**Course Name- Nanophotonics, Plasmonics and Metamaterials**

**Professor Name- Dr. Debabrata Sikdar**

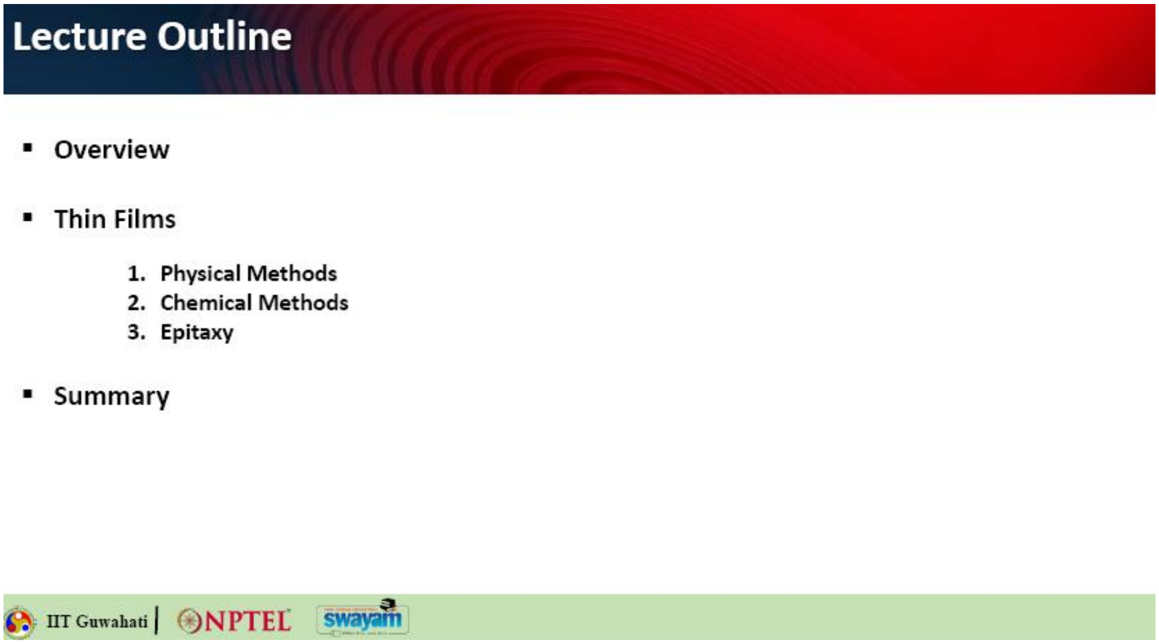
**Department Name- Electronics and Electrical Engineering**

**Institute Name- Indian Institute of Technology Guwahati**

**Week-12**

**Lecture -34**

Hello everyone, welcome to lecture 34 of the online course on Nanophotonics, Plasmonics and Metamaterials. Today's lecture will be on Nanofabrication. So, in this lecture we will see the most mostly used nanofabrication methods and we will discuss about thin films and different ways of making thin films like physical methods, chemical methods and epitaxy and then we will conclude this lecture. So, this particular module will give you a brief overview of how different fabrication methods can help you realize the structures that we have studied in this particular course. So, it will not be a very extensive overview or in detail study of the different fabrication methods. I will try to catch and touch upon different topics so that you have basic idea of how to realize the structures that we have discussed.



## Lecture Outline

- Overview
- Thin Films
    1. Physical Methods
    2. Chemical Methods
    3. Epitaxy
- Summary

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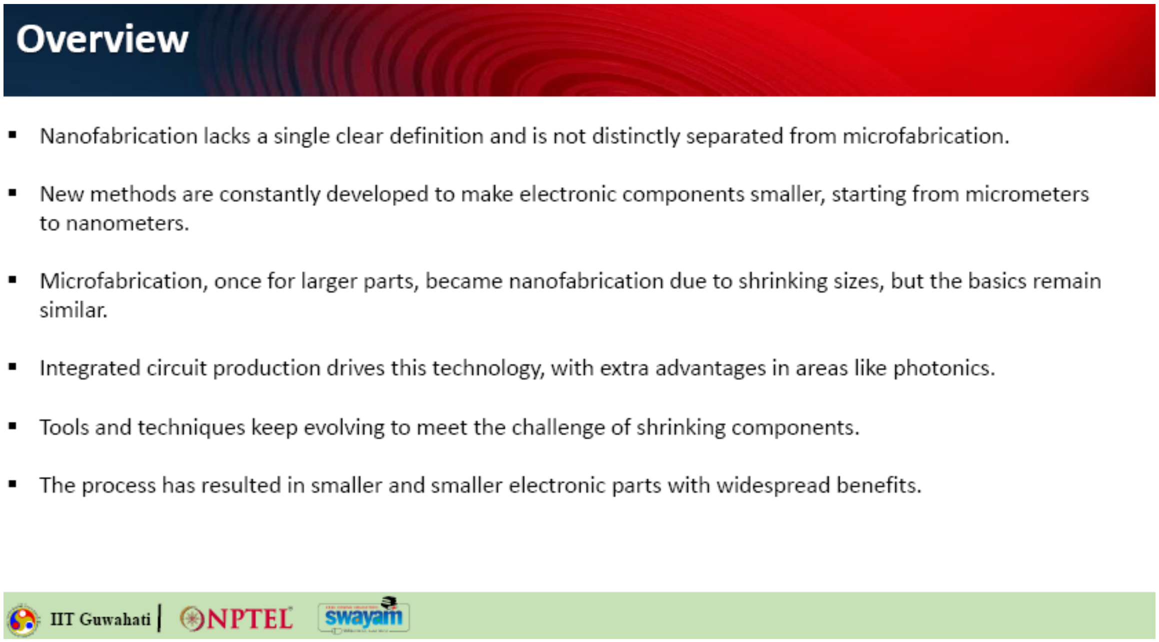
So, when we talk about nanofabrication, nanofabrication lacks a clear definition and it is not very distinctly separated from the term microfabrication. So, new methods are constantly developed to make electronic components smaller starting from micrometers to nanometers and the same techniques can also be used for nanophotonics, plasmonics and metamaterials. So, microfabrication that those are typically done for larger parts will become nanofabrication when the parts shrink and the dimensions become almost comparable to nanometers ok. So, the basics remain similar.

Now, integrated circuit production drives this particular technology and they provide extra advantages in the areas like photonics. Tools and techniques keep evolving with time there is a constant research and updation going on to make the process more robust so that there are less fabrication error and the yield increases and there are also challenges coming from continuous shrinking of the component sizes.



## Overview

- Nanofabrication lacks a single clear definition and is not distinctly separated from microfabrication.
- New methods are constantly developed to make electronic components smaller, starting from micrometers to nanometers.
- Microfabrication, once for larger parts, became nanofabrication due to shrinking sizes, but the basics remain similar.
- Integrated circuit production drives this technology, with extra advantages in areas like photonics.
- Tools and techniques keep evolving to meet the challenge of shrinking components.
- The process has resulted in smaller and smaller electronic parts with widespread benefits.

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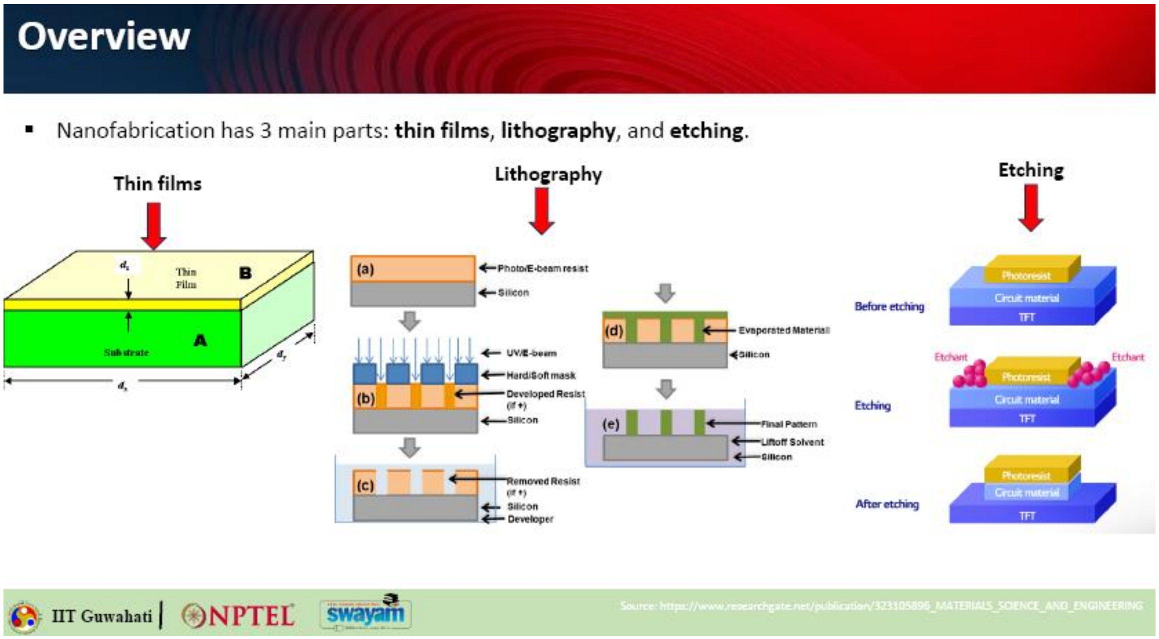
So, the process has resulted in smaller and smaller electronic parts with widespread benefits that is why you see all these devices they are becoming very lightweight and small compact these days. So, that is because of the advancement in nanotechnology that allows the scientists and engineers to fabricate structures which are really really small. Now, if you look into nanofabrication there are mainly three parts thin films lithography and etching.

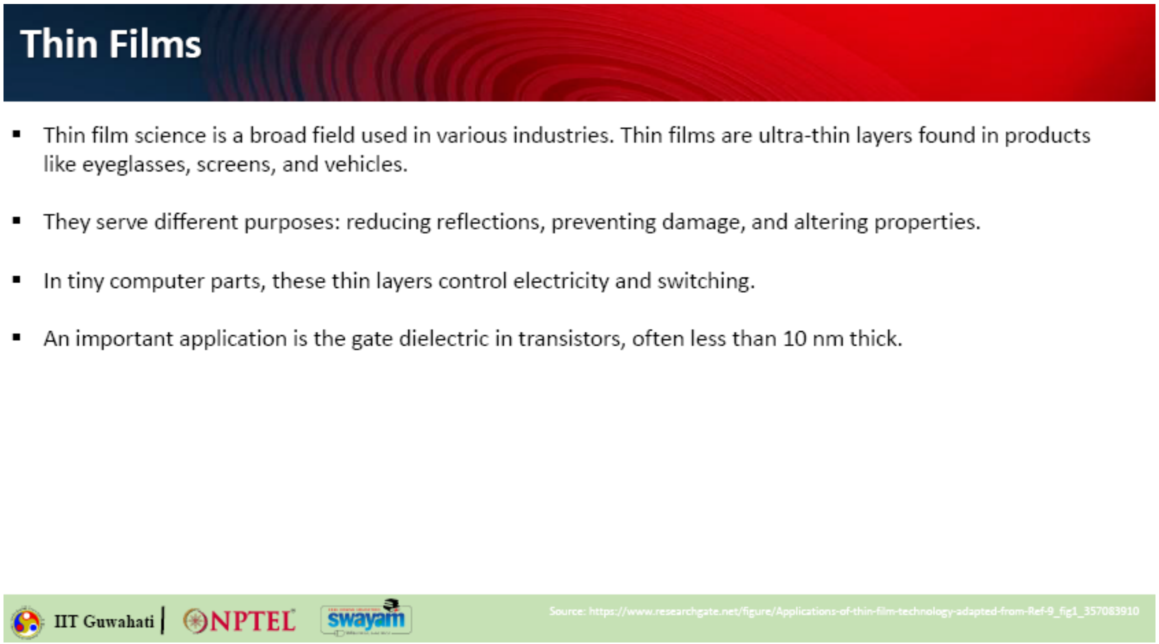


## Overview

- Nanofabrication has 3 main parts: **thin films**, **lithography**, and **etching**.

Source: https://www.researchgate.net/publication/323105896_MATERIALS_SCIENCE_AND_ENGINEERING

So, thin films as you can see there will be a substrate and you can develop a thin film on top of that this film thickness can be typically few to several nanometers ok or even micrometers ok those are thin films. Then you have lithography lithography is basically a process of making patterns ok. So, you can see it starts with a silicon substrate which is coated with a photo or e-beam resist. We will come into the details of this in the next lecture, but let us quickly go through what it looks like. Then you will basically have a hard or soft mask which actually got the pattern that you want to develop and then when you expose UV or electron beam ok your your photoresist ok if they are positive photoresist they get developed ok and then they can be etched away by some kind of solvent and this is the pattern of the resist that remains ok.



## Thin Films

- Thin film science is a broad field used in various industries. Thin films are ultra-thin layers found in products like eyeglasses, screens, and vehicles.
- They serve different purposes: reducing reflections, preventing damage, and altering properties.
- In tiny computer parts, these thin layers control electricity and switching.
- An important application is the gate dielectric in transistors, often less than 10 nm thick.

