

## Thin film processes

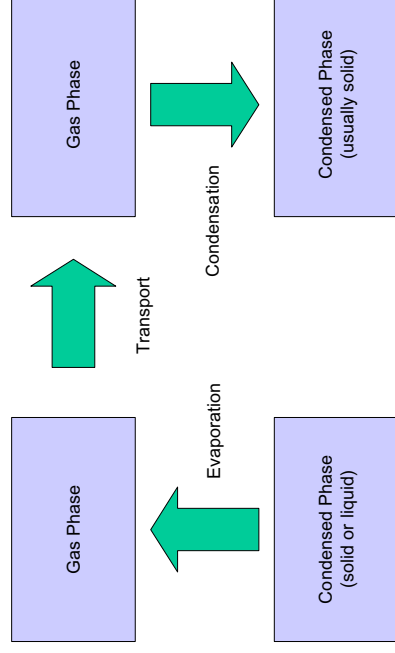
- “grown” films
  - typically “converted” from original substrate material
    - example: SiO<sub>2</sub> formed by oxidation of Si substrate
- “deposited” films
  - crystalline, poly crystalline, amorphous
  - electro-deposition
    - not standard IC process
  - liquid phase deposition
    - not standard IC process
  - vapor phase deposition
    - PVD: physical vapor deposition
    - CVD: chemical vapor deposition

## CVD, Oxidation, and Diffusion

### Fundamentals of Micromachining

Dr. Bruce K. Gale  
BIOEN 6421  
EL EN 5221 and 6221  
ME EN 5960 and 6960

## Physical Vapor Deposition

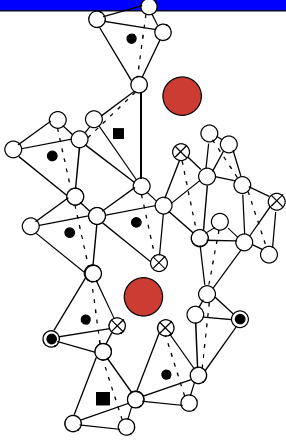


## Thin-Film Deposition

- Spin-on Films
  - Polyimide (PI), photoresist (PR)
  - Spin-on glass (SOG)
- Physical Vapor Deposition (PVD)
  - Evaporation
  - Sputtering
- Chemical Vapor Deposition (CVD)
  - Oxidation
  - LPCVD
  - PECVD

## Silicon Oxides: SiO<sub>2</sub>

- **Uses:**
  - diffusion masks
  - surface passivation
  - gate insulator (MOSFET)
  - isolation, insulation
- **Formation:**
  - grown / "native"
    - thermal: "highest" quality
    - anodization
  - deposited:
    - CVD, evaporate, sputter
- **amorphous silica: material is a GLASS under "normal" circumstances**
  - can also find "crystal quartz" in nature
- **m.p. 1732° C; glass is "unstable" below 1710° C**
  - BUT devitrification rate (i.e. crystallization) below 1000° C negligible



- bridging oxygen
- ⊗ non-bridging oxygen
- silicon
- network modifier
- network former
- hydroxyl group

## Stages of Thin Film Growth

- Island Stage
- Coalescence Stage
- Channel Stage
- Continuous Film Stage

## Thermal Oxidation of Silicon

- Formation of the oxide of silicon on the silicon surface is known as oxidation .
- Thermal Oxidation is characterized by high temperatures (900 - 1200 C) .
- Two main processes :
  - Dry Oxidation
    - $\text{Si(s)} + \text{O}_2 \rightarrow \text{SiO}_2$  1 atm, 1000 C
  - Wet Oxidation
    - $\text{Si(s)} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2$
- Dry oxidation produces a better (more dense) oxide as compared to wet oxidation.

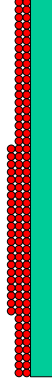
## Modes of Thin Film Growth

(1) Volmer-Weber: (island growth):



M. Volmer and A. Weber, *Z. Phys. Chem.* **119**, p. 277 (1926).

(2) Frank- Van der Merwe: (layer growth; ideal epitaxy):



F. C. Frank and J. H. Van der Merwe, *Proc. R. Soc. London, Ser. A* **198**, p. 205 (1949).

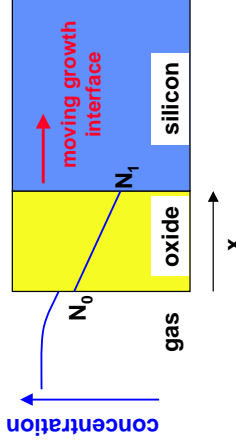
(3) Stranski-Krastanov: (layers + islands):



