


Fundamentals of Micro and Nanofabrication
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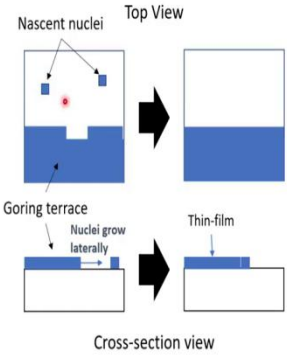
Lecture – 20
Chemical Vapor Deposition: Other Details

Under special cases, you can have a 2D growth where the nuclei have surface energy such that the contact angle with the substrate is very small. In layman's terms, the nuclei like to stick to the substrate. In that case, 2D growth may be preferred over 3D growth.

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Effect of Surface Energy: 2D Growth



- Material wets the surface, nuclei grow laterally
 - Not vertically
- 2D growth tends to be uniform
 - Fewer defects
 - Desirable for epitaxy
 - Common during homoepitaxy
 - E.g. Si on Si wafer
 - Called Franck-van Der Merwe growth
- 100% coverage even in thin films

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Here is a nascent nucleus which is subcritical and will coalesce with the larger nucleus. The nascent nucleus, instead of growing on top of the other, tends to stay on the substrate and diffuse to the edge of the larger nucleus and get coalesced. What you end up forming is a very thin film, in extreme cases, a 2D film or a monolayer of atoms growing laterally across the substrate. From an epitaxial point of view, this mode is preferred because a 3D growth tends to have a lot of grain boundaries and a lot of other issues that this does not. Thankfully, this is also a common occurrence in homoepitaxy, which is when you are trying to grow silicon on silicon. This is called Franck- van- Der- Merwe growth.

The advantage is that even for very thin films, you will get 100 % coverage, or conversely, to get very thin films with 100 % coverage, you should select the conditions that promote 2D growth.

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Growth: Surface Diffusion

CENSE

- For lattice matching, atoms need to move to a suitable lattice site via surface diffusion
 - Coalescing of small nuclei with large ones
 - Reduces number of growing nuclei
- Surface diffusion is thermally activated
 - $D \propto e^{-\frac{E_a}{kT}}$
 - E_a is typically 25-50% of the bulk value
 - $D_{surface}$ can be 100 times faster than D_{bulk}

What can we say about grain-size?

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What is the mechanism by which these grains coalesce? Thermodynamics tells us that a subcritical nucleus will shrink and a supercritical nucleus will grow, but what is the mechanism of this transport? Given an infinite amount of time, this process will happen, but how fast this process will happen can only be answered if we understand its kinetics. Most simply, you can imagine that this transport will occur through surface diffusion. The way this subcritical nucleus approach this larger grain is through surface diffusion. Surface diffusion is a temperature activated process with a rate $\propto e^{-\frac{E_a}{kT}}$, where E_a is the activation energy for surface diffusion.

Typically, the activation energy for surface diffusion is around 25 to 50 % smaller than the bulk diffusion. In the diffusion lecture, we talked about impurities and how these impurities diffuse in bulk via the substitutional or interstitial mechanism. For the surface diffusion, E_a tends to be 25 to 50 % smaller, which means the surface diffusion is much faster than bulk diffusion. This is important because bulk diffusion is a relatively slow process and only happens at high temperatures but surface diffusion can happen at a lower temperature. You can theoretically have high-quality epitaxial growth at lower temperatures. Otherwise, you have to wait for a long time for your grain to grow.

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Nucleation: Nuclei Concentration & Rate

- Concentration of nuclei that are growing or critical nuclei (n_{crit}) is given by:

$$n_{crit} = n_0 e^{-\Delta G_{crit}/kT}$$
 where, $\Delta G_{crit} = \frac{16\pi\gamma^3}{3\Delta G_{V \rightarrow S}^2}$
- $\frac{P_{surf}}{P_{\infty}} \uparrow$ i.e. supersaturation \uparrow
 $\Rightarrow \Delta G_{V \rightarrow S}$ becomes more negative
 \Rightarrow Number of nuclei that are growing (n_{crit}), increase *significantly*

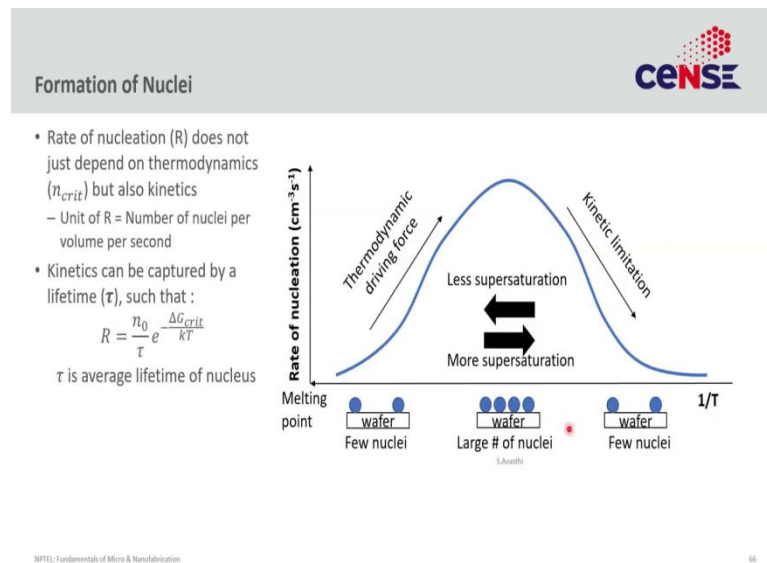
This square *inside* exponential. VERY SENSITIVE

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Nuclei will form if the supersaturation condition is achieved. More the supersaturation, the more the nuclei will form, but what is the average distance between two nuclei? The average distance between the two nuclei is inversely proportional to the critical nuclei concentration. The concentration of the critical nuclei depends upon the critical Gibbs free energy change ΔG_{crit} that we saw in the previous lecture.