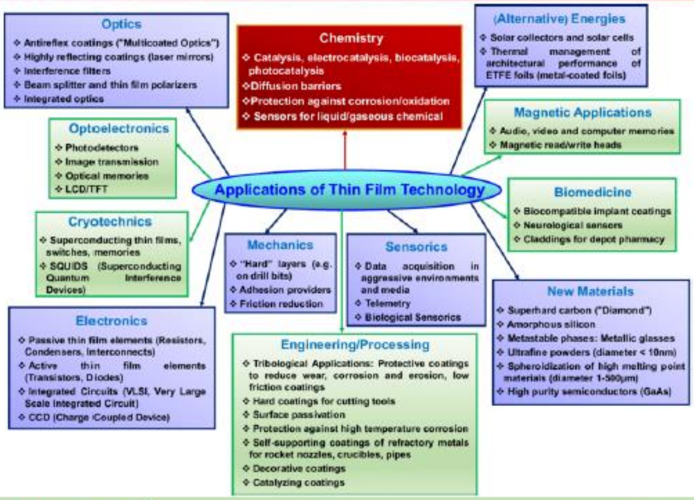
Source: https://www.researchgate.net/figure/Applications-of-thin-film-technology-adapted-from-Ref-9_fig1_357083910

So, after that you can evaporate material and that material fills in this particular gap and then when you remove this photoresist completely these are the patterns which are basically developed on the silicon. So, you can this is done by putting this in a lift of solvent. So, all these are the standard processes in nanofabrication technology. So, we will look into this in the next lecture. Today we will be mainly covering thin films and in the last lecture of this module we will be covering etching ok.

So, here you can see that you have got a circuit material that needs to be etched and you develop a photoresist first on that ok and then you can expose these areas of the circuit material to the etch they can etch away those circuit material and this is what you get after etching. So, these are the 3 methods that actually help you develop those structures that you have seen in this particular course ok. So, these as you can see these methods are very much standardized and optimized for semiconductor industry and that is where people are actually aiming towards making photonics material CMOS compatible. So, that the same foundry with some minor modification can help us fabricate those nanophotonic structures or plasmonic structures. If we are going for totally different materials that might be difficult for mass production at this current stage when the foundry is not supporting those kind of material fabrication.

So, if you look into the thin film industry, thin film size science is basically a broad field which is used in various industries ok and thin films are ultra thin layers that can be found in products such as eyeglasses ok screens and vehicles and these are different kind of purposes something like reducing reflection preventing damage and altering properties. In tiny computer parts these thin films can control electricity and help you switch ok. So, another important application you can think of is the gate direct link in transistors which is often less than 10 nanometer thick. So, those are also thin films. So, here you can see applications of thin film in different different disciplines.

# Applications of thin film technology



Applications of Thin Film Technology

**Optics**
- ❖ Antireflex coatings ("Multicoated Optics")
- ❖ Highly reflecting coatings (laser mirrors)
- ❖ Interference filters
- ❖ Beam splitter and thin film polarizers
- ❖ Integrated optics

**Chemistry**
- ❖ Catalysis, electrocatalysis, biocatalysis, photocatalysis
- ❖ Diffusion barriers
- ❖ Protection against corrosion/oxidation
- ❖ Sensors for liquid/gaseous chemical

**(Alternative) Energies**
- ❖ Solar collectors and solar cells
- ❖ Thermal management of architectural performance of ETFE foils (metal-coated foils)

**Optoelectronics**
- ❖ Photodetectors
- ❖ Image transmission
- ❖ Optical memories
- ❖ LCD/TFT

**Magnetic Applications**
- ❖ Audio, video and computer memories
- ❖ Magnetic read/write heads

**Cryotechnics**
- ❖ Superconducting thin films, switches, memories
- ❖ SQUIDS (Superconducting Quantum Interference Devices)

**Biomedicine**
- ❖ Biocompatible implant coatings
- ❖ Neurological sensors
- ❖ Claddings for depot pharmacy

**Mechanics**
- ❖ "Hard" layers (e.g. on drill bits)
- ❖ Adhesion providers
- ❖ Friction reduction

**Sensorics**
- ❖ Data acquisition in aggressive environments and media
- ❖ Telemetry
- ❖ Biological Sensorics

**Electronics**
- ❖ Passive thin film elements (Resistors, Condensers, Interconnects)
- ❖ Active thin film elements (Transistors, Diodes)
- ❖ Integrated Circuits (VLSI, Very Large Scale Integrated Circuit)
- ❖ CCD (Charge Coupled Device)

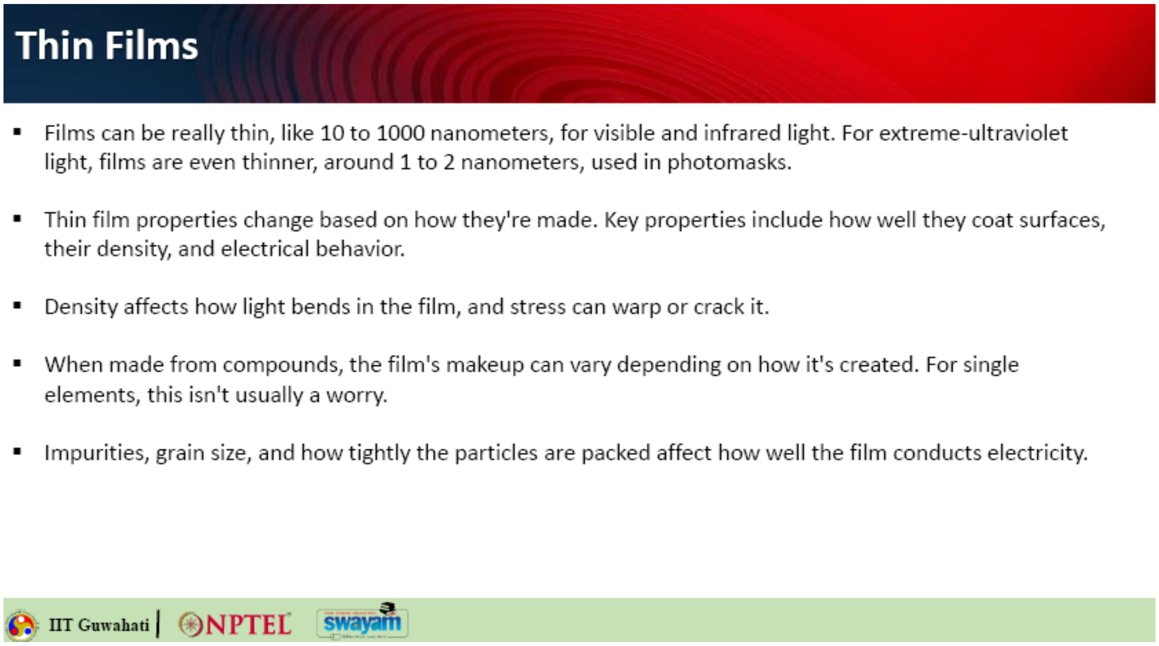
**Engineering/Processing**
- ❖ Tribological Applications: Protective coatings to reduce wear, corrosion and erosion, low friction coatings
- ❖ Hard coatings for cutting tools
- ❖ Surface passivation
- ❖ Protection against high temperature corrosion
- ❖ Self-supporting coatings of refractory metals for rocket nozzles, crucibles, pipes
- ❖ Decorative coatings
- ❖ Catalyzing coatings

**New Materials**
- ❖ Superhard carbon ("Diamond")
- ❖ Amorphous silicon
- ❖ Metastable phases: Metallic glasses
- ❖ Ultrafine powders (diameter < 10nm)
- ❖ Spheroidization of high melting point materials (diameter 1-500µm)
- ❖ High purity semiconductors (GaAs)

Source: https://www.researchgate.net/figure/Applications-of-thin-film-technology-adapted-from-Ref-9_fig1_357083910

So, if you think of optics it can give you anti reflection coating, highly reflected coating something like laser mirrors you can have interference filters beam splitter then thin film polarizers integrated optics and so on. If you think of optoelectronics you can use them for photo detectors image transmission optical memories LCD TFTs and all this. If you think of electronics they can be like passive thin film elements like resistors condensers and interconnects you can think of active thin film elements like transistors and diodes ok and integrated circuits like VLSI circuits they also use a lot of thin films. Then CCD charge coupled device you can think of chemistry where catalysis electro catalysis biocatalysis photo catalysis all those things are the application you can think of sensors you can think of magnetic applications engineering and processing and also new materials I will not read out all of them, but you can always see that there are lot of applications of thin films. They are also very useful in biomedicine where you can have neurological sensors you can have claddings for a depot pharmacy and biocompatible implant coatings.

So, all these things are possible. So, there are vast application of thin film technology not only in the area of semiconductor or photonics they can actually have applications in lot more other disciplines ok. They can be used for alternative energy or green energy something like in solar collectors or solar cells and so on ok. So, as I mentioned earlier this thin films can be really really thin and they can be from 10 to 1000 nanometers. So, typically 10 nanometer to 1 micron that is what we call them as thin films ok and these are for visible and infrared light and for extreme UV light the films will become even more thinner because extreme UV light has got a very short wavelength and in that case you can actually use thin films of 1 to 2 nanometer thickness and these are typically used in photo masks will come into this.



## Thin Films

- Films can be really thin, like 10 to 1000 nanometers, for visible and infrared light. For extreme-ultraviolet light, films are even thinner, around 1 to 2 nanometers, used in photomasks.
- Thin film properties change based on how they're made. Key properties include how well they coat surfaces, their density, and electrical behavior.
- Density affects how light bends in the film, and stress can warp or crack it.
- When made from compounds, the film's makeup can vary depending on how it's created. For single elements, this isn't usually a worry.
- Impurities, grain size, and how tightly the particles are packed affect how well the film conducts electricity.

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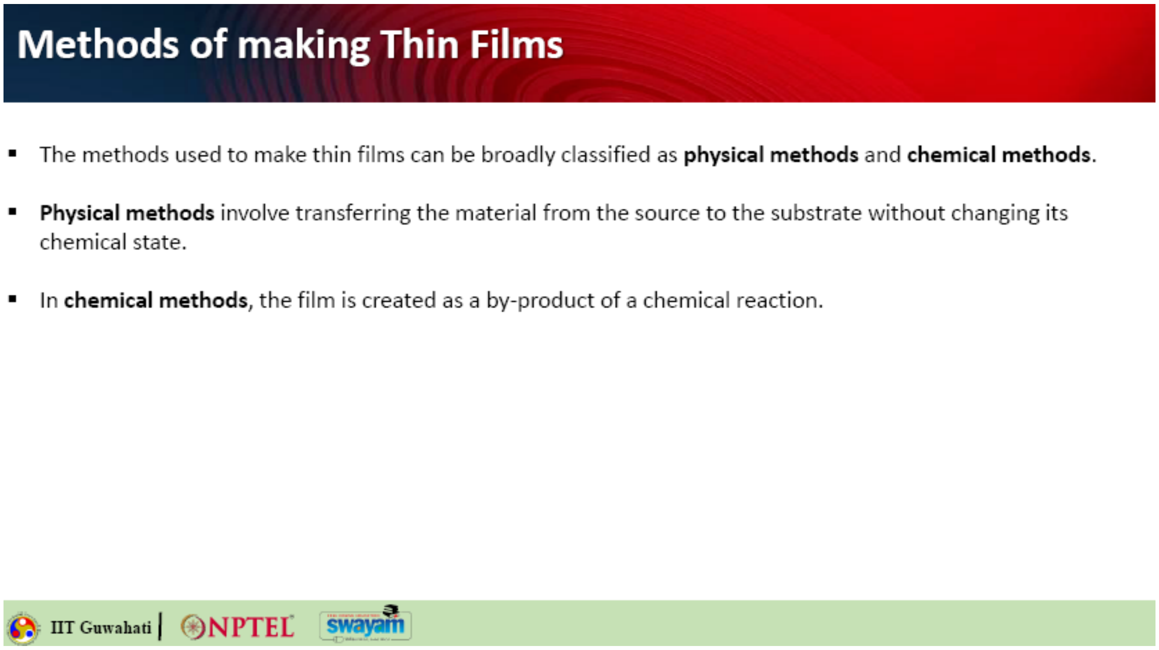
So, right now just keep this new terms in mind we will discuss about this new terms soon in this lecture or in the subsequent lectures. Now, thin film properties change based on how they are made. So, the key properties include how well they coat the surfaces, their density and their electrical behavior and density affects how light bands in the film and stress can wrap or crack it.



## Methods of making Thin Films

- The methods used to make thin films can be broadly classified as **physical methods** and **chemical methods**.
- **Physical methods** involve transferring the material from the source to the substrate without changing its chemical state.
- In **chemical methods**, the film is created as a by-product of a chemical reaction.

