Fundamentals of Micro and Nanofabrication
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Lecture – 17
Chemical Vapor Deposition: Precursor Transport

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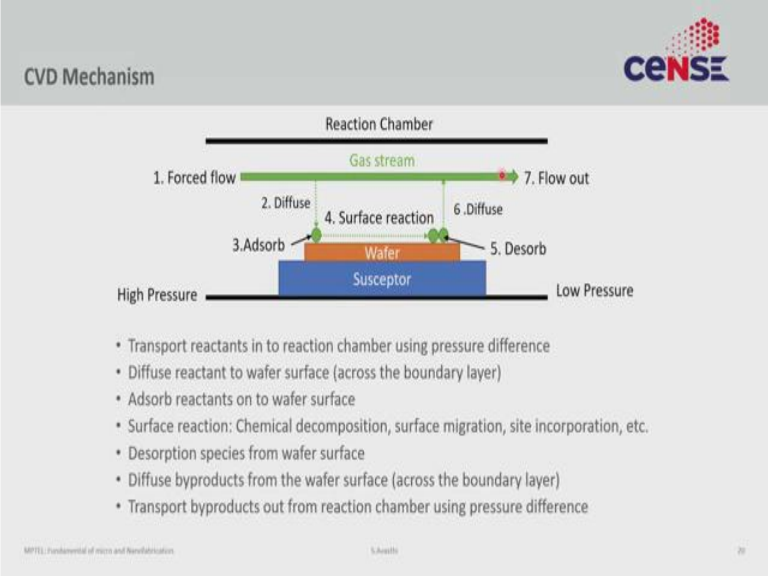

CVD Mechanism

- Transport reactants in to reaction chamber using pressure difference
- Diffuse reactant to wafer surface (across the boundary layer)
- Adsorb reactants on to wafer surface
- Surface reaction: Chemical decomposition, surface migration, site incorporation, etc.
- Desorption species from wafer surface
- Diffuse byproducts from the wafer surface (across the boundary layer)
- Transport byproducts out from reaction chamber using pressure difference

Before we go look at other components such as the susceptor, the chamber, the substrate, let's think about how the CVD happens. This discussion will span a couple of lectures. Here is a list of processes that must happen in order for the CVD to occur. We have already discussed precursors. The precursors are in the gas stream here. How does this gas stream flow inside the reactor? We have discussed some basics of fluid dynamics or viscous flow. CVD happens is in the viscous flow regime. The gas flow depends upon the geometry of the reactor, and that is where the reactor design and various other aspects come in. After understanding the gas flow inside a CVD reactor, you must also look at how the precursor makes its way to the surface. In general, that happens through diffusion, and not drift because we form a boundary layer and then the only way things move through the boundary layer is by diffusion. Then the precursor must be adsorbed on the surface, where it will do a surface reaction and form these particle nuclei, which must nucleate to form a film. The byproducts must diffuse out back into the gas stream that flows out of your vacuum chamber.

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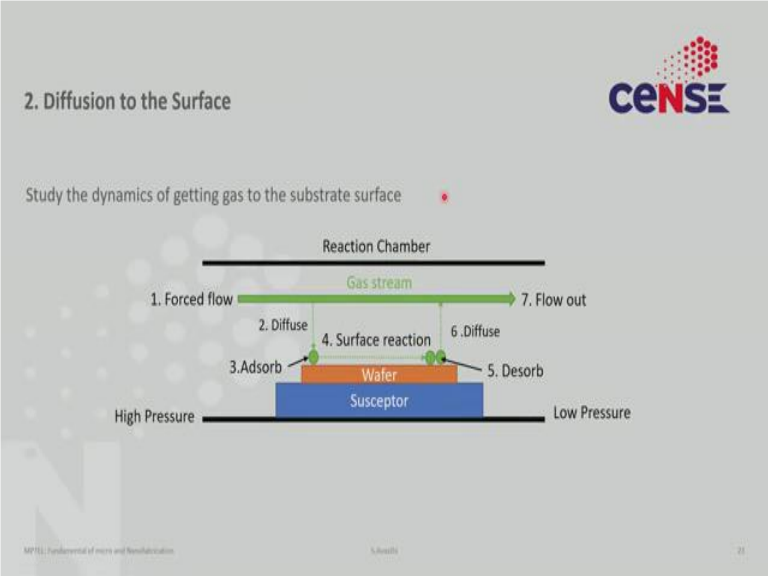

2. Diffusion to the Surface

Study the dynamics of getting gas to the substrate surface

Let’s first talk about diffusion or getting the precursor to the surface.

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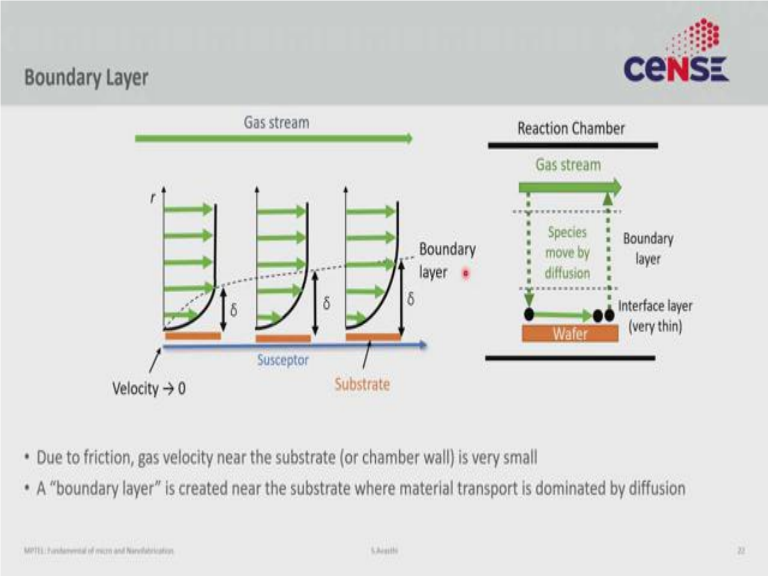

Boundary Layer

- Due to friction, gas velocity near the substrate (or chamber wall) is very small
- A “boundary layer” is created near the substrate where material transport is dominated by diffusion

The glass frame that you use is a boundary for the gas stream. So are the wafers and the susceptor on which they sit. Imagine three wafers sitting on a susceptor. This susceptor is one of the boundaries of the gas flow, and the other boundary is somewhere far away and not shown here. You are looking at a zoomed-in image of your reactor very close to the susceptor. You can see the flow lines and velocity profile of the gas in the chamber. As we have discussed, the reason for this unique shape is the no-slip boundary condition.

