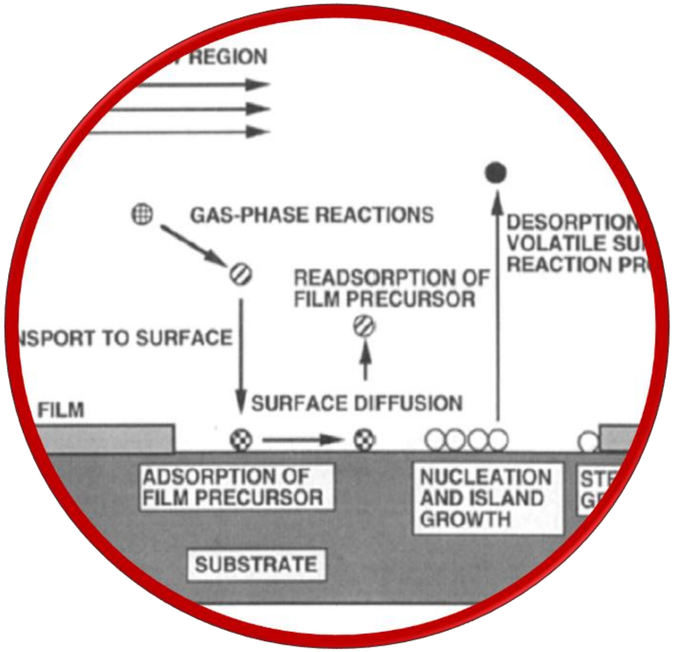
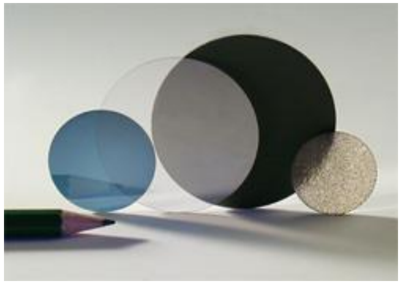
Chemical vapor deposition



application examples

Forming and cutting tools



CVD diamond

Inner coating of
pharmazeutical glassware

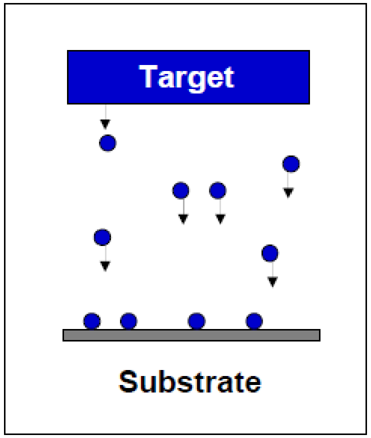
MOCVD of LEDs

http://www.richterprecision.com/services/cvd-coatings/
https://www.schott.com/rd/german/coating/picvd.html?highlighted_text=CVD
https://www.aixtron.com/innovation/technologien/How_MOCVD_works.pdf

content

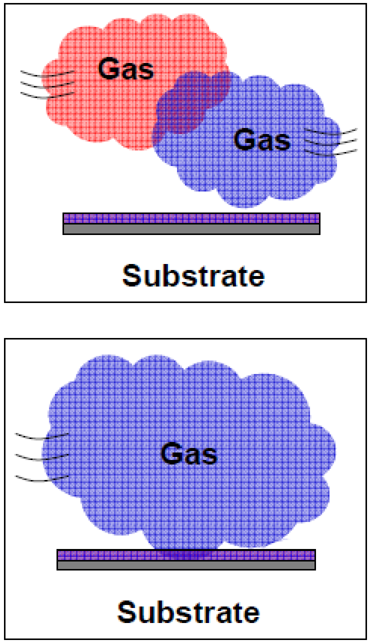
PVD – CVD - ALD

Physical Vapor Deposition (PVD)



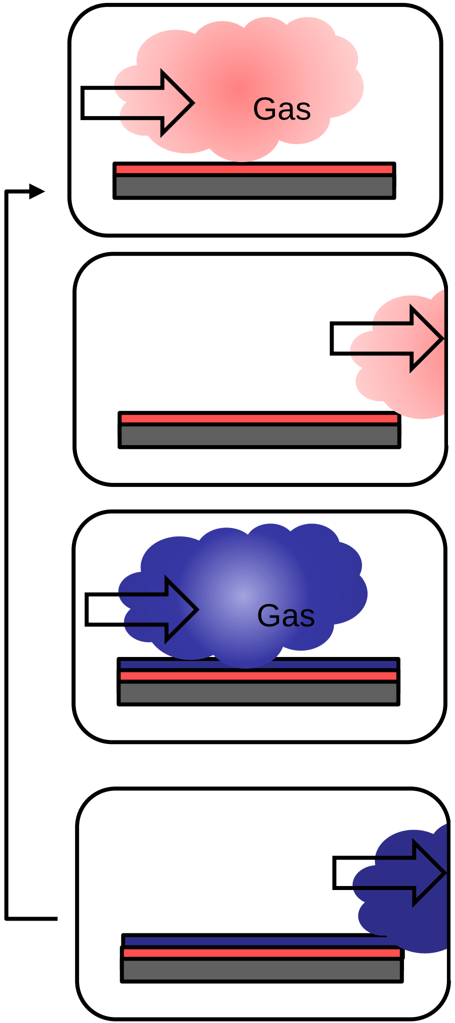
Impingement of atoms or molecular species

Chemical Vapor Deposition (CVD)



Chemical Reaction Promoted by
Heat
UV
Plasma
Electrons/Ions

Atomic Layer Deposition (ALD)



Surface Reactions only

introduction

Chemical vapor deposition (CVD) is the process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomistically on a suitably placed substrate.

It differs from physical vapor deposition (PVD), which relies on material transfer from condensed-phase evaporant or sputter target sources.

An advantage is the affordable cost of the equipment and operating expenses. Because of this, many variants of CVD processing have been researched and developed, including atmospheric pressure (APCVD), low-pressure (LPCVD), plasma-enhanced (PECVD), and laser-enhanced (LECVD) chemical vapor deposition.

CVD processes are extremely complex and involve a series of gas-phase and surface reactions. They are often summarized by overall reaction schemes.

introduction

The fundamental sequential steps that occur in every CVD process are:

1. **Convective and diffusive transport** of reactants from the gas inlets to the reaction zone

2. **Chemical reactions in the gas phase** to produce new reactive species and by-products

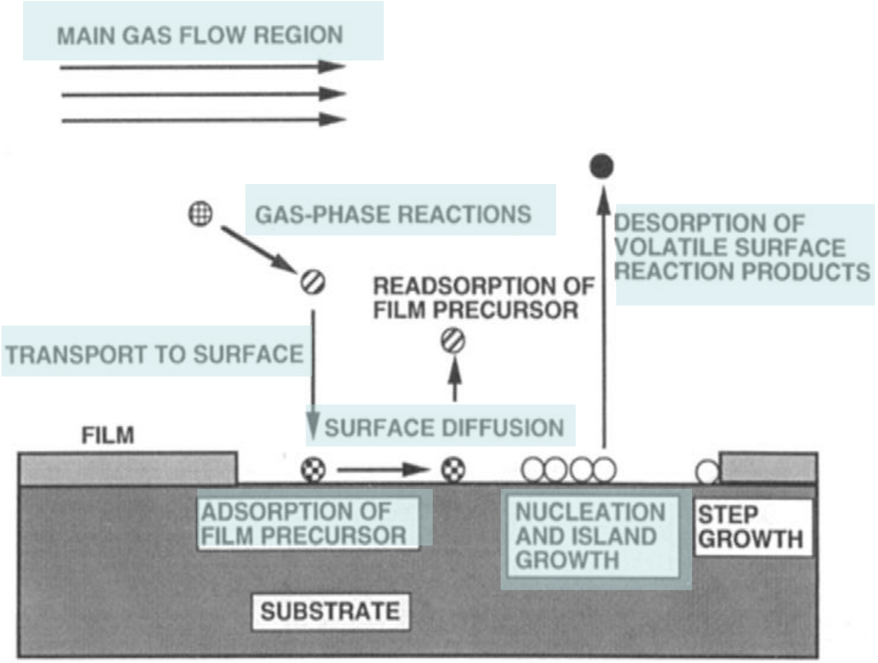
3. **Transport** of the initial reactants and their products **to the substrate surface**

4. **Adsorption** (chemical and physical) **and diffusion** of these species on the substrate surface

5. **Heterogeneous reactions catalyzed by the surface** leading to film nucleation and growth

6. **Desorption** of the **volatile by-products** of surface reactions

7. **Convective and diffusive transport of the reaction by-products away** from the reaction zone



Ohring 2002

introduction

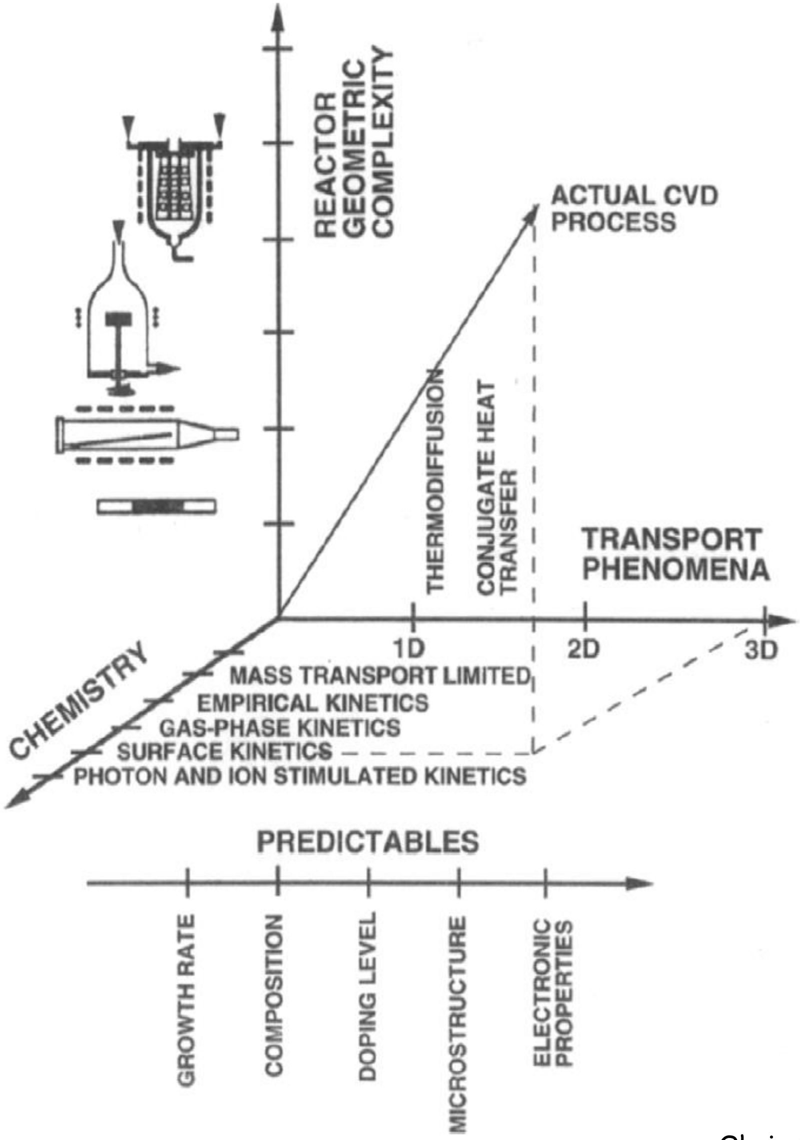
Schematic diagram of the

chemical,

transport, and

geometrical complexities

involved in modeling CVD processes



Ohring 2002

reaction types

General: Gaseous precursor + surface reaction ➔ solid film + gaseous byproducts

Pyrolisis

$$SiH_{4(g)} \rightarrow Si_{(s)} + 2H_{2(g)} \qquad (650^\circ C)$$

$$Ni(CO)_{4(g)} \rightarrow Ni_{(s)} + 4CO_{(g)} \qquad (180^\circ C)$$

Reduction

$$SiCl_{4(g)} + 2H_{2(g)} \rightarrow Si_{(s)} + 4HCl_{(g)} \qquad (1200^\circ C).$$

Oxidation

$$SiH_{4(g)} + O_{2(g)} \rightarrow SiO_{2(s)} + 2H_{2(g)} \qquad (450^\circ C)$$

Compound formation

$$SiCl_{4(g)} + CH_{4(g)} \rightarrow SiC_{(s)} + 4HCl_{(g)} \qquad (1400^\circ C)$$

Disproportionation

$$2GeI_{2(g)} \underset{600^\circ C}{\overset{300^\circ C}{\rightleftharpoons}} Ge_{(s)} + GeI_{4(g)}$$

Reversible transfer

$$As_{4(g)} + As_{2(g)} + 6GaCl_{(g)} + 3H_{2(g)} \overset{750^\circ C}{\rightleftharpoons} 6GaAs_{(s)} + 6HCl_{(g)}.$$

Ohring 2002

Thermal CVD silicon

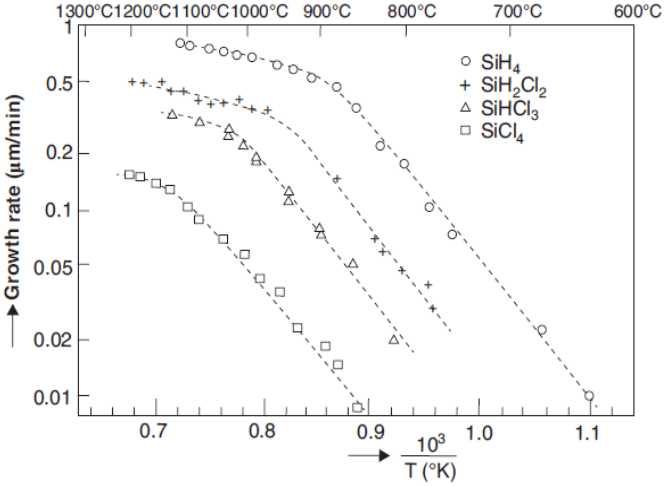
In the early days **single crystal wafers were not pure enough** to allow integrated circuits to be built into them directly. The **CVD silicon films could be grown at very high purity** from carefully purified reactant gases.