Notice that ΔG_{crit} itself depends upon the supersaturation, but it depends on the square of the supersaturation and this square is inside an exponent. This $e^{-\frac{1}{x^2}}$ dependence is a very sensitive dependence. Very small changes in supersaturation cause very large changes in critical concentration. In general, as we increase the supersaturation, the $\Delta G_{V \rightarrow S}$ becomes more negative and the number of critical or supercritical nuclei keeps growing.

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Let's talk about the kinetics of nucleation. Nucleation rate (R) is the rate at which the critical (stable) nuclei form in a given volume (or area). In this simple model, we assume that the growing nuclei don't consume so much material that the supersaturation and n_{crit} get significantly affected. This nucleation rate (R) depends on the concentration of critical nuclei n_{crit} and an average lifetime τ of the nuclei: $R = \frac{n_{crit}}{\tau}$. The average lifetime is how long the nuclei last before coalescing into the larger ones.

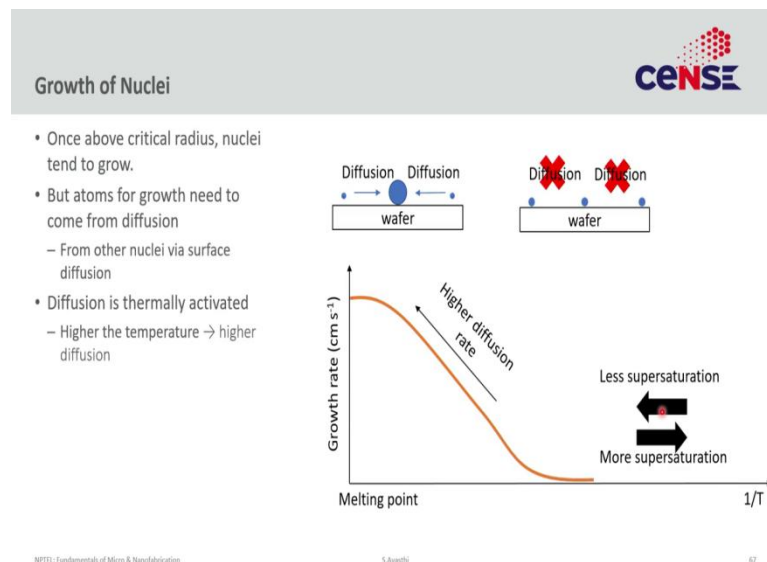
Here is an Arrhenius like plot of the rate of nucleation as a function of temperature. With the melting point on the left, the temperature reduces with increasing $1/T$. The supersaturation increases with increasing $1/T$. The nucleation rate vs $1/T$ is a U-shaped curve. At high temperatures, near the melting point, the nucleation rate is very small because the system is near the phase equilibrium. At equilibrium, you theoretically form no nuclei. As you increase the supersaturation (reduce the temperature), the thermodynamic force for the nucleation increases. As an example, take water below the melting point. Below the melting point, water is super cool and wants to nucleate. More you cool the water below its melting point, the more the driving force for nucleation grows. As the probability of nucleation increases, the nucleation rate increases.

At some point, however, it peaks and then falls again because of the kinetic limitation. Nucleation occurs by agglomerating subcritical nuclei and that process requires the movement of material which happens via diffusion. There is a kinetic limit on the speed.

If you reduce the temperature too much, even though the driving force for forming the nuclei is very large, the speed at which the nuclei can form is so small that you do not really create nuclei. This leads to a U-shaped curve. The nucleation rate peaks somewhere in the middle, and is not highest at the melting point.

What does that tell us about the CVD process? At the temperatures very close to the melting point, you will have very few nuclei and the average distance between two nuclei will be large. At a temperature where the nucleation rate is the highest, you will have the maximum density of nuclei; a lot of small nuclei all over the place. If you reduce the temperature further, at some point, you will again have very few nuclei with a large average distance.

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Large nuclei (with the radius above the critical radius) will grow in size at the expense of the smaller nuclei that get consumed. This process happens through surface diffusion. The speed at which the large nuclei grow is decided by how fast the material can transport (diffuse) from small nuclei to large nuclei. Since diffusion has such a strong dependence on temperature, you can expect a curve where the growth rate for the supercritical nuclei versus temperature looks Arrhenius. At higher temperatures (lower 1/T), the diffusion is higher and so is the growth rate of the supercritical nuclei.

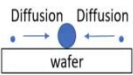
At high temperature, the surface diffusion is fast, so critical nuclei will grow in size at a high growth rate. At lower temperatures, even though you have nuclei, they don't grow appreciably as the diffusion is slow - the growth rate falls.

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Growth of Nuclei



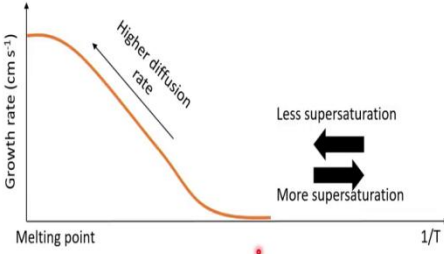
- Once above critical radius, nuclei tend to grow.
- But atoms for growth need to come from diffusion
 - From other nuclei via surface diffusion
- Diffusion is thermally activated
 - Higher the temperature → higher diffusion



Diffusion Diffusion
wafer



~~Diffusion~~ ~~Diffusion~~
wafer



Growth rate (cm s^{-1})

Melting point

$1/T$

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Putting these two (nucleation and growth rate) together, we can figure out the temperature at which we should grow things in CVD? Nucleation rate is a U shaped curve, while the growth rate is a monotonically decreasing function with $1/T$.