J. N. Stranski and L. Krastanov, *Ber. Akad. Wiss. Wien* **146**, p. 797 (1938).

## Oxide growth kinetics

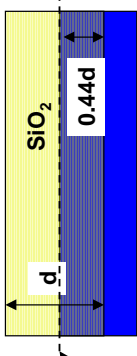
- basic model is the Grove and Deal Model
  - supply of oxidizer is limited by diffusion through oxide to growth interface
  - Fick's First Law: flux  $j = -D \frac{\partial N_{\text{oxidizer}}}{\partial x}$



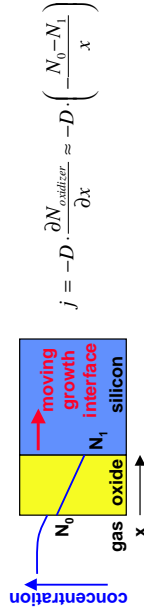
- simplest approximation:  $\frac{\partial N}{\partial x} = -\frac{N_0 - N_1}{x}$

## Growth of SiO<sub>2</sub> from Si

- in dry (<< 20 ppm H<sub>2</sub>O) oxygen
  - Si + O<sub>2</sub> → SiO<sub>2</sub>
  - once an oxide is formed, how does this chemical reaction continue?
    - does the oxygen go "in" or the silicon go "out"?
- density / formula differences
  - $\rho_{\text{SiO}_2} = 2.25 \text{ gm/cm}^3$ , GMW = 60
  - $\rho_{\text{Si}} = 2.3 \text{ gm/cm}^3$ , GMW = 28
  - oxide d thick consumes a layer 0.44d thick of Si original silicon surface
- "bare" silicon in air is "always" covered with about 15-20 Å of oxide, upper limit of ~ 40 Å
  - it is possible to prepare a hydrogen terminated Si surface to retard this "native" oxide formation



## Oxidizer concentration gradient and flux



$$j = -D \cdot \frac{\partial N_{\text{oxidizer}}}{\partial x} \approx -D \left( -\frac{N_0 - N_1}{x} \right)$$

- N<sub>0</sub> is limited by the solid solubility limit of the oxidizer in the oxide!
  - N<sub>0</sub><sup>O<sub>2</sub></sup> ~ 5 x 10<sup>16</sup> cm<sup>-3</sup> @ 1000° C
  - N<sub>0</sub><sup>H<sub>2</sub>O</sup> ~ 3 x 10<sup>19</sup> cm<sup>-3</sup> @ 1000° C
- flux of oxidizer j' at SiO<sub>2</sub> / Si interface consumed to form new oxide
  - $j' = k \cdot N_1$
- k is the chemical reaction rate constant
- in steady state, flux in must equal flux consumed

$$j'_{\text{steady state}} = j \Rightarrow k \cdot N_1 = -D \cdot \left( -\frac{N_0 - N_1}{x} \right)$$

solve for N<sub>1</sub>, sub back into flux eq

$$j = \frac{D \cdot N_0}{x + D/k}$$

## "Wet" oxidation of Si

- overall reaction is
    - Si + 2 H<sub>2</sub>O → SiO<sub>2</sub> + H<sub>2</sub>
  - proposed process
    - H<sub>2</sub>O + Si-O-Si → Si-OH + Si-OH
    - diffusion of hydroxyl complex to SiO<sub>2</sub> -Si interface
- $$\begin{array}{l} \text{Si - OH} \\ \text{Si - O - Si} \\ \text{Si - O - Si} \end{array} + \text{Si - Si} \rightarrow \begin{array}{l} \text{Si - O - Si} \\ \text{Si - O - Si} \end{array} + \text{H}_2$$
- this results in a more open oxide, with lower density, weaker structure, than dry oxide
    - $\rho_{\text{wet}} \approx 2 \cdot 15 \text{ gm/cm}^3$

## Limiting behavior of Grove & Deal oxidation model

$$x(t) = \frac{A}{2} \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right]$$

- “short times”

$$t + \tau \ll A^2/4B$$

$$x(t) = \frac{A}{2} \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right] \xrightarrow{\text{yellow}} x(t) \approx \frac{A}{2} \left[ \left( 1 + \frac{1}{2} \cdot \frac{t+\tau}{A^2/4B} \right) - 1 \right] = \frac{B}{A} (t+\tau)$$

- thickness is linearly increasing with time
- characteristic of a reaction rate limited process
- B/A is the “linear rate constant”

$$\frac{B}{A} = \left( \frac{2 \cdot DN_{SiO_2}}{n} \right) / \left( \frac{2 \cdot D}{k} \right) = \frac{N_{SiO_2} \cdot k}{n}$$

- linear rate constant depends on
  - reaction rate between oxidizer and silicon (**k**) AND
  - solid solubility of oxidizer in oxide (**N<sub>0</sub>**)
  - temperature dependence mainly from reaction rate