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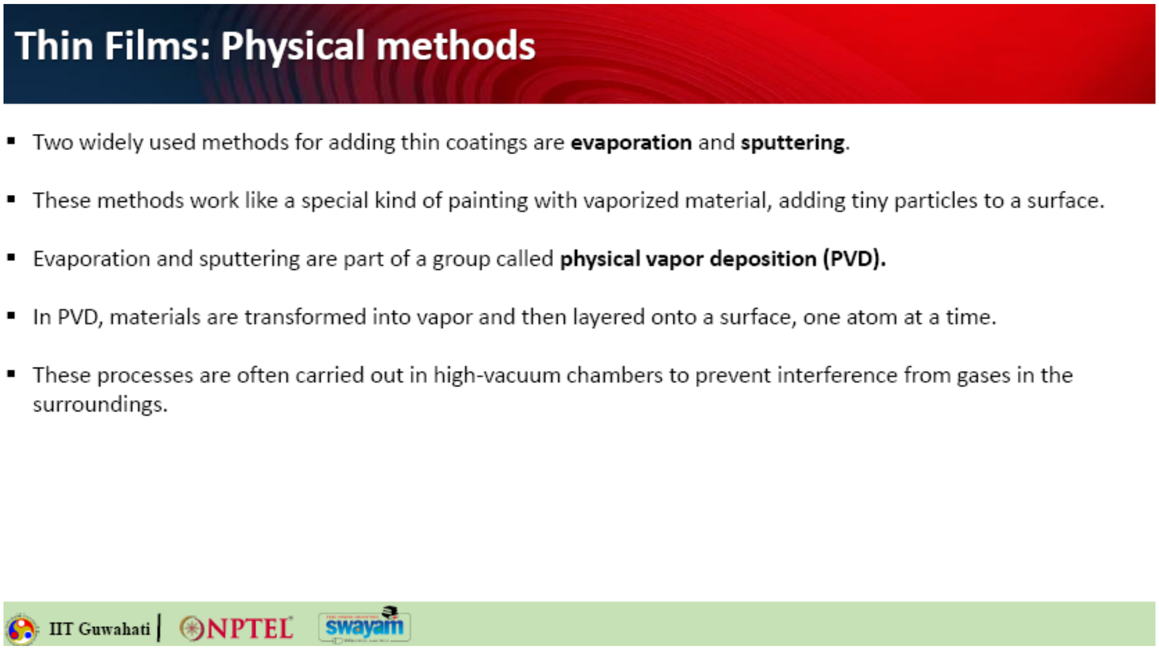
So, this is the effect of density when the thin films are made from compounds the films make up can vary depending on how it is created and for single element thin films it is not usually of a worry and when you develop thin films the impurities grain size and how tightly the elements of the particles are packed they also affect how well the thin film will conduct electricity. So, their conductivity depends on all these parameters.

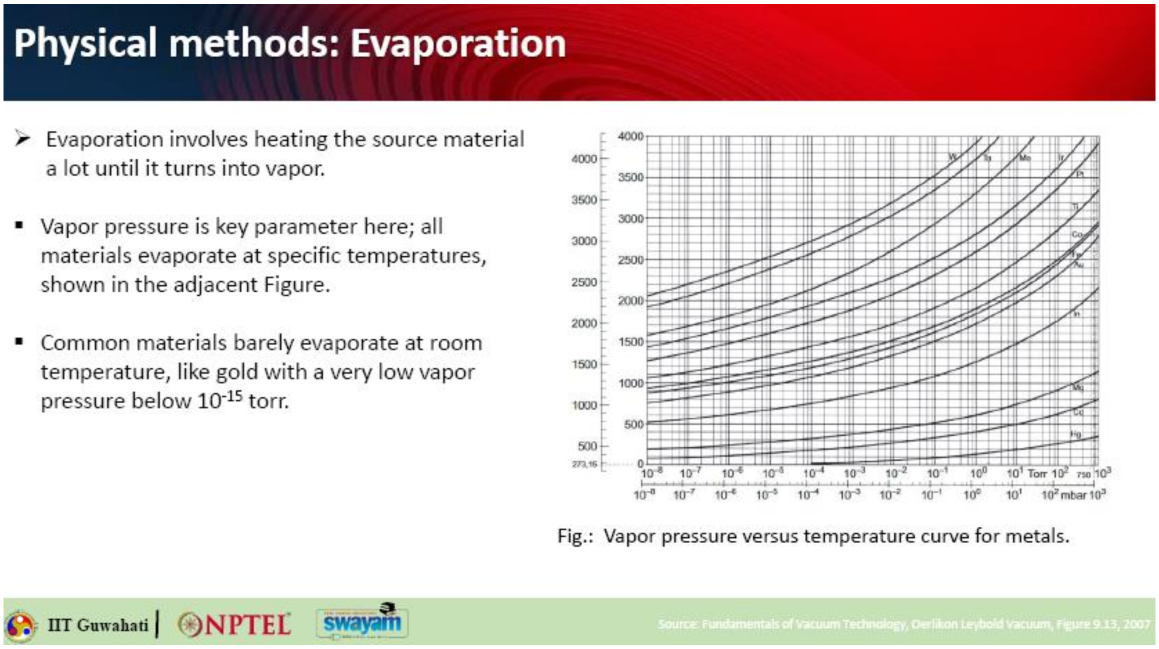


## Thin Films: Physical methods

- Two widely used methods for adding thin coatings are **evaporation** and **sputtering**.
- These methods work like a special kind of painting with vaporized material, adding tiny particles to a surface.
- Evaporation and sputtering are part of a group called **physical vapor deposition (PVD).**
- In PVD, materials are transformed into vapor and then layered onto a surface, one atom at a time.
- These processes are often carried out in high-vacuum chambers to prevent interference from gases in the surroundings.

Now, how do you make thin films? So, the process of making thin films can be broadly classified into 2 categories physical methods and chemical methods. Physical methods involve transferring the material from the source to the substrate without changing its chemical state. So, it is a physical method. On the other hand when you think of chemical method it the film is basically created as a byproduct of some chemical reaction. So, let us look into the physical methods first.

So, when you talk about physical methods there are 2 widely used methods for adding thin films one is evaporation another is sputtering. So, this methods work like a special kind of painting with the vaporized material adding tiny particles to a particular substrate that will be the surface that you will be coating with the thin material. Evaporation or sputtering are part of a group called physical vapor deposition or PVD. In PVD the materials are transformed into vapor and then layered onto a surface one atom at a time and these processes are often carried out in high vacuum chambers that prevent interference from gases in the surrounding. So, if we look into the evaporation method evaporation method involves heating the source material a lot until it turns into vapor and vapor pressure plays a very important role here because all materials evaporate at specific temperatures as you can see here.



## Physical methods: Evaporation

- ➢ Evaporation involves heating the source material a lot until it turns into vapor.
- Vapor pressure is key parameter here; all materials evaporate at specific temperatures, shown in the adjacent Figure.
- Common materials barely evaporate at room temperature, like gold with a very low vapor pressure below $10^{-15}$ torr.

Fig.: Vapor pressure versus temperature curve for metals.

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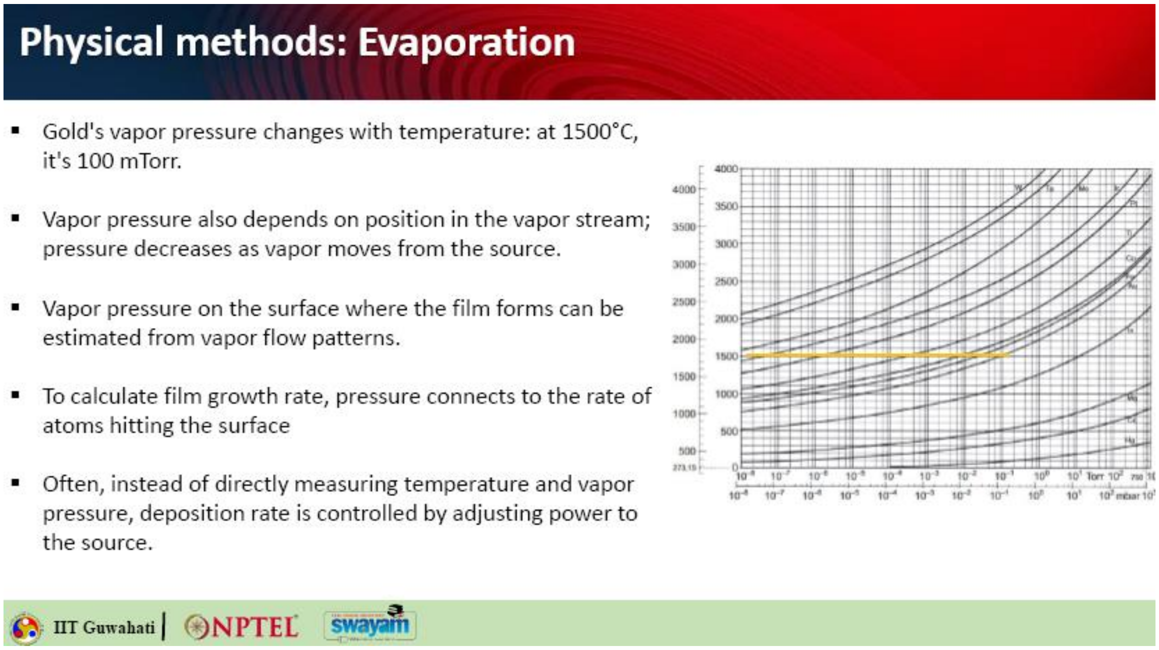
Source: Fundamentals of Vacuum Technology, Oerlikon Leybold Vacuum, Figure 9.13, 2007

So, this is basically the pressure it is given in millibar this one is in torr and this is the temperature scale ok. So, that is in centigrade and that is in Kelvin ok. So, and here are the materials like tungsten, gold, magnesium there are many more all listed here ok. So, this is basically a vapor pressure versus temperature curve for different kind of metals. So, commonly used materials barely evaporate at room temperature right.

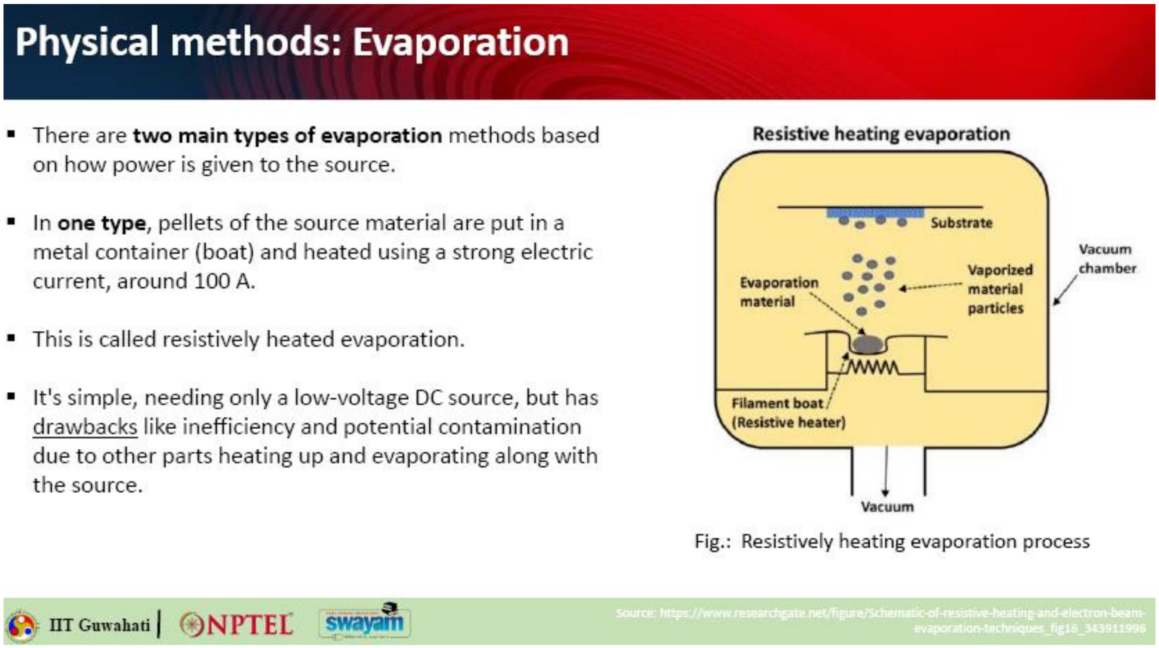
So, you can see that gold with a very low vapor pressure below $10^{-15}$ torr at room temperature ok. Now, when you see how the vapor pressure for gold is changing ok with temperature. So, you can see that at 1500 degree centigrade it actually changes to 100 milli torr ok. And the vapor pressure also depends on the position in the vapor stream. So, the pressure decreases as the vapor moves away from the source, make sense.



## Physical methods: Evaporation

- Gold's vapor pressure changes with temperature: at 1500°C, it's 100 mTorr.
- Vapor pressure also depends on position in the vapor stream; pressure decreases as vapor moves from the source.
- Vapor pressure on the surface where the film forms can be estimated from vapor flow patterns.
- To calculate film growth rate, pressure connects to the rate of atoms hitting the surface
- Often, instead of directly measuring temperature and vapor pressure, deposition rate is controlled by adjusting power to the source.

