5

Depositions and Reactions of Metals and Metal Compounds

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I. FUNCTIONS OF METALS IN INTEGRATED CIRCUITS

Tiny strips of metal form the electrical connections between the millions of transistors on a computer chip. These metals pass the signals from one transistor to another, and to and from the world outside the chip. The name *integrated circuits* is appropriate because these electrical connections are made through connections integrated into the structure, rather than through the external wires used in older electrical devices.

These structures are formed by depositing metal layers and etching them into the intricate patterns required to connect the circuits. The performance and sta

bility of these structures are related to their thermodynamic properties and the interactions at their interfaces.

An interconnect generally consists of an electrically conductive metal film deposited on top of an insulator (usually silicon dioxide, SiO_2), which covers the semiconductor (usually silicon). As sketched in Fig. 1, the metal contacts the silicon through holes in the insulating layer, these holes being termed contact windows. In modern devices, additional layers of patterned insulators and metals are added on top of the layers shown in Fig. 1, to form multilayer interconnections, as shown in Fig. 9 of Chapter 2.

There are several requirements for industrially useful interconnects:

1. "Proper" electrical contact to adjacent layers
2. Low electrical resistance along their length
3. Stability during formation and under operating conditions

For connections to the sources and drains of transistors (see Fig. 5 in Chapter 1), "proper" electrical contacts have low contact resistance, in order to carry the required electrical currents. Gate electrodes, on the other hand, require high contact resistance to the silicon. Gate electrodes are simpler, and so their structures and means of formation will be discussed first, followed by the low-resistance contacts to sources and drains.

II. PROCESSES FOR MAKING METAL SILICIDES

Gate electrodes apply a voltage to a transistor without allowing a significant current to flow. Thus, they require a high-resistance contact to the silicon, which

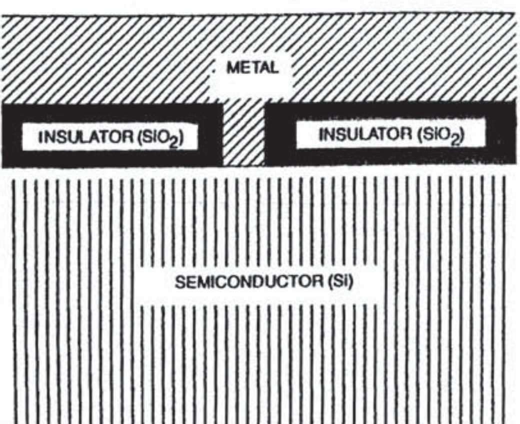


Figure 1 Cross section of a metal contact to a semiconductor device.

is achieved by forming a thin (about 10 to 20 nm) layer of silicon dioxide on the silicon by oxidation at high temperatures, before the gate electrode is deposited. The electrical resistance along the gate electrode must be sufficiently low to maintain a constant voltage over the electrode.

A. Polycrystalline Silicon

Traditionally, gate electrodes in microcircuits have been made from highly phosphorus-doped polycrystalline silicon, deposited by chemical vapor deposition (CVD) onto the crystalline silicon substrate covered with a thin layer of insulating silicon oxide (see Fig. 5, Chapter 1). Doped polycrystalline silicon, however, has a rather high resistivity. Therefore, the resistances along gate electrodes are often reduced by forming more conductive layers on top of the polycrystalline silicon. Metal silicides, such as titanium disilicide ($TiSi_2$), tungsten disilicide (WSi_2), or cobalt silicide ($CoSi_2$), are typically used for this purpose.

The methods used to deposit the metals or their silicides include both sputtering and chemical vapor deposition. Sputtering has been the most commonly used deposition method in the past, but CVD processes have become more popular and are necessary to achieve the smaller dimensions in the advanced microelectronic circuits of the 1990s.

B. Titanium Disilicide

Titanium disilicide is usually formed by depositing titanium metal on polycrystalline silicon and then heating it to a temperature above about 600°C to form the silicide:

$$2Ti + Si \rightarrow TiSi_2 \quad (1)$$

Heating (annealing) to temperatures above 700°C is usually required to transform the resulting titanium silicide from the initially formed, metastable crystal structure (called C49) with a high resistivity (over 60 μΩ-cm), into the stable crystal structure (C54) with a lower electrical resistivity (13 μΩ-cm).

Titanium silicide can also be formed by a CVD process based on the reaction

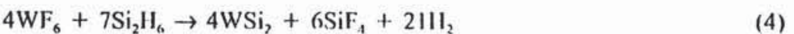
$$TiCl_4 + 2SiH_4 \rightarrow TiSi_2 + 4HCl + 2H_2 \quad (2)$$

This reaction deposits $TiSi_2$ rapidly at temperatures of 500–700°C.

C. Tungsten Disilicide

Tungsten disilicide may be made by any one of several CVD reactions. For example, reaction of tungsten hexafluoride with silane,

$$2WF_6 + 7SiH_4 \rightarrow 2WSi_2 + 3SiF_4 + 14H_2 \quad (3)$$



operates at temperatures from about 150 to 500°C. Still lower deposition temperatures (down to about 100°C) can be achieved by using disilane (Si_2H_6) in place of silane (SiH_4):

$$4WF_6 + 7Si_2H_6 \rightarrow 4WSi_2 + 6SiF_4 + 2H_2 \quad (4)$$

The initially deposited tungsten silicide has a relatively high resistivity (often over 600 μΩ-cm). Annealing at temperatures over 900°C causes the resistivity to decrease to values (around 40 μΩ-cm) almost as low as the bulk resistivity (33 μΩ-cm).

During these CVD reactions, some of the fluorine atoms are not removed, and they remain as impurities in the tungsten silicide, typically at a concentration of about 10^{20} cm^{-3}. This fluorine can cause changes in the insulating gate oxide, decreasing the breakdown field (deleterious) and decreasing the interface state density (advantageous).

The dichlorosilane reaction

$$WF_6 + 10SiH_2Cl_2 \rightarrow 2WSi_2 + 3SiF_4 + 3SiCl_4 + 8HCl + 6H_2 \quad (5)$$

produces a purer form of tungsten silicide, with much less fluorine as an impurity (below 10^{17} cm^{-3}), than does the silane reaction (3), perhaps because it operates at higher substrate temperatures (usually 400–600°C). These low levels of fluorine appear, however, to be too small to alter device properties.

D. Cobalt Disilicide

Cobalt disilicide, $CoSi_2$, is usually made by sputtering cobalt onto silicon, followed by heating to about 700°C. The structure of cobalt disilicide is a close match (1.2% difference in size) to the lattice of silicon, and so it can be grown epitaxially on silicon. This opens up the theoretical possibility of growing epitaxial single-crystal silicon on top of metallic cobalt disilicide, to form multilayer semiconductor devices integrated in three dimensions.

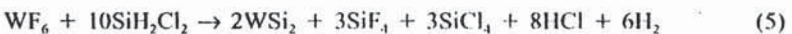
Cobalt monosilicide may be deposited from a single source, silyl cobalt tetracarbonyl,

$$H_3SiCo(CO)_4 \rightarrow CoSi + \frac{3}{2}H_2 + 4CO \quad (6)$$

This reaction produces single-phase cobalt monosilicide at about 500°C.

E. Platinum Silicide

Platinum silicide, PtSi, is usually made by sputtering platinum onto silicon, and heating. One CVD source for platinum is the volatile liquid tetrakis-(trifluorophosphine)platinum, $Pt(PF_3)_4$, whose vapors decompose at about 400°C to form platinum metal.



