Fundamentals of Micro and Nanofabrication

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Lecture - 23
Physical Vapor Deposition: Basics

We will start the module on Physical Vapor Deposition (PVD) in our ongoing discussion on additive processing. In this lecture, we will focus on basics and terminology.

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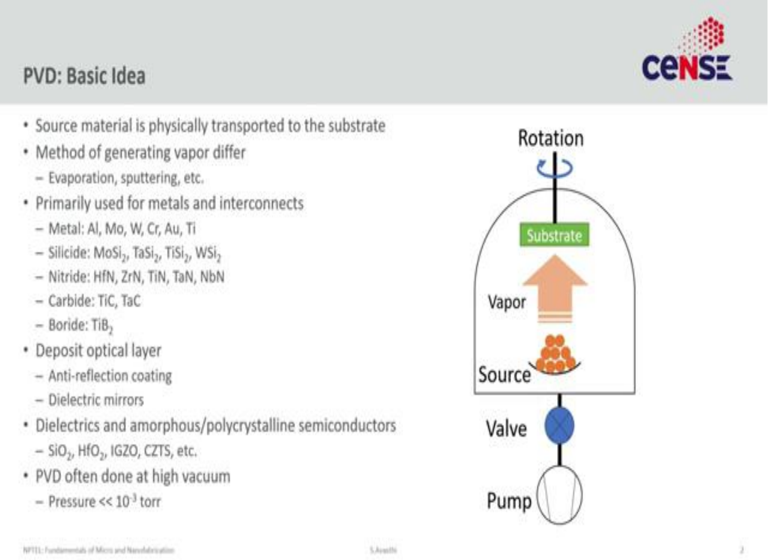

PVD: Basic Idea

- Source material is physically transported to the substrate
- Method of generating vapor differ
  - Evaporation, sputtering, etc.
- Primarily used for metals and interconnects
  - Metal: Al, Mo, W, Cr, Au, Ti
  - Silicide: $MoSi_2$, $TaSi_2$, $TiSi_2$, WSi_2
  - Nitride: HfN, ZrN, TiN, TaN, NbN
  - Carbide: TiC, TaC
  - Boride: TiB_2
- Deposit optical layer
  - Anti-reflection coating
  - Dielectric mirrors
- Dielectrics and amorphous/polycrystalline semiconductors
  - SiO_2, HfO_2, IGZO, CZTS, etc.
- PVD often done at high vacuum
  - Pressure << 10^{-3} torr

We have looked at the basic idea of PVD in the first lecture. Unlike CVD, where you make the material in situ, on top of the substrate, in PVD, the material is ready-made, typically in the solid form. All you have to do is to convert it into vapor, and then transport that vapor to the substrate and deposit it. For uniformity, the substrates are often rotated. If you deposit aluminum, you do not want it to react with oxygen and form aluminum oxide. To avoid contamination, you generate and deposit the vapors inside a vacuum chamber, so you need valves and pumps. There are different ways to make these vapors like sputtering or evaporation.

Primarily, we use these to deposit films that are not of electronic quality. We don’t care about the crystallinity or orientation. We often deposit metal, silicide, nitride, or polycrystalline thin films through PVD. You can deposit optical films like anti-reflection coating in solar cells or dielectric mirrors or photonic devices using PVD. You can also deposit dielectrics, but they are not as good in quality as grown dielectrics. However, for various applications, they work well. For semiconductors that are defect tolerant and you do not care about grain boundaries too much or are trying to be low cost, for example, CZTS, IGZO etcetera, you can use PVD.

The most important aspect is that PVD often requires a high vacuum. High vacuum means pressure way lower than 10^{-3} torr. In CVD, the pressures were in millitorr to torr regime. There, we had viscous flow, and we talked about the Reynolds number. At very low pressures, these concepts don't work. We are now in the molecular flow regime.