So, the closest it is to the source it will be the highest vapor pressure. So, vapor pressure on the surface where the film forms can be estimated from the vapor flow patterns. And to calculate the film growth rate pressure connects to the rate of atoms hitting the surface. So, that way you can calculate the rate at which your thin film will be growing. Often instead of directly measuring the temperature and vapor pressure deposition rate is controlled by adjusting the power to the source.



## Physical methods: Evaporation

- There are **two main types of evaporation** methods based on how power is given to the source.
- In **one type**, pellets of the source material are put in a metal container (boat) and heated using a strong electric current, around 100 A.
- This is called resistively heated evaporation.
- It's simple, needing only a low-voltage DC source, but has drawbacks like inefficiency and potential contamination due to other parts heating up and evaporating along with the source.

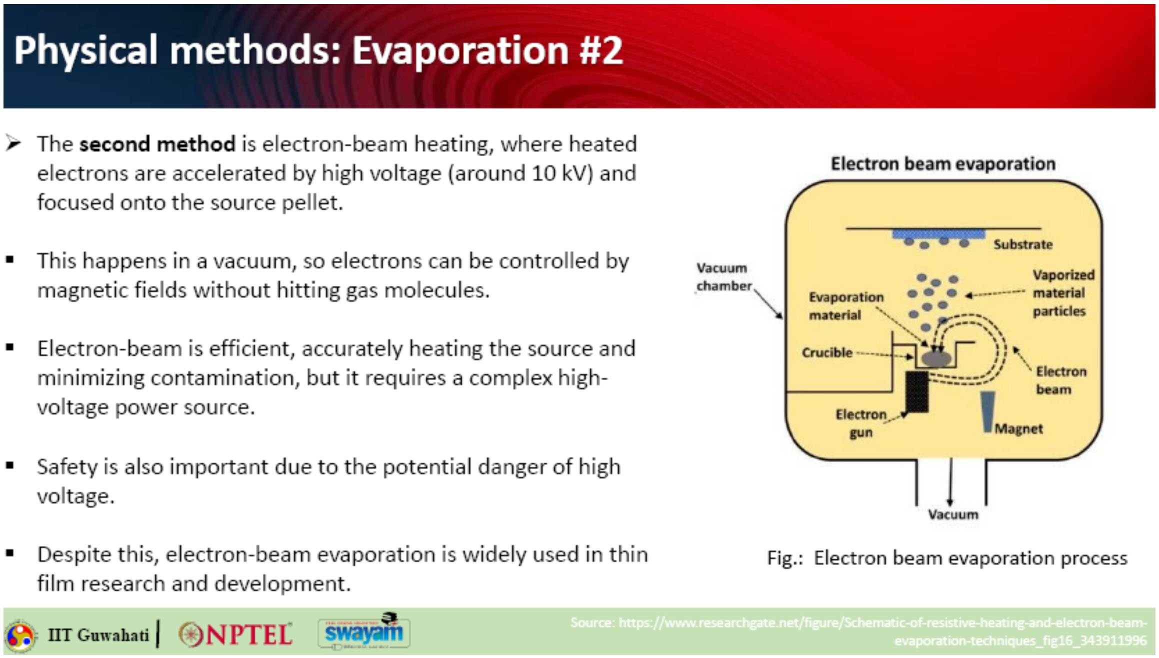
**Resistive heating evaporation**

Fig.: Resistively heating evaporation process

Source: https://www.researchgate.net/figure/Schematic-of-resistive-heating-and-electron-beam-evaporation-techniques_fig16_343911996

So, that is also another method to adjust how much the temperature how much thickness will be deposited. So, among the two methods of evaporation you can see here one method is called resistively heating evaporation process. So, in this particular process there are two methods. So, this is the one the other one will show in the next slide. So, in this one the palette of the source material that is here it is actually put in a metal container like a boat ok and it is heated using a strong electric current around 100 amperes.

So, this is particularly called resistively heated evaporation. So, it is very simple needing only a low voltage DC source, but it has got some drawbacks. Drawback something like it is inefficient and there are chances of potential contamination due to other parts also getting heated up and evaporating along with the source. So, this boat material or other parts also may get heated up and they they will also vaporize along with the source material. So, this is how it works the source material or evaporation material is here the filament or the heater element is here.



## Physical methods: Evaporation #2

- The **second method** is electron-beam heating, where heated electrons are accelerated by high voltage (around 10 kV) and focused onto the source pellet.
- This happens in a vacuum, so electrons can be controlled by magnetic fields without hitting gas molecules.
- Electron-beam is efficient, accurately heating the source and minimizing contamination, but it requires a complex high-voltage power source.
- Safety is also important due to the potential danger of high voltage.
- Despite this, electron-beam evaporation is widely used in thin film research and development.

Fig.: Electron beam evaporation process

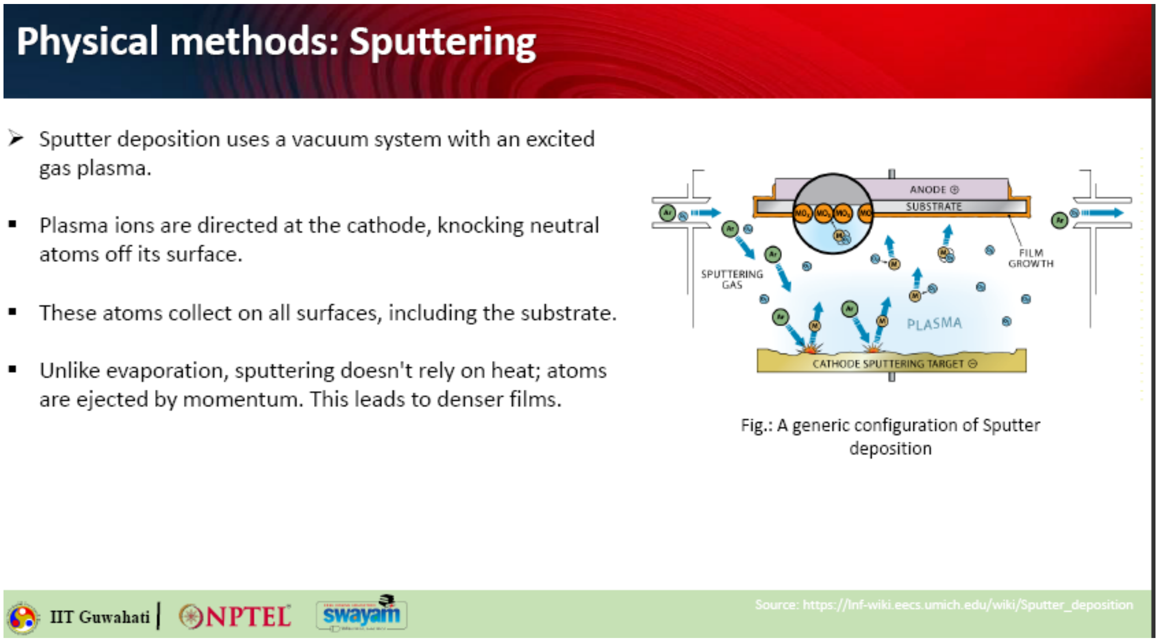
Source: https://www.researchgate.net/figure/Schematic-of-resistive-heating-and-electron-beam-evaporation-techniques_fig16_343911996

So, it hits this one up the vaporized material particles they actually go and settle down on the substrate which is kept right on top of it and this is done in a vacuum chamber. The second method is called a electron beam heating ok where the heated electrons are basically accelerated by high voltage. So, here you see the amount of voltage requirement goes very very high it is around 10 kilovolt and then it is focused this particular electron beam is focused on to the source palette. So, this happens again inside a vacuum. So, the electrons can be controlled by magnetic field ok and without heating the gas molecules.

This particular method of electron beam evaporation is pretty efficient and here accurately heating of the source can be obtained. So, that it minimizes the contamination and therefore, it is a good process of developing in a high quality thin films, but only problem is that it requires a complex high voltage power source. And safety also becomes important here because you are dealing with very high voltage. Now, despite this electron beam evaporation is widely used in thin film research and development the reason you get a very high quality film. Now, the next method of developing thin film is called sputtering.

So, sputtering also uses a vacuum system with an excited gas plasma ok. So, this is the typical setup for sputtering. So, here you can see that there is a gas inlet this is the outlet and the sputtering gas comes in and it hits the cathode sputtering target ok. So, that knocks out the metallic particles or atoms and they actually go and settle down on the substrate forming a thin film ok.

So, here you can see how it works. So, plasma ions so these are the plasma ions which are so this is plasma and then the sputtering gas enters and the plasma ions are basically directed at the cathode and they could knock the neutral atoms of the surfaces. You can see here M is the metal that is been knocked off ok and these atoms they collect on all surfaces including the substrate. So, you can see a thin film being growing on this it is because of this ok. Now, in this particular method unlike evaporation it does not depend on heating ok. So, what is the method of atoms coming out? The the atoms are basically ejected by momentum.



## Physical methods: Sputtering

- Sputter deposition uses a vacuum system with an excited gas plasma.
- Plasma ions are directed at the cathode, knocking neutral atoms off its surface.
- These atoms collect on all surfaces, including the substrate.
- Unlike evaporation, sputtering doesn't rely on heat; atoms are ejected by momentum. This leads to denser films.

Fig.: A generic configuration of Sputter deposition

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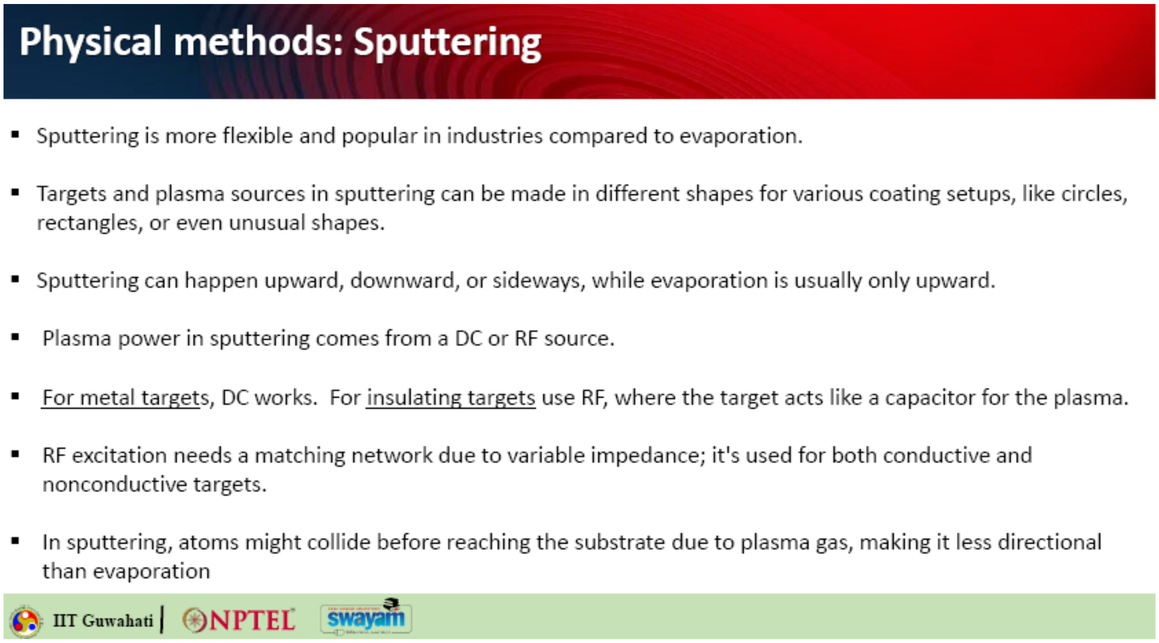
Source: https://lnf-wiki.eecs.umich.edu/wiki/Sputter_deposition

So, this leads into much denser films ok. However, there are some benefits with sputtering because it is more flexible and that is why it is popular in the industries compared to evaporation. Heating is not required high voltage requirement is not there. So, it is pretty good. Targets and plasma sources in sputtering can be made of different shapes for various coating setups something like circles rectangles or any other unusual shape you can coat ok.