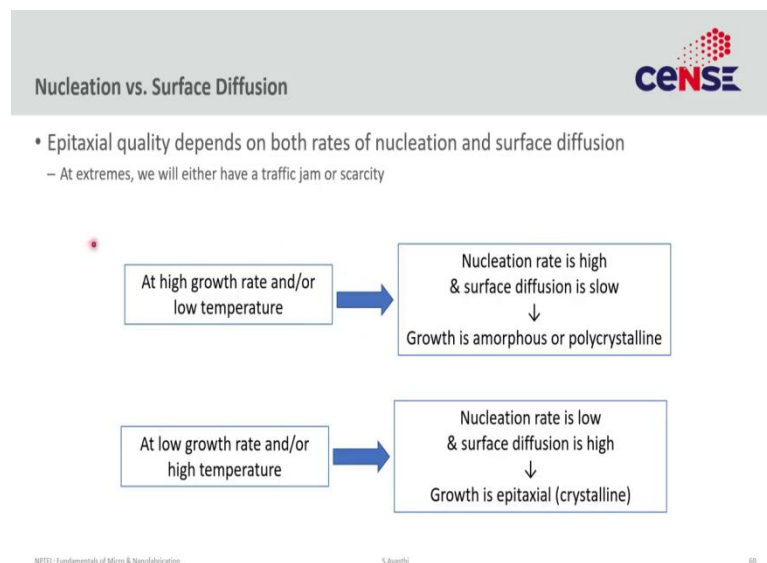
You can ideally do the growth very close to the melting point. For example, if you take a water bottle and keep it in the freezer, it can go below the melting point without freezing. At that point, the bottle is metastable. If you just bang it on a counter, suddenly you will see the ice form. That is because water wants to freeze, but it has not yet found nuclei. Why? Because the nucleation rate near the melting point is negligible. It doesn't freeze even though there is a thermodynamic imperative. The challenge is that thermodynamics predicts things that will happen given infinite time, while kinetics tells you how fast that process will occur. So, in practical systems, in a finite time, kinetics can give different phase from the equilibrium phase predicted by thermodynamics.

Coming back to the question of suitable temperature for CVD growth - this metastable region near the melting point is not very useful for CVD as the nucleation rate is small even though the growth rate is very large. As you reduce the temperature from the melting point, you get to a case where you have both the nucleation and an appreciable

growth rate. A lot of CVD happens here because you have both growth and nucleation. If you further reduce the temperature, you get to a regime of large nucleation rate but low growth rate. You don't get complete coverage but droplets or islands instead. This is not useful for CVD because often we want smooth films. It may be useful for quantum dots or something like that, not for thin films.

At high temperatures, where both nucleation and growth happens, you may have to wait for a very long time to get a thick film with a large grain size, because of a low nucleation rate. The growth of an individual nucleus may be fast, but the film growth rate may be slow. People sometimes do a two-step CVD. They start at a lower temperature, where the nucleation rate is high. The number of nuclei created in this step (or the average distance between nuclei) sets the grain size. And then transition to a higher temperature so, they can then also get a higher growth rate and don't have to wait for a very long time to get a certain thickness. That is essentially the optimization between the nucleation rate and growth rate. This has a consequence on the epitaxy.

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The film's growth has two components – nucleation and surface diffusion. At the two extremes, either nucleation or surface diffusion rate is dominant.

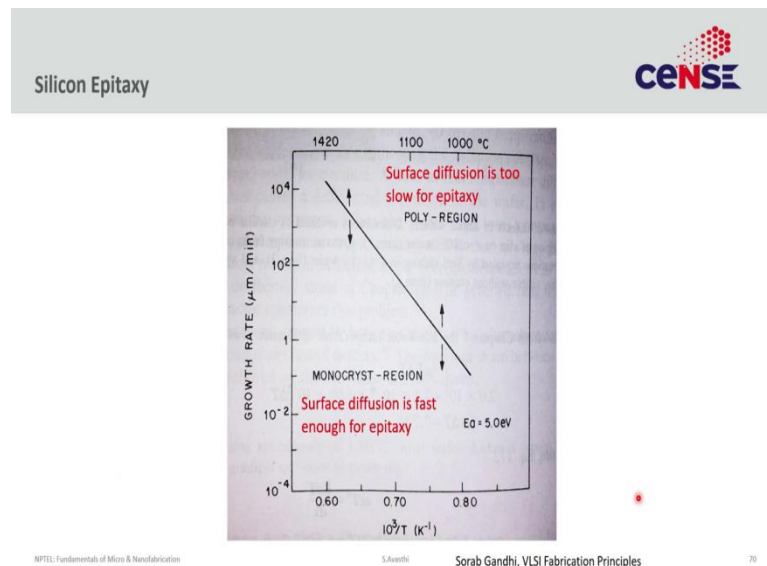
In a case of higher film growth rate or lower temperature, the nucleation rate is relatively high. Note that this is the growth rate of the film, not individual nuclei. You have very high partial pressures and are transporting a lot of material on to the surface. This

increases supersaturation, which in turn causes more nucleation. The surface diffusion rate is lower either because of lower temperatures or lack of enough time for the nuclei to diffuse. The distance they will travel is some version of \sqrt{Dt} . Even if D is large, the diffusion length is small if it does not have enough time to diffuse.

If you pile up material so fast that the material has does not have that time to reorganize itself on the surface, then it cannot do the epitaxy. The whole point of epitaxy is that the silicon underneath orients with itself the nuclei that are on the top. As these nuclei grow, that orientation is maintained and you get an epitaxially oriented film on top. In cases where the film growth rate is very high or the temperature is very low, that cannot happen. Often in these cases, the growth is amorphous or polycrystalline as there is not enough time for the material to orient.

In the case where the film growth is very low, you have a lower flux or partial pressure of the precursor. The supersaturation is low or the temperature is high. In these cases, the nucleation tends to be lower and the surface diffusion higher. There is a lot of time before more material gets dumped in, for the nuclei that are growing to diffuse and orient themselves. In these cases, the growth is often epitaxial or crystalline.