## Limiting behavior of Grove & Deal oxidation model

$$x(t) = \frac{A}{2} \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right]$$

- “long times”

$$t + \tau \gg A^2/4B$$

$$x(t) = \frac{A}{2} \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right] \xrightarrow{\text{yellow}} x(t) \approx \frac{A}{2} \left[ \sqrt{\frac{t+\tau}{A^2/4B}} \right] = \sqrt{B \cdot (t+\tau)}$$

- dependence is “parabolic”: (thickness)<sup>2</sup> ∝ time
- characteristic of a diffusion limited process
- B is the “parabolic rate constant”

$$B = \frac{2 \cdot D \cdot N_0}{n}$$

- parabolic rate constant depends on
  - diffusivity of oxidizer in oxide (**D**) AND
  - solid solubility of oxidizer in oxide (**N<sub>0</sub>**)
  - temperature dependence mainly from diffusivity

## Relation between flux and interface position

- flux: #oxidizer molecules crossing interface per unit area per unit time
  - # cm<sup>2</sup> sec<sup>-1</sup>
- rate of change of interface position: dx / dt (interface velocity)
  - cm sec<sup>-1</sup>
- n: # of oxidizer molecules per unit volume of oxide:
  - # cm<sup>-3</sup>
  - $n = \frac{\rho_{SiO_2} \cdot N_A}{GMW_{SiO_2}} \cdot \begin{cases} 2 & \text{for H}_2\text{O} \\ 1 & \text{for O}_2 \end{cases} = 2.25 \times 10^{22} \text{ cm}^{-3} \cdot \begin{cases} 2 & \text{for H}_2\text{O} \\ 1 & \text{for O}_2 \end{cases}$
- then relation is just
  - $\frac{dx}{dt} = \frac{j}{n} = \frac{DN_{O_2}/n}{x + D/k}$
  - now integrate with appropriate initial condition

## Grove and Deal relation

- setting
  - $2D/k = A$
  - function of what's diffusing, what it's diffusing in, and what it reacts with
  - $2DN_0/n = B$
  - function of what's diffusing and what it's diffusing in
  - initial condition  $x(t=0) = x_i$
  - integration gives

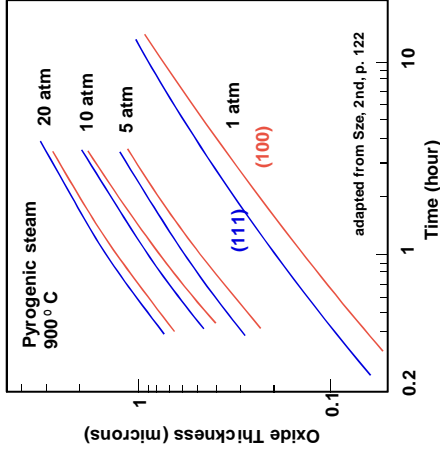
$$x(t) = \frac{A}{2} \left[ \sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right]$$

- where  $\tau$  represents an “offset” time to account for any oxide present at  $t = 0$

$$\tau = \frac{(x_i)^2 + A \cdot x_i}{B}$$

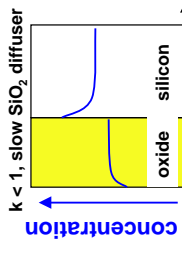
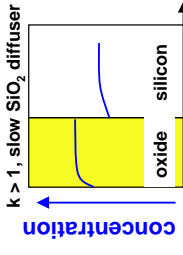
## Pressure Effects on Oxidation

- grow thick oxides at reduced time / temperature product
  - use elevated pressures to increase concentration of oxidizer in oxide
    - for steam, both B and B/A ~ linear with pressure
    - rule of thumb: constant growth rate, if for each increase of 1 atm pressure, temperature is reduced ~ 30° C.
  - pressures up to 25 atm have been used (commercial systems: HIPOX, FOX)



## Effect of Si doping on oxidation kinetics

- boron**
  - $k = C_{ox} / C_{Si} \sim 3$
  - dopants accumulate in oxide
    - little effect on linear rate constant B/A (=  $N_b k / n$ )
    - can increase parabolic rate constant B (=  $2DN_b / n$ )
      - really only significant for  $N_{boron} > \sim 10^{20} \text{ cm}^{-3}$
- phosphorus**
  - $k = C_{ox} / C_{Si} \sim 0.1$
  - dopants “pile-up” at silicon surface
    - little effect on parabolic rate constant B
    - increases linear rate constant B/A
      - again, really only significant for  $N_{phosphorus} > \sim 10^{20} \text{ cm}^{-3}$

