Chapter 7

Polysilicon and Dielectric Film Deposition

Professor Paul K. Chu

Thin Films in Microelectronics

- Polycrystalline silicon or polysilicon
- Doped or undoped silicon dioxide
- Stoichiometric or plasma-deposited silicon nitride

Polysilicon

- Gate electrode material in MOS devices
- Conducting materials for multilevel metallization
- Contact materials for devices with shallow junctions

Polysilicon can be undoped or doped with elements such as As, P, or B to reduce the resistivity. The dopant can be incorporated in-situ during deposition, or later by diffusion or ion implantation. Polysilicon consisting of several percent oxygen is a semi-insulating material for circuit passivation.

Dielectric Thin Films

- Insulation between conducting layers
- Diffusion and ion implantation masks
- Diffusion sources (doped oxide)
- Capping doped films to prevent dopant loss
- Gettering impurities
- Passivation to protect devices from impurities, moisture, and scratches

- Phosphorus-doped silicon dioxide, commonly referred to as P-glass or phosphosilicate glass (PSG), is especially useful as a passivation layer because it inhibits the diffusion of impurities (such as Na), and it softens and flows at 950^{o}C to 1100^{o}C to create a smooth topography that is beneficial for depositing metals
- Borophosphosilicate glass (BPSG), formed by incorporating both boron and phosphorus into the glass, flows at even lower temperatures between 850^{o}C and 950^{o}C
- The smaller phosphorus content in BPSG reduces the severity of aluminum corrosion in the presence of moisture

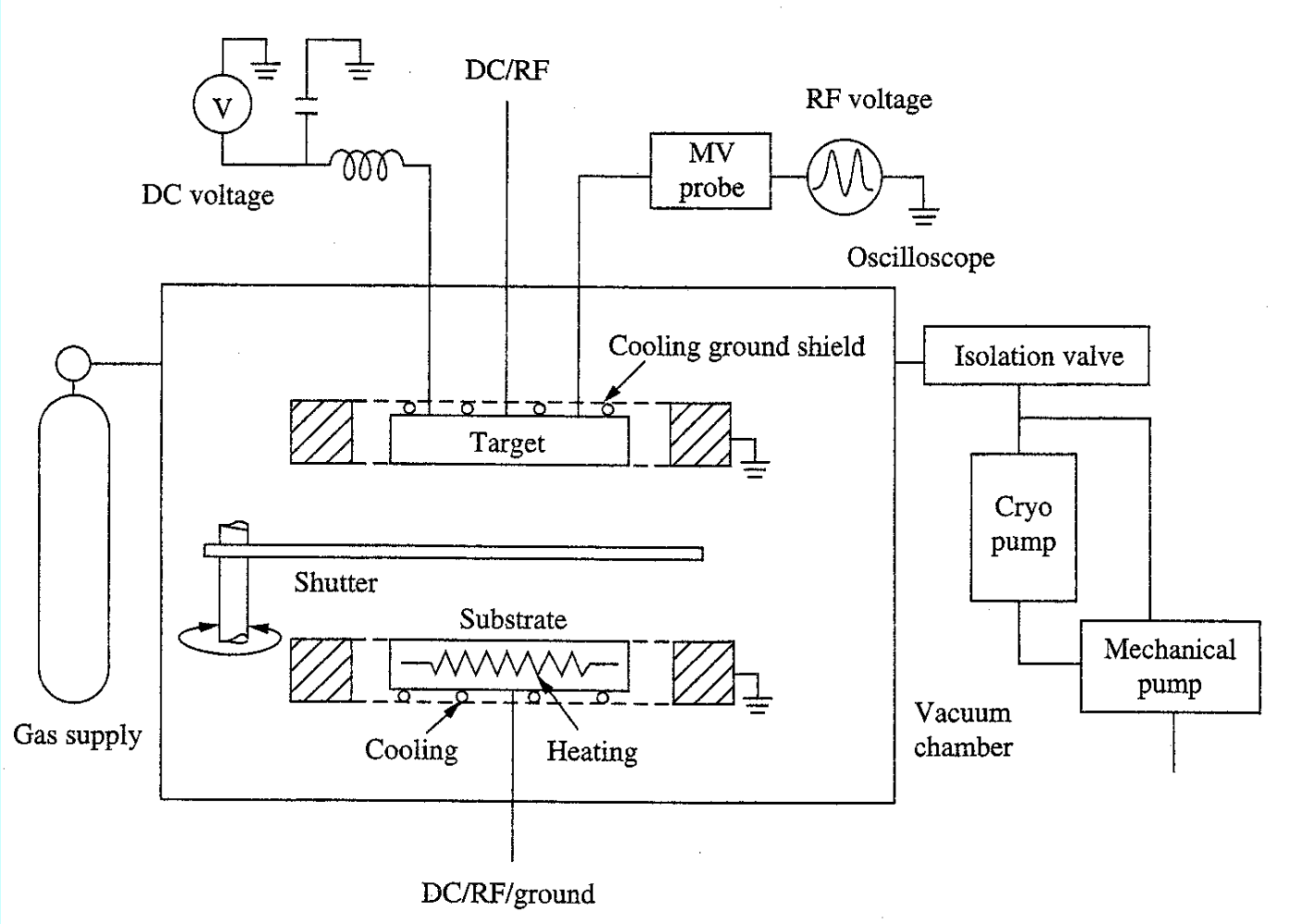
- Silicon nitride is a barrier to sodium diffusion, is nearly impervious to moisture, and has a low oxidation rate
- The local oxidation of silicon (LOCOS) process also uses silicon nitride as a mask
- The patterned silicon nitride will prevent the underlying silicon from oxidation but leave the exposed silicon to be oxidized
- Silicon nitride is also used as the dielectric for DRAM MOS capacitors when it combines with silicon dioxide

Physical Vapor Deposition (PVD)

