### Thin film processes

- "grown" films
  - typically "converted" from original substrate material
    - example: SiO2 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

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

- Uses:
  - diffusion masks
  - surface passivation
  - gate insulator (MOSFET)
  - isolation, insulation
- Formation:
  - grown / "native"
    - thermal: "highest" quality
    - anodization
  - deposited:
    - C V D, evaporate, sputter
- vitreous 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



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

- in dry (<< 20 ppm H2O) oxygen
  - Si +  $O_2 \rightarrow SiO_2$
  - once an oxide is formed, how does this chemical reaction continue?
    - does the oxygen go "in" or the silicon go "out"?
- density / formula differences
  - $ρ_{siO2}$  = 2.25 gm/cm<sup>3</sup> , GMW = 60
  - $-~\rho_{\text{Si}}$  = 2.3 gm/cm<sup>3</sup> , 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

### "Wet" oxidation of Si

- overall reaction is
  - $\hspace{0.1 cm} \text{Si} + 2 \hspace{0.1 cm} \text{H}_2 \text{O} \hspace{0.1 cm} \rightarrow \hspace{0.1 cm} \text{SiO}_2 \hspace{0.1 cm} + \hspace{0.1 cm} \text{H}_2$
- proposed process
  - H<sub>2</sub>O + Si-O-Si  $\rightarrow$  Si-OH + Si-OH
  - diffusion of hydroxyl complex to SiO<sub>2</sub> -Si interface

 $\begin{array}{ccc} \text{Si} - \text{OH} & & \text{Si} - \text{O} - \text{Si} \\ & & + \text{Si} - \text{Si} \rightarrow & & + \text{H}_2 \\ \text{Si} - \text{OH} & & & \text{Si} - \text{O} - \text{Si} \end{array}$ 

 this results in a more open oxide, with lower density, weaker structure, than dry oxide

 $- \rho_{wet} \approx 2.15 \text{ gm} / \text{cm}^3$ 

#### **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:

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

# Oxidizer concentration gradient and flux



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

• N<sub>0</sub> is limited by the solid solubility limit of the oxidizer in the oxide!

- N<sub>0</sub><sup>H2O</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

$$j' = j \implies k \cdot N_1 = -D \cdot \left(-\frac{N_0 - N_1}{x}\right) \rightarrow j' = \frac{D \cdot N_0}{x + \frac{D}{k}}$$

# 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:

$$n = \frac{\rho_{SiO_2} \cdot N_A}{GMW_{SiO_2}} \cdot \begin{bmatrix} 2 & \text{for } H_2O \\ 1 & \text{for } O_2 \end{bmatrix} = 2.25 \times 10^{22} \text{ cm}^{-3} \cdot \begin{bmatrix} 2 & \text{for } H_2O \\ 1 & \text{for } O_2 \end{bmatrix}$$

– **# cm**<sup>-3</sup>

• then relation is just

$$\frac{d x}{d t} = \frac{j}{n} = \frac{D N_0/n}{x + D/k}$$

now integrate with appropriate initial condition

#### **Grove and Deal relation**

- setting
  - 2D/k = A
    - function of what's diffusing, what it's diffusing in, <u>and what it</u> 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

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

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

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

#### **Limiting behavior of Grove & Deal** oxidation model $x(t) = \frac{A}{2} \cdot \left[ \sqrt{1 + \frac{t + \tau}{A^2/4B}} - 1 \right]$

• "short times"

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

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

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

$$\frac{B}{A} = \left(\frac{2 DN}{n}\right) \left(\frac{2 D}{k}\right) = \frac{N_0 \cdot k}{n}$$

- linear rate constant depends on
  - reaction rate between oxidizer and silicon (k) AND
  - solid solubility of oxidizer in oxide  $(N_0)$
  - temperature dependence mainly from reaction rate

#### **Limiting behavior of Grove & Deal** oxidation model $x(t) = \frac{A}{2} \cdot \left[ \sqrt{1 + \frac{t + \tau}{A^2/4B}} - 1 \right]$

• "long times"