Assume that the gas that is very close to the interface does not have any velocity. As you go further away from the interface, the velocity increases until it becomes v_o, which is the velocity in the center of the flow. As there is no velocity of gas near the susceptor or the wafer, there is no way of transporting material to the wafer or away from it. A boundary layer or an arbitrary line representing the stagnant layer forms on top of the wafer because of no-slip boundary condition. Any fresh precursor or byproducts must diffuse through this stagnant boundary layer to get to the wafer and do the chemical reaction and deposition. Also, this boundary layer is not uniform. It might be very small at the start of the boundary, but as you go further in the flow direction, the boundary layer becomes thicker and hence, the diffusion of the precursor/byproducts becomes harder because of the distance that the material has to travel increases.

Inside the reaction chamber, you have a gas stream and a boundary layer or dead layer of varying thickness depending upon the distance. The precursors must move from the gas stream to the wafer surface and the byproducts from the wafer to the stream. The shape and thickness of this boundary layer are important aspects of reactor design.

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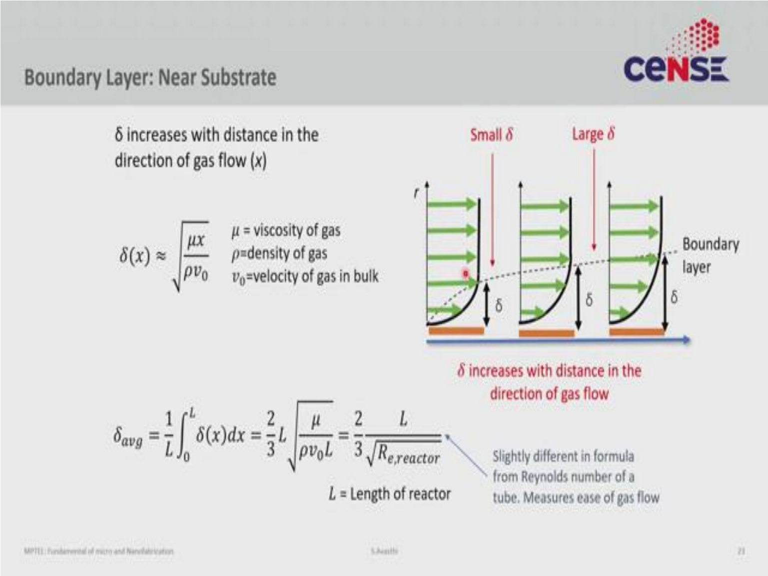

Boundary Layer: Near Substrate

δ increases with distance in the direction of gas flow (x)

$$\delta(x) \approx \sqrt{\frac{\mu x}{\rho v_0}}$$

μ = viscosity of gas
ρ=density of gas
v_0=velocity of gas in bulk

δ increases with distance in the direction of gas flow

$$\delta_{avg} = \frac{1}{L}\int_0^L \delta(x)dx = \frac{2}{3}L\sqrt{\frac{\mu}{\rho v_0 L}} = \frac{2}{3}\frac{L}{\sqrt{R_{e,reactor}}}$$

L = Length of reactor

Slightly different in formula from Reynolds number of a tube. Measures ease of gas flow

Solving simple laminar flow equations in this system, you see that the boundary layer is approximately given by this formula. It depends upon the viscosity of the gas μ, the density of the gas ρ and the velocity of the gas in bulk v_o, far away from the boundary, in the middle of the chamber. For a given reactor, you can define a certain Reynolds number or

Re of the reactor is slightly different from a tube, but essentially measures how easy it is to flow gas through a reactor.

For a thin boundary layer or stagnant layer, most of the reactor the gas can flow easily and it is only mitigated in the boundary layer. If a reactor has a very thick boundary layer, the gas will feel a lot of impedance and the actual gas flow will be restricted in a narrower region. For a simplified 1D case, the boundary layer starts from 0 and increases as you go further into the reactor. The average boundary layer thickness which is the first moment of this equation $\delta_{avg} \propto L$, where L is the length of the reactor along the blue line. Re for a given reactor is a constant that captures the ability of gas to flow inside it. Re depends upon the gases flowing inside, the precursors, and the gas flow velocity which is constant for fixed pumping and the pressures. The gas velocity depends upon the pumping pressure by Ohm's law of gases we looked at it in the last lecture.

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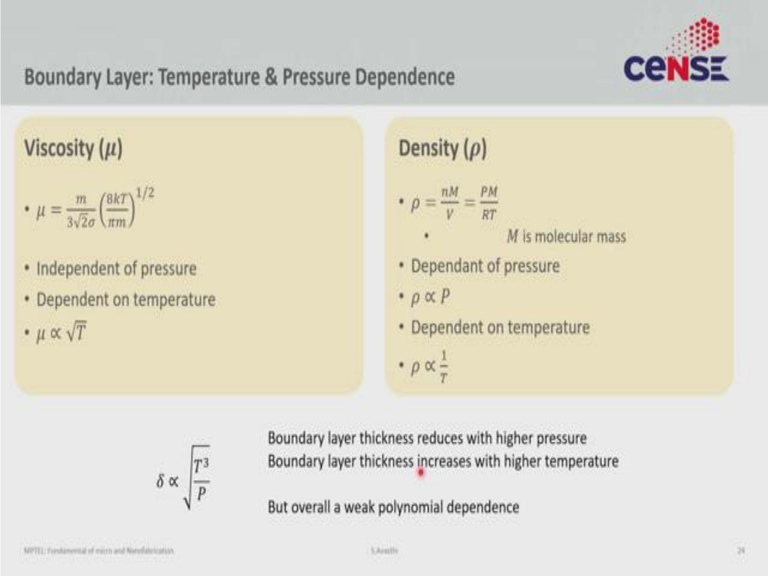

Boundary Layer: Temperature & Pressure Dependence

Viscosity (μ)