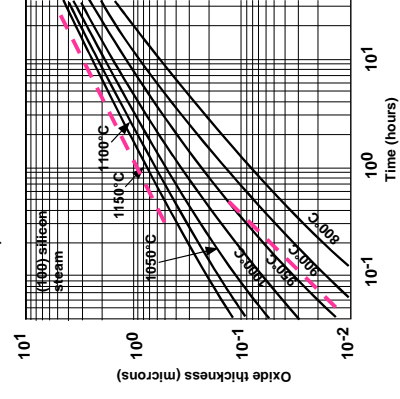
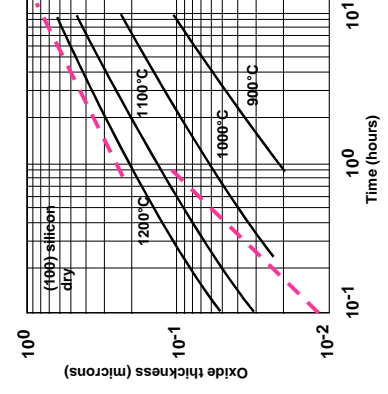


## Types of CVD

- Atmospheric Pressure CVD (APCVD)
- Low Pressure CVD (LPCVD)
- Plasma Enhanced CVD (PECVD)

## Oxidation thicknesses

- dry oxidation
  - 1200°C
  - 1100°C
  - 1000°C
  - 900°C
- wet oxidation
  - 640 Torr partial pressure is typical (vapor pressure over liquid water @ 95°C)
  - 1150°C
  - 1100°C
  - 1050°C
  - 1000°C
  - 900°C
  - 800°C



## Chemical Vapor Deposition (CVD)

- CVD = formation of non-volatile solid film on substrate by reaction of vapor phase chemicals
- Steps in CVD
  - Gases are introduced into a reaction chamber
  - Gas species move to the substrate
  - Reactants are adsorbed on the substrate
  - Film-forming chemical reactions
  - Desorption and removal of gaseous by-products

## Low Temperature Oxidation of Silicon

- (LTO) SiO<sub>2</sub> is formed using three types of CVD Processes.
- APCVD (Most commonly used method), LPCVD and PECVD
- SiH<sub>4</sub> + O<sub>2</sub> : ----->SiO<sub>2</sub> + 2H<sub>2</sub> (240 - 550 C)
- (200 - 500 nm/min optimal) and (1400 nm/min possible).
- Deposition rate increases slowly with increased T (310- 450 C)
- Deposition rate can also be increased by increasing the O<sub>2</sub>/SiH<sub>4</sub> ratio
- APCVD : 325 C ratio 3:1 , 475 C ratio 23:1 , 550 C ratio 60: 1
- LPCVD : 360 C ratio 1:1 , 450 C ratio 1.45 : 1
- Deposition can occur in the APCVD as low as 130 C
- For LPCVD Window (100 - 330 C) 2-12 torr and 14 nm/min at 300 C

## CVD reactions

- Heterogeneous = occur at wafer surface
  - Desirable
  - Produce good quality films
- Homogeneous = occur in gas phase
  - Undesirable
  - Form gas phase clusters of material
  - Consume reactants
  - Reduce deposition rate

## Chemical vapor deposition

- **general characteristic of gas phase chemical reactions**
  - pressures typically atmospheric to 50 mTorr
    - $\lambda$  ranges from  $\ll 1 \mu\text{m}$  to  $\sim 1 \text{mm}$
  - reactions driven by
    - thermal: temperatures 100° - 1000° C
      - higher temperature processes increase surface migration/mobility
    - plasma
    - optical
- **example materials**
  - polycrystalline silicon (poly)
  - silicon dioxide
  - phosphosilicate, borosilicate, borophosphosilicate glasses
    - PSG, BSG, BPSG
  - silicon nitride

## Low Temperature oxide formation by APCVD /LPCVD/ PECVD vs. Thermal Oxidation of Silicon

- **ADVANTAGES**
- Low temperatures
- Fast Deposition rates especially APCVD .
- Good Step Coverage especially PECVD.
- **DISADVANTAGES**
- Contamination especially PECVD.
- Inferior electrical properties of PECVD films as compared with thermally grown ones.
- Less dense films are obtained .