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

$$SiCl_4\,(g) + 2H_2 \rightarrow Si\,(s) + 4HCl$$

$$SiH_2Cl_2\,(g) \rightarrow Si\,(s) + 2HCl$$

$$SiHCl_3\,(g) + H_2 \rightarrow Si\,(s) + 3HCl$$

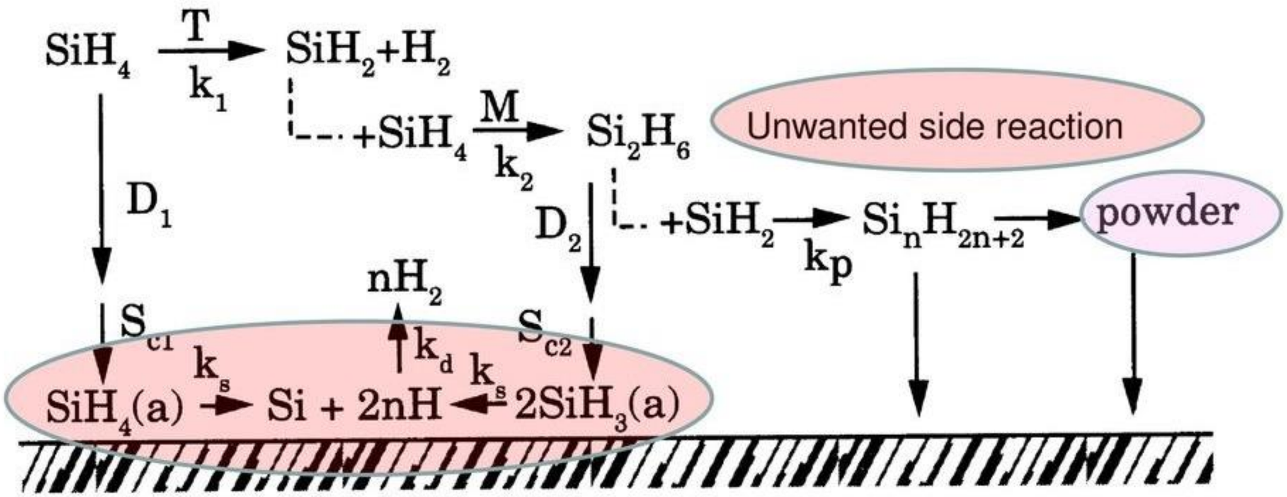


Any of these four reactions can be used to deposit silicon, and the film morphology can be single crystal, polycrystalline or amorphous, depending on the deposition temperature.

As can be seen, the **lowest growth rates at a given temperature** are for the silicon tetrachloride reaction because this molecule is **the most stable of the four silicon precursors**. The **highest growth rates** are seen for **the silane reaction** as this molecule is the **least stable** of the four.

Kääriäinen 2013

Gas-phase and surface reactions : Thermal CVD of Si



Wanted deposition reaction

Source: Smith, Thin film deposition

Thermodynamics – feasibility of reaction

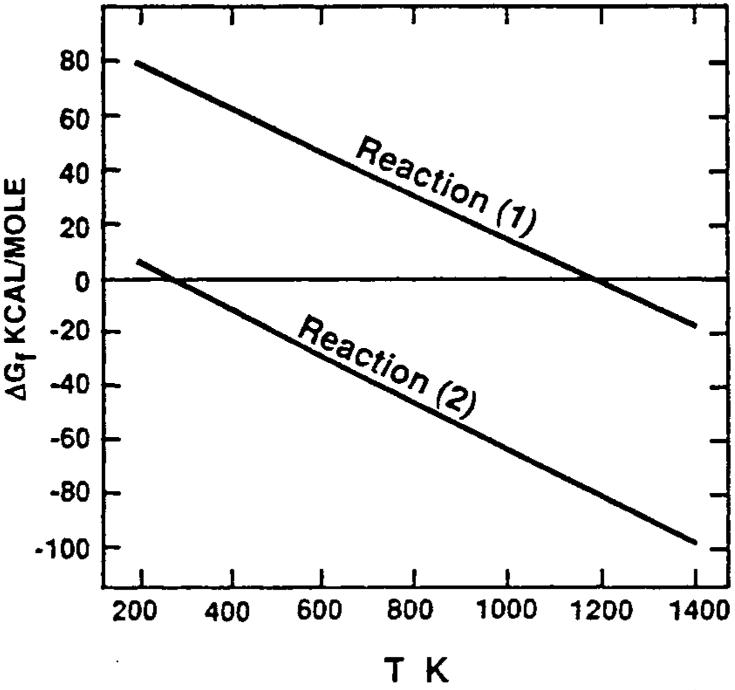
Is given **chemical reaction feasible or not**?

Once it is decided that a reaction is possible, **thermodynamic calculation** can frequently **provide information on the partial pressures** of the involved gaseous species and **the direction of transport in the case of reversible reactions**.

Thermodynamics **does not, however, address questions related to the speed of the reaction and resulting film growth rates**. Indeed, processes which are thermodynamically possible frequently proceed at such low rates because of both vapor transport kinetics and vapor-solid reaction limitations that they are unfeasible in practice.

Furthermore, the use of **thermodynamics implies that chemical equilibrium has been attained**. Although this may occur in a closed system, **it is generally not the case in an open or flow reactor** where gaseous reactants and products are continuously introduced and removed.

$\Delta G < 0$ for reaction to take place



(1) $TiCl_4 + 2BCl_3 \longrightarrow TiB_2 + 10HCl$

(2) $TiCl_4 + B_2H_6 \longrightarrow TiB_2 + H_2 + 4HCl$

Pierson: Handbook of CVD

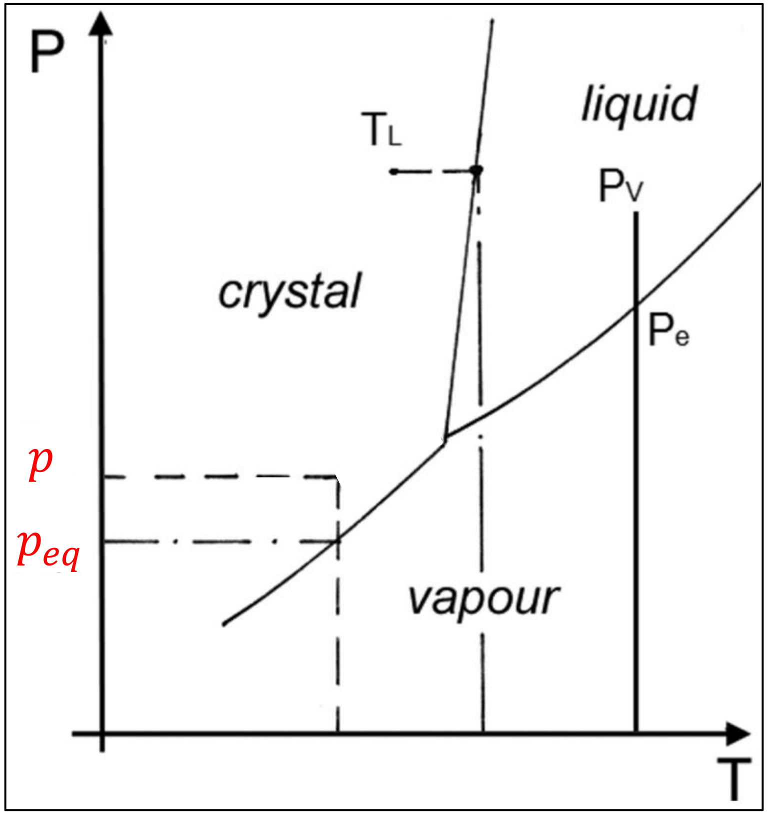
Vapour Supersaturation β

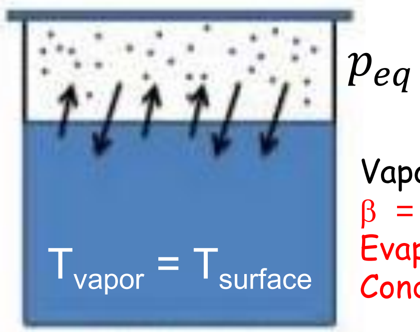
Vapour supersaturation quantifies the off-equilibrium state when the vapour above a compound has higher/lower (partial) pressure than the vapour pressure of that compound (at given temperature) → condensation (deposition) vs evaporation.

$$\Delta\mu = -kT\ln\left(\frac{p}{p_{eq}}\right) = -kT\ln(\boldsymbol{\beta})$$

$\Delta\mu$ is the thermodynamical supersaturation

$\beta = p/p_{eq}$ is the vapour supersaturation

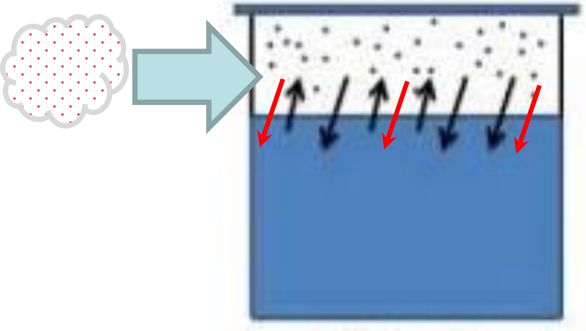




Vapour pressure

β = 1

Evaporation = Condensation



Supersaturated Vapour

β > 0

Condensation > Evaporation

→ Growth

Graphics source : internet

Thermal CVD silicon

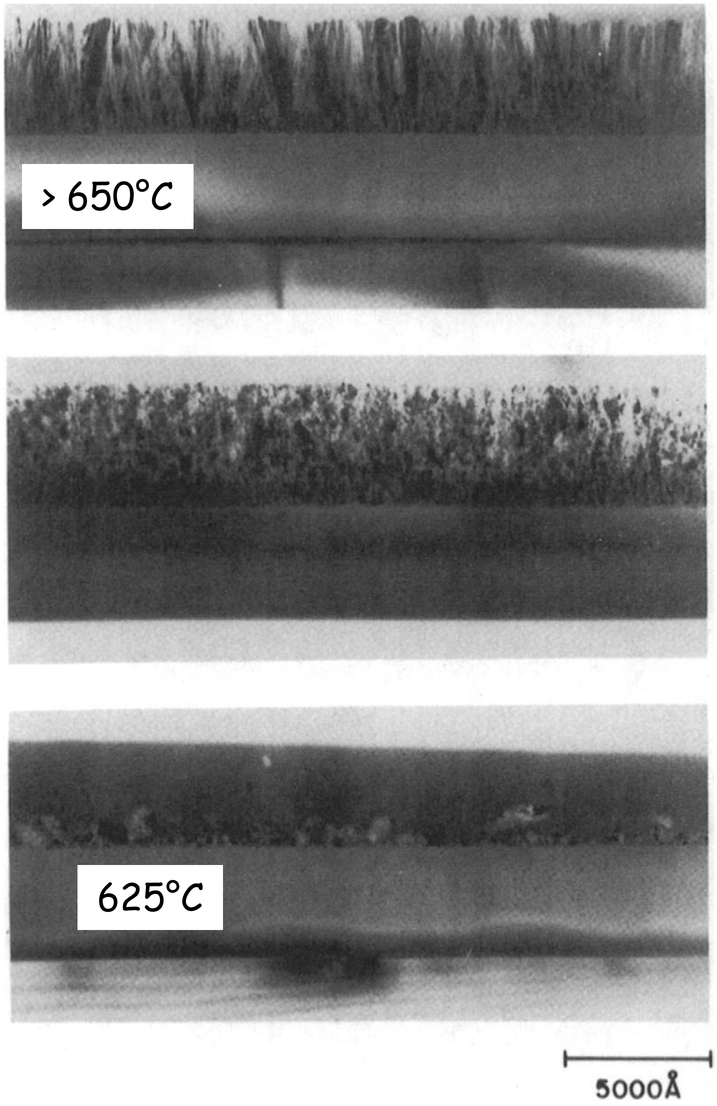
$$[\mathrm{SiH_4}]_{(g)} \xrightarrow{500\text{–}800^\circ\mathrm{C}} \mathrm{Si}_{(s)} + 2\mathrm{H}_{2(g)}\uparrow$$

Example: Decomposition of silane at temperatures of about 600°C and below yields amorphous films with no detectable structure. Polysilicon films deposited from 600°C to 650°C have a columnar structure with grain sizes ranging from 0.03 to 0.3 μm, and possess a [110] preferred orientation. Larger Si crystallites form at higher temperatures.

Perhaps the two most important variables affecting growth morphologies **are vapor supersaturation and substrate temperature.**

Vapor supersaturation influences the film **nucleation rate**
Large values give many and small nuclei
Small values give few but large nuclei
→ **Large grain growth and single crystal growth**
@ low supersaturations
→ **Amorphous or ultrananograin growth favoured**
@ high supersaturations

High temperature facilitates surface diffusion and arrangement into large nuclei and consequently large crystalline grains
Low temperature favours amorphous material deposition



Ohring 2002

gas transport

Gas transport is the process by which volatile species flow from one part of a reactor to another. It is important **to understand gas transport phenomena in CVD** systems for the following reasons:

1. The deposited **film or coating thickness uniformity** depends on the delivery of equal amounts of reactants to all substrate surfaces.