- $\mu = \frac{m}{3\sqrt{2}\sigma}\left(\frac{8kT}{\pi m}\right)^{1/2}$
- Independent of pressure
- Dependent on temperature
- $\mu \propto \sqrt{T}$

Density (ρ)

- $\rho = \frac{nM}{V} = \frac{PM}{RT}$
  - M is molecular mass
- Dependant of pressure
- $\rho \propto P$
- Dependent on temperature
- $\rho \propto \frac{1}{T}$

$$\delta \propto \sqrt{\frac{T^3}{P}}$$

Boundary layer thickness reduces with higher pressure
Boundary layer thickness increases with higher temperature

But overall a weak polynomial dependence

The viscosity and density of gas are slightly different from that of a liquid. Assuming the kinetic theory of gases, viscosity and density are given by these formulae and are temperature dependent quantities. Viscosity increase with temperature for gases and density decreases with temperature. Overall the boundary layer thickness δ depends on both μ and ρ and has $T^{3/2}$ dependence on temperature, and an inverse dependence on pressure. However, it doesn't have an exponential dependence on either of these quantities. The boundary layer does not change by an order of magnitude with the temperature or pressure of the growth. It is a weak polynomial dependence, which is a good thing because CVD often is done over a very wide range of temperatures and pressure. If the boundary layer kept changing, then all the parameters in the optimization of the CVD would also keep changing, and it would be very hard.

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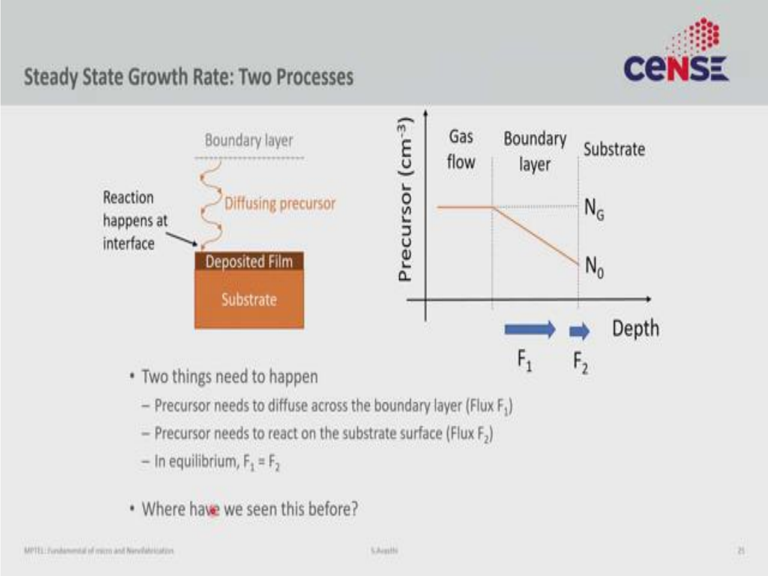

Steady State Growth Rate: Two Processes

- Two things need to happen
  - Precursor needs to diffuse across the boundary layer (Flux F_1)
  - Precursor needs to react on the substrate surface (Flux F_2)
  - In equilibrium, $F_1 = F_2$
- Where have we seen this before?

Now that we have understood that there is the stagnant boundary layer of varying thicknesses that forms on top of a wafer, we can do a little bit more in terms of growth mechanism. If you remember the lecture on native oxide growth, you will find this to be eerily similar where we had assumed that there is a gas flow region, a certain region through which the precursor diffuses and the reaction happens on the substrate. The only difference was that instead of the boundary layer, the diffusion was happening through silicon dioxide, and instead of the reaction happening on top of the substrate, the reaction was occurring between silicon dioxide and silicon on the buried interface, not at the top of the interface.

In that case (oxide growth), we had completely ignored the gas flow and assumed the gas concentration outside to be constant. In this case (CVD), we cannot assume that. The concentration of gases beyond the boundary layer can be assumed to be constant, but diffusion must occur through the boundary, and the material must get to the top of the deposited film, where the reaction will occur. These two fluxes, the flux of diffusion and the flux of surface reaction must be equal under equilibrium. So, $F_1 = F_2$.

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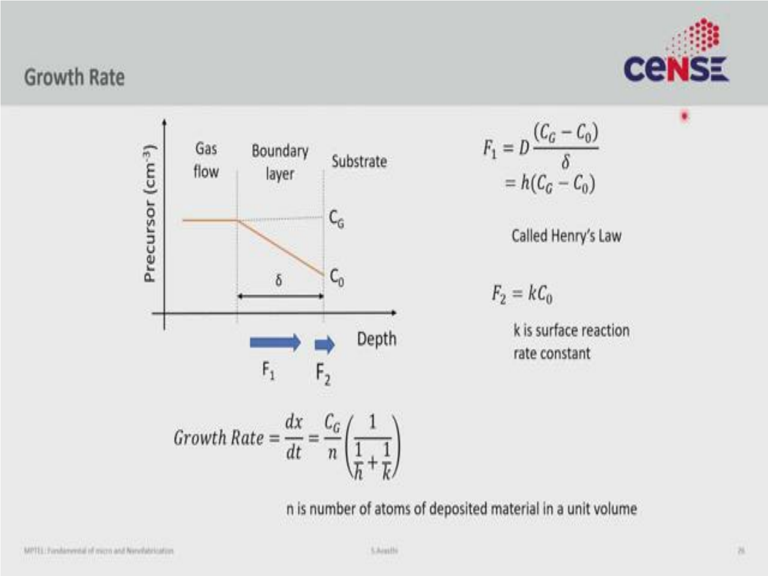

Growth Rate

$$F_1 = D\frac{(C_G - C_0)}{\delta}$$
$$= h(C_G - C_0)$$

Called Henry's Law

$$F_2 = kC_0$$

k is surface reaction rate constant

$$Growth\ Rate = \frac{dx}{dt} = \frac{C_G}{n}\left(\frac{1}{\frac{1}{h}+\frac{1}{k}}\right)$$

n is number of atoms of deposited material in a unit volume

The diffusion flux (F_1) is given by Fick's law, which is simply the diffusion coefficient multiplied by the gradient. To first order, we can assume the gradient to be linear (a flat line), which is $\frac{C_G - C_o}{\delta}$, where δ is the boundary layer thickness, C_o is the concentration at the substrate, and C_G is the concentration of gas in the middle of the reactor. This is often called Henry's law. This D/δ is converted into a constant called h for ease. For a given reactor, the value of h is known.

