

Nanotechnology Applications

E SC 215

Unit 4

Oxidation and Dielectric Materials

Lecture 1

Dielectrics by Growth and Deposition

Outline

- Introduction – Silicon Dioxide
- Types of Oxide
- Furnace Deposition
 - Dry Oxidation
 - Wet Oxidation
- High Pressure Oxidation
- Chemical Vapor Deposition
- Modifying Dielectric Constant

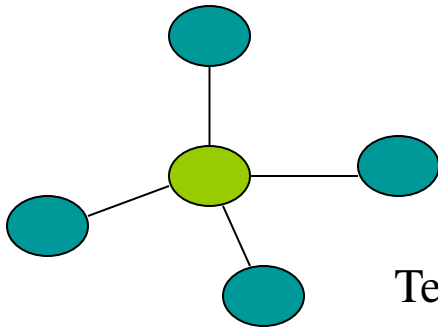
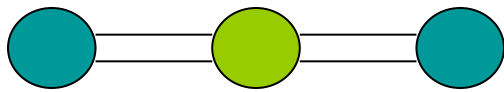
Oxidation

- Oxidation is a chemical reaction in which silicon and oxygen form a stable material called silicon dioxide.

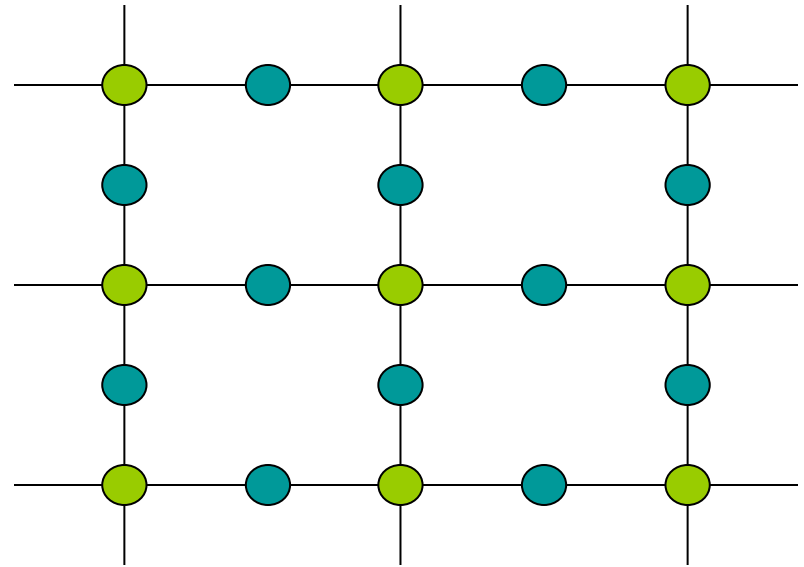
Silicon Dioxide

- A high quality, stable electrical insulator material
- Grows naturally on silicon
- Has many uses

Silicon Dioxide



Tetrahedral
Structure of oxide



Oxide Lattice

Key:

Oxygen

Si



Oxide Quality

- Determined by checking:
 - Film thickness and uniformity (nm)
 - Defects (#/volume)
 - Dielectric strength (MV/cm²)
 - Stress (MPa)
 - Interface properties

Film Thickness

- Oxide film thickness can be roughly judged by the color of the oxide.
- This is a general measurement, but can be useful.

