
MICROCHIP MANUFACTURING

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CVD OF AMORPHOUS AND POLYCRYSTALLINE THIN-FILMS

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"A well-designed apparatus will do its work without effort. It will cost considerably less than one improperly planned and in whose design established principles have been overlooked. It will also perform with greater economy of steam, which is always an important consideration."

A.L. Weber,
Evaporation, The Chemical
Catalog Co, New York, 1926.

PECVD system for 300-mm wafers. Shown is the Novellus VECTOR® PECVD tool. Courtesy of Novellus Systems, Inc.

Chemical vapor deposition (CVD) is a process by which a solid-film is deposited on a substrate by reacting vapor-phase chemicals that contain the constituents of the film. The reactant-gases are fed into a reaction chamber. There they decompose and/or react at a heated-surface to form the thin-film (Fig. 16-1). Note that in CVD the reactant-gases do not react with (and therefore do not consume) any substrate-surface-material.

A wide-variety of the thin-films used in ULSI fabrication are formed by CVD. The deposition of amorphous and polycrystalline thin-films is the subject of this chapter. The growth of single-crystal silicon films by epitaxial CVD-techniques is described in Chap. 17.

CVD involves many scientific disciplines, including gas-phase reaction-chemistry, thermodynamics, kinetics, heat-transfer, fluid-mechanics, surface-reactions, plasma-reactions, film-growth phenomena, and reactor-engineering. Obviously these interdisciplinary principles can only be introduced here. Interested readers are advised to consult the references

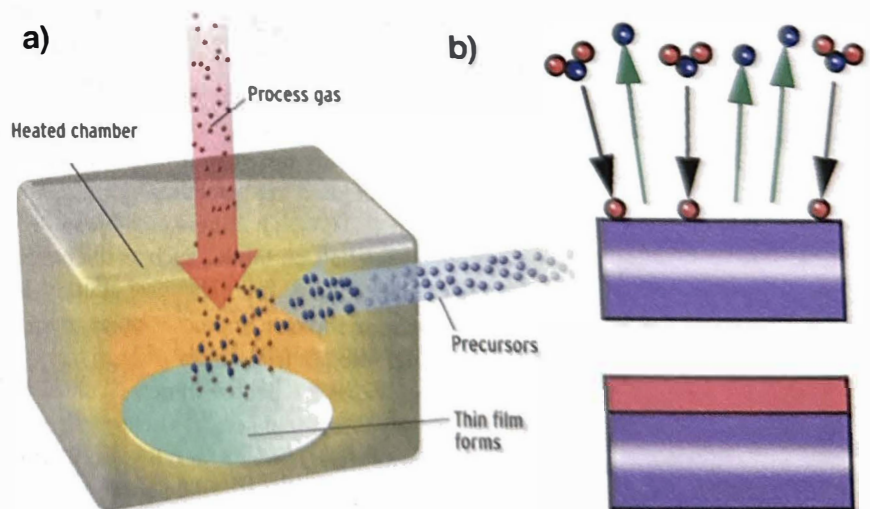


Fig. 16-1 Chemical-vapor-deposition (CVD) produces a solid-film on a substrate by reacting vapor-phase chemicals that contain the constituents of the film. The reactant-gases do not react with (and therefore do not consume) any substrate surface-material: (a) Macroscopic perspective; and (b) Microscopic perspective of CVD.

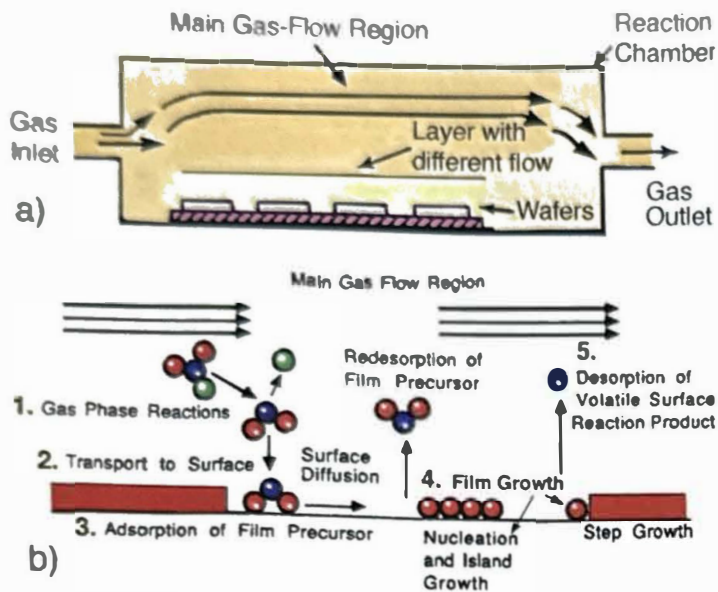


Fig. 16-2 The CVD-process from: (a) a *macroscopic perspective*; and (b) a *microscopic perspective*. In part (a) a CVD reaction-chamber is shown with gases flowing into and out of it. In part (b) the five sequential-steps of a CVD-process are depicted.

for more information on these topics.¹⁻⁴

In this chapter, the mechanisms and a model for thin-film growth in CVD are discussed first. Next, the deposition-technology and equipment used to prepare such films by CVD are covered. Finally, the properties and deposition conditions of some of the most widely-used films deposited by CVD (including polycrystalline-silicon, silicon-dioxide, silicon-nitride, tungsten, and titanium-nitride) are covered. Measurement of many of the properties of CVD-films is virtually identical to the measurement of the same properties in other thin-films. Consult the index to find information on various generic thin-film measurement methods.

As discussed in Chap. 7, thin-films are used in a host of different applications in ULSI fabrication, and can be prepared using a variety of techniques. Regardless of the method by which they are formed, the process must be economical, and the resultant films must exhibit the following characteristics: **a)** good thickness-uniformity; **b)** high-purity and density; **c)** controlled-composition and stoichiometry; **d)** a high-degree of structural-perfection; **e)** good

electrical-properties; **f)** excellent adhesion; **g)** good step-coverage; and **h)** low defect-density.

Specific deposition methods have been developed to fabricate such thin-films, based on the capabilities for satisfying these demanding criteria. CVD-processes are often selected over other competing techniques because they offer the following advantages: **a)** high-purity deposits can be achieved; **b)** a great variety of chemical-compositions can be deposited; **c)** some films cannot be deposited with acceptable film properties by any other method; and **d)** good economy and process-control are possible for many CVD films.

16.1 THE BASIC ASPECTS OF CHEMICAL VAPOR DEPOSITION (CVD)

A CVD-process consists of the following five steps:

1. Reactant-gases (frequently diluted by mixing with a *carrier-gas* [or *diluent-gas*]) are introduced into a reaction-chamber. They move from the inlet to the outlet in the *main gas-flow region* (see Fig. 16-2a). While flowing through the chamber, they come into the vicinity of the wafers in it.
2. The gases are transported by *diffusion* to the wafer-surface through a sector called the *boundary-layer*. That is, a *boundary-layer* in the gas exists between the main gas-flow region and the surface of the wafer (see Figs. 16-2a and b).
3. The reactants are *adsorbed* on the substrate-surface (whereupon they are called *adatoms*).
4. These adatoms migrate to growth-sites, where the *film-forming chemical-reactions* take place. These reactions create the *solid-film* and *gaseous by-products*.
5. The *gaseous by-products* of the reaction desorb from the surface, diffuse through the boundary-layer near the surface, into the main- gas-flow region, and are removed from the chamber as the main-gas-flow moves toward the outlet.