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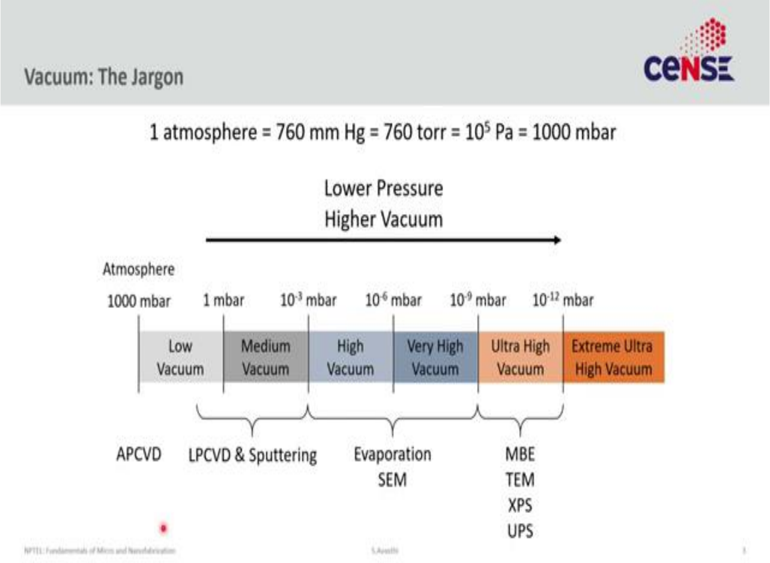

Vacuum: The Jargon

1 atmosphere = 760 mm Hg = 760 torr = 10^5 Pa = 1000 mbar

Let us get the jargon of vacuum out of the way. 1 atmosphere is 760 mm of mercury at sea level. Each mm of mercury is called a torr, 1 atmosphere is 760 torr. It is an imperial unit of pressure. The SI unit is the pascal (N/m^2), and 1 atmosphere is roughly 10^5 Pa or a bar. The range of pressure starting from 1 atmosphere to 10^{-3} of 1 atm, around 1 mbar, is called low-vacuum. Atmospheric pressure CVD is typically done around atmospheric pressure. LPCVD is done in a medium vacuum. Below 10^{-3} mbar, it is a high vacuum, and from 10^{-6} to 10^{-5} mbar, very high vacuum.

These are the regimes in which we do PVD. Even though sputtering happens in medium-vacuum, at the start, you pump down the chamber to high-vacuum or very high vacuum levels. You can attain even better vacuums - 10^{-9}, or in extreme cases better than 10^{-12} mbar. This is the kind of pressure you find in space. You do not typically deposit at these levels of the pressure. It is very hard to achieve an ultra-high vacuum, and the deposition rates are very low. MBE is an exception, which you often do under ultra-high vacuum conditions. However, a lot of characterization like TEM, XPS, or UPS happens here. We will concentrate on what happens in this high vacuum and very high vacuum regime.

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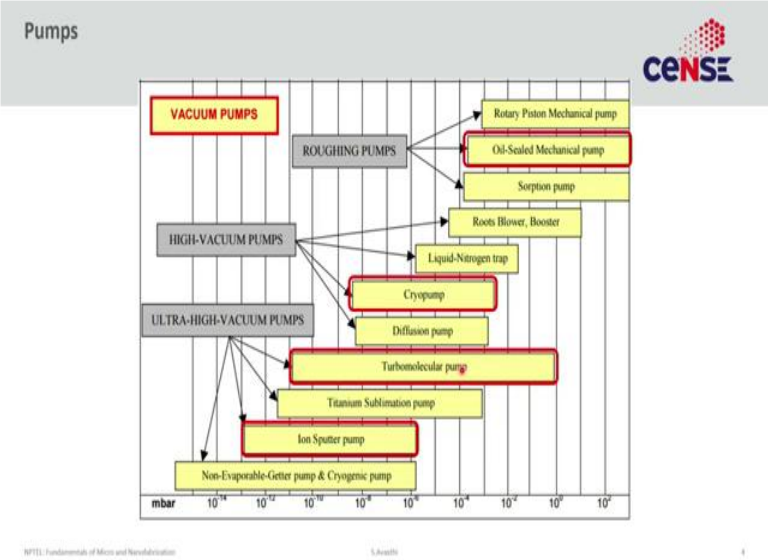

Pumps

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What kinds of pumps can we use to get to these pressures? Pumps come in different sizes and with different techniques. You have to select a specific pump for a given application, and each pump works in a specific pressure range. Pumps like rotary piston mechanical pump, oil-sealed mechanical pump only work under high pressure. Once you get to the base pressure of that pump, you cannot gain any further vacuum just by pumping longer. No matter how long you put an oil seal pump to a vacuum chamber, you never get lower than 10^{-4} mbar vacuum, because that is a limit of that pump.