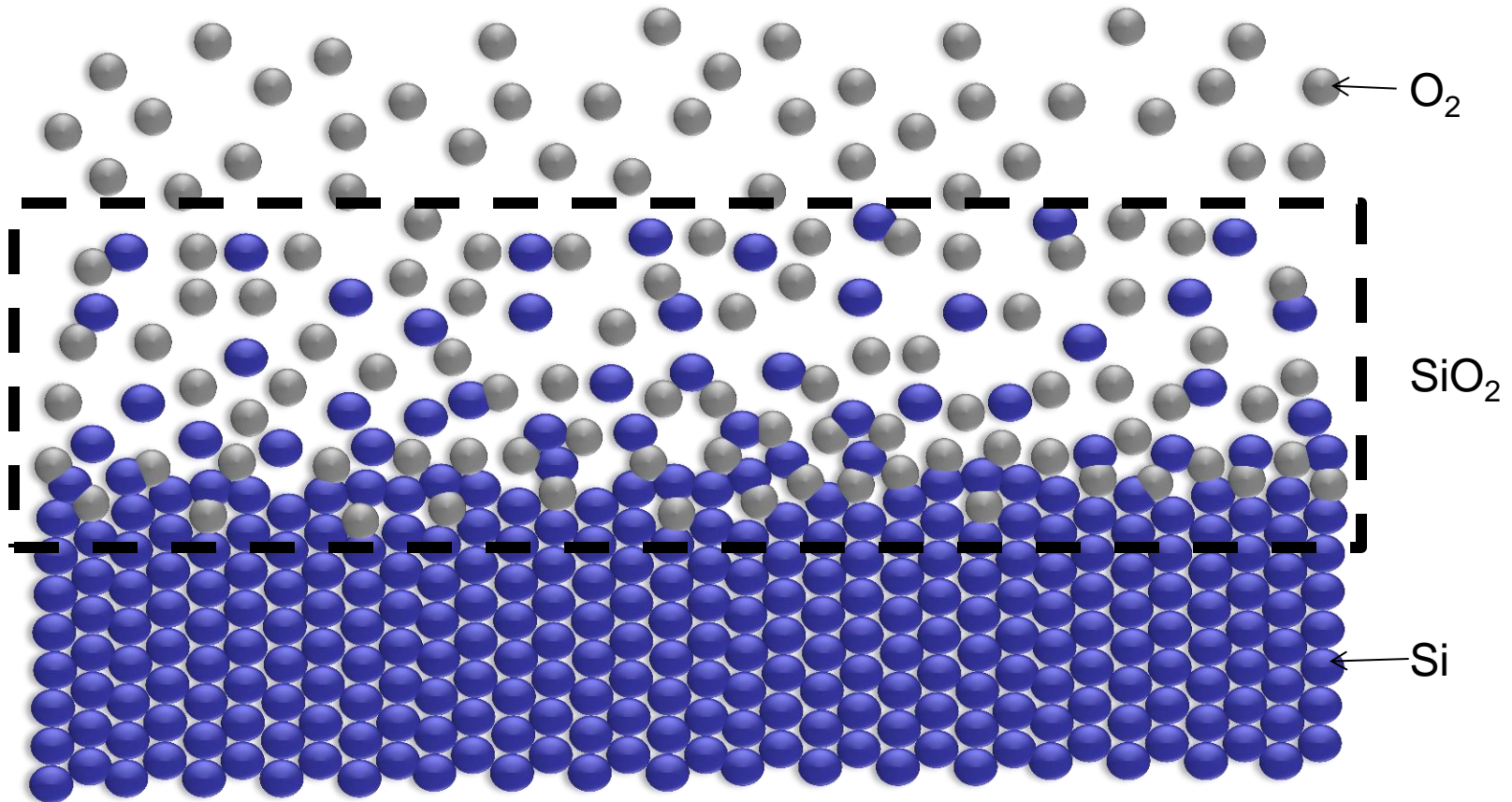
Silicon Dioxide Thickness

Thickness	Color	Thickness	Color
0.05 μm	Tan	0.54	Yellow-green
0.12	Royal Blue	0.57	Yellow to “yellowish”
0.17	Metallic to v. light yellow-green	0.60	Carnation Pink
0.22	Gold w/ orange-yellow	0.63	Violet-red
0.27	Red-violet	0.80	Orange
0.32	Blue to Blue-green	0.85	Dull, light Red-violet
0.36	Yellow-green	0.87	Blue-violet
0.39	Yellow	0.92	Blue-green
0.42	Carnation Pink	0.97	Yellow to “yellowish”
0.50	Blue-green	1.00	Carnation Pink

Mechanism

- Oxygen moves through the oxide layer to react with the silicon below.
- Oxygen diffuses from an area of high concentration (gas) to an area of low oxygen conc. (silicon).
- Fick's first law states that the particle flow per unit area, J (particle flux), is directly proportional to the concentration gradient of the particle:
 - $J = -D\partial N(x,t)/\partial x$

Diffusion of Oxygen



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Mechanism

- Silicon in the wafer is consumed as the oxide grows.
- Typically, for every 1000Å of oxide grown, 400Å of silicon is consumed.
- For a 1000Å layer of oxide, the wafer physically grows only 600Å.

Outline

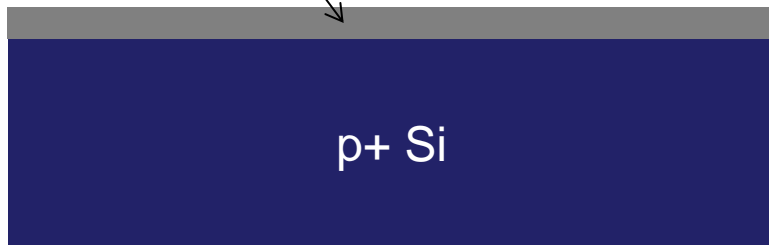
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Types of Oxides

- Native Oxide
 - Considered a contaminant. It grows naturally on silicon at room temperature due to the presence of O_2 in the ambient environment.
 - Can reach a maximum thickness of $\sim 40\text{\AA}$.
- Gate Oxide
 - A highly pure, specifically grown oxide that acts as a dielectric between the gate, source, and drain on the MOS structure.
 - Optimal thickness is between 20\AA and several hundred \AA .
 - Higher purity and thinner oxides lead to the production of faster devices.

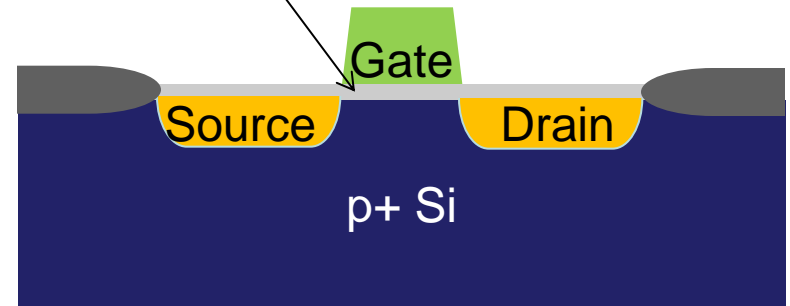
Types of Oxide

SiO₂ Native Oxide (200nm)