2. Rapid deposition **growth rates** are dependent on optimizing **the flow of reactants** through the system and to substrates.

3. More **efficient utilization** of generally **expensive process** gases can be achieved as a result.

4. Computer **modeling of CVD processes** will be more **accurate enabling improved reactor design** and better predictive capability with regard to performance.

It is important to **distinguish between diffusion** and **bulk flow processes** in gases.

Diffusion involves the motion of **individual atomic** or molecular species.

In bulk transport processes such as **viscous flow** or **convection**, parts of the **gas move as a whole**.

different driving forces and **resulting transport equations** define and characterize these two broad types of gas flow.

diffusion in gases

The phenomenon of diffusion applies to mass transport in gases as well as condensed phases.

In the case of **two different gases** that are initially separated and then allowed to mix, each **will interdiffuse** and increase the entropy of the system.

Diffusion coefficients in gases are many orders of magnitude **higher than even the largest values in solids**.

convection

Convection is a bulk gas-flow process that can be **distinguished from both diffusion and viscous flow.**

Whereas gas diffusion involves the statistical motion of atoms and molecules driven by concentration gradients, **convection arises from the response to gravitational, centrifugal, electric, and magnetic forces**.

It is manifested in CVD reactors when there are **vertical gas-density or temperature gradients**.

An important example occurs in **cold-wall reactors**. **Cooler, more dense gases then lie above hotter, less dense gases**. The resultant convective instability causes an overturning of the **gas by buoyancy effects**.
Subsequently, a complex coupling of mass and heat transfer serves to reduce both density and temperature gradients in the system.

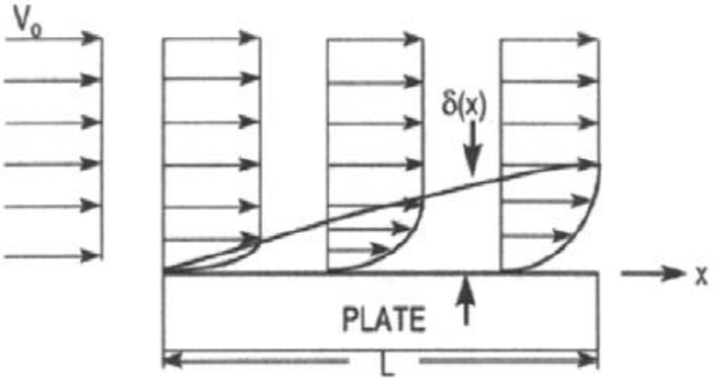
viscous flow

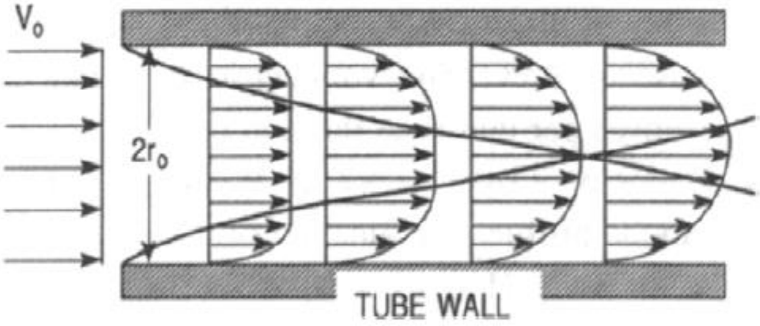
The **viscous flow regime** is operative when **gas transport occurs at pressures of roughly 0.01 atm** and above **in reactors of typical size**. This is the pressure range characterisic of most CVD systems.

At typical **flow velocities of tens of centimeters per second, the reactant gases exhibit what is known as laminar** or **streamline flow.**

We consider the fluid mechanics
Of two simple geometries: flat plate & tube

The **flow velocity has a uniform value v_o,** but only prior to impinging on the leading edge of the plate.
However, **as flow progresses, velocity gradients must form because the gas clings to the plate.** Far away the velocity is still uniform but **drops rapidly to zero at the plate surface, creating a boundary layer**.





Ohring 2002

viscous flow

The latter **grows with distance along the plate and has a thickness δ(x)** given by

$$\delta(x)=\frac{5x}{\sqrt{R_e}}$$

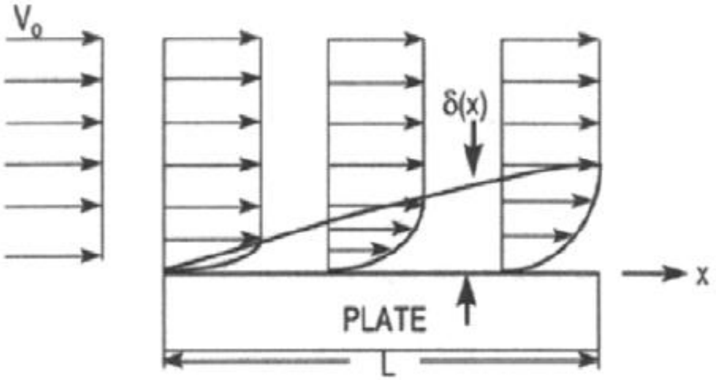
where Re is the Reynolds number defined as

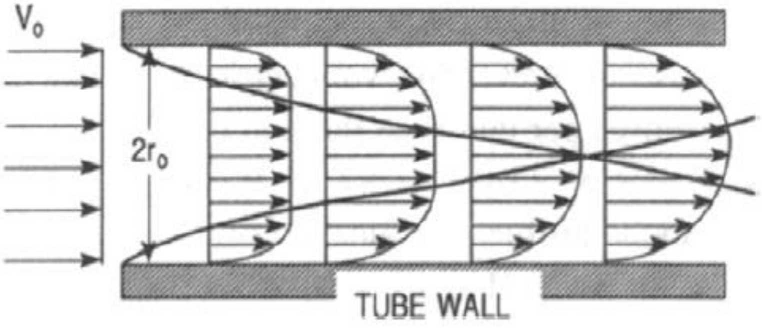
$$R_e=\frac{\rho x v_0}{\eta}$$

The quantities η and ρ are gas viscosity and density, respectively.

Low values of δ(x) are desirable in enhancing mass-transport rates. This can be practically achieved by increasing R_e.

Typical values of **Re in CVD reactors range up to a few hundred**. If, however, **Re exceeds approximately 2100, a transition from laminar to turbulent flow occurs**. The resulting erratic gas eddies and swirls are not conducive to uniform, defect-free film growth and are to be avoided.





Ohring 2002

Growth Regimes

A crucial factor that determines the relative importance of each regime is the pressure of the CVD reactor.

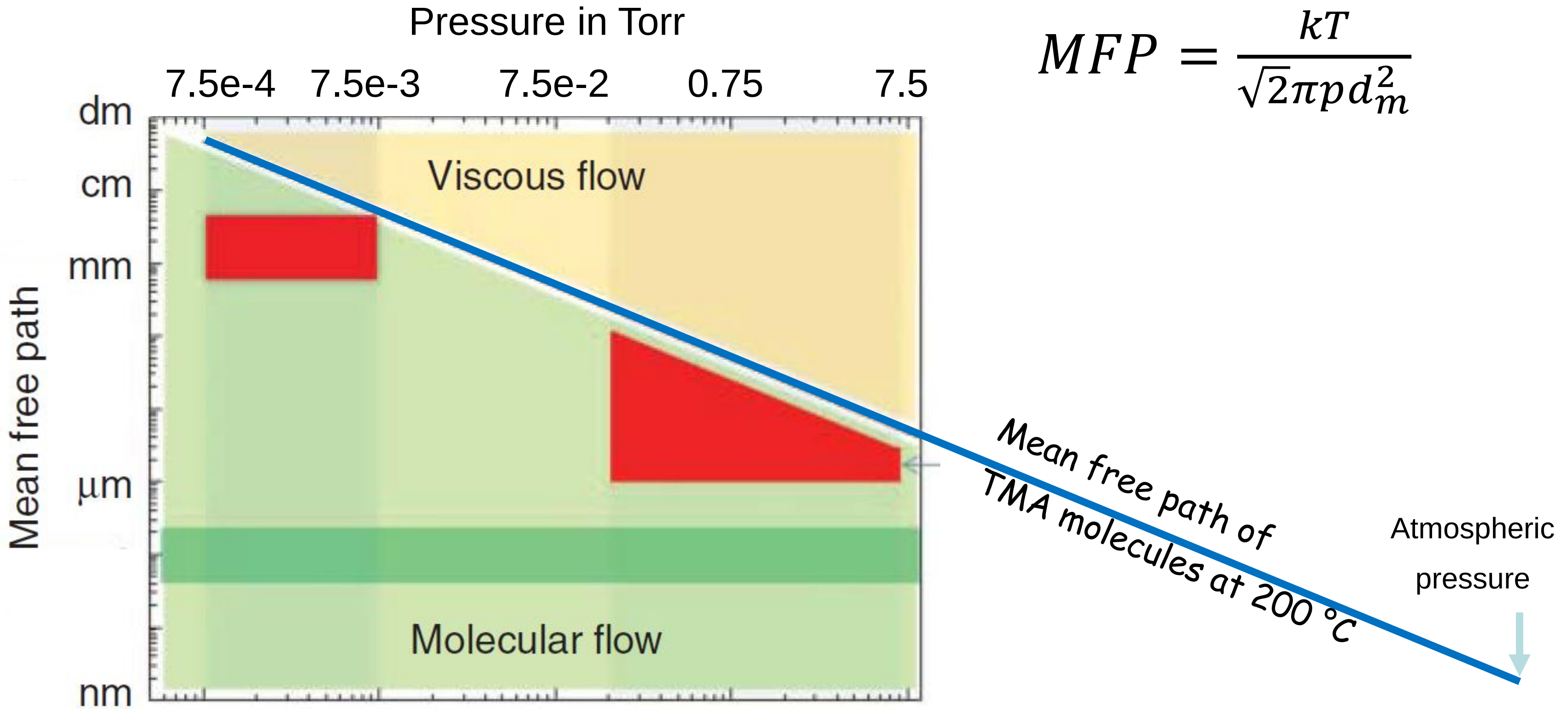
10^3 – 10mbar: gas phase reactions are important and, in addition, a **significant boundary layer is present**. Kinetics and mass transport can both play a significant role in deposition.

<1 mbar: As the pressure falls gas phase reactions tend to become less important, and particularly at pressures below 1 mbar **layer growth is often controlled by surface reactions**.

$< 10^{-4}$ mbar: layer growth is **primarily controlled by the gas and substrate temperature** and by **desorption of precursor fragments** and matrix elements from the growth surface.

Source: CVD, Jones & Hitchman

Growth Regimes vs CVD pressure



$$MFP = \frac{kT}{\sqrt{2}\pi p d_m^2}$$

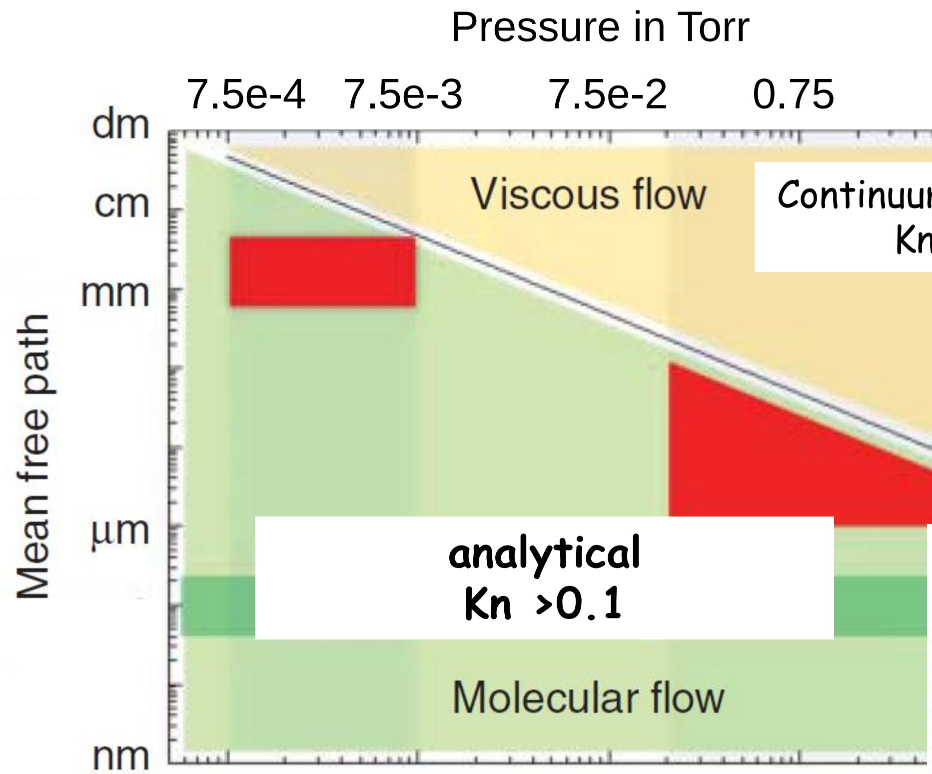
Molecule-surface collisions dominant
→Only surface reactions
molecular flow (reactor dimension < MFP)
→No stagnant boundary layer
→Easy trajectory calculation!!

