate

(25) Lewis, B.; Anderson, J. C. *Nucleation and Growth of Thin Films*; Academic Press: New York, 1978; p 504.

ratios (R).²⁶ The growth surface was silicon, located at the bottom of the vias, and the nongrowth surface was silicon oxide. In all three micrographs on the left-hand side of the figure, tungsten completely covered the silicon. Analysis of the tungsten coverage of the nongrowth surface yielded values of selectivities ($^{Si}S_{SiO_2}$) of 0.995 for $R = 0.6$ and 0.919 for $R = 0.75$. From these numbers, it suggests that selective processes may be described in much the same way as the purity of chemicals is often discussed. Metallic copper, for example, can be purchased that is 99.999%, or five-nines, pure. The depositions shown in Figure 4 are two-nines and one-nine pure for $R = 0.6$ and 0.75, respectively. For the film grown at $R = 0.6$, removal of all of the tungsten particles except the largest on the nongrowth surface would increase the value of $^{Si}S_{SiO_2}$ to 0.998. If the diameter of this remaining particle was reduced by a factor of three, $^{Si}S_{SiO_2}$ would equal 0.9998 (nearly four-nines selectivity). In the above discussion, it is assumed that the error in the measurements warrants the number of significant figures.

An entirely nonselective process would give $^{ns}S_{ns} = 0$, whereas a perfectly selective deposition would yield a value of 1. Rather than stating a particular deposition exhibited a value of 1.0, it should be described as an inequality, $^{Si}S_{SiO_2} > 0.99\dots$, where the specific value is established by the minimum particle size measured by the probe used to evaluate selectivity.

The definition of selectivity (eq 5) is similar in form to that used to describe the enantiomeric excess of an asymmetric chemical reaction and offers some advantages. First, the fractional coverages of *both* surfaces are combined into one expression which gives a more realistic assessment of the selectivity. The second advantage of this definition of selectivity stems from the shortcut in the analysis that occurs as soon as the growth surface is fully covered. At this point, which will occur early in any reasonably selective process, all that remains to be established is θ_{ns} which involves measuring far fewer particles.

An alternative definition of selectivity as the ratio of nuclei creation rate to the metal deposition rate has been used²⁴ and offers the advantage of being somewhat more tractable from the viewpoint of optimization. Using such as definition selectivity would vary from 1 for a nonselective process to infinity for a completely selective one.

2.2. Effect of Time and Temperature. As suggested in eq 6 selectivity for a given materials system (precursor, growth surface, and nongrowth surface) is not a constant but a complex function of the experimental conditions:

$$^{ns}S_{ns} = f(\text{time, temperature, pressures, flow rates, reactor design, impurities, defects, surface preparation, etc.}) \quad (6)$$

Figure 5 typifies the change in coverage and selectivity as a function of time, and it highlights the dependence of this behavior on the cause of nucleation. For the case involving intrinsic nucleation, the maximum value of selectivity is 0.78 (not particularly selective) in this example and occurs prior to the onset of the coalescence of nuclei on the GS. The value of the maximum is especially important because it represents the time-independent

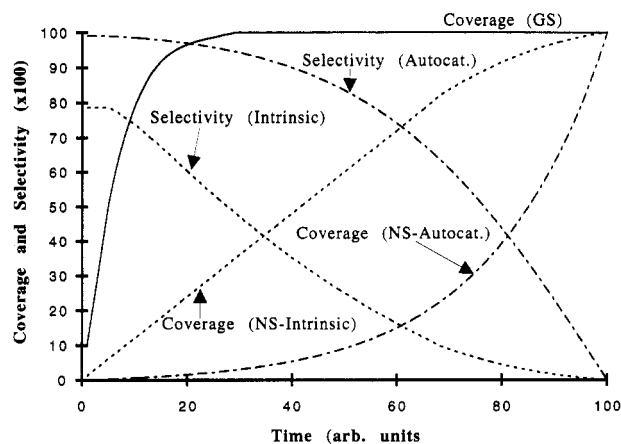


Figure 5. Conceptual diagram showing the time-dependent relationship of coverage and selectivity for a deposition in which nucleation occurred by an intrinsic (cause 1) process compared to a deposition in which the formation of nuclei was autocatalytic (cause 3).

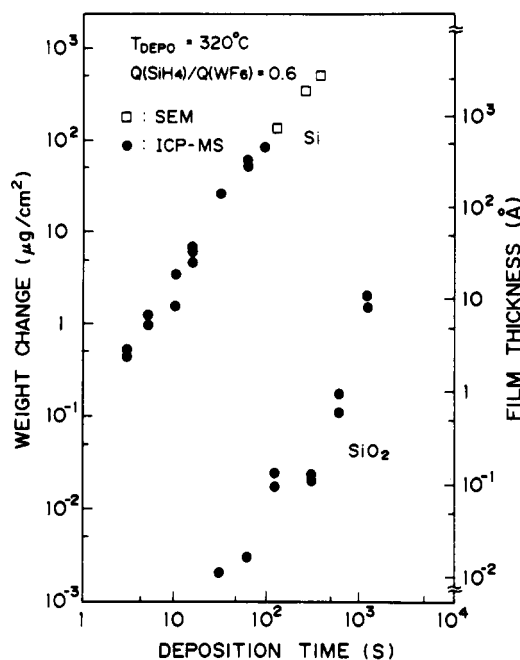


Figure 6. Comparison of the growth rates of W on Si and SiO₂ using WF₆ and SiH₄.²⁷ [Reprinted with permission from the Materials Research Society.]

selectivity of the deposition for a given set of processing parameters. For the situation involving the autocatalytic generation of nuclei, as is observed in many selective tungsten depositions, $^{ns}S_{ns} = 0.99$ at the outset (for this example) but decreases exponentially as a function of time.

During the period described in Figure 5 the thickness of the film will increase and continue to do so at the steady state rate after the coverage saturates. Eventually the growth rates on the two surfaces will become equal. Figure 6 shows an experimental measurement of this induction period for the growth of W on Si/SiO₂.²⁷ For a selective deposition to be useful for a given application, the requisite film thickness must be achieved before $^{ns}S_{ns}$ degrades.

In addition to time, increasing temperature is widely recognized as degrading selectivity. Figure 7 shows one

(26) Ahn, K. Y.; Fryer, P. M.; Harper, J. M. E.; Joshi, R. V.; Miller, C. W.; Colgan, E. G. In *Tungsten and Other Refractory Metals for VLSI Applications IV*; Blewer, R. S., McConica, C. M., Eds.; Materials Research Society: Pittsburgh, PA, 1989; p 35.

(27) Itoh, H.; Nakata, R.; Kaji, N.; Endo, T.; Watanabe, T.; Okano, H. In *Tungsten and Other Advanced Metals for VLSI/ULSI Applications V*; Wong, S. S., Furukawa, S., Eds.; Materials Research Society: Pittsburgh, PA, 1990; p 23.

THERMAL OXIDE

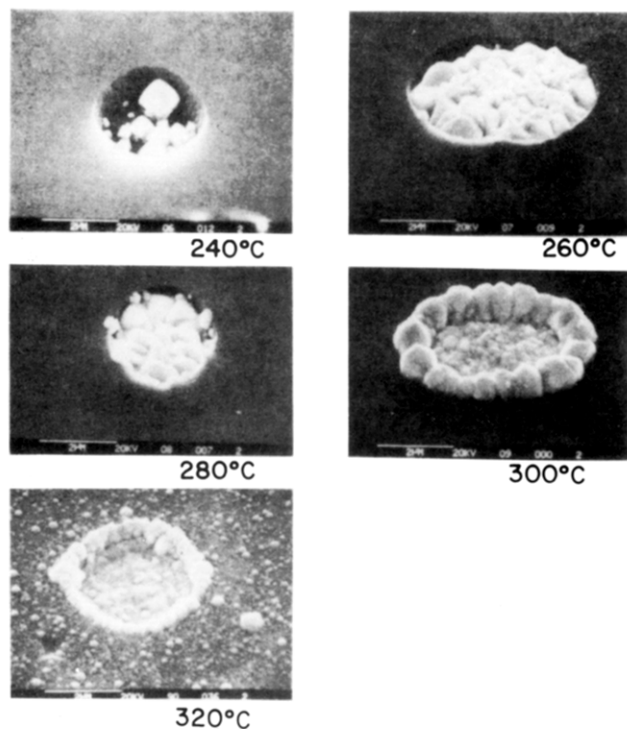
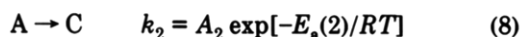
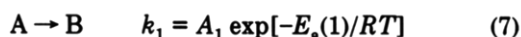


Figure 7. Selectivity loss at higher temperatures. All depositions above were conducted for 115 second at a total pressure of 60 mTorr. The gas flow rates in sccm were $WF_6 = 4$, $SiH_4 = 3.5$, $H_2 = 50$, $Ar = 30$.²⁶ [Reprinted with permission from the Materials Research Society.]

example of the loss of selectivity of W grown on Si/SiO_2 substrates as the growth temperature reaches 320 °C.²⁶ Although kinetic schemes describing nucleation rates will be far more complex, one aspect of this behavior can be anticipated based on the simple kinetic system involving two parallel first order processes (eqs 7 and 8). Upon



completion of the reaction, the ratio of B to C would equal the ratio of the specific rate constants (k_1/k_2). Substituting the Arrhenius expression for these constants, the ratio of B to C becomes proportional to $\exp[E_a(2) - E_a(1)/RT]$. As temperature is increased, the selectivity will decrease. A slightly more detailed presentation of the effect of temperature on the selective growth of Al on Si and SiO_2 has appeared.²⁸ Additional parameters effecting the selectivity of a specific deposition will be discussed in greater detail in section 3.

