Principles of Micro- and Nanofabrication for Electronic and Photonic Devices

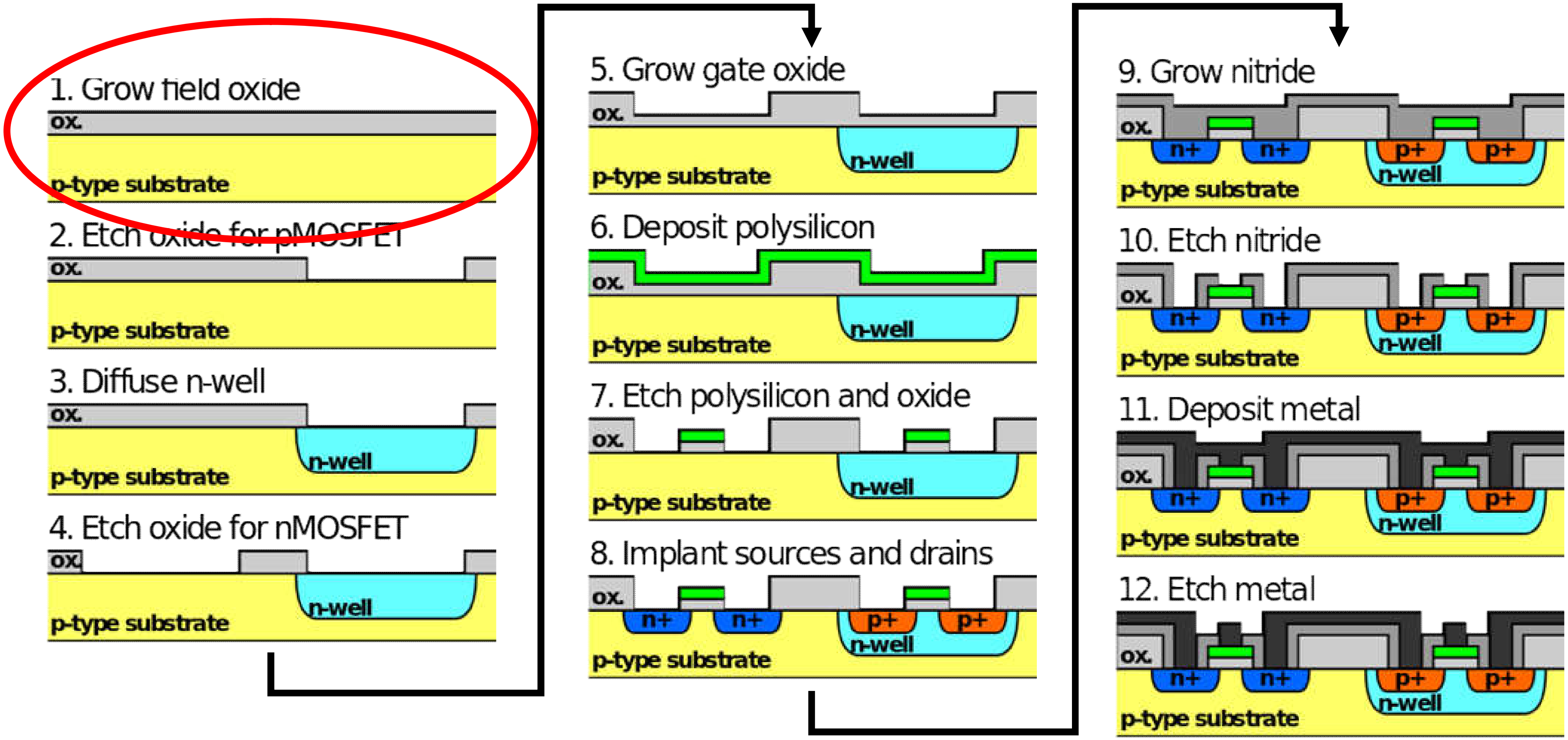
Film Deposition

Part II: Si Oxidation

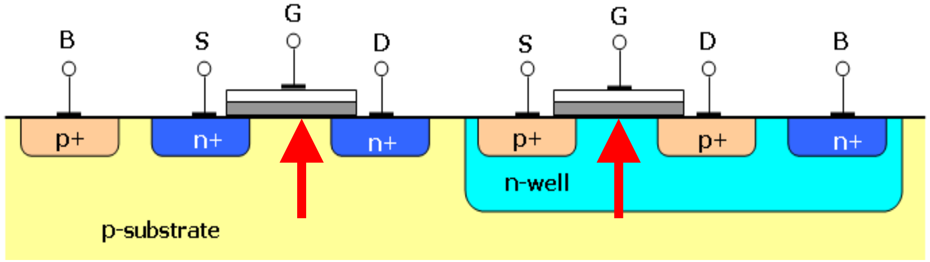
Xing Sheng 盛兴

Department of Electronic Engineering
Tsinghua University
xingsheng@tsinghua.edu.cn

CMOS Transistors



1. Grow field oxide
2. Etch oxide for pMOSFET
3. Diffuse n-well
4. Etch oxide for nMOSFET
5. Grow gate oxide
6. Deposit polysilicon
7. Etch polysilicon and oxide
8. Implant sources and drains
9. Grow nitride
10. Etch nitride
11. Deposit metal
12. Etch metal



Properties of SiO_2

- Very stable
  - for Ge, GeO_2 is soluble in water, and decompose at 450 °C
  - for GaAs, GaO_x and AsO_x have many defects
- Easily etched
  - wet etch (HF solution) or dry etch (F based plasma)
- Good diffusion barrier (low dopant diffusivity $D_{ox} << D_{Si}$)
- High quality insulator
  - band gap ~ 8 eV, resistivity > 10^{16} Ω*cm
- High dielectric strength (> 500 V/μm)
- Low interface state / defect density (< 10^{10} cm^{-2})

Properties of SiO_2

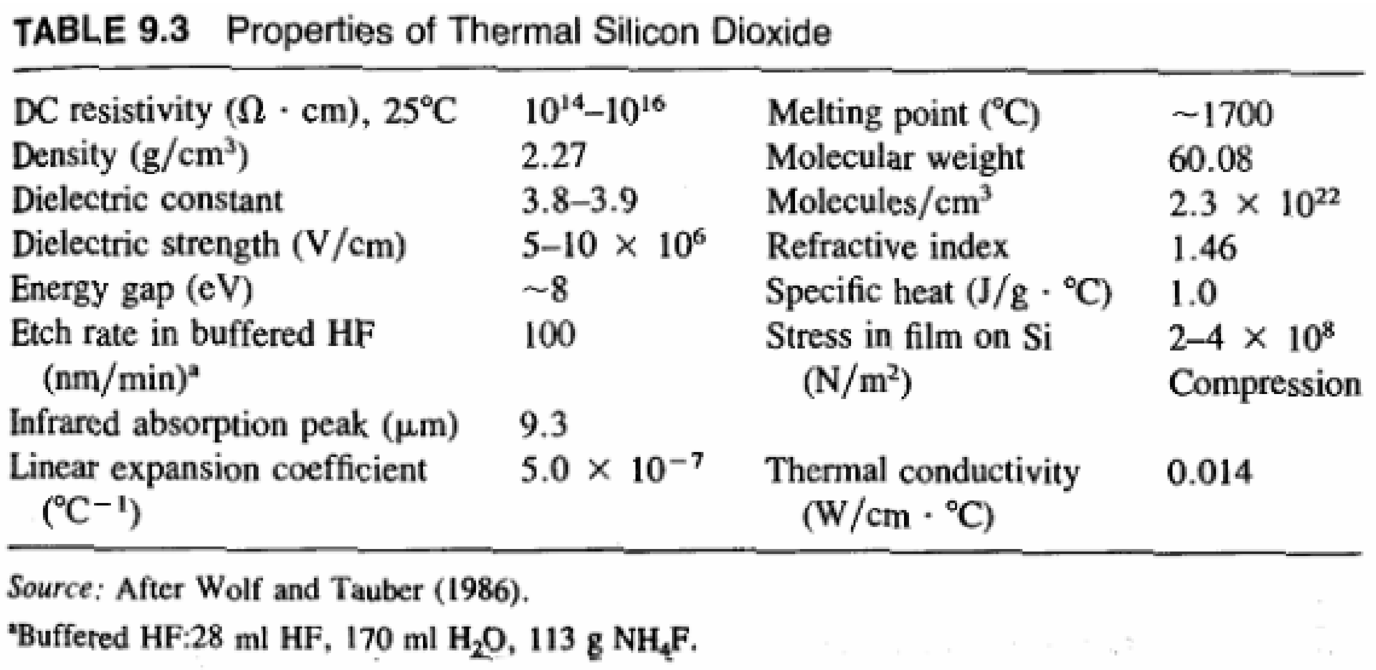


TABLE 9.3 Properties of Thermal Silicon Dioxide

DC resistivity (Ω · cm), 25°C	10^{14}–10^{16}	Melting point (°C)	~1700
Density (g/cm^3)	2.27	Molecular weight	60.08
Dielectric constant	3.8–3.9	Molecules/cm^3	2.3×10^{22}
Dielectric strength (V/cm)	$5–10 \times 10^6$	Refractive index	1.46
Energy gap (eV)	~8	Specific heat (J/g · °C)	1.0
Etch rate in buffered HF (nm/min)[a]	100	Stress in film on Si (N/m^2)	$2–4 \times 10^8$ Compression
Infrared absorption peak (μm)	9.3		
Linear expansion coefficient (°C^{-1})	5.0×10^{-7}	Thermal conductivity (W/cm · °C)	0.014

Source: After Wolf and Tauber (1986).

[a] Buffered HF:28 ml HF, 170 ml H_2O, 113 g NH_4F.