+ 
$$\tau >> A^2/4 B$$

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

- dependence is "parabolic": (thickness)<sup>2</sup>  $\propto$  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  $(N_0)$
  - temperature dependence mainly from diffusivity

# Effect of Si doping on oxidation kinetics

#### • boron

- k = C<sub>ox</sub> / C<sub>Si</sub> ~ 3
- dopants accumulate in oxide
  - little effect on linear rate constant B/A ( = N<sub>o</sub>k / n)
  - can increase parabolic rate constant B ( = 2DN<sub>o</sub> / 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  $N_{phosphorus} > \sim 10^{20} \text{ cm}^{-3}$





#### **Oxidation thicknesses**







• dry oxidation

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#### **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)



13

## **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

## Kinetic theory of gases

- for a gas at STP:
  - N ~ 2.7 x 10<sup>19</sup> 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 ~ 10<sup>-5</sup> atms
- fraction of molecules traveling distance d without colliding is

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

$$\lambda \text{ is the mean free path } \lambda = \frac{k \cdot \tilde{T}}{P \cdot \pi \cdot \sigma^2 \cdot \sqrt{2}}$$
• at room temp
$$\lambda \sim 0.7 \text{ cm / P (in pascals)}$$

$$\sim 5.3 \times 10^{-3} \text{ cm / P (in Torr)}$$
• at room temp and one atmosphere

λ ~ 0.07 μm

## **Velocity distribution**

- for ideal gas, velocity distribution is Maxwellian
  - we'll use  $\bar{c} = \sqrt{\frac{kT}{2\pi m}}$
  - ~ 900 miles/hour at rm temp
- rate of surface bombardment (flux)

$$i_{gas} (\#/unit \ area \cdot time) = n_{gas}^{unit \ volume} \cdot velocity$$

$$= \underbrace{\left(\frac{P}{kT}\right)}_{ideal \ gas \ law} \cdot \overline{c} = \frac{P}{\sqrt{2\pi m kT}}$$

$$ideal \ gas \ law$$

$$P \cdot \underbrace{V}_{unit \ vol} = n \cdot k \cdot T$$

$$unit \ vol$$

- j = 3.4 x 10<sup>22</sup> (# / cm<sup>2</sup> sec) P /  $\sqrt{MT}$ 
  - P in Torr, M is gram-molecular mass
- monolayer formation time  $\tau$ 
  - # molecules per unit area / bombard rate

 $\tau \approx \frac{10^{15} cm^{-2}}{j}$  $\approx \frac{2.6 \times 10^{-6}}{P(in \ Torr)} \sec \frac{1}{10^{-6}}$ 

# Impact of pressure on deposition conditions

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

|                     | pressure<br>(Torr)       | number<br>density<br>(#/cm <sup>3</sup> ) | λ            | N <sub>d=1m</sub>    | τ        |
|---------------------|--------------------------|-------------------------------------------|--------------|----------------------|----------|
| rough<br>vacuum     | 760                      | 2.7 x 10 <sup>19</sup>                    | 0.07 µm      | ~ 0                  | 3.3 nsec |
|                     | 10 <sup>-3</sup>         | 3.5 x 10 <sup>13</sup>                    | 5 cm         | 2x10 <sup>-7</sup> % | 2.5 msec |
| nigh vacuum         | 10 <sup>-6</sup>         | 3.5 x 10 <sup>10</sup>                    | 50 m         | 98 %                 | 2.5 sec  |
| very<br>high vacuum | 10 <sup>-9</sup>         | 3.5 x 10 <sup>7</sup>                     | 50 km        | 100 %                | 42 min   |
|                     | <b>10</b> <sup>-12</sup> | 3.5 x 10 <sup>4</sup>                     | 50,000<br>km |                      | 29 days  |

17

# Impact of pressure on deposition conditions

- material arrival angular distribution
  - depends on mean free path compared to both size of system and size of wafer "steps"
- Case I: "atmospheric pressure": 760 Torr  $\Rightarrow \lambda = 0.07 \ \mu m$ 
  - $\lambda \ll$  system & steps
  - isotropic arrival on ALL surfaces
    - flat surfaces:
       180°
    - inside corners: 90°
       ➡ thinner
    - outside corners: 270°
       ➡ thicker





assume material does NOT migrate after arrival!!