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Here is an Arrhenius plot of the film growth rate. This line represents the separation between the region where you tend to grow polycrystalline and monocrystalline silicon.

At lower temperatures and high growth rates, you don't give enough time for the film to orient itself. So, you get polycrystalline silicon. At higher temperatures and low growth rates, you get epitaxial growth. This sort of insight is important when you are trying to do epitaxial growth so that you can appropriately tune the temperature, supersaturation, pressure, etc...

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Condition for Good Epitaxy?


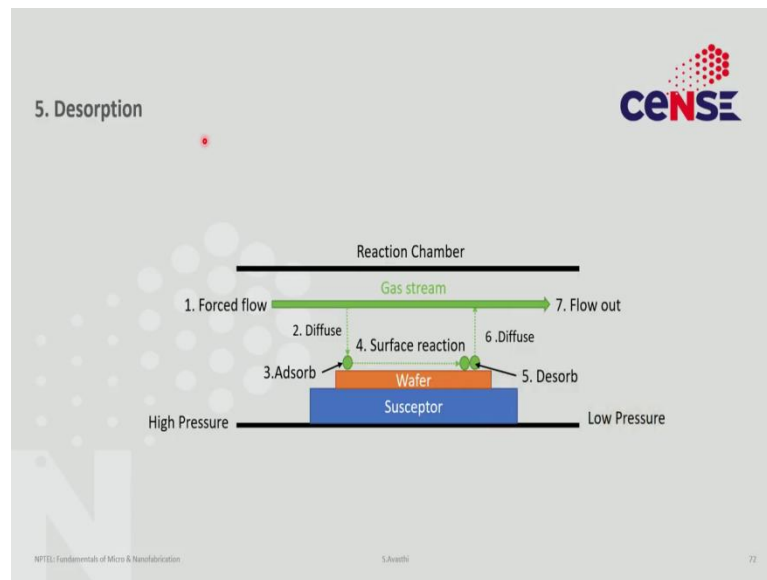
Conditions	Reason	Expression	Downside
High temperature	Faster surface diffusion	$D = D_0 e^{-\frac{E_a}{kT}}$	Bulk diffusion is higher Dopant diffusion is higher
Lower partial pressure (i.e. lower super-saturation)	Lower nucleation rate	$R \propto e^{-\frac{16\pi\gamma^3}{3k^3T^3 \left(\ln\left(\frac{P_{surf}}{P_{\infty}}\right)\right)^2}}$	Slower growth



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The conditions for good epitaxy are higher temperatures and lower partial pressures. Typically higher temperatures allow material to move better. For CVD, low partial pressure means a low nucleation rate. Here, the nuclei are very far or sparse. So, the incoming material has a lot of time to reorganize. However, these are also the conditions for slow growth rates. Often epitaxial growth is excruciatingly slow. If you just want a polycrystalline film, you can get much higher growth rates.

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With that, we come to the end of the part on nucleation and growth. Till now, we have discussed how flow affects growth in a CVD reactor, how things diffuse through the boundary layer on to the surface, adsorb on the surface, does chemical reaction which leads to nucleation and growth. Now we talk about desorption.

Byproducts of the chemical reaction in the CVD need to desorb and again diffuse through the boundary layer out into the gas stream and to get pumped out. On top of that, often these other components, for example, hydrogen might do their side reaction on the surface and the byproducts from those reactions must also desorb.

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Desorption

- Desorption happens by diffusion
 - Against the same boundary layer
 - Similar math
- Usually not the bottleneck so ignored
- However, Si epitaxy is often H-desorption limited.

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From a mathematical standpoint, desorption and adsorption are similar; just the direction is different. In both cases, you are dealing with the boundary layer and the material being absorbed or desorbed must diffuse through it. So, the maths is very similar.

All these processes happen in series and the slowest step decides the growth rate. Desorption usually is not a bottleneck, as it is not the slowest step. So, often it is ignored. However, there is an important aspect of the silicon epitaxy that you can only understand if you understand hydrogen desorption.

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Si Epitaxy: H₂ Desorption

- In most Si CVD H₂ is the carrier gas
- H₂ gets adsorbed on to the surface (bonds to Si atoms)
 - It competes with Si from SiH₄ for Si atoms on the substrate
- In most Si CVD, growth rate is limited by H desorption

The graph shows the Open Site Fraction (y-axis, logarithmic scale from 10⁻⁴ to 10⁰) versus Temperature in Celsius (x-axis, linear scale from 500 to 1100). Two curves are shown: a blue curve for a partial pressure of H₂ = 10 mTorr and an orange curve for a partial pressure of H₂ = 6000 mTorr. Both curves show an increase in Open Site Fraction with temperature, with the 10 mTorr curve consistently higher than the 6000 mTorr curve.

From PhD Thesis of K. Chung, Princeton University

The graph shows Growth Rate (y-axis) versus SiH₄ partial pressure (x-axis). The curve starts with a linear region, followed by a region labeled 'Waiting on H₂ to desorb' where the growth rate plateaus, and finally a region labeled 'Desorption limited' where the growth rate begins to decrease.