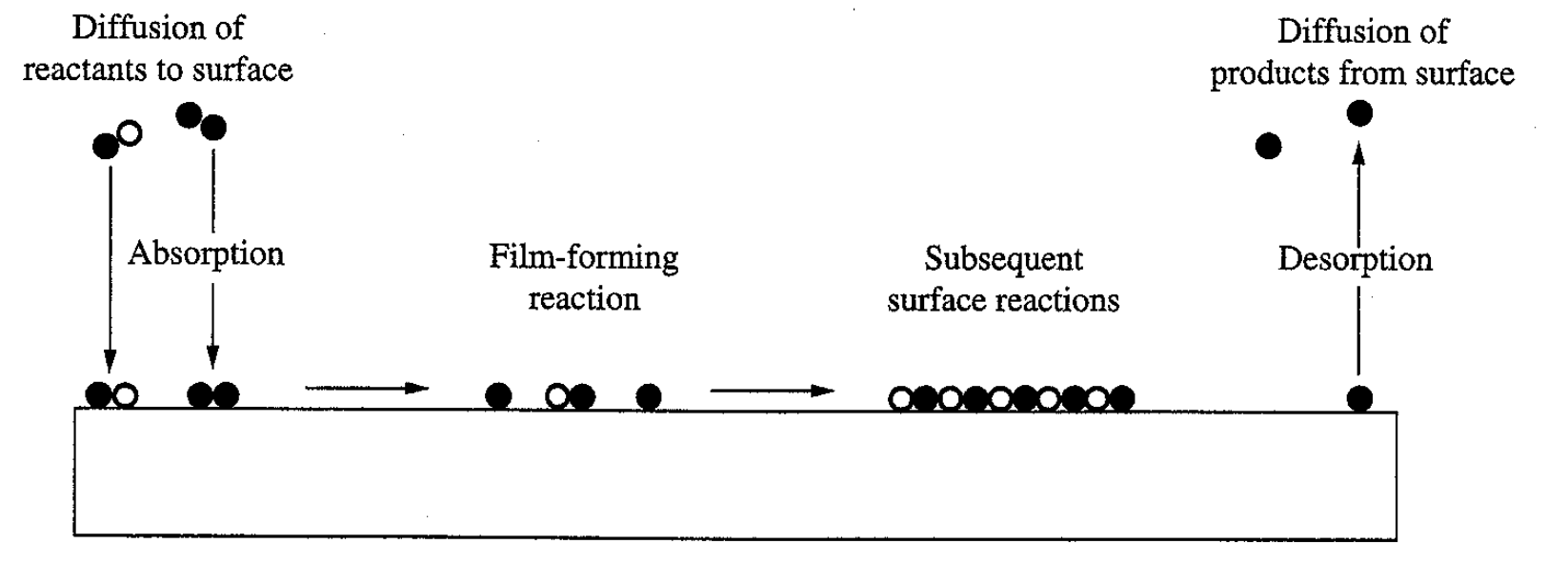
- **Evaporation**: A vapor is first generated by evaporating a source material in a vacuum chamber and then transported from the source to the substrate and condensed to a solid film on the substrate surface.

- **Sputtering**: The process involves the ejection of surface atoms from an electrode surface by momentum transfer from the bombarding ions to the electrode surface atoms. The generated vapor of electrode material is then deposited on the substrate. Sputtering processes, unlike evaporation, are very well controlled and generally applicable to all materials such as metals, insulators, semiconductors, and alloys.

Typical Sputtering System

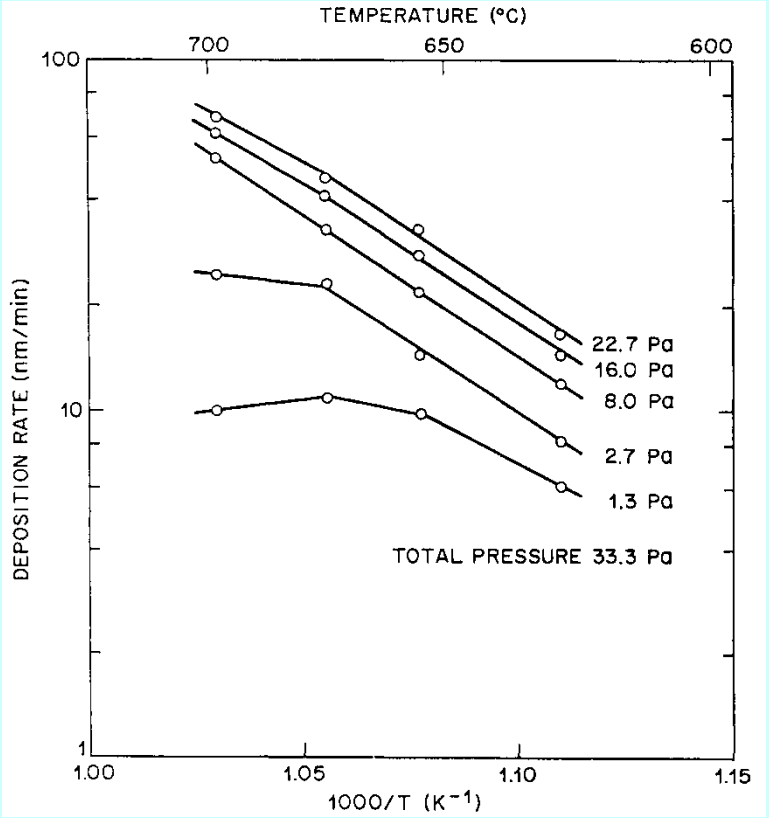


Chemical Vapor Deposition (CVD)



- Atmospheric-pressure chemical vapor deposition (**APCVD**)
- Low-pressure chemical vapor deposition (**LPCVD**)
- Plasma-enhanced chemical vapor deposition (**PECVD**)

- Since the steps in a CVD process are sequential, the one that occurs at the slowest rate will determine the deposition rate and the rate-determining steps can be grouped into gas-phase and surface processes
- Gas-phase processes dictate the rate at which gases impinge on the surface and since such transport processes occur by gas-phase diffusion proportional to the diffusivity of the gas and the concentration gradient across the boundary layer, they are only weakly influenced by the deposition temperature
- The surface reaction rate is greatly affected by the deposition temperature. At low temperature, the surface reaction rate is reduced so much that the arrival rate of reactants can exceed the rate at which they are consumed by the surface reaction process. Under such conditions, the deposition rate is surface-reaction-rate-limited, and at high temperature, it is usually mass-transport-limited.



Arrhenius Equation

$$R = A \exp\{-qE_a / kT\}$$

where R is the deposition rate, A is the frequency factor, q is the electronic charge, E_a is the activation energy, k is the Boltzmann's constant, and T is the absolute temperature