The flux F_2 again is due to a chemical reaction. Assuming first-order kinetics, we have $F_2 = kC_o$, where C_o is the concentration of the reactant at the substrate and k is a surface reaction rate constant. And if $F_1 = F_2$, you can do a little bit of math and come up with a growth rate: $\frac{dx}{dt} = \frac{C_G}{n}(\frac{1}{\frac{1}{h}+\frac{1}{k}})$, where n is the number of atoms per unit volume or atomic density.

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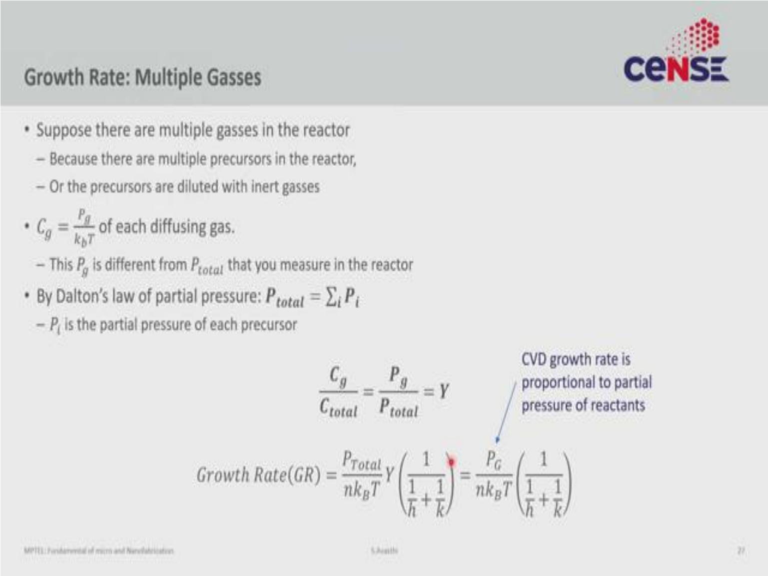

Growth Rate: Multiple Gasses

- Suppose there are multiple gasses in the reactor
  - Because there are multiple precursors in the reactor,
  - Or the precursors are diluted with inert gasses
- $C_g = \frac{P_g}{k_b T}$ of each diffusing gas.
  - This P_g is different from P_{total} that you measure in the reactor
- By Dalton's law of partial pressure: $P_{total} = \sum_i P_i$
  - P_i is the partial pressure of each precursor

$$\frac{C_g}{C_{total}} = \frac{P_g}{P_{total}} = Y$$

CVD growth rate is proportional to partial pressure of reactants

$$Growth\ Rate(GR) = \frac{P_{Total}}{nk_B T} Y \left(\frac{1}{\frac{1}{h} + \frac{1}{k}}\right) = \frac{P_G}{nk_B T}\left(\frac{1}{\frac{1}{h} + \frac{1}{k}}\right)$$

If you have multiple precursors, things become a little more complicated. If you have multiple gases in the reactor, you must talk about each individual component. The concentration C_G can be converted to pressure because the pressure is what we actually measure, which we know is proportional to C_G: $C_G = \frac{P_G}{k_B T}$, where k_B is the Boltzmann constant.

According to Dalton's law of partial pressure, the total pressure is the sum of all these component pressures. If P_i is the partial pressure of each precursor, $P_{Total} = \sum_i P_i$. The fractional concentration of a certain gas is the partial pressure of that gas divided by the total pressure. Y is the ratio of partial pressure to total pressure. The growth rate equation that I showed before can then be written in terms of what we actually control – pressure and temperature. Boltzmann constant is a constant and n is a material property.

This equation $GR = \frac{P_{Total} Y}{nk_B T} \left(\frac{1}{\frac{1}{h}+\frac{1}{k}}\right)$ is extremely useful. In the first generalization, the growth rate depends upon the total pressure. This is true across all CVD. If you want to increase your growth rate, you must increase your pressure.

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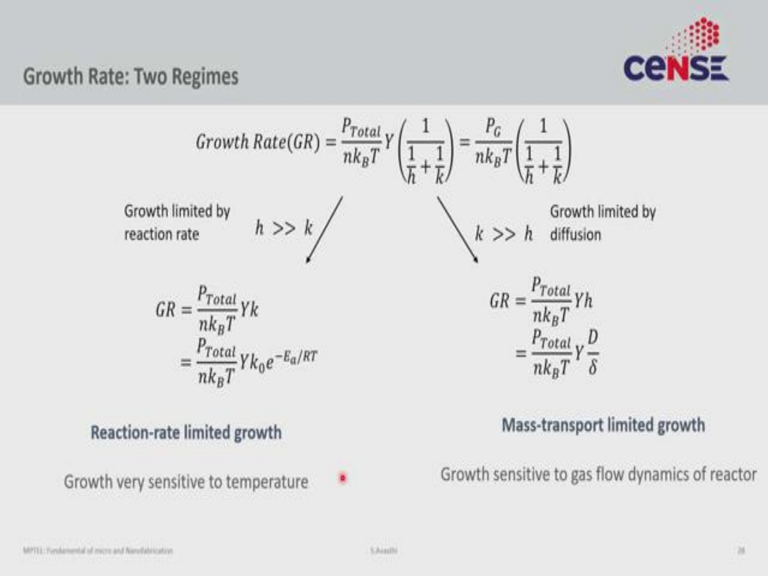

Growth Rate: Two Regimes

$$Growth\ Rate(GR) = \frac{P_{Total}}{nk_BT}Y\left(\frac{1}{\frac{1}{h}+\frac{1}{k}}\right) = \frac{P_G}{nk_BT}\left(\frac{1}{\frac{1}{h}+\frac{1}{k}}\right)$$

Growth limited by reaction rate $h >> k$

$$GR = \frac{P_{Total}}{nk_BT}Yk = \frac{P_{Total}}{nk_BT}Yk_0e^{-E_a/RT}$$

Reaction-rate limited growth

Growth very sensitive to temperature

$k >> h$ Growth limited by diffusion

$$GR = \frac{P_{Total}}{nk_BT}Yh = \frac{P_{Total}}{nk_BT}Y\frac{D}{\delta}$$

Mass-transport limited growth

Growth sensitive to gas flow dynamics of reactor

Once again, there are two regimes. Assume two cases; one, where the h >> k or the fast diffusion case. If diffusion is very fast in a process and two processes are happening in series, then diffusion is not the bottleneck but the reaction rate or F_2 is. In that case, the growth rate can be given by this equation: $GR = \frac{P_{Total}}{nk_BT}Yk$. k is the chemical reaction rate constant which by Arrhenius equation must be exponentially related to temperature. Overall, if you look at this expression, you realize that the growth rate is linearly dependent on pressure, but is exponentially depends on temperature. The growth in the reaction rate limited regime is extremely sensitive to temperature. A 50^o change in temperature up or down can change the growth rate by orders of magnitude.