## Physical methods: Sputtering

- Sputtering is more flexible and popular in industries compared to evaporation.
- Targets and plasma sources in sputtering can be made in different shapes for various coating setups, like circles, rectangles, or even unusual shapes.
- Sputtering can happen upward, downward, or sideways, while evaporation is usually only upward.
- Plasma power in sputtering comes from a DC or RF source.
- For metal targets, DC works. For insulating targets use RF, where the target acts like a capacitor for the plasma.
- RF excitation needs a matching network due to variable impedance; it's used for both conductive and nonconductive targets.
- In sputtering, atoms might collide before reaching the substrate due to plasma gas, making it less directional than evaporation

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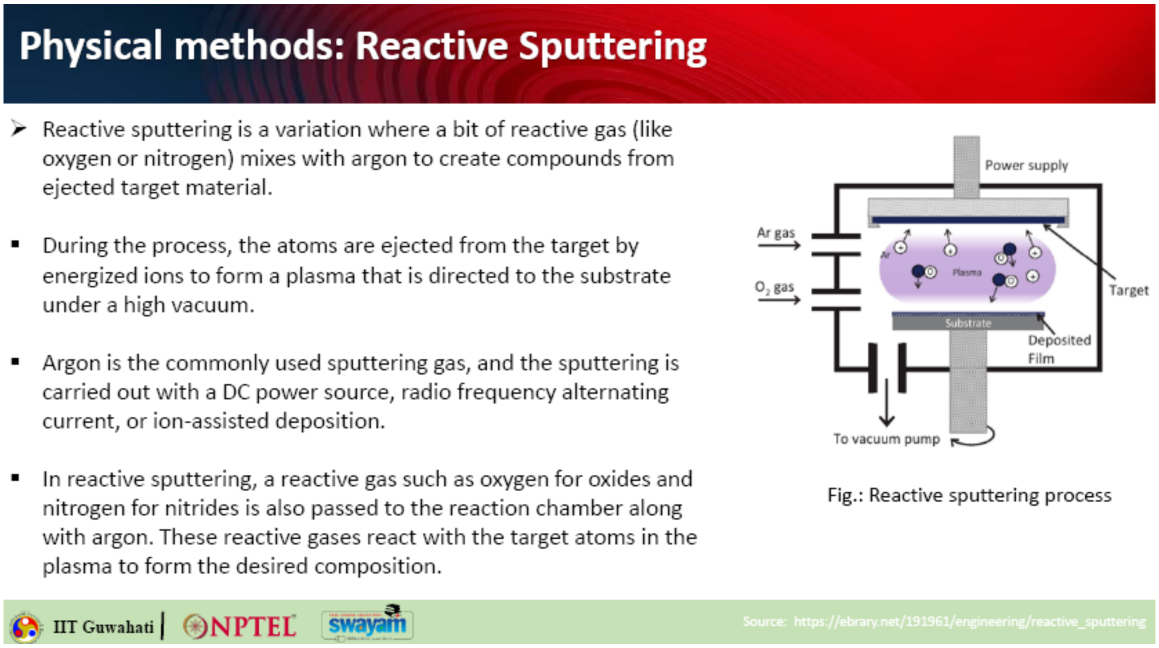
Sputtering can happen upward downward or sideways while evaporation happens only upward ok. So, these are the flexibilities with the sputtering technique. Moreover, the plasma power in the sputtering comes from a DC or RF source ok. So, for metal targets DC sputtering works whereas, for insulating targets RF sputtering is used where the target acts as the capacitor for the plasma. We will not go into too much of detail, but it is good to know what are the different techniques being used for developing what kind of films.



## Physical methods: Reactive Sputtering

- ➢ Reactive sputtering is a variation where a bit of reactive gas (like oxygen or nitrogen) mixes with argon to create compounds from ejected target material.
- During the process, the atoms are ejected from the target by energized ions to form a plasma that is directed to the substrate under a high vacuum.
- Argon is the commonly used sputtering gas, and the sputtering is carried out with a DC power source, radio frequency alternating current, or ion-assisted deposition.
- In reactive sputtering, a reactive gas such as oxygen for oxides and nitrogen for nitrides is also passed to the reaction chamber along with argon. These reactive gases react with the target atoms in the plasma to form the desired composition.

Fig.: Reactive sputtering process

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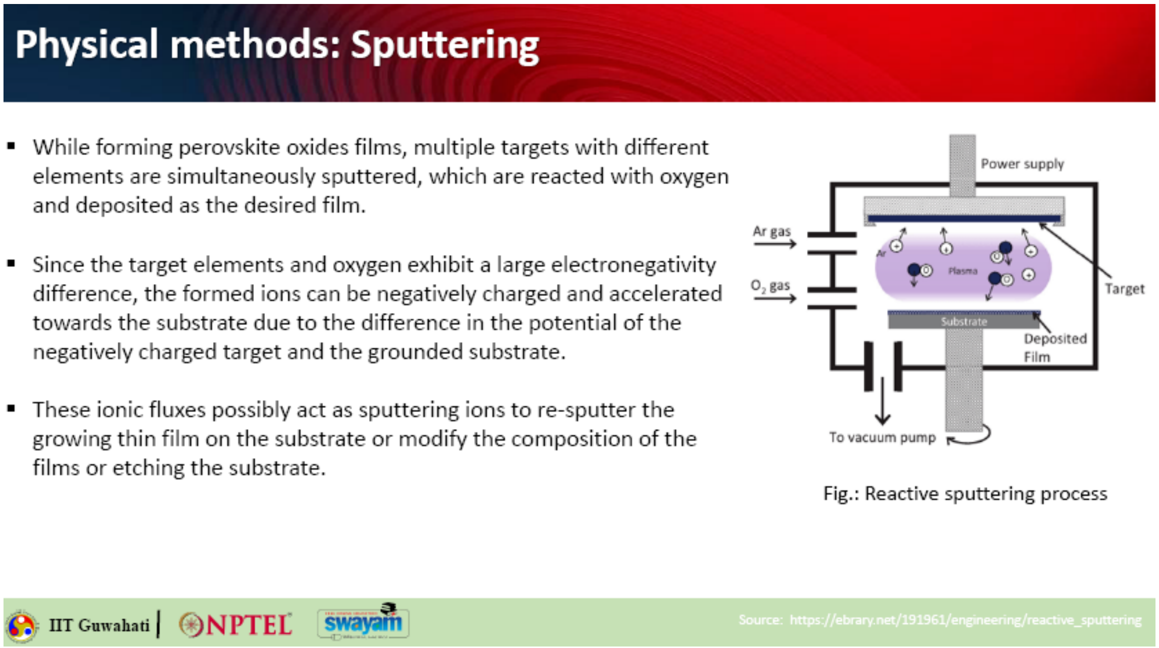
Source: https://ebrary.net/191961/engineering/reactive_sputtering

So, RF excitation needs a matching network due to variable impedance and it is used for both conductive and non-conductive targets ok. In sputtering the atoms collide before reaching the substrate due to plasma gas making it less directional than evaporation. So, these are couple of pros and cons of sputtering as compared to evaporation. There is a variation to it which is called reactive sputtering and in reactive sputtering what happens a bit of reactive gas like oxygen or nitrogen mixes with the argon gas to create compounds from ejected target molecule ok. So, the setup looks like this you have got a power supply here this is the target which is kept this is the plasma formation you have got argon gas and also you get some reactive gas and this is the vacuum chamber ok.

And from the target these are knocked off and then the materials or nanoparticles which are ejected from this target gets reacted with this reacting gas and then the compound gets deposited on the substrate. So, during this process as you can see the atoms are ejected from the target by energized ions to form a plasma that is directed to the substrate under a high vacuum. Argon is commonly used as the sputtering gas and the sputtering is carry out with DC power source and RF alternating current or ion assisted deposition there are 3 methods. So, mainly DC and RF sputtering are used and in this particular case of reactive sputtering a reactive gas such as oxygen are used for getting oxides. You can use nitrogen if you want to create thin films of nitrides ok.



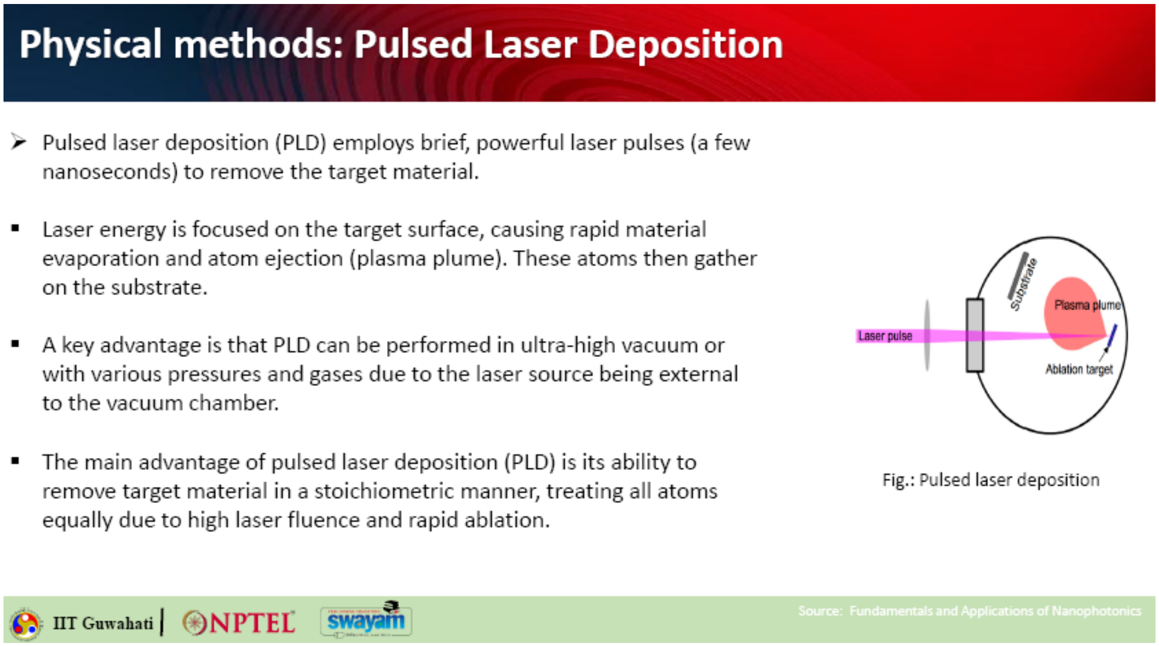
## Physical methods: Sputtering

- While forming perovskite oxides films, multiple targets with different elements are simultaneously sputtered, which are reacted with oxygen and deposited as the desired film.
- Since the target elements and oxygen exhibit a large electronegativity difference, the formed ions can be negatively charged and accelerated towards the substrate due to the difference in the potential of the negatively charged target and the grounded substrate.
- These ionic fluxes possibly act as sputtering ions to re-sputter the growing thin film on the substrate or modify the composition of the films or etching the substrate.

Fig.: Reactive sputtering process

Source: https://ebrary.net/191961/engineering/reactive_sputtering

They are also passed to the reaction chamber along with the argon gas that you can see here and this reactive gases react with the target atoms in the plasma to form the desired composition and then they get deposited in the film as I explained before. So, while forming perovskite oxide films multiple targets with different elements are simultaneously sputtered which are reacted with oxygen and they deposit as the desired film. Since the target elements and oxygen exhibit a large electronegativity difference the formed ions can be negatively charged and they can be accelerated towards the substrate due to the difference in the potential of the negatively charged target and the grounded substrate ok. So, the substrate is grounded ok. This ionic fluxes possibly act as sputtering ions to re sputter the growing thin films onto the substrate or modify the composition of the films or etching the substrate ok.



## Physical methods: Pulsed Laser Deposition

- Pulsed laser deposition (PLD) employs brief, powerful laser pulses (a few nanoseconds) to remove the target material.
- Laser energy is focused on the target surface, causing rapid material evaporation and atom ejection (plasma plume). These atoms then gather on the substrate.
- A key advantage is that PLD can be performed in ultra-high vacuum or with various pressures and gases due to the laser source being external to the vacuum chamber.
- The main advantage of pulsed laser deposition (PLD) is its ability to remove target material in a stoichiometric manner, treating all atoms equally due to high laser fluence and rapid ablation.

Fig.: Pulsed laser deposition

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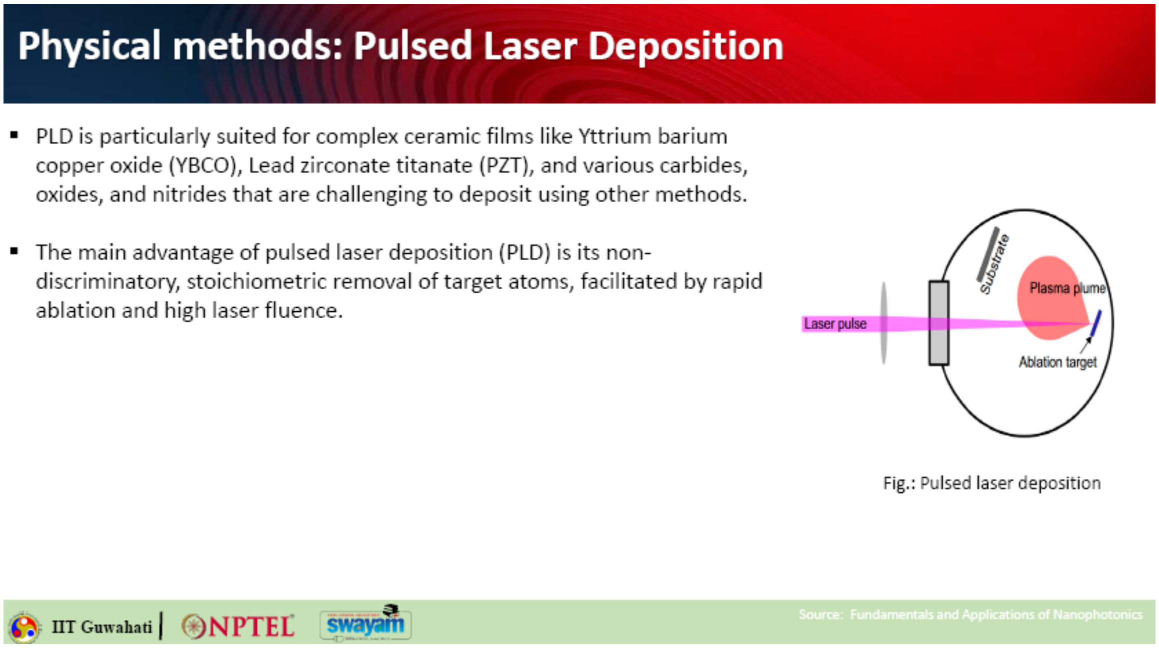
Source: Fundamentals and Applications of Nanophotonics

So, the next method to develop thin film is pulsed laser deposition. So, here the name itself tells you that you are going to use a laser pulse ok for depositing thin films. So, how it works? So, pulsed laser deposition or PLD employs brief powerful laser pulses which are as short as few nanoseconds to remove the target material. So, you can see in the diagram here you have got a laser pulse you focus it and you hit the target ok. And then there is a plasma plume that goes towards the substrate and it gets deposited.