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

- Case II: 10<sup>-1</sup> Torr  $\Rightarrow \lambda = 0.5 \text{ mm}$ 
  - 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  $\Rightarrow \lambda = 5$  meters
  - long compared to almost everything
- anisotropic arrival at all surfaces!
  - geometric "shadowing" dominates



- "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!!

# Physical vapor deposition: thermal evaporation

- high vacuum to avoid contamination
  - "line-of-sight" deposition, poor step coverage
- heating of source material
  - potential problem: thermal decomposition
- rates ~ 0.1- few nm/sec
  - typically P<sub>vapor</sub> ~ 10<sup>-4</sup> Torr <u>immediately above source</u>
  - "pressure" at sample surface is much lower
    - few monolayers per sec ⇒
       P<sub>equiv</sub> ~ 10<sup>-6</sup> Torr



## **Thermal evaporation**

- main heating mechanisms
  - resistively heat "boat" containing material



tungsten (mp 3410°C), tantalum (mp 2996°C), molybdenum (mp 2617°C) very common "heater" materials

22

- reaction with boat potential problem
- electron beam evaporator
  - source material "directly" heated by electron bombardment
    - can generate x-rays, can damage substrate/devices
  - I<sub>beam</sub> ~ 100 mA, V<sub>acc</sub> ~ kV ➡ P ~ kWatts



essentially eddy current losses



## **Sputtering**

- use moderate energy ion bombardment to eject atoms from target
- "purely" physical process
  - can deposit almost anything



# **Sputtering**

- plasma generates high density, energetic incident particles
  - magnetic field used to confine plasma, electric field ("bias") to accelerate
  - dc plasma: metals
    - rates up to ~1 µm / minute
  - rf plasma: dielectrics
- typically inert (noble) gas used to form incident ions
  - ion energies ~ few hundred eV ; ejected atoms ~ tens eV
  - ~10<sup>-2</sup> Torr,  $\lambda$  ~ 5 mm
  - better step coverage than evaporation



planar magnetron



adapted from: Campbell, p. 298

Dean P. Neikirk © 2001, last update February 2, 2001

## **Chemical vapor deposition**

- general characteristic of gas phase chemical reactions
  - pressures typically atmospheric to 50 mTorr
    - $\lambda$  ranges from << 1  $\mu$ m to ~ 1 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

#### **CVD** system design: hot wall reactors



## **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

# 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

$$\frac{\text{gas flow lines } \mathbf{x} \rightarrow \mathbf{a} \mathbf{d}}{\text{substrate}} \quad d = \sqrt{\frac{\mu \cdot x}{\rho \cdot v}}$$

- v: velocity; ρ: density; μ: viscosity
- reactant supply limited by diffusion across boundary layer

gas flow line

- geometry of wafers relative to gas flow critical for film thickness uniformity
  - to improve boundary layer uniformity can tilt wafer wrt gas flow

# **Basic configurations**

horizontal tube reactor



• parallel plate plasma reactor



- barrel reactor
- single wafer systems

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

![](_page_28_Picture_8.jpeg)

![](_page_28_Picture_9.jpeg)

## Material examples: polysilicon

- uses
  - gates, high value resistors, "local" interconnects
- deposition
  - silane pyrolysis:  $600^{\circ}$ -700° C SiH<sub>4</sub> → Si + 2H<sub>2</sub>
    - atmospheric, cold wall, 5% silane in hydrogen, ~1/2 μm/min
    - LPCVD (~1 Torr), hot wall, 20-100% silane, ~hundreds nm/min
  - grain size dependent on growth temperature, subsequent processing
    - 950° C phosphorus diffusion, 20 min: ~1 μm grain size
    - 1050° C oxidation: ~1-3 µm grain size
- in-situ doping
  - p-type: diborane  $B_2H_6$ : ρ ~ 0.005 Ω-cm (B/Si ~ 2.5x10<sup>-3</sup>)
    - can cause substantial increase in deposition rate
  - n-type: arsine AsH<sub>3</sub>, phosphine PH<sub>3</sub> :  $\rho \sim 0.02 \Omega$ -cm
    - can cause substantial decrease in deposition rate
- dope after deposition (implant, diffusion)