III. LOW-RESISTANCE ELECTRICAL CONTACTS TO SILICON

A. Factors that Contribute to Contact Resistance

In many parts of microcircuits, the purpose of the metal contact to the silicon is to provide low electrical resistance between the metal and the silicon. In order to achieve and maintain this low resistance, three conditions must be met:

1. High free carrier concentration near the surface of the silicon.
2. No insulating silicon oxide layer between the silicon and the metal.
3. The interfaces remain chemically and mechanically stable.

A high free carrier concentration (of either electrons or holes) means that many carriers are available to move into or out of the silicon through its interface with the metal. Although there often is an electrical barrier to this movement of the carriers due to carriers trapped at the interface, when the carrier concentration is very high (around 10^{20} cm^{-3}), the barrier is effectively very narrow (a few nanometers), since the other carriers screen the charges giving rise to the barrier. According to the laws of quantum mechanics, the carriers can tunnel efficiently through a narrow barrier.

When exposed to air, silicon quickly becomes covered with a thin layer of insulating silicon oxide. In order for a low-resistance electrical contact to be formed, this silicon oxide layer must be removed or otherwise avoided.

No single metal has been found to meet simultaneously the three requirements just listed. In practice, metal interconnects need to be formed by combining at least three different metal sublayers:

1. A reactive metal, such as titanium, forms the electrical contact layer.
2. A low-resistance metal, such as aluminum, tungsten, or copper, forms the bulk of the interconnect.
3. A nonreactive barrier metal, such as titanium nitride, stabilizes the interface between the other two metals.

Figure 2 indicates this type of triple metal layer, the details of which we will discuss in terms of their respective functions as successful interconnects in modern integrated circuits.

B. Processes for Making Low-Resistance Electrical Contacts

Several processing steps are needed to achieve low-resistance electrical contac between silicon and a metal.

The high carrier concentration in the silicon is achieved by various alternative methods for placing dopants in the silicon layer (diffusion, ion implantation

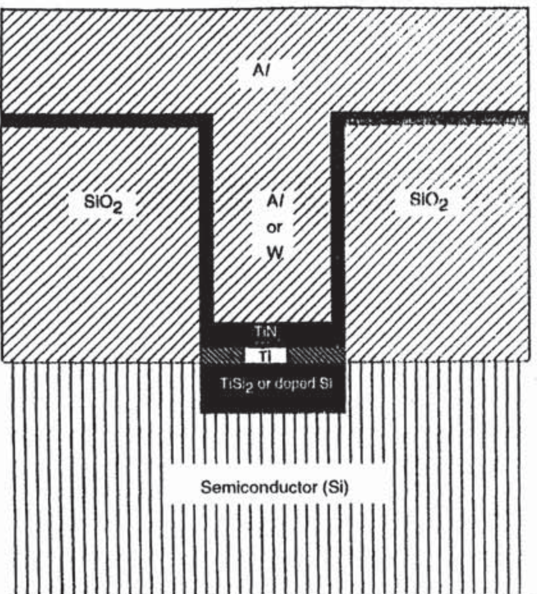


Figure 2 Cross section of a multilayer metal contact.

epitaxial growth), and activating them, if necessary, by an annealing process to remove defects. See Chapters 2–4 for more details about forming a highly conductive silicon layer.

The most effective and reliable way to eliminate the insulating effect of a thin silicon oxide layer on silicon is to convert it with a reactive metal such as titanium into a conducting metal oxide. For example, if a thin titanium layer is sputtered onto a silicon surface that is covered with a thin layer of silicon oxide, the titanium metal removes the oxygen from the silicon, by reactions such as the following:

$$9Ti + 3SiO_2 \rightarrow Ti_5Si_3 + 2Ti_2O_3 \qquad (7)$$

A remarkable feature of this transformation is that the product materials, titanium silicide and titanium(III) oxide, are both metallic electrical conductors. Thus, the insulating silicon dioxide layer has been converted into an electrically conducting layer by this reaction.

Titanium is the *only* metal that can achieve this spontaneous reduction of silicon oxide to highly conductive products. Some metals (such as zirconium)

can also reduce silicon oxide by spontaneous chemical reactions, but the product metal oxides (such as ZrO_2) are electrical insulators. Other metals (such as vanadium and niobium) can form conducting oxides, but their reduction reactions with silicon are not as rapid, and the thin films of their silicides have higher resistances than titanium silicide.

Normally, there is only a thin silicon oxide layer (about 2–3 nm thick) remaining on a contact window area of silicon after the thick (about 1000 nm) layer of silicon dioxide is opened by etching. Sputtering from a titanium target is normally used to deposit the titanium metal, to a thickness of 10 or 20 nm. Then the structure may be annealed (heated) in a vacuum or an inert (e.g., argon) atmosphere, in order to induce the reduction reaction (7), with more than enough titanium available to react with the SiO_2. During the anneal, at temperatures of 700–800°C, the remaining titanium reacts with more of the silicon to form more titanium disilicide, by reaction (1).

The top surface of the silicon, which is thus converted into titanium silicide, often contains defects and impurities, which would increase the contact resistance between the silicon and a metal. In the final structure of the contact, the more perfect underlying silicon becomes a fresh surface in contact with the metallic titanium disilicide, forming a very-low-resistance contact. Values of contact resistance as low as 10^{-7} Ω-cm^2 can be achieved in this way. This means that a contact window 0.5 μm in diameter contributes about 50 Ω to the resistance of its circuit.

C. Metals Used for the Electrical Connections

A primary requirement for an electrical interconnection is that it must have a low, stable electrical resistance. It also must remain chemically stable during all manufacturing steps and through long-term use. Aluminum and tungsten are the primary metals used for electrical connections within integrated circuits. Copper is considered a possible future replacement for these metals, for reasons that will be explained. Some properties of these metals are given in Table 1.

1. Silver

Although silver has the lowest resistance for a given size interconnect, it has not been used in integrated circuits because of its electrical instability when too large an electrical current is drawn through it. The current tends to move silver atoms by a process called electromigration, which can cause breaks in the electrical connection. Silver corrodes easily in the presence of many oxygen and sulfur containing materials encountered during the manufacturing processes, as well as in typical computer operating environments. Also, silver very readily diffuses into silicon, in which it catalyzes the recombination of electrons and holes.

Table 1 Properties of Bulk Metals

Metal	Electrical resistivity ($\mu\Omega$-cm)	Melting point (°C)	Chemical stability	Electrical stability
Ag	1.6	962	Poor	Poor
Cu	1.7	1083	Poor	Good
Al	2.7	660	Fair	Poor
W	5.3	3410	Good	Good
$TiSi_2$	13	1540	Good	Good
$CoSi_2$	15	1277	Good	Good
TiN	22	2930	Good	Good
PtSi	28	1100	Good	Good
WSi_2	38	2050	Good	Good
CoSi	168	1395	Good	Good

2. Aluminum

Aluminum has been and remains the predominant workhorse of interconnect technology. It has a fairly low electrical resistivity (about 1.7 times that of silver). Although aluminum is very reactive, its surface becomes covered with a thin (about 5 nm thick) oxide layer, which generally protects it against further oxidation. Aluminum is easily deposited by several methods, including sputtering, evaporation, and chemical vapor deposition. Patterns can be etched into aluminum by either wet (solution) or dry (gaseous) processes.