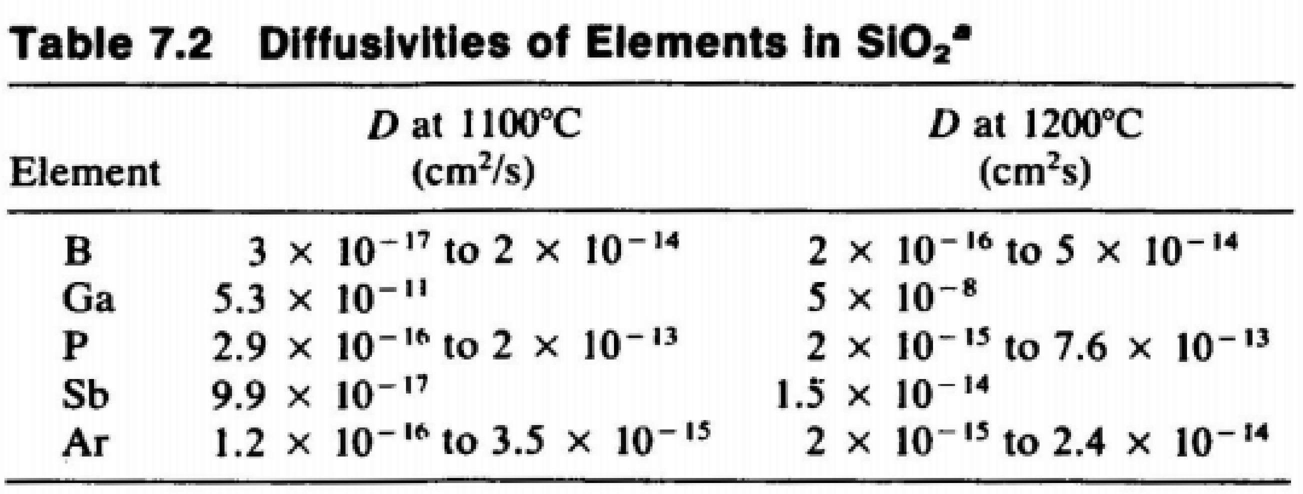
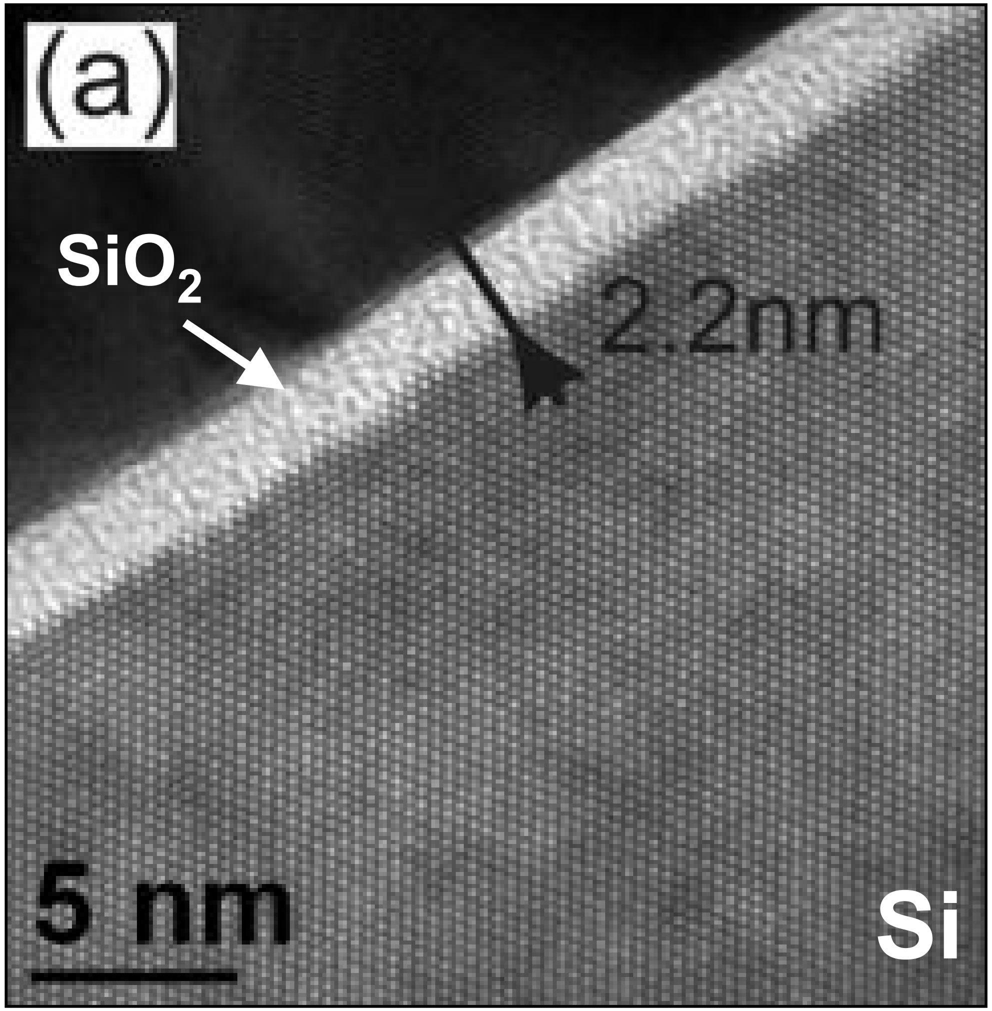


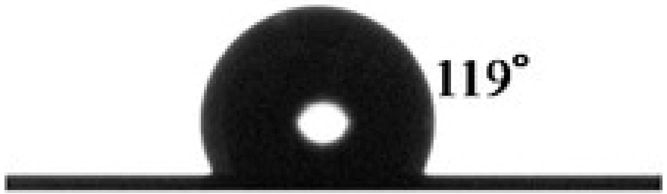
Table 7.2 Diffusivities of Elements in SiO_2[a]

Element	*D* at 1100°C (cm^2/s)	*D* at 1200°C (cm^{2}s)
B	3×10^{-17} to 2×10^{-14}	2×10^{-16} to 5×10^{-14}
Ga	5.3×10^{-11}	5×10^{-8}
P	2.9×10^{-16} to 2×10^{-13}	2×10^{-15} to 7.6×10^{-13}
Sb	9.9×10^{-17}	1.5×10^{-14}
Ar	1.2×10^{-16} to 3.5×10^{-15}	2×10^{-15} to 2.4×10^{-14}

Native Oxide



clean Si (oxide removed by HF)
hydrophobic



Si with native oxide
hydrophilic

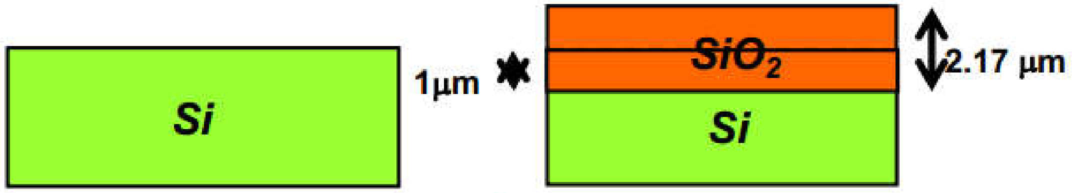
Si forms native oxide in the air (1~2 nm, a few hours)

Q: amorphous or crystalline SiO_2 ?

Thermal Oxide Growth

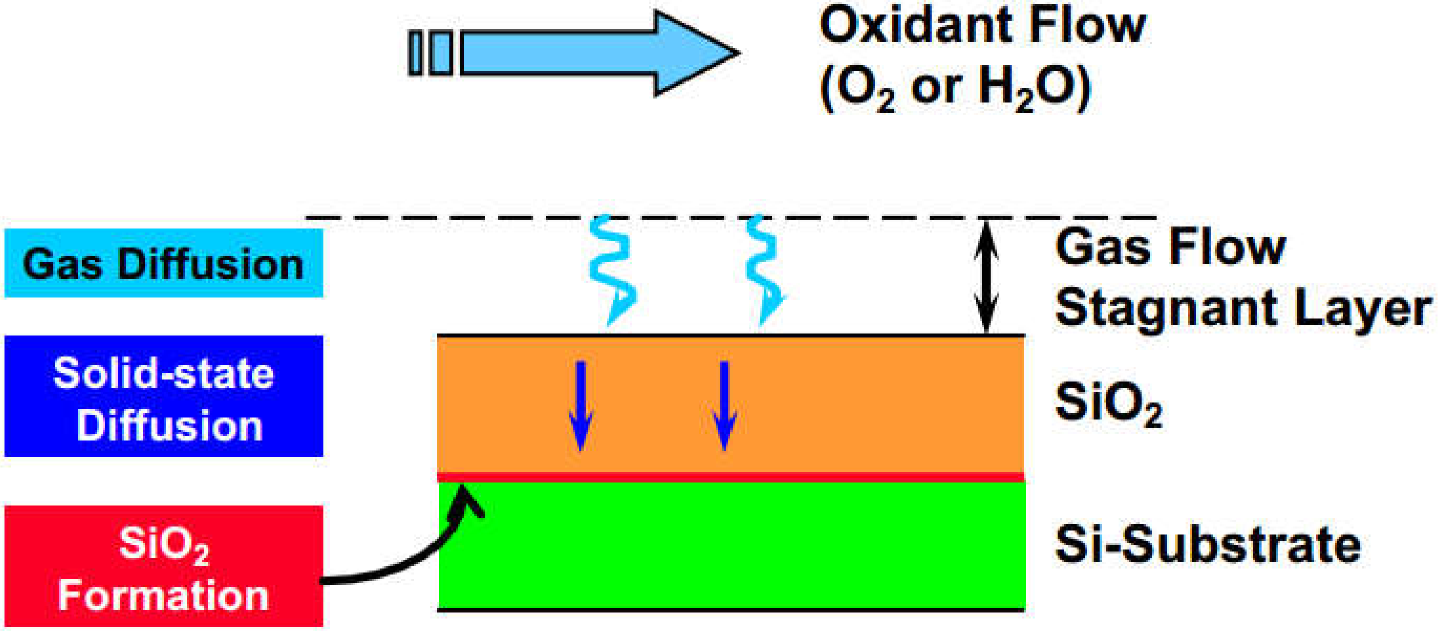
dry oxidation $Si\ (s) + O_2\ (g) = SiO_2\ (s)$