Native Oxide

Gate Oxide

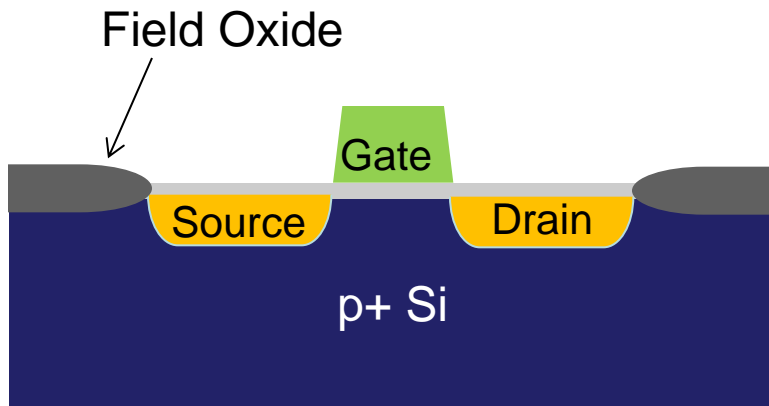


Gate Oxide

Types of Oxide

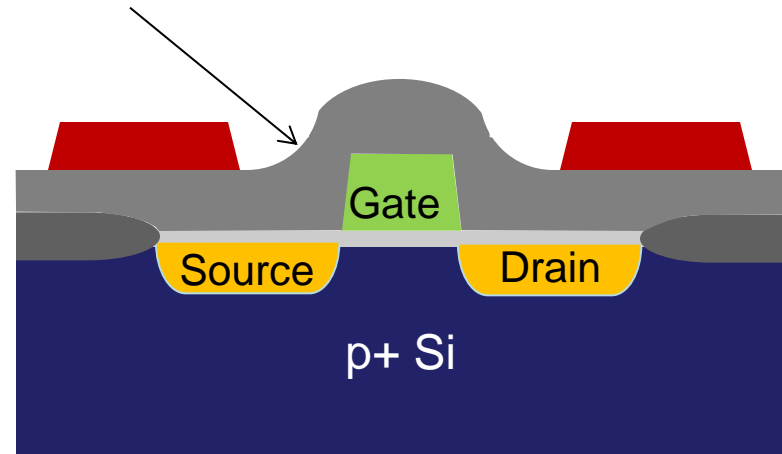
- Field Oxide (FOX)
 - Used to isolate individual transistors from each other on a wafer
 - Ideal thickness is between 2,500Å – 15,000Å.
- Barrier Oxide
 - Protects active devices and silicon from further processing
 - Ideal thickness is usually several hundred Å

Types of Oxide



Field Oxide

Barrier Oxide

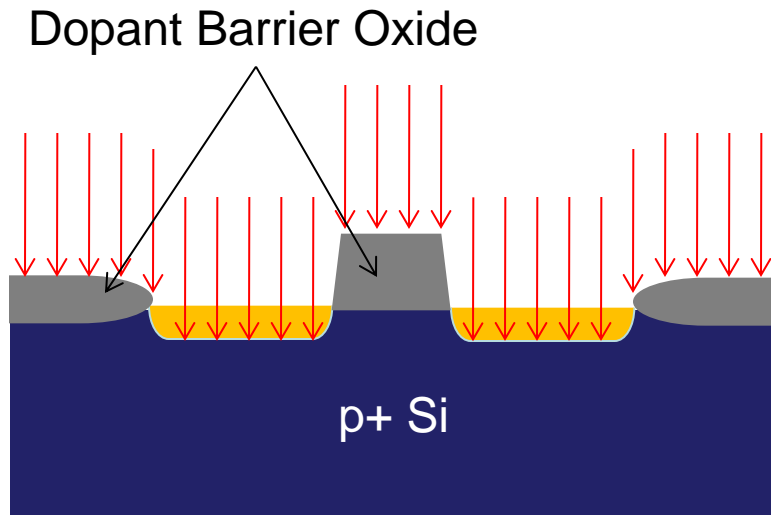


Barrier Oxide

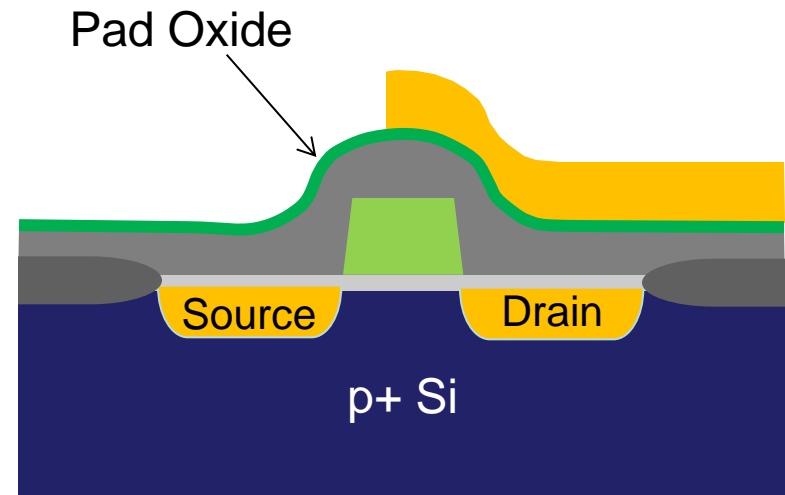
Types of Oxide

- Barrier
 - Used as a mask to prevent doping in unwanted areas
 - Also used in patterning of wafers. Its chemical resistance provides a strong barrier for etching/depositing/etc. patterns in a wafer
 - Optimal thickness $\sim 400\text{\AA} - 1,200\text{\AA}$, but it depends on the doping process.
- Pad Oxide
 - Reduces stress for Si_3N_4
 - Thickness is kept very thin.