Aluminum is also subject to electromigration instability. This effect can be reduced by the addition of small amounts (1–2%) of copper and silicon to the aluminum. Such additives, however, increase the electrical resistance of the aluminum by 10–20%. Even with these stabilizing additives, current densities must be kept below about 2×10^5 amperes/cm^2 in order to avoid electromigration.

3. Tungsten

Tungsten has the highest melting temperature (3410°C) of any metal. This fact illustrates the very strong bonds between tungsten atoms, which also makes tungsten resist electromigration much better than aluminum does. It is possible to deposit tungsten by CVD selectively on the silicon in contact windows, while avoiding deposition on neighboring areas of silicon oxide. This selective deposition process makes it easier to maintain a level topography for deposition of subsequent layers, by forming tungsten "plugs" inside the contact windows. Because of these advantages, tungsten is receiving increasing use in integrated circuits.

A disadvantage of tungsten is that its electrical resistivity is higher than that of aluminum. The circuits of the same size operate more slowly if made with tungsten metallurgy rather than with aluminum.

4. Copper

Although no full-scale use has been made of copper within integrated circuits, it has the potential advantages of lower resistance than aluminum and tungsten, and much better stability toward electromigration than aluminum. Copper can reliably carry current densities up to 5×10^6 amperes/cm^2. The necessary currents could flow through narrower copper interconnects; this advantage will be particularly important for metal linewidths below 0.25 μm. Thus, copper would have a very significant advantage over aluminum or tungsten in permitting size and cost reduction and higher operating speeds (an estimated 50% increase for devices with channel lengths of 0.25 μm).

Copper's disadvantages are similar to those of silver. Copper diffuses easily into silicon, in which it acts as a recombination center. Thus, improved diffusion barriers must be developed for use between copper and silicon. Copper is also easily corroded by water and oxygen, and so greater protection may be needed in handling partially completed devices during the manufacture of a chip. Furthermore, encapsulation of the final devices may need to be improved, in order to protect the copper adequately during long-term use. In particular, plastic encapsulation may not be sufficiently protective for copper circuits, and more expensive inorganic glass encapsulation may be needed.

5. Refractory Metal Silicides

The silicides of refractory metals, such as titanium disilicide ($TiSi_2$), cobalt disilicide ($CoSi_2$), and tungsten disilicide (WSi_2), are metallic compounds that have higher resistivities than the elemental metals already discussed. They are extremely stable against chemical attack, diffusion, and electromigration, and they are finding increasing use for short interconnections for which their higher resistances still allow acceptable device performance.

IV. DEPOSITION PROCESSES FOR ELEMENTAL METALS

A. Deposition of Metals by Sputtering

In current technology, sputtering is usually used to deposit aluminum. Sputtering is a physical deposition process carried out in a vacuum chamber. Electrical energy is applied to a low-pressure nonreactive gas, such as argon, within the chamber, forming some positive ions, such as argon ions, and free electrons. On one side of the chamber there is a plate of the metal to be sputtered, called the target. The positive argon ions are accelerated electrically toward the surface

of the metal target, from which they dislodge metal atoms. These freed metal atoms travel across the vacuum chamber to the other side, where they coat the substrate with metal.

An advantage of sputtering is its flexibility; almost any metal can be deposited simply by making the appropriate target. Alloy films, such as aluminum stabilized with 1–3% copper and silicon, can be made from targets of essentially the same composition. Metals generally sputter with different efficiencies, and so the first few films made from a new alloy target may be enriched in the element that sputters most easily. However, after a few depositions, the face of the target becomes enriched in the less easily sputtered element, and the deposited films approach the bulk composition of the target.

Sputtering has some disadvantages. Bombardment by ions and electrons from the plasma discharge can generate damage (defects and impurities) in the substrate and on its surface. Sputtering also has some difficulty filling narrow holes and trenches with metal, because the metal atoms tend to stick to the upper part of the walls. As this deposit gets thicker, it can eventually block off the top of the hole, leaving a void in the metal deposit near the bottom of the hole. Stages in this process are illustrated in Fig. 3. This type of deposit represents an example of poor "step coverage." For comparison, Fig. 4 shows a CVD deposit with excellent step coverage, in which the coating thickness is nearly the same on the upper surface, the sidewalls, and the bottom of the contact hole.

The voids left in a deposit with poor step coverage increase the electrical resistance of the interconnect, and they may lead to failure by electromigration of the metal, induced by the high current densities through the adjacent thin metal.

This void formation by sputtering can be avoided by inserting a plate with narrow holes (called a collimator) between the target and the substrate. The collimator only passes metal atoms that are traveling nearly perpendicular to the substrate. In this way, most of the metal atoms are delivered directly to the bottom of the contact window, so that a dense, void-free plug of metal can be formed. A disadvantage of collimated sputtering is a reduced deposition rate, which tends to increase needed maintenance to replace the collimators before deposits on them start to flake off and contaminate the substrates.

Collimated sputtering appears to be adequate for fabricating typical integrated circuits into the mid-1990s. The insulating layers are not likely to be much thinner in the future designs, because adequate separation must be maintained between the different circuits. Although the height (around 1 μm) of the via holes for the metal will remain about the same, their widths will be smaller, and thus the ratio of height to width (called the "aspect ratio") will be larger. In 1994, aspect ratios of 1–2 are typically used, while future devices call for aspect ratios of 3–4 or more. Deposition of metal by collimated sputtering cannot be used to fill holes with these high aspect ratios.

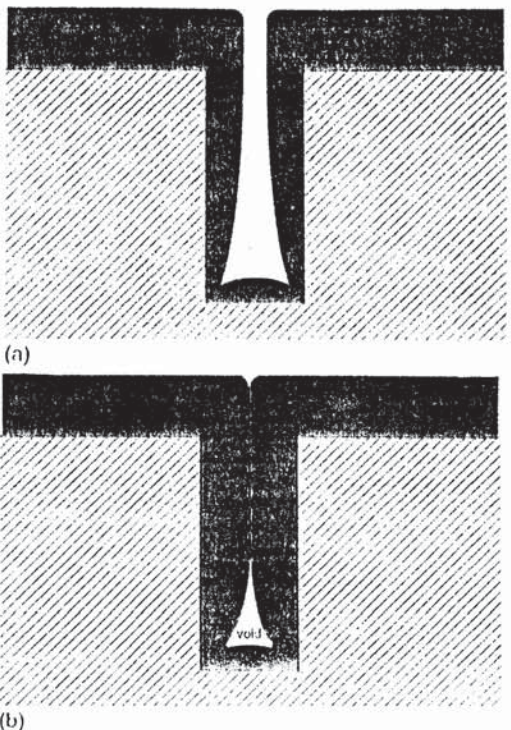


Figure 3 Cross section of a deposit with poor step coverage, leading to a void: (a) early stage of film growth; (b) at end of film growth.