wet oxidation $Si\ (s) + H_2O\ (g) = SiO_2\ (s) + H_2\ (g)$

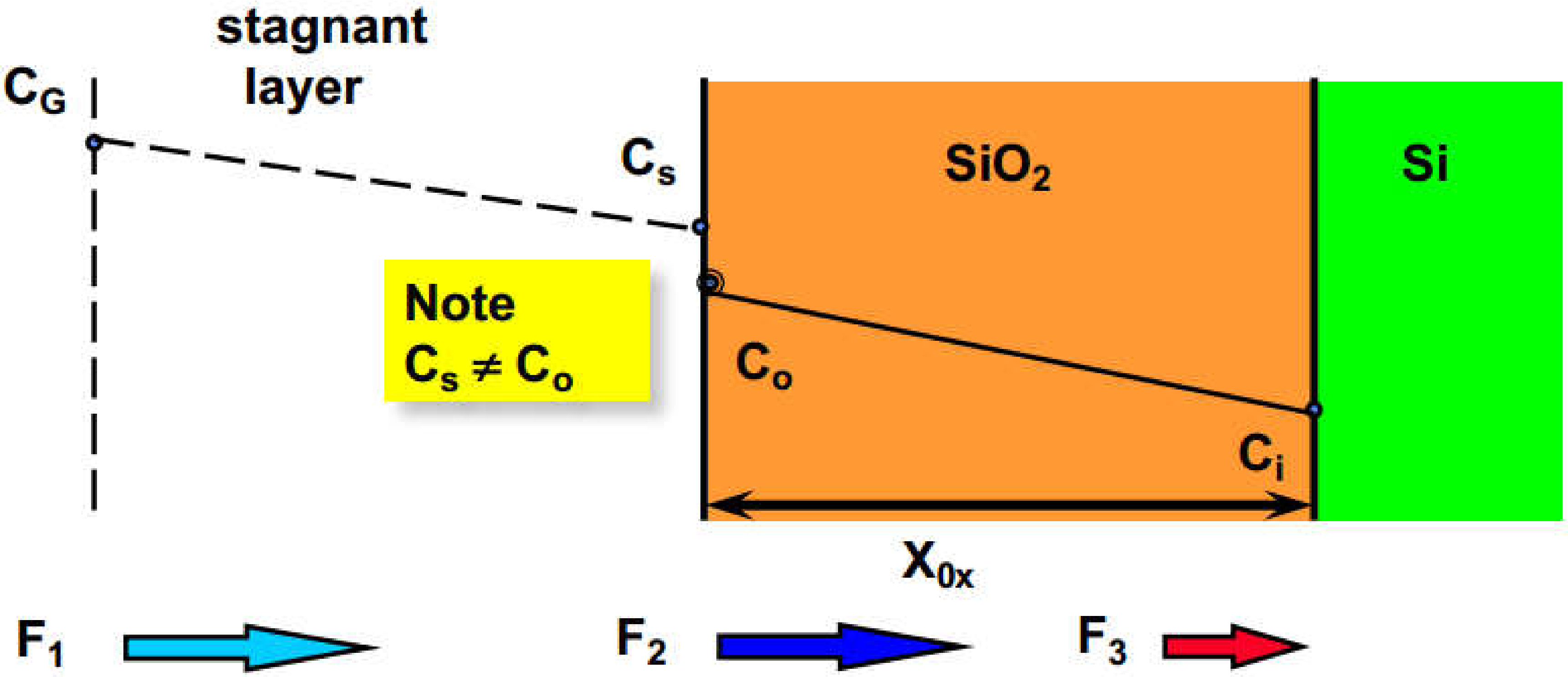


1μm Si oxidized → 2.17 μm SiO_2

Video



The Deal-Grove (D-G) Model



Note
$C_s \neq C_o$

gas transport flux

diffusion flux through SiO_2

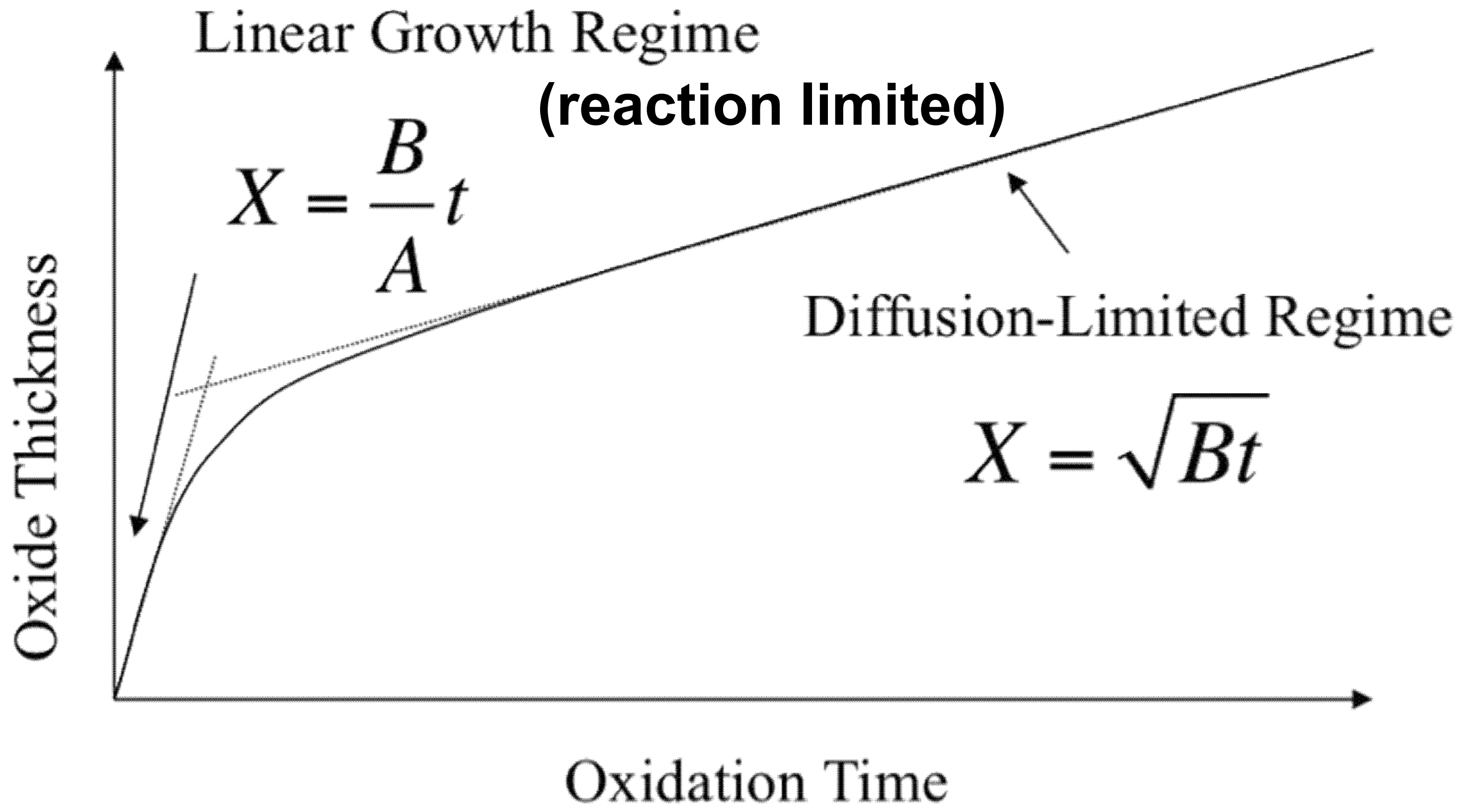
reaction flux at interface

- F: oxygen flux –
  the number of oxygen molecules that crosses a plane per unit area per second

The Deal-Grove (D-G) Model

$$\boxed{X_{ox} = \frac{A}{2}\left\{\sqrt{1+\left(\frac{t+\tau}{A^2/4B}\right)}-1\right\}}$$

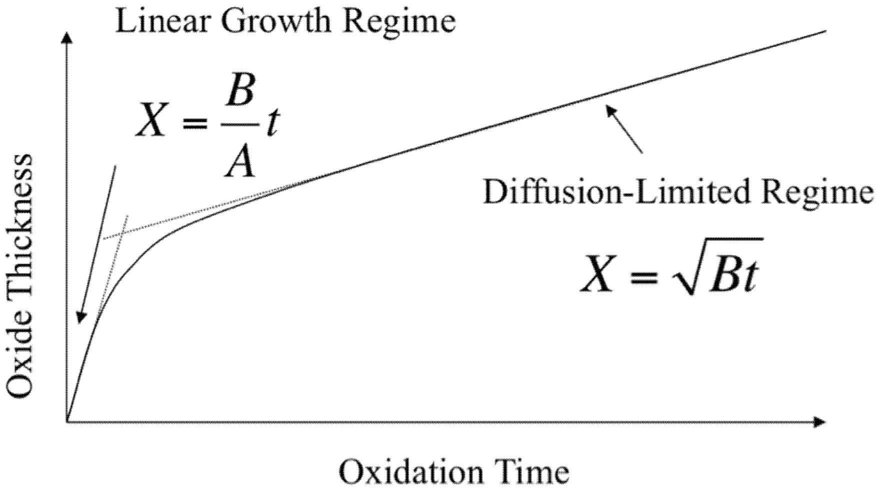
A	**related to reaction**
B	**related to diffusion**
τ	**initial native oxide**



Thermal Oxidation

- **Process Parameters**
  - Time
  - Temperature
  - Gas type (O_2, H_2O, ...)
  - Gas pressure
  - Crystal orientation
  - Dopant (B, P, As, ...)

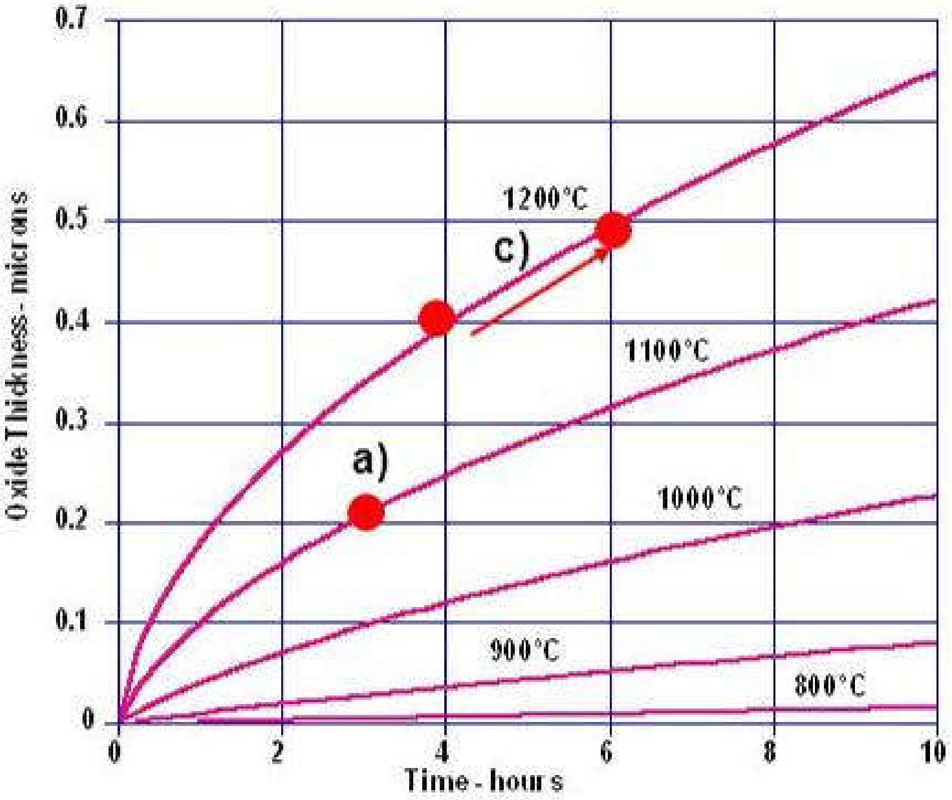
$$X_{ox} = \frac{A}{2}\left\{\sqrt{1+\left(\frac{t+\tau}{A^2/4B}\right)}-1\right\}$$



- **Control Parameters**
  - Oxide thickness
  - Film quality (defects, dielectric strength, ...)

