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: SiO₂

- 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 SiO₂ 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/cm³ , GMW = 60
 - $-~\rho_{\text{Si}}$ = 2.3 gm/cm³ , 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
 - H₂O + Si-O-Si \rightarrow Si-OH + Si-OH
 - diffusion of hydroxyl complex to SiO₂ -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



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

• N₀ is limited by the solid solubility limit of the oxidizer in the oxide!

- N₀^{H2O} ~ 3 x 10¹⁹ cm⁻³ @ 1000° C
- flux of oxidizer j' at SiO₂ / 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⁻² sec⁻¹
- rate of change of interface position: dx / dt (interface velocity)
 - cm sec⁻¹
- 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**⁻³

• 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 τ 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)² \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_{ox} / C_{Si} ~ 3
- dopants accumulate in oxide
 - little effect on linear rate constant B/A (= N_ok / n)
 - can increase parabolic rate constant B (= 2DN_o / 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)



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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 10¹⁹ molecules/cm³
 - N \propto pressure
 - one atmosphere = 1.0132×10^5 pascal
 - = 760 Torr (mm Hg)
 - 1 Pascal = 1/132 Torr ~ 10⁻⁵ 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 10²² (# / cm² sec) P / \sqrt{MT}
 - P in Torr, M is gram-molecular mass
- monolayer formation time τ
 - # 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 (Torr)	number density (#/cm ³)	λ	N _{d=1m}	τ
rough vacuum	760	2.7 x 10 ¹⁹	0.07 µm	~ 0	3.3 nsec
	10 ⁻³	3.5 x 10 ¹³	5 cm	2x10 ⁻⁷ %	2.5 msec
nigh vacuum	10 ⁻⁶	3.5 x 10 ¹⁰	50 m	98 %	2.5 sec
very high vacuum	10 ⁻⁹	3.5 x 10 ⁷	50 km	100 %	42 min
	10 ⁻¹²	3.5 x 10 ⁴	50,000 km		29 days

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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: 10⁻¹ 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: λ > system, λ >> step

- case III: 10⁻⁵ 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_{vapor} ~ 10⁻⁴ Torr <u>immediately above source</u>
 - "pressure" at sample surface is much lower
 - few monolayers per sec ⇒
 P_{equiv} ~ 10⁻⁶ 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

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- reaction with boat potential problem
- electron beam evaporator
 - source material "directly" heated by electron bombardment
 - can generate x-rays, can damage substrate/devices
 - I_{beam} ~ 100 mA, V_{acc} ~ 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
 - ~10⁻² Torr, λ ~ 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
 - λ ranges from << 1 μ 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





Material examples: polysilicon

- uses
 - gates, high value resistors, "local" interconnects
- deposition
 - silane pyrolysis: 600° -700° C SiH₄ → Si + 2H₂
 - 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 ~ 2.5x10⁻³)
 - can cause substantial increase in deposition rate
 - n-type: arsine AsH₃, phosphine PH₃ : $\rho \sim 0.02 \Omega$ -cm
 - can cause substantial decrease in deposition rate
- dope after deposition (implant, diffusion)

Metal CVD

- tungsten
 - WF₆ + 3H₂ \leftrightarrows W + 6HF
 - cold wall systems
 - − ~300°C
 - can be selective
 - adherence to SiO₂ 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 β -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)
 - fluorinated oxides, spin-on glasses, organics
 - high k dielectrics: k > ~25-100's
 - gate insulators, de-coupling caps

summary of SiO₂ characteristics

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

adapted from Sze, 2nd, p. 259.

Silicon nitride Si₃N₄

• 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 Si₃N₄
 - 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/cm³ ; n ~ 2.0; k ~ 6-7
 - stress: ~10 Gdyne/cm², 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/cm³; n ~ 1.8-2.5; k ~ 6-9
 - stress: ~2C 5T Gdyne/cm²

Safety issues in CVD

- most gases used are toxic, pyrophoric, flammable, explosive, or some combination of these
 - silane, SiH₄
 - · 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