B. Chemical Vapor Deposition of Tungsten

The CVD process has been used since the early 1990s to deposit tungsten into holes with high aspect ratios. General aspects of CVD have been discussed in Chapters 3 and 4. Tungsten CVD is usually carried out at moderately low gas pressures, on the order of 10 torr, although higher pressures, up to 1 atm (760 torr), have also been used successfully. An ideal CVD reactor would provide a uniform flux of reactant gases to all parts of the reactor surface, to give a uniformly thick layer of tungsten. Detailed modeling of the flow, diffusion, and reaction of gases in a CVD reactor are needed in general to determine the flux distribution of the gases (see Chapter 3). Low gas pressure promotes uniform distribution of the gases, because diffusion constants increase with lower pressure. Proper design of the inlet gas nozzle is also very important; often, "show-

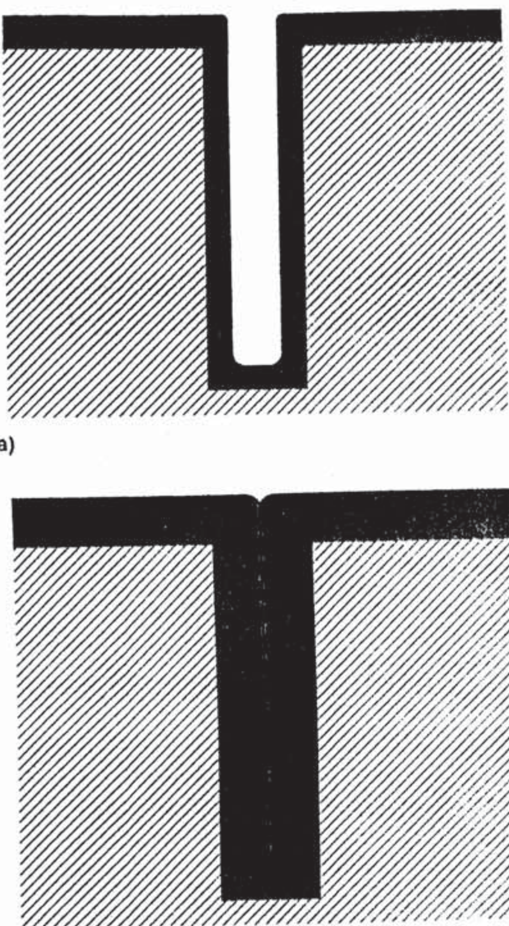


Figure 4 Cross section of a deposit with excellent step coverage at (a) an early stage of film growth, and at (b) the end of film growth, showing complete plug filling.

erhead'' designs are used, in which the gas enters the CVD chamber through many small holes. Rotation of the substrate may be used to make the film thickness more uniform. At higher pressures (0.1 to 1 atm), it is usually impossible to distribute the gases uniformly over a large wafer. In such cases, uniform thickness may still be achieved by distributing the gases uniformly from a

straight slot, and moving the substrate (for example, on a belt or platform) past the slot.

For tungsten, the most commonly used CVD source is tungsten hexafluoride gas, WF_6. Chemical reactions convert the source gas into the metal to be deposited. For example, hydrogen may be mixed with the tungsten hexafluoride, so that the following reduction reaction can take place:

$$WF_6 + 3H_2 \rightarrow W + 6HF \tag{8}$$

The by-product hydrogen fluoride, HF, is a gas that is pumped out of the deposition chamber and neutralized for disposal. The hydrogen fluoride may also cause problems by reacting with silicon dioxide insulating layers. This substrate etching must be prevented by first depositing a barrier layer on the substrate, as discussed in Sec. V.A.

According to thermodynamics, the hydrogen reduction of tungsten hexafluoride should be spontaneous, since it has a negative free energy change (−138 kJ/mol at 523°C). At temperatures below about 300°C, however, the rate of the reaction is negligibly slow, even though it should happen spontaneously if one waited long enough. In the range 300–450°C the deposition rate increases rapidly with temperature, with an activation energy of about 67 kJ/mol, according to the expression (in nanometers per minute):

$$\frac{\text{thickness}}{\text{time}} \approx 7.8 \times 10^5\, e^{-8040/T} P_{H_2}^{\ 1/2} \tag{9}$$

in which T is the temperature in degrees Kelvin. The growth rate is proportional to the square root of the hydrogen partial pressure, P_{H_2}, in Pascals, at the surface of the substrate. It does not depend on the tungsten hexafluoride concentration, as long as it is larger than some minimum value (around 10 mtorr).

Above about 500°C, the deposition rate increases only slowly with temperature. In this higher temperature range, the reaction rate is so fast that the slowest step in the process (the rate-limiting step) is the diffusion of the reactants to the surface. Diffusion rates increase only slowly with temperature, and thus the overall deposition rate increases only slowly at high temperatures.

There is, however, evidence that the chemical reaction steps in the reduction of tungsten hexafluoride by hydrogen (reaction (8)) occur on the surface of the deposited tungsten metal, which catalyzes the reaction. (Reactions also occur in the gas phase during most CVD processes.) In general, clean, oxide-free metal surfaces catalyze this reaction, but most insulator surfaces, such as silicon dioxide or silicon nitride, do not promote it.

A CVD reaction has good step coverage when its slowest (rate-limiting) step occurs on the surface and is slow compared with the arrival rate of the reactants. Thus, tungsten deposited by the hydrogen reduction of tungsten hexafluoride in the lower temperature range, 300–450°C, shows good step coverage, because of

the slow rate of reaction at the surface. For example, at 430°C, over 80% step coverage has been achieved by this reaction in vias with an aspect ratio of 3:1, at a modest deposition rate of 25 nm/min. As the deposition temperature increases, so does the surface reaction rate, and the step coverage becomes poorer. The good step coverage found for the hydrogen reduction may be attributed to either the slow adsorption of hydrogen or to the slow desorption of HF by-product from the surface.

Silicon also catalyzes the deposition of tungsten. Initially, the silicon itself is the reductant, according to the reaction

$$2WF_6 + 3Si \rightarrow 2W + 3SiF_4 \qquad (10)$$

This silicon reduction of tungsten hexafluoride stops after a thin layer of tungsten is deposited, because the tungsten layer prevents contact between the gas-phase reactant (WF_6) and the silicon surface, which has become covered with tungsten. However, the deposition of tungsten can be continued by shifting to the hydrogen reduction (Eq. 8) catalyzed by the initially deposited layer of tungsten over the silicon. Therefore, selective deposition of tungsten on silicon contacts is possible. The tungsten nucleates on the silicon at the bottom of the contact hole and grows to form a ''plug'' through the silicon dioxide insulator layer, but it does not grow on top of the silicon dioxide. The resulting structure has a nearly planar surface, onto which a layer of lower-resistance interconnect metal (such as aluminum) can be deposited and then etched into the required pattern of connections.

Although this selective tungsten process has been studied extensively, it has not yet (in 1994) come into widespread commercial use for the production of tungsten plugs in contact holes. One problem is that the removal of silicon by reaction (10) may interfere with the operation of shallow semiconductor devices. Also, practical difficulties have arisen in completely preventing growth on various insulator surfaces. Unwanted tungsten growth may occur on insulator surfaces because of catalytic action of a variety of contaminants, including some less volatile tungsten fluorides that occur as intermediates in the reduction reactions. Use of a cold-wall reactor, in which only the substrate is heated, tends to trap the lower tungsten fluoride by-products and maintain selectivity better than hot-wall reactors do.