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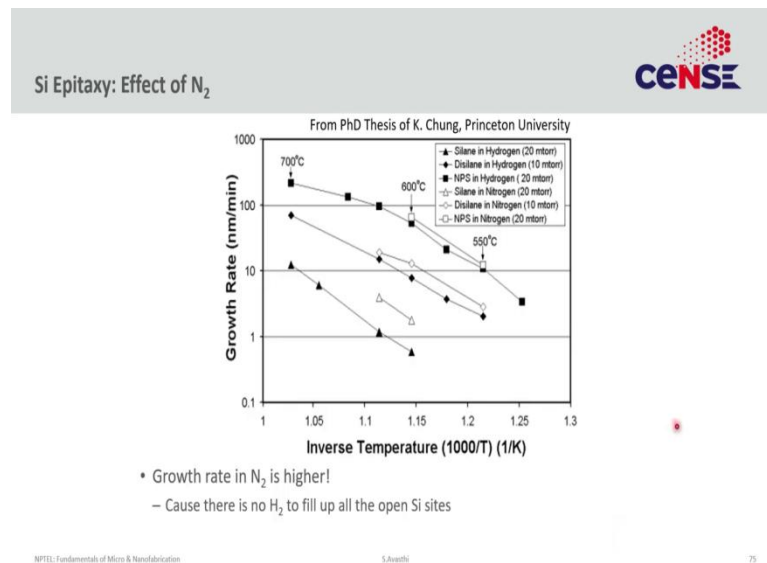
Let's have a slide on that. What happens in silicon when you use hydride precursors? A lot of silicon epitaxy happens through hydrides. Precursors like silane, dichlorosilane, disilane contain hydrogen. Silicon has a great affinity for hydrogen. Even in the cleaning lecture, we discussed how a monolayer of Si-H bonds form when you dip the wafer in hydrochloric acid. That H passivation is very strong and useful. The same thing happens in silicon CVD. The presence of a large amount of hydrogen in the atmosphere passivates the dangling bonds of silicon on the surface with Si-H bonds.

Now, if you were to add another silicon atom to make this layer a little thick, you first need to break the Si-H bond so you can make a Si-Si bond. For that, hydrogen must desorb from the surface and that requires certain energy. Often in silicon epitaxy, that is the bottleneck. In most CVD, desorption is not a bottleneck, so we do not talk about it, but in silicon epitaxy, at relative at moderate temperatures, hydrogen desorption is the bottleneck. Here is nice data from the Ph.D. thesis of one of my seniors at Princeton.

Open sites are silicon atoms on the surface that are not bonded (to hydrogen). These open sites are where the growth can occur by the addition of new silicon atoms. If silicon is already bonded to hydrogen, then it will not bond to other silicon atoms. The open site fraction is important. This curve shows the open site fraction as a function of temperature for different hydrogen partial pressures. At very high H_2 partial pressures, the open site fraction is lower because there is more hydrogen. Hydrogen reacts with silicon dangling bonds and passivates them, filling the open sites. As you reduce this hydrogen partial pressure, the open site fraction increase.

Look at the growth rate as a function of silane partial pressure. Initially, you get a higher growth rate which is what you would expect from a simple CVD process; the higher the partial pressure, the higher the growth rate. This linear region is what you expect, but at some point, it becomes sublinear and then self-limiting. At higher silane partial pressures, you are not starved of silicon. What you are starved of is open sites. Hydrogen bonded to the substrate surface atom prevents further reaction from occurring. You are always waiting for that hydrogen to desorb from the surface before a silicon atom can attach. Where does this hydrogen come from? Silicon formation from silane produces a lot of hydrogen. Silane itself is a source of hydrogen. Secondly, a lot of these reactions are done in a hydrogen ambient. So, you also flow several liters of hydrogen per minute to dilute the silane.

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You can see the effect of hydrogen if you look at the growth rate as a function of $1/T$ for different precursors. You have seen some version of this figure before when we were talking about the growth rate in mass flow limited and reaction rate limited regimes. You can see the growth rates for hydrogen and nitrogen dilution. Black triangles represent silane in hydrogen (20 m torr) and the open triangles, silane in nitrogen (20 m torr). The growth rate is higher for silane in nitrogen dilution. We have not changed the silane flow. All we have done is instead of diluting it in hydrogen, we have diluted in nitrogen. Since nitrogen is inert, it does not make a Si-N bond at the surface and has no passivating effect. It has no impact on open sites. So, in a nitrogen atmosphere, you have a lot more open sites than in a hydrogen atmosphere and because of this, there is a sudden jump in the growth rate right. You get several times higher growth rate in nitrogen than in hydrogen.

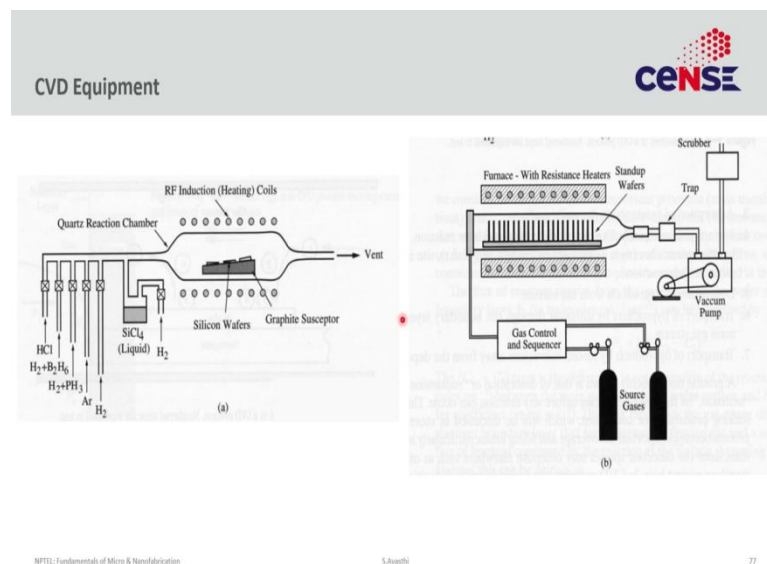
Why do people use hydrogen at all? Well, the slower growth rate has advantages. A couple of slides ago, we saw that a very high growth rate tends to cause polycrystalline growth. That hydrogen is useful as it tempers the growth rate and allows for more epitaxial and high-quality films to be formed, but if your goal just is a higher growth rate, you may consider doing your silicon growth in nitrogen.