Finally, even the design of the substrates used to evaluate selectivity can affect the result. Special care should be exercised when trying to correlate the rates of nucleation and growth on two independent (unattached) substrates to a selectivity observed when one substrate contains both surfaces. One of the mechanisms that leads to the loss of selectivity in the tungsten system is the desorption of subfluorides from the metallic tungsten surface. Read-sorption of these molecules on the adjacent dielectric leads

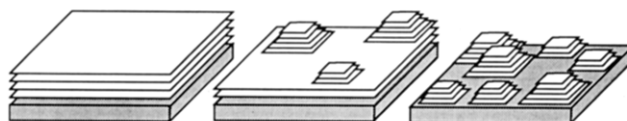


Figure 8. Thin-film growth modes. Layer-by-layer (left), layer-by-layer plus island (center), and island (right).

to nucleation and growth of tungsten particles.²²⁻²⁴ Clearly the proximity of the two surfaces is a factor contributing to the overall selectivity. In studies of the selective deposition of semiconductors, the geometry of the pattern itself was found to be important in some cases.^{15-18,29} As the ratio of the areas of the growth to nongrowth surfaces (termed the fill factor¹⁶) decreased, the rate of deposition on the growth surface increased. The cause was proposed to be the increased flux of precursor due either to surface migration or to desorption-readsorption from the nongrowth surface onto the growth surface.^{16,18}

2.3. Analytical Methods for Assessing Selectivity. Thin-film formation can occur by one of the three classic modes: (1) layer-by-layer (Frank-van der Merwe) growth, (2) island (Volmer-Weber) growth, and (3) layer-by-layer plus island (Stranski-Krastanov) growth (Figure 8).²⁵ The choice of the proper analytical method to evaluate selectivity will depend on which of these modes is operating. This concern is less of a problem for the nongrowth surface (usually the dielectric) because island growth is expected due to the large differences between the structure and properties of the materials, i.e., a metal and a dielectric.

Scanning electron microscopy is the most useful method for evaluating selective depositions. As mentioned above, however, the problem arises when the thin film deposit does not exhibit any new morphologies on the substrate. Even when distinct structures can be assigned to islands of the deposit, the investigator should corroborate that the apparently unchanged portion of the micrograph is still the original substrate material. Although many SEMs are equipped with energy dispersive spectrometers, their sampling depth can often be greater than the thickness of the film.³⁰ This makes it difficult to obtain quantitative and sometimes even qualitative information. In principle, the backscattered electron image can be used to establish the elemental distribution of a deposit in cases where morphology alone is not sufficient. The success of the analysis, however, is highly dependent on the relative Z values for the substrates and deposit.³⁰ For example, the ability to detect W on Si/SiO_2 is good, while differentiating Al on Si/SiO_2 is difficult.

Particle counters based on light-scattering and optical microscopy can be used to evaluate selectivity. The former method can be automated and can scan a larger surface area relatively quickly. Only the most elaborate (costly) counters can be used with substrates that have patterns on their surfaces. The lower size limit of detectable particles is approximately 0.2 μm .

The usual surface spectroscopic methods, X-ray photoelectron (XPS), and Auger electron (AES) spectroscopies, can be used to evaluate selective deposition of thin films. The critical requirement is that the beam be small enough and accurately controlled to accommodate

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(30) Goldstein, J. I.; Newbury, D. E.; Echlin, P.; Joy, D. C.; Fiori, C.; Lifshin, E. *Scanning Electron Microscopy and X-Ray Microanalysis*; Plenum Press: New York, 1981; p 673.

(28) Lee, K.-I.; Kim, Y.-S.; Joo, S.-K. *J. Electrochem. Soc.* **1992**, *139*, 3578.

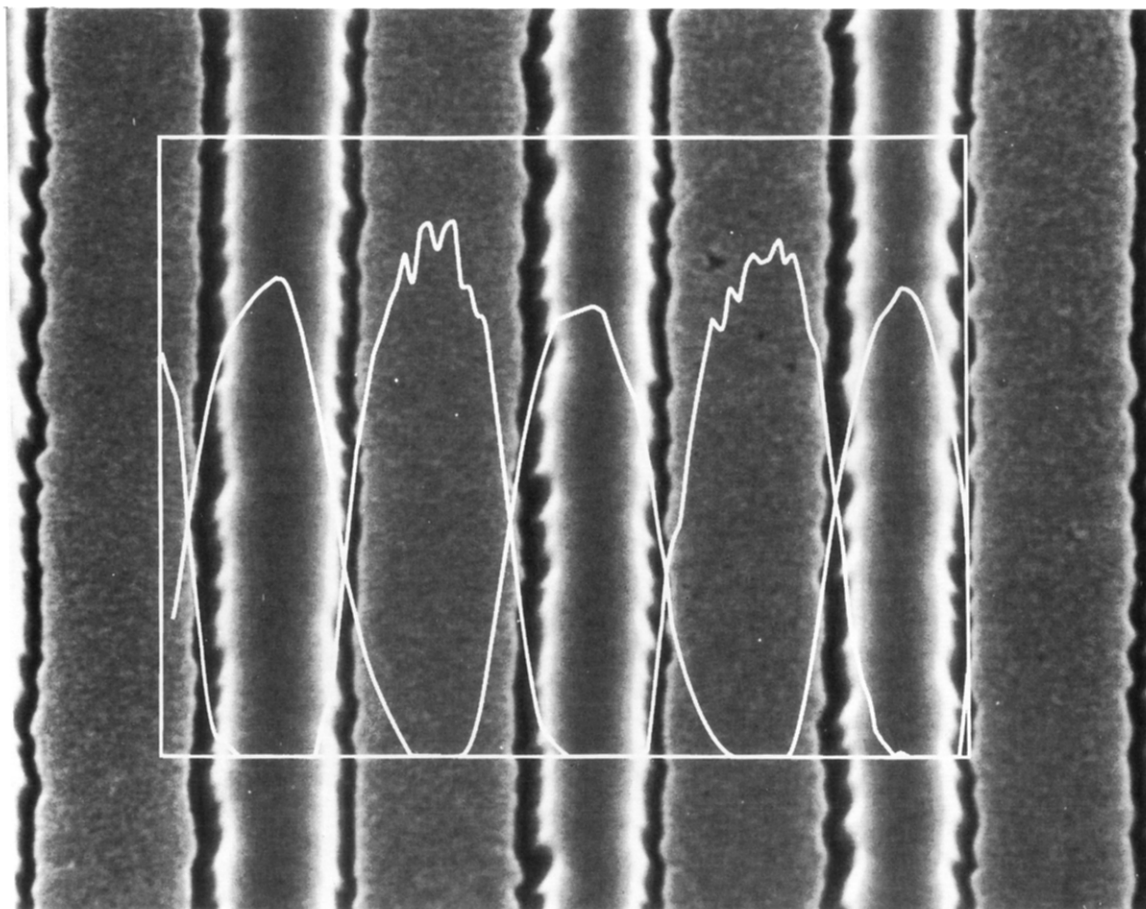


Figure 9. Correlation of SEM and SAM results is shown for the selective deposition of aluminum on gold in the presence of SiO_2 using dimethylethylamine alane. The line showing the first maximum on the left-hand side of the figure is the Auger line for silicon; the other trace is for aluminum. The combined results establish that no detectable aluminum had formed on the oxide surface. The widths of the aluminum lines are $3 \mu\text{m}$. For this deposition $^{A\text{u}}\text{SiO}_2 > 0.9999$.

the small size of the patterns on the surface. A scanning Auger spectrometer is particularly well-suited for this purpose as exemplified in Figure 9. Although the resolution is not typically as high as an SEM, it is satisfactory for all but the smallest structures. It is noteworthy that in both the copper and aluminum³¹⁻³³ selective depositions in which SiO_2 is the nongrowth surface that some precursor does stick to the SiO_2 and can be observed by electron spectroscopies. When this happens additional studies should be undertaken to establish its chemical state, i.e., whether or not it is metallic, before calculating the selectivity.

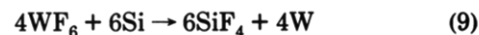
3. Selective Metallization Systems

Tungsten deposition is by far the most thoroughly studied selective metallization and will be the first process reviewed. Recent advances in selective deposition of copper and to a lesser extent aluminum will then be discussed. A few observations of selectivity have been made for other metals, but few systematic studies³⁴ of the phenomena have yet appeared.

3.1. Selective Tungsten Deposition. Tungsten hexafluoride (WF_6) is a gas at room temperature and is

the reagent of choice for the CVD of tungsten thin films.³ The recent publication of a comprehensive review³ and other more focused reviews of W CVD^{35,36} makes it unnecessary to present an entirely separate summary in this article.

During selective W deposition some metal and semiconductor surfaces reduce or catalyze the reduction of WF_6 creating tungsten nuclei, eq 9. This reaction is fast relative



to the subsequent reduction by hydrogen or silane and in most studies it is self-limiting.³⁷⁻³⁹ When the W film thickness reaches a few hundred angstroms, the rate of eq 9 usually drops significantly. Once formed these nuclei, or more precisely this layer, catalyze the further reduction of WF_6 with the gaseous reducing agent, hydrogen or silane (eqs 10 and 11), which leads to the steady-state growth of the tungsten film. Important to achieving selectivity is the fact that reduction does not occur when WF_6 collides with dielectrics such as SiO_2 , Si_3N_4 , borophosphosilicate glass (BPSG), and polyimide.

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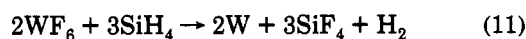
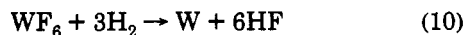
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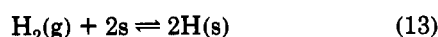
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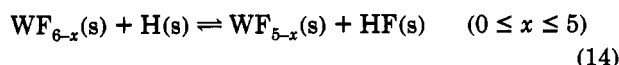
3.1.1. $\text{WF}_6 + \text{H}_2$. The kinetics of the steady-state growth of W have been studied in both hot-wall and cold-wall CVD reactors.^{37,40,41} Although there is widespread agreement regarding the experimental observation that the growth rate is zero order with respect to the partial pressure of WF_6 and one-half order with respect to hydrogen (eq 12), there is less agreement on the mechanism.^{36,40} In the

$$\text{growth rate (nm/min)} = k_0 \exp[-E_a/RT](p_{\text{H}_2})^{0.5} \quad (12)$$

cold-wall reactor $k_0 = 4.7 \times 10^7 \text{ nm min}^{-1} \text{ Torr}^{-0.5}$ and $E_a = 17 \text{ kcal/mol}$ ⁴⁰ yielding a growth rate at 287 °C and 0.9 Torr of H_2 of 6 nm/min. The half-order dependence on the H_2 pressure derives from the equilibrium to produce adsorbed H atoms (eq 13), which are consumed in



subsequent steps in the mechanism. One proposed mechanism involves³⁵ the reaction of adsorbed WF_6 with the adsorbed hydrogen atoms through the series of reductions represented by eq 14.