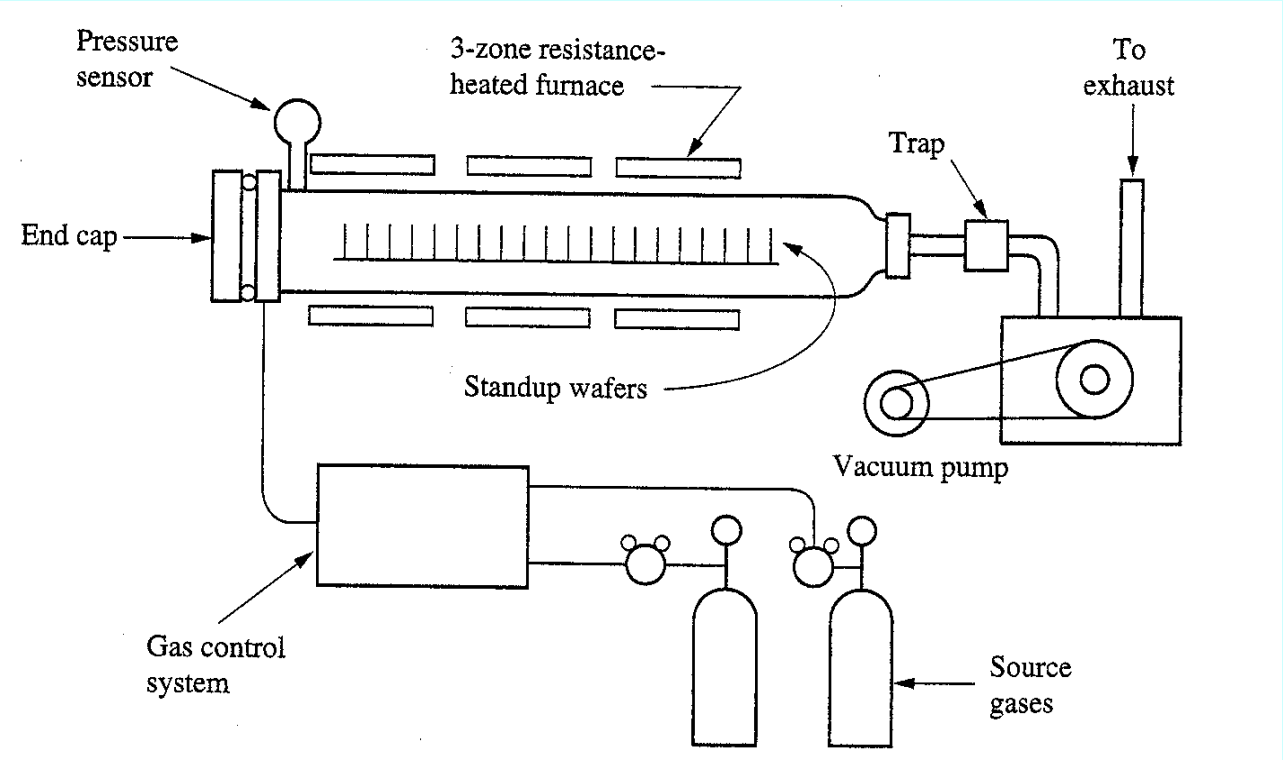
The activation energy calculated from the slope of the straight-line plots is roughly 1.7 eV.

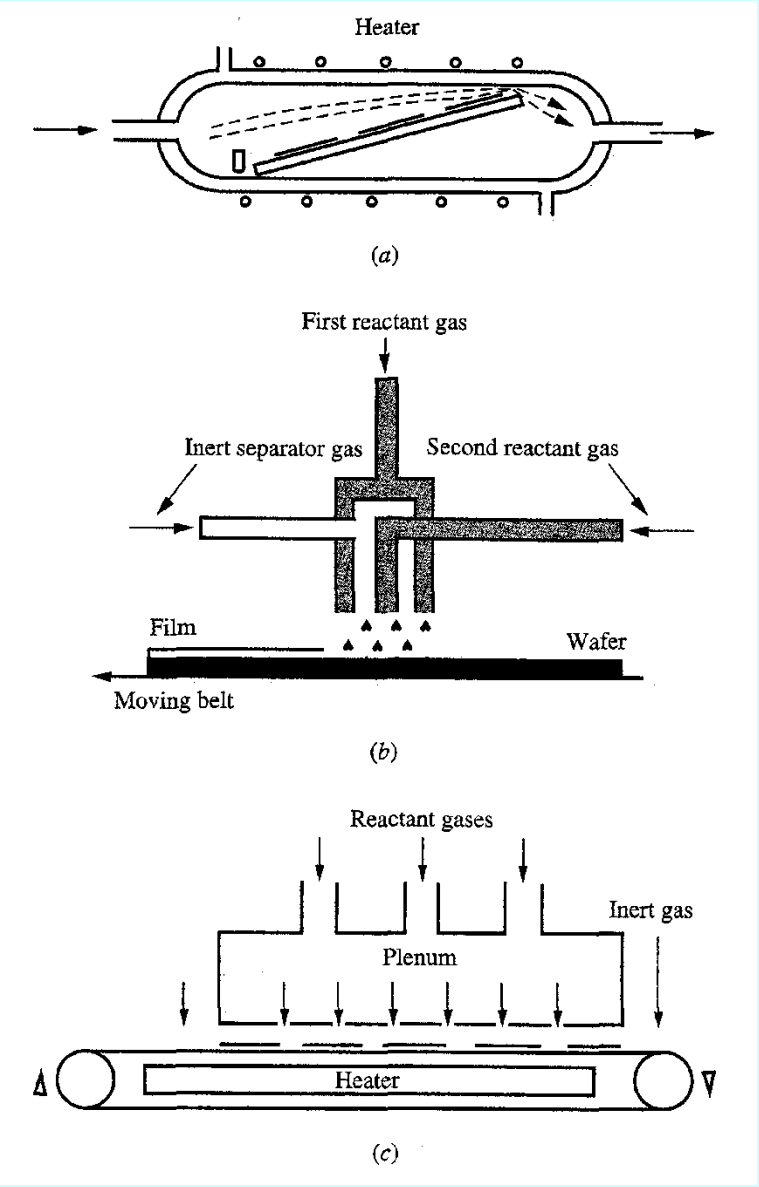
At high temperature, the reaction becomes faster than the rate at which unreacted silane arrives at the surface. The reaction in this temperature regime is mass-transport limited, as exemplified by the high temperature (or small 1/*T*) data. The linear portion of the lines show the surface-reaction limited conditions, that is, the rate of reaction is slower than the rate of reactant arrival.

Characteristics and Applications of CVD Processes

Process	Advantages	Disadvantages	Applications
APCVD (low T)	Simple reactor, fast deposition, low temperature	Poor step coverage, particle contamination, low throughput	Doped/undoped low T oxides
LPCVD	Excellent purity & uniformity, conformal step coverage, large wafer capacity, high throughput	High temperature, low deposition rate	Doped/undoped high T oxides, silicon nitride, polysilicon, tungsten, WSi_2
PECVD	Low temperature, fast deposition, good step coverage	Chemical (e.g. H_2) and particle contamination	Passivation (nitride), low T insulators over metals

Simple Commercial Hot-Wall, Low-Pressure Reactor for High Wafer Capacity Deposition of Polysilicon