## CVD Reaction Rate (R)

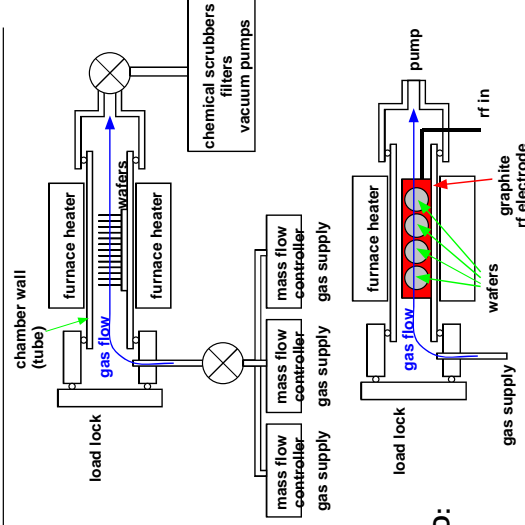
- $R = R_0 \exp(-E_a/kT)$ 
  - where  $E_a$  = activation energy (eV)
  - $k$  = Boltzmann constant
  - $T$  = temperature (K)
- Surface reaction rate increases with increasing temperature at very high temperature
  - Reaction rate > reactant arrival rate
  - Mass-transport limited
- At low temperatures
  - Reaction rate < reactant arrival rate
  - Reaction rate limited

## PECVD

- $\text{SiH}_4 + 2\text{N}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{N}_2 + 2\text{H}_2$  (200- 400 C) , RF, 0.1 - 5 torr .
- Low ratio of  $\text{N}_2\text{O} / \text{SiH}_4$  will increase “n” leading to formation of silicon rich films .
- Lower deposition temperatures and higher ratios of  $\text{N}_2\text{O} / \text{SiO}_2$  will lead to less dense films and faster etch rates
- HF etch rate is a measure of the film’s density
- Densification of films

## CVD system design: hot wall reactors

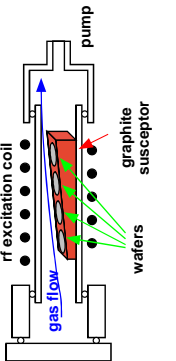
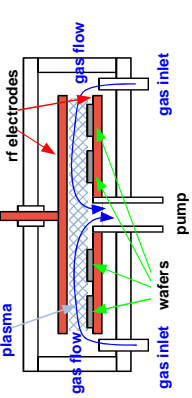
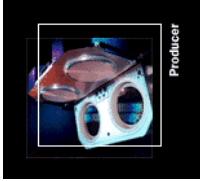
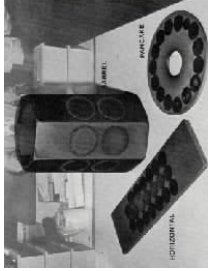
- **heat entire system:** thermally driven reactions
  - requires leak-tight, sealed system
    - avoid unwanted contamination, escape of hazardous materials (the reactants)
  - atmospheric: high deposition rates
  - low pressure (LPCVD): lower rates, good uniformity



## plasma assisted CVD: PECVD



## Basic configurations

- horizontal tube reactor
 
  - parallel plate plasma reactor
 
- “pancake” configuration is similar
- barrel reactor
 
  - single wafer systems
 

from:  
<http://www.appliedmaterials.com/prod/ucts/pdd.html>

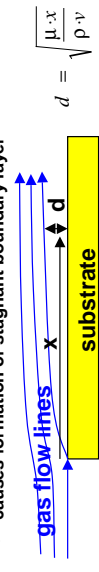
## Cold wall reactors

- heat substrate “only” using
  - resistive heating (pass current through “susceptor”)
  - inductive heating (external rf fields create eddy currents in conductive susceptor)
  - optical heating (lamps generate IR, absorbed by susceptor)
- advantages
  - reduces contamination from hot furnace walls
  - reduces deposition on chamber walls
- disadvantages
  - more complex to achieve temperature uniformity
  - hard to measure temperature
    - inherently a non-isothermal system

## CVD Chemistries

- Silicon Oxide
  - Dry Oxidation:  $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$
  - Wet Oxidation:  $\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2$
  - $\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2$
  - $\text{SiH}_4 + \text{N}_2\text{O} \rightarrow \text{SiO}_2 + \text{by-products}$
  - $\text{SiCl}_2\text{H}_2 + \text{N}_2\text{O} \rightarrow \text{SiO}_2 + \text{by-products}$
  - $\text{Si}(\text{OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 + \text{byproducts}$

## Gas flow in CVD systems

- purely “turbulent” flow
    - reactants are well mixed, no “geometric” limitations on supply of reactants to wafer surface
      - typical of LPCVD tube furnace design
  - interaction of gas flow with surfaces
    - away from surfaces, flow is primarily laminar
    - friction forces velocity to zero at surfaces
      - causes formation of stagnant boundary layer
- 
- $$d = \sqrt{\frac{\mu \cdot x}{\rho \cdot v}}$$
- v: velocity;  $\rho$ : density;  $\mu$ : viscosity
  - reactant supply limited by diffusion across boundary layer
  - geometry of wafers relative to gas flow critical for film thickness uniformity
    - to improve boundary layer uniformity can tilt wafer wrt gas flow