In the above mechanism the reactions occur between two intermediates adsorbed on the surface (as required in the Langmuir-Hinselwood kinetic model of surface reactions). An alternative explanation³¹ of the kinetics involves the Rideal-Eley mechanism in which a species in the gas phase (e.g., WF_6) approaches and reacts with a surface-bound intermediate (e.g., W-H) without prior adsorption on the surface. This mechanism has the attractive feature of explaining how a molecule of WF_6 might initially interact with the surface. Because of the large number of elementary steps required, it is possible that both mechanisms are involved at different stages of the reduction.

3.1.2. $\text{WF}_6 + \text{SiH}_4$. The use of SiH_4 to reduce the WF_6 results in substantially higher deposition rates at significantly lower temperatures compared to the hydrogen reductions.³ The deposition is complicated by the formation of various tungsten silicides as the SiH_4/WF_6 ratio increases. When this ratio lies between 0.5 and approximately 1.3, α -W is produced. As the ratio exceeds the stoichiometric ratio (eq 11), β -W and an amorphous silicide phase is observed, and above 2.0 only amorphous silicide is found.⁴² Similar to the hydrogen reduction, kinetic studies established that the growth rate was zero order with respect to the partial pressure of WF_6 ; however, it was first order with respect to the silane partial pressure.³ To date, no mechanistic proposals have been offered that explain the data.

Increasing the temperature of the W deposition using silane above approximately 320 °C results in complete loss of selectivity (Figure 7). It can also be seen in Figure 4 that the selectivity decreases as the SiH_4/WF_6 flow rate ratio increases.

3.1.3. *Nature of Substrates*. The growth surfaces include silicon, aluminum, TiN, and metal silicides (WSi_x , TiSi_x , etc.). Selective tungsten growth has required that a facile reaction occur between the growth surface and WF_6 , as exemplified in eq 9, or the ability of the substrate to dissociate H_2 .

The nongrowth surfaces studied include a variety of dielectrics upon which tungsten formation does not occur easily because these materials do not act as reducing agents nor do they provide a facile means to activate hydrogen to produce a metal hydride reducing agent. Polyimide was also found to be an effective dielectric for selective depositions.⁴³ Studies of the interaction of WF_6 with SiO_2 surfaces under UHV conditions using soft X-ray photoemission showed no measurable W growth at any temperature up to 850 °C.⁴⁴ It was found, however, that exposure (1000 L) of a *partial* oxide surface on a Si(111) wafer at room temperature did result in the incorporation of tungsten on the surface. The tungsten was present in several oxidation states, but it was not possible to determine whether the metal was coordinated just to fluorine or to a mixture of oxygen and fluorine.⁴⁴

Differences in selectivity among various dielectric materials have been observed. In a study the selectivity of deposition on silicon in the presence of silicon nitride, oxynitride, oxide, and phosphorous-doped oxide was evaluated.⁴⁵ Figure 10 shows a plot of the density of nuclei as a function of deposition time. Nuclei formed more readily on nitrogen-containing surfaces whereas the presence of phosphorous seemed to inhibit nucleation.

3.1.4. *Causes of Selectivity Loss*. Achieving and maintaining selective deposition for the maximum length of time possible require careful attention to the cleanliness of the reactor, the purity of the gases, preparation of the substrates, and control of reactor dynamics during deposition. Even under the best conditions, however, selectivity can eventually be lost during a deposition. The following discussion outlines some of the proposed causes of selectivity loss.

In several of the studies on selective deposition of tungsten in hot-wall reactors, it was noted that selectivity significantly worsened as distance of the wafer from the gas entrance increased.^{3,36,46} The buildup of tungsten on the walls of the reactor also caused a decrease in the selectivity as did increases in the number of substrates and the fractional area to be coated. These observations are characteristic of nucleation caused by a product or an intermediate of the deposition whose concentration increases as the WF_6 collides with the reactive surfaces. Once a fully developed tungsten film has formed on the growth surface, HF is the only volatile product of the hydrogen reduction. Although HF is thought to inhibit rather than enhance the kinetics of tungsten growth, it has been

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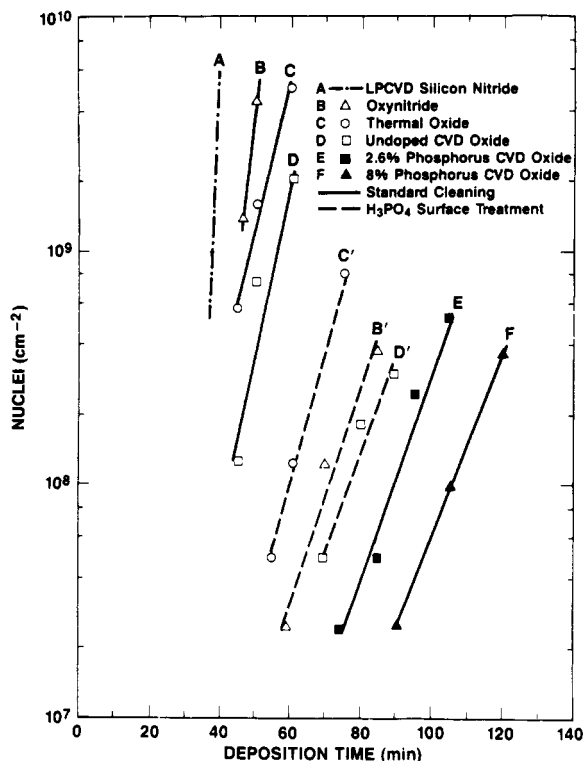


Figure 10. Formation of tungsten nuclei on selected dielectric surfaces.⁴⁵ [Reprinted by permission of the publisher, The Electrochemical Society, Inc.]

suggested that it could cause selectivity loss by reacting with SiO_2 to produce H_2O and silicon fluorides (SiF_x), either of which could be the species responsible for inducing W nucleation.^{3,35,36,46} Water reacts rapidly with WF_6 to produce volatile oxyfluorides such as WOF_4 which have also been suggested to cause selectivity loss.⁴¹ During the early stage of W deposition on silicon when eq 9 is the dominant reaction, production of SiF_4 (or SiF_2 above 450 °C) has also been proposed to cause selectivity loss.⁴⁷ In silane reductions of WF_6 , SiF_4 would be the volatile product of the reaction.

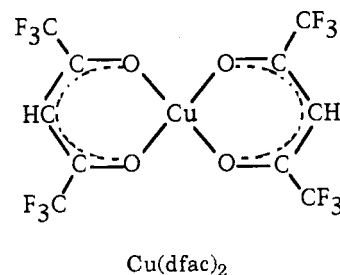
The most convincing scenario of selectivity loss, and the only one for which experimentation has provided a step-by-step pathway outlining the formation of tungsten nuclei, involves the formation of desorbed subfluorides of tungsten, formed as intermediates in the reduction on W surfaces, which readsorb and induce W nucleation on nearby nongrowth surfaces.^{22,23,48} Volatile WF_5 is formed when WF_6 comes into contact with a hot surface of tungsten (typically >500 °C). This can readsorb on other surfaces in the reactor including the dielectric. If the temperature of this surface is higher than about 350 °C, the WF_5 will disproportionate to give WF_6 and W, which can nucleate and then catalyze the growth of tungsten as long as a reducing agent is also present. The rate of WF_5 formation from 300 to 400 °C is 2×10^{11} to 3×10^{12} molecules/cm² s. Given that selectivity loss is significant when tungsten particle densities reach 10^8 – 10^{110} /cm², the observed rates of subfluoride formation could account for this level of particle formation.^{22,23} Overall nucleation kinetics of W

on a thermal oxide surface agree with this picture.²⁴ The SiO_2 was unaltered unless a region of metallic W (in these studies the heater block was composed of W) was nearby.

In light of this mechanism for loss of selectivity, it is worth reconsidering some of the earlier studies⁴⁵ on the effect of the composition of the dielectrics. Now the question becomes how do Si_3N_4 , SiO_2 , and phosphorous-containing glasses effect the adsorption and subsequent disproportionation of WF_5 ?

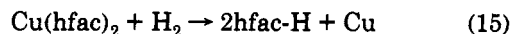
3.2. Selective Copper Deposition. Copper has attracted much attention recently for use in microelectronic applications because of the increasing demands for smaller feature size and lower resistance. Its low resistivity ($1.67 \mu\Omega \text{ cm}$) is second among the metals only to silver. Although easily deposited using evaporation or sputtering methods, problems with adhesion have limited its use. In addition, copper is more difficult to pattern because of the lack of an effective etchant.^{10,11} This is one of the strongest arguments supporting the need for a selective copper CVD process. Copper does see widespread use on circuit boards. For many of these applications the copper is deposited by electroless, electrochemical, or often a combination of both methods. Within the past few years there has been a surge of studies^{10,11} on the chemical vapor deposition of copper films, and several of these have commented on the ability to deposit copper selectively on metallic substrates. The molecular precursors can be subdivided into two classes based on the oxidation state of the copper. The following presentation will summarize the reports of selectivity first for the divalent and then the monovalent complexes.