Dry vs. Wet Oxidation

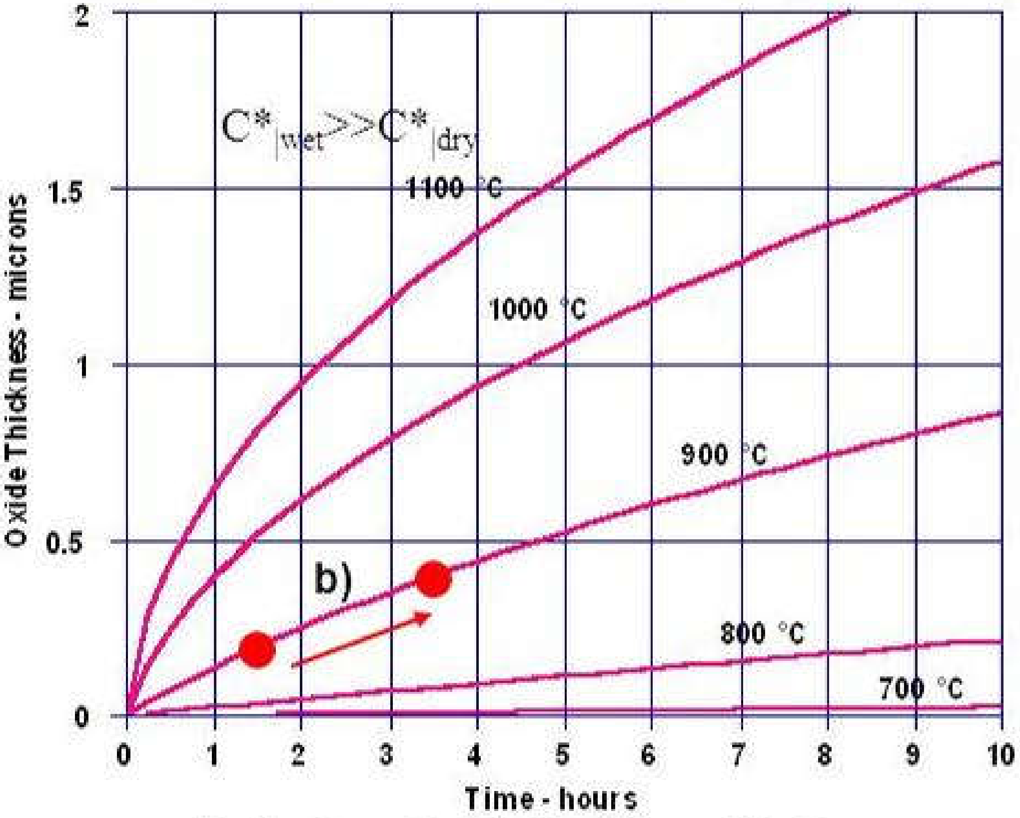
Dry oxidation - used up to 100-200 nm



Calculated (100) silicon dry O_2 oxidation rates using Deal Grove.

Video

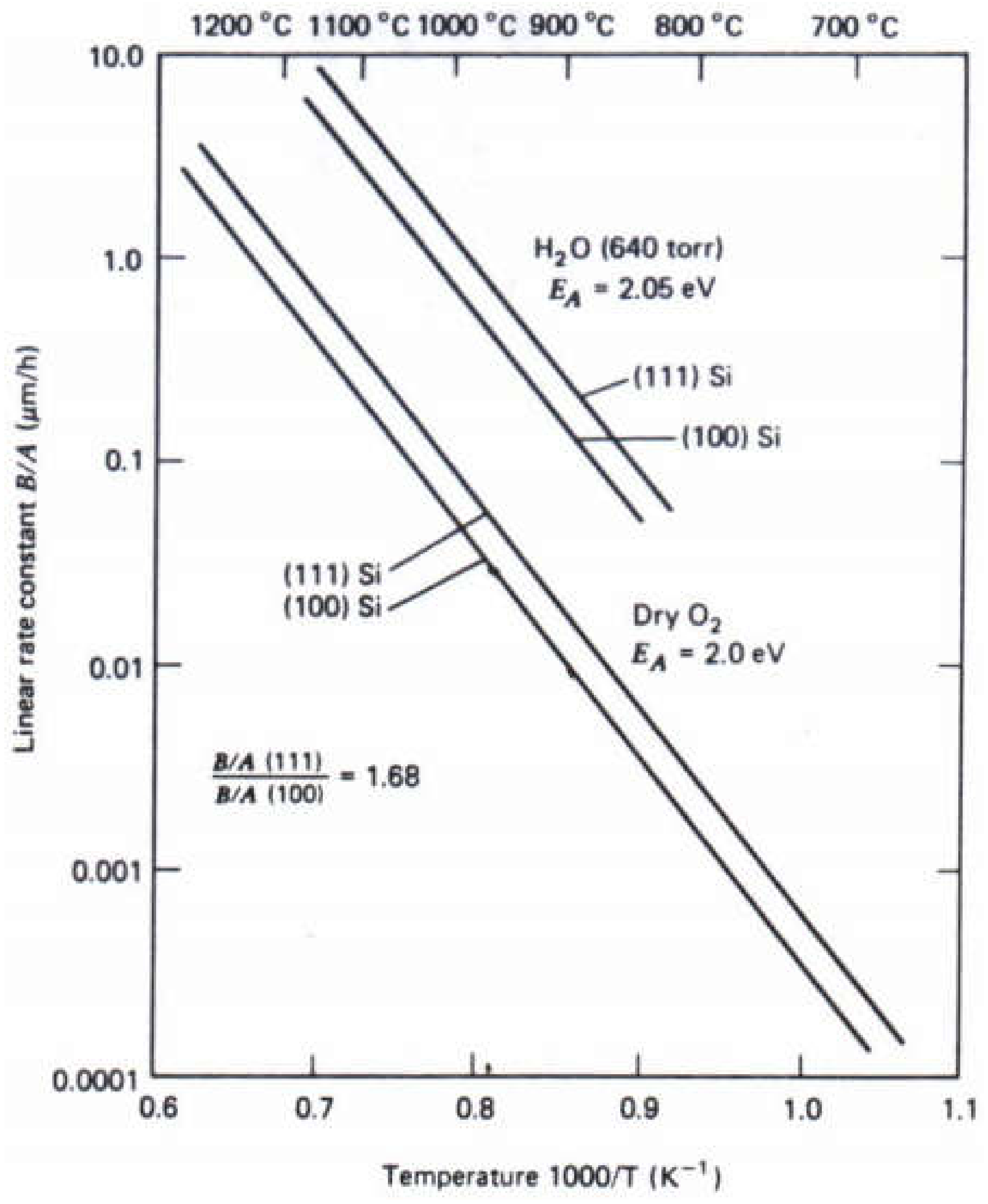
Wet oxidation - used for thicker oxides



Calculated (100) silicon H_2O oxidation rates using Deal Grove.

wet oxidation is 10~100 times faster than dry oxidation because H_2O has higher solubility/diffusivity in SiO_2

Crystal Orientation

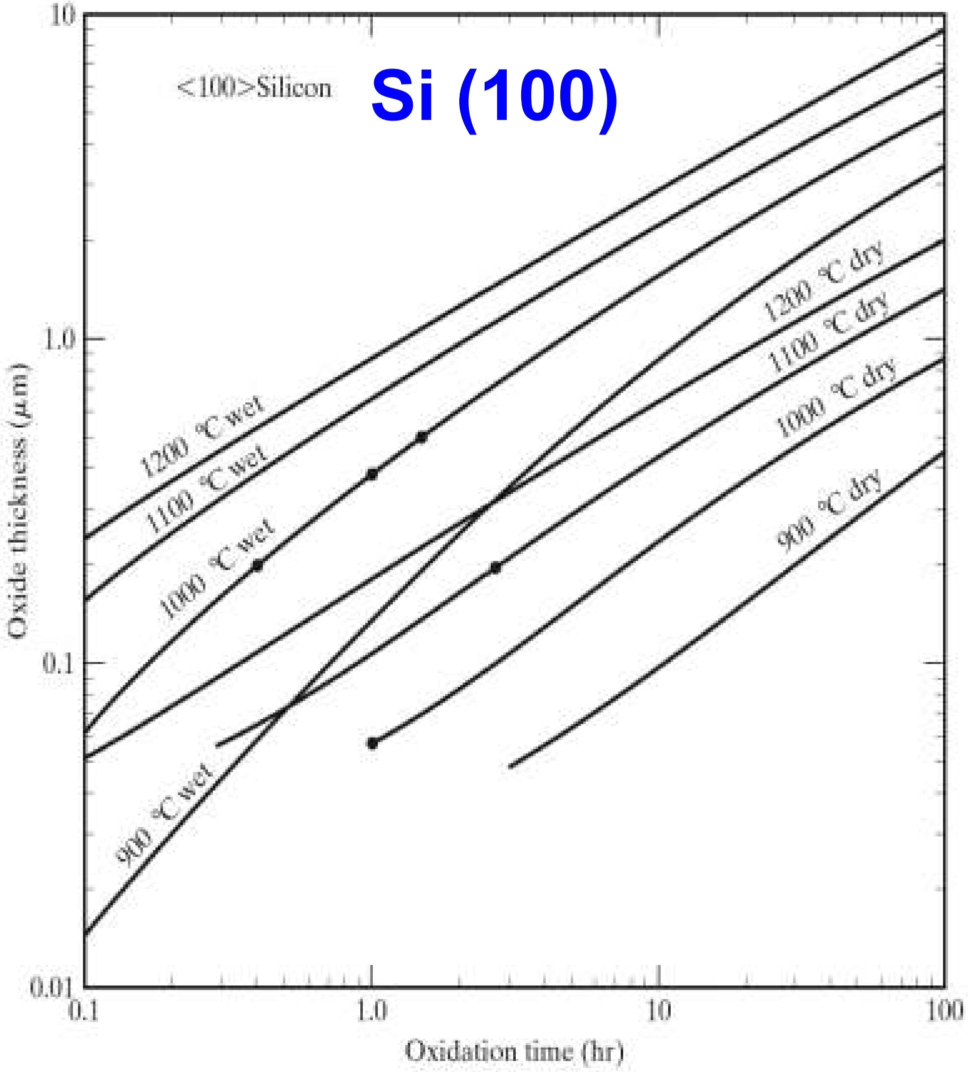


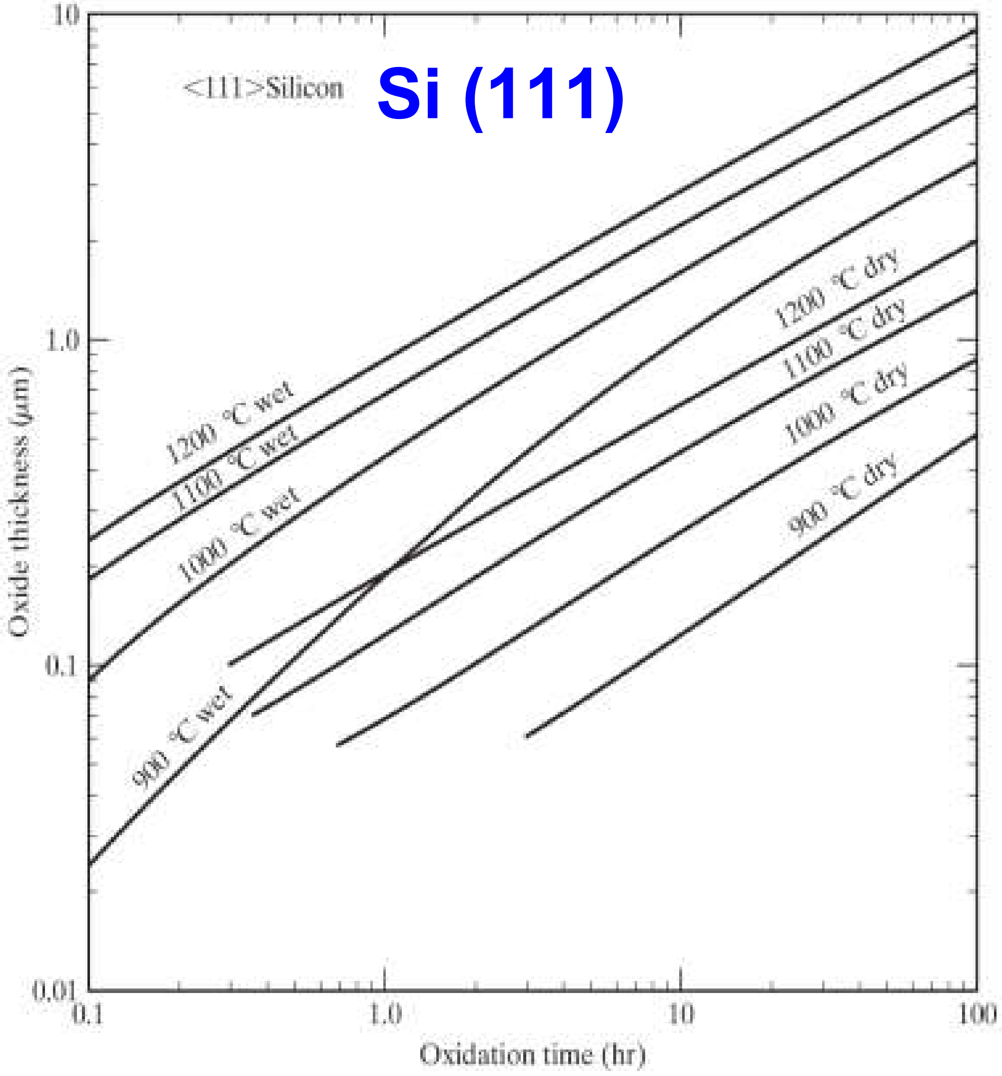
Si (111) has smaller *A*, but same *B* with Si (100)

higher growth rate at initial stage

why ??