Because of the difficulty of reproducing selective tungsten growth, tungsten plugs are usually deposited by the so-called ''blanket tungsten process.'' In this process, tungsten is deposited over the entire wafer surface, and then etched away in all areas except for the thicker regions deposited within the contact holes. Nonselective deposition on all surfaces, including insulators as well as metals and silicon, is achieved by beginning the reaction with silane as a reductant:

$$2WF_6 + 3SiH_4 \rightarrow 2W + 3SiF_4 + 6H_2 \qquad (11)$$

The silane reduction proceeds without the need for any catalytic action by the surface, and it deposits tungsten rapidly and nonselectively on all surfaces. In fact, it can even nucleate spontaneously in the gas phase, yielding undesirable tungsten particles. To avoid vapor-phase nucleation reactions, the silane reduction reaction is normally run with low partial pressures of the reactants (less than 1 torr). At low pressures, the rate of deposition by this reaction is proportional to the flux of silane gas to the surface of the film, and it is essentially independent of the tungsten hexafluoride concentration (provided it exceeds some very small value).

Because of its rapid surface reaction, the silane reduction reaction yields rather poor step coverage. For example, with equal gas concentrations of silane and tungsten hexafluoride, only 25% step coverage is found at 430°C in holes with an aspect ratio of 3:1. The growth rate under these conditions is more than four times higher than achieved by the hydrogen reduction reaction. In practice, because of this poor step coverage, only a thin initial layer is produced by silane reduction. Then, the silane flow is terminated, while the hydrogen flow is initiated. The hydrogen reduction reaction (reaction (8)) is then used to deposit tungsten over the entire surface to benefit from the catalytic effect of the thin tungsten layer already produced by the silane reduction reaction.

Another approach that has been taken to initiate tungsten deposition onto titanium nitride barrier/adhesion layers (see Sec. V.D) is to flow hydrogen gas over the titanium nitride surface prior to beginning the flow of tungsten hexafluoride gas. Presumably, some of the hydrogen chemisorbs onto the titanium nitride surface, leading to almost immediate initiation of tungsten film growth. In contrast, if the tungsten hexafluoride gas is started first or at the same time as the hydrogen, then there is a long delay (many minutes) before the tungsten growth begins, and the interface between the titanium nitride and the tungsten appears to be contaminated by significant amounts of fluorine.

Because the step coverage of the hydrogen reduction reaction is good, ''blanket'' deposited tungsten fills the contact holes and covers the rest of the insulator surface to a nearly planar level. Then the tungsten is etched by a fluorine-containing plasma, so that only the tungsten within the contact holes remains. Alternatively, mechanical polishing is also used to remove the blanket tungsten layer, leaving contact holes filled with tungsten up to the flat surface of the silicon dioxide insulator.

Stress is another important property of thin films. A film is said to be in tensile stress if it is stretched over the substrate, and in compressive stress if it is squeezed by the substrate. In the case that the tensile stress in a film is too large, cracks may form in it, and/or it may result in delaminations off the substrate. Large compressive stresses may result in delaminations off the substrate

in the form of bubbles or blisters. During a CVD process a certain amount of stress is built into the film, with tensile stress being more common than compressive stress. Tensile stress may arise because some of the ligands are lost from the surface layers of the growing film, leaving metal atoms separated by distances larger than usual for the bulk material. Compressive stress is more common in sputtered films, perhaps because of the bombardment of the film surface by fast-moving ions. Stress can also be changed (either increased or decreased) as the film and substrate are cooled from the deposition temperature to room temperature.

Normally, CVD tungsten films have high tensile stress (more than 10^{10} dynes/cm^2). By reducing the concentration of tungsten hexafluoride gas, the stress in tungsten films may be reduced or even made slightly compressive. The lower growth rates under these conditions presumably allow more time for the tungsten atoms to rearrange at the growth surface before being covered by a new layer of atoms. Poorer step coverage may, however, be obtained in tungsten deposited under these conditions.

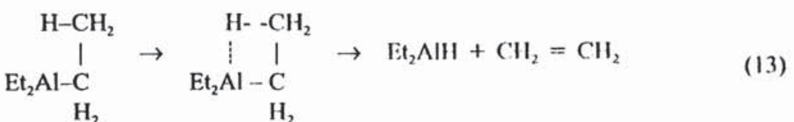
C. Chemical Vapor Deposition of Aluminum

Several different compounds of aluminum have been used as sources for CVD. Aluminum alkyls, such as triisobutylaluminum (TIBA), allows deposition at substrate temperatures in the range 200–400°C:

$$AlR_3 \rightarrow Al + H_2 + \text{olefins} \quad (12)$$

(R is a hydrocarbon radical, such as isobutyl, C_4H_9.)

These temperatures (200–400°C) are not high enough to break the strong aluminum–carbon bonds (about 280 kJ/mol) directly. Instead, there is evidence that a bond between aluminum and hydrogen forms at the same time that the aluminum–carbon bond is breaking, in what is called a beta-hydride elimination, as illustrated by



$$Et_2Al\text{–}C(H_2)\text{–}CH_2\text{–}H \rightarrow Et_2Al\text{–}C(H_2)\text{–}CH_2 \cdots H \rightarrow Et_2AlH + CH_2 = CH_2 \quad (13)$$

Two more beta-hydride elimination reactions result in AlH_3, which quickly decomposes to aluminum and hydrogen at temperatures above 100°C:

$$AlH_3 \rightarrow Al + \frac{3}{2}H_2 \quad (14)$$

The effect of temperature on the deposition rate of aluminum from triisobutylaluminum is shown in Fig. 5. Below 400°C, the rate increases rapidly

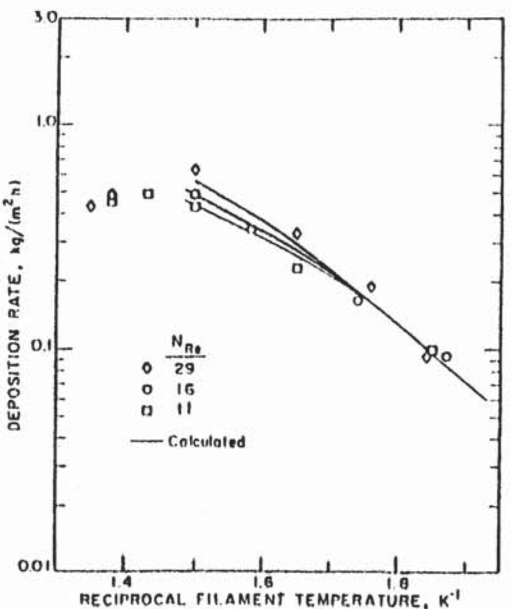


Figure 5 Temperature dependence of the deposition rate of aluminum from triisobutylaluminum. (From A. Malazgirt and J. W. Evans, *Metall. Trans. 11B*:225 (1980).)

with temperature, because of the activation barrier to the beta-hydride elimination reactions. Above 400°C, the diffusion of reactants to the surface becomes rate-limiting, and the deposition rate becomes nearly constant.

Not all of the aluminum–carbon bonds are eliminated during the decomposition of aluminum alkyls, which thus leave some carbon contamination in the aluminum film, particularly at higher substrate temperatures. Another problem with this CVD process for aluminum is that the deposited aluminum film tends to be somewhat rough, because of large crystallites, which can cause problems forming narrow interconnections. Heated liquid aluminum alkyls undergo some beta-hydride elimination of ligands before they are even vaporized, resulting in complex mixtures containing variable amounts of mixed aluminum alkyl-hydride species of lower volatility. Premature source decomposition may be mitigated by using an alkene carrier gas, such as isobutylene. Also, the aluminum alkyls associate in the liquid state by strong intermolecular interactions, which slow down the kinetics of vaporization and make it difficult to obtain reproducible vapor concentrations. Close control of the temperature of the liquid

aluminum alkyl is insufficient to ensure a reproducible rate of vapor delivery, because the slow vaporization kinetics results in a less than saturated vapor pressure. Thus, the concentration of vapor delivered depends on the carrier gas flow rate, the volume of liquid remaining, and so on. These difficulties contribute to the slow introduction of the commercial use of aluminum alkyl CVD for use in microelectronic circuit fabrication.