Energy to drive the film-forming reactions is supplied by one or more of the following energy-sources: thermal energy; photons; or electrons. *Thermal energy* is

by far the most common energy-source used.

Many types of chemical-reactions are employed in CVD to fabricate the various kinds of films needed in ICs, including: *pyrolysis* (thermal-decomposition); *reduction*; and *oxidation* of the reactants.

Several other practical aspects of CVD processes should be mentioned. First, the deposition-time needed to form the film with the desired thickness must be sufficiently-short to permit adequate wafer-throughput. Second, the process-temperature must be low-enough so that it does not adversely impact the stability of previously-deposited layers (e.g., low-melting-point metal layers such as Al may already be on a wafer). Third, the CVD-process should not allow by-products of the reactant-gases to become incorporated into the growing films (but this is sometimes unavoidable, such as when a significant-amount of hydrogen is incorporated in PECVD silicon-nitride films - see Sect. 16.5).

The chemical-reactions leading to the formation of the solid that makes up the deposited-film may, in practice, take place not only on (or very-close-to) the wafer-surface (*heterogeneous-reaction*), but also in the gas-phase (*homogeneous-reaction*). Heterogeneous-reactions are preferred, as they occur selectively only on heated-surfaces, and produce good-quality films. Homogeneous-reactions are undesirable because they form solid-clusters of the depositing material in the gas-phase. These clusters can rain-down on the film being grown on the wafers, causing defects in this film (as well as other problems, including poor-adhesion and low film-density). In addition, homogeneous-reactions also consume reactants, and thus cause the deposition-rate to decrease. As a result, one important characteristic of a chemical-reaction for CVD-application is the degree to which heterogeneous-reactions are favored over gas-phase (homogeneous) reactions.

16.1.1 A Simplified CVD Film-Growth Model

Since the steps of a CVD process are sequential, the one which occurs at the slowest-rate will determine the overall-rate of film deposition. This slowest-step is referred to as the *growth-rate-limiting step*. Since

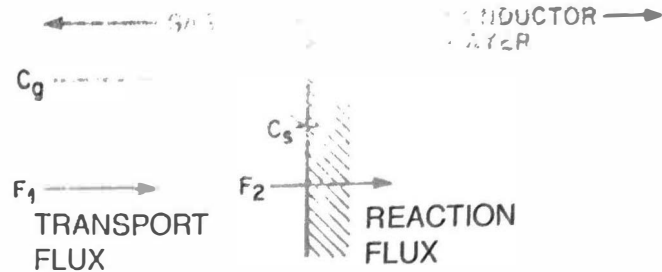


Fig. 16-3 Grove's model of the CVD-process depicting the transport-flux F_1 and the reaction-flux F_2 .⁵

high growth-rates are essential for making a deposition-process economically feasible, knowing which one limits the growth-rate can be valuable. Once identified, process-modifications can be explored to speed-up that step, perhaps allowing the overall deposition-rate to be increased.

A model that permits the growth-rate of CVD-films to be predicted is also a useful tool for developing CVD-processes. However, deriving a simple mathematical-relationship which predicts CVD growth-rates based on all five-steps of the above CVD process-sequence has proven difficult, even up to this time. Instead, less-complex growth-rate models have been created, based on the observation that the 5-steps of the CVD-process can be grouped into two-categories: **1)** those that occur in the gas-phase (*gas-phase processes*); and **2)** those that occur on the substrate surface or chamber-wall surface (*surface processes*). By using this observation, a simple CVD growth-rate model can be established.

This model assumes that *only one of the gas-phase growth steps* (i.e., transport of the reactants across the boundary-layer - Step 2), or *only one of the surface-processes* (i.e., the surface chemical-reaction - Step 4) *is the rate-limiting step*.⁵ This model explains many phenomena observed in CVD-processes, and predicts the growth-rates of many films quite accurately.

Figure 16-3 is a schematic depicting the essentials of this model. It shows the concentration distribution of the reactant-gas and the *flux* (number of atoms or molecules crossing a unit-area in a unit-time; e.g., atoms/cm² sec) from the bulk of the gas to the surface

of the growing-film, as F_1 . A second-flux (which corresponds to the consumption of the reactant-gas at the surface to form the solid-film) is also shown, and is termed F_2 . The choice of gas-species does not affect the basic-principles described by the model. The flux F_1 is approximated by assuming it is linearly-proportional to the concentration-difference between the reactant in the bulk of the gas C_g and that at the surface of the substrate, C_s . The constant of proportionality is termed the *gas-phase mass-transfer-coefficient*, h_g . The relationship for F_1 is thus:

$$F_1 = h_g (C_g - C_s) \quad (16.1)$$

The flux F_2 is assumed to be linearly-proportional to the surface-concentration of the reactant, and the constant of proportionality is the *chemical surface-reaction-rate-constant*, k_s . The expression for F_2 is:

$$F_2 = k_s C_s \quad (16.2)$$

Under *steady-state-deposition* conditions the two-fluxes must be equal: $F_1 = F_2 = F$. As noted earlier, in many CVD-processes the reactant-gas is diluted in a *carrier* (or *diluent*) gas. In such cases, the concentration of the reactant in the gas-phase can be defined as $C_g = C_T Y$, where Y is the mole-fraction of the reaction-species and C_T is the total-number of molecules (including the carrier-gas) per cm^3 in the chamber. In this case, an equation that calculates the *growth-rate of the film* G can be derived from this model, and is given by:

$$G = \frac{k_s h_g}{k_s + h_g} \frac{C_T}{N_1} Y \quad (16.3)$$

where N_1 is the number of atoms incorporated into a unit-volume of the film. (Recall that the value of N_1 for silicon is 5×10^{22} -atoms/ cm^3 .) The detailed derivation of this equation is given in Appendix D.

There are two limiting-cases of Eq. 16-3. If $k_s \ll h_g$, this is termed the *surface-reaction-rate-limited* regime. On the other hand, if $h_g \ll k_s$, this is termed the *mass-transfer-rate-limited* regime. In either of these two regimes, the *growth-rate at constant C_g (or Y) is controlled (in the limits) by the smaller-value of k_s and h_g* . This means that in these limiting-cases, the growth-rates are given by:

$$G = (C_T k_s Y) / N_1 \quad k_s \ll h_g \quad \text{(surface-reaction-rate-limited)} \quad (16.4)$$

or by:

$$G = (C_T h_g Y) / N_1 \quad h_g \ll k_s \quad \text{(mass-transfer-rate-limited case)} \quad (16.5)$$

Basically, if the CVD-process is being operated in the surface-reaction-rate-limited regime, then the growth-rate is very sensitive to variations in the temperature. This also implies that as the temperature is reduced, the surface-reaction-rate is reduced. At sufficiently-low temperatures, the arrival-rate of reactants eventually exceeds the rate at which they are consumed by the surface-reaction, and the deposition-rate becomes *surface-reaction-rate-limited*.

The surface reaction-rate also increases exponentially with increasing-temperature (see Appendix D). For a given surface-reaction, if the temperature rises high enough, the reaction-rate will exceed the rate at which reactant-species arrive at the surface. In such cases, the reaction cannot proceed any more rapidly than the rate at which reactant-gases are supplied to the substrate by mass-transport, no matter how-high the temperature is increased. Then the growth-rate becomes *mass-transport-limited*.