Transition pressure range

Many molecule-molecule collisions
→ gas phase reactions are important
viscous flow (reactor dimension >> MFP)
→significant stagnant boundary layer
→Diffusive Mass Transport

Modified from Dendooven & Detavernier 2012

Molecular Flow vs Viscous Flow

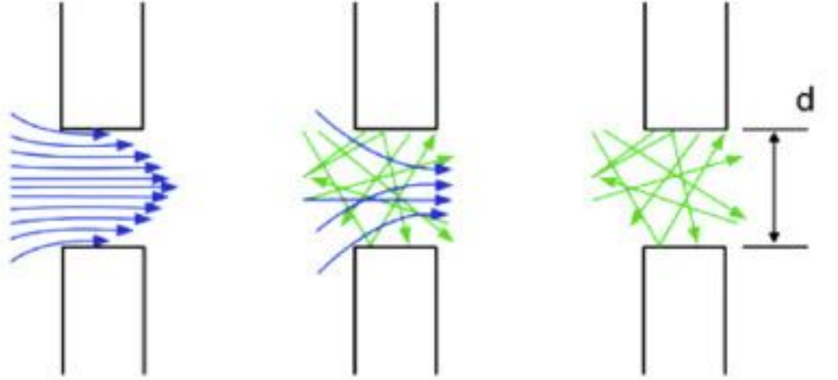


Continuum modelling
Kn <0.1

analytical
Kn >0.1

Knudsen number

$$Kn = \frac{MFP}{dimension}$$



Continuous flow
Kn < 0.01
Low vacuum

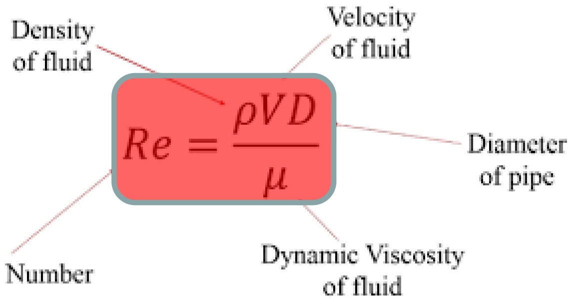
Knudsen flow
0.01 < Kn < 0.5
Medium vacuum

Molecular flow
Kn > 0.5
High/Ultra-high vacuum

Modified from Dendooven & Detavernier 2012; sciencedirect

Viscous vs Turbulent Flow

Reynolds number

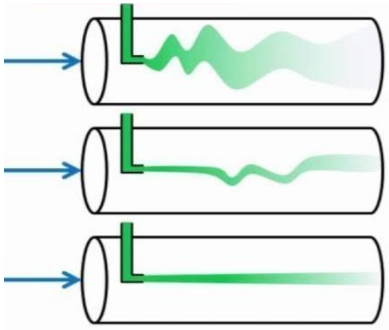


$$\rho = MR/pT$$

$$Re = \frac{\rho V D}{\mu}$$

$$\mu = \mu_0 (T/T_0)^m$$

Pipes

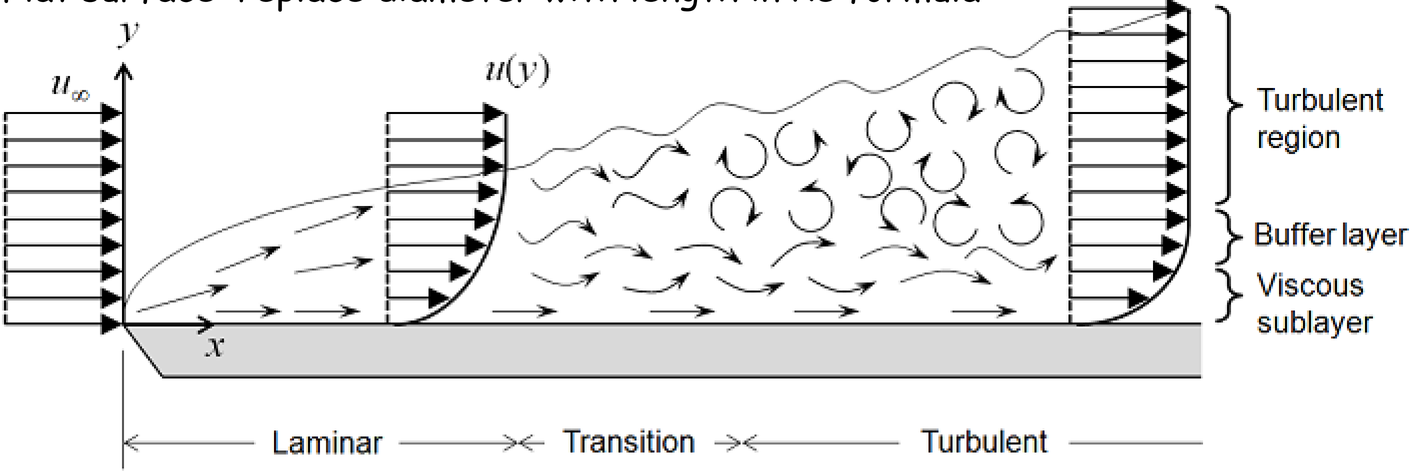


$Re > 4000$
turbulent (unpredictable, rapid mixing)

$2300 < Re < 4000$
transitional (turbulent outbursts)

$Re < 2300$
laminar (predictable, slow mixing)

Flat surface: replace diameter with length in Re formula



Graphics source : internet

Complex gas transport effects

When gas transport is physically more complex because of combined flows in three dimensions, the fundamental equations of fluid dynamics become the starting point of the analysis.

1. Continuity: The **conservation of mass requires** that the net rate of mass accumulation in a region be equal to the difference between the rate of mass flow in and out.

2. Navier-Stokes: **Momentum conservation** requires that the net rate of momentum accumulation in a region be equal to the difference between the rate of momentum in and out, plus the sum of forces acting on the system.

3. Energy: **Energy balance** means that the rate of accumulation of internal and kinetic energy in a region is equal to the net rate of internal and kinetic energy in by convection, plus the net rate of heat flow by conduction, minus the rate of work done by the fluid.

In **practice exact solutions are rare** and only exist in the simplest cases. For this reason **numerical methods based on finite-element analysis are often used** to analyze gas flow in reactors of complex geometry where steep temperature gradients exist.

Complex gas transport effects

Before starting, however, it is often found to be very useful to **transform the equations into dimensionless forms by scaling the variables** and properties that describe gas behavior relative to reference values.

Although only **Damkohler numbers** $\mathbf{Da_g}$ **and** $\mathbf{Da_s}$ specifically refer to chemical reaction rates among species within the gas or at the substrate surface, the **other dimensionless groups describe gas transport in both multicomponent and homogeneous systems**.

In particular, the **Peclet**, **Grashof/Rayleigh**, **Reynolds**, **Damkohler**, and **Knudsen** numbers are important descriptors of CVD reactor processes.

For example, when the **Peclet** number is large, species transfer is mainly due to convection, and downstream reaction products and impurities will not diffuse back to the reaction zone; for small Peclet numbers, transport due to diffusion dominates the flow

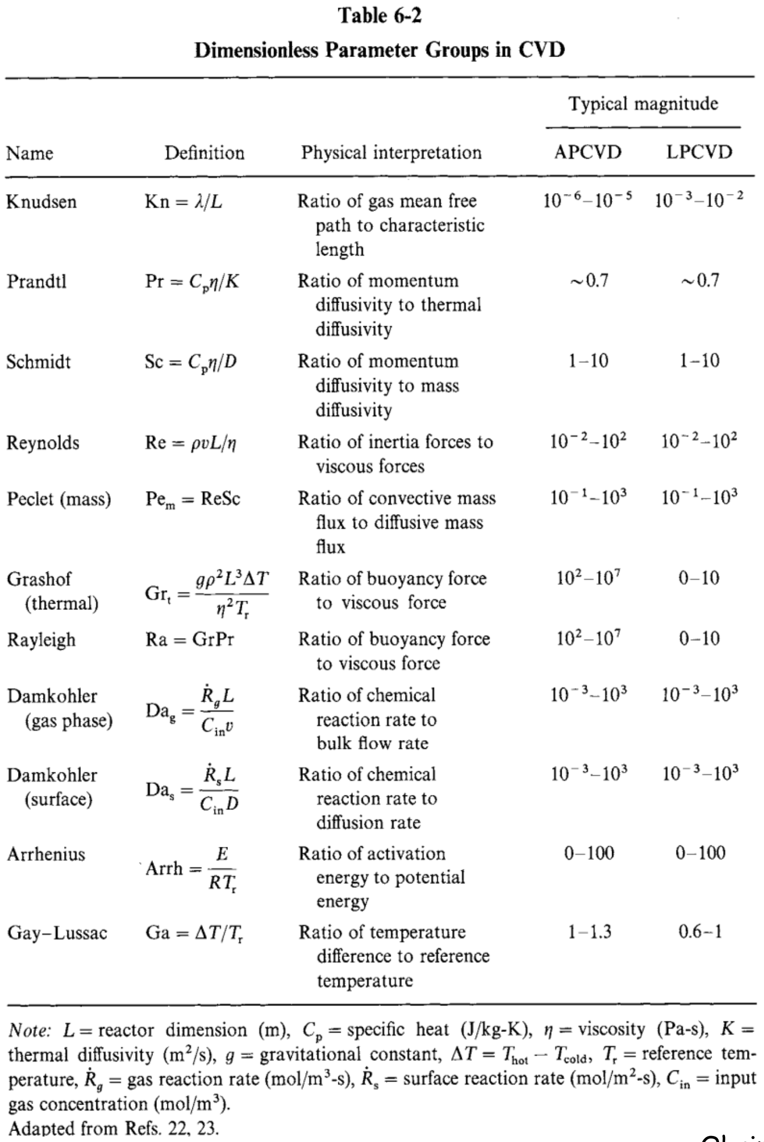


Table 6-2

Dimensionless Parameter Groups in CVD

Name	Definition	Physical interpretation	Typical magnitude	
			APCVD	LPCVD
Knudsen	$\mathrm{Kn} = \lambda/L$	Ratio of gas mean free path to characteristic length	10^{-6}–10^{-5}	10^{-3}–10^{-2}
Prandtl	$\mathrm{Pr} = C_p\eta/K$	Ratio of momentum diffusivity to thermal diffusivity	~0.7	~0.7
Schmidt	$\mathrm{Sc} = C_p\eta/D$	Ratio of momentum diffusivity to mass diffusivity	1–10	1–10
Reynolds	$\mathrm{Re} = \rho vL/\eta$	Ratio of inertia forces to viscous forces	10^{-2}–10^{2}	10^{-2}–10^{2}
Peclet (mass)	$\mathrm{Pe_m} = \mathrm{ReSc}$	Ratio of convective mass flux to diffusive mass flux	10^{-1}–10^{3}	10^{-1}–10^{3}
Grashof (thermal)	$\mathrm{Gr_t} = \dfrac{g\rho^2L^3\Delta T}{\eta^2T_r}$	Ratio of buoyancy force to viscous force	10^{2}–10^{7}	0–10
Rayleigh	$\mathrm{Ra} = \mathrm{GrPr}$	Ratio of buoyancy force to viscous force	10^{2}–10^{7}	0–10
Damkohler (gas phase)	$\mathrm{Da_g} = \dfrac{\dot{R}_gL}{C_{\mathrm{in}}v}$	Ratio of chemical reaction rate to bulk flow rate	10^{-3}–10^{3}	10^{-3}–10^{3}
Damkohler (surface)	$\mathrm{Da_s} = \dfrac{\dot{R}_sL}{C_{\mathrm{in}}D}$	Ratio of chemical reaction rate to diffusion rate	10^{-3}–10^{3}	10^{-3}–10^{3}
Arrhenius	$\mathrm{Arrh} = \dfrac{E}{RT_r}$	Ratio of activation energy to potential energy	0–100	0–100
Gay–Lussac	$\mathrm{Ga} = \Delta T/T_r$	Ratio of temperature difference to reference temperature	1–1.3	0.6–1

Note: L = reactor dimension (m), C_p = specific heat (J/kg-K), η = viscosity (Pa-s), K = thermal diffusivity (m^2/s), g = gravitational constant, $\Delta T = T_{hot} - T_{cold}$, T_r = reference temperature, $\dot{R}_g$ = gas reaction rate (mol/m^3-s), $\dot{R}_s$ = surface reaction rate (mol/m^2-s), C_{in} = input gas concentration (mol/m^3).
Adapted from Refs. 22, 23.