3.2.1. Divalent Copper Precursors. The basic molecular structure of divalent copper precursors uses the β -diketonate type of ligand. By far the most studied example used for CVD copper is bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II) ($\text{Cu}(\text{hfac})_2$), which has a vapor



pressure of 0.06 Torr at room temperature.¹¹ Both blanket and selective depositions of copper have been described using $\text{Cu}(\text{hfac})_2$. Related β -ketoiminato ligands have also been used to deposit copper selectively onto SiO_2 .⁴⁹

Although some initial reports suggested $\text{Cu}(\text{hfac})_2$ could be used to form copper in the absence of any external reducing agent,⁵⁰ it is now accepted that films of greater purity are obtained by conducting the deposition in the presence of hydrogen (eq 15).⁵¹ The depositions are usually conducted in the temperature range 250–400 °C, and



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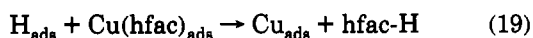
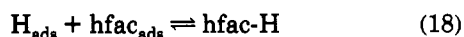
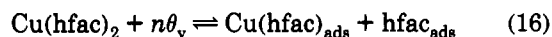
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growth rates up to 180 nm/min have been reported.⁵¹ As always the specific value is critically dependent on the reactor design and conditions of the deposition. Experimental evidence has suggested that the deposition rate saturates at commonly used partial pressures of Cu(hfac)₂.⁵² This fact along with an observed first-order rate dependence on the hydrogen pressure and the inhibition by excess hfac-H allowed the derivation of a Langmuir-Hinshelwood kinetic expression. The zero-order kinetics with respect to the precursor was interpreted to mean that the reaction proceeds through an adsorbed intermediate whose surface concentration saturates under normal conditions. The following microscopic events are invoked to explain the observations.^{11,52} The symbol θ_v is used to represent a vacant site on the surface.



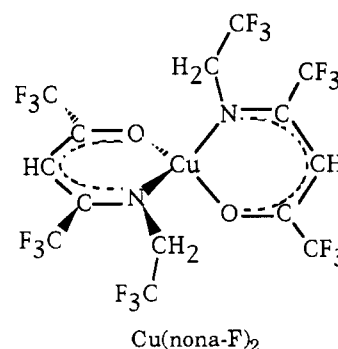
Studies of the adsorption of Cu(hfac)₂ in UHV conditions establish that eq 16 occurs below room temperature.⁵³⁻⁵⁶ Under these conditions, the clean, hydrogen-free surface reacts with Cu(hfac)_{ads} and hfac_{ads}, eventually degrading the ligand and causing contamination of the surface with carbon and fluorine. Directly dosing a copper surface at room temperature with hfac-H leads, by the reverse of eq 18, to adsorbed hfac.⁵⁶ The observation that hfac-H is a reaction product under normal deposition conditions suggests that either eq 18 or 19 or both must be fast enough to compete with the ligand degradation events.

Selective deposition using Cu(hfac)₂ was observed on metallic substrates in the presence of SiO₂ and Si₃N₄. The best results required hydrogen as the carrier gas, and in the range 300-350 °C yielded growth rates up to 15 nm/min. This process was used to fill successfully 10 000 vias that had a diameter of 1000 nm.⁵⁷

Selectivity was observed on a series of SiO₂ substrates exposed in certain areas to an evaporative source of Pt, Cu, Pd, Au, and W.⁵⁸ These metals formed a discontinuous, prenucleation layer upon which the copper grew following exposure of the substrates to Cu(hfac)₂ in hydrogen at 300-400 °C. The nominal thickness of the prenucleation layers ranged from 0.01 to 3 nm. Examination of Pt layers using TEM established that isolated particles of Pt had diameters from 1.5 to 2 nm for films having a nominal thickness of 0.25 nm. For thinner films, the particles were not observed by TEM yet their catalytic effect on copper growth was still evident.⁵⁸ These interesting results begin to address the question of the size of

particle required to observe steady-state growth using Cu(hfac)₂. The addition of water to the gas stream accelerated the rate of growth both on the prenucleated surface and on the SiO₂.⁵⁹ Above a 15:1 ratio of partial pressures of H₂O to Cu(hfac)₂ all selectivity was lost. There is no explanation for the rate enhancement caused by water; however, the importance of water on the nucleation, especially on the SiO₂ surface, is consistent with observations made in depositions using copper(I) precursors discussed below.

Changing the structure of the ligand has the remarkable effect of reversing the selectivity. Replacing the trifluoromethyl groups of hfac with *tert*-butyl groups in Cu(dpm)₂ (dpm = dipivaloylmethyl) resulted in selective deposition of copper on SiO₂ in the presence of silicon at temperatures below 300 °C.⁶⁰ Conversion of one of the keto groups of the ligand into an imino group yields a reasonably volatile precursor as long as the organic side chain is fluorinated. The compound Cu(nona-F)₂ depos-



ited copper selectively on SiO₂ in the presence of W and TiN surfaces. In addition to differences in the first coordination sphere of the Cu, the nona-F ligand causes the structure of the complex to distort toward tetrahedral (instead of square-planar) geometry as suggested in the Cu(nona-F)₂ structure.⁴⁹

The picture of selective deposition of copper using divalent precursors remains unclear. The current mechanism for the steady-state growth offers insight into the events that are occurring on the growth surface, and it is likely that similar reactions will occur on other metallic surfaces. Little is understood, however, about the interaction between the copper(II) precursors and the surface of SiO₂ and the causes for the reverse selectivity due to changes in the ligand.

3.2.2. Monovalent Copper Precursors. The structures of representative monovalent copper precursors used for the deposition of copper films are shown in Figure 11.¹⁰ Reports of selective depositions focus on the class of complexes which contain one hfac ligand and one two-electron donor ligand. Because the interest of most of the researchers working in this area lies heavily on the side of precursor development and/or elucidating the surface chemistry that leads to selectivity, fundamental studies have outpaced the development of the processing conditions necessary to achieve selectivity. In the following discussion I will summarize what little is known about the

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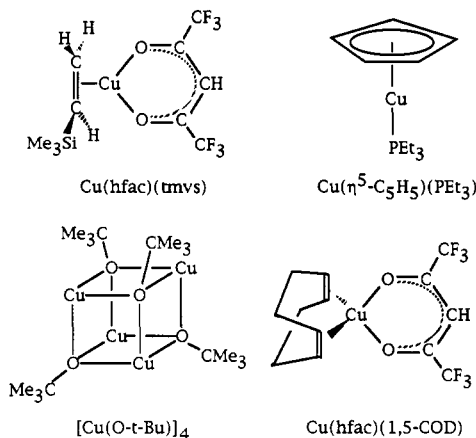


Figure 11. Structures of selected monovalent copper precursors.

Table I. Reports of Selectivity for Monovalent Copper Complexes

| precursor | selectivity(GS vs NS) | temp (°C) | ref |
|-------------------------------------------------|------------------------------------------------------------------------------------------------------|-----------|--------|
| $\text{Cu}(\text{C}_6\text{H}_5)(\text{PEt}_3)$ | W vs SiO_2 | 175 | 65 |
| $\text{Cu}(\text{hfac})(\text{tmvs})^b$ | W vs SiO_2 | 120–420 | 66 |
| $\text{Cu}(\text{hfac})(\text{tmvs})$ | Ta, Al, and TiN vs SiO_2 | 150–180 | 66 |
| $\text{Cu}(\text{hfac})(\text{tmvs})$ | PtSi vs SiO_2 | 150–200 | 66 |
| $\text{Cu}(\text{hfac})(1,5\text{-COD})^a$ | Ta, Cu, Ag, Au, and Cr vs SiO_2 and Si_3N_4 (certain degree of selectivity) | <200 | 64, 67 |
| $\text{Cu}(\text{hfac})(\text{MeCCMe})$ | Co and Mo vs SiO_2 (certain degree of selectivity) | 150 | 61, 68 |
| $\text{Cu}(\text{hfac})(\text{PMe}_3)$ | Pt, W, Cu vs SiO_2 | 150–300 | 62, 69 |
| $\text{Cu}(\text{tfac})(\text{PMe}_3)$ | Pt, W, Cu vs SiO_2 | 100–150 | 62 |
| $\text{Cu}(\text{acac})(\text{PMe}_3)$ | Pt, W, Cu vs SiO_2 | <80 | 62 |

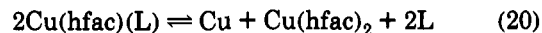
^a 1,5-COD = 1,5-cyclooctadiene. ^b tmvs = $\text{Me}_3\text{SiCH}=\text{CH}_2$.

processing and follow this with a summary of the surface studies. While the surface studies have not answered all of the questions about the nucleation and growth process on both the growth and nongrowth surfaces, the critical insight that such research has provided will be invaluable to those who wish to develop a working process.

In general, the temperatures required for copper deposition using the monovalent precursors are substantially lower than those needed for the analogous divalent complexes. Table I summarizes the results as a function of the two-electron-donor ligand. The literature also contains reports that contradict some of the claims for selectivity outlined in Table I.^{61–64} As described in more detail below, the sensitivity of nucleation to many of the processing parameters including substrate preparation, undoubtedly contributes to the problem. In general, the purity of the copper films deposited from the Cu(I)

precursors under typical conditions was very high and resistivities usually approached the value of bulk copper.

All of the copper(I) precursors containing hfac and related ligands appear to disproportionate according to the stoichiometry shown in eq 20.⁷⁰ The reversible nature



of this reaction has been used as a dry etch process for copper.⁶⁶ The only liquid (at room temperature) precursor of those studied thus far contains the trimethylvinylsilane (tmvs) ligand. Figure 12 shows the result of copper deposited onto tungsten lines in the presence of SiO_2 barriers. The pressure of the deposition was 0.1 Torr and growth rates approaching 100 nm/min were achieved. Studies of the effect of temperature established that this growth rate was limited by mass transport to the substrates. In this study, a selective deposition was defined as exhibiting less than 1 detectable grain of copper on the nongrowth surface (SiO_2) per $10^4 \mu\text{m}^2$ of total W and SiO_2 surface. The resistivity of the copper films grown using $\text{Cu}(\text{hfac})(\text{tmvs})$ was generally $2 \mu\Omega \text{ cm}$.⁶⁶ It was also reported⁷¹ that the selectivity of deposition using $\text{Cu}(\text{hfac})(\text{tmvs})$ at 160 °C (wafer temperature) on TiN was dependent on the processing history of the SiO_2 or related nongrowth surfaces. Deposition methods that involved high temperatures such as used to growth a thermal oxide yielded selective deposition of the copper on TiN. Blanket deposition occurred on wafers comprised of TiN and SiO_2 or Si_3N_4 grown using plasma-enhanced CVD. Selectivity could be improved, however, when these samples were annealed at 700 °C under nitrogen prior to copper deposition. These results are consistent with other studies described below in suggesting that surface hydroxyls can induce nucleation on the nongrowth surface.