This CVD-growth-model also gives insight into CVD-processes. For example, in CVD-processes run under *surface-reaction-rate-limited* conditions the *process-temperature* is the key-parameter. In such processes, uniform deposition-rates throughout a reactor require conditions that maintain a constant surface reaction-rate. This, in turn, implies that a constant-temperature must also exist everywhere at all wafer-surfaces. Thus, controlling the temperature becomes the main-issue in the reactor-design. Under such conditions, the rate at which reactant-species arrive at the surface is not as important (since their concentration does not limit the growth-rate). Thus, it is not as critical that a reactor be designed to supply an equal-flux of reactants to all-locations of a wafer-surface. It will be seen that in low-pressure-CVD (LPCVD) reactors, wafers can be stacked at very-close-spacing because such-systems operate in

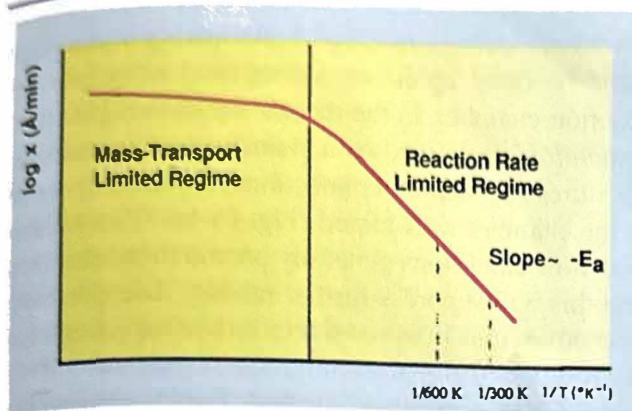


Fig. 16-4 Temperature-dependence of the growth-rate for CVD films.

a surface-reaction-rate-limited mode.

In deposition-processes that are *mass-transport-limited*, the temperature-control is not nearly as critical because the mass-transport process that limits the growth-rate is only weakly-dependent on temperature. In these processes, it is very important that the *same concentration of reactants* be present in the main (or bulk) gas-flow-regions adjacent to all locations of a wafer, since the arrival-rate is directly proportional to the concentration in the bulk-gas. Thus, to insure *uniform film-thickness* across a wafer, reactors which are operated in the mass-transport-limited regime must be designed so that all locations of wafer-surfaces are supplied with an equal-flux of reactant-species. Atmospheric-pressure-CVD (APCVD) reactors that deposit SiO_2 at $\sim 400^\circ\text{C}$, and epitaxial-reactors operating at $\geq 1000^\circ\text{C}$, operate in the mass-transport-limited regime. The most widely-used APCVD- SiO_2 reactor-designs provide a uniform-supply of reactants by horizontally-positioning the wafers and moving them under a stream of reactant gases.

To Summarize: At high-temperatures, the deposition is usually *mass-transport-limited*, while at lower-temperatures it is usually *surface-reaction-rate-limited* (Fig. 16-4). In actual-processes, the temperature at which the deposition-condition moves from one of these growth-regimes to the other is dependent on the activation-energy of the reaction and the gas-flow-conditions in the reactor.

16.2 CHEMICAL-VAPOR-DEPOSITION SYSTEMS

In this section the equipment used in CVD-processes is described. The general terminology of CVD-tech is first presented, and then the particular CVD-reactor types are discussed.

16.2.1 Components of CVD-Systems

Figure 16-5 shows some of the reactor types that have been used for CVD-processes. CVD-reactors are generally *open-flow* systems, in which gases continuously flow into the reaction-chamber (where the deposition occurs). Reactant-gases are frequently carried by *diluent* (or *carrier*) gases such as H_2 , N_2 , or Ar, depending on the specific CVD-process. Gaseous by-products are exhausted together with the diluent-gas (and any unused reactant-gases). Gas-flows in the chamber are slow enough so that the pressure can be considered to be uniform. Corrosive and hazardous-gases pumped from the chamber are removed from the exhaust-gas flow by a *scrubber* (see Chap. 29), and the remainder

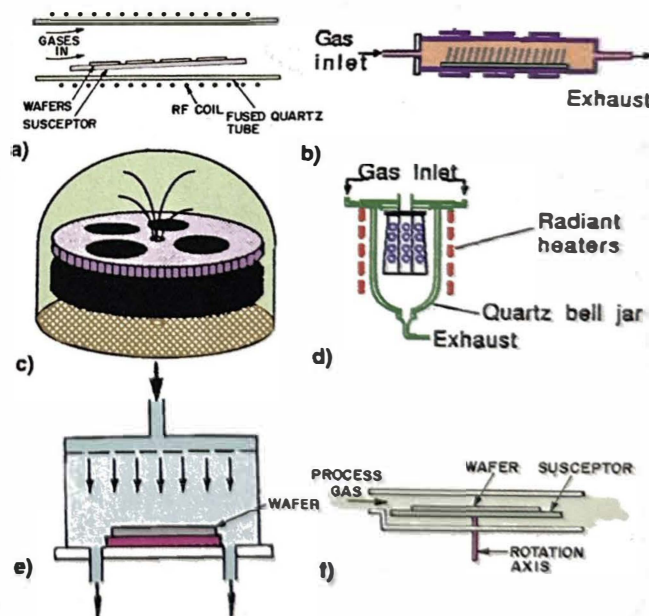


Fig. 16-5 CVD-reactor types: (a) Horizontal-flow reactor with tilted susceptor; (b) Horizontal-flow reactor with wafers stacked vertically; (c) Pancake reactor; (d) Barrel reactor; (e) Single-wafer reactor with showerhead gas-injector; (f) Horizontal-flow single-wafer reactor with rotating susceptor.

are vented to the atmosphere.

CVD-systems usually contain the following subsystems: **a)** gas-sources; **b)** gas feed-lines; **c)** mass-flow controllers (for metering the gases into the system); **d)** a reaction-chamber (or reactor); **e)** a method for heating the wafers onto which the film is to be deposited (and in some types of systems, for adding additional-energy by other means); and **f)** temperature sensors. LPCVD and PECVD systems also contain pumps for establishing the reduced-pressure and for exhausting gases from the chamber. Vacuum considerations and mass-flow-controllers (MFCs) are covered in Chap. 6. In this section gas-sources and heating-techniques in CVD-reactors are covered. CVD reactor-configurations are discussed in later sections.

16.2.2 Gas Sources & Delivery Systems for CVD

Gas-handling systems are used to supply and deliver the reactant-gases to the CVD-reactor, and these are

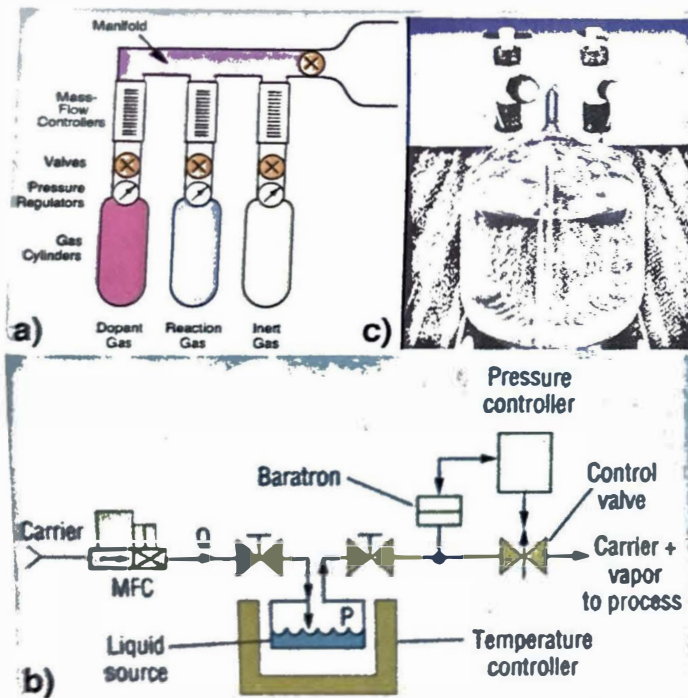


Fig. 16-6 (a) Gas-source manifold. (b) Bubbler-system for vapor-flow control. A mass-flow controller (MFC) delivers a carrier-gas into a temperature-controlled container holding the liquid-source, where the gas becomes saturated with the reactant-vapor.⁶ (c) Photograph of a bubbler vapor-source. Courtesy of Schumacher.

discussed in detail in Chap. 5. Premixing of the gases must be done upon (or just before) entry into the reaction-chamber, in the reactor *supply manifold* (a *manifold* is defined as a chamber having multiple apertures for making connections) so that they arrive at the chamber well-mixed (Fig. 16-6a). That is, laminar-flow conditions generally prevail in the chamber and this will suppress further mixing. Attention must be paid to fluid-flow considerations at the gas-inlet to the reaction-chamber to minimize turbulence.