## Material examples: polysilicon

- **uses**
  - gates, high value resistors, “local” interconnects
- **deposition**
  - silane pyrolysis:  $600^{\circ}\text{--}700^{\circ}\text{C}$   $\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$ 
    - atmospheric, cold wall, 5% silane in hydrogen,  $\sim 1/2$   $\mu\text{m}/\text{min}$
    - LPCVD ( $\sim 1$  Torr), hot wall, 20-100% silane,  $\sim$ hundreds  $\text{nm}/\text{min}$
  - grain size dependent on growth temperature, subsequent processing
    - $950^{\circ}\text{C}$  phosphorus diffusion, 20 min:  $\sim 1$   $\mu\text{m}$  grain size
    - $1050^{\circ}\text{C}$  oxidation:  $\sim 1\text{--}3$   $\mu\text{m}$  grain size
- **in-situ doping**
  - p-type: diborane  $\text{B}_2\text{H}_6$ :  $\rho \sim 0.005$   $\Omega\text{-cm}$  (B/Si  $\sim 2.5 \times 10^{-3}$ )
    - can cause substantial increase in deposition rate
  - n-type: arsine  $\text{AsH}_3$ , phosphine  $\text{PH}_3$ :  $\rho \sim 0.02$   $\Omega\text{-cm}$ 
    - can cause substantial decrease in deposition rate
- **dope after deposition (implant, diffusion)**

## Metal CVD

- **tungsten**
  - $\text{WF}_6 + 3\text{H}_2 \rightleftharpoons \text{W} + 6\text{HF}$
  - cold wall systems
  - $\sim 300^{\circ}\text{C}$
  - can be selective
  - adherence to  $\text{SiO}_2$  problematic
    - TiN often used to improve adhesion
    - causes long “initiation” time before W deposition begins
  - frequently used to fill deep (“high aspect ratio”) contact vias
- **aluminum**
  - tri-isobutyl-aluminum (TIBA)
  - LPCVD
  - $\sim 200^{\circ}\text{--}300^{\circ}\text{C}$ , tens  $\text{nm}/\text{min}$  deposition rate
- **copper**
  - Cu  $\beta$ -diketones,  $\sim 100^{\circ}\text{--}200^{\circ}\text{C}$

## CVD Chemistries

- **Silicon Nitride**
  - $3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2$
  - $\text{SiCl}_2\text{H}_2 + \text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + \text{by-products}$
  - $\text{SiH}_4 + 4\text{N}_2\text{O} \rightarrow \text{Si}_3\text{N}_4 + \text{by products}$
  - $\text{SiH}_4 + \text{N}_2 \rightarrow \text{Si}_3\text{N}_4 + \text{by products}$

## CVD Chemistries

- **Polysilicon:**  $\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$
- **Silicon Carbide**
- **Polycrystalline Diamond**
- **Parylene (polymerized p-xylylene)**
- **Refractory Metals:**
  - $2\text{WF}_6 + 3\text{SiH}_4 \rightarrow 2\text{W} + 3\text{SiF}_4 + 6\text{H}_2$
- **II-VI compounds (e.g., CdSe)**

## Safety issues in CVD

- most gases used are toxic, pyrophoric, flammable, explosive, or some combination of these
  - silane,  $\text{SiH}_4$ 
    - toxic, burns on contact with air
  - phosphine
    - very toxic, flammable
  - ammonia
    - toxic, corrosive
- how to deal with this?
  - monitor!
  - limit maximum flow rate from gas sources
    - helps with dispersal problem associated with gases
  - double walled tubing, all welded distribution networks

## CVD silicon dioxide

- thermally driven reaction
  - mid-temperature:  $\sim 500^\circ\text{C}$ 
    - "LTO" (low-temp. oxide)  $T < \sim 500^\circ\text{C}$
    - $\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + \text{H}_2$
    - cold-wall, atmospheric,  $\sim 0.1 \mu\text{m}/\text{min}$
    - hot-wall, LPCVD,  $\sim 0.01 \mu\text{m}/\text{min}$
  - plasma-enhanced reaction (PECVD)
    - low temperature:  $\sim 250^\circ\text{C}$
    - high temperature:  $\sim 700^\circ\text{C}$ 
      - tetraethyl orthosilicate (TEOS)
        - $\text{Si}(\text{OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 + \text{by-products}$
  - new materials
    - low "k" dielectrics
      - interlevel insulation with lower dielectric constants ( $k < \sim 3$ )
        - fluorinated oxides, spin-on glasses, organics
      - high k dielectrics:  $k > \sim 25\text{-}100$ 's
        - gate insulators, de-coupling caps