The other well-studied complex which contained an alkene coordinated to the copper was $\text{Cu}(\text{hfac})(1,5\text{-COD})$.^{64,67} Depositions were conducted in a stainless steel reactor in which the walls were maintained at 70 °C to prevent condensation of the precursor.⁶⁷ Helium carrier gas was passed through the solid precursor which had a vapor pressure of 0.056 Torr at 62 °C. Between 178 and 198 °C the growth rate varied from 10 to 20 nm/min and yielded an activation energy of 29.8 kcal/mol.⁶⁷ A slightly lower value of 26 kcal/mol was obtained in an independent study.⁶⁴ A certain degree of selectivity was observed on sputter-cleaned metals compared to SiO_2 and Si_3N_4 , but this was difficult to maintain, and above 200 °C no selectivity was found.⁶⁷

The alkyne complex, $\text{Cu}(\text{hfac})(\text{MeCCMe})$, has been found to give copper films at rates approaching 1000 nm/min at 200 °C (precursor partial pressure = 0.050 Torr). The activation energy for the deposition between 150–200 °C was 23 kcal/mol.^{61,62} Some selectivity was observed on metal surfaces;⁶⁸ however, both sets of studies of this precursor have focused on blanket deposition.

Phosphine ligands, especially alkylphosphines, are far stronger donors than either alkenes or alkynes, and the stability of the corresponding $\text{Cu}(\text{hfac})(\text{PR}_3)$ complexes is somewhat greater. Most of the research has focused on

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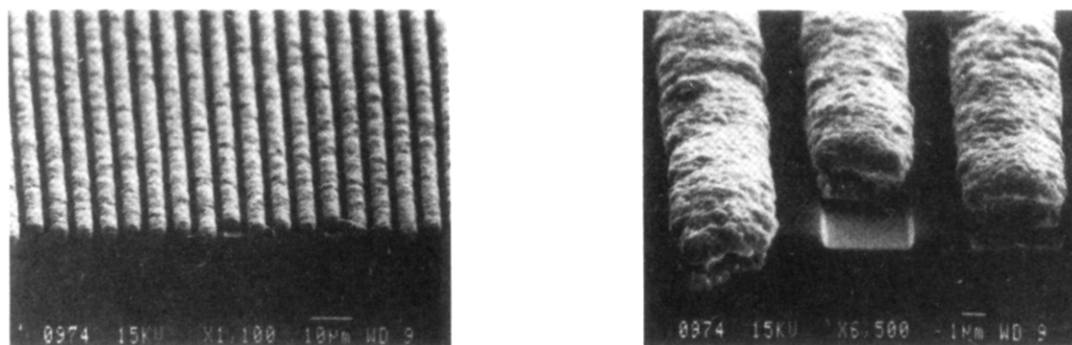


Figure 12. Selective via filling using $\text{Cu}(\text{hfac})(\text{tmvs})$.⁶⁶ [Reprinted with permission from *J. Phys. (Paris)*.]

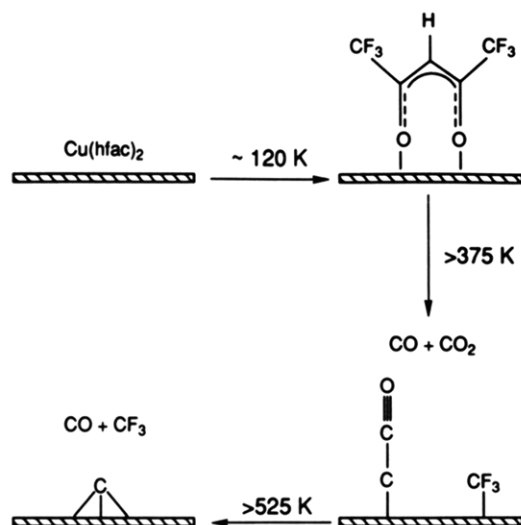
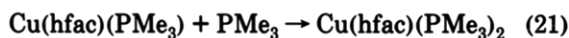


Figure 13. Proposed surface degradation of the hfac ligand.⁵⁶ [Reprinted with permission from *J. Am. Chem. Soc.* 1993, 115, 1015. Copyright 1993 American Chemical Society.]

the trimethylphosphine complex which deposits copper films at temperatures between 150 and 400 °C.^{62,69} At the latter temperature, the rate was 120 nm/min. As with many solid precursors the partial pressure was difficult to control and depended to some extent on the grain size of the crystalline precursor. The chemistry occurring in the growth chamber appears to be more complex than suggested by eq 20. Trimethylphosphine liberated during the deposition reacts, eq 21, with the starting precursor



to give the stable complex having two phosphines. Higher concentrations of phosphine sometimes resulted in the formation of a white solid near the exit of the reactor. Complete characterization of this species established that it was the ionic complex, $[\text{Cu}(\text{PMe}_3)_4][\text{hfac}]$.^{62,72}

Selective deposition on metallic surfaces in the presence of SiO_2 was observed with $\text{Cu}(\text{hfac})(\text{PMe}_3)$ from 150 to 300 °C.^{62,69} Film thicknesses achieved during a selective deposition reached 1500 nm. Because $\text{Cu}(\text{hfac})_2$ is formed during these depositions and is known to deposit copper with less selectivity, it was suggested that this reaction byproduct may cause the loss of selectivity of $\text{Cu}(\text{hfac})(\text{PMe}_3)$ above 300 °C. In these same studies, the nature of the anionic group was changed to 1,1,1-trifluoro-2,4-pentanedionato (tfac) and 2,4-pentanedionato (acac) ligands. Although each complex deposited copper, the

maximum temperature at which selectivity could be observed was lowered in the order $\text{hfac} > \text{tfac} > \text{acac}$.⁶² In the same reactor under similar conditions selectivity was found for $\text{L} = \text{PMe}_3$ and PEt_3 (in $\text{Cu}(\text{hfac})(\text{L})$) but not for tmvs , 1,5-COD, or 2-butyne.

A study of the ligand desorption rates from $\text{Cu}(100)$ using temperature-programmed desorption established a link between the strength of the Cu-L bond and the selectivity. The activation energies in parentheses for the series of ligands 2-butyne (8.5 kcal/mol), tmvs (12.0), COD (14.2), and PMe_3 (28.0) show some correlation with the selectivity data observed in the CVD experiments.⁷³ The hypothesis offered to explain the relationship was that the stronger Cu-L bond in $\text{Cu}(\text{hfac})(\text{PMe}_3)$ allowed the molecule to desorb intact or to diffuse to the growth surface.

The only monovalent copper complex that exhibits selectivity but does not have an acac type of ligand is $\text{Cu}(\eta^5\text{-C}_5\text{H}_5)(\text{PEt}_3)$. Upon deposition two cyclopentadienyl ligands combine to form 9,10-dihydrofulvalene. Although most reports have focused on its use for the blanket deposition of copper, some selectivity was observed below 175 °C.⁶⁵ The analogous PMe_3 complex also deposits copper films, but no selectivity data were reported.⁷⁴

3.2.3. Surface Chemistry of Copper Precursors. Several studies of the surface chemistry of $\text{Cu}(\text{hfac})(\text{L})$ complexes under ultrahigh-vacuum conditions on copper,⁵⁶ silver,^{53,75} and titanium nitride^{55,63} have led to similar conclusions. At temperatures below ambient, the precursor, either $\text{Cu}(\text{hfac})(\text{COD})$ ^{53,75} or $\text{Cu}(\text{hfac})(\text{tmvs})$,⁵⁶ adsorbed on the substrate with little detectable change. If the surface temperature was raised, or if the precursor was dosed at room temperature, complete loss of the neutral ligand (COD or tmvs) occurred leaving a residual $\text{Cu}(\text{hfac})$ group. In each of the studies, spectroscopy (IR⁵⁶ or XPS^{53,75}) established a similarity between the adsorbed species produced from either of the $\text{Cu}(\text{I})$ precursors and $\text{Cu}(\text{hfac})_2$. In addition, dosing hfac-H directly onto a clean copper surface also yielded this species that was assigned the formula $\text{Cu}(\text{hfac})_{\text{ads}}$.⁵⁶ The vibrational spectrum of the adsorbed fragment established that the plane of the hfac ligand was perpendicular to the metal surface (Figure 13)

Heating copper surfaces that were covered with $\text{Cu}(\text{hfac})_{\text{ads}}$ produced no $\text{Cu}(\text{hfac})_2$, the product of the deposition reaction (eq 20). Instead degradation of the hfac ligand itself was the predominant reaction occurring under high-vacuum conditions. Infrared spectroscopy of a surface