The other case is where k >> h and F_2 is not the bottle-beck. The reaction can happen at arbitrarily higher speeds and the problem is getting the reactant to the surface of the wafer. So, in that case, we are limited by diffusion and hence, it is called a growth limited by diffusion or mass transport. The growth rate in this case: $GR = \frac{P_{Total}}{nk_BT}Y\frac{D}{\delta}$, where δ is the boundary layer thickness. the growth rate is proportional to pressure but unlike the reaction rate limited regime, the temperature dependence only comes because of this T, and some from D and δ. All of these are polynomial, so the growth rate is much more insensitive to temperature. However, it is sensitive to δ, which is sensitive to the gas flow dynamics of the reactor. The reactor shape and flow dynamics are very critical in mass transport limited regime and the temperature in reaction rate limited regime.

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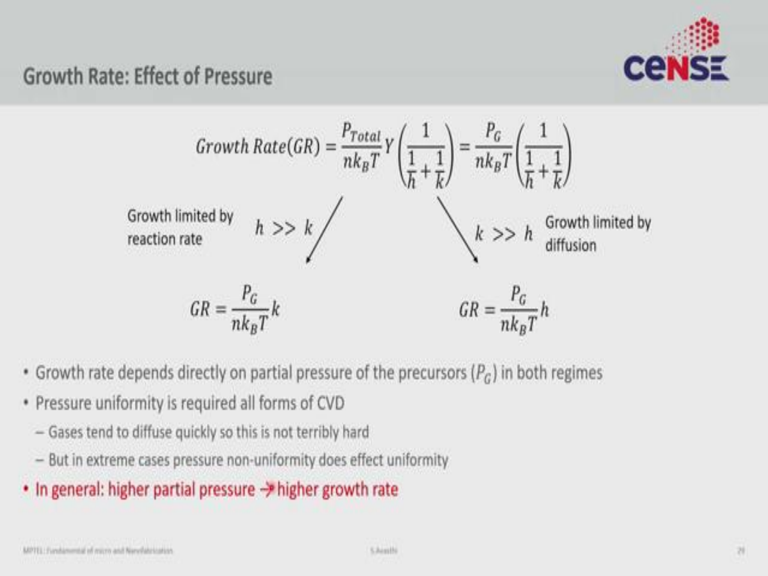

Growth Rate: Effect of Pressure

$$Growth\ Rate(GR) = \frac{P_{Total}}{nk_BT}Y\left(\frac{1}{\frac{1}{h}+\frac{1}{k}}\right) = \frac{P_G}{nk_BT}\left(\frac{1}{\frac{1}{h}+\frac{1}{k}}\right)$$

Growth limited by reaction rate $h >> k$

$$GR = \frac{P_G}{nk_BT}k$$

$k >> h$ Growth limited by diffusion

$$GR = \frac{P_G}{nk_BT}h$$

- Growth rate depends directly on partial pressure of the precursors (P_G) in both regimes
- Pressure uniformity is required all forms of CVD
  - Gases tend to diffuse quickly so this is not terribly hard
  - But in extreme cases pressure non-uniformity does effect uniformity
- In general: higher partial pressure → higher growth rate

The growth rate depends on pressure, so, the pressure uniformity sort of required in all the types of CVD. Thankfully this is not too much of a problem as the gases tend to diffuse very quickly. It is very hard to maintain a very large gradient of gaseous precursors inside the reactor.

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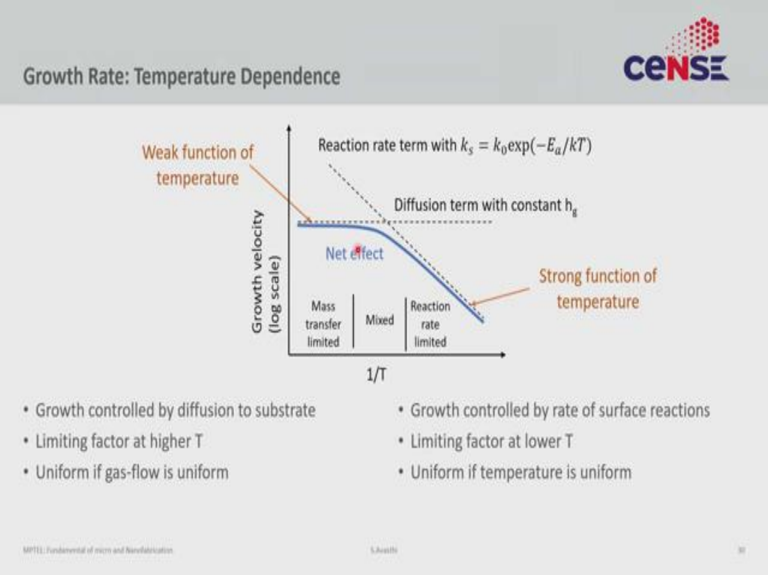

Growth Rate: Temperature Dependence

- Growth controlled by diffusion to substrate
- Limiting factor at higher T
- Uniform if gas-flow is uniform

- Growth controlled by rate of surface reactions
- Limiting factor at lower T
- Uniform if temperature is uniform

Overall, the growth rate (plotted in Arhennius form) shows the following temperature dependence. You have the two regimes, demonstrated as tangents to the growth rate curve. In reaction rate limited regime, where the reaction rate is the bottleneck, the rate depends upon the temperature exponentially. In mass transport limited case, where the reaction rate is very fast but the diffusion is slow, the rate is limited by h. For the sake of argument, let’s assume h to be constant with temperature. In that case, the growth velocity will be an independent function of temperature and will be completely flat. At lower temperatures, because of this exponential relationship, k’s are very small, so you often are reaction rate limited. As the temperature goes up, the value of k grows and at some point, it becomes higher than h, and you the mass transport limited regime, where the reaction rates are very fast, but precursors are not coming in. Somewhere in the middle, you have this mixed regime.