Types of Oxide



Dopant Barrier Oxide

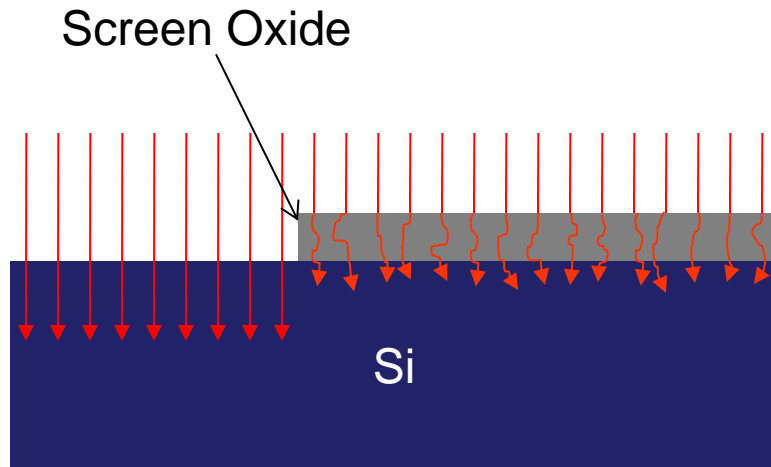


Pad Oxide

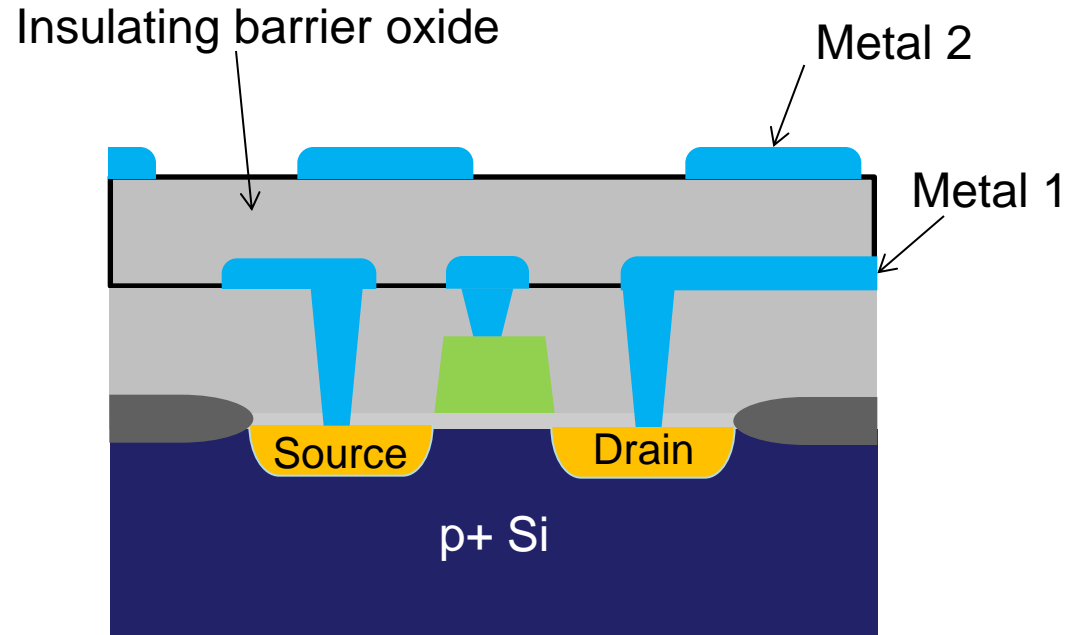
Types of Oxide

- Implant Screen Oxide
 - Used to prevent/minimize implant channeling and damage.
 - Thickness varies depending on implant depth.
- Insulating Barrier
 - Placed between metal layers to prevent electrical shorts
 - Used because of its insulating properties (does not conduct electricity)
 - This layer is deposited (as opposed to grown) and the required thickness varies.

Types of Oxide



Implant Screen Oxide



Insulating Barrier Oxide

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Oxidation

- Three methods for **growing** oxide:
 - High temperature oxidation (furnace)
 - w/ oxygen: dry oxidation
 - w/ steam: wet oxidation
 - High-pressure oxidation – HiPOx
- One method of **depositing** oxide:
 - CVD – chemical vapor deposition

Furnace Oxidation

- Important parameters for furnace processes:
 - Time
 - Temperature
 - Temperature gradients
 - Gas composition and purity
 - Gas flow rate
 - Thermal stress management

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Dry Oxidation

- Oxidation that occurs as a result of oxygen reacting with silicon
 - $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$
- Grows high quality thin layers of oxide (i.e. gate oxides)
- Grows oxide at a slow rate.

Dry Oxidation

- The process is performed in the furnace at a high temperature (normally above 1000°C)
- Uses oxygen as the process gas
- May use HCl in process to reduce charges at the wafer surface.