## Deposited thin films

- need to be able to add materials "on top" of silicon
  - both conductors and insulators
- deposition methods
  - physical vapor deposition (PVD)
    - thermal evaporation
    - sputtering
  - chemical vapor deposition (CVD)
- general requirements
  - good electrical characteristics
  - free from pin-holes, cracks
  - low stress
  - good adhesion
  - chemical compatibility
    - with both layer "below" and "above"
    - at room temperature and under deposition conditions

## Silicon nitride $\text{Si}_3\text{N}_4$

- uses
  - diffusivity of  $\text{O}_2$ ,  $\text{H}_2\text{O}$  is very low in nitride
  - mask against oxidation, protect against water/corrosion
  - diffusivity of Na also very low
  - protect against mobile ion contamination
- deposition
  - stoichiometric formulation is  $\text{Si}_3\text{N}_4$ 
    - in practice Si/N ratio varies from 0.7 (N rich) to 1.1 (Si rich)
  - LPCVD:  $\sim 700^\circ\text{C} - 900^\circ\text{C}$ 
    - $3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2$ ;  $3\text{Si}_2\text{Cl}_2\text{H}_2 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 6\text{HCl} + 6\text{H}_2$
    - Si/N ratio 0.75, 4-8% H
    - $\rho \sim 3 \text{ g}/\text{cm}^3$ ;  $n \sim 2.0$ ;  $k \sim 6\text{-}7$
    - stress:  $\sim 10 \text{ Gdyne}/\text{cm}^2$ , tensile
  - PECVD:  $\sim 250^\circ\text{C} - 350^\circ\text{C}$ 
    - $\text{aSiH}_4 + \text{bNH}_3 \rightarrow \text{Si}_x\text{N}_y\text{H}_z + \text{cH}_2$
    - $\text{aSiH}_4 + \text{bN}_2 \rightarrow \text{Si}_x\text{N}_y\text{H}_z + \text{cH}_2$
    - Si/N ratio 0.8-1.2,  $\sim 20\%$  H
    - $\rho \sim 2.4\text{-}2.8 \text{ g}/\text{cm}^3$ ;  $n \sim 1.8\text{-}2.5$ ;  $k \sim 6\text{-}9$
    - stress:  $\sim 2\text{-}5 \text{ T Gdyne}/\text{cm}^2$

# Impact of pressure on deposition conditions

- pressure influences
  - mean free path:  $\lambda \propto 1/P$
  - "contamination rate":  $\tau \propto 1/P$

pressure (Torr)	number density (#/cm <sup>3</sup> )	$\lambda$	$n_{d=1m}$	$\tau$
760	$2.7 \times 10^{19}$	0.07 $\mu\text{m}$	~ 0	3.3 nsec
$10^{-3}$	$3.5 \times 10^{13}$	5 cm	$2 \times 10^{-7}$ %	2.5 msec
$10^{-6}$	$3.5 \times 10^{10}$	50 m	98 %	2.5 sec
$10^{-9}$	$3.5 \times 10^7$	50 km	100 %	42 min
$10^{-12}$	$3.5 \times 10^4$	50,000 km		29 days

rough vacuum  
 high vacuum  
 very high vacuum

# Kinetic theory of gases

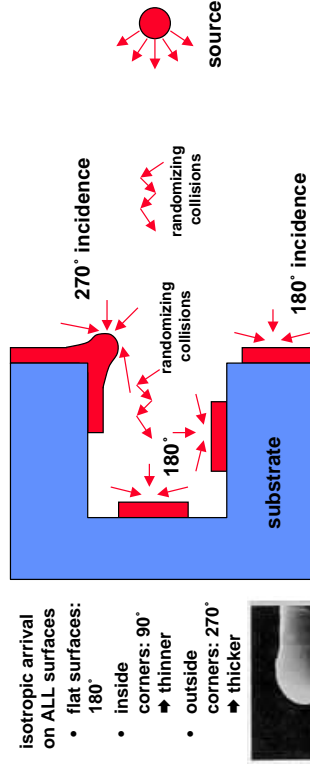
- for a gas at STP:
  - $N \sim 2.7 \times 10^{19}$  molecules/cm<sup>3</sup>
  - $N \propto$  pressure
    - one atmosphere =  $1.0132 \times 10^5$  pascal = 760 Torr (mm Hg)
    - 1 Pascal = 1/132 Torr  $\sim 10^{-5}$  atms
- fraction of molecules traveling distance  $d$  without colliding is

$$\frac{n_{no\ collisions}}{n_{gas}} = e^{-\frac{d}{\lambda}}$$

- $\lambda$  is the mean free path  $\lambda = \frac{k \cdot T}{P \cdot \pi \cdot \sigma^2 \cdot \sqrt{2}}$ 
  - at room temp  $\lambda \sim 0.7$  cm / P (in pascals)
  - $\sim 5.3 \times 10^{-3}$  cm / P (in Torr)
- at room temp and one atmosphere  $\lambda \sim 0.07$   $\mu\text{m}$

# Impact of pressure on deposition conditions

- material arrival angular distribution
  - depends on mean free path compared to both size of system and size of water "steps"
- Case 1: "atmospheric pressure": 760 Torr  $\rightarrow \lambda = 0.07$   $\mu\text{m}$ 
  - $\lambda \ll$  system & steps



assume material does NOT migrate after arrival!