Surfaces of many clean, oxide-free metals, including aluminum itself, catalyze the deposition of aluminum. On the other hand, film growth does not occur readily on some other surfaces, such as oxides. In principle, this distinction could form the basis for a selective aluminum process. However, a reproducible selective aluminum process has been difficult to demonstrate.

Another type of aluminum precursor is aluminum hydride, AlH_3, which was previously mentioned (Eq. 14) as a likely intermediate compound formed during the decomposition of aluminum alkyls. AlH_3 might seem to be the ideal source for deposition of aluminum, because it contains no carbon that could enter the film as an impurity, and it decomposes at a low enough temperature (around 100°C) so that the aluminum crystallites would remain small. The normal, stable form of AlH_3 is a solid material that cannot be vaporized without decomposition. However, when it is complexed with a tertiary amine, in the form of an amine-alane, $R_3N \cdot AlH_3$, it becomes volatile enough to serve as a CVD precursor at low reaction temperatures (100–200°C):

$$R_3N \cdot AlH_3 \rightarrow Al + \frac{3}{2}H_2 + R_3N \qquad (15)$$

R is a hydrocarbon radical, usually methyl (CH_3) or ethyl (C_2H_5).

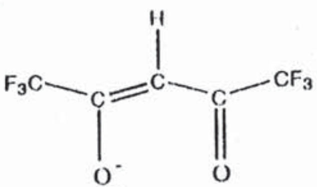
These amine-alane reagents begin to decompose by breaking the relatively weak bond between nitrogen and aluminum:

$$R_3N \cdot AlH_3 \rightarrow AlH_3 + R_3N \qquad (16)$$

The carbon is removed very completely by this dissociation reaction. The AlH_3 then decomposes according to equation (14), leaving the aluminum film free of carbon contamination. The films are also smoother because of the smaller crystallites formed at these lower deposition temperatures. Trimethylamine-alane ($R = CH_3$) and triethylamine-alane ($R = CH_2CH_3$) are solids, which are less reproducible vapor sources than liquids. The mixed alkyl-amine, dimethylethylamine-alane, is a liquid source that tends to give more reproducible amounts of vapor. On storage, however, some of the amine is lost from this dimethylethylamine-alane, and so it may be necessary to add dimethylethylamine vapor to the carrier gas in order to prevent decomposition. Dimethylethylamine-alane is being actively studied for possible application to microelectronics.

D. Chemical Vapor Deposition of Copper

Copper CVD precursors are based on compounds containing the hexafluoroacetylacetonate ligand (abbreviated as hfa):



This fluorinated ligand yields more volatile precursors than the corresponding ligand with hydrogen in place of the fluorine. At temperatures of about 250–400°C, hydrogen reduces vapors from the solid compound copper(II)-hexafluoroacetylacetonate to deposit copper according to the reaction

$$Cu(hfa)_2 + H_2 \rightarrow Cu + 2H(hfa) \qquad (17)$$

A lower-temperature CVD source for copper is the reaction

$$2Cu(hfa)L \rightarrow Cu + Cu(hfa)_2 + 2L \qquad (18)$$

in which L is a neutral ligand such as an olefin or trimethylphosphine. Most of these starting materials of the type Cu(hfa)L are solids, but for L = vinyltrimethylsilane, it is a liquid, and thus it is more easily vaporized than are solids.

Resistivities as low as 2 μΩ-cm have been obtained, close to that of bulk copper (1.7 μΩ-cm). These reactions can produce a high deposition rate of copper, approaching one micron per minute. The temperature dependence of the deposition rate is shown in Fig. 6. At temperatures below 200°C the deposition rate increases steeply with increasing temperature, according to an Arrhenius rate law, probably due to the rate-limiting step being a surface reaction with an activation energy near 96 kJ/mol (23 kcal/mol). Above 200°C, the deposition rate becomes nearly independent of temperature, because the surface reaction is very fast and the rate-limiting step is then the rate of diffusion of reactants to the surface.

Selective growth of copper from reaction (18) has been demonstrated on various metals, including copper itself and metallic titanium nitride, at rather low temperatures of 150–200°C. No growth of copper occurs on dry oxide surfaces, but moisture or other contaminants lead to unwanted spurious growth of copper and loss of selectivity. Better understanding of these and other growth parameter effects is required to achieve a practical selective copper process.

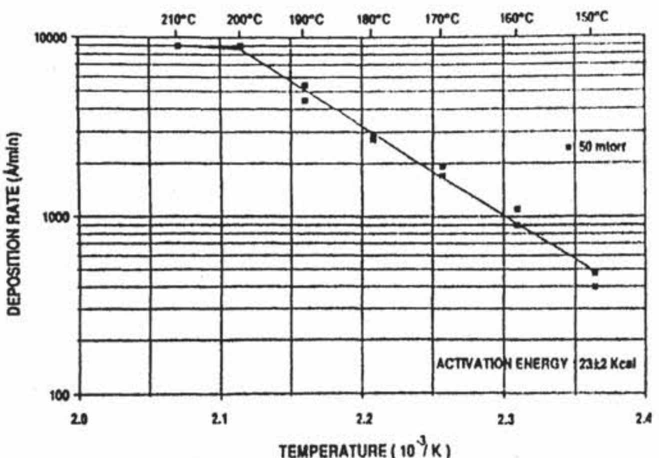


Figure 6 Chemical vapor deposition rate of copper from the precursor (hexafluoroacetylacetonate)copper(2-butyne) as a function of deposition temperature at a precursor partial pressure of 50 mtorr. (From A. Jain, K.-M. Chi, T. T. Kodas, M. J. Hampden-Smith, J. D. Farr, and M. F. Paffett, *Chem. Mat.* 3:995 (1991).)

The likely mechanism of this selective CVD reaction involves dissociation of the precursor on the surface of a metal to form a copper(I) surface species and the free gaseous ligand:

$$Cu(hfa)L(s) \rightarrow Cu(hfa)(s) + L(g) \quad (19)$$

Two adjacent copper(I) species then disproportionate to give the surface-bound product copper and a volatile copper(II) by-product, which sublimes into the gas phase:

$$2Cu(hfa)(s) \rightarrow Cu + Cu(hfa)_2(g) \quad (20)$$

V. BARRIER AND ADHESION LAYERS

A. The Need for a Diffusion Barrier for Aluminum Interconnects

A chemical instability occurs when aluminum comes into direct contact with silicon. Aluminum and silicon react to form a compound (called a eutectic) with a relatively low melting point of 577°C. The interface between aluminum and silicon becomes unstable when heated, even to temperatures somewhat below the eutectic temperature, causing etch pits in the silicon to such a depth that

they short out pn junctions near the surface of the silicon. These etch pits can even form through a thin titanium silicide contact layer.

This undesirable interaction is prevented in practice by placing a barrier material on the contact silicide prior to depositing the aluminum. The barrier material must not react with silicon, titanium silicide, or aluminum, and it must not allow the aluminum, titanium, or silicon to penetrate or diffuse through it.

The most commonly used barrier material is titanium nitride, TiN. A TiN layer only 20 nm thick prevents interdiffusion of the contact structure shown in Fig. 2 even when it is heated to a temperature of 500°C for an hour.