Ohring 2002

Plasma-enhanced CVD (PECVD)

Example of Plasma CVD

Plasma generates reactive gas species
(also effects surface and surface reaction products)

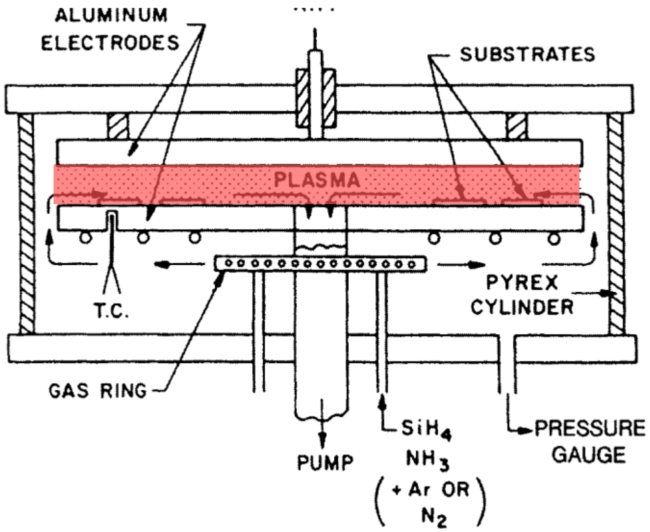
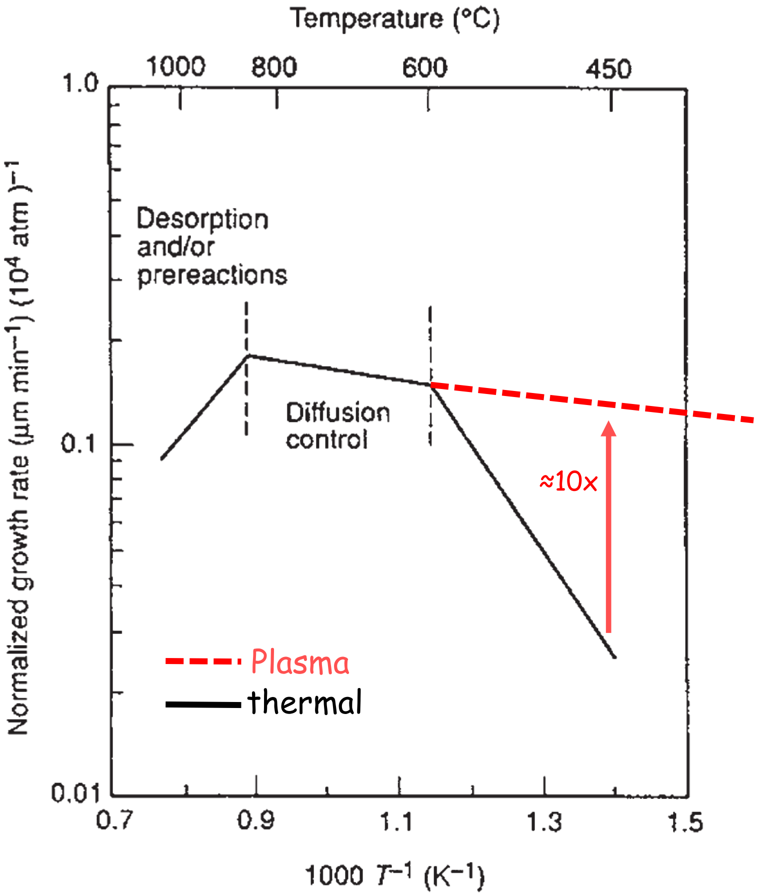


Figure 6-18 Reinberg-type cylindrical radial-flow plasma reactor for the deposition of silicon-nitride films. [From M. J. Rand, *J. Vac. Sci. Technol.* **16**(2), 420 (1979). Reprinted with permission.]

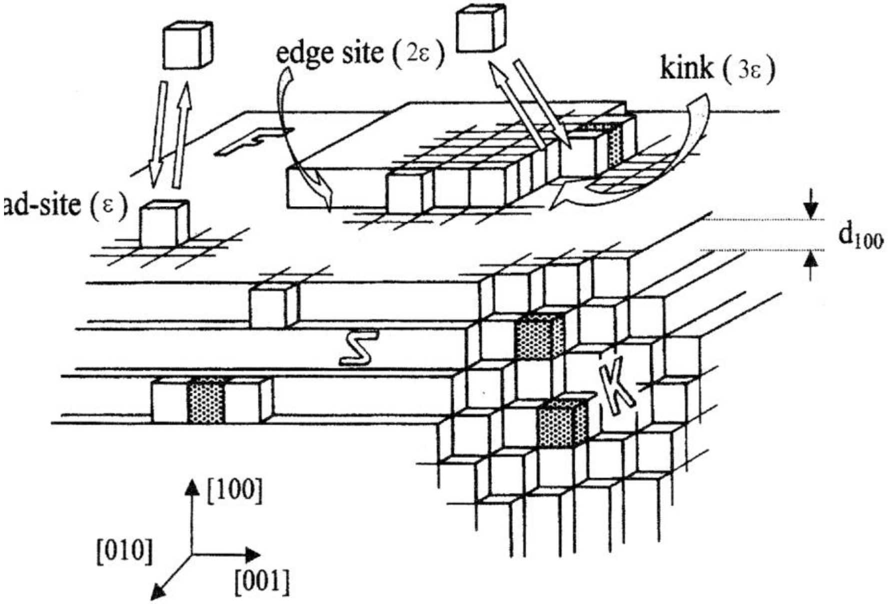


source : Ohring?

Growth rate

Vapour supersaturation is a thermodynamic parameter. Growth depends furthermore strongly on surface kinetics meaning the adsorption processes on the surface, hence the number of adsorption sites and their related reactivity.

Idealized model: **Kossel crystal**



source : Rubbo 2013

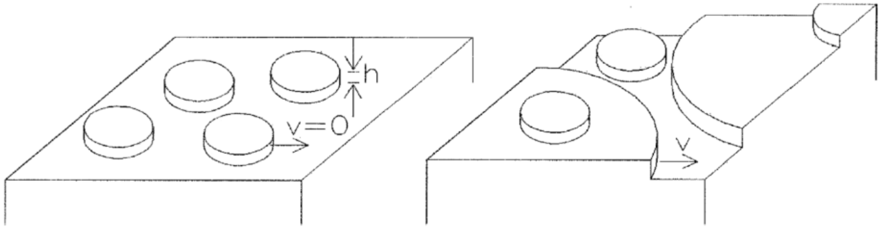
Growth Rate

The K and S faces can grow by uncorrelated addition of vapour atoms impinging on step and kink sites.

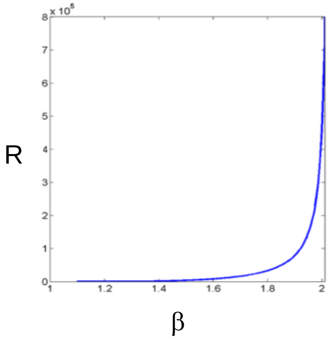
$$R = VJ = V\frac{p_{eq}}{\sqrt{2\pi mkT}}(\beta - 1)$$

J is the flux of atoms
V the atomic volume
m the atomic mass

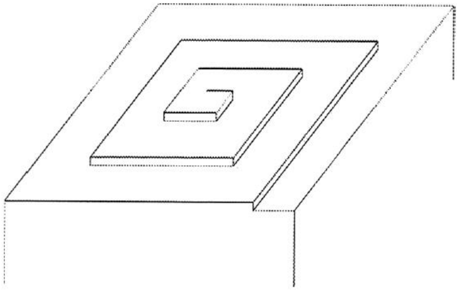
Two-dimensional (2D) nucleation kinetics on a flat (F) face



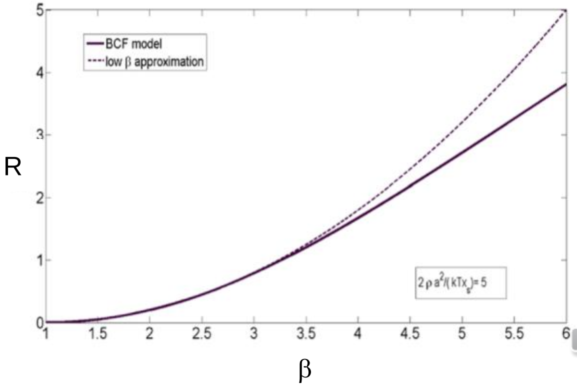
$$R \sim \exp(..)\,(..)^{\frac{3}{2}}\,\mathrm{erf}(..)\;\dots\dots..\,one\ page\ expression$$



Spiral growth mode on flat (F) fACE : self generating step source at screw dislocation (Burton/Cabrera/Frank theory)



$$R \sim (\beta - 1)\ ^2 tanh(1/(\beta - 1))$$



source : Rubbo 2013

Thermal CVD complexity

When changing (substrate) temperature we inevitably change the vapor supersaturation.

In concert they influence whether epitaxial films, platelets, whiskers, dendrites, coarse-grained polycrystals, fine-grained polycrystals, amorphous deposits, gas-phase powder, or some combination of these form.

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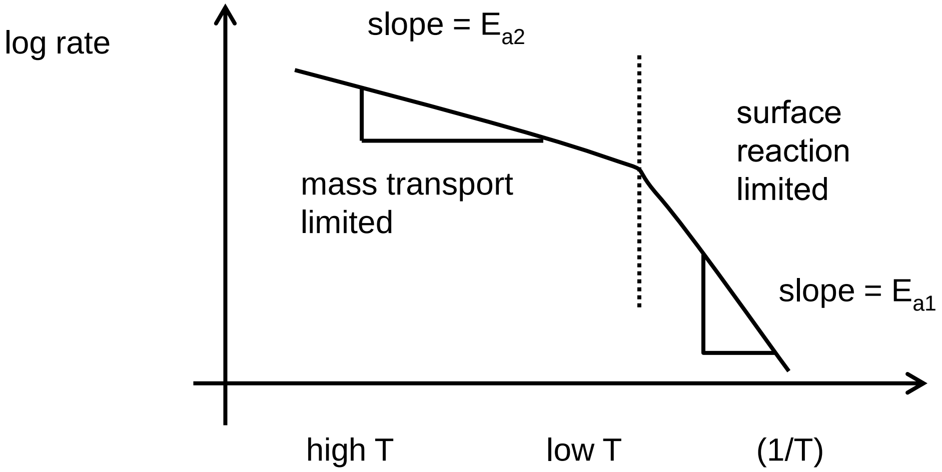
Surface limited vs. mass transport limited reactions

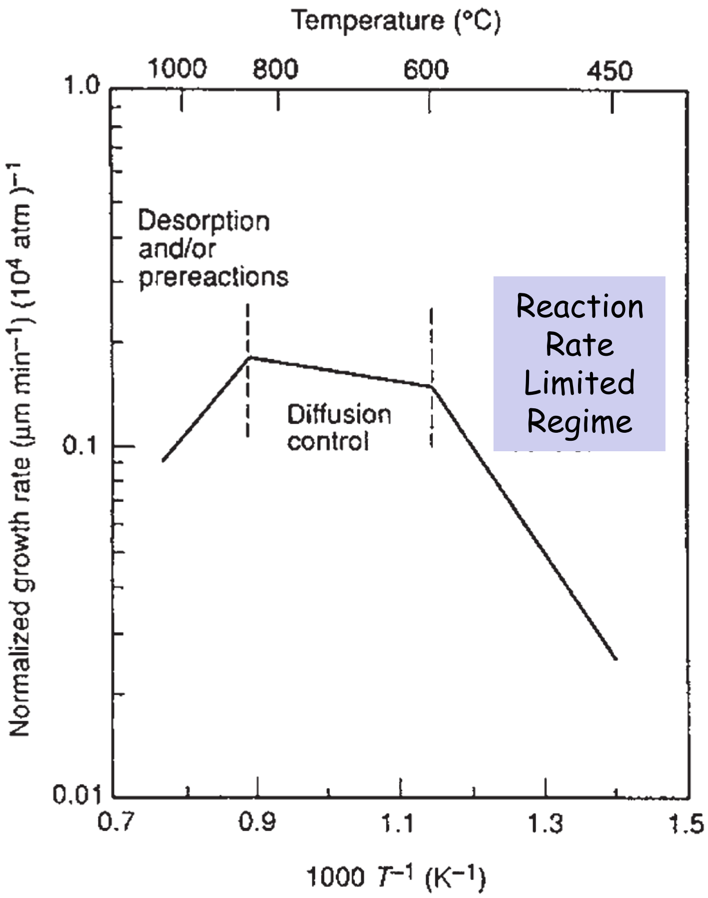


When **temperature is low**, surface reaction rate is slow, and overabundance of reactants is available. Reaction is then **surface reaction limited**.

Above a certain **high temperature all source** gas molecules react immediately. The reaction is then in **mass-transport limited regime** (also known as diffusion limited and supply limited regime).

Growth Regimes

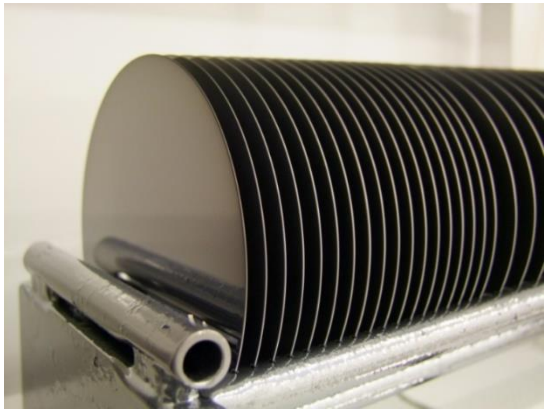
Example: GaAs by MOCVD using Me_3Ga and AsH_3



Reaction Rate Limited Regime

Rate limiting step is the gas phase or surface reaction – its rate is ~$\exp(E_r/RT)$

→ Reaction kinetics



Reaction Rate Limited Regime

Regime of choice for batch coating using hot wall CVD reactors

Why?

Source: CVD, Jones & Hitchman

Thermal CVD: RRL Regime

One of the important advantages of CVD methods is the ability to **batch coat large numbers of small tools** at one time. For this purpose **commercial hot-wall reactor** systems capable of individual or sequential **TiC, TiN, and Al_2O_3 film depositions** have been constructed.