# Velocity distribution

- for ideal gas, velocity distribution is Maxwellian

$$c = \sqrt{\frac{kT}{2\pi m}}$$

- we'll use  $c = \sqrt{\frac{kT}{2\pi m}}$
- ~ 900 miles/hour at rm temp

- rate of surface bombardment (flux)

$$j_{gas} (\# / \text{unit area} \cdot \text{time}) = n_{gas} \cdot v_{unit\ volume} \cdot \text{velocity}$$

$$= \left( \frac{P}{kT} \right) \cdot c = \frac{P}{\sqrt{2\pi m kT}}$$

$$P \cdot \frac{V}{unit\ vol} = n kT$$

- $j = 3.4 \times 10^{22}$  (# / cm<sup>2</sup> • sec) • P /  $\sqrt{MT}$

- P in Torr, M is gram-molecular mass

- monolayer formation time  $\tau$

$$\tau \approx \frac{10^{15} \text{ cm}^{-2}}{j} \approx \frac{2.6 \times 10^{-6}}{P \text{ (in Torr)}} \text{ sec}$$

- # molecules per unit area / bombard rate

## summary of SiO<sub>2</sub> characteristics

temperature	plasma ~200°C	SiH <sub>4</sub> + O <sub>2</sub> ~450°C	TEOS ~700°C	thermal ~1000°C
composition	SiO <sub>1.9</sub> (H)	SiO <sub>2</sub> (H)	SiO <sub>2</sub> conformal	SiO <sub>2</sub> "conformal"
step coverage	non-conformal loses H	non-conformal densifies	stable	stable
thermal stability	2.3	2.1	2.2	2.2
density (g/cm <sup>3</sup> )	3C - 3T	3T	1C	3C
stress (Mdyne/cm <sup>2</sup> )	3-6	8	10	11
dielectric strength (MV/cm)	1.47	1.44	1.46	1.46
index of refraction (632.8 nm)	4.9	4.3	4.0	3.9

adapted from Sze, 2nd, p. 259.

## "low" pressure: $\lambda \ll$ system, $\lambda >$ step

- Case II: 10<sup>-1</sup> Torr →  $\lambda = 0.5$  mm

- small compared to system, large compared to wafer features
- isotropic arrival at "flat" surface

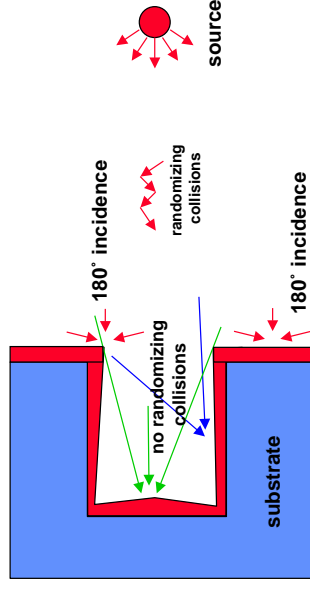
- BUT no scattering inside "hole"!!**

- top flat surface: 180°

- "inside" surface: depends on location!

- shadowing by corners of features

- "anisotropic" deposition



assumes material does NOT migrate after arrival!!

## "vacuum" conditions: $\lambda >$ system, $\lambda >$ step

- case III: 10<sup>-5</sup> Torr →  $\lambda = 5$  meters

- long compared to almost everything

- anisotropic arrival at all surfaces!

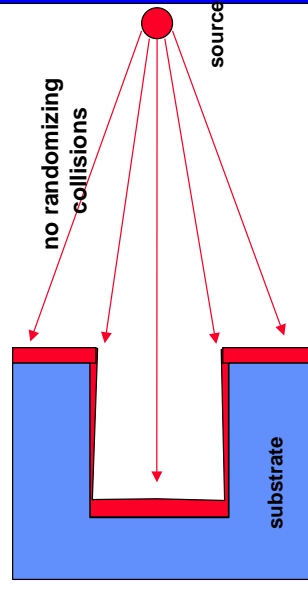
- geometric "shadowing" dominates

- anisotropic deposition

- "line-of-sight" deposition

- very thin on "side walls"

- very dependent on source configuration relative to sample surface



assumes material does NOT migrate after arrival!!