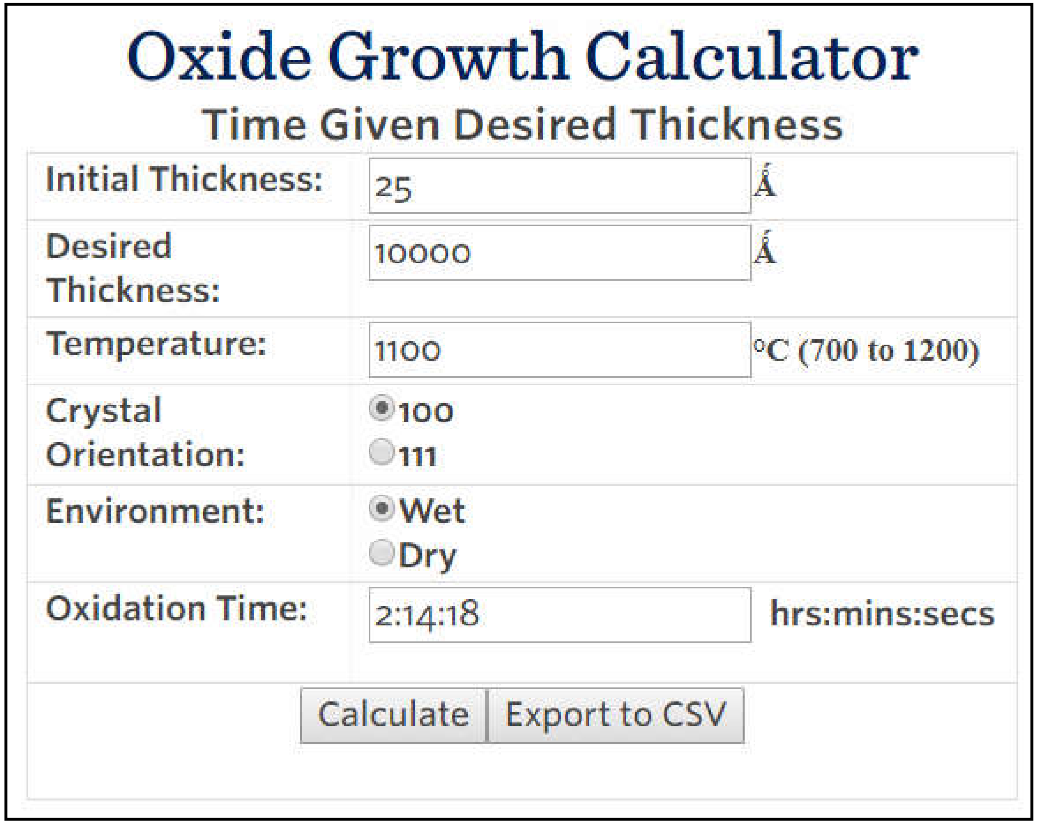
Crystal Orientation





similar rates at long time oxidation (diffusion limited)

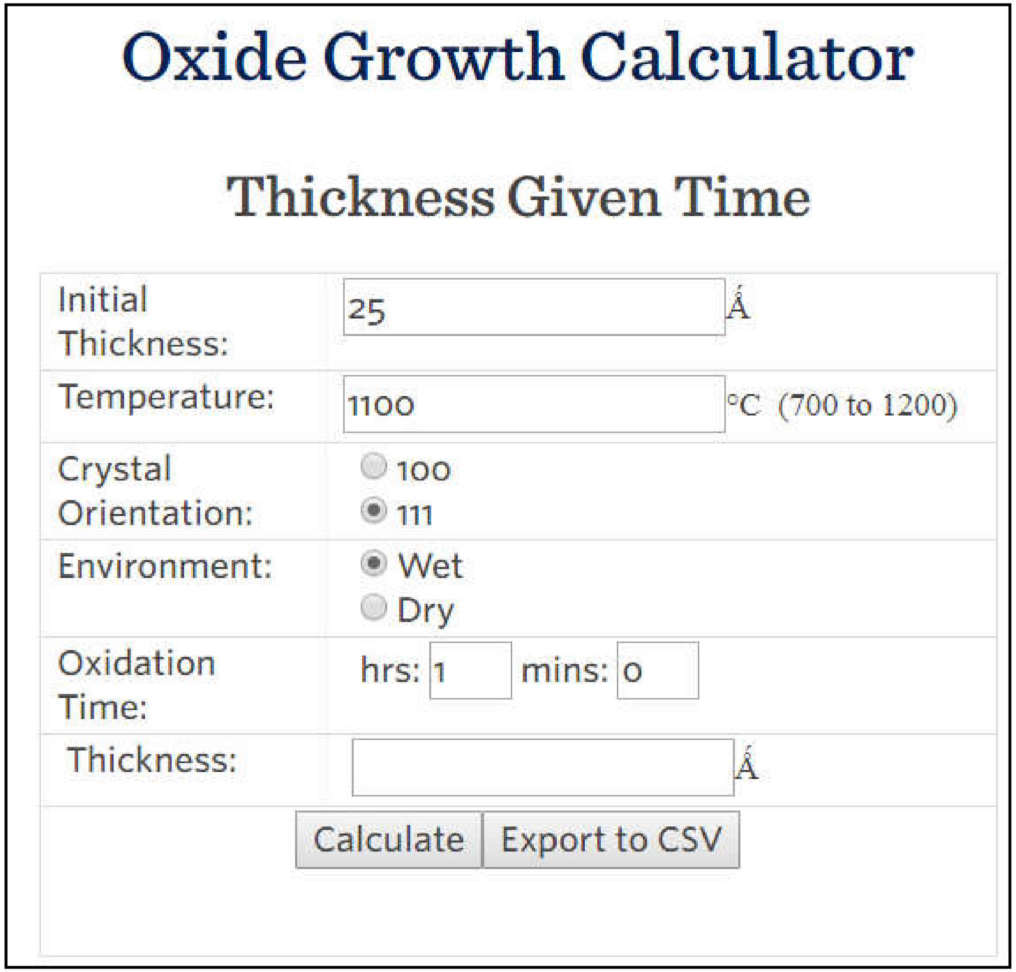
Thermal Oxidation - Simulation



Oxide Growth Calculator

Time Given Desired Thickness

Initial Thickness:	25	Á
Desired Thickness:	10000	Á
Temperature:	1100	°C (700 to 1200)
Crystal Orientation:	● 100 ○ 111	
Environment:	● Wet ○ Dry	
Oxidation Time:	2:14:18	hrs:mins:secs