For example, TiN can be deposited by CVD over a broad range of temperatures using the same $TiCl_4$ precursor. Some typical reactions are

1. High temperature, $1200°C > T > 850°C$:

$$2TiCl_4 + N_2 + 4H_2 \rightarrow 2TiN + 8HCl$$

2. Moderate temperature, $850°C > T > 700°C$:

$$TiCl_4 + CH_3CN + 5/2H_2 \rightarrow Ti(C, N) + CH_4 + 4HCl$$

Perhaps **billions of cemented tungsten-carbide cutting tools have now been coated since the mid-1960s** in such reactors.

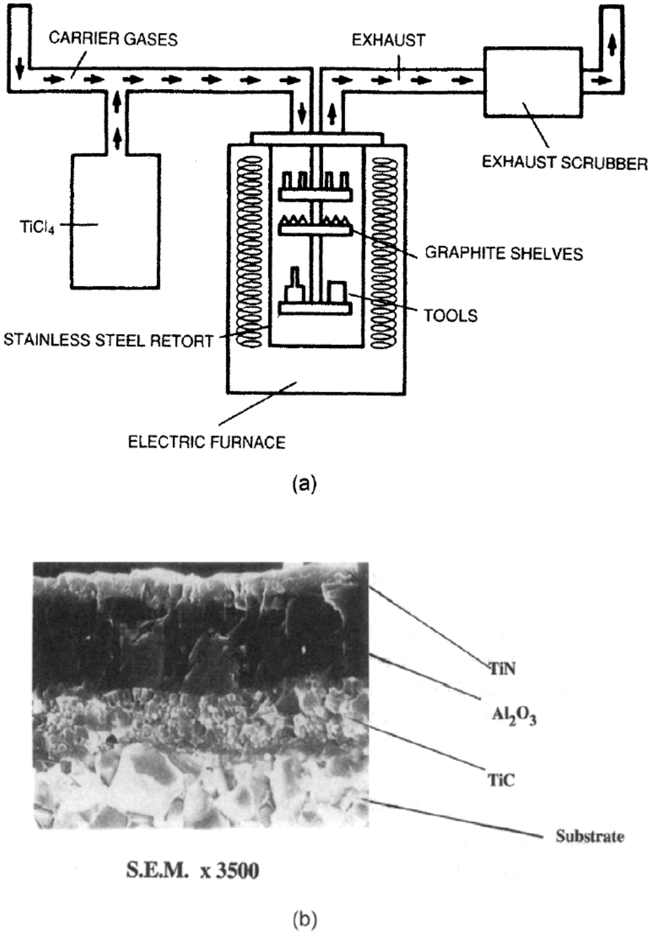


Figure 6-16 Schematic view of a commercial CVD reactor for deposition of TiC, TiN, and Al_2O_3 on carbide cutting tools. (Courtesy of A. Gates, Multi-Arc Scientific Coatings Inc.) (b) SEM image of CVD multilayer coating for cutting tool inserts. Carbide substrate/TiC/Al_2O_3/TiN (3500 ×). Courtesy of S. Wertheimer, ISCAR Ltd.

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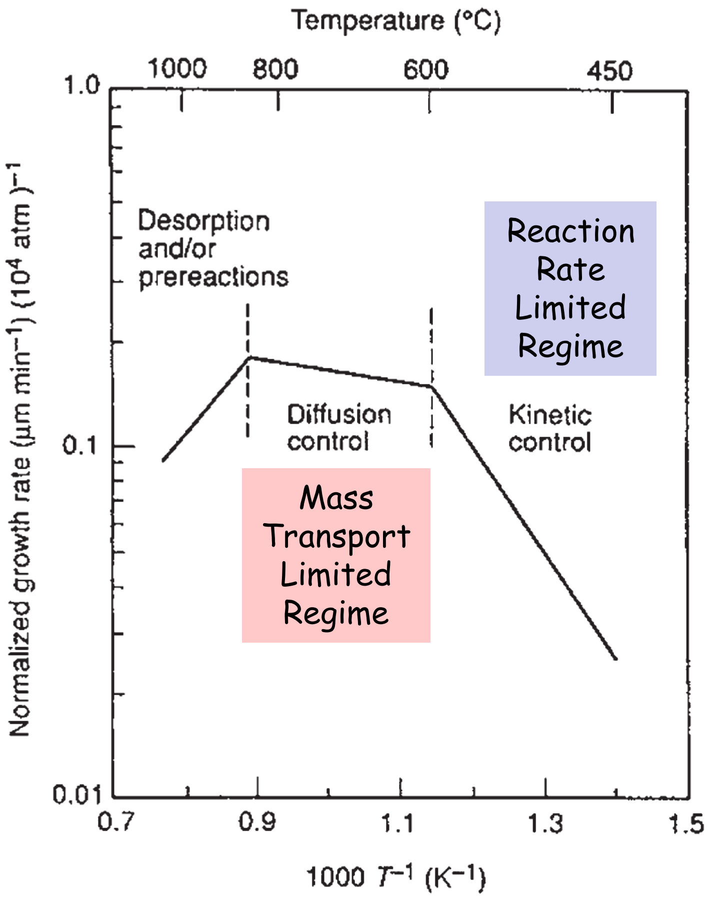
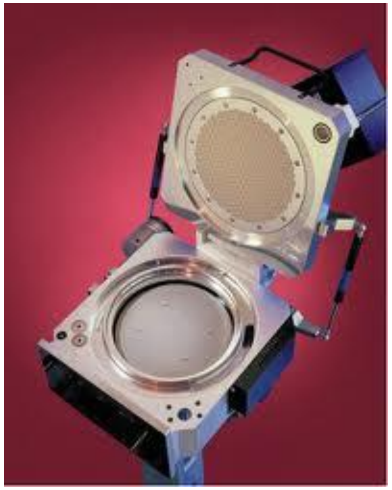
Growth Regimes

Example: GaAs by MOCVD using Me_3Ga and AsH_3



Mass Transport Limited Regime

Rate limiting step is the transport of gas molecules into the reactor and through the stagnant layer, nearly independent of temperature.



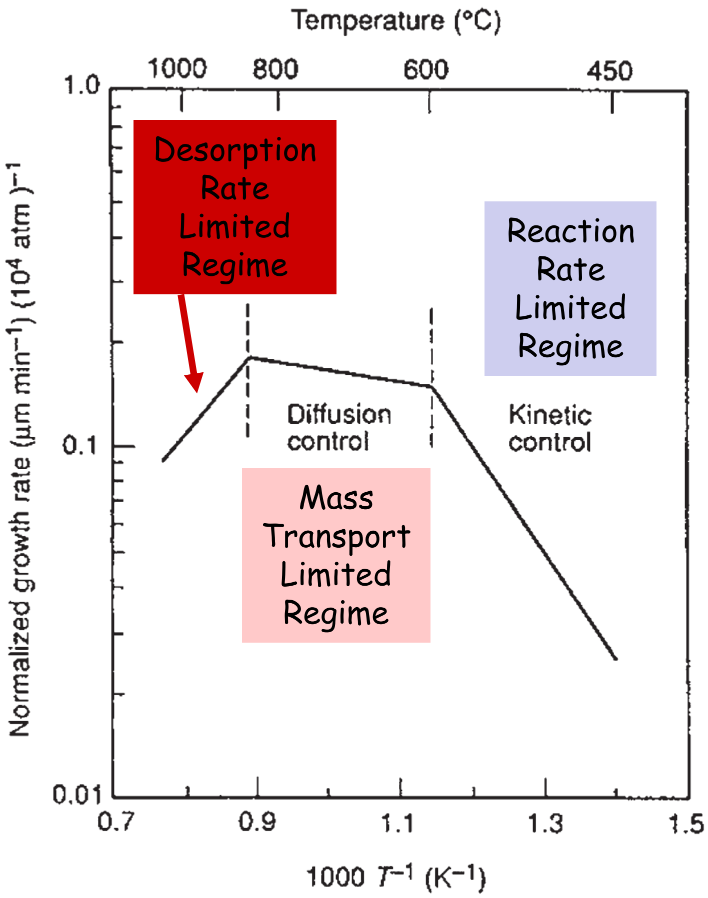
Mass Transport Limited Regime

Single wafer reactors for high growth speed, single crystal, epitaxy.

Source: CVD, Jones & Hitchman

Growth Regimes

Example: GaAs by MOCVD using Me_3Ga and AsH_3

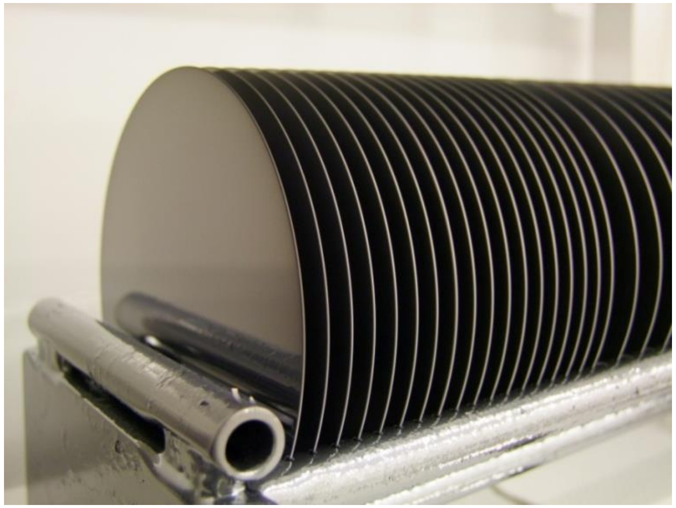


Desorption Rate Limited Regime

Rate limiting step is the desorption of molecules at high temperatures. The growth rate decreases. The surface mobility of the adsorbates increases.

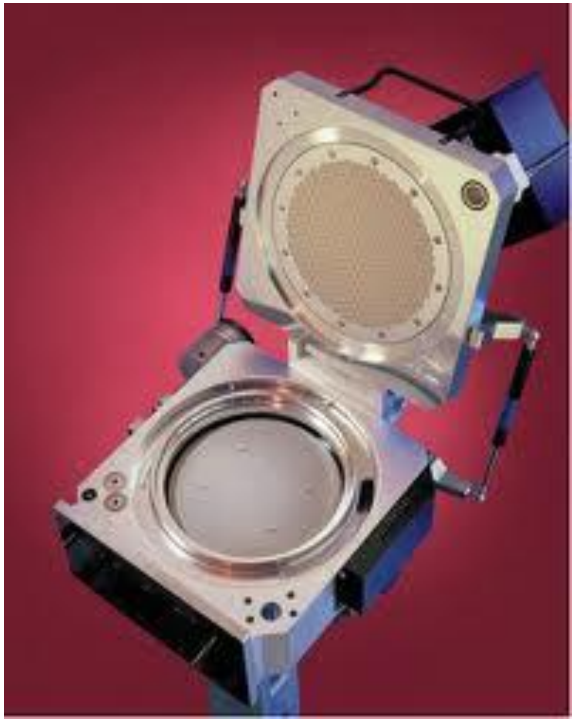
Source: CVD, Jones & Hitchman

Surface limited vs. mass transport limited reactions



A batch reactor operating in surface reaction limited mode:

- -slow reaction
- -many wafers



A mass transport limited reactor:

- -single wafer
- -high deposition rate

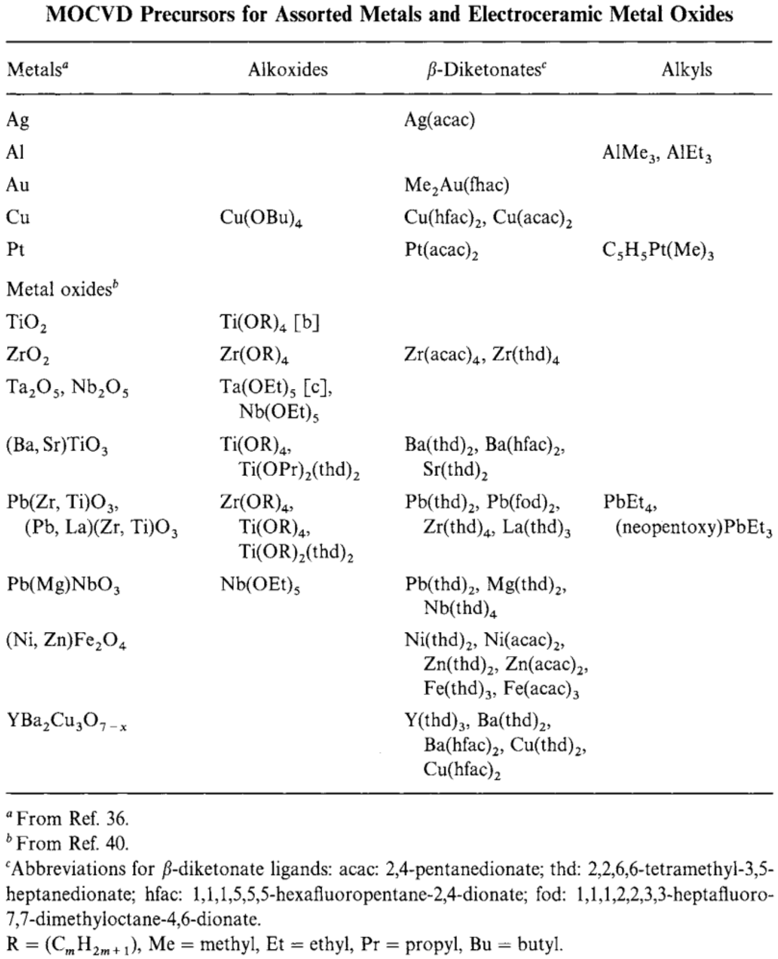
Metalorganic CVD (MOCVD)

The great **advantage of metalorganics** is their generally **high volatility at moderately low temperatures.**

Since all constituents are in the vapor phase, **precise electronic control of gas flow rates** and partial pressures is possible **without dealing with troublesome liquid or solid sources** in the reactor.