In CVD both gaseous and liquid sources are available. For example, both silane SiH_4 (a gas) and tetraethoxysilane TEOS (a liquid) are reactants used in CVD- SiO_2 . The gaseous forms of the CVD reactants have been widely-used since the outset of the IC industry, but they are being replaced by liquid sources. Gaseous-precursors can be metered directly into the process chamber with a mass-flow controller. However, liquid-sources are preferred for a number of reasons. First, many of the gases used in CVD are hazardous-materials, posing one or more of the following dangers: being toxic, pyrophoric, or corrosive (see Chap. 29). Such hazardous compounds are inherently safer if they are liquids at room-temperature than if they are in gaseous form. That is, the vapor-pressure of the liquid is much lower than that of the gas, and hence the danger of inhaling a lethal-dose in case of a leak is smaller for liquids. In addition, liquid-spills are limited to a defined area, and in most cases there is no plume of toxic-gas. (An exception involves chlorinated liquids. These can react with water in the air to form a hazardous plume of HCl .) Besides safety considerations, many liquid-sources produce CVD-films with better characteristics, as will be discussed later.

However, if the source of the reactant-gas at the elevated process temperatures is a liquid at room-temperature, it must be vaporized before being delivered to the reaction-chamber. The lower a material's vapor-pressure, the more difficult it is to deliver it to the reactor. This, perhaps more than any other factor, determines which of the seemingly-endless number of possible organic-compounds are suitable for IC production use. Delivery of the vapors of a liquid-source

is usually done by one of several methods, including: 1) *bubblers*; 2) heated source-containers; and 3) *direct-liquid-injection* systems.

A common technique for delivering material from a liquid source to the CVD-chamber is with a *bubbler*. Here, a carrier-gas (e.g., N_2 , H_2 , or Ar) is metered through a mass-flow controller, and this gas is bubbled through the liquid to sweep the liquid-source molecules into the reaction-chamber (Fig. 16-6b). The carrier-gas becomes saturated with the reactant-vapor at the temperature of the liquid in the carefully-temperature-controlled bubbler. A control-loop on the downstream-side of the bubbler controls exhaust-pressure and vapor-flow into the reactor.

The main disadvantage of a bubbler is that the flow of the precursor-species is only indirectly controlled via the control of the carrier-gas flow. This can represent a significant control problem if the precursor has a steep vapor-pressure curve. For example, the vapor-pressure of TEOS will fluctuate by 32% if the bubbler-temperature fluctuates from 60 to 62°C. Bubblers also have problems in delivering materials with very-low vapor-pressures. These tend to condense between the source and the chamber. To avoid this problem the lines from the bubbler to the reaction-chamber must be heated to prevent deposition on the walls of the tubing by condensation.

Several alternatives to conventional bubbler-technology are available, including the two listed above. In the first, the source is heated and the vapor is drawn off and controlled directly by a vapor mass-flow controller. It also requires heated gas-supply-lines. Such *direct-vapor-pressure systems* are capable of delivering materials with vapor-pressures from 1-torr up to atmospheric-pressure.

The second alternative-delivery method is *direct-liquid-injection* (Fig. 16-7). In this method, the liquid remains at room-temperature until it is pumped into the vaporizer. There it is vaporized and then injected into the process-chamber. This feature is needed when the precursors are temperature-sensitive or when they decompose after long periods of heating (such as Cu [I][hfac], a liquid-source used in the CVD of Cu).

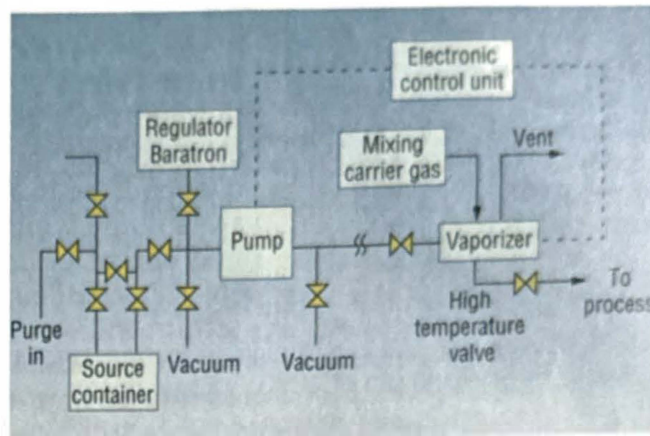


Fig. 16-7 Direct-liquid-injection (DLI) precursor delivery system.⁶

Such alternative-delivery systems offer the promise of being cleaner, cost-effective, and more reliable than bubbler-systems.

16.2.3 Heating-Sources for CVD Reaction-Chambers

In essentially all CVD-processes, films are deposited at temperatures significantly higher than room-temperature. The walls of the reaction-chamber are maintained at T_W . The wafers rest on a holder maintained at temperature T_S . In some cases $T_W = T_S$, and these are called *hot-wall-CVD-reactors*. In others $T_W < T_S$, and these are termed *cold-wall-CVD reactors*. Note that just because the temperatures of the walls of cold-wall reactors are lower than that of the wafers, they may still be significantly hotter than room-temperature. In fact, in some cold-wall systems, significant chamber-wall-heating can still take place. To limit reactions or depositions from occurring there, provisions for cooling the walls must be implemented (e.g., by water-cooling). The temperature of the gas as it enters the reaction-chamber is assumed to be equal to T_W . There are a number of methods used to raise the temperature to that required by the process, as described here.

In the first, coils of resistive-elements are wrapped around the outside of the reactor-tube. Since the hot-coils heat the entire volume they surround, the reactor-walls (as well as the wafers) have the same

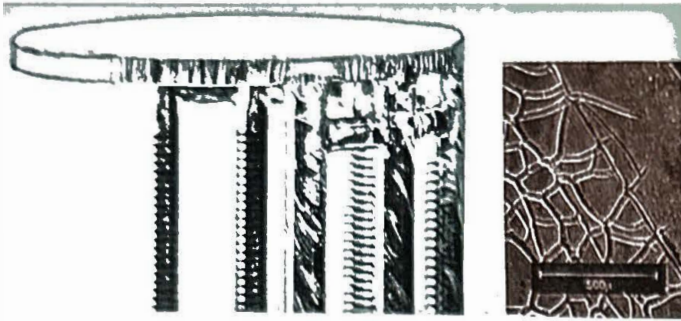


Fig. 16-8 Polysilicon film build-up and cracking on the wafer holder of a vertical LPCVD polysilicon-reactor.

temperature ($T_W = T_S$), making this a *hot-wall system*. Since the CVD-processes that are run in such systems are typically surface-reaction-rate-limited, the temperature must be uniform throughout the chamber and tightly-controlled. Control of better than 5°C at 1000°C can be achieved with such coil-resistive-heating methods.