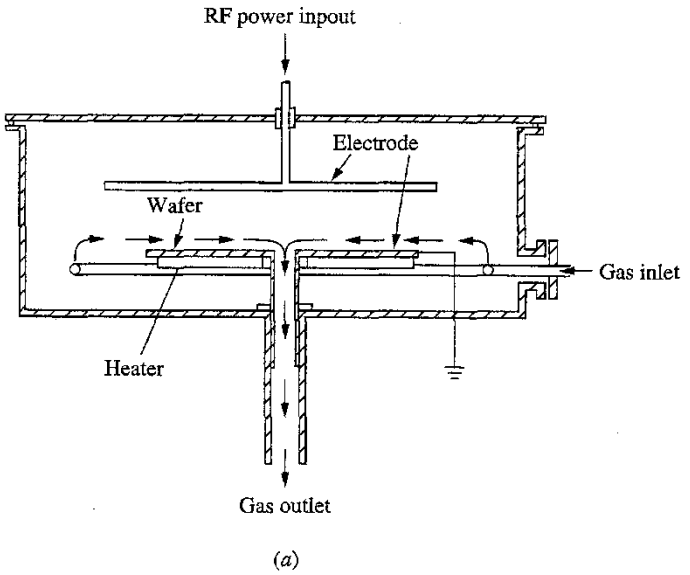




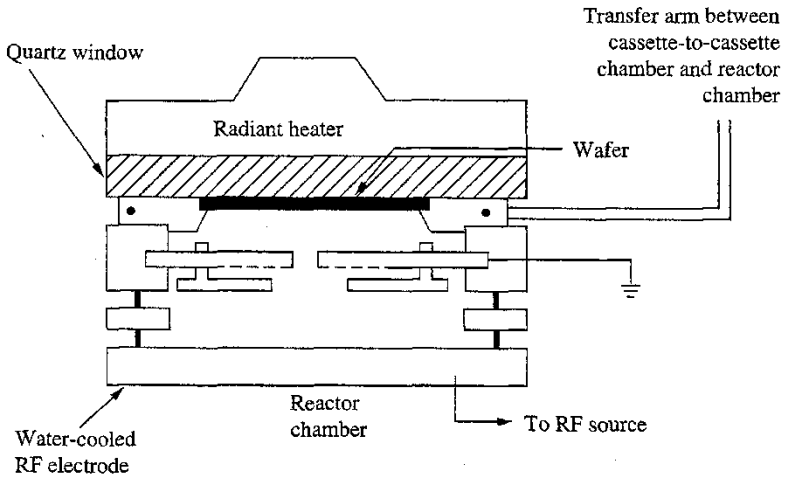
Horizontal Tube APCVD Reactor

Gas Injection-Type Continuous-Processing APCVD Reactor

Plenum-Type Continuous-Processing APCVD Reactor



(a)

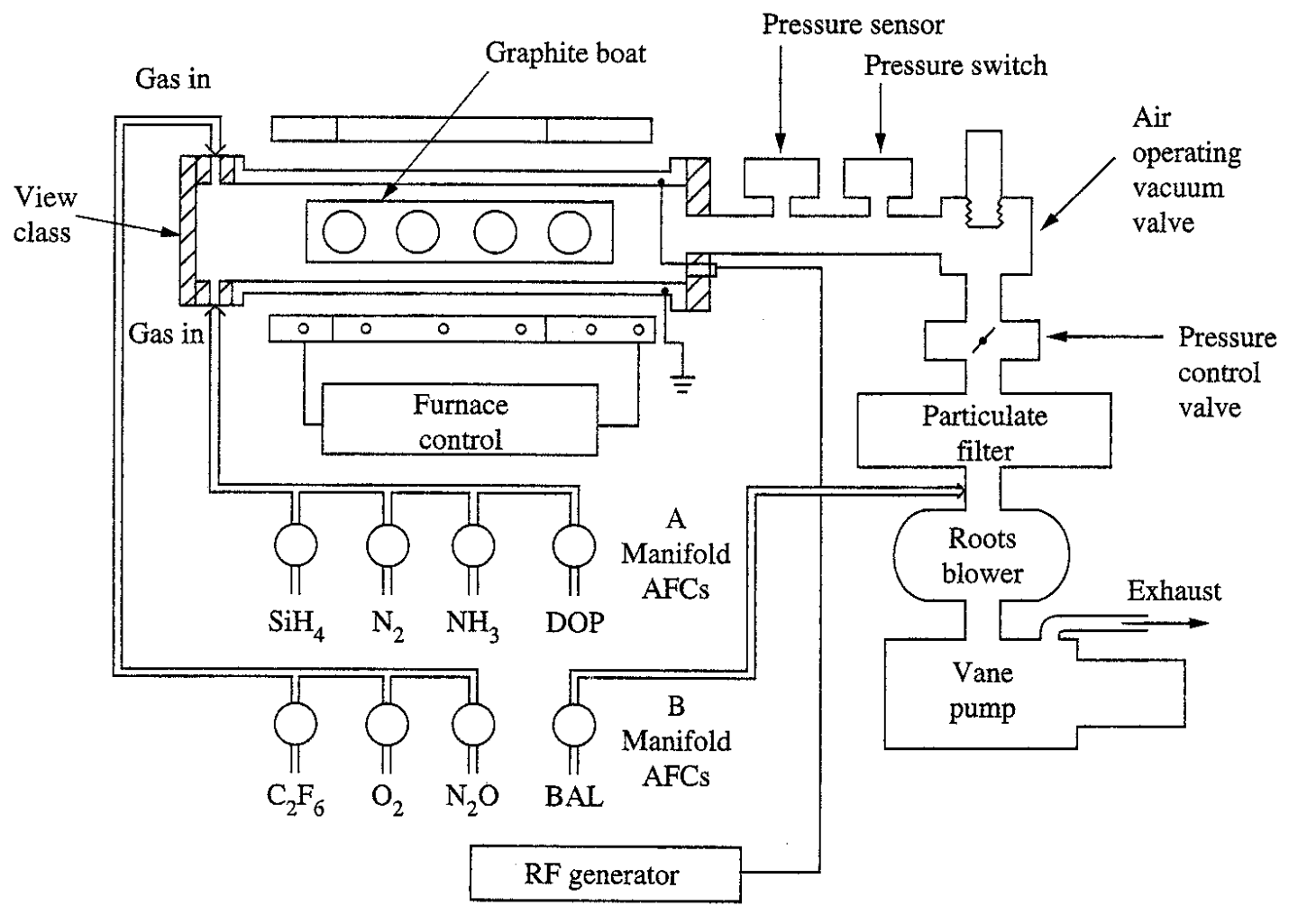


(b)