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Let us talk about some other issues such as hardware, doping etcetera to round up this lecture on CVD.

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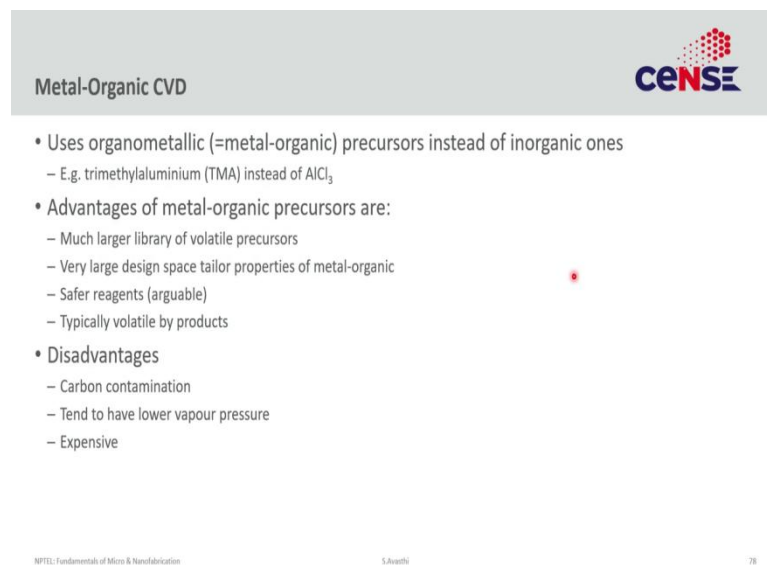


This is what typical equipment looks like. At this point, you probably expect something like this, because we have seen the same in native oxide growth and diffusion. There is a quartz chamber that can be heated. Here, I am trying to show an atmospheric pressure CVD. APCVD does not necessarily have any pump, because there is no pressure being created. The gases are just vented. Precursors come from the left. They can be a liquid -

for example, silicon tetrachloride is a liquid. There is a graphite susceptor that heats by RF power. This is a cold walled reactor. The boundary layer is a big problem because this is an APCVD reactor. So, you load the wafers at an angle such that you get a uniform deposition of the film.

Compare this to an LPCVD system. You see a vacuum pump to pull the chamber to a lower pressure, a scrubber to scrub off the exhaust, and some gas sources with very precise control and sequence - which gasses to flow and when. This is a hot walled chamber with a resistive heater and a susceptor. The wafers are mounted axially because the flow, to a first-order, does not affect things too much. All you need to do is maintain temperature uniformity. These are the typical versions of CVDs that you see. There is a general class of CVD called MOCVD or metal-organic CVD.

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Metal-Organic CVD

CENSE

- Uses organometallic (=metal-organic) precursors instead of inorganic ones
 - E.g. trimethylaluminium (TMA) instead of AlCl_3
- Advantages of metal-organic precursors are:
 - Much larger library of volatile precursors
 - Very large design space tailor properties of metal-organic
 - Safer reagents (arguable)
 - Typically volatile by products
- Disadvantages
 - Carbon contamination
 - Tend to have lower vapour pressure
 - Expensive

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It is not a different type of CVD. The name simply refers to the fact that the precursors can be metal-organic. We have seen precursors such as silane. The problem is that it is a dangerous gas. It is pyrophoric, which means it will catch fire if ever exposed to air. That is a problem because safety is a huge consideration in industrial manufacturing. One way of making safer precursors is converting this Si-H bond into a silicon metal-organic bond. However, it is not done in silicon because of carbon addition (silicon carbide formation).

A major advantage of metal-organic precursors is the ability to tune the vapor pressure. For example, in AlGaAs deposition, you use TMA or trimethylaluminum instead of, say, AlCl₃, as AlCl₃ tends to be very low vapor pressure (~300 times, at 100°C) and is a little hard to deal with. There is a large library of different types of precursors you can make. You can tune the volatility by selecting an appropriate organic ligand. There is very large design space. Though TMA is also a fairly bad material, you can theoretically make some safer reagents. MOCVD typically leads to very volatile byproducts, because they mostly are organic and organics like alcohols, acetones, ketones, methane, ethane, all tend to be very volatile. At very low temperatures, they leave the surface.

The disadvantage is it leads to carbon contamination. Compared to hydrides, they tend to lower vapor pressures and are very expensive because you have to do a lot of chemical synthesis and purification. Where carbon contamination is an issue, you may have to rethink the use of metal-organic CVD.

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Plasma Enhanced CVD (PECVD)


- Instead of thermal energy, use electrical energy to break down the precursor
- Use when CVD temperatures are too high
- Compared to thermal CVD, film quality is poorer
 - Surface diffusion is too slow to allow reorganization
- Compared to PVD methods, films quality is good
 - Reasonable deposition rates
 - Conformal

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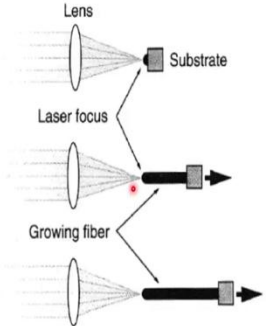
You may have heard the term plasma-enhanced CVD or PECVD. We will not go into more detail here. In CVD that we have discussed, the energy for the chemical reaction was coming thermally, by setting appropriate temperature. In PECVD, the energy comes from the plasma. In the introductory lecture, we discussed dry etching and sputtering, where also we use plasma. The same plasma can provide energy for the activation of the chemical reaction. That allows you to do the deposition at much lower temperatures.

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Laser CVD



- Use energy from a laser to break down the precursor
- Forms continuous thin rods or fibers by pulling substrate away from a stationary laser
- Can grow fibers of silicon, carbon, boron, oxides, nitrides, carbides, borides, and metals such as aluminum.
- Growth rate is 100-1000 $\mu\text{m/s}$




The diagram illustrates the Laser CVD process in three stages. In the first stage, a lens focuses a laser beam onto a substrate. In the second stage, the substrate is pulled away from the laser focus, creating a growing fiber. In the third stage, the fiber is fully formed and continues to grow as the substrate is pulled further away.