Resistive-heating can also be used to heat *only the wafer holder* by providing electrical-contacts to elements in the heater-block beneath the wafer-holder to external power-supplies. Since heat is transferred directly to the wafer-holder, it and the wafers are hotter than the reactor-walls, making this a *cold-wall configuration* ($T_W < T_S$).

Heating can also be performed *inductively* or with *high-intensity-radiation lamps*. Both of these methods primarily heat only the wafers and the wafer-susceptor, again resulting in cold-wall reactor configurations. Inductive-heating of a conductive-susceptor (such as graphite), is done by wrapping cooled rf-coils outside and around the chamber. The rf-power coupled from these coils induces eddy-currents in the susceptor, which cause its temperature to increase. The non-conductive (e.g., fused-silica) chamber-walls are not heated by the rf-field, and they remain substantially cooler than the susceptor. For the lamp-heated case, chamber-walls are made of materials that are largely transparent to light. Thus, they are not heated as much as the opaque wafers and susceptor, which absorb more of the incident-light-energy.

Hot-wall and cold-wall reactor-configurations both have advantages and disadvantages. In hot-wall

reactors $T_W = T_S$. Since the reaction is driven, CVD film-forming-reactions (and hence deposition) can take place on their chamber walls and wafer-holders (as well as on the wafer-surfaces). While many films grown in hot-wall reactors are dense, adherent deposits, after a number of wafers are processed, these deposits on the walls can become thick enough to begin flaking-off. To prevent contamination from such sources, hot-wall systems require periodic cleaning. Figure 16-8 shows polysilicon build-up and cracking on a wafer-holder of a vertical hot-wall LPCVD polysilicon-reactor.

In cold-wall reactors, less-deposition occurs on the reactor-walls, since their temperature is lower than that of the susceptor and wafers. However, some material is still deposited on the cooler walls, and it is often more porous and less adherent. Thus, particle detachment can still be a problem and cleaning must still be employed. Some single-wafer reactors use an *in-situ* cleaning-process after each film-deposition step to keep the film-buildup on the walls to a minimum, and to provide the same chamber-surface conditions for each wafer.

16.2.4 The Terminology of CVD-Reactor-Design

The design and operation of CVD-reactors depends on a variety of factors, and hence they can be categorized in several ways. Figure 16-9 illustrates one way of grouping CVD reactor types. The first distinction between reactor types (i.e., *hot-wall* versus *cold-wall* reactors), has already been indicated. The next criterion used to distinguish reactor-types is their pressure-

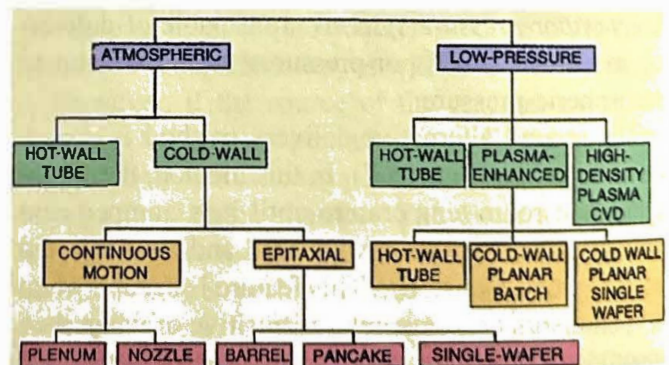


Fig. 16-9 Chart of CVD-reactor types.

Table 16-1. CHARACTERISTICS and APPLICATIONS OF CVD-REACTORS

PROCESS	ADVANTAGES	DISADVANTAGES	APPLICATIONS
APCVD	Simple Reactor, Fast Deposition, Low Temperature	Poor Step Coverage, Particle Contamination	Low Temperature Oxides, both doped and undoped; Epi films
LPCVD	Excellent Purity and Uniformity, Conformal Step Coverage, Large Wafer Capacity	High Temperature Low Deposition Rate Source Depletion	High Temperature Oxides, both doped & undoped, Silicon Nit- ride, Poly-Si, W, WSi ₂
PECVD	Low Temperature, Fast Deposition, Good Step Coverage	Chemical (e.g., H ₂) and Particulate Contam- ination	Low Temperature Insulators over Metals, Passiva- tion (Nitrides)

regime of operation (i.e., *atmospheric-pressure* versus *reduced-pressure* reactors). Finally, the reduced pressure group is split into: (a) low-pressure reactors (the so-called *low-pressure-CVD*, or *LPCVD*-reactors), in which the energy-input is entirely thermal; and (b) those in which energy is partially supplied by a plasma as well as by thermal-energy. The latter are known as *plasma-enhanced-CVD*, or *PECVD*-reactors. Newer high-density-plasma (HDP) reactors for CVD are also now available (see Chap. 22). Each of the reactor-types in the two pressure-regimes are further divided into sub-groups, defined by reactor-configuration and method of heating (see Fig. 16-9).

Reactor-geometry is constrained by the pressure-regime and energy-source used, and is an important factor in wafer-throughput. Since atmospheric-pressure-reactors by and large operate in the mass-transport-limited regime, they must be designed so that an equal flux of reactants is delivered to each wafer, and to all locations of the wafer. As a result, wafers in APCVD reactors are never stacked at close spacing, but are laid flat on a horizontal-surface. An undesirable consequence of this design is that the growing films on the wafer-surfaces can incorporate particles that fall upon them. LPCVD hot-wall-reactors are not constrained by the mass-transfer-rate limitation,

allowing designs that accommodate a larger number of wafers per run. That is, wafers can be stacked side-by-side, only a few-mm apart in a quartz reaction-tube. Quartz wafer-holders (boats) can hold up to 200-wafers. Since LPCVD-reactors operate in the surface-reaction-rate-limited mode, they must, however, be capable of precise temperature-control. Table 16-1 summarizes the characteristics and applications of the various CVD reactor-designs.

16.2.5 Atmospheric-Pressure (APCVD) Reactors

Atmospheric-pressure-CVD reactors (APCVD) were the first CVD-reactors to be used by the microelectronics industry. Their early applications included CVD-oxide and epitaxial film-deposition, and they are still used for these purposes. Operation at atmospheric-pressures keeps reactor-design simple and allows high film-deposition-rates. APCVD, however, is susceptible to gas-phase reactions, and silane-chemistry-based SiO₂-films deposited by APCVD exhibit poor step-coverage. Since APCVD-processes are also generally conducted in the mass-transport-limited regime, the reactant-flux to all parts of every substrate in the reactor must be well controlled. This places constraints on reactor-geometry and gas-flow patterns. Although APCVD-processes for deposition

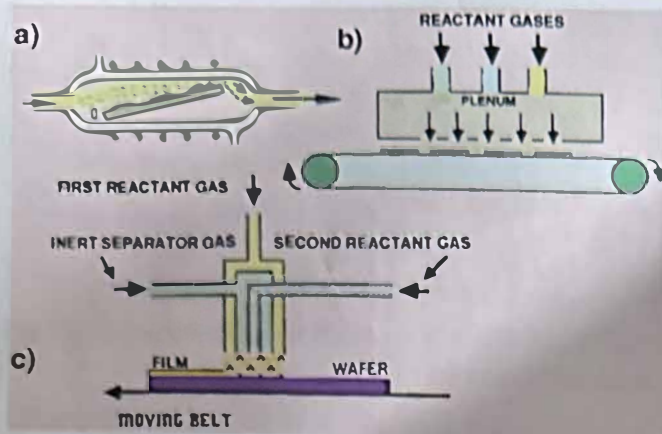


Fig. 16-10 (a) Horizontal-tube APCVD-reactor. (b) Plenum-type continuous-processing APCVD-reactor (c) Gas-injector type continuous-processing APCVD-reactor.

of nitrides and polysilicon were also developed, they were replaced by LPCVD-processes (see below).