To get a better vacuum, you need pumps with different techniques. The common ones are, for example, cryo-pump or diffusion pump, but these cannot function at higher pressures. So, instead of having one pump, you have two in series. At higher pressures, you use roughing pumps to get to a certain low value, and once it is there, you engage these pumps to pump it even further.

If you want to get to an ultra-high vacuum, even cryo or diffusion pumps are not good enough. You have to use a titanium sublimation pump or ion sputter pump, and these again have limits. In this case, you have a cascade of three pumps to get to 10^{-12}. The complexity keeps increasing. The most common pump used in the modern age is the oil seal mechanical pumps. These are the simple vacuum pumps. If you do not know which pump you have, you probably have this pump. Cyro pumps are very common. Diffusion pumps used to be very popular, but not so much anymore. The turbo-molecular pump has replaced them. Ion sputter pumps are popular for ultra-high vacuum applications.

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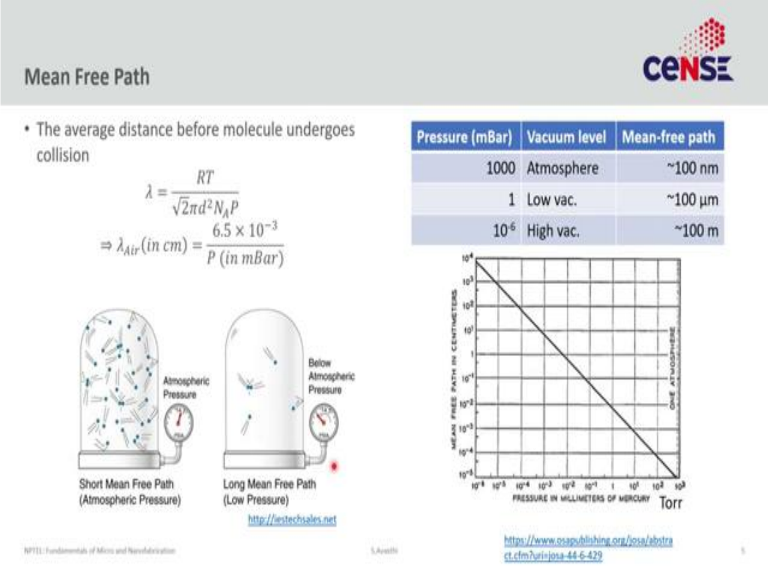

Mean Free Path

- The average distance before molecule undergoes collision

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P}$$

$$\Rightarrow \lambda_{Air}(in\ cm) = \frac{6.5 \times 10^{-3}}{P\ (in\ mBar)}$$

Pressure (mBar)	Vacuum level	Mean-free path
1000	Atmosphere	~100 nm
1	Low vac.	~100 µm
10^{-6}	High vac.	~100 m

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To understand the molecular flow regime, we have to understand what is the mean free path. The concept comes from the kinetic theory of gases. The basic idea is gas molecules move around and continue to move in a direction until they hit another molecule. On collision, they do not lose energy but change the direction, and these collisions happen all the time. The average distance that a gas molecule travels between two collisions is the mean free path. That would depend, of course, on the pressure. More the pressure, the shorter the distance. The mean free path (λ) must be inversely proportional to pressure. It also depends on temperature, along with certain geometric factors. Higher the temperature, the longer the distance.

As you go to lower and lower pressures, you keep increasing the value of λ. This formula is to give you context for actual numbers. At atmospheric pressure, the mean free path is around 100 nm. Gas molecules, on average, move 100 nm before colliding. As you get to low-vacuum, say at LPCVD level, this number becomes 100 µm. Once you get to high-vacuum where you often do PVD, these values are 100 m. The mean free paths become much longer than the chamber size. That has a consequence, and this is the pictorial view of that. Initially, the collisions happen at a scale much smaller than the chamber size. Once you pump the chamber to high-vacuum, the gas molecules do not collide with each other anymore. They collide only with the chamber surface because the mean free path is much larger than the chamber size.