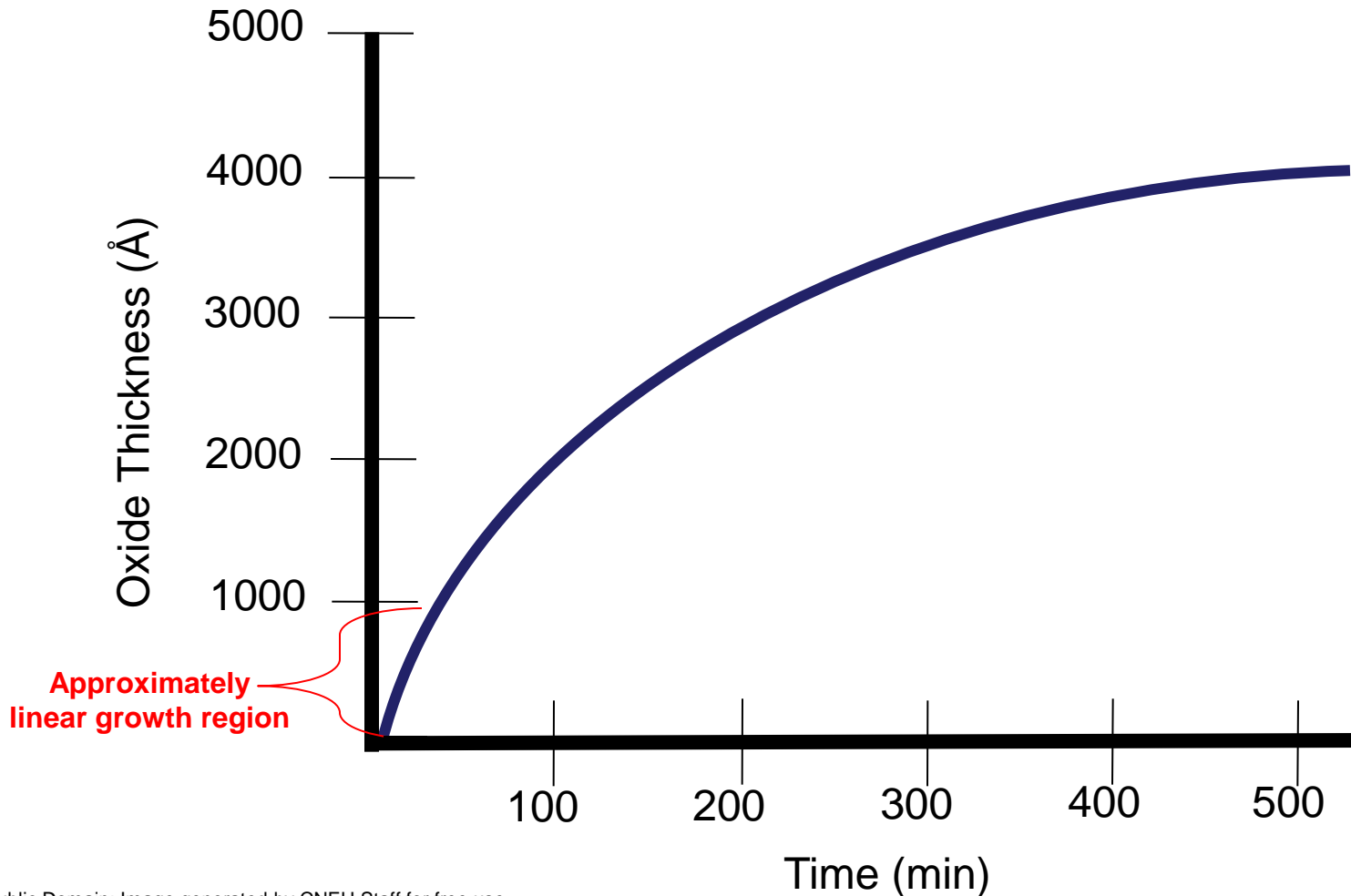
Dry Ox. Process Recipe

Step	Time (min)	Temp. (°C)	Gas Flow (SLM)		
			N ₂	O ₂	HCL
1) Idle state		850	3	0	0
2) Push wafer into furnace	5	850	3	0	0
3) Ramp up temp.	15	10°C/min	3	0	0
4) Temp. stabilization	5	1000	3	0	0
5) Dry oxide growth	30	1000	0	2.5	.067
6) Anneal	30	1000	3	0	0
7) Ramp down temp.	75	-2°C/min	3	0	0
8) Retrieve wafer	850	3	0	0	

Ramping

- With any furnace process, temperatures need to be changed slowly when wafers are present.
- The ramp-up rate (in this recipe) is $10^{\circ}\text{C}/\text{min}$. The ramp-down rate is $-2^{\circ}\text{C}/\text{min}$.
- These slow rates are necessary to prevent warping or other thermal stress problems in the silicon wafers.

Dry Ox. Growth Rate



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Wet Oxidation

- Oxidation that occurs as a result of steam reacting with silicon
 - $\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2$
- Grows oxide at a much faster rate and produces a lower quality oxide
- Use this technique when very thick oxides (i.e. field oxide) are needed rather than high quality

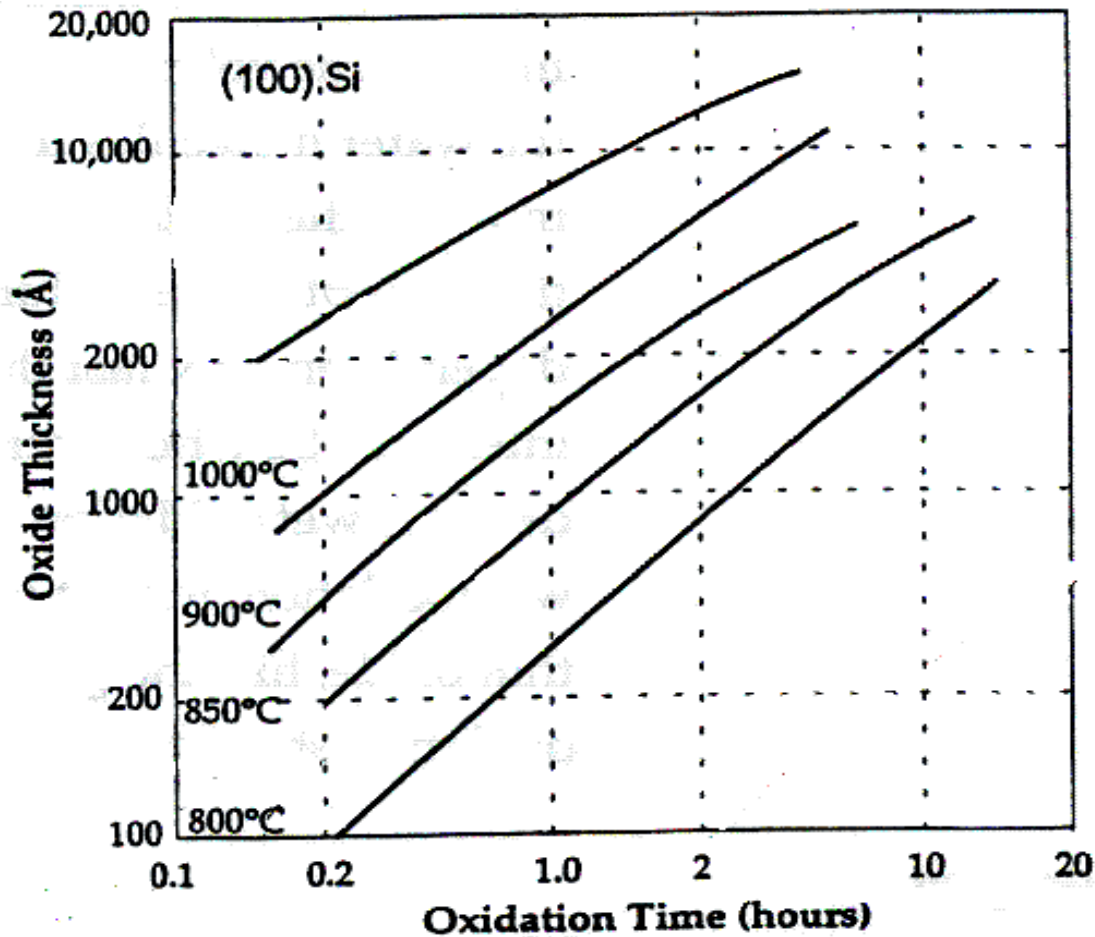
Wet Oxidation

- The process is performed in the furnace at high temperatures (normally 1000°C)
- Uses steam as the process gas
 - Steam is pyrolytic meaning that in high heat H_2 and O_2 are reacted together to create water vapor molecules
 - This produces a much purer steam for oxidation

Chlorinated Agents

- Using chlorinated gases in the oxidation process can neutralize charge accumulation at the silicon oxide interface.
- Chlorinated agents are kept under 3% so instability is not created in the oxide layer.
- Chlorinate agents can increase growth rates by 10-15%. This mechanism is poorly understood.
- Trichloroethane (TCA), an organochloride, offers low corrosion to the oxidation system.