Figure 16-10 shows schematics of three types of atmospheric-CVD systems. The first is the *horizontal-tube* (Fig. 16-10a). Such systems have a horizontal quartz-tube, with the wafers lying flat on a fixed horizontal plate, while gas in the main-flow region moves parallel to the wafer-surface. Reactant-gases are metered into one end of the tube, and unused (or by-product) gases are exhausted through the other. Energy is supplied by radiant-heating from

resistance-heated coils that surround the tube (hot-wall), or inductive-coils that heat only the susceptor (cold-wall). It is possible to deposit a variety of films in these systems, but since they suffer from low-throughput, poor-uniformity and particulate-contamination, such systems find little use in VLSI and ULSI fabrication today.

The second type is the *continuous-processing APCVD-reactor* (Figs. 16-10b and 16-10c). This configuration was widely-used design for depositing low-temperature CVD-SiO₂-films in production applications in the 1980's. Continuous-processing APCVD-reactors move the wafers at constant-speed through a heated reaction-chamber, either on a moving-plate or a continuous conveyor-belt. The deposition-region is carefully isolated from outside air by curtains of flowing inert-gas. In the continuous-reactor, the reaction-chamber is at steady-state, with reactant-gases and wafers being continuously introduced and removed from the reaction-area. Reactant-gases in earlier systems were mixed in a *plenum* (i.e., from the Latin word *full*), which is a confined-volume filled with flowing process-gases at a positive pressure (slightly greater than atmospheric-pressure). But this approach causes excessive particulate-formation from gas-phase nucleation.

In a third type of APCVD-reactor (sold by Watkins-

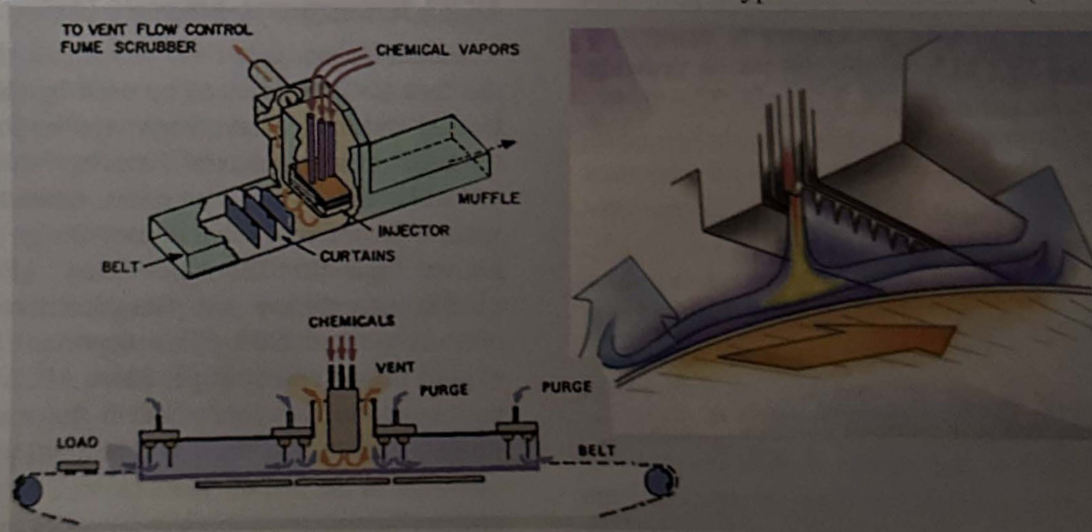


Fig. 16-11 Schematic of a conveyORIZED APCVD reactor with gas injection.

ic-acid [P_2O_5] crystallites occurs, which can then lead to the formation of insoluble BPO_4 -crystallites during the reflow-process). Such precipitation degrades the film properties since the acid-particles (though soluble) leave pits in the glass that are decorated later, and they leave local areas of low dopant-concentration that affect the flow-performance of the glass. The BPO_4 -particles also remain behind as defects.

16.5 PROPERTIES AND CHEMICAL-VAPOR-DEPOSITION OF SILICON-NITRIDE

Silicon-nitride (SiN) films are amorphous, insulating-materials that find many applications in ULSI-fabrication, including: **1)** as a final-passivation and mechanical-protective-layer for ICs (especially for parts encapsulated in plastic-packages); **2)** as a mask for the selective-oxidation of silicon; **3)** as one of the dielectric-materials in the stacked oxide-nitride-oxide (ONO) layers in DRAM-capacitors; **4)** as sidewall-spacers in MOSFETs (where they are used to form lightly-doped-drain structures [LDD], and also serve as sidewall-passivation-structures during salicide-processes); **5)** as a CMP-stop layer in shallow-trench-isolation processes (see Chap. 4); and **6)** as an etch-stop layer in Damascene-structures (see Chap. 24).

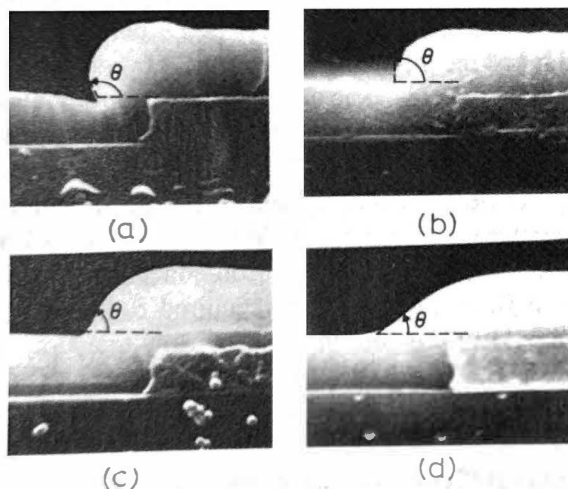


Fig. 16-33 SEM cross-sections (10,000X) of samples annealed in steam at 1100°C for 20-min for the following weight of phosphorus: (a) 0.0 wt.% P; (b) 2.2 wt.% P; (c) 4.6 wt.% P; and (d) 7.2 wt.% P.¹⁴ Reprinted by permission of the publisher, the Electrochemical Society, Inc.

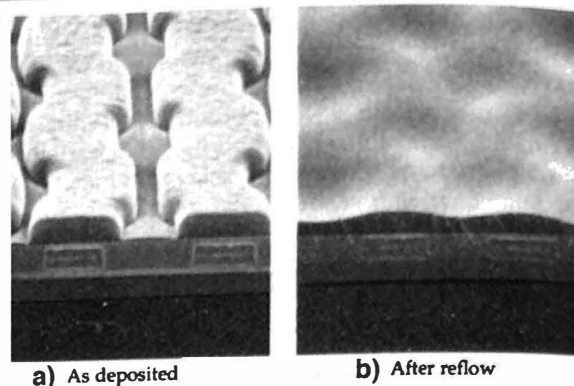
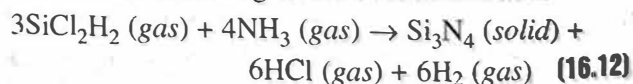


Fig. 16-34 Reflow of a BPSG-film containing 5%-B and 5%-P for 30-min in N_2 : (a) Before reflow; (b) After reflow. Courtesy of Applied Materials

However, since silicon-nitride has a higher-dielectric-constant than SiO_2 (6–9 versus ~ 4.2), it is not used for interlevel-dielectric applications. (It would increase the value of the interlevel-capacitance, which would result in a reduction of the circuit-speed.)