Parallel Plate PECVD Reactor

Single Wafer PECVD Reactor

Typical Commercial PECVD System



Common Gases Used in CVD

Gas	Formula	Hazards	Flammable Exposure Limits in Air (vol %)	Toxic Limit (ppm)
Ammonia	NH_3	Toxic, corrosive	16-25	25
Argon	Ar	Inert	--	--
Arsine	AsH_3	Toxic	--	0.05
Diborane	B_2H_6	Toxic, flammable	1-98	0.1
Dichlorosilane	SiH_2Cl_2	Toxic, flammable	4-99	5
Hydrogen	H_2	Flammable	4-74	--
Hydrogen chloride	HCl	Toxic, corrosive	--	--
Nitrogen	N_2	Inert	--	--
Nitrogen Oxide	N_2O	Oxidizer	--	--
Oxygen	O_2	Oxidizer	--	--
Phosphine	PH_3	Toxic, flammable	Pyrophoric	0.3
Silane	SiH_4	Toxic, flammable	Pyrophoric	0.5

Polysilicon Deposition

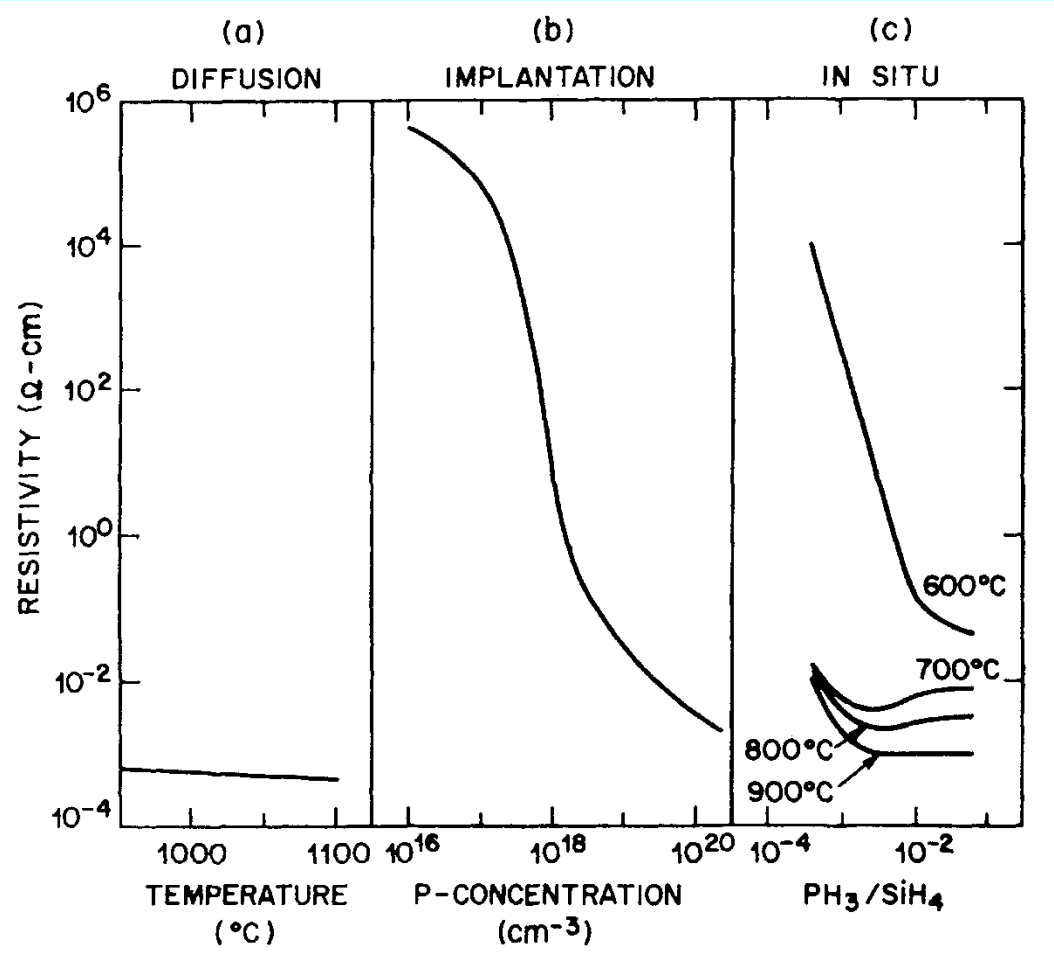
Polysilicon is deposited by pyrolyzing silane between 575°C and 650°C in a low-pressure reaction:

$$SiH_4\ (g) \rightarrow\ Si\ (s) + 2H_2\ (gas)$$

Either pure silane or 20 to 30% silane in nitrogen is bled into the LPCVD system at a pressure of 0.2 to 1.0 torr. The properties of the LPCVD polysilicon films are determined by the deposition pressure, silane concentration, deposition temperature, and dopant content.

Polysilicon can be doped by adding phosphine, arsine, or diborane to the reactants (in-situ doping). Adding diborane causes a large increase in the deposition rate because diborane forms borane radicals, BH_3, that catalyze gas-phase reactions and increase the deposition rate. In contrast, adding phosphine or arsine causes a rapid reduction in the deposition rate, because phosphine or arsine is strongly adsorbed on the silicon substrate surface thereby inhibiting the dissociative chemisorption of SiH_4.

The dopant concentration in diffused polysilicon often exceeds the solid solubility limit, with the excess dopant atoms segregated at the grain boundaries.



The high resistivity observed for lightly implanted polysilicon is caused by carrier traps at the grain boundaries. Once these traps are saturated with dopants, the resistivity decreases rapidly and approaches that for implanted single-crystal silicon.

Silicon Dioxide Deposition

Silicon dioxide films can be deposited at lower than 500°C by reacting silane, dopant (phosphorus in this example), and oxygen under reduced pressure or atmospheric pressure

$$SiH_4\,(g) + O_2\,(g) \rightarrow SiO_2\,(s) + 2H_2\,(g)$$

$$4PH_3\,(g) + 5O_2\,(g) \rightarrow 2P_2O_5\,(s) + 6H_2\,(g)$$

The process can be conducted in an APCVD or LPCVD chamber. The main advantage of silane-oxygen reactions is the low deposition temperature allowing films to be deposited over aluminum metallization. The primary disadvantages are poor step coverage and high particle contamination caused by loosely adhering deposits on the reactor walls.

Silicon dioxide can be deposited at 650°C to 750°C in an LPCVD reactor by pyrolyzing tetraethoxysilane, $Si(OC_2H_5)_4$. This compound, abbreviated **TEOS**, is vaporized from a liquid source

$$\mathbf{Si(OC_2H_5)_4\ (l) \rightarrow SiO_2\ (s) + by\text{-}products\ (g)}$$

The by-products are organic and organosilicon compounds. LPCVD TEOS is often used to deposit the spacers beside the polysilicon gates. The process offers good uniformity and step coverage, but the high temperature limits its application on aluminum interconnects.