Wet Ox. Growth Rate



Wet Vs. Dry Oxidation

- Dry Ox. Grows higher quality oxides
 - In Wet Ox., steam reacts with silicon and produces hydrogen molecules. These molecules become trapped in the oxide and change the stoichiometry of the oxide
 - Stoichiometry indicates how closely the deposited film approaches the ratio of the elements given by its chemical formula

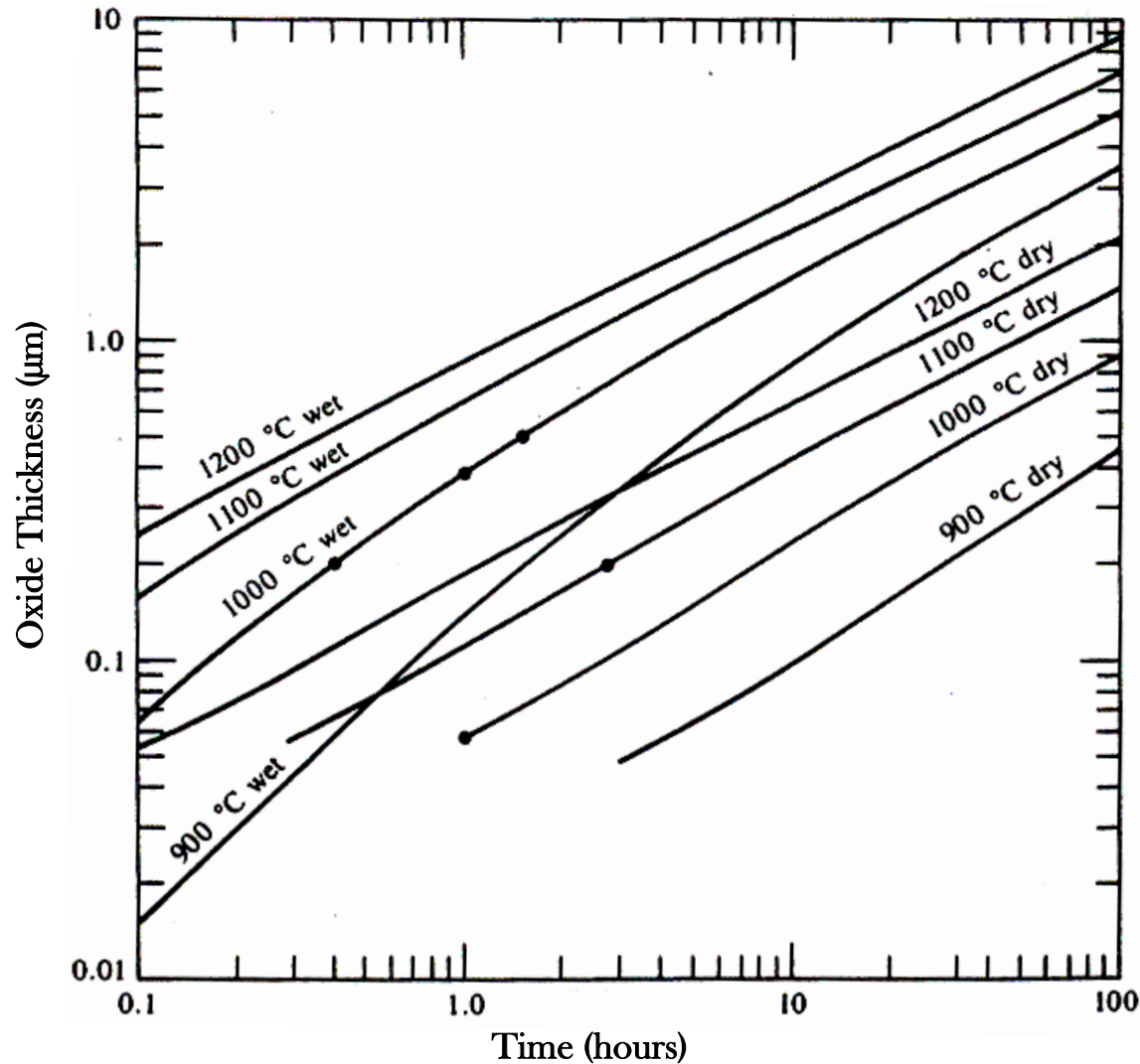
Wet Vs. Dry Oxidation

- Wet Ox. grows oxides faster
 - At 1000°C, the solubility of water in silicon (total amount of water that can be present in a certain volume of silicon) is 600 times that of oxygen in silicon.
 - Even though oxygen diffuses faster, it has a lower solubility and physically can fit fewer atoms in the silicon.