As shown in Table 16-2, two CVD-techniques are used for depositing SiN . When used as a mask for selective-oxidation (or as a dielectric-layer in DRAM-capacitor-structures), SiN is generally-deposited by a medium-temperature (700–800°C) *LPCVD-technique* (for reasons of film-uniformity and lower-processing-cost). When used as a passivation-layer, the deposition-process must be compatible with such low-melting-point metals as aluminum. Thus, a lower-temperature process is needed (200–400°C). For such applications, *PECVD* is the deposition method-of-choice, as it can deposit SiN -films at 200–400°C. However, *PECVD-SiN* is non-stoichiometric and contains substantial-quantities of atomic-H (10–30-atomic %). Thus, it is sometimes chemically-represented as $Si_xN_yH_z$. Table 16-2 also compares the properties of *LPCVD* and *PECVD* silicon-nitride films.

LPCVD-silicon-nitride is most commonly deposited by reacting dichlorosilane ($SiCl_2H_2$) and ammonia (NH_3) at temperatures between 700–800°C in a hot-wall reactor according to the overall-reaction:



Silicon-nitride depositions by *LPCVD* are controlled

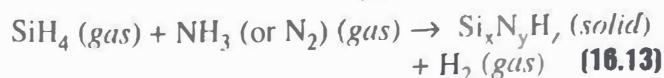
by a large-number of deposition-parameters including: temperature, total-pressure, reactant-ratios, and temperature-gradients in the reactor. A temperature-ramp along the tube-length is required for obtaining uniform-depositions (as is discussed in the section on hot-wall tube-LPCVD-reactors, Sect 16.2.6).

In general, LPCVD-SiN-films have high-density ($2.9\text{--}3.1\text{-g/cm}^3$), a dielectric-constant of 6, and a hydrogen-content (up to 8-at%) that is lower than in PECVD-SiN-films. In addition, they exhibit excellent step-coverage and relatively-low particulate-contamination. Such films, however, have high-tensile-stresses ($\sim 1 \times 10^{10}$ dynes/cm², about an order-of-magnitude higher than TEOS-deposited-SiO₂). This can cause cracking in LPCVD-SiN-films thicker than 200-nm.

Silicon-nitride-deposition by PECVD was first described in 1965, and SiN-films were the first-materials to be deposited by the PECVD-technique on a large-production-scale. The overall PECVD-deposi-

tion-reaction is written as:

(200-400°C, rf)



where silane and ammonia (or nitrogen) are reacted in a plasma at 200-400°C.

Hydrogen in PECVD-SiN can reach 18-22-at% in films deposited near 300°C. The presence of large quantities of hydrogen is harmful to IC-devices. It leads to significant threshold-voltage shifts, and the film-etching-characteristics (both wet and dry) are impacted. Processing-techniques that reduce H-concentration-levels in PECVD-SiN have been pursued.

Table 16-3 is a summary of the CVD-reactions for polysilicon, SiO₂, PSG, BPSG, and silicon-nitride.

16.6 SILICON-OXYNITRIDES DEPOSITED BY CVD

Materials can be prepared with characteristics between those of nitrides and oxides, and these are called *silicon-oxynitrides* [$\text{SiO}_x\text{N}_y(\text{H}_z)$]. Such films are less-permeable to moisture and other contaminants than deposited-oxides. They are formed by reacting SiH₄ with N₂O and NH₃, usually by PECVD. Properties can be tailored for improved-thermal-stability, low-stress, and crack-resistance. For example, the composition and properties of the SiO_xN_y-films can be varied smoothly by changing the flow-rates of the three-reactants.

16.7 CVD OF METALS, SILICIDES, AND NITRIDES FOR ULSI-APPLICATIONS

CVD has also been pursued as a deposition-technology for a number of metals used as ULSI-interconnects, including tungsten, aluminum, titanium, and copper. Of this group, only CVD of tungsten has found wide-acceptance as a production-process. CVD of the other metals has not been able to displace PVD (sputtering) as the main deposition-technology. Here we describe the deposition by CVD of tungsten and titanium-nitride. CVD of CU is covered in Chap. 24.

16.7.1 CVD of Tungsten (W)

Refractory-metals (i.e., W, Ti, Mo, and Ta) have been investigated for various applications in the intercon-

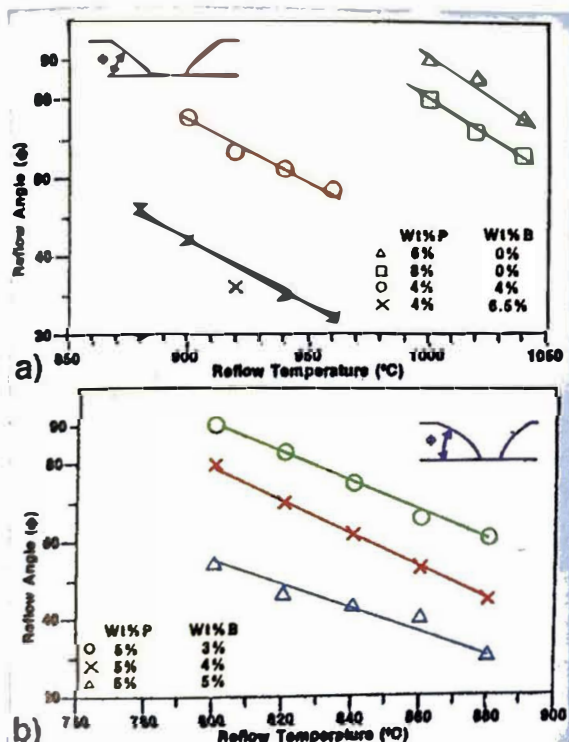


Fig. 16-35 (a) Reflow-angle vs. reflow-temperatures in a nitrogen-ambient (30 min). (b) Reflow-angle versus reflow-temperatures in a steam-ambient (30 min). Reprinted by permission of Solid State Technology.¹⁵

TABLE 16-2 PROPERTIES OF HIGH-TEMPERATURE-CVD-SILICON-NITRIDE AND PECVD-SILICON-NITRIDE

Property	HT-CVD—NP 900°C	PE-CVD—LP 300°C
Composition	Si ₃ N ₄	Si ₃ N ₂ H ₂
Si/N ratio	0.75	0.8–1.0
Density	2.8–3.1 g/cm ³	2.5–2.8 g/cm ³
Refractive index	2.0–2.1	2.0–2.1
Dielectric constant	6–7	6–9
Dielectric strength	1 × 10 ⁷ V/cm	6 × 10 ⁶ V/cm
Bulk resistivity	10 ¹⁵ –10 ¹⁷ ohms/cm	10 ¹⁵ ohms/cm
Surface resistivity	> 10 ¹³ ohms/square	1 × 10 ¹³ ohms/square
Stress at 23°C on Si	1.2–1.8 × 10 ¹⁰ dyn/cm ² (tensile)	1–8 × 10 ⁹ dyn/cm ² (compressive)
Thermal expansion	4 × 10 ⁻⁶ /°C	> 4 < 7 × 10 ⁻⁶ /°C
Color, transmitted	None	Yellow
Step coverage	Fair	Conformal
H ₂ O permeability	Zero	Low–none
Thermal stability	Excellent	Variable > 400°C
Solution etch rate		
HFB 20–25°C	10–15 Å/min	200–300 Å/min
49% HF 23°C	80 Å/min	1500–3000 Å/min
85% H ₃ PO ₄ 155°C	15 Å/min	100–200 Å/min
85% H ₃ PO ₄ 180°C	120 Å/min	600–1000 Å/min
Plasma etch rate		
70% CF ₄ /30% O ₂ , 150 W, 100°C	200 Å/min	500 Å/min
Na ⁺ penetration	< 100 Å	< 100 Å
Na ⁺ retained in top 100 Å	> 99%	> 99%
IR absorption		
Si–N max	~ 870 cm ⁻¹	~ 830 cm ⁻¹
Si–H minor	—	2180 cm ⁻¹