This, combined with **pyrolysis reactions which are relatively insensitive to temperature**, allows for efficient and reproducible deposition.

Carbon contamination of films is a disadvantage, however.



MOCVD Precursors for Assorted Metals and Electroceramic Metal Oxides

Metals[a]	Alkoxides	β-Diketonates[c]	Alkyls
Ag		Ag(acac)	
Al			$AlMe_3$, $AlEt_3$
Au		$Me_2Au(fhac)$	
Cu	$Cu(OBu)_4$	$Cu(hfac)_2$, $Cu(acac)_2$	
Pt		$Pt(acac)_2$	$C_5H_5Pt(Me)_3$
Metal oxides[b]			
TiO_2	$Ti(OR)_4$ [b]		
ZrO_2	$Zr(OR)_4$	$Zr(acac)_4$, $Zr(thd)_4$	
Ta_2O_5, Nb_2O_5	$Ta(OEt)_5$ [c], $Nb(OEt)_5$		
$(Ba, Sr)TiO_3$	$Ti(OR)_4$, $Ti(OPr)_2(thd)_2$	$Ba(thd)_2$, $Ba(hfac)_2$, $Sr(thd)_2$	
$Pb(Zr, Ti)O_3$, $(Pb, La)(Zr, Ti)O_3$	$Zr(OR)_4$, $Ti(OR)_4$, $Ti(OR)_2(thd)_2$	$Pb(thd)_2$, $Pb(fod)_2$, $Zr(thd)_4$, $La(thd)_3$	$PbEt_4$, (neopentoxy)$PbEt_3$
$Pb(Mg)NbO_3$	$Nb(OEt)_5$	$Pb(thd)_2$, $Mg(thd)_2$, $Nb(thd)_4$	
$(Ni, Zn)Fe_2O_4$		$Ni(thd)_2$, $Ni(acac)_2$, $Zn(thd)_2$, $Zn(acac)_2$, $Fe(thd)_3$, $Fe(acac)_3$	
$YBa_2Cu_3O_{7-x}$		$Y(thd)_3$, $Ba(thd)_2$, $Ba(hfac)_2$, $Cu(thd)_2$, $Cu(hfac)_2$	

[a] From Ref. 36.

[b] From Ref. 40.

[c] Abbreviations for β-diketonate ligands: acac: 2,4-pentanedionate; thd: 2,2,6,6-tetramethyl-3,5-heptanedionate; hfac: 1,1,1,5,5,5-hexafluoropentane-2,4-dionate; fod: 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate.

$R = (C_mH_{2m+1})$, Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl.

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Plasma-enhanced CVD (PECVD)

In PECVD processes, **glow-discharge plasmas are sustained within chambers** where **simultaneous vapor-phase chemical reactions** and film deposition occur.

In **the majority of PECVD** processing activity, glow-discharge plasmas are excited by an **RF field**. The reason is that most films deposited by this method are dielectrics and DC discharges are not feasible.

The energetic discharge is sufficient to **decompose gas molecules into a variety of component species,i.e., ions, atoms and molecules in ground** and **excited states, molecular fragments, free radicals**, etc.

The net effect of the interactions among these reactive entities is to **cause chemical reactions to occur at much lower temperatures** than in thermal CVD reactors not benefiting from plasma activation. Therefore, previously unfeasible high-temperature reactions can be made to occur on temperature-sensitive substrates.

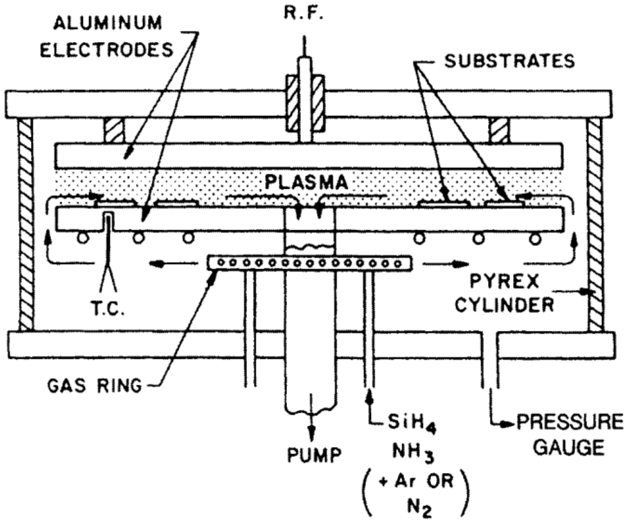

Figure 6-18 Reinberg-type cylindrical radial-flow plasma reactor for the deposition of silicon-nitride films. [From M. J. Rand, *J. Vac. Sci. Technol.* **16**(2), 420 (1979). Reprinted with permission.]

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Plasma-enhanced CVD (PECVD)

The **parallel-plate**, plasma-deposition reactor of the Reinberg type has been a very widely used configuration for PECVD.

Reactant gases first flow along the axis of the chamber and then radially outward across rotating substrates which rest on one plate of an RF-coupled capacitor.

This diode configuration enables reasonably uniform and controllable film deposition to occur.

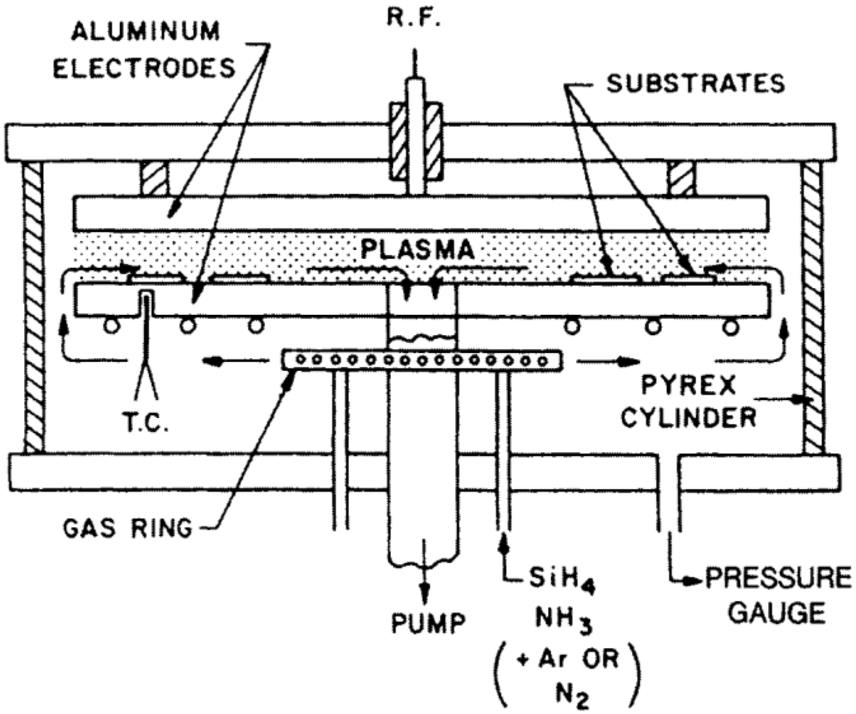

Figure 6-18 Reinberg-type cylindrical radial-flow plasma reactor for the deposition of silicon-nitride films. [From M. J. Rand, *J. Vac. Sci. Technol.* **16**(2), 420 (1979). Reprinted with permission.]

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Plasma-enhanced CVD (PECVD)

Example of Plasma CVD

Plasma generates reactive gas species
(also effects surface and surface reaction products)

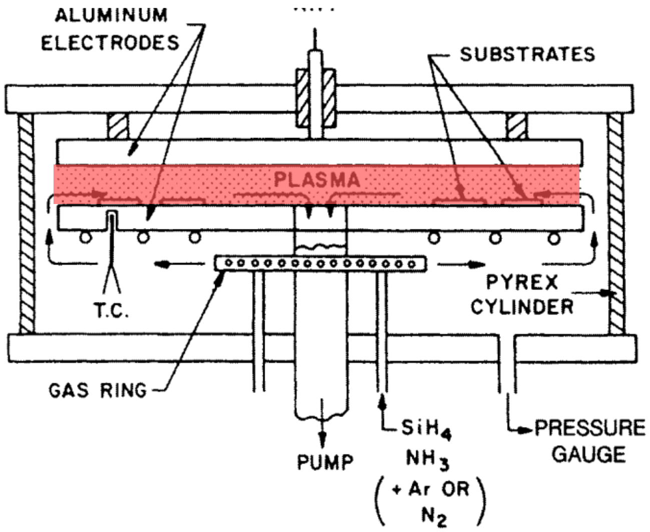
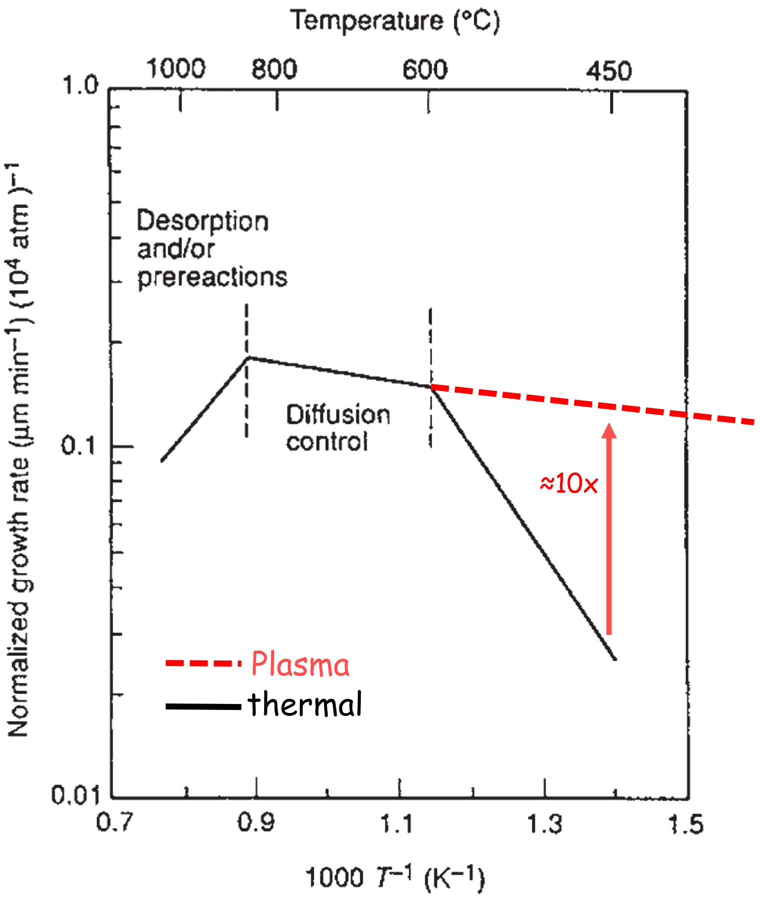


Figure 6-18 Reinberg-type cylindrical radial-flow plasma reactor for the deposition of silicon-nitride films. [From M. J. Rand, *J. Vac. Sci. Technol.* **16**(2), 420 (1979). Reprinted with permission.]



source : Ohring?

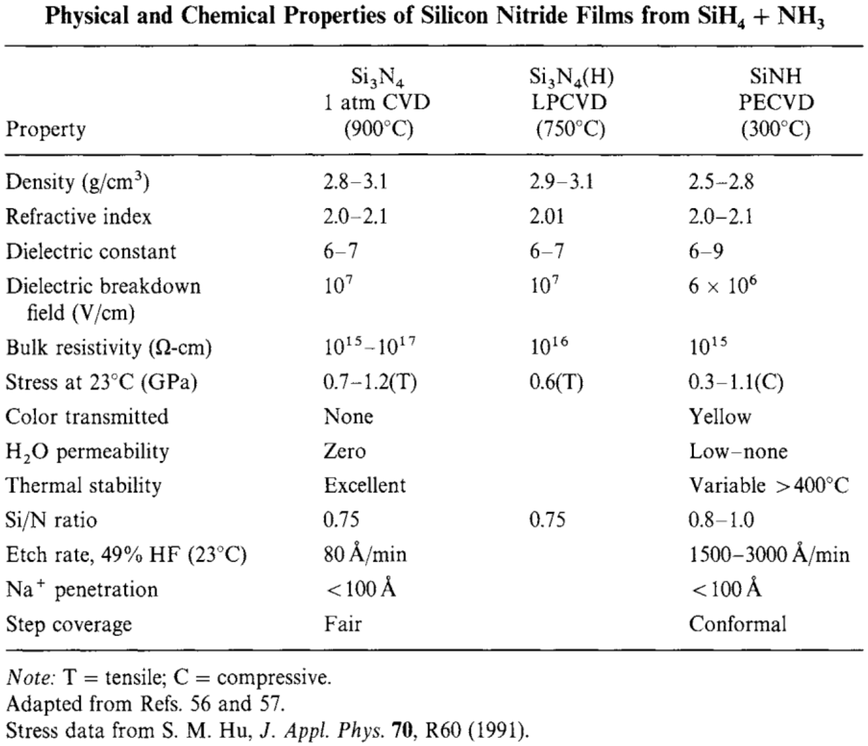
amorphous silicon nitride films

Silicon nitride is normally prepared by reacting **silane with ammonia** in **an argon plasma**

During plasma deposition, as much **as 30 at.% hydrogen** can be incorporated which apparently forms bonds to both Si and N. It is in this sense that silicon nitride is often described as a **ternary solid-solution alloy, SiNH**.