Wet Vs. Dry Oxidation

Oxide Type	Temp (°C)	Thickness (Å)	Time
Dry	1000	1000	2 hours
Wet	1000	1000	12 minutes

Wet and Dry Oxide Growth



Increasing Temp. – Decreasing Time

- There are many problems with increasing the temperature at which a process runs.
 - Increased diffusion of impurities present in the wafer
 - Crystal defects (stacking faults)
 - Permanent damage from thermal stress
 - Equipment damage/more costly equipment to run at higher temperatures

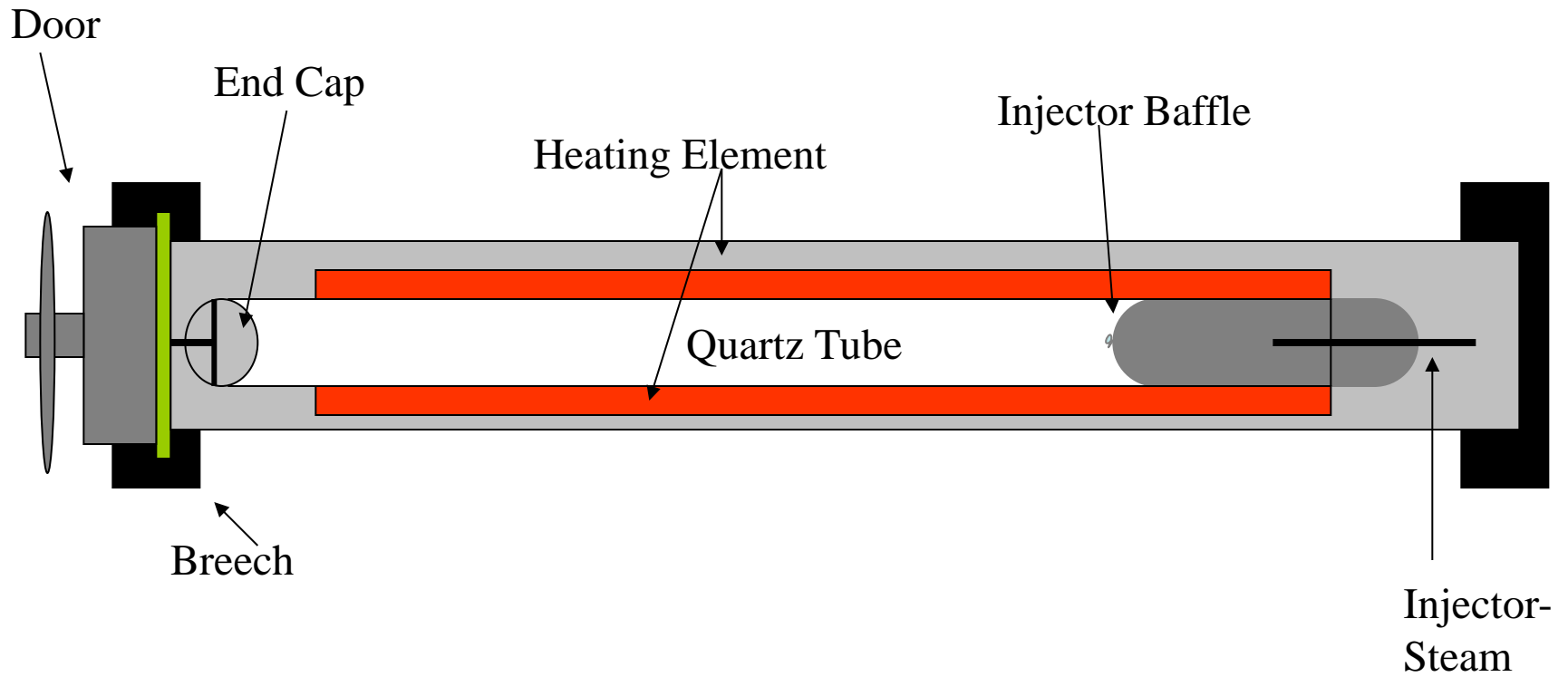
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High Pressure Oxidation - HiPOx

- Used to grow thick layers of oxide in reduced time and temperature (i.e. field oxide)
- Uses steam and oxygen as process gases
- Has special HiPOx system equipment

HiPOx System



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HiPOx

- Runs at reduced temperatures:
 - ~ 650°C – 900°C
- And increased pressures:
 - ~ 5 – 20 atm.

HiPOx Relationships

- Time and pressure are inversely related:

Temp. (°C)	Pressure (atm.)	Time
900	1	5 hours
900	5	1 hour
900	25	12 minutes

*Assuming that the wafers are of the same thickness

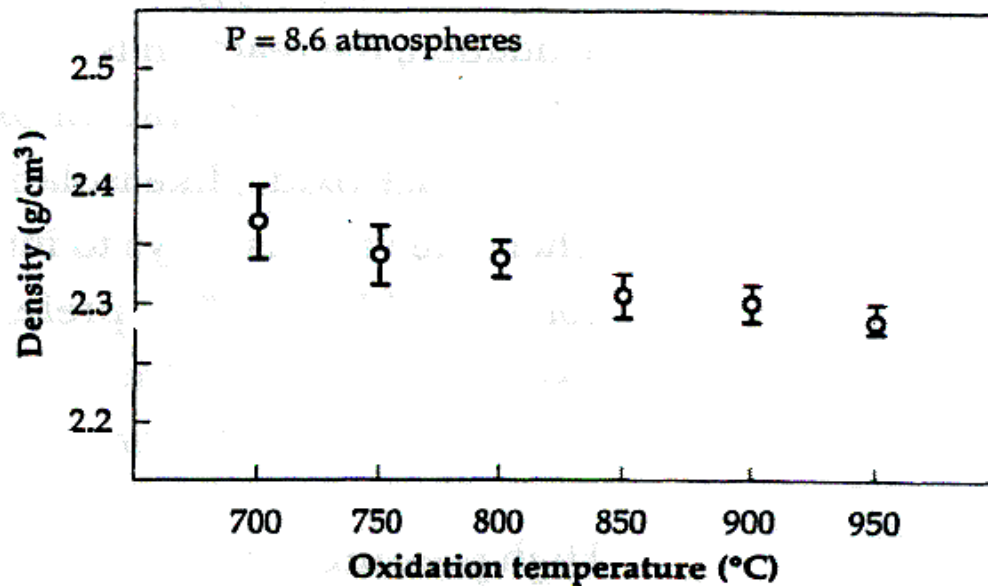
HiPOx Relationships

- Temperature and Pressure:
 - For every increase of one atmosphere, the temperature can be dropped by 30°C to obtain the same thickness in the same time

Time (hours)	Pressure (atm.)	Temp. (°C)
5	1	1000
5	10	700

HiPOx Relationships

- Temperature and oxide density:
 - As temperature decreases, oxide density increases.