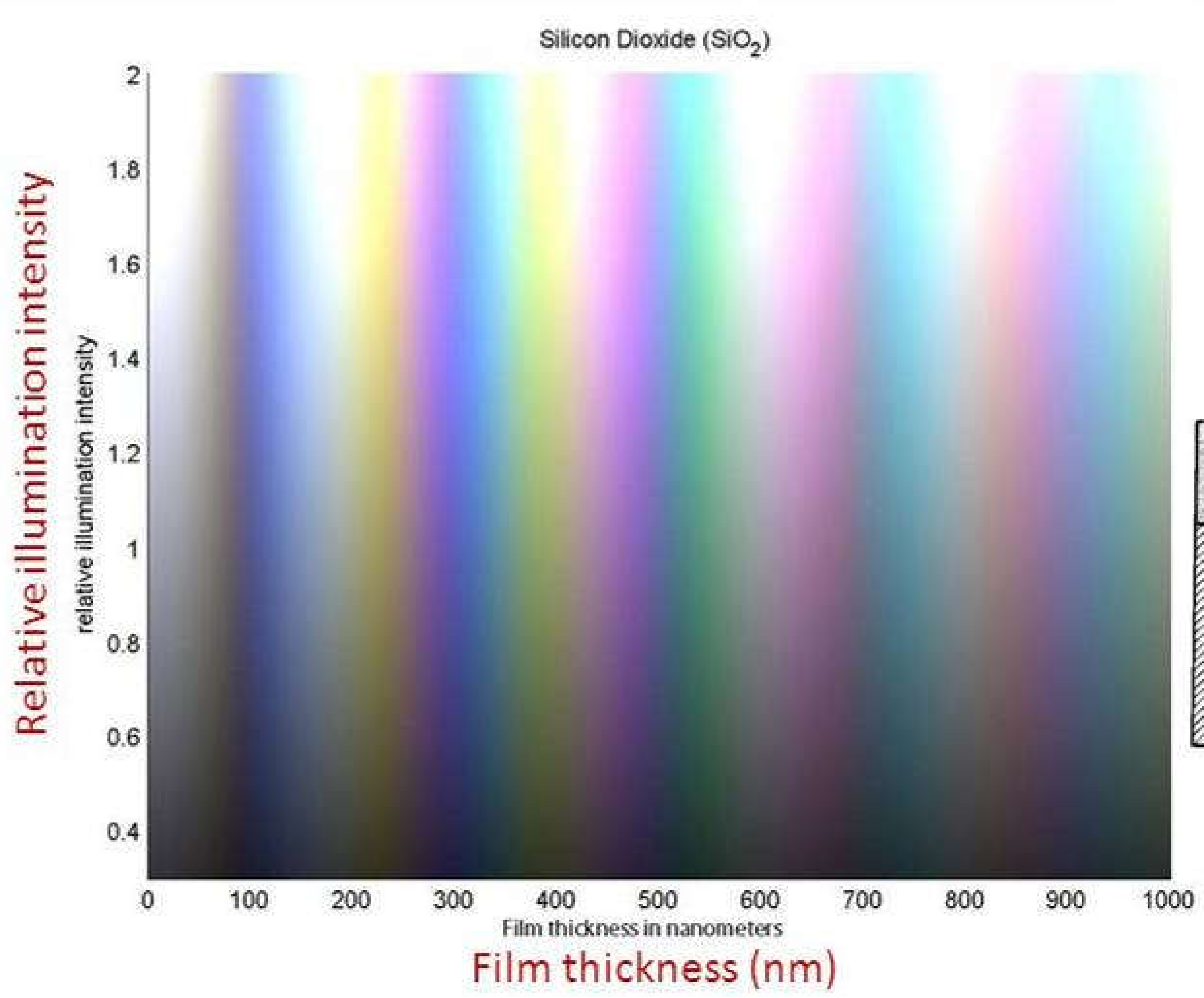
Oxide Growth Calculator

Thickness Given Time

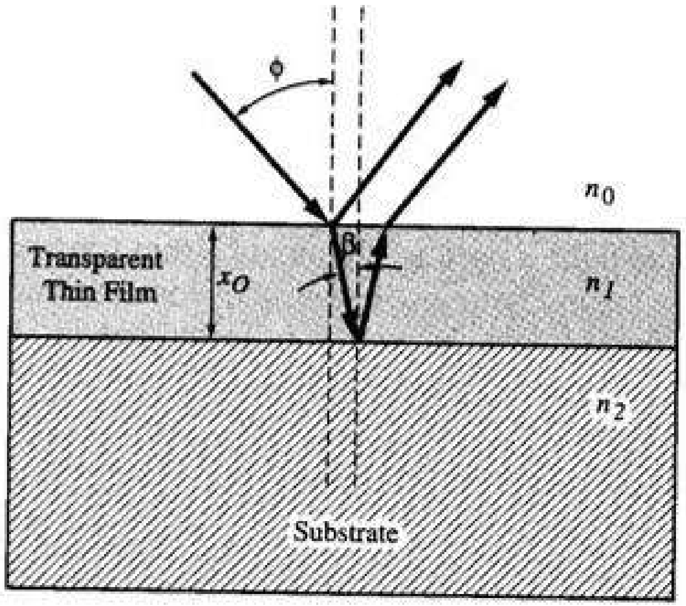
Initial Thickness:	25	Á
Temperature:	1100	°C (700 to 1200)
Crystal Orientation:	○ 100 ● 111	
Environment:	● Wet ○ Dry	
Oxidation Time:	hrs: 1 mins: 0	
Thickness:		Á