In mass transport limited regime, at high temperatures, the problem is getting the material to the substrate. The growth rate is uniform if the gas flow is uniform as it makes h uniform. However, in a reaction rate limited case, the problem is the reaction at the substrate and you are limited by the temperature. The growth rate is proportional to k or the reaction rate constant and it is uniform if the temperature on top of the wafer is uniform.

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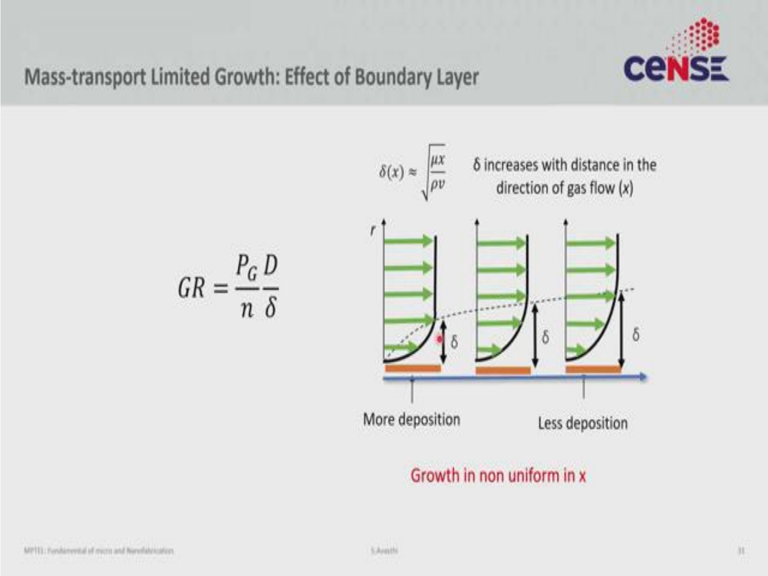

Mass-transport Limited Growth: Effect of Boundary Layer

$$GR = \frac{P_G}{n}\frac{D}{\delta}$$

$\delta(x) \approx \sqrt{\frac{\mu x}{\rho v}}$ δ increases with distance in the direction of gas flow (x)

More deposition

Less deposition

Growth in non uniform in x

Let’s look into the mass transport limited regime in a little more detail. It must be obvious to you by now that there would be an effect of the boundary layer as the growth rate $\frac{P_G}{nk_BT}\frac{D}{\delta}$ depends on D as well as δ. δ or the boundary layer thickness changes from the left of the reactor to the right side of the reactor and also changes across a wafer right. The edge that is facing the incoming gas flow will have a smaller boundary layer and the edge that faces the trailing the gas flow will always have a thicker boundary layer. As the growth rate depends on δ, we get a non-uniformity in the thickness because of δ non-uniformity.

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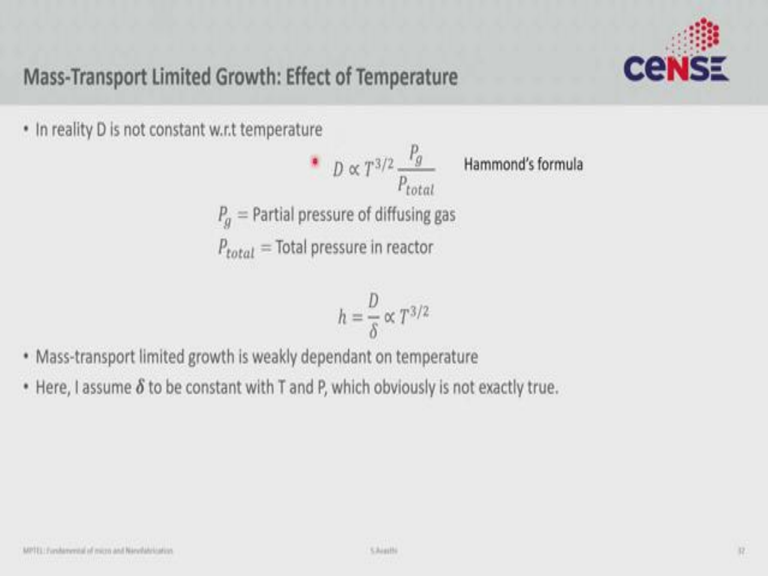

Mass-Transport Limited Growth: Effect of Temperature

- In reality D is not constant w.r.t temperature
  - $D \propto T^{3/2} \frac{P_g}{P_{total}}$ **Hammond's formula**

P_g = Partial pressure of diffusing gas

P_{total} = Total pressure in reactor

$$h = \frac{D}{\delta} \propto T^{3/2}$$

- Mass-transport limited growth is weakly dependant on temperature
- Here, I assume δ to be constant with T and P, which obviously is not exactly true.

Even D is not exactly uniform because D depends on temperature as described by Hammond's law, $D = T^{\frac{3}{2}} \frac{P_G}{P_{Total}}$, where D depends on $T^{\frac{3}{2}}$ but linearly on pressure or the ratio of partial pressure to total pressure. Overall, h dependence on both; D and δ and hence, $h \propto T^{\frac{3}{2}}$. Here, we assume delta to be independent of T and P while just a couple of slides before we had seen that it is not exactly the case. So, is this formula exactly true? No, but in general reactions, there are a lot of second or third-order effects, so it is very hard to give exact exponents. The take-home message here is that there is some weak polynomial dependence of Henry's constant on temperature – 1.5, 1.6, 1.8 or 1.2 really depends upon the details.