HiPOx

- HiPOx allows the oxidation to occur at a lower temperature and higher pressure.
- As shown, HiPOx will produce a higher quality (greater density) oxide in a shorter time than dry or wet oxidation can produce (for equal thickness).

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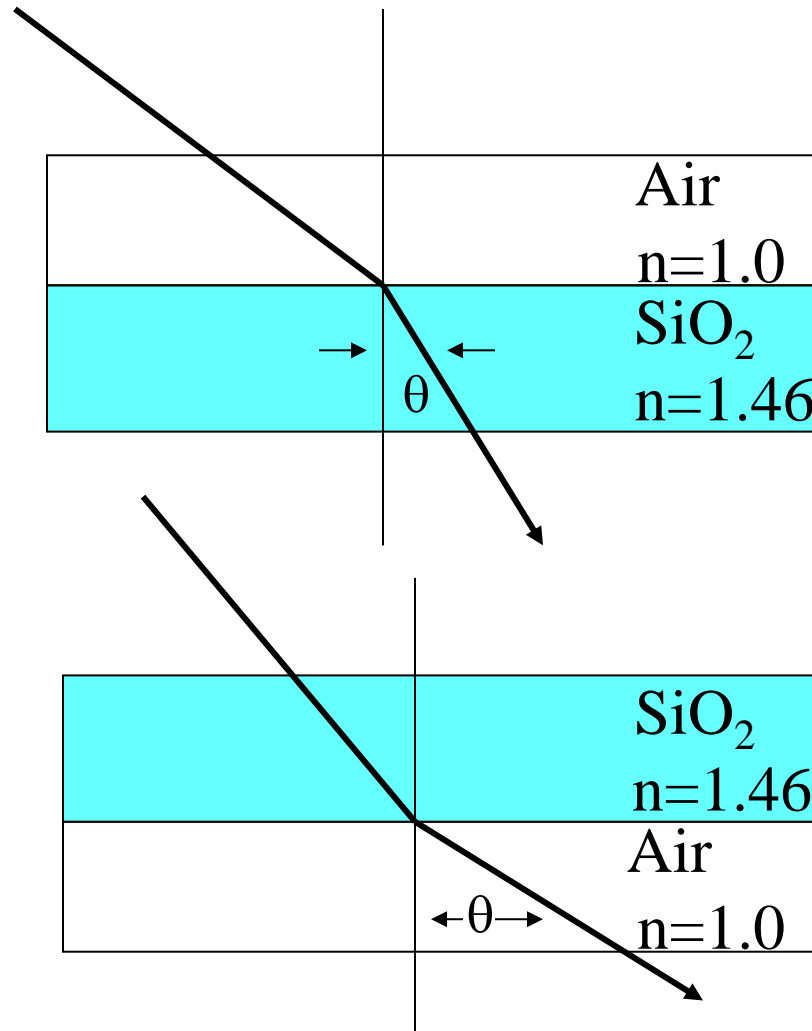
CVD

- The deposition of oxide onto a wafer using the decomposition of silane.
 - $\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2$
- “Deposits” a layer of oxide as opposed to the other techniques that “grow” the oxide.

CVD

- Oxide is deposited at $\sim 350^{\circ}\text{C}$.
- Silicon and oxygen react in plasma and deposit onto the wafer (other techniques diffuse O_2 into the wafer and use the wafer's silicon to produce oxide)
- Creates a nearly stoichiometric layer

Index of Refraction



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CVD

- Nitrous oxide (N_2O) or carbon dioxide (CO_2) are actually preferred over oxygen.
- The oxygen reacts too easily in the plasma and can cause poor film quality.

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Engineering Dielectric Constant (k)

- This concept centers around capacitance (C) and its relationship to signal time (T) when fabricating integrated circuits

$$C = \frac{k \epsilon_0 A}{d}$$

- k= dielectric constant
- ϵ_0 = permittivity of free space (constant)
- A= area
- d= distance between features

Engineering Dielectric Constant (k)

- Signal Time (T)

$$T = RC$$

- R= resistance of metals
- C= capacitance
- In IC fabrication, the idea is to use the correct dielectric material with the right constants for a desired process
 - Keeps the capacitance the same to insure the signal time is not compromised

Engineering Dielectric Constant (k)

- Figure of Merit
 - The figure of merit is a number expressed in farads/meter and is calculated by dividing capacitance (C) by area (A)
$$C/A = \text{figure of merit}$$
 - Used as a constant in IC fabrication
 - If device scaling changes, the dielectric material must change to maintain the figure of merit's value

Engineering Dielectric Constant (k)

- Interconnects- wiring
 - The wire lines must be as close as possible in order to fit the maximum amount of transistors on a chip
 - The distance must be minimized, therefore; the dielectric material must have a low k
 - As d decreases, k must also decrease

Engineering Dielectric Constant (k)

- Gates
 - Uniformity is a key quality parameter
 - It is easier to make the gates thicker, to insure that any variation in uniformity won't impact device performance as drastically
 - Example 1: If a gate is 30Å:
 - Material uniformity that varies by 10Å drastically alters performance
 - Example 2: If a gate is 100Å
 - Material uniformity that varies by 10Å does not impact performance that drastically

Engineering Dielectric Constant (k)

- Gates
 - A thicker gate requires a dielectric material with a high k value
 - As d increases, k must also increase

High k Dielectric Materials

- Ta_2O_5 , $k = 22\text{-}30$
- TiO_2 , $k = 20\text{-}85$
- Nb_2O_5 , $k = 11$
- HfO_2 , $k = 17$
- Y_2O_3 , $k = 15$

Low k Dielectric Materials

- FSG, $k = 3.4-4.1$
- HSQ, $k = 2.9$
- Nanoporous silica, $k = 1.3-2.5$
- Fluorinated polyimide, $k = 2.6-2.9$
- PTFE, $k = 1.9$
- DVS-BCB, $k = 2.65$
- Aromatic hydrocarbon, $k = 2.65$