https://cleanroom.byu.edu/processes#Microfab_OxideGrowth

SiO_2 Film Thickness Measurement

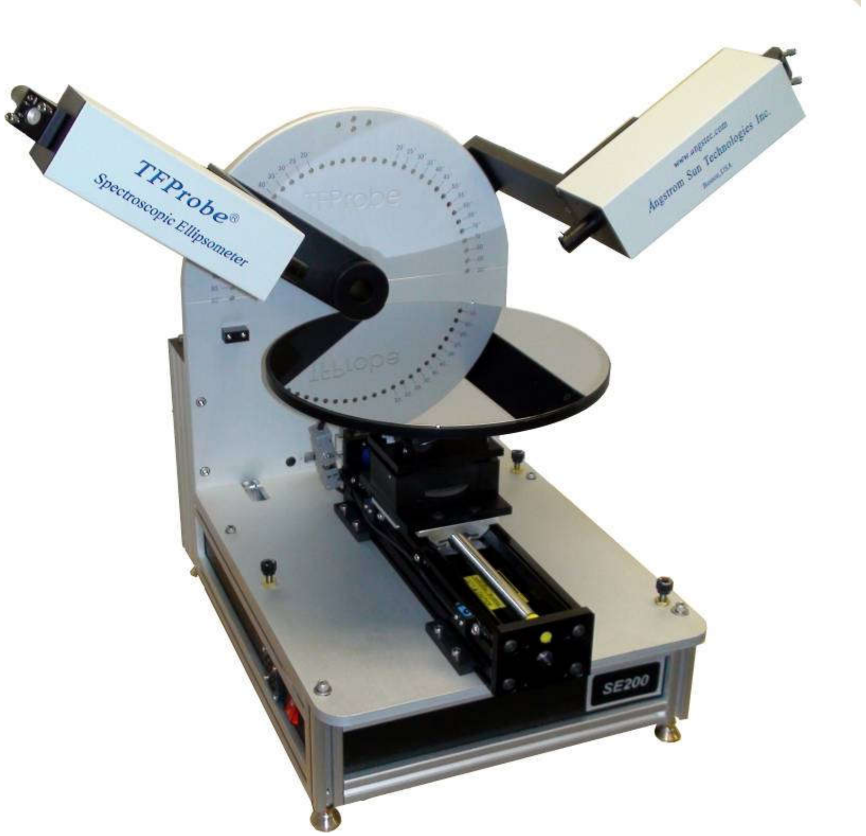


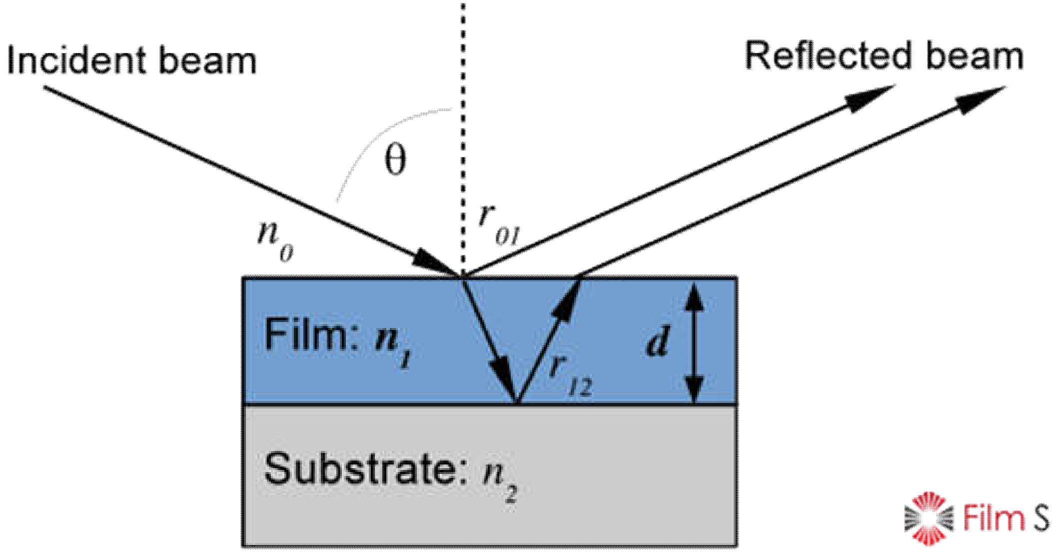
color difference



SiO_2 Film Thickness Measurement

Spectroscopic Ellipsometer

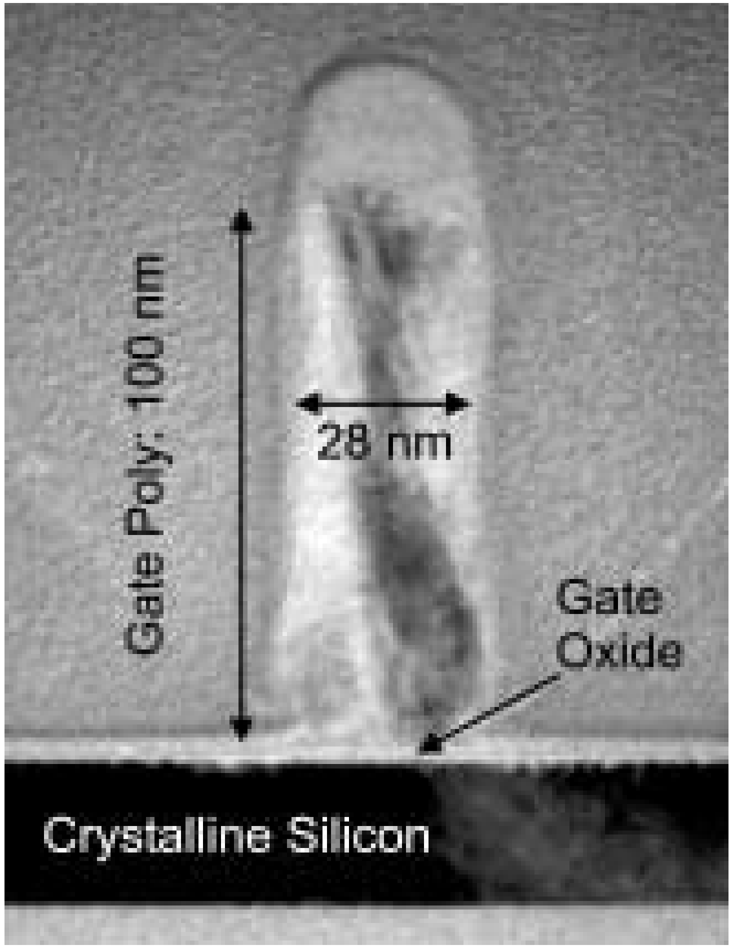


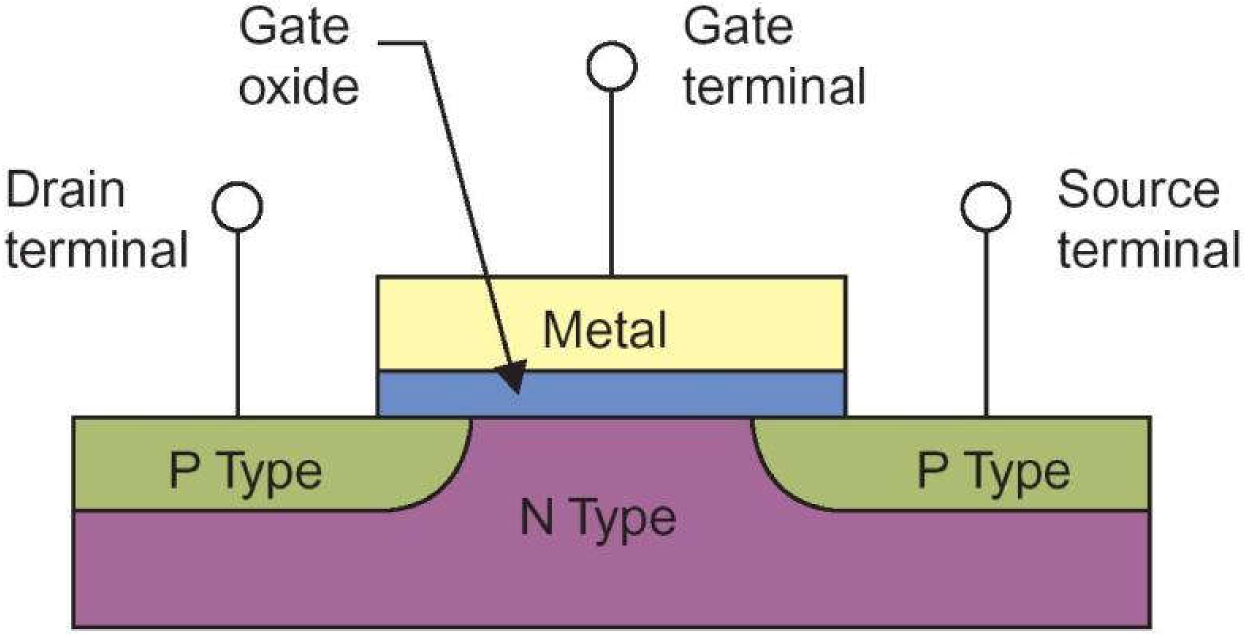


SiO_2 in CMOS

gate oxide for transistors

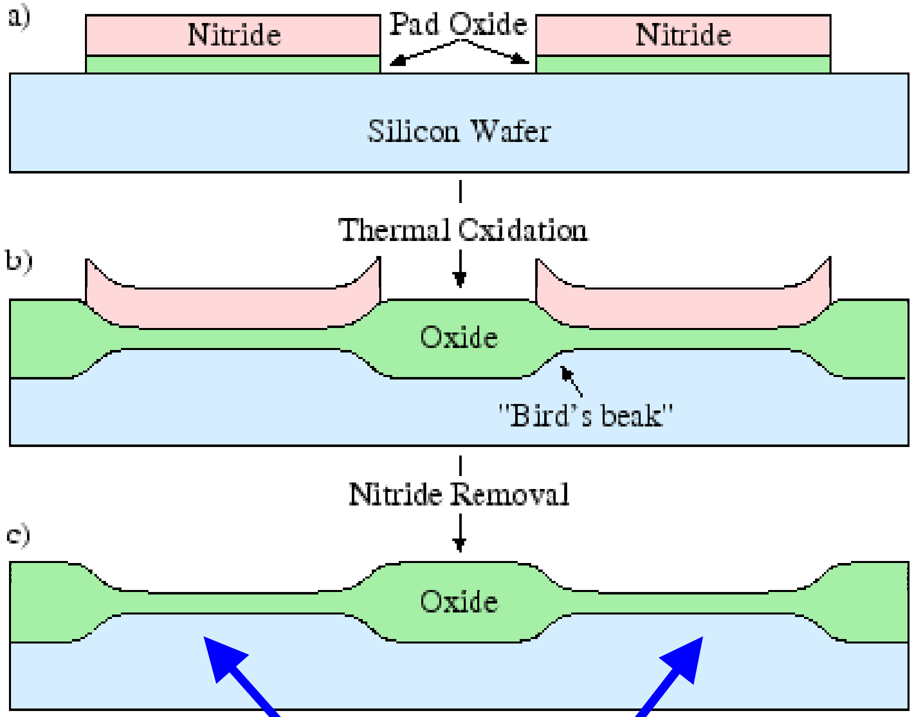
$$I_{D,Sat} = \frac{W}{L}\mu C\frac{(V_G - V_{th})^2}{2}$$

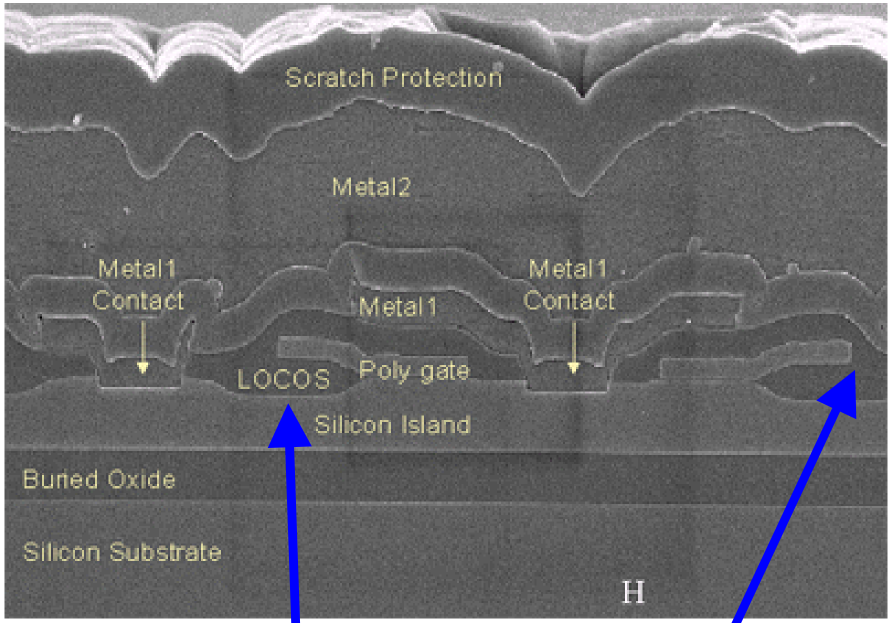




SiO_2 in CMOS

Local Oxidation of Si (LOCOS)





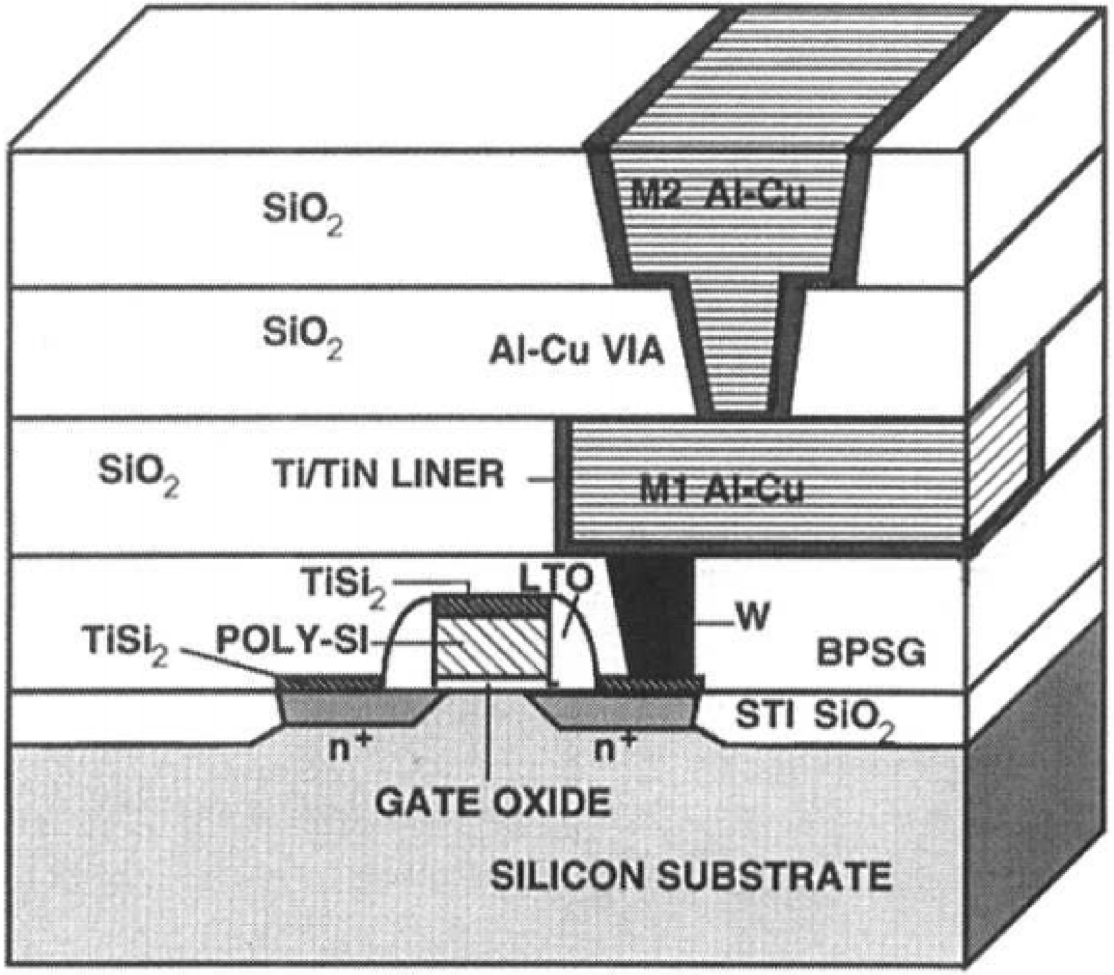
For isolation

transistor region

SiO_2 in CMOS

other methods to deposit SiO_2

temperature



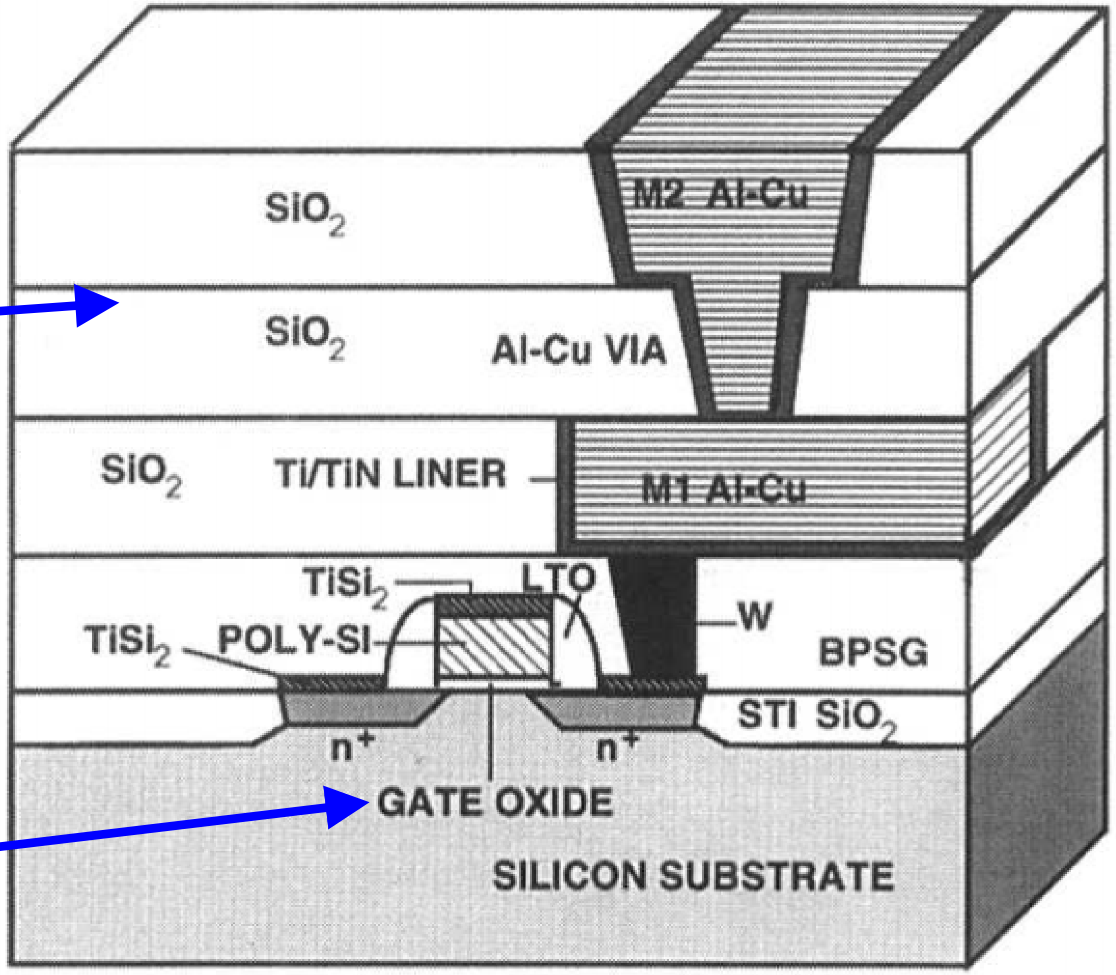
Q: why?