Silicon dioxide can be deposited by LPCVD at about 900^{o}C by reacting dichlorosilane with nitrous oxide

$$\mathbf{SiCl_2H_2\ (g) + 2N_2O\ (g) \rightarrow SiO_2\ (s) + 2N_2\ (g) + 2HCl\ (g)}$$

This deposition technique provides excellent uniformity, and like LPCVD TEOS, it is employed to deposit insulating layers over polysilicon. However, this oxide is frequently contaminated with small amounts of chlorine that may react with polysilicon causing film cracking.

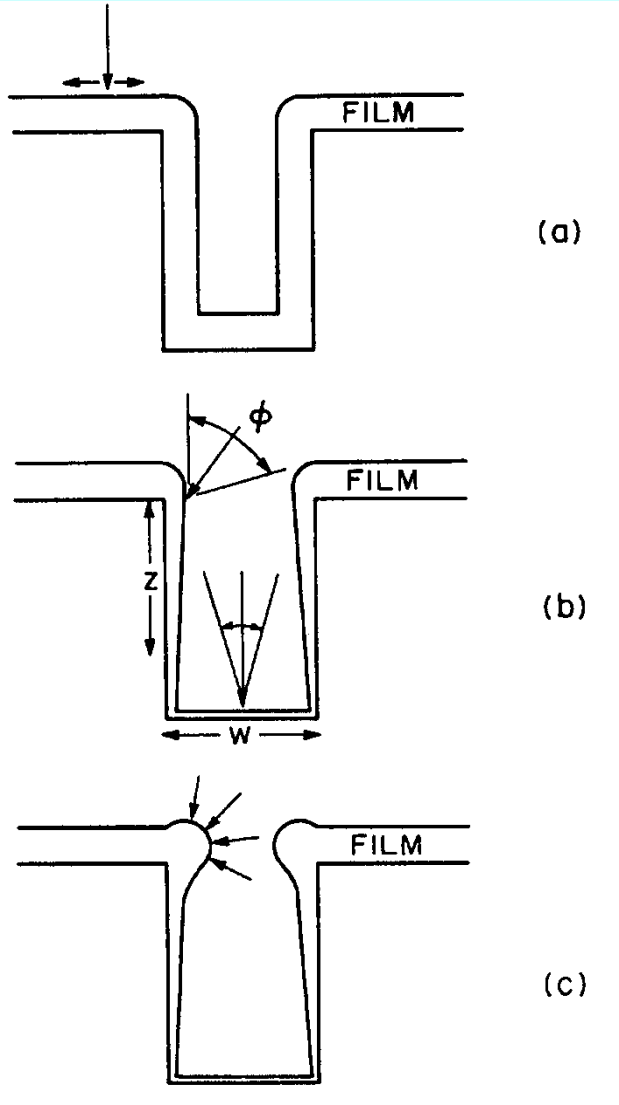
Plasma-assisted CVD requires the control and optimization of the RF power density, frequency, and duty cycle in addition to the conditions similar to those of an LPCVD process such as gas composition, flow rate, deposition temperature, and pressure. Like LPCVD at low temperature, the PECVD process is surface-reaction-limited, and adequate substrate temperature control is necessary to ensure film thickness uniformity.

By reacting silane and oxygen or nitrous oxide in plasma, silicon dioxide films can be formed by the following reactions:

$$\mathbf{SiH_4\,(g) + O_2\,(g) \rightarrow SiO_2\,(s) + 2H_2\,(g)}$$

$$\mathbf{SiH_4\,(g) + 4N_2O\,(g) \rightarrow SiO_2\,(s) + 4N_2\,(g) + 2H_2O\,(g)}$$

Step Coverage



A uniform or conformal step coverage depicted in **(a)** results when reactants or reactive intermediates adsorb and then migrate promptly along the surface before reacting.

When the reactants adsorb and react without significant surface migration, the deposition rate is proportional to the arrival angle of the gas molecules. If the mean free path of the gas is much larger than the dimensions of the step **(b)**, the arrival angle and consequently the film thickness vary. The film is thin along the vertical walls and may have a crack at the bottom of the step caused by self-shadowing.

When there is minimal surface mobility and the mean free path is short, the arrival angle at the top of the step is 270^{o}, thus giving a thicker deposit. The arrival angle at the bottom of the step is only 90^{o}, and so the film is thin **(c)**. The thick cusp at the top of the step and the thin crevice at the bottom combine to give a re-entrant shape that is particularly difficult to cover with metal.

Reflow

- Doped oxides used as diffusion sources contain 5 to 15 weight % of the dopant
- Doped oxides for passivation or interlevel insulation contain 2 to 8 wt. % phosphorus to prevent the diffusion of ionic impurities to the device
- Phosphosilicate glass (PSG) used for the reflow process contains 6 to 8 wt. % phosphorus

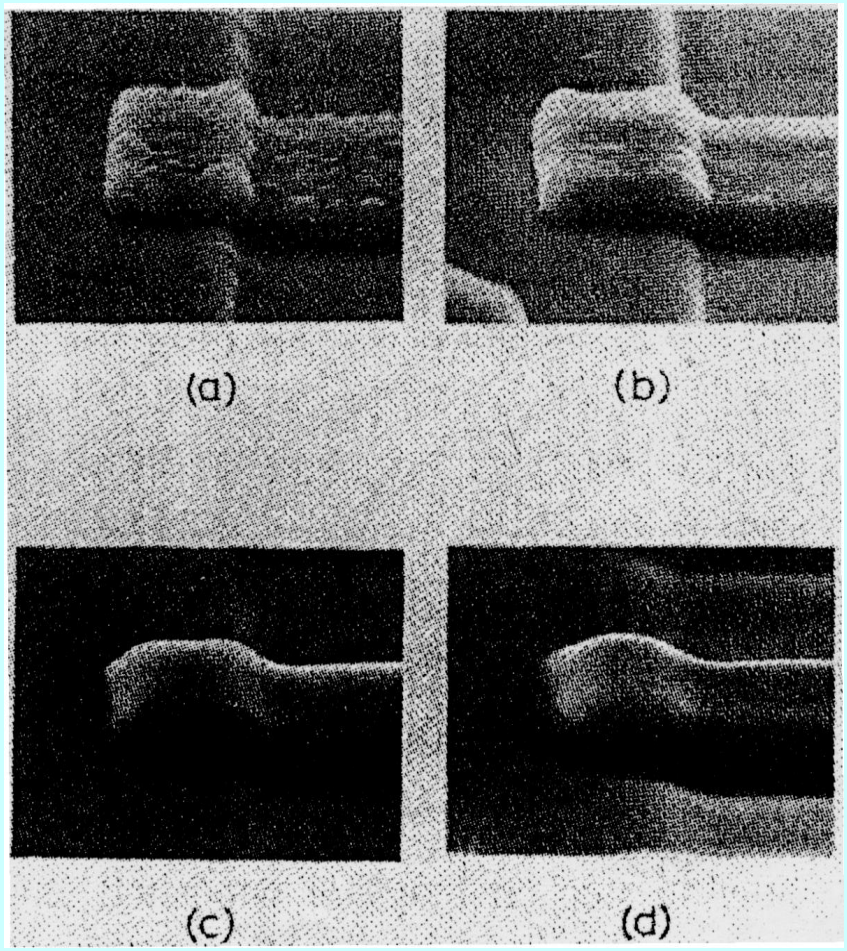
- Oxides with lower phosphorus concentrations will not soften and flow, but higher phosphorus concentrations can give rise to deleterious effects for phosphorus can react with atmospheric moisture to form phosphoric acid which can consequently corrode the aluminum metallization