So, the laser energy here is focused on the target subs surface causing rapid material evaporation and atom injection. So, that gives you this plasma plume ok and the atoms then they gather on the surface to give you that thin film. So, what is the key advantage of this PLD? It can be performed in ultra high vacuum or with various pressures and gases due to the laser source being external to the vacuum chamber. So, that that is the flexibility it provides and the main advantage of PLD is its ability to remove target materials in stoichiometric manner that treating all atoms equally due to high laser fluency and rapid ablation. So, that way you are able to deposit uniform films using pulsed laser deposition.



## Physical methods: Pulsed Laser Deposition

- PLD is particularly suited for complex ceramic films like Yttrium barium copper oxide (YBCO), Lead zirconate titanate (PZT), and various carbides, oxides, and nitrides that are challenging to deposit using other methods.
- The main advantage of pulsed laser deposition (PLD) is its non-discriminatory, stoichiometric removal of target atoms, facilitated by rapid ablation and high laser fluence.

Fig.: Pulsed laser deposition

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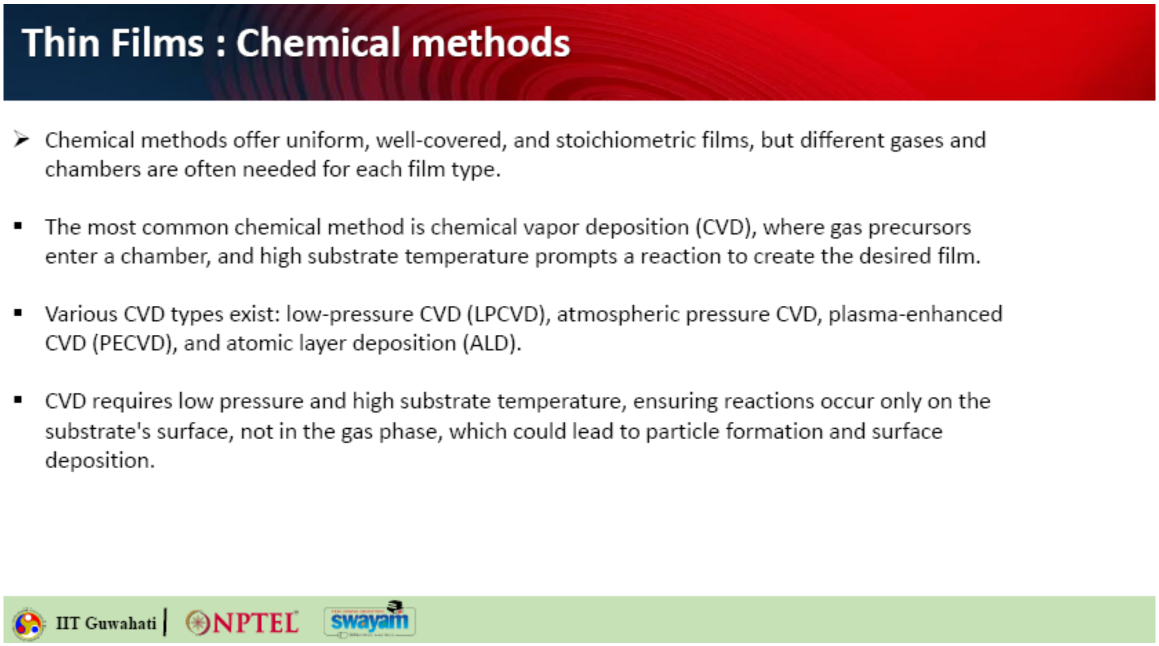
Source: Fundamentals and Applications of Nanophotonics

So, PLD is particularly suited for complex ceramic films like yttrium barium copper oxide YBCO lead zirconate titanate PZT and different other carbides oxides nitrides ok that are challenging to deposit using other methods. So, you can actually deposit this kind of films using PLD method. So, as I told you that the main advantage of PLD is that it is non discriminatory and it gives you stoichiometric removal of target atoms ok and it facilitates and it comes from rapid ablation and high laser fluency. So, quickly this evaporation takes place and it takes place from all from the entire target.

So, that happens very very quickly. So, with that we more or less cover all the basic methods in this particular physical methods of depositing thin films. Now, let us look into the chemical methods of depositing thin films. As we mentioned before that chemical methods will deposit the thin films as a byproduct of some chemical reaction. So, chemical methods they offer uniform well covered and stoichiometric films, but different gases and chambers are often required for each type of film.



## Thin Films : Chemical methods

- ➢ Chemical methods offer uniform, well-covered, and stoichiometric films, but different gases and chambers are often needed for each film type.
- The most common chemical method is chemical vapor deposition (CVD), where gas precursors enter a chamber, and high substrate temperature prompts a reaction to create the desired film.
- Various CVD types exist: low-pressure CVD (LPCVD), atmospheric pressure CVD, plasma-enhanced CVD (PECVD), and atomic layer deposition (ALD).
- CVD requires low pressure and high substrate temperature, ensuring reactions occur only on the substrate's surface, not in the gas phase, which could lead to particle formation and surface deposition.

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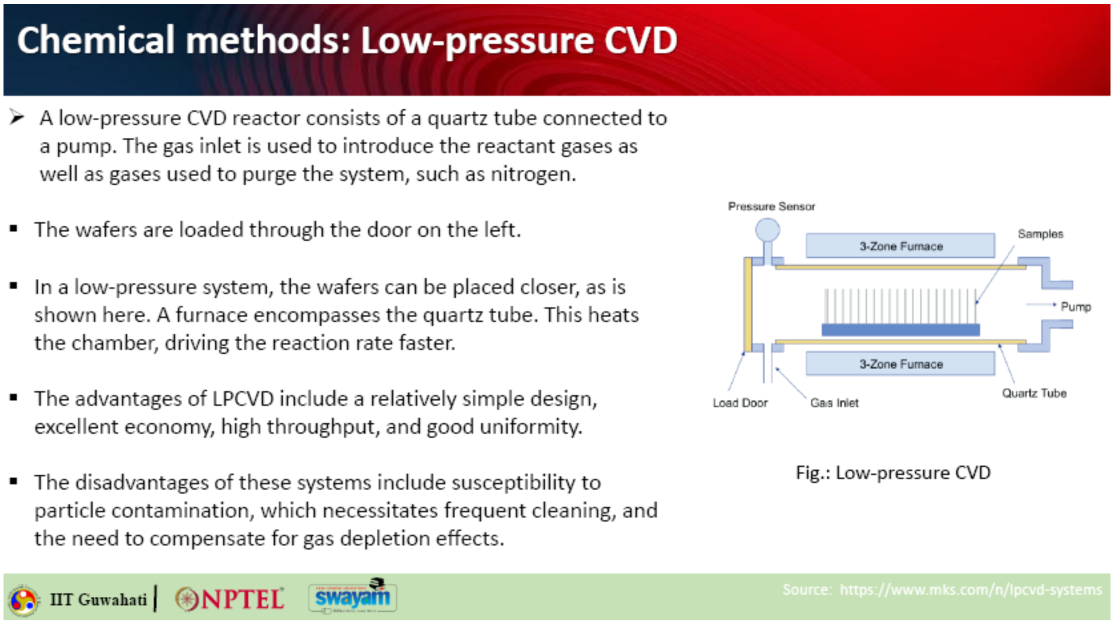
So, that makes it very very specific. So, so and it is that makes it also costly if you are experimenting in different films because and using different gases. So, you need different different chambers for different film types. So, the most common chemical method is chemical vapor deposition where gas precursors enter a chamber and the high substrate temperature prompts a reaction to build the desired film. So, different types of CVDs are there one is called low pressure CVD, you have atmospheric pressure CVD, you have plasma enhanced CVD and atomic layer deposition. So, CVD requires low pressure and high substrate temperature that ensures that the reaction occurs only on the substrates surface and not in the gas phase which could lead to particle formation and surface deposition.

So, here is the setup typically used for low pressure CVD. So, in this particular case of low pressure CVD the reactor consists of a quartz tube that you see here this quartz tube that is connected to a pump ok and the gas inlet is used to introduce the reactant gases as well as the gases needs to purge the system. You typically nitrogen is used for purging and the wafers are loaded through the door which is on the left. So, you can open this door and you can load this sample ok. In low pressure system the wafers can be placed closer as you can see here a furnace.



## Chemical methods: Low-pressure CVD

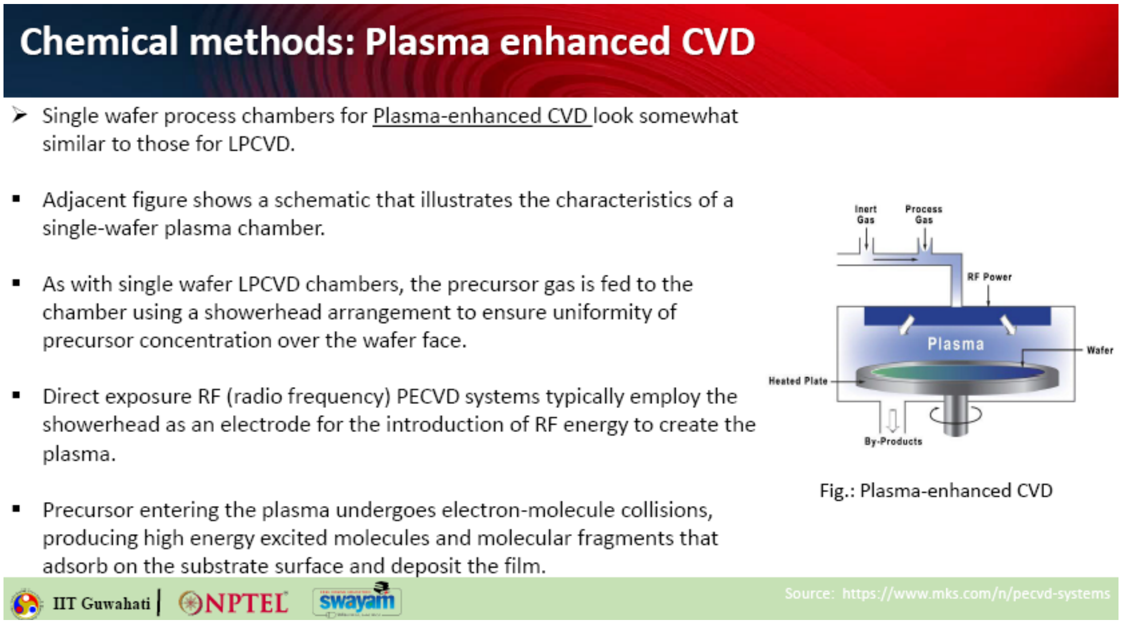
- A low-pressure CVD reactor consists of a quartz tube connected to a pump. The gas inlet is used to introduce the reactant gases as well as gases used to purge the system, such as nitrogen.
- The wafers are loaded through the door on the left.
- In a low-pressure system, the wafers can be placed closer, as is shown here. A furnace encompasses the quartz tube. This heats the chamber, driving the reaction rate faster.
- The advantages of LPCVD include a relatively simple design, excellent economy, high throughput, and good uniformity.
- The disadvantages of these systems include susceptibility to particle contamination, which necessitates frequent cleaning, and the need to compensate for gas depletion effects.

Fig.: Low-pressure CVD

Source: https://www.mks.com/n/lpcvd-systems

So, this is a three zone furnace that is there from the three sides ok top back and bottom ok. And this particular one actually encompasses the quartz tube and this heats up the chamber which drives the reaction rate faster. Now, what is the advantages of low pressure CVD? The first thing is it is a relatively simple design. So, excellent economy it gives you high throughput and very good uniformity of the thin films.

But there are some disadvantages also. So, you can say what are the disadvantages? They are susceptible to particle contamination. So, it requires frequent cleaning of this setup and also you need to compensate for gas depletion effects. Next methods we will see is plasma enhanced CVD. Now single wafer process chambers for plasma CVD look somewhat similar to this low power CVD ok. Adjustment figure here it shows a schematic that tells you how exactly single wafer plasma chamber will look like.