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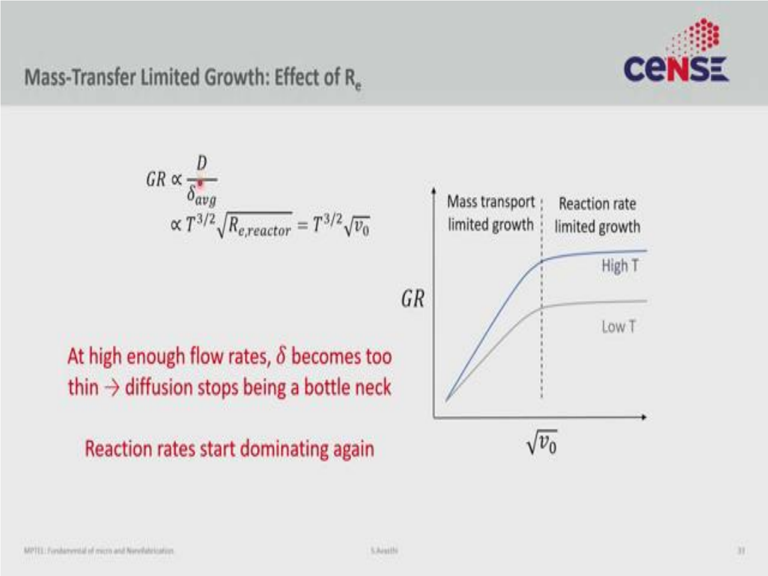

Mass-Transfer Limited Growth: Effect of R_e

$$GR \propto \frac{D}{\delta_{avg}}$$
$$\propto T^{3/2}\sqrt{R_{e,reactor}} = T^{3/2}\sqrt{v_0}$$

At high enough flow rates, δ becomes too thin → diffusion stops being a bottle neck

Reaction rates start dominating again

Overall, the growth rate on an average depends upon the D_{avg} and δ_{avg}. δ_{avg} which is the average thickness of the boundary layer and is related to the Reynolds number of the reactor, which is related to the velocity of flow inside the reactor. What happens if we increase v_o? If you took a reactor and pumped it harder or created a larger pressure differential between the two sides of the reactors or increase the conductance of the reactor, it increases the velocity of the flow and the Reynolds number. So, the boundary layer will become thinner and the diffusion becomes faster. If you keep making the diffusion faster and faster, at some point, you will not remain a mass transport limited but will become reaction rate limited. You are mass transport limited for a certain range of velocities, but beyond a certain point, you become reaction rate limited.

This transition can also occur at higher temperatures because, at high temperatures, the growth rate becomes faster because the D is larger and the diffusion stops being the bottleneck.

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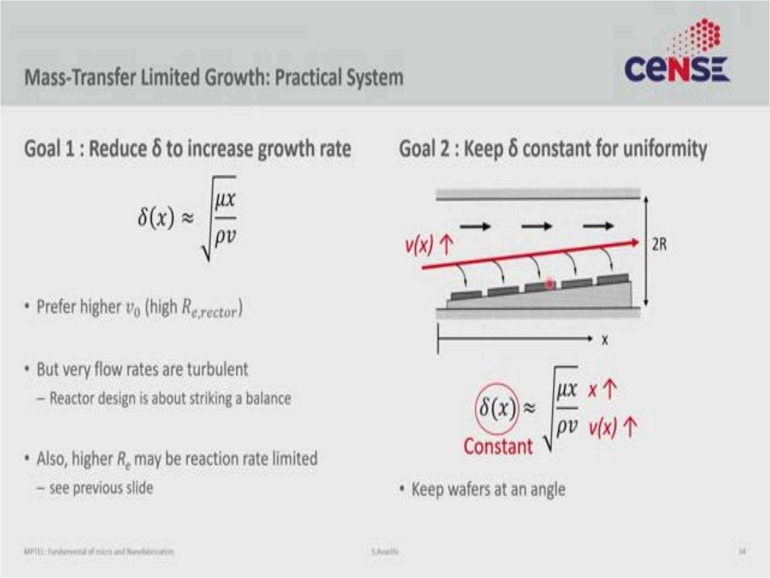

Mass-Transfer Limited Growth: Practical System

Goal 1 : Reduce δ to increase growth rate

$$\delta(x) \approx \sqrt{\frac{\mu x}{\rho v}}$$

- Prefer higher v_0 (high $R_{e,rector}$)
- But very flow rates are turbulent
  - Reactor design is about striking a balance
- Also, higher R_e may be reaction rate limited
  - see previous slide

Goal 2 : Keep δ constant for uniformity

$$\boxed{\delta(x)} \approx \sqrt{\frac{\mu x}{\rho v}} \quad x \uparrow \quad v(x) \uparrow$$

Constant

- Keep wafers at an angle

If you want to make a practical system that works under mass transport limited growth, your goal would be twofold; you want a system that has as high growth rate as possible because that saves time, and time is money, and you want it to be uniform. Given all the non-idealities we have discussed, how do we actually get that? First, just notice this δ. The growth rate $GR \propto \frac{1}{\delta}$ because thicker the boundary layer, more the film has to diffuse. The easiest way to reduce the boundary layer thickness is to increase the velocity of flow; higher the velocity of flow, lower the boundary layer thickness. Higher v_o means we design a reactor with a higher Reynolds number, but there is a limit. At very high Reynolds numbers, the flow becomes turbulent and there are other kinds of non-uniformities that occur. Also at very high v_o, you tend to become reaction rate-limited.

The second goal is to keep whatever value of δ we have constant across the wafer. The easiest way to do that is to load the wafers at an angle. By doing that, you change the velocity of the gas as it goes from left to right. The effective cross-section of the reactor reduces from left to right. Since mass cannot be created or destroyed, the effective velocity must increase as you go from left to right. You can come up with an angle or a shape, where the increase in the velocity exactly compensates for the increase in distance, keeping δ(x) constant. Keeping wafers at an angle is the easiest way to get a relatively uniform boundary layer and hence, relatively uniform deposition.