- Addition of boron to PSG further reduces the reflow temperature without exacerbating this corrosion problem

- Borophosphosilicate glass (BPSG) typically contains 4 to 6 wt. % P and 1 to 4 wt. % B

SEM photographs (3200x) showing surfaces of 4.6 wt. % P-glass annealed for different times in steam at 1100°C

0 minute



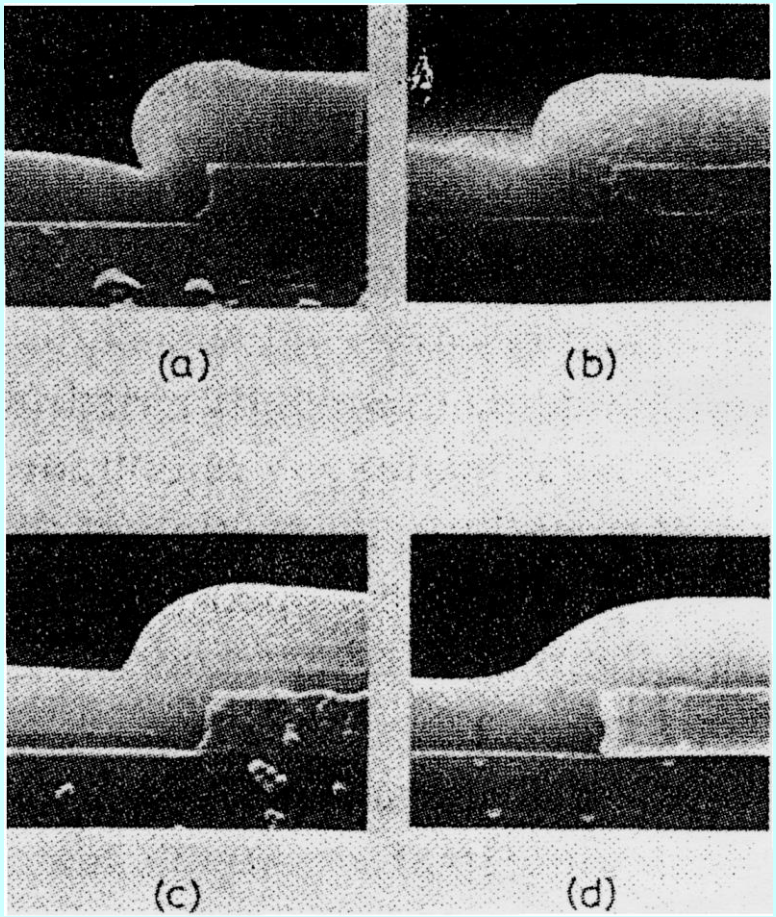
20 minutes

40 minutes

60 minutes

SEM cross sections (10,000x) of samples with different weight percent of phosphorus annealed in steam at 1100°C for 20 minutes

0.0 wt. % P

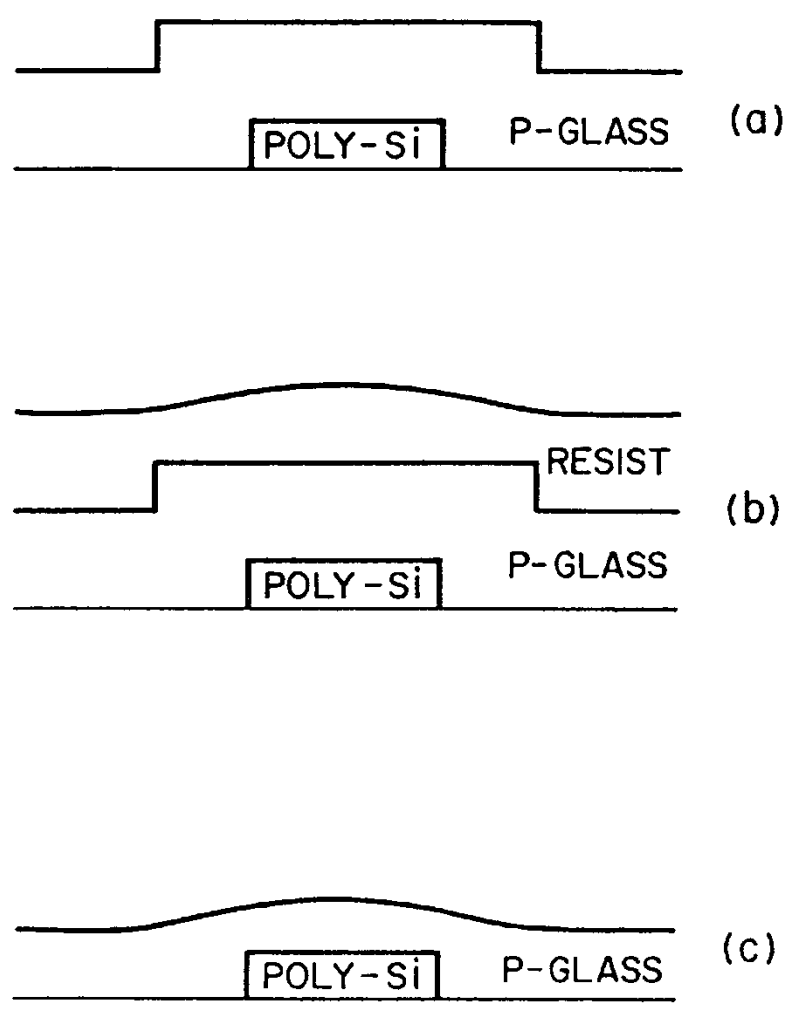


2.2 wt. % P

4.6 wt. % P

7.2 wt. % P

Planarization



The step coverage of deposited oxides can be improved by planarization or etch-back techniques.

Since the organic resist material has a low viscosity, reflow occurs during application or the subsequent bake. The sample is then plasma etched to remove all the organic coating and part of the PSG, as long as the etching conditions are selected to remove the organic material and PSG at equal rates.