# Chemical methods: Plasma enhanced CVD

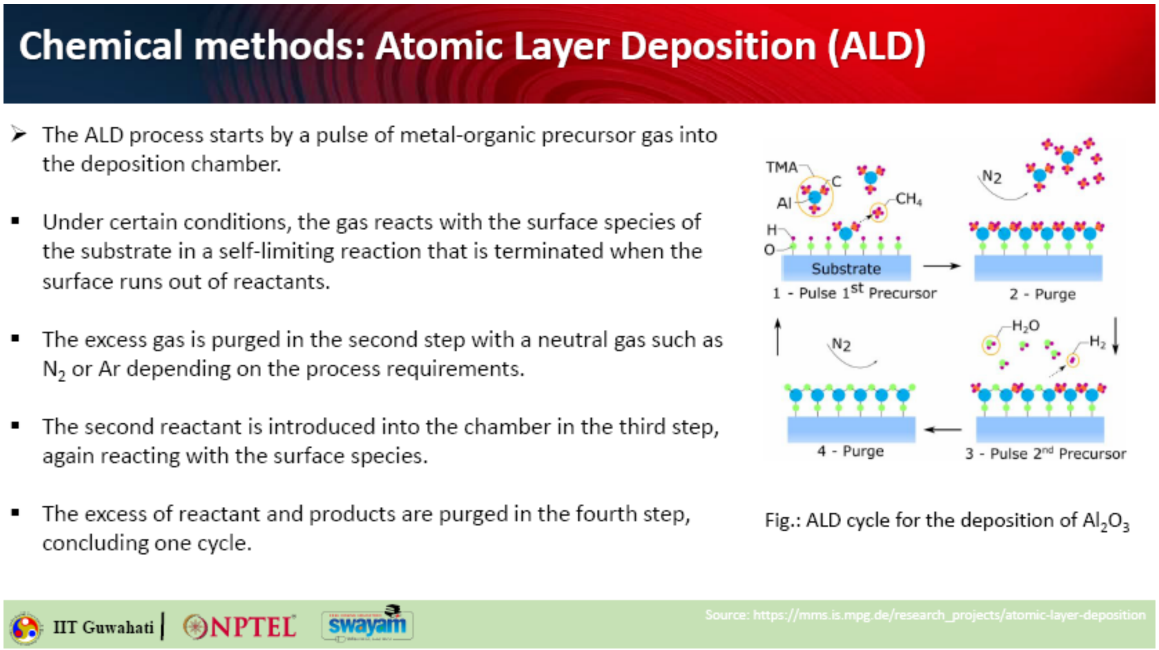
- Single wafer process chambers for Plasma-enhanced CVD look somewhat similar to those for LPCVD.
  - Adjacent figure shows a schematic that illustrates the characteristics of a single-wafer plasma chamber.
  - As with single wafer LPCVD chambers, the precursor gas is fed to the chamber using a showerhead arrangement to ensure uniformity of precursor concentration over the wafer face.
  - Direct exposure RF (radio frequency) PECVD systems typically employ the showerhead as an electrode for the introduction of RF energy to create the plasma.
  - Precursor entering the plasma undergoes electron-molecule collisions, producing high energy excited molecules and molecular fragments that adsorb on the substrate surface and deposit the film.

Fig.: Plasma-enhanced CVD

Source: https://www.mks.com/n/pecvd-systems

So, as with the single wafer LP CVD chambers here also the precursor gas is fed to the chamber using the shower head ok. So, you see here and that ensure the uniformity of the precursor concentration over the wafer phase. So, this is where the wafer is kept and this is basically on a heated plate ok. So, the wafer sits on a heated plate and the byproduct gases are exhausted through this outlet which is below the wafer level ok. Now with direct exposure RF PECVD systems typically employ shower head as an electrode for the introduction of the RF energy to create the plasma that is see here ok.

The precursor entering the plasma undergoes electron molecule collisions producing high energy excited molecules and molecular fragments that absorb on the substrate surface and deposit the film. So, these are the gas inlets ok. So, the next method is atomic layer deposition. So, atomic layer deposition or ALD it starts by a pulse ok of metal organic precursor gas into a deposition chamber as you can see here this is the first stage. Under certain conditions the gas will react with the surface species of the substrate in a self limiting reaction that is terminated when the surface runs out of the reactants.



## Chemical methods: Atomic Layer Deposition (ALD)

- The ALD process starts by a pulse of metal-organic precursor gas into the deposition chamber.
- Under certain conditions, the gas reacts with the surface species of the substrate in a self-limiting reaction that is terminated when the surface runs out of reactants.
- The excess gas is purged in the second step with a neutral gas such as $N_2$ or Ar depending on the process requirements.
- The second reactant is introduced into the chamber in the third step, again reacting with the surface species.
- The excess of reactant and products are purged in the fourth step, concluding one cycle.

Fig.: ALD cycle for the deposition of $Al_2O_3$

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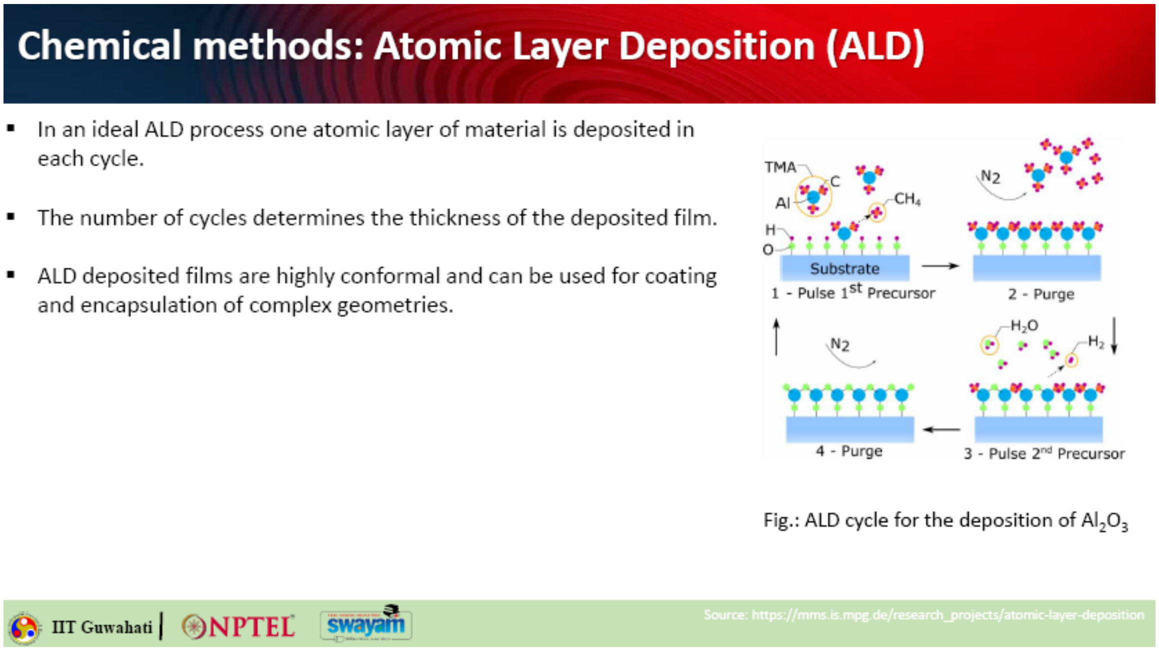
Source: https://mms.is.mpg.de/research_projects/atomic-layer-deposition

So, that is why it is called self-limiting reaction and the excess gas is purged in the next step with a neutral gas. So, as you can see here nitrogen is being used for doing the purging you can also use argon depending on the process requirements. So, the second reactant is then introduced into the chamber in the third stage. So, here the second one is introduced and again that starts reacting with the surface species like that and the excess reactant is again purged in the fourth step.

So, that that gives you one particular cycle and then it is repeated. So, you can actually atomic layer deposition as the name tells you we can actually deposit layer by layer of atoms and grow your thin film. So, in an ideal ALD process one atomic layer of material is deposited in each cycle that is what it does. So, you can actually precisely control the thickness of the films using this particular method. The number of cycles will then determine the overall thickness of the film okay and ALD deposited films are highly conformal and they can be used for coating and encapsulating of complex geometries because you have complete control on the thickness of the films that are being deposited ok. So, with that we move on to the third method of depositing thin films that is epitaxy.



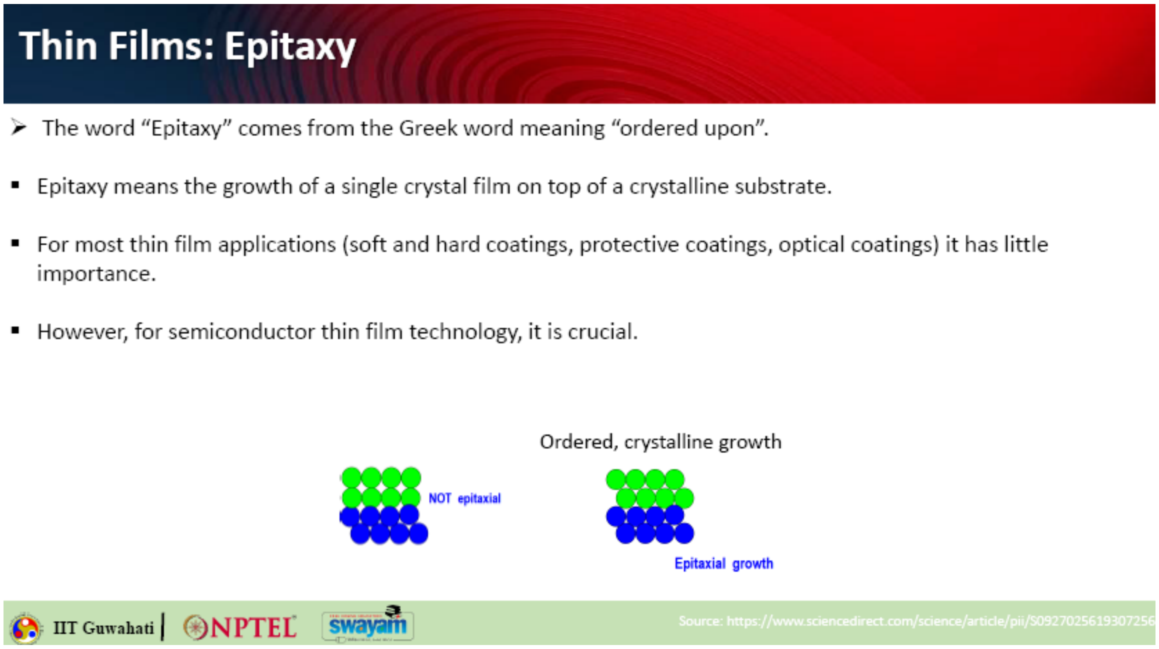
## Chemical methods: Atomic Layer Deposition (ALD)

- In an ideal ALD process one atomic layer of material is deposited in each cycle.
- The number of cycles determines the thickness of the deposited film.
- ALD deposited films are highly conformal and can be used for coating and encapsulation of complex geometries.

Fig.: ALD cycle for the deposition of $Al_2O_3$

Source: https://mms.is.mpg.de/research_projects/atomic-layer-deposition

So, when we talk about epitaxy it basically this word comes from a Greek word which means ordered upon. So, epitaxy means basically the growth of a single crystal film on top of a crystalline substrate. So, for most of the thin film application which includes soft or hard coating, protective coating, material coating it has little importance. However, when you go for semiconductor thin film technology this becomes very very crucial the crystalline growth becomes very very crucial.



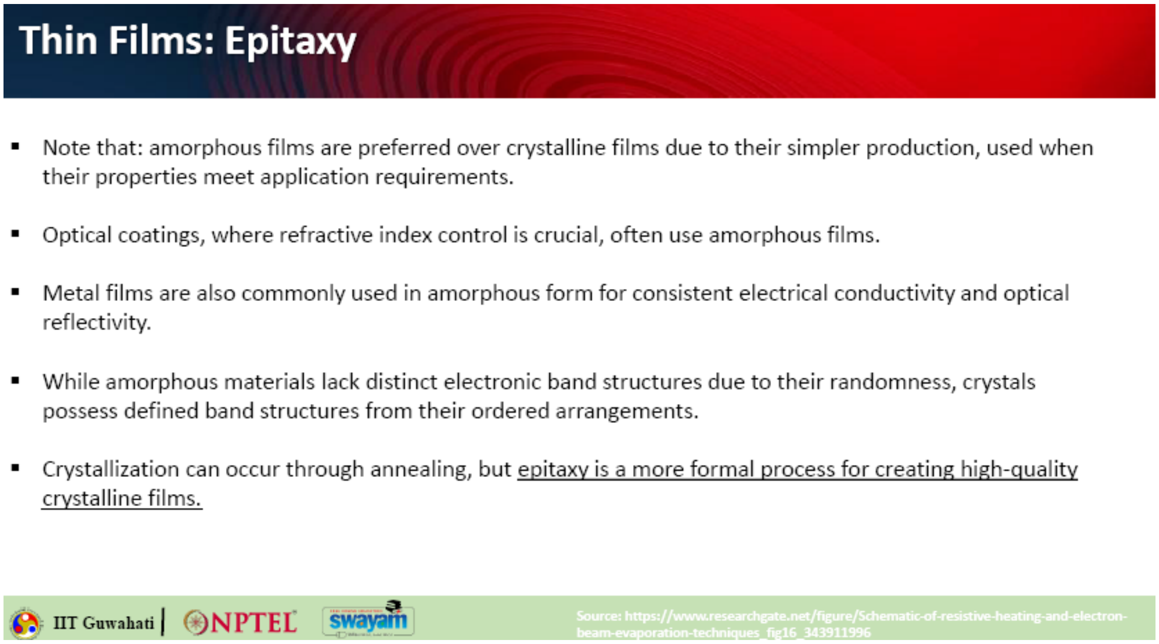
## Thin Films: Epitaxy

- ➢ The word "Epitaxy" comes from the Greek word meaning "ordered upon".
- Epitaxy means the growth of a single crystal film on top of a crystalline substrate.
- For most thin film applications (soft and hard coatings, protective coatings, optical coatings) it has little importance.
- However, for semiconductor thin film technology, it is crucial.