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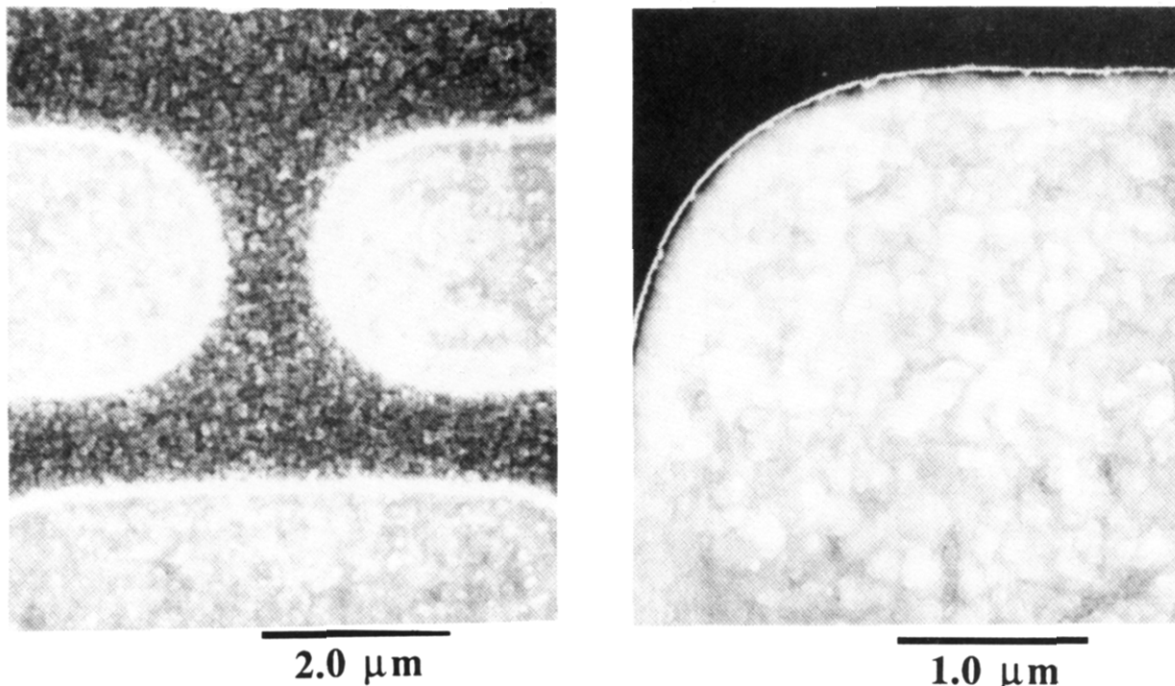
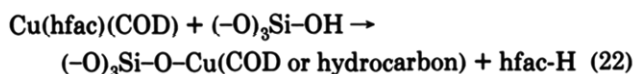


Figure 14. Selectivity of copper deposition before and after treatment of the surface with chlorotrimethylsilane.⁷⁷ [Reprinted with permission from the American Institute of Physics.]

treated with Cu(hfac)(tmvs) revealed the appearance of a new absorption at 1205 cm^{-1} at $102\text{ }^{\circ}\text{C}$.⁵⁶ This was attributed to the symmetric C–F stretch of a surface-bound CF_3 ligand. Upon further heating to $152\text{ }^{\circ}\text{C}$ another new band appeared at 2038 cm^{-1} , which was assigned to a ketenylidene (CCO) ligand (Figure 13). Above $300\text{ }^{\circ}\text{C}$ the CCO group loses the CO, leaving the surface contaminated with carbon.⁵⁶ On silver surfaces, no infrared absorption was observed that could be attributed to a ketenylidene ligand; however some decomposition of the hfac ligand was noted.^{53,75} Likewise on TiN, decomposition of the hfac ligand was found and, in addition to carbon, resulted in contamination of the surface with fluorine.^{55,63}

Two studies have focused on the critical question of the nature of the interaction between the nongrowth surface, SiO_2 , and the copper precursors. There are three important differences between these reports; the nature of the precursor [Cu(hfac)(COD)⁷⁶ vs Cu(hfac)(tmvs)⁷³], the nature of the surface (a thin oxide on a silicon wafer⁷⁶ vs high surface area silica⁷³), and the spectroscopic probe (XPS⁷⁶ vs transmission FTIR spectroscopy⁷³). Examination by XPS of a 1.0–1.2-nm oxide layer on a silicon substrate dosed with Cu(hfac)(COD) at room temperature revealed a single C 1s feature at 283.0 eV. If an intact hfac group were present, it would be expected to give three well-separated peaks due to the CF_3 , C=O, and C–H groups. It was concluded that on an SiO_2 surface Cu(hfac)(COD) reacts by cleavage of the hfac ligand from the copper to give hfac-H which subsequently desorbs (eq 22).



The conclusion of this study was that selectivity in the copper depositions was attributable to different chemical reactions of the precursor on the growth and nongrowth surfaces. Although copper remained on both the growth and nongrowth surfaces following their respective reactions, it was stabilized in a higher oxidation state on the

oxide compared to a metal surface. This leads to a much slower rate of nucleation on SiO_2 .⁷⁶

The interaction between Cu(hfac)(tmvs) and a pressed wafer composed of a high surface area fumed silica (Cab-O-Sil) was studied using transmission FTIR spectroscopy. The wafer was dehydrated by heating to $507\text{--}727\text{ }^{\circ}\text{C}$ for several hours leaving fewer than 1 isolated hydroxyl/nm². Dosing the cooled wafer ($-78\text{ }^{\circ}\text{C}$) with the precursor resulted in the adsorption of intact molecules of Cu(hfac)(tmvs) which desorbed cleanly as the temperature was raised to $47\text{ }^{\circ}\text{C}$. Separate dosing of hfac-H and tmvs established that neither interacts strongly with SiO_2 . These data suggested that one possible explanation for the lack of nucleation of SiO_2 was the low sticking coefficient of the precursor. Predosing the SiO_2 wafer with water formed hydrogen-bonded hydroxyl groups (distinguishable by the O–H stretching frequency) which were responsible for dramatically altering the reactivity of Cu(hfac)(tmvs). Exposure of Cu(hfac)(tmvs) to the hydrogen-bonded surface at $27\text{ }^{\circ}\text{C}$ produced a vibrational spectrum similar to Cu(hfac)₂ with complete loss of tmvs. The spectroscopic signature for the adsorbed hfac groups eventually disappeared as the sample was heated. Presumably the hfac was desorbed as hfac-H. Additional observations made in this study were the formation of copper films on dehydrated wafers that were too hot or on dehydrated wafers exposed to residual precursor remaining of the walls of the reactor. Taken together, these studies established that the selectivity of a copper deposition is very sensitive to many of the processing procedures.⁷³

Use of chlorotrimethylsilane to pretreat wafers patterned with W and SiO_2 resulted in the passivation of the SiO_2 surface and allowed the copper to be grown selectively on the tungsten for each of the monovalent copper precursors studied ($L = \text{PMe}_3$, tmvs, COD, and 2-butyne).⁷⁷

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Selective deposition (Figure 14) continued for at least 1 min at 170 °C and a precursor pressure of 1–10 mTorr and yielded thicknesses from 100 to 300 nm. Selectivity was lost at longer deposition times. Chlorotrimethylsilane would be expected to convert the reactive surface hydroxyls on the SiO₂ into unreactive, nonpolar trimethylsilyl ethers above 300 °C. At the lower temperatures (57 °C) used for the pretreatment in this study only a small portion of the –OH groups were irreversibly reacted. Transmission FTIR spectroscopic studies conducted on pressed wafers of Cab-O-Sil revealed that most of the chlorotrimethylsilane, adsorbed following exposure for 15 min at 0.15 Torr and 57 °C, had desorbed upon evacuation of the chamber. It was suggested that most of the chlorotrimethylsilane was weakly hydrogen-bonded to the surface and that the loss of selectivity corresponded to the desorption of the Me₃SiCl. The infrared spectral studies indicated that the intensities of the peaks due to Cu(hfac)(tmvs) adsorbed on the SiO₂ surface were nearly an order of magnitude smaller than those of Cu(hfac)(tmvs) adsorbed on an untreated SiO₂ surface under identical conditions.⁷⁷

3.2.4. Gas-Phase Reactions of Copper Precursors. Concern over precursor reaction in the gas phase, especially in hot-wall reactors, has led to the study of Cu(hfac)(tmvs) in a molecular beam apparatus in which the effects of surface chemistry could be minimized.⁷⁸ Mass spectrometric and infrared spectroscopic probes established that the reaction represented in eq 20, where L = tmvs, was complete when the temperature of the beam was raised to 250 °C. At 50 °C, however, little or no gas-phase decomposition had occurred during the course of the experiment. No evidence was found for the existence of gas-phase intermediates such as Cu(hfac). These observations are especially important to the selective deposition because atomic copper is a presumed product which, if formed, could easily lead to the loss of selectivity.

3.3. Selective Aluminum Deposition. Although aluminum is the most commonly used metal in microelectronic applications,^{79–81} relatively little has been reported in the way of selective CVD except through the use of laser CVD processing.² This stems from the fact that Al films are currently deposited by physical vapor depositions and that aluminum is easily etched and, therefore, patterned with little difficulty using routine lithographic methods. A further complication to using CVD grown material comes from the interest in combining a few percent of copper with the aluminum to minimize the problems associated with electromigration. Figure 15 shows the structures of the organometallic complexes that have demonstrated selective growth. Each will be discussed in the following sections.

3.3.1. Triisobutylaluminum (TIBA). This is the most extensively studied precursor for the growth of aluminum films.^{82–94} Under typical conditions (220–300 °C, 0.2–0.5

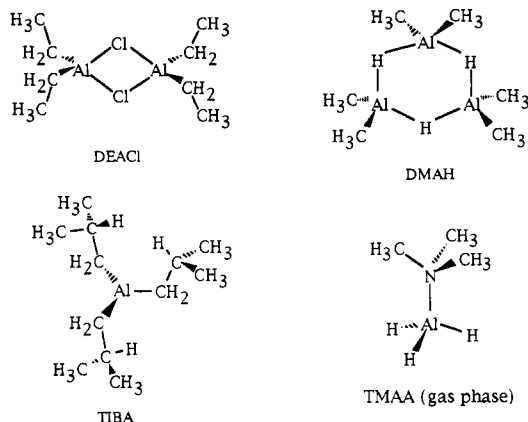


Figure 15. Structures of precursors for selective deposition of Al.