Silicon Nitride Deposition

(1) Stoichiometric silicon nitride (Si_3N_4) can be deposited at 700°C to 800°C at atmospheric pressure:

$$\mathbf{3SiH_4\ (g)\ + 4NH_3\ (g) \rightarrow Si_3N_4\ (s) + 12H_2\ (g)}$$

(2) Using LPCVD, silicon nitride can be produced by reacting dichlorosilane and ammonia at temperature between 700°C and 800°C:

$$\mathbf{3SiCl_2H_2\ (g)\ + 4NH_3\ (g) \rightarrow Si_3N_4\ (s) + 6H_2\ (g)}$$

The reduced-pressure technique has the advantage of yielding good uniformity and higher wafer throughput.

Silicon Nitride Plasma Deposition

Hydrogenated silicon nitride films can be deposited by reacting silane and ammonia or nitrogen in plasma at reduced temperature:

$$SiH_4\,(g) + NH_3\,(g) \rightarrow SiN:H\,(s) + 3H_2\,(g)$$

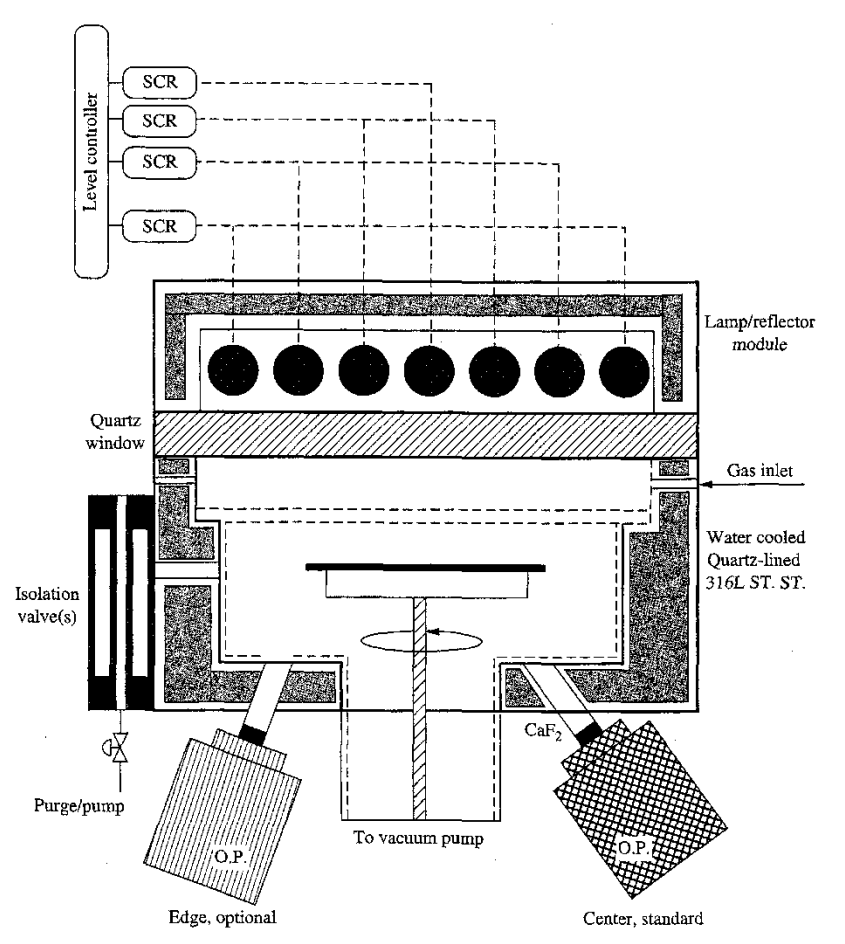
$$SiH_4\,(g) + N_2\,(g) \rightarrow 2SiN:H\,(s) + 3H_2\,(g)$$

Plasma-assisted deposition is conducted at low temperature by reacting the gases in a glow discharge. Two plasma deposited materials, plasma deposited silicon nitride (SiNH) and plasma deposited silicon dioxide, are useful in VLSI. On account of the low deposition temperature, 300^{o}C to 350^{o}C, plasma nitride can be deposited over the final device metallization. Plasma-deposited films contain large amounts of hydrogen (10 to 35 atomic %) bonded to silicon as Si-H, to nitrogen as N-H, and to oxygen as Si-OH and H_2O.

Properties of Silicon Nitride Films

Deposition	LPCVD	Plasma
Temperature (^oC)	700-800	250-350
Composition	Si_3N_4 (H)	SiN_xH_y
Si/N ratio	0.75	0.8-1.2
Atom % H	4-8	20-25
Refractive index	2.01	1.8-2.5
Density (g/cm^3)	2.9-3.1	2.4-2.8
Dielectric constant	6-7	6-9
Resistivity (ohm-cm)	10^{16}	10^6-10^{15}
Dielectric strength (10^6V/cm)	10	5
Energy gap (eV)	5	4-5
Stress (10^9 dyne/cm^2)	10T	2C-5T

Rapid Thermal Chemical Vapor Deposition (RTCVD) System



RTCVD requires higher temperature but shorter time to deposit the same material compared to LPCVD.

Temperature is the switch that turns the RTP deposition process on or off, avoiding the long ramp-up and ramp-down times required in conventional methods.

- To be commercially viable, RTCVD systems must be able to process a single wafer in 1 to 2 minutes, giving a corresponding throughput of 30 to 60 wafers per hour

- For relatively thick deposited films of 100 to 200 nm, this requires deposition rates greater than 100 nm/min

- In comparison, the typical deposition rate in conventional batch LPCVD processes is about 10 nm/min

The RTCVD of SiO_2 by pyrolysis of TEOS is believed to occur by the reaction:

$$\mathbf{Si(OC_2H_5)_4 \rightarrow SiO_2\ (s) + 2H_2O + 4C_2H_4}$$

Below 800^{o}C, the deposition rate is controlled by surface reaction processes with activation energy of 3.3 eV. This large sensitivity to temperature thus demands tight temperature control for thin oxide deposition at low temperature. Above 800^{o}C, the deposition rate of SiO_2 approaches 100 nm/min with a lower activation energy, which meets the throughput and deposition control requirements of the RTCVD system. The high operating temperature makes it infeasible for back end steps in multilevel-metallization technologies that use aluminium.

Thin oxide applications include in-situ deposition of MOS gate structures where Si surface cleaning, gate oxide formation, and polysilicon gate electrode deposition would all occur in a low-pressure, multi-chamber cluster tool. RTCVD yields high-quality films through the use of ultraclean gases in a chamber with a highly regulated ambient, and examples of these reactions are:

$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$$

$$SiH_4 + 2N_2O \rightarrow SiO_2 + 2N_2 + 2H_2O$$

$$3SiH_2Cl_2 + 10NH_3 \rightarrow Si_3N_4 + 6NH_4Cl + 6H_2$$

$$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$$

$$SiH_4 \rightarrow Si + 2H_2$$