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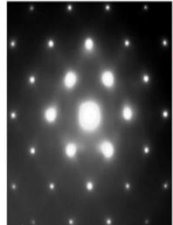

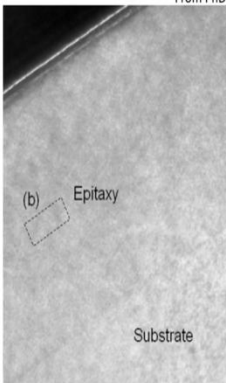
Something that I find very interesting is laser CVD, where you provide the energy to break the precursor through laser radiation. It is not very useful for growing films over large substrates, but if you want to grow a wire, laser CVD is sometimes used. In that case, the growth rates can be fairly high.

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Silicon Epitaxy



From PhD Thesis of K. Chung, Princeton University



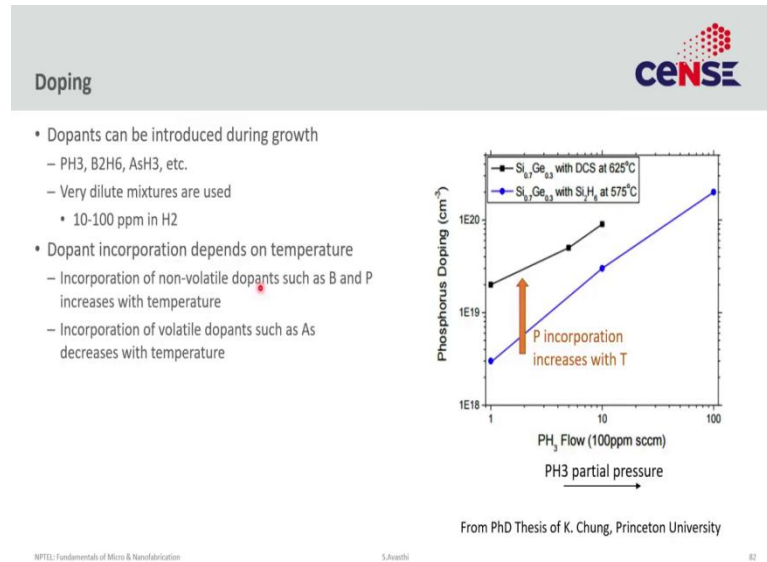
(b) Epitaxy
Substrate
80 nm epitaxy
Si lattice
Electron diffraction pattern

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What is the quality of silicon that we get with the modern epitaxy? The answer is extremely good. You have seen this figure in the introductory lecture. This is a cross-sectional TEM of epitaxial silicon grown on the silicon substrate. By and large, the film

is indistinguishable from the substrate save for this one line that you see at the interface. If you zoom in, you see the perfect silicon lattice. People know how to do silicon epitaxy for extremely high-quality films.

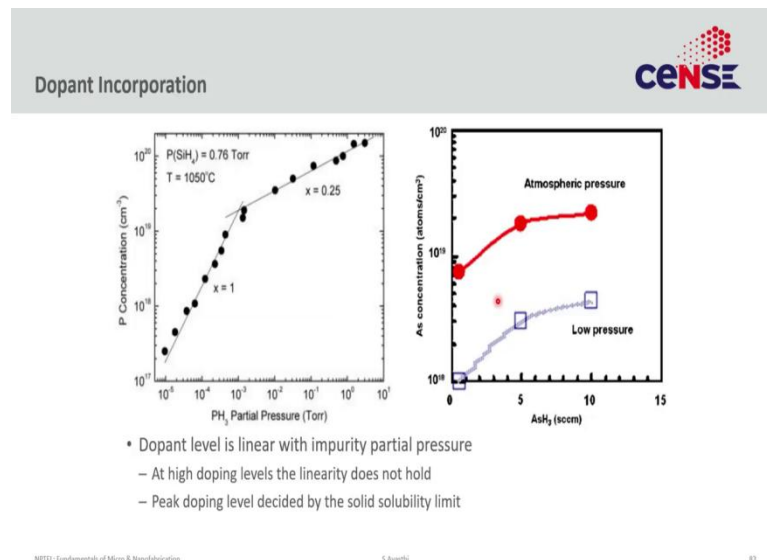
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Let's discuss a couple of points on doping. If you want to grow a doped film, the easiest way is to incorporate the dopants while you are doing CVD. If you want phosphorus doping, introduce phosphine, diborane for boron doping. Compared to the silicon atomic density, the doping density needs to be much lower. Phosphine and diborane must also be very low in concentration. We get low concentrations by making very dilute mixtures. Instead of having 100 % arsine or 100 % phosphine, you have, say, 10 ppm of arsine or 10 ppm of phosphine in hydrogen. There are few complications though. The first complication is that the amount of doping you get is a function of