Torr of partial pressure of TIBA) aluminum films grew at a rate of 20–80 nm/min.⁸⁹ Nucleation of the aluminum films on insulators and semiconductors has been a problem, and most processes involved the pretreatment of the surface with TiCl₄ to increase the density of nucleation sites.^{88–91} This led to mirrorlike coatings compared to rough surfaces if no pretreatment was used. On clean silicon substrates, mirror smooth, epitaxial aluminum films can be grown without a nucleating agent by heating both the substrate and the precursor.^{92–94} Selective deposition on silicon occurred on patterned Si/SiO₂ substrates under similar conditions provided no TiCl₄ was used to pretreat the surface.^{95–101} Other materials, including W, Mo, Ti, and various silicides acted as nucleation promoters.⁹⁹

The mechanism of steady state growth of aluminum using TIBA has been elucidated and is shown in Figure 16.^{102–105} Following irreversible adsorption, the three alkyl groups migrate to separate metal sites and in the rate-

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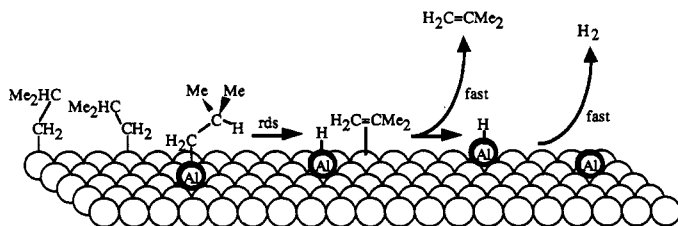


Figure 16. Aluminum growth mechanism using TIBA.¹⁰⁴

determining step undergo β -hydrogen elimination at the same rate. Neither hydrogen nor isobutene stick to aluminum above 60 °C so that once formed, they immediately dissociate and expose a fresh surface to more precursor. The kinetic model used to quantify the behavior is shown in eq 23. Although this was derived from

$$\text{rate of Al deposition} = \frac{An_s \exp(-E_a/RT)}{(An_s/\sigma s) \exp(-E_a/RT) + 1} \quad (23)$$

experiments under high vacuum conditions, it gave remarkably good agreement with kinetics obtained under typical CVD conditions. In eq 23, n_s is the number of adsorbed TIBA molecules per unit area at saturation coverage ($1.4 \times 10^{14} \text{ cm}^{-2}$), σ is the flux of TIBA to the growth surface, s is the sticking probability of TIBA on Al (1.0), R is the gas constant, T is the absolute temperature, A is the preexponential factor ($3.8 \times 10^{11} \text{ s}^{-1}$ for Al(111)), and E_a is the activation energy (27.7 kcal/mol for Al(111)).¹⁰⁴

X-ray photoelectron spectroscopic studies of the interaction between TIBA and Si and SiO₂,^{31,32,106–108} established that exposure of a clean surface of SiO₂ to less than a monolayer coverage of TIBA at room temperature led to rapid loss of two isobutyl groups. The C:Al ratio at this point was approximately 4/1, and this remained unchanged even at temperatures as high as 450 °C. The binding energies of the Al 2p and C 1s peaks were observed to move to higher and lower values, respectively, as a function of time. This indicated that although the ratio was unchanged, the nature of the carbon species was changing. Exposure of a SiO₂ surface that had already reached the 4/1 ratio of C/Al to additional TIBA increased the ratio to 12/1; the same as the precursor itself. The interpretation of these results was that once the SiO₂ was saturated with partially reacted TIBA, the surface no longer reacted with additional precursor. In other words, the SiO₂ surface was poisoned by an unreactive intermediate. The aluminum atoms that are present on the surface at the 4/1 C/Al ratio point are immobile and do not readily nucleate.

TIBA reacted on the silicon surface to form aluminum islands. In the absence of oxygen, the aluminum atoms

remained mobile and nucleated.³¹ Once this occurs, growth continued in the manner suggested in Figure 16.

3.3.2. Tertiary Amine Complexes of Alane. Trimethylamine alane (TMAA),^{109–116} triethylamine alane (TEAA),^{116–118} and dimethylethylamine alane (DMEAA)^{20,21,119} have vapor pressures between 0.5 and 1.5 Torr at room temperature and have been used for the CVD of aluminum films. The results of these are very similar to those found for TIBA except that the temperatures required for the deposition are lower by approximately 150 °C. The lowest temperature used in most of the studies was 100 °C, and TiCl₄ pretreatment was required to produce continuous, fine-grained, specularly reflective deposits.^{109,111} The morphology of the aluminum was dependent on the nature of the substrate. Deposition on untreated silicon, SiO₂, or other insulating surfaces yielded large grains and resulted in a rough surface. Somewhat smoother surfaces were grown on conducting surfaces such as TiN and copper.¹¹⁵ It was also noted that the minimum temperature required to induce growth on these conducting surfaces was substantially lower than untreated surfaces of silicon or SiO₂.

Reports of selective growth are just beginning to appear. Using TMAA, aluminum grew preferentially on W lines patterned on a silicon wafer using a contact shadow mask.¹¹³ Using a similar masking technique to create a gold pattern on Si(100), we have shown that DMEAA will deposit selectively on the gold in the presence of SiO₂.¹¹⁹ The conditions for this experiment included a wafer temperature in a hot-wall reactor of 180 °C, a partial pressure of DMEAA of 0.3 Torr, and a H₂ carrier gas pressure and flow rate of 3 Torr and 100 sccm, respectively. The thickness of the aluminum film deposited for 4 min was 600 nm. In a related study, solutions of TEAA were found to deposit aluminum selectively between 70 and 110 °C on KrF laser patterned palladium surfaces.¹²⁰

In recent experiments¹²¹ using a cold-wall reactor, a lithographically patterned substrate containing gold at the bottom of vias and barriers composed of thermal SiO₂ was treated under similar conditions as just described. Figure 9 shows an SEM of the surface on which aluminum growth (100 nm) was detectable only on the Au. Scanning Auger microscopy (Figure 9) verified that the gold surface was completely covered, but careful analysis of individual spots on the SiO₂ did show a small signal due to aluminum.

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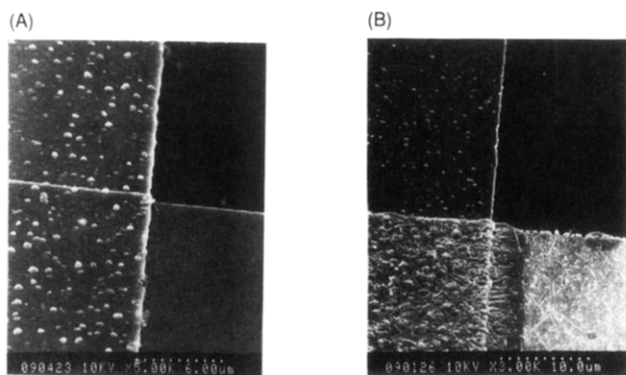


Figure 17. Selective deposition of Al on Ti (lower half of each photo) in the presence of regions of poly Si (upper left) and Si_3N_4 (upper right) using DMEAA: (A) before Al growth; (B) after exposure to DMEAA for 2.5 min at 100 °C.

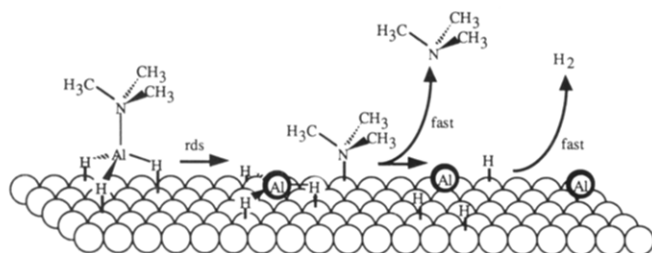


Figure 18. Aluminum growth mechanism using TMAA.¹²²

Whether this was the result of the initial stage of growth of aluminum or, in analogy to TIBA, the irreversible adsorption of a monolayer of the precursor is unknown and will be the subject of further study.

A more complex pattern, shown in Figure 17A, simultaneously exposed three different surfaces to the precursor flux; phosphorus-doped polysilicon, silicon nitride, and a metal. The metals studied include platinum, titanium, zirconium, tungsten, nickel-chromium alloy, and titanium nitride. In each case the substrate was treated at 100 or 140 °C at 0.3 Torr of partial pressure of DMEAA. Figure 17B shows that the deposition is selective for 2 min of growth on the metallic (in this case titanium) surface. After longer exposures (10 m), the selectivity ($T_i\text{Si}$) dropped to 0.8, while $T_i\text{Si}_3\text{N}_4$ dropped to 0.9.¹²¹

The mechanisms for steady state growth of aluminum using TMAA and TEAA have been studied, and the sequence of reactions are shown in Figure 18.^{118,122} Despite their similarities the two precursors exhibited different rate-determining steps. For TMAA, the cleavage of the Al-N bond was rate determining,¹²² while the desorption of hydrogen was rate determining for TEAA.¹¹⁸ The difference arose from the slightly weaker Al-N bond strength in TEAA. The selectivity itself may be related more to the ability of the growth surface to promote the desorption of molecular hydrogen. The reductive elimination of H_2 from isolated molecules of TMAA is expected to be unfavorable at low temperatures due to the relative instability of Al^+ compared to Al^{3+} . Binding TMAA to a metallic surface may allow the hydrogens to disperse and the aluminum to be reduced rapidly to the metallic state. Desorption of H_2 from many metallic surfaces, including aluminum is facile. At this point much of this is still speculative and more research is needed to clarify the role of the metal surface in inducing nucleation. In addition,

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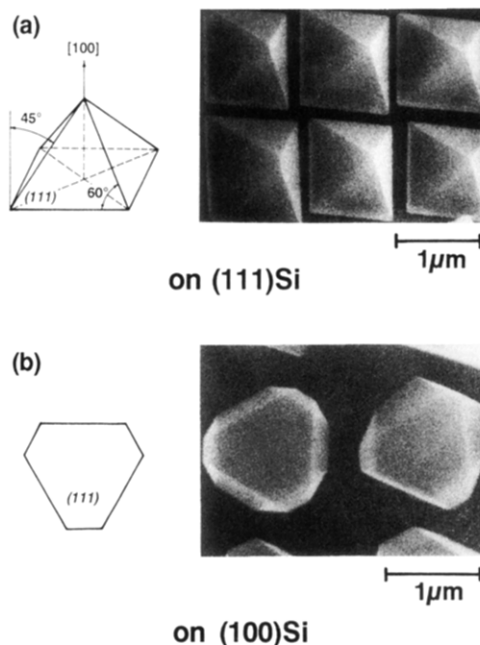
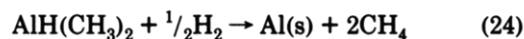


Figure 19. Selective via filling on Si in the presence of SiO_2 using DMAH.¹²⁵ [Reprinted with permission from the American Institute of Physics.]

the nature of the interaction between the amine alanes and the nongrowth surfaces needs to be explored.³³

3.3.3. Dimethylaluminum Hydride (DMAH). As with most Al CVD processes the current work focuses on low-pressure reactors.¹²³⁻¹²⁶ The vapor pressure of DMAH is approximately 2 Torr at room temperature, and most depositions use partial pressures from the mTorr range to the hundreds of mTorr range. Hydrogen usually at a partial pressure of 1-3 Torr was used as the carrier gas because the suggested stoichiometry of the deposition requires an additional source of hydrogen atoms (eq 24).