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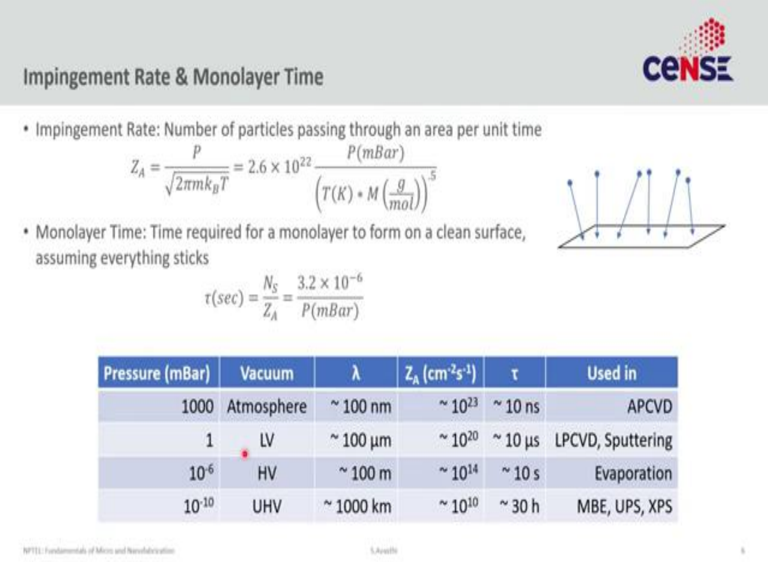

Impingement Rate & Monolayer Time

- Impingement Rate: Number of particles passing through an area per unit time

$$Z_A = \frac{P}{\sqrt{2\pi m k_B T}} = 2.6 \times 10^{22} \frac{P(mBar)}{\left(T(K) * M\left(\frac{g}{mol}\right)\right)^{.5}}$$

- Monolayer Time: Time required for a monolayer to form on a clean surface, assuming everything sticks

$$\tau(sec) = \frac{N_S}{Z_A} = \frac{3.2 \times 10^{-6}}{P(mBar)}$$

Pressure (mBar)	Vacuum	λ	Z_A ($cm^{-2}s^{-1}$)	τ	Used in
1000	Atmosphere	~ 100 nm	~ 10^{23}	~ 10 ns	APCVD
1	LV	~ 100 µm	~ 10^{20}	~ 10 µs	LPCVD, Sputtering
10^{-6}	HV	~ 100 m	~ 10^{14}	~ 10 s	Evaporation
10^{-10}	UHV	~ 1000 km	~ 10^{10}	~ 30 h	MBE, UPS, XPS

Once you understand the concept of the mean free path, you can ask - what is the impingement rate? The impingement rate is the number of atoms/molecules that impinge on a given area per unit time. You can calculate that using the kinetic theory of gases, and it is related to λ and is given by this formula. Once you know the impingement rate, you can calculate monolayer formation time. It is the time required to form a monolayer on top of an imaginary surface assuming the atoms that impinge on the surface stick to it.

Look at these numbers to get the context. At atmospheric pressures, λ is 100 nm and impingement rates are in the order of 10^{23}. While sitting in this room, 10^{23} atoms hit my face every second, per cm^2, and the time to a monolayer is 10 ns. If you expose a wafer with a ‘pure’ surface to the atmosphere, it gets covered in a monolayer in ~ 10 ns. That is what happens under APCVD conditions. As you get to LPCVD, the impingement rate reduces to 10^{20}, and the time to a monolayer is now 10 µs but is still short. Once you get to 10^{-6} regimes, the impingement rate is only 10^{14}, and it takes 10 s to form a monolayer.

Now we are getting into regions where it takes some amount of time to form a monolayer. And if you go to ultra-high vacuum (at 10^{-10} mbar), the time to monolayer is 30 hr, and this is the reason why you need an ultra-high vacuum to do characterization like TEM. If you do this inside a chamber where time to monolayer is less than the time it takes for you to do the imaging, you would mostly see junk all the time. The only sane way is to do it inside a chamber where the time to a monolayer is significantly larger than the time it takes for you to take the image. Only then do you have a good chance of looking at your sample, and not just the crud of that gets deposited on top of it.