Amorphous silicon nitride should be distinguished from the **stoichiometric compound, Si_3N_4,** formed **by reacting silane and ammonia at 900°C in an atmospheric CVD reactor.** It is instructive to further compare the physical and chemical property differences in three types of silicon nitride.

While **Si_3N_4 is denser and more resistant to chemical attack** and has higher resistivity and dielectric breakdown strength, **SiNH tends to provide better step coverage**.



Physical and Chemical Properties of Silicon Nitride Films from $SiH_4 + NH_3$

Property	Si_3N_4 1 atm CVD (900°C)	$Si_3N_4(H)$ LPCVD (750°C)	SiNH PECVD (300°C)
Density (g/cm^3)	2.8–3.1	2.9–3.1	2.5–2.8
Refractive index	2.0–2.1	2.01	2.0–2.1
Dielectric constant	6–7	6–7	6–9
Dielectric breakdown field (V/cm)	10^7	10^7	6×10^6
Bulk resistivity (Ω-cm)	10^{15}–10^{17}	10^{16}	10^{15}
Stress at 23°C (GPa)	0.7–1.2(T)	0.6(T)	0.3–1.1(C)
Color transmitted	None		Yellow
H_2O permeability	Zero		Low–none
Thermal stability	Excellent		Variable >400°C
Si/N ratio	0.75	0.75	0.8–1.0
Etch rate, 49% HF (23°C)	80 Å/min		1500–3000 Å/min
Na^+ penetration	<100 Å		<100 Å
Step coverage	Fair		Conformal

Note: T = tensile; C = compressive.
Adapted from Refs. 56 and 57.
Stress data from S. M. Hu, *J. Appl. Phys.* **70**, R60 (1991).

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Diamondlike and amorphous carbon

Amorphous carbons containing hydrogen, are identified as a-C:H materials and possess diamondlike properties. Films are formed when hydrocarbons impact relatively low-temperature substrates with energies in the range of a few hundred eV. **Plasma CVD techniques employing RF and DC glow discharges in assorted hydrocarbon gas mixtures** commonly produce a-C:H deposits.

Substrate **temperatures below 300°C** are required to prevent graphitization and film softening. The **energetic molecular ions disintegrate upon hitting the surface** and this explains why the resulting film properties are insensitive to the particular hydrocarbon employed.

Amorphous Carbon (a-C) are prepared **at low temperatures in the absence of hydrocarbons by ion-beam-assisted or sputter-deposition techniques**. Both essentially involve deposition of carbon under the bombardment of energetic ions. Simple thermal evaporation of carbon will, however, yield highly conductive, soft films whose properties are far removed from the hard, very resistive, high-energy bandgap diamond-like materials. Ion impact energy, therefore, appears to be critical in establishing the structure of the deposit. More diamond-like properties are produced at lower energies; microcrystalline diamond ceases to form when the ion energy exceeds 100 eV, in which case the amorphous structure prevails.

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Diamond CVD

Thin diamond films involve metastable synthesis in the low-pressure graphite region of the phase diagram. The possibility of synthesizing diamond in this region is based on the small free-energy difference, i.e., 500 cal/mol, between diamond and graphite under ambient conditions.

Therefore, a finite probability exists that both phases can nucleate and grow simultaneously, especially under conditions where kinetic factors dominate, i.e., high energy or supersaturation.

In particular, the key is to prevent graphite from forming or to remove it preferentially, leaving diamond behind. The way this is done practically is to generate a supersaturation of atomic H. The latter has been most commonly produced utilizing 0.2-2% CH_4-H_2 mixtures in DC, RF, and microwave plasmas, or in thermal CVD reactors containing hot filaments.

Large thermal stress upon cooling

Under these conditions the atomic H that is generated fosters diamond growth by inhibiting graphite formation, by dissolving it if it does form, by stabilizing sp3 bonding, or by promoting some combination of these factors.

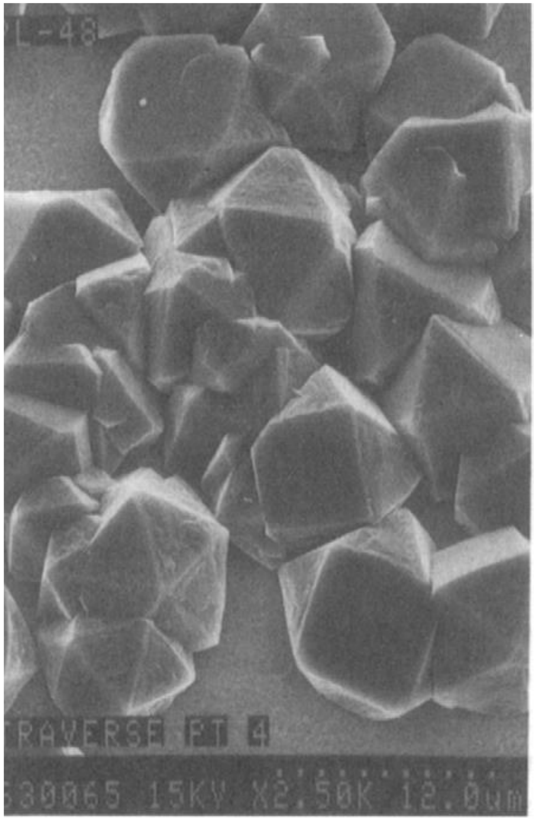

Figure 6-24 Diamond crystals grown by CVD employing combined microwave and heated filament methods. (Courtesy of T. R. Anthony, GE Corporate Research and Development.)

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Safety issues with CVD

In the case of CVD reactant or product gases we are typically dealing with **toxic**, **flammable**, **pyrophoric**, or **corrosive** substances.

Because they frequently possess a combination of these attributes, they present particular **health hazards to humans**.

Exposure of reactor hardware and associated gas-handling equipment to corrosive environments also causes significant maintenance problems and losses due to downtime.

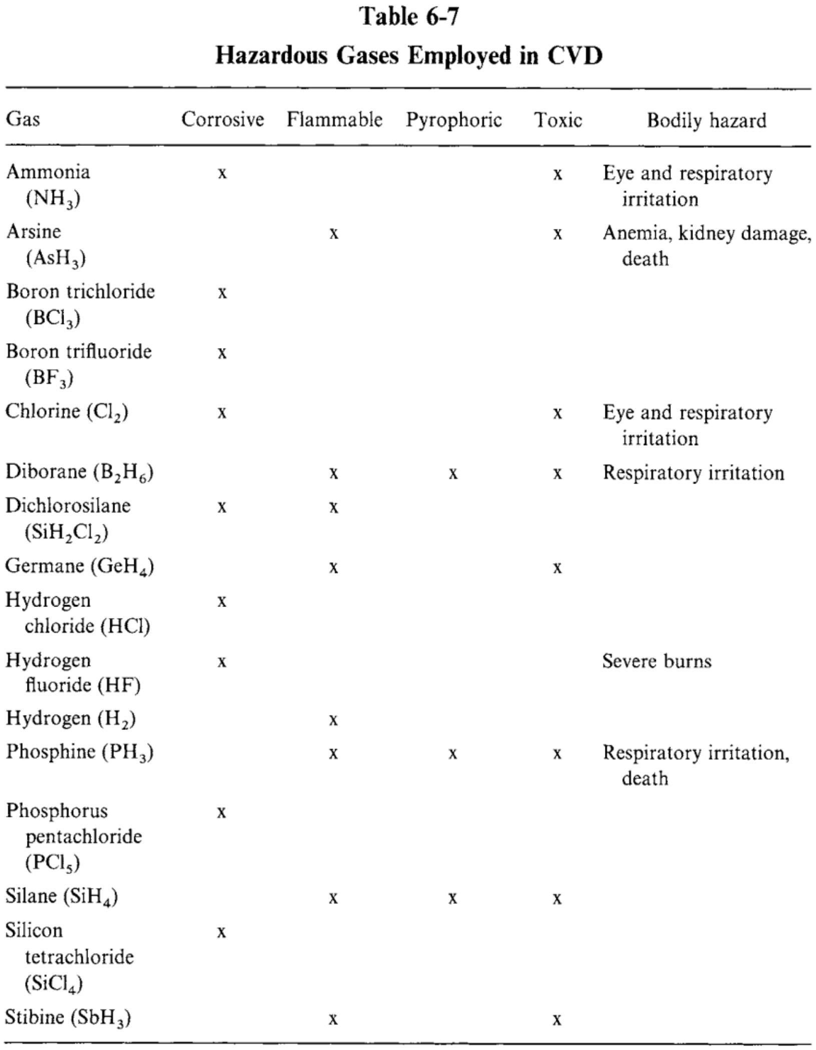

Table 6-7

Hazardous Gases Employed in CVD

Gas	Corrosive	Flammable	Pyrophoric	Toxic	Bodily hazard
Ammonia (NH_3)	x			x	Eye and respiratory irritation
Arsine (AsH_3)		x		x	Anemia, kidney damage, death
Boron trichloride (BCl_3)	x				
Boron trifluoride (BF_3)	x				
Chlorine (Cl_2)	x			x	Eye and respiratory irritation
Diborane (B_2H_6)		x	x	x	Respiratory irritation
Dichlorosilane (SiH_2Cl_2)	x	x			
Germane (GeH_4)		x		x	
Hydrogen chloride (HCl)	x				
Hydrogen fluoride (HF)	x				Severe burns
Hydrogen (H_2)		x			
Phosphine (PH_3)		x	x	x	Respiratory irritation, death
Phosphorus pentachloride (PCl_5)	x				
Silane (SiH_4)		x	x	x	
Silicon tetrachloride ($SiCl_4$)	x				
Stibine (SbH_3)		x		x	

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Summary

- Instead of the physical transfer of atoms from a condensed evaporation source or sputtering target to the substrate, CVD relies on gas phase and gas-solid chemical reactions to produce thin films.
- Fundamental steps at the surface are: Convective and diffusive transport of reactants, Chemical reactions in the gas phase, Transport to the substrate surface, Adsorption and diffusion, chemical reaction at surface, desorption of volatile by-products, Convective and diffusive transport of the reaction by-products away
- Reaction types are Pyrolisis, Reduction, Oxidation, Compound formation, Disproportionisation or reversible Transfer
- Thermal CVD of silicon exploits the silane reaction as silane is less stable as Chloride based precursors -> highest growth rate for all thermodynamic possible reactions
- Vapour supersaturation determines the grain size in CVD
- Nucleation rate on various surfaces: K, S, F faces; linear, exponential, and square dependence
- Diffusion involves motion of individual atoms, but viscous flow and convection moves the gas as a whole
- convection arises from the response to gravitational, centrifugal, electric, and magnetic forces
- Molecular flow vs viscous flow vs turbulent flow and its relation to boundary layer thickness

- Viscous flow happens above 0.01atm. A boundary layer establishes at tube/reactor where the the velocity drops to zero.
- The Reynolds number defines the boundary layer thickness and marks the transition from laminar to turbulent flow above Re>2100.
- Growth regimes are determined by pressure and the related mean free path of species (Knudsen number): atm-10mbar: kinetics and mass transport dominant, <1mbar surface reactions are important, <10^{-4}mbar temperature of gas and surface and desorption of precursor fragments

Summary

- Turbulent flow happens at Re>2100. Note role of pipe diameter or length of surface along gas flow
- Modelling mostly numerical, but dimensionless numbers such as Knudsen, Peclet, or Reynolds guide the process
- Thermal CVD: active surface sites are important, temperature drives vapor supersaturation. Growth regimes are reaction rate limited, diffusion/mass transport limited and desortption rate limited
- Batch processing ideally in surface reaction limited mode
- MOCVD precursors exhibit high volatility at moderately low temperatures which allows control of gas flow rates instead controlling vapour pressure of solids.
- PECVD expoits rf diode discharges to decompose gas molecules into a variety of reactive species enabling lower process temperatures
- Silicon nitride is stoichiometric with thermal CVD at 900° and amorphous & hydrogenated after PECVD at 300°.
- Example carbon: DLC as low-T PECVD and diamond as Thermal CVD
- CVD precursors and reaction products are typically toxic, flammable, pyrophoric, or corrosive substances and are therefore a health hazard to humans

In General because they are subject to thermodynamic and kinetic limitations and constrained by the flow of gaseous reactants and products, CVDprocesses are generally more complex than those involving PVD. An impressive number of different CVD materials (metals, elemental and compound semiconductors, oxides, nitrides, carbides, diamond, etc.) can be synthesized. These materials and applications needs have been fulfilled through a variety of CVD processes involving different reactor designs and operating conditions.

exercises

- Compare CVD, ALD and PVD and explain at least 3 fundamental differences
- What are the different steps governing the mechanisms of CVD?
- Give 3 examples of reaction types in CVD (chemical reaction formulas)
- Why is silane preferred over chlorine based precursors in thermal CVD of silicon?
- Explain the relation between vapor supersaturation and grain size
- Explain the difference between diffusion, convection and viscous flow
- How does the pressure influence CVD processes. Use the Knudsen number for your arguments
- Explain viscous vers Turbulent flow. How can we estimate the transition. Use the Reynolds number equation to discuss strategies to avoid turbulent flow.
- Explain surface /Reaction Rate) vs mass transport limited reactions
- Explain desorption rate limited Regime
- How does pressure affect deposition rate?
- How does one switch between reaction controlled and diffusion-controlled regimes? •
- How does the regime (reaction- vs. diffusion controlled) affect CVD system design?
- Why is the Reaction Rate Limited Regime the Regime of choice for batch coating using hot wall CVD reactors
- Why is MOCVD so popular in terms of process control?
- Explain the advantages and disadvantages of atmospheric CVD, LPCVD, and PECVD

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