B. The Need for a Barrier/Adhesion Layer Under Tungsten

When tungsten is used as an interconnect metal, there are two problems that may occur with a substrate made of silicon and silicon dioxide. The initial reaction of tungsten hexafluoride with the silicon substrate occurs via reaction (10), which consumes some of the silicon surface. Etching of the silicon dioxide can be caused by the hydrogen fluoride by-product of the hydrogen reduction reaction (8), when hydrogen is used as a reactant gas,

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \quad (21)$$

These reactions remove silicon and silicon dioxide from the substrate, and they can leave etch pits, often described as "wormholes," due to uneven etching across the surface.

Another problem that arises is that the tungsten does not adhere well to the silicon dioxide.

In order to protect the substrate during tungsten CVD and to cause the tungsten to adhere, the substrate must first be protected by a layer that is both impervious to attack by the chemicals present in the CVD chamber and adherent to the tungsten. Titanium nitride has been found to be effective in this role, since it does not react either with tungsten hexafluoride or with hydrogen fluoride, and the deposited tungsten adheres well to the titanium nitride layer.

C. The Need for a Diffusion Barrier Layer Under Copper

Copper diffuses rapidly through many solid materials, including silicon. Inside silicon, copper impurities catalyze the recombination of electrons and holes. Early in the development of solid state transistors, many experimental devices failed because of an unknown contaminant, nicknamed "deathnium," later identified as copper. Thus, if copper is ever to be used as a viable interconnect metal for microcircuits, a very effective diffusion barrier is needed under the copper.

Titanium nitride is effective against the diffusion of copper. Furthermore, very thin layers of amorphous alloys containing tantalum, nitrogen, and silicon have also been demonstrated to be effective as diffusion barriers.

D. CVD of Titanium Nitride Barrier and Adhesion Layers

As indicated, titanium nitride layers serve as barrier films for each of the three common interconnect metals. Titanium nitride layers have generally been made by reactive sputtering of a titanium target in a nitrogen atmosphere. This sputtering process is adequate to fill holes and trenches with aspect ratios under about 2 or 3. However, if the aspect ratio is too large, the sputtered titanium nitride layer is very nonconformal, resulting in only a few tens of nanometers on the bottoms and sidewalls of the holes. Therefore, alternative CVD processes have been investigated, in order to more uniformly fill the narrow holes, or to coat contoured surfaces.

Titanium tetrachloride vapor reacts with ammonia at temperatures above 500°C to deposit titanium nitride with excellent step coverage as per

$$6TiCl_4 + 8NH_3 \rightarrow 6TiN + 24HCl + N_2 \quad (22)$$

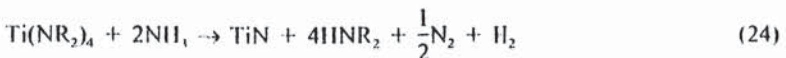
However, it is important that these reactants are not mixed at ambient temperatures, in which case a rapid acid–base reaction precipitates an unwanted salt or adduct, by reactions such as

$$TiCl_4 + 2NH_3 \rightarrow TiCl_4 \cdot 2NH_3 \quad (23)$$

To avoid reaction (23), the reactants are separately preheated to temperatures around 250–300°C. The mixed reactants then maintain a homogeneous vapor phase sufficiently long to deposit a relatively pure TiN film at substrate temperatures above about 600°C. This temperature is low enough to allow its use in commercial depositions of diffusion barriers on silicon microelectronic devices, at the first level of metallization. The same method is also employed to produce titanium nitride solar control coatings on large areas of window glass.

The deposition temperature for this reaction is, however, too high to be used between upper layers of metals, if some aluminum has already been deposited on the wafer. Another disadvantage of this reaction is that some chlorine remains in the deposited film, where it may later cause corrosion of the metal layers. Also, solid by-products of the CVD reaction, such as ammonium chloride, generate particles, which can contaminate wafers and cause problems in handling the reactor exhaust gases.

An alternative CVD process operating at lower temperatures (typically, 200–400°C) and involving no chlorine is that of tetrakis(dialkylamido)titanium reacting with ammonia as per

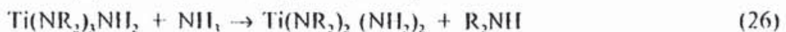


$$Ti(NR_2)_4 + 2NH_3 \rightarrow TiN + 4HNR_2 + \frac{1}{2}N_2 + H_2 \quad (24)$$

in which R represents either methyl or ethyl groups. This CVD process yields better step coverage than sputtering, but it is inferior to that produced by the chloride CVD process (22). However, these films are more effective diffusion barriers between metals and silicon compared with the commonly used sputtered TiN films.

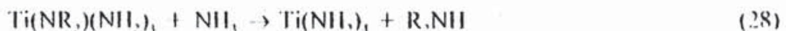
The chemical mechanism of the CVD reaction between tetrakis-(dialkylamido)titanium compounds and ammonia is partly understood. The reaction begins very rapidly as soon as the reactants are mixed in the gas phase. By analogy to similar solution-phase reactions, it seems likely that these initial gas-phase reactions are transaminations:

$$Ti(NR_2)_4 + NH_3 \rightarrow Ti(NR_2)_3\,NH_2 + R_2NH \quad (25)$$



$$Ti(NR_2)_3NH_2 + NH_3 \rightarrow Ti(NR_2)_2\,(NH_2)_2 + R_2NH \quad (26)$$

$$Ti(NR_2)_2(NH_2)_2 + NH_3 \rightarrow Ti(NR_2)(NH_2)_3 + R_2NH \quad (27)$$



$$Ti(NR_2)(NH_2)_3 + NH_3 \rightarrow Ti(NH_2)_4 + R_2NH \quad (28)$$

Flow tube experiments have confirmed that these fast reactions produce dimethylamine (in the case R = methyl), and they have measured the rate constants for these fast transamination reactions. The transamination reactions become slower with bulkier ethyl groups. This mechanism also predicted that the nitrogen in the film comes from the ammonia, rather than from the nitrogen initially bound to the titanium. Isotopic tracer experiments have subsequently verified this source of the nitrogen, giving further suppot to the transamination mechanism.

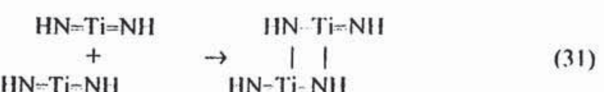
The resulting titanium amide, $Ti(NH_2)_4$, is not a known compound. It is likely to undergo rapid unimolecular decomposition reactions, eliminating ammonia:

$$Ti(NH_2)_4 \rightarrow HN{=}Ti(NH_2)_2 + NH_3 \quad (29)$$

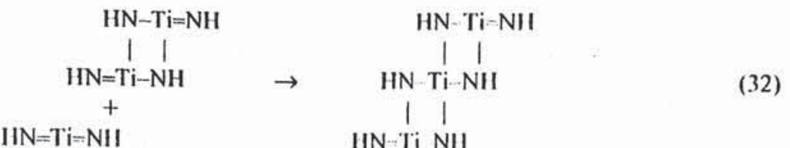
$$HN{=}Ti(NH_2)_2 \rightarrow HN{=}Ti{=}NH + NH_3 \quad (30)$$

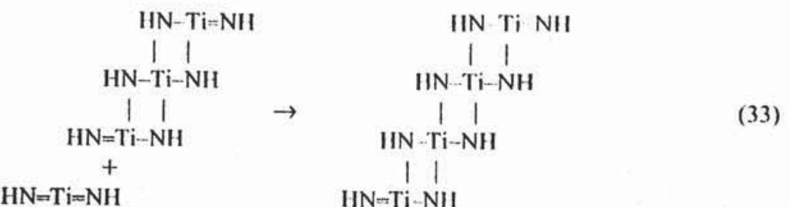
The elimination reactions should be somewhat endothermic, since they convert two titanium–nitrogen single bonds into one double bond of lower bond strength. The resulting titanium diimide, HN=Ti=NH, should have a high sticking coefficient on the surface of the growing film, because the titanium atom has only two shielding ligands. Thus, the titanium diimide is a likely growth species leading to a material with a transition composition of (TiN_2H_2). Subsequent loss of some nitrogen and hydrogen from the solid would then lead to the observed composition of nitrogen-rich titanium nitride with some residual hydrogen.