Ordered, crystalline growth

Source: https://www.sciencedirect.com/science/article/pii/S0927025619307256

So, this is what we mean by crystalline growth. So, this is not epitaxial, but this is epitaxial ok. So, it is a crystalline growth ordered and crystalline growth. Now note that when we talk about the other thin films if they are not crystalline they are typically amorphous ok. So, amorphous films are preferred over thin films due to the simpler production ok used when their properties can meet the application requirement. So, if you are able to provide a amorphous film that can serve your purpose you stick to that you do not need to develop a crystalline film or a very ordered film because that makes it very expensive ok.



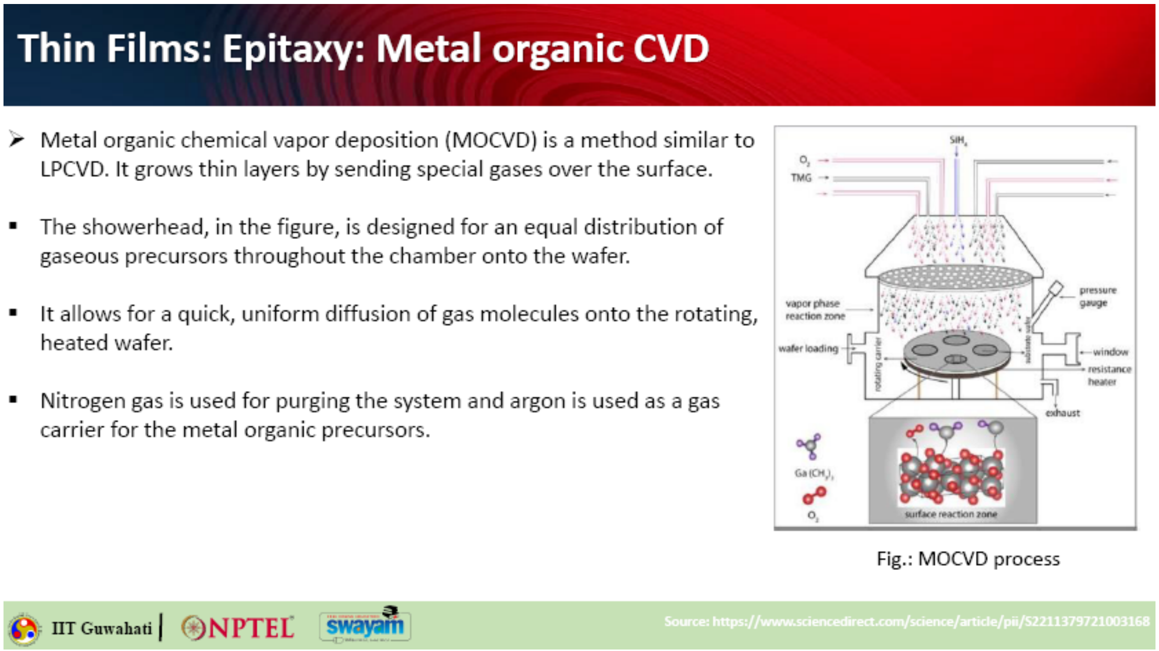
## Thin Films: Epitaxy

- Note that: amorphous films are preferred over crystalline films due to their simpler production, used when their properties meet application requirements.
- Optical coatings, where refractive index control is crucial, often use amorphous films.
- Metal films are also commonly used in amorphous form for consistent electrical conductivity and optical reflectivity.
- While amorphous materials lack distinct electronic band structures due to their randomness, crystals possess defined band structures from their ordered arrangements.
- Crystallization can occur through annealing, but epitaxy is a more formal process for creating high-quality crystalline films.

Source: https://www.researchgate.net/figure/Schematic-of-resistive-heating-and-electron-beam-evaporation-techniques_fig16_343911996

Now when we talk about the optical coatings where the refractive index control is crucial you actually use amorphous films ok that works for you. Metal films are commonly used in amorphous form for consistent electrical conductivity and optical reflectivity. While amorphous materials they lack distinct electronic band structure due to their randomness crystals process defines band structure with their ordered arrangements and crystallization can occur through annealing ok, but epitaxy is a more formal process for creating high quality crystalline films. So, here is an example of method of epitaxy which is metal organic CVD. So, this is very very similar to LPCVD that you have seen it grows thin layers by sending special gases over the substrate.

Now if you see the shower head here ok in this particular figure it is designed for equal distribution of gaseous precursors through the chamber onto the wafer. So, these are different gases which comes in ok. It allows a quick and uniform diffusion of gas molecules onto a rotating heated wafer. So, this the wafer which is being on a rotating platform and which is also heated. So, nitrogen gas is typically used for purging the system and argon gas can be used as the carrier of the metal organic precursors.



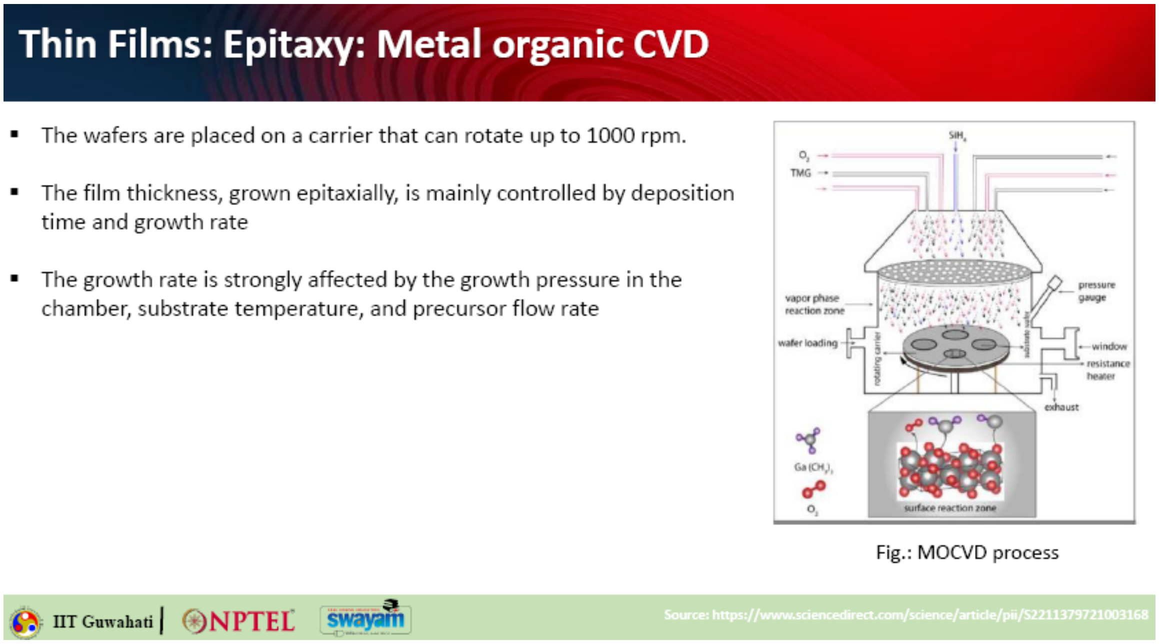
## Thin Films: Epitaxy: Metal organic CVD

- Metal organic chemical vapor deposition (MOCVD) is a method similar to LPCVD. It grows thin layers by sending special gases over the surface.
- The showerhead, in the figure, is designed for an equal distribution of gaseous precursors throughout the chamber onto the wafer.
- It allows for a quick, uniform diffusion of gas molecules onto the rotating, heated wafer.
- Nitrogen gas is used for purging the system and argon is used as a gas carrier for the metal organic precursors.

Fig.: MOCVD process

Source: https://www.sciencedirect.com/science/article/pii/S2211379721003168

These are the wafer loading window this is the exhaust ok and this is where the resistance heater is that heats up the platform ok. So, you can actually see that this this particular wafer at rotates on this platform at a speed up to 1000 rpm. The film thickness which is grown epitaxially that means, orderly ok is mainly controlled by deposition time and the growth rate. And growth rate is also strongly affected by the growth pressure in the chamber substrate temperature and the precursor flow rate. So, these are the factors they they actually decide what will be the growth rate of the film.



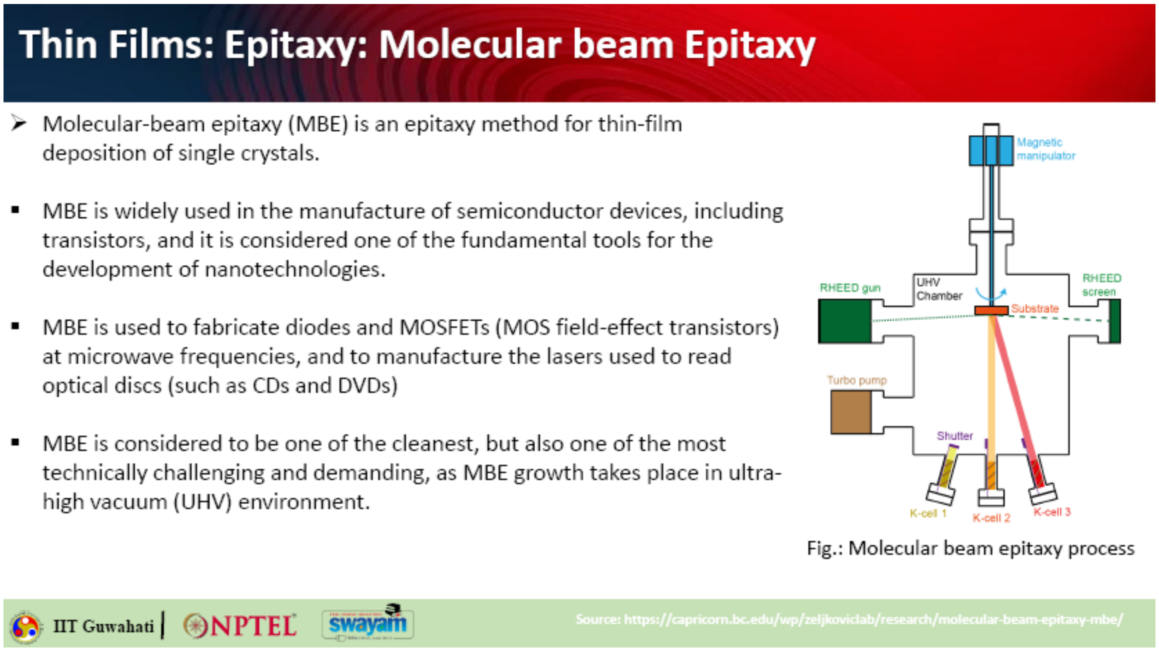
## Thin Films: Epitaxy: Metal organic CVD

- The wafers are placed on a carrier that can rotate up to 1000 rpm.
- The film thickness, grown epitaxially, is mainly controlled by deposition time and growth rate
- The growth rate is strongly affected by the growth pressure in the chamber, substrate temperature, and precursor flow rate

Fig.: MOCVD process

Source: https://www.sciencedirect.com/science/article/pii/S2211379721003168

The other method is called molecular beam epitaxy. This is an epitaxy method where thin film deposition of single crystals take place. So, in this particular method it is widely used in manufacturing semiconductor devices something like transistors and it is considered as one of the fundamental tools for development of nanotechnology. So, MBE molecular beam epitaxy is used to fabricate diodes and and MOSFETs MOS means metal oxide semiconductor FETs ok working at microwave frequencies ok and to manufacture the lasers used to read optical disks such as CD and DVDs. So, I will go into the process soon.



## Thin Films: Epitaxy: Molecular beam Epitaxy

- Molecular-beam epitaxy (MBE) is an epitaxy method for thin-film deposition of single crystals.
- MBE is widely used in the manufacture of semiconductor devices, including transistors, and it is considered one of the fundamental tools for the development of nanotechnologies.
- MBE is used to fabricate diodes and MOSFETs (MOS field-effect transistors) at microwave frequencies, and to manufacture the lasers used to read optical discs (such as CDs and DVDs)
- MBE is considered to be one of the cleanest, but also one of the most technically challenging and demanding, as MBE growth takes place in ultra-high vacuum (UHV) environment.

Fig.: Molecular beam epitaxy process

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