# **Metal CVD**

- tungsten
  - WF<sub>6</sub> + 3H<sub>2</sub>  $\leftrightarrows$  W + 6HF
  - cold wall systems
  - − ~300°C
  - can be selective
  - adherence to SiO<sub>2</sub> 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
  - ~200°-300° C, tens nm/min deposition rate
- copper
  - Cu  $\beta$ -diketones, ~100°-200° C

# **CVD** silicon dioxide

- thermally driven reaction
  - mid-temperature: ~ 500°C
    - "LTO" (low-temp. oxide) T < ~500°C
  - $\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + \text{H}_2$
  - cold-wall, atmospheric, ~0.1 μm/min
  - hot-wall, LPCVD, ~0.01 µm/min
- plasma-enhanced reaction (PECVD)
  - low temperature: ~250°C
- high temperature: ~700°C
  - tetraethyl orthosilicate (TEOS)
    - $Si(OC_2H_5)_4 \rightarrow SiO_2 + by-products$
- new materials
  - low "k" dielectrics
    - interlevel insulation with lower dielectric constants (k < ~3)</li>
      - fluorinated oxides, spin-on glasses, organics
  - high k dielectrics: k > ~25-100's
    - gate insulators, de-coupling caps

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

|                                   | plasma                 | SiH <sub>4</sub> + O <sub>2</sub> | TEOS             | thermal          |
|-----------------------------------|------------------------|-----------------------------------|------------------|------------------|
| temperature                       | ~200°C                 | ~450°C                            | ~700°C           | ~1000°C          |
| composition                       | SiO <sub>1.9</sub> (H) | SiO <sub>2</sub> (H)              | SiO <sub>2</sub> | SiO <sub>2</sub> |
| step coverage                     | non-<br>conformal      | non-<br>conformal                 | conformal        | "conformal"      |
| thermal stability                 | loses H                | densifies                         | stable           | stable           |
| density (g/cm <sup>3</sup> )      | 2.3                    | 2.1                               | 2.2              | 2.2              |
| stress<br>(Mdyne/cm²)             | 3C - 3T                | 3Т                                | 1C               | 3C               |
| dielectric strength<br>(MV/cm)    | 3-6                    | 8                                 | 10               | 11               |
| index of refraction<br>(632.8 nm) | 1.47                   | 1.44                              | 1.46             | 1.46             |
| $\epsilon_r$ (low freq.)          | 4.9                    | 4.3                               | 4.0              | 3.9              |

adapted from Sze, 2nd, p. 259.

# Silicon nitride Si<sub>3</sub>N<sub>4</sub>

#### • uses

- diffusivity of  $O_2$ ,  $H_2O$  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 Si<sub>3</sub>N<sub>4</sub>
    - in practice Si/N ratio varies from 0.7 (N rich) to 1.1 (Si rich)
  - LPCVD: ~700°C 900°C
    - $3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$ ;  $3Si_2CI_2H_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCI + 6H_2$
    - Si/N ratio 0.75, 4-8% H
    - ρ ~ 3 g/cm<sup>3</sup> ; n ~ 2.0; k ~ 6-7
    - stress: ~10 Gdyne/cm<sup>2</sup>, tensile
  - PECVD: ~250°C 350°C
    - $aSiH_4 + bNH_3 \rightarrow Si_xN_yH_z + cH_2$
    - $aSiH_4 + bN_2 \rightarrow Si_xN_yH_z + cH_2$
    - Si/N ratio 0.8-1.2, ~20% H
    - ρ ~ 2.4-2.8 g/cm<sup>3</sup>; n ~ 1.8-2.5; k ~ 6-9
    - stress: ~2C 5T Gdyne/cm<sup>2</sup>

# Safety issues in CVD

- most gases used are toxic, pyrophoric, flammable, explosive, or some combination of these
  - silane, SiH<sub>4</sub>
    - · 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