SiO$_2$ in CMOS

$$\boxed{C = \frac{\kappa \varepsilon_0 A}{t}}$$

low κ dielectric for insulating reduce *RC* delay

high κ dielectric for gate oxide



$$\boxed{I_{D,Sat} = \frac{W}{L} \mu C \frac{(V_G - V_{th})^2}{2}}$$

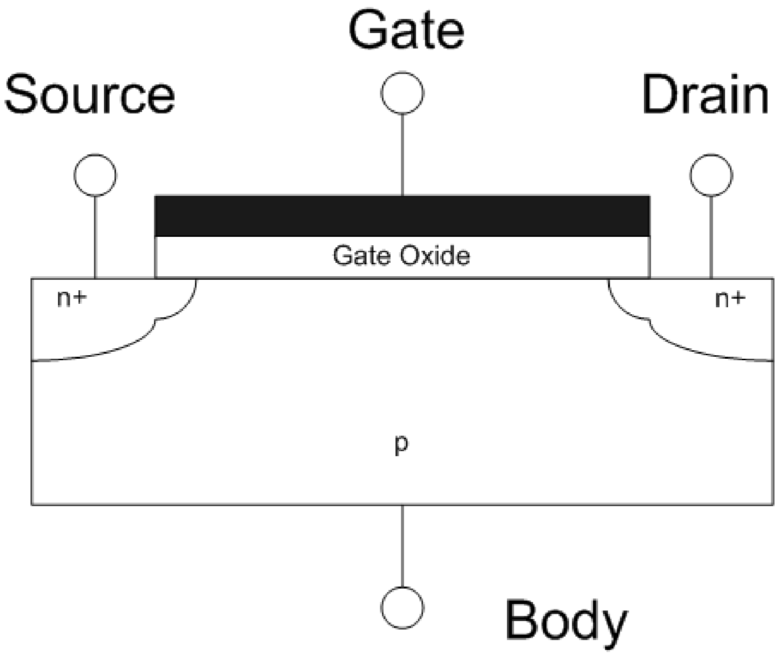
Oxide for High κ Dielectric

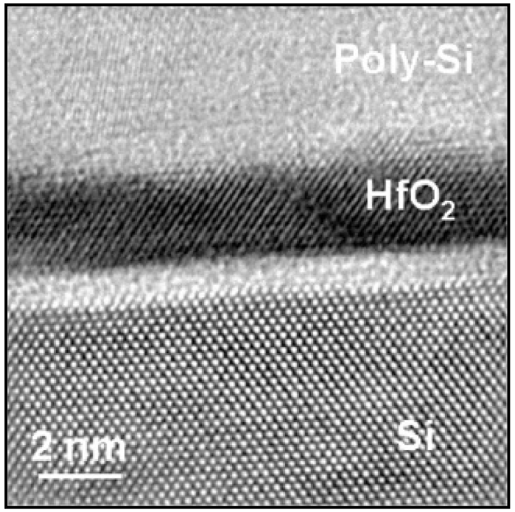
$$I_{D,Sat} = \frac{W}{L}\mu C \frac{(V_G - V_{th})^2}{2}$$

$$C = \frac{\kappa \varepsilon_0 A}{t}$$

thickness t is already ~ nm

high κ -> large C -> large I_D





Film Type	Thermal SiO_2	Al_2O_3	Ta_2O_5	ZrO_2	HfO_2
Dielectric Constant	3.95	9	26	25	25–40
Bandgap (eV)	8.9	8.7	4.5	7.8	5.7
Barrier Height to Silicon	3.2	2.8	1–1.5	1.4	1.5
Deposition Technique	Thermal Growth	CVD	CVD	CVD	CVD

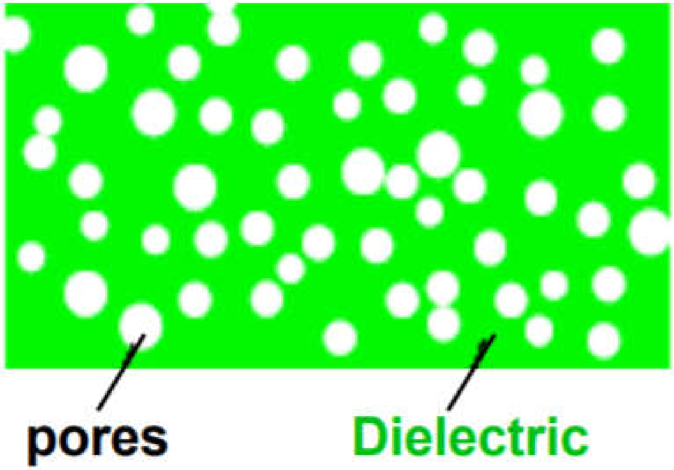
Porous SiO_2 for Low κ Dielectric

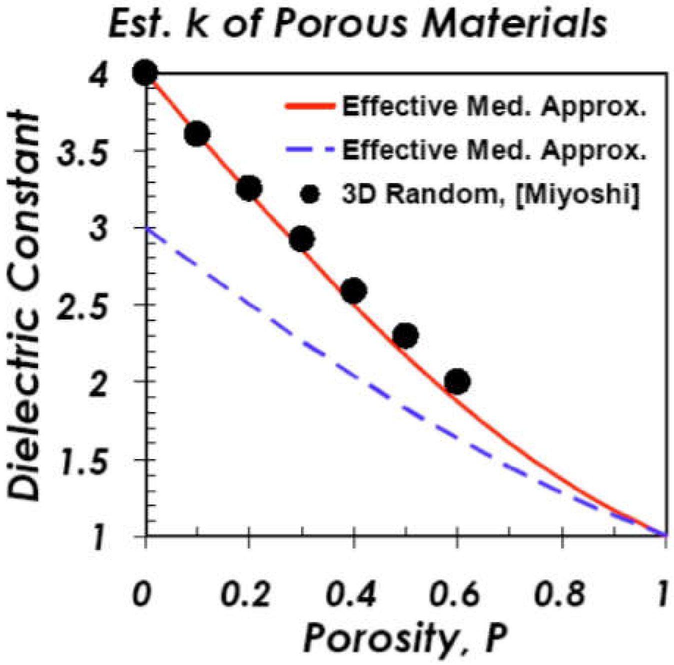
SiO_2

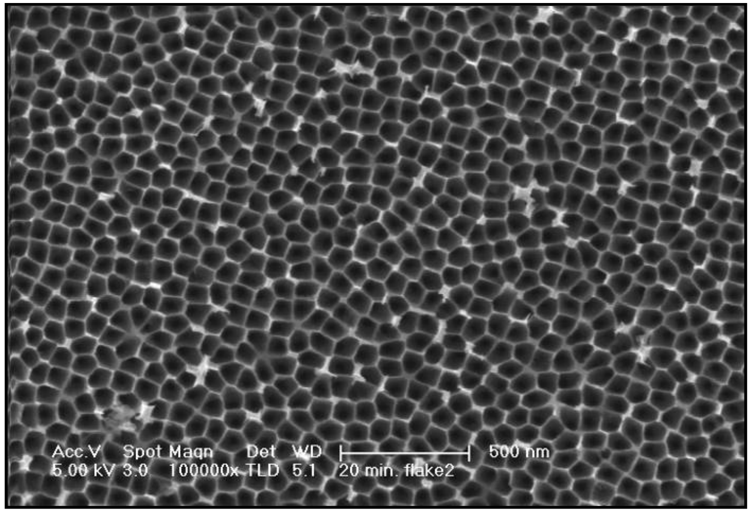
$\kappa = 3.9$

air

$\kappa = 1.0$

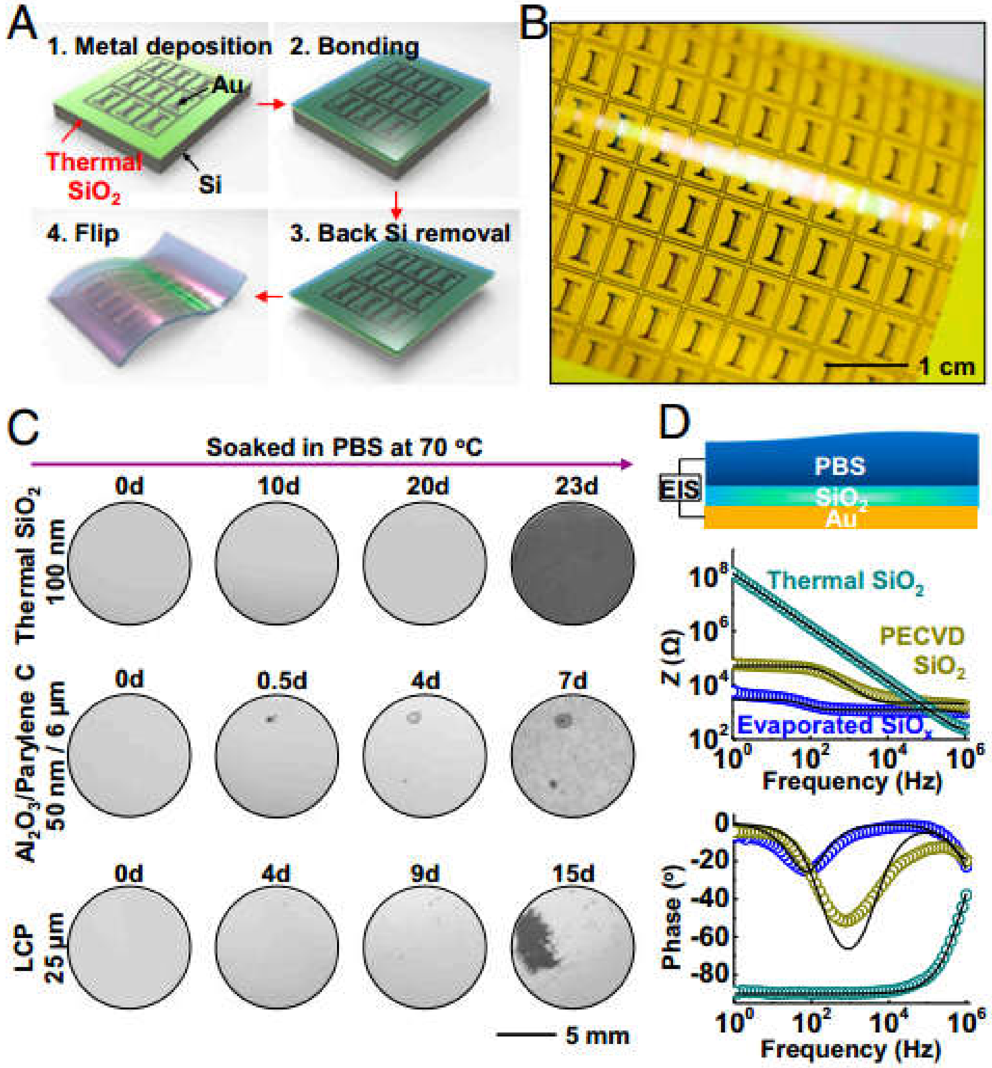






SiO_2 in Biointegrated Devices

Thermal oxide is an ideal moisture barrier



useful for implantable devices

At room temperature, it will take > 100 years to dissolve 1 μm thermal SiO_2 in water

H. Fang, *et al.*, *Proc. Natl. Acad. Sci.* **113,** 11682 (2016)