Dimerization reactions are also likely for the titanium diimide:


(31)

These are likely to be followed by polymerization reactions such as the following:


(32)


(33)

The polymerization reactions should be exothermic, due to the exchange of a Ti=N double bond for two single Ti–N bonds, the latter of which are each more than half as strong as a double bond. The rates of polymerization are likely to be fast and nearly independent of temperature. Extensive polymerization could lead to the formation of particles. By making the gas residence time in the CVD reactor as short as possible, the growth of particles is limited by reduced polymerization. Gas-phase polymers may also add to the surface of the growing film, resulting in more material of the same composition, $(TiN_2H_2)_n$. With the sticking coefficients of the polymeric species likely to be higher than those of the monomer, the physical properties of the film deposited from polymers may differ from those of films deposited from monomers. Gas-phase polymerization occurring before film deposition will therefore reduce the step coverage, density, and conductivity of films. The best film properties are thus obtained when the reactant gases are mixed as close to the growth surface as possible. Special showerheads have been developed with two interspersed sets of holes to bring the titanium precursor and the ammonia gas in separately, so that they mix close to the wafer surface. Rapid mixing by fans between the showerhead and the substrate has also been used to improve film properties. Better properties (step coverage and conductivity) are obtained from the ethyl precursor (tetrakis(diethylamido)titanium, TDEAT) than from the analogous methyl precursor (TDMAT), presumably because the transamination reactions are slower and

subsequent deleterious polymerization reactions are more limited in the ethyl case.

VI. ETCHING PROCESSES FOR METALS

In order to form the intricate patterns of metal lines connecting the various electrical components on a microcircuit, etching processes remove parts of the metal layers not covered by photolithographically produced mask layers (see Chapter 6). The removal of metal can be achieved by appropriate solutions (wet etching), or by reactive gases or by plasmas (dry etching; see Chapter 7). There are several chemical approaches used to etch metals.

A. Wet Etching

Aluminum can be dissolved by aqueous hydrochloric acid, unless its covering aluminum oxide layer is too thick.

One wet tungsten etch is aqueous hydrogen peroxide, H_2O_2. Another is a solution obtained by combining potassium ferrocyanide, potassium hydroxide, and potassium acid phosphate ($K_3Fe(CN)_6 + KOH + KH_2PO_4$).

Copper may be dissolved by an aqueous solution of ferric chloride ($FeCl_3$).

Titanium and titanium nitride may be etched by an aqueous solution containing hydrogen peroxide and ammonia. The solution remains active for a few hours, after which the hydrogen peroxide decomposes. Since this solution does not dissolve titanium silicide, it permits the selective removal of titanium and is the basis of the widely used self-aligned silicide ("salicide") patterning process.

Tungsten silicide may be dissolved in an HF/HNO_3 acid solution. The practical usefulness of this etch is limited because it also dissolves silicon and silicon dioxide.

Wet etching processes are simple to carry out in the laboratory, but they have some practical disadvantages in chip production. In some cases, bubbles of gaseous by-products hinder complete removal of the metal. Rinsing and drying steps are needed to clean the wafers after wet etching. Spent etching solutions must be neutralized, and in some cases toxic metals must be removed before disposal. For these reasons, dry etching processes have often become the preferred means for manufacture of microcircuits.

B. Dry (Gaseous) Etching

Aluminum can be removed by first sputtering in an argon atmosphere to remove the thin surface layer of aluminum oxide, and then applying carbon tetrachloride plasma. It is likely that the CCl_4 plasma converts the aluminum to the more

volatile aluminum chloride, $AlCl_3$. The detailed mechanism of this reaction is not known, but it probably involves chlorine atoms and various chlorine-containing free radicals, such as CCl_3.

Tungsten is etched by a carbon tetrafluoride plasma, in which it may be converted to gaseous tungsten hexafluoride.

Chlorine-containing plasmas etch copper if it is held at temperatures above 250°C, so that the by-product Cu_3Cl_3 has a sufficiently high vapor pressure. Copper can also be removed by using the reverse of the CVD reaction (18), using a vapor mixture of copper(II)hexafluoroacetylacetonate (hfa) and vinyltrimethylsilane (L):

$$Cu + Cu(hfa)_2 + 2L \rightarrow 2Cu(hfa)L \tag{34}$$

Titanium and titanium nitride are etched by a chlorotrifluoromethane plasma, which may convert them into titanium tetrachloride vapor.

VII. SUMMARY

Metal interconnections in microelectronic circuits consist on multiple layers. One layer, typically aluminum or tungsten, forms the low-resistance pathway for the electric current to travel between different parts of the silicon semiconductor wafer. Other layers, typically titanium nitride, provide stability to structure by preventing reaction between the metal and the silicon, and by making a stronger bond between tungsten and silicon dioxide insulators. Additional layers, such as titanium metal, are often used to lower the electrical resistance between the metals and the silicon. Very stable metal silicides, such as titanium silicide and tungsten silicide, are being used as gate electrodes that are more conductive than polysilicon, the material traditionally used for gate electrodes.

Sputtering has traditionally been the most common method of applying these metallic layers to silicon substrates. During the 1990s, increasing use has been made of chemical vapor deposition for this purpose, because CVD can fill more completely the very tiny holes and channels in modern microcircuits. But CVD involves complex chemical reactions, which in many cases are only partly understood. Better knowledge of CVD mechanisms is aiding in the optimization and control of known reactions, and in the design of new CVD processes.

EXERCISES

1. Titanium and zirconium are metals in the same group of the periodic table, and they have similar, but not identical, properties. Why do you think that titanium is preferred over zirconium as a contact metal in silicon semiconductor devices?

2. What deleterious effect would be noticed in a microcircuit's operation if the titanium layer in Fig. 2 were omitted from the contact structure? What deleterious effect would be noticed in a microcircuit's operation if the titanium nitride layer in Fig. 2 were omitted from the contact structure?
3. Consider the tungsten CVD reactions (8), (10), and (11). Suggest appropriate chemical reactions that could be used to convert the gaseous by-products from these reactions into safe, nontoxic chemicals suitable for recycling and/or disposal in an environmentally sound manner.
4. Suppose you have carried out a CVD process, and found a void structure in the deposited material, similar to that shown in Fig. 3. What changes in the processing might you suggest to form a dense, void-free deposit?
5. Which of the CVD reactions discussed in this chapter are reversible? Give the conditions that would drive the reaction to the right, and those that would drive it to the left.

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