The films grown under these conditions were pure and exhibited resistivities near the value of bulk aluminum ($2.7 \mu\Omega \text{ cm}$). The minimum temperature required for deposition was 230 °C, and the maximum value studied was 350 °C.

Selective growth of high-purity aluminum was observed on Si, Ti, and TiN in the presence of SiO_2 .¹²⁵ As with other selective processes, it was sensitive to the actual temperature of the deposition. The highest temperatures reported¹²⁴ to give the optimum selectivity was in the range 240-270 °C. At the higher of these temperatures the growth rate was 80 nm/min. An intriguing observation was reported^{123,125} while using DMAH to fill 1 μm via holes in SiO_2 on top of Si. From the shape of the growth it was clear that a single crystal of aluminum had filled the entire via (Figure 19). In addition it was observed that on Si(100) the Al crystal was oriented with the (111) plane parallel to the surface. On Si(111), the Al(100) plane was found

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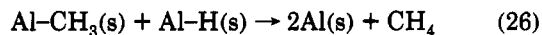
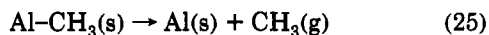
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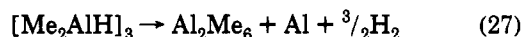
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to be parallel to the substrate. The cause of these effects is unknown.

Little is known about the mechanism of this reaction. The absence of β -hydrogens means that the Al-C bond-cleaving mechanism must differ from the well-studied precursor, triisobutylaluminum. The fact that methane was stated^{123,125} to be the only gaseous product limits the Al-C bond-cleaving step to two mechanisms, homolysis of the Al-CH₃ bond to give methyl radicals (eq 25) or the



reductive elimination of methane from the surface (eq 26). In studies of the chemistry of Al(CH₃)₃, Al-C bond homolysis was found to occur,¹²⁷⁻¹³² but the temperature required was substantially higher than that required for Al deposition using DMAH. The stabilizing effect of the aluminum surface could lead to a substantial lowering of the activation barrier for dissociation. The reductive elimination of methane is a possible alternative except for the fact that hydrogen must be activated by the aluminum surface. The dissociative adsorption of molecular hydrogen on clean aluminum is unfavorable. Atomic hydrogen, however, will stick to aluminum at low temperatures, but it desorbs as H₂ rapidly above 60 °C.¹³³ One possible explanation for the low carbon content is the reaction shown in eq 27,^{134,135} which may proceed through the



formation of alane (AlH₃) by a ligand redistribution reaction. This path, however, requires more than methane as a product of the reaction. Clearly more research into the fundamental reactions on aluminum are required to interpret the observations.

In another study, selective aluminum growth was used to fill Si vias in SiO₂. Subsequent to lighting a rf plasma, nonselective growth was used to planarize the entire substrate.¹²³ The effect of the plasma was suggested to provide electrons and hydrogen atoms to the surface of the oxide that induce nucleation of aluminum by reacting with the molecular precursor.

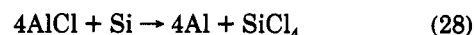
The nature of the initial reaction with silicon, the growth surface, was proposed to involve the reaction between DMAH and a Si-H group that was formed by pretreatment of the wafer with dilute HF.¹²⁵ This hypothesis can and should be tested because it has important ramifications

for reproducing the results. As for the interaction between DMAH and the nongrowth surface, SiO₂, it seems reasonable to expect behavior analogous to that found for TIBA. The residual Al-CH₃ would be expected to be stable and protect the surface from further reaction with fresh DMAH. At this time there is insufficient information available to assign a cause to the loss of selectivity that is observed at temperatures above 300 °C.

In an exciting extension of this work, an electron beam was used to create a pattern by desorbing hydrogen from a H-terminated silicon wafer. Transfer of the wafer through air into a CVD reactor, followed by treatment at 270 °C with DMAH produced selective deposition of aluminum only on the surface that was not exposed to the electron beam. In essence the H termination was used as an atomic layer resist.¹³⁶

3.3.4. Diethylaluminum Chloride (DEACl). Only one report has appeared which describes the selectivity of this precursor.¹³⁷ At temperatures between 313 and 380 °C aluminum was grown selectively on Si in the presence of SiO₂. Hydrogen was used as the carrier gas and was maintained at 90 Torr, and the flow rate through the bubbler (heated to 60 °C) containing DEACl was 200 sccm. The initial growth rate was 37 nm/min, but this diminished as the thickness of the film increased. On substrates that consisted of a 50-nm-thick layer of polysilicon on SiO₂, the growth stopped after the aluminum thickness reached approximately 50 nm. Upon removal of the aluminum layer using H₃PO₄, no silicon layer was found. These results establish that the decomposition requires a stoichiometric amount of silicon as was found for the reaction between WF₆ and Si. Mass spectrometry was used to determine that ethylene was the gaseous byproduct once metallic aluminum had begun to form. Butane and some ethane were also observed during the earliest stages of growth.

It was suggested that the reaction shown in eq 28 was responsible for the consumption of the silicon and the aluminum deposition. It seems likely, however, that the



initial steps in the mechanism (once nucleation has occurred) must involve the adsorption of DEACl on the surface of aluminum. In analogy to the chemistry of TIBA, the ethyl groups should disperse and eventually undergo β -hydrogen elimination of ethene and subsequent desorption of H₂. This would leave the Cl group bonded to the aluminum surface which should have a relatively small impact on the kinetic barrier for the β -hydrogen elimination. In support of this hypothesis it was found that alkyl halides, especially iodides, react with single-crystal aluminum surfaces with cleavage of the C-X bond.^{138,139} The rate of subsequent reactions of the alkyl moiety were similar to alkyl groups adsorbed using the corresponding trialkylaluminum on halide-free surfaces. To eliminate SiCl₄, the chloride must eventually collide with a silicon atom. At the reasonably high temperatures required for this deposition, it is possible the limited solubility of silicon

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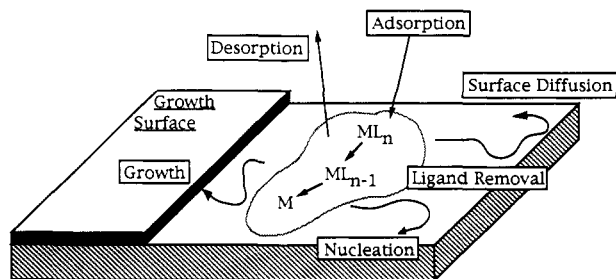


Figure 20. Results of competition among events on the nongrowth surface determines whether or not selectivity is observed.

in aluminum would provide the source of silicon to form the product. Alternatively, diffusion of the reactants along grain boundaries could occur.

4. Generalizations

Figure 20 attempts to summarize the generic microscopic events that take place following the collision of a molecular precursor with the nongrowth surface. Once on the surface, the molecular precursor (or a partially reactive fragment) will (1) react to form a metal atom itself or a species that leads to nucleation of the metal (perhaps by collision with a defect or an impurity), (2) desorb, or (3) diffuse along the surface until it reacts or desorbs. When attempting to understand the details of a selective deposition, it is critical to consider the constant competition among these processes. Also, when sorting out the causes for selectivity it is important to understand the nature of both the precursor/nongrowth surface interactions and those between the precursor and the growth surface. In any well-mixed system the flux of precursor will be constant to both surfaces. The same generic events (Figure 20) occur on the growth surface although the specific mechanisms and their relative rates will differ from those on the nongrowth surface.

This review has revealed several common features of the diverse processes for selective deposition of metals. On the nongrowth surface, the precursor either does not stick directly, as is the case with WF_6 on SiO_2 , or it reacts and saturates the surface with a relatively stable layer to which additional precursor does not stick or react. The latter scenario was established for the interaction between SiO_2 and $Al(i-Bu)_3$ and between SiO_2 and $Cu(hfac)(COD)$. Purposely passivating the nongrowth surface with a

molecule other than the precursor (chlorotrimethylsilane) successfully improved the selectivity.

In recent years numerous research efforts have focused on designing molecules that lower the temperature required for a given CVD process. As discussed in section 2.2.2, this should be beneficial for selectivity as long as the difference in the kinetic barriers toward nucleation on the growth and nongrowth surface remains unchanged or increases. It is, however, more likely that changes in the molecular structure of the precursor designed to lower the growth temperature will cause this difference to decrease. A molecule on the verge of decomposing is less likely to discriminate among the possible sites for reaction. As an example of this behavior, the selectivities of the $Cu(hfac)(L)$ precursors parallel their stabilities.

A common feature of the selective metallizations is that almost all will selectively deposit on metal surfaces in the presence of insulators or semiconductors. This is not surprising given the similarities in reactivity patterns among the metals. In addition, the differences in the structures and bonding among the metals are small compared to the differences between a metal and a semiconductor or an insulator. These similarities contribute to a lowering of the nucleation barrier.

The role of the growth surface can involve either a purely catalytic effect on the nucleation of the depositing film as is the usual situation when the growth surface is a metal, or the growth surface itself can undergo a stoichiometric reaction during nucleation as is usually true with growth surfaces that are semiconductors. In the deposition of W on silicon, the first stage on the process is the stoichiometric reaction between WF_6 and Si. This produces metallic W which is necessary to activate H_2 and sustain a steady state growth process. The selective deposition of Al on Si using Et_2AlCl is driven by the related reaction to form $SiCl_4$ and reduced Al.

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