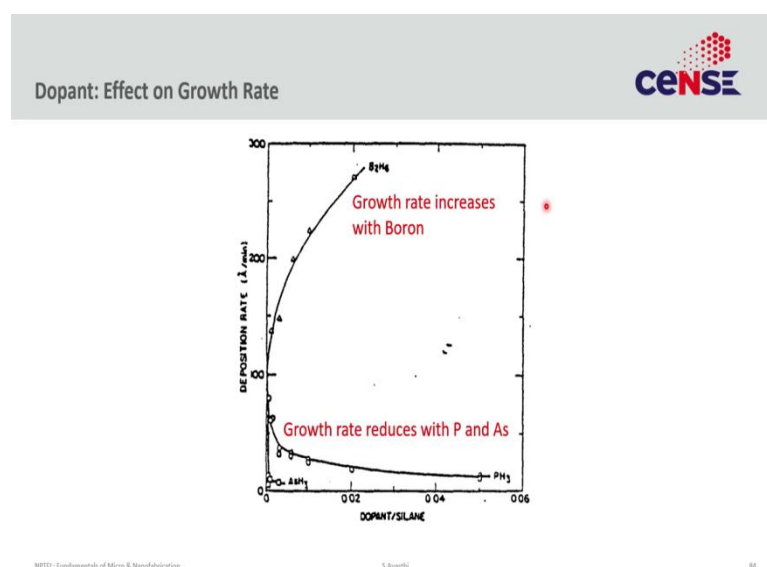
- Dopant precursor partial pressure: more precursor you put, more doping you get.
- The material you deposit with: depending on the silicon precursor used, for example, dichlorosilane vs disilane, you get different doping concentration in the doped silicon CVD film.

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The other complication is that often the dopant incorporation is not linear. At lower partial pressures, for every phosphorous atom, you get a dopant, but at very high partial pressures, the incorporation of phosphorus tends to become sublinear. For every atom of phosphorus you add, you get ~ 0.25 dopant incorporated. The concentration also depends upon the deposition pressure. It has something to do with open sites. We will not discuss the mechanism here. The eventual concentration depends on the solid solubility of the dopants in the film. CVDs are equilibrium processes. In general, you cannot get higher doping than the thermodynamic solid solubility limit.


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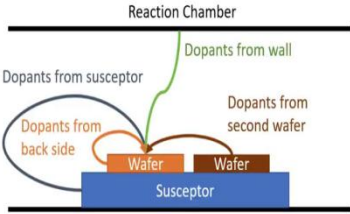
Dopants sometimes have a catalytic effect that might enhance the film growth rate. If you add just 1-2 % of diborane, the deposition rate of silicon itself increases. Boron-doped silicon grows faster than intrinsic or phosphorus/arsenic doped silicon.

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Autodoping



- Adsorbed atoms may cause unintentional doping
- Adsorption could be on:
 - wafer frontside
 - wafer backside and edges
 - other wafers
 - Susceptor
- Hot-wall vs cold-wall reactors behave differently.
- Some reactors come with turbo pump to just pump-out adsorbed impurities.
- Some reactors use HCl chemistry to etch the chamber surface and clean the chamber
- Almost all reactors have background doping of $10^{15} - 10^{16} \text{ cm}^{-3}$



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Autodoping refers to the fact that there is some unintentional doping in any reactor. Suppose, you are trying to deposit a film on two wafers in your reactor, and one wafer has higher doping. The dopants might get from that wafer to the wafer with lower doping, and the substrate. If you have a highly doped layer on the backside of this wafer, that might also come out and go to the top. Maybe the person before you who did a very highly doped run and the susceptor and chamber walls are now full of dopants that will get on to the wafer.

There is a complicated history here. That history depends upon what somebody has used the reactor for, before you. It is almost impossible to grow undoped layers in CVD. Virtually every reactor will have some background doping that causes auto doping. Hot wall cylinder and cold wall cylinder behave differently. Some reactors come with turbopumps, that you do not use during the growth, but to suck out all the contamination before the growth starts. Some reactors come with HCl chemistry to etch the chamber and the susceptor a little bit, so, that you clean up all the gunk and have a virgin surface to start from. Even then, most reactors have some background doping of $10^{14} - 10^{16} \text{ cm}^{-3}$.

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Selective Epitaxial Growth


• Leveraging different desorption rates of SiO_2 and Si can do selective epitaxial growth (SEG)
– E.g. Si epitaxy on Si but not on SiO_2

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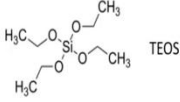
Selective epitaxial growth: till now, we had talked about CVD that was done on plain, unpatterned silicon. In practice, you probably will have patterned silicon with silicon dioxide patterns. When you grow silicon, you either get a conformal growth or selective growth. Conformal growth, where you get growth both on silicon dioxide and silicon, is not good, because silicon dioxide is not crystalline and will not seed the layer. It will impede the single-crystalline growth from the silicon. What you prefer is selective growth, where the growth only happens over the exposed silicon and nowhere else.

This example is from one of the papers, where there is no growth happening on the oxide, but only on the exposed silicon. This can be done by an appropriate selection of precursors, leveraging the desorption and the absorption rates on silicon dioxide versus silicon, incorporation of chlorine or no chlorine incorporation, etching, or no etching etcetera. I have just said that this concept exists, without explaining how it is done.

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SiO₂ CVD 

- Typically used at the back-end
 - Due to metal, temperatures need to be <500 C
- SiH₄ and TEOS are popular precursors

 TEOS

- TEOS = Tetraethyl orthosilicate
- For TEOS, deposition peaks at 380 C

https://booksite.elsevier.com/9781437778731/past_edition_chapters/Chemical_Vapor.pdf

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Let's have a slide on CVD of materials other than silicon, for example, silicon oxide. You can flow silane and oxygen to get silicon dioxide. Another very popular material is TEOS or siloxane, which contains Si-O. As you heat it, the molecule decomposes and you form the SiO₂ layer.

With that, we come to the end of the CVD. In this module, we discussed what is CVD, what precursor is, how the vapors are transported, a little bit of the viscous flow regime, how you design the flow in the reactor, how the Reynolds number of the reactor will tell you about the boundary layer, and the presence or absence of the boundary decides whether the film deposition will be uniform or not, etcetera.

We looked at two special cases of APCVD reactors and LPCVD reactors and discussed hot wall vs cold wall, nucleation, competition between nucleation and growth, and how that leads to epitaxy or polycrystalline growth. We then looked at equipment details and some special topics such as doping, selective growth, and silicon dioxide CVD. In the next lecture, we will talk about atomic layer deposition.