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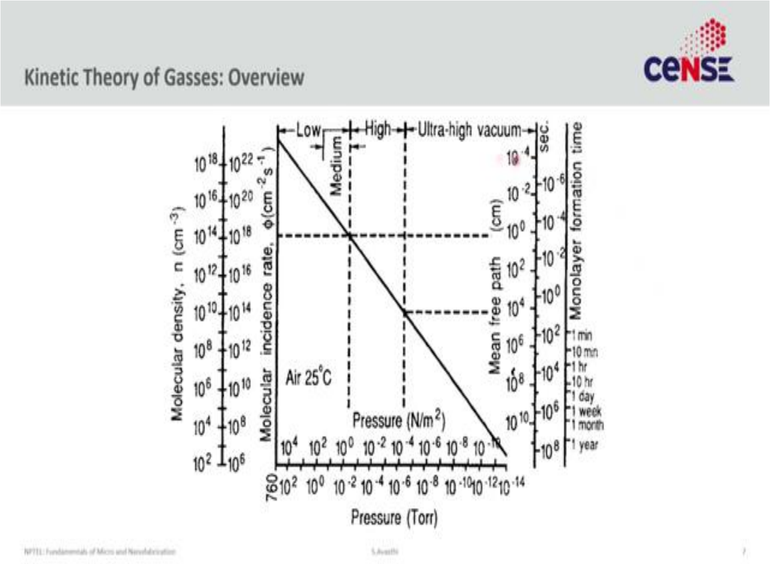

Kinetic Theory of Gasses: Overview

This is why a lot of the characterization equipment like UPS, XPS require an ultrahigh vacuum. PVD does not, as it is happy with this kind of time to a monolayer. This figure captures everything we have discussed. There is a molecule incidence rate, mean free path, and monolayer formation time. All of these are strong functions of pressure. We typically operate PVD in a high-vacuum regime.

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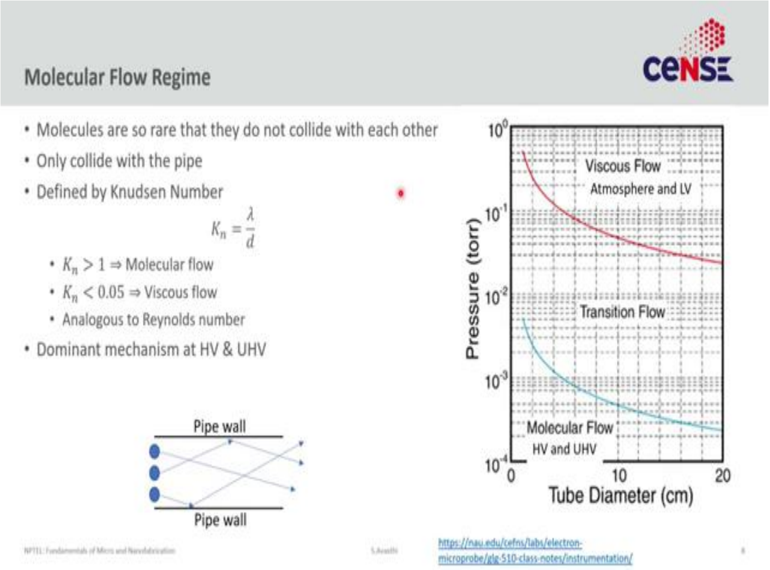

Molecular Flow Regime

- Molecules are so rare that they do not collide with each other
- Only collide with the pipe
- Defined by Knudsen Number

$$K_n = \frac{\lambda}{d}$$

  - $K_n > 1 \Rightarrow$ Molecular flow
  - $K_n < 0.05 \Rightarrow$ Viscous flow
  - Analogous to Reynolds number
- Dominant mechanism at HV & UHV

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https://nau.edu/cefns/labs/electron-microprobe/glg-510-class-notes/instrumentation/

We have some numbers to look at in the molecular flow regime, similar to what we had in the viscous flow regime. There it was Reynolds number. Here it is Knudsen number. In the viscous flow regime, there was a laminar flow because the molecules were interacting with each other. One molecule collided with the other molecule every 10 ns, and it was very much aware of its presence. So, they all went into streamlines because of the interaction. However, in the molecular flow regime, molecules do not interact with each other at all, because the size of the pipe or the chamber is smaller than the mean free path. The only thing the molecules interact with is the chamber wall. The flow in this regime is very different from the laminar flow. It does not depend upon the pressure or the characteristics of the gas. It depends only on the dimension of the pipe.

This ends the short introduction to the molecular flow regime and concepts related to high-vacuum. In the next lecture, we shall focus on the details of evaporation and sputtering.