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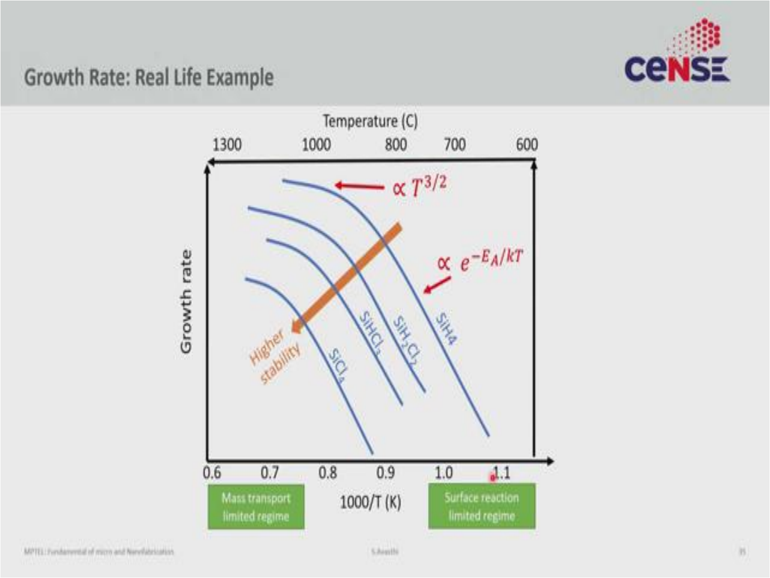

Growth Rate: Real Life Example

The overall growth rate looks like this, where we have various precursors. At low-temperature (high 1000/T), you are often limited by reaction rate. So, you have exponential dependence with T, which in the log scale, looks linear. As T increases, the growth rate transitions into the mass transport limited regime, where you have a $T^{\frac{3}{2}}$ temperature dependence. Different precursors will give you slightly different curves. As the stability of the precursor increases, it tends to decompose slower and lowers the growth rate. As you go from SiH_4 to $SiCl_4$, the growth rates keep coming down.

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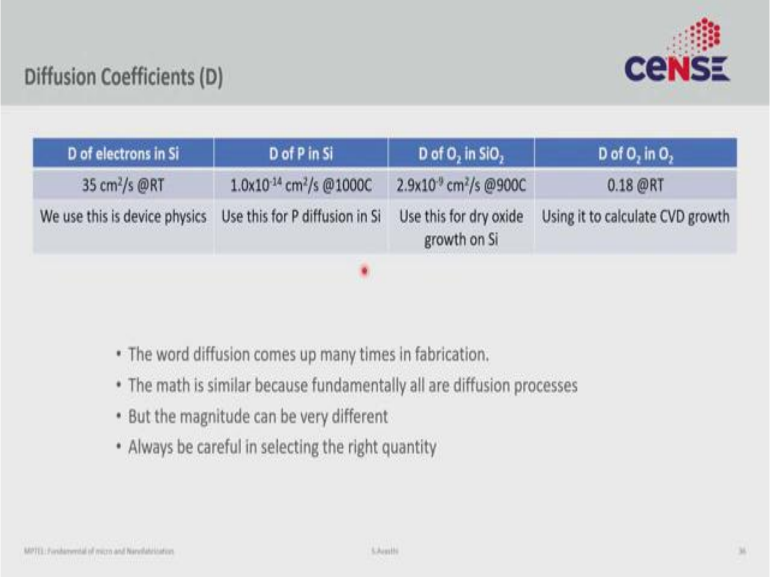

Diffusion Coefficients (D)

D of electrons in Si	D of P in Si	D of O_2 in SiO_2	D of O_2 in O_2
35 cm²/s @RT	1.0x10^{-14} cm²/s @1000C	2.9x10^{-9} cm²/s @900C	0.18 @RT
We use this is device physics	Use this for P diffusion in Si	Use this for dry oxide growth on Si	Using it to calculate CVD growth

- The word diffusion comes up many times in fabrication.
- The math is similar because fundamentally all are diffusion processes
- But the magnitude can be very different
- Always be careful in selecting the right quantity

A little note on this diffusion coefficient D. I have used D in several contexts. D of electrons in silicon is around 35 cm^2/s. We use this in device physics. We looked at the diffusion of phosphorus in silicon when we were discussing diffusion. We looked at diffusion of oxygen in silicon dioxide when we were discussing thermal oxidation and right now, we are talking of D of oxygen in oxygen in CVD. Be very careful with these very different Ds, as they mean different things and have different orders of magnitude right from 10^{-14} to 10^{-8} to 0.18 cm^2/s. Always ask the question: diffusion of what, in what and at what temperature?

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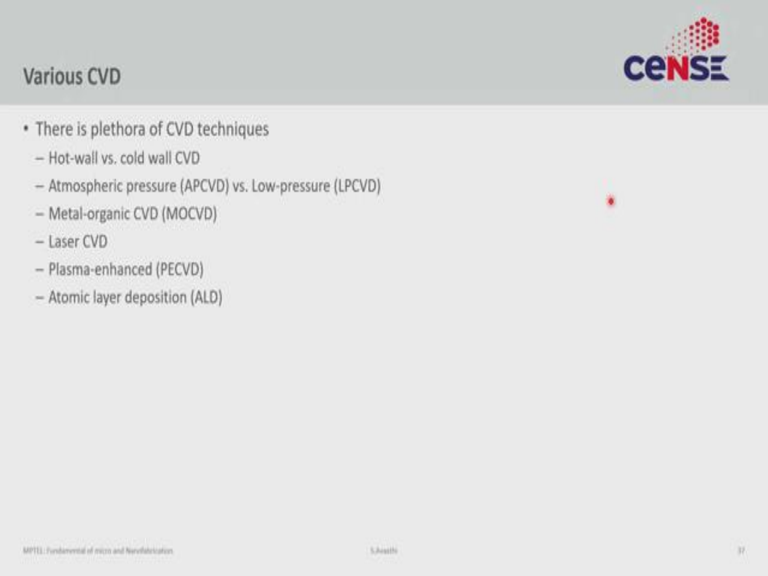

Various CVD

- There is plethora of CVD techniques
  - Hot-wall vs. cold wall CVD
  - Atmospheric pressure (APCVD) vs. Low-pressure (LPCVD)
  - Metal-organic CVD (MOCVD)
  - Laser CVD
  - Plasma-enhanced (PECVD)
  - Atomic layer deposition (ALD)

I will just list out the various types of CVD equipment you can design. There are a plethora of techniques, hot walled versus cold walled, atmospheric pressure CVDs versus low-pressure CVD, metal-organic CVD, laser CVD, PECVD, ALD etcetera. We will discuss each of these in a slight level of detail in the next lecture.