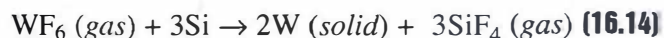
nect-systems of silicon-ICs. Their resistivities are higher than those of Al and its alloys, but lower than those of the refractory-metal-silicides and nitrides. Of these metals, tungsten (W) has adopted for several interconnect-applications,¹⁶ the most important being that of a *plug* (i.e., a material that can completely-fill vias between aluminum-films, as well as contact-holes). It is used as a plug-material because CVD-W provides superior via-filling-capabilities than does PVD-aluminum. PVD-films cannot completely-fill contact-holes and vias. A method to *completely-fill* the contact-holes was therefore sought. CVD-W was able to do this. Blanket-W-CVD deposition-and-etch-back-processes are used for W-plug-applications.

CVD-tungsten exhibits high-thermal-stability (having the highest-melting-point of all metals - 3410°C), excellent conformal-step-coverage, and its

thermal-expansion-coefficient closely matches that of silicon. In addition, it has excellent electromigration and corrosion-resistance. Some of its disadvantages include: **a)** its resistivity, although 200-times lower than that of heavily-doped-polysilicon, is still about twice as high as that of Al-alloy-films; **b)** W-films adhere poorly to oxides and nitrides; and **c)** oxides form on W-films when temperatures exceed 400°C (and thus care must be exercised to prevent oxidation, especially during subsequent dielectric-deposition).

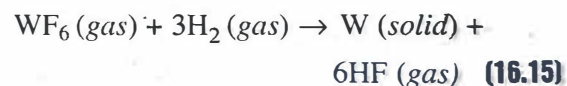
16.7.2 The Chemistry of CVD-Tungsten

The chemical-vapor-deposition of tungsten is generally performed in cold-wall, low-pressure systems (an example is shown in Fig. 16-36). Although tungsten can be deposited either from WF₆ or WCl₆, tungsten-hexafluoride (WF₆) is better suited as the W-source gas, since it is a liquid that boils below room-temperature (17°C). On the other hand, WCl₆ is a solid that melts at 275°C. The low boiling-point makes WF₆ much easier to meter into process-chambers in a reproducible way. The main-drawback of WF₆ is its high-cost. Three reactions are used in CVD-W, namely reduction of WF₆ by: 1) silicon; 2) hydrogen; and 3) silane (since it can be reduced by all of these materials). The *silicon-reduction reaction* is given by:



This reaction is normally produced by allowing the WF₆-gas to react with regions of exposed solid-silicon on a wafer-surface at a temperature of about 300°C. The reaction is self-limiting when the film reaches a thickness of 10–15-nm, since the W-film serves as a diffusion-barrier between the Si and WF₆ once this thickness is reached. No deposit occurs on wafer-regions covered with SiO₂ during this reaction.

The *hydrogen-reduction-reaction* is given by:



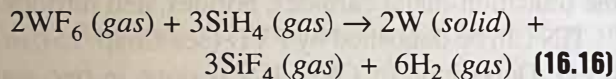
The process is carried out at reduced-pressures, usually at temperatures below 450°C. The resistivity of W-films deposited by hydrogen-reduction is in the 7–12-μΩ-cm range. Because W does not adhere-well

Table 16-3 CVD DEPOSITION REACTIONS

PRODUCT	REACTANTS	METHOD	TEMP (°C)	COMMENTS
Polysilicon	SiH ₄	LPCVD	580–650	may be <i>in situ</i> doped
Silicon Nitride	SiH ₄ + NH ₃	LPCVD	700–900	
	SiCl ₂ H ₂ + NH ₃	LPCVD	650–750	
	SiH ₄ + NH ₃	PECVD	200–350	
	SiH ₄ + N ₂	PECVD	200–350	
Silicon Dioxide (SiO ₂)	SiH ₄ + O ₂	APCVD	300–500	poor step coverage
	SiH ₄ + O ₂	PECVD	200–350	good step coverage
	SiH ₄ + N ₂ O	PECVD	200–350	
	Si(OC ₂ H ₅) ₄ (TEOS)	LPCVD	650–750	liquid source, conformal
	SiCl ₂ H ₂ + N ₂ O	LPCVD	850–900	conformal
Doped SiO ₂	SiH ₄ + O ₂ + PH ₃	APCVD	300–500	PSG
	SiH ₄ + O ₂ + PH ₃	PECVD	300–500	PSG
	SiH ₄ + O ₂ + PH ₃ + B ₂ H ₆	APCVD	300–500	BPSG, low temperature flow
	SiH ₄ + O ₂ + PH ₃ + B ₂ H ₆	PECVD	300–500	BPSG, low temperature flow

to SiO₂, an adhesion-layer is first deposited onto the SiO₂, and the W is then deposited onto it.

The overall *silane-reduction-reaction* is given by:



This reaction (LPCVD at ~300°C) is used to produce a W-nucleation-layer for the hydrogen-reaction. Better-nucleation is consistently obtained with the silane-reduction on most surfaces, including TiN.

As noted earlier, CVD of tungsten is performed in cold-wall, low-pressure-CVD (LPCVD) reactors. The wafers are held on a heated-chuck opposite a showerhead through which a premixed-flow of WF₆ and one of the reducing-agent-gases (H₂, or SiH₄) is injected. Hot-wall systems are not used because W would deposit on the quartz furnace-tube-walls. Since W doesn't adhere to SiO₂, such films would soon-delaminate from the walls and create particles. Frequent-cleaning would be necessary to keep this problem under control. Furthermore, once the fused-silica furnace-walls are coated with W they become opaque. IR-radiation from the heating-coils would no

longer be transmitted as efficiently through the walls as when the fused-silica was transparent.

16.7.3 Blanket CVD-W and Etchback

Tungsten can be deposited by CVD using either a selective or blanket-process. Only blanket W-deposition has emerged as a production-proven process (Fig. 16-37). Blanket-CVD-W-and-etchback (or CMP) has found widespread-use for contact-hole and via-filling applications in IC-technologies below about 1-μm. Both applications require adherent, low-cost-films. The plug-applications, however, call for high step-coverage and thickness-uniformity, but can tolerate higher-resistivity than is needed for W-films used as interconnects. For filling contact-holes, this W-plug-formation process has six steps (Fig. 16-38):

1. An *in-situ* surface-pre-clean is performed;
2. A contact-forming layer is deposited (usually a Ti-film formed by sputtering or CVD);
3. An adhesion/barrier-layer is deposited (typically a TiN-film formed by sputtering or CVD);
4. A blanket-CVD W-film is formed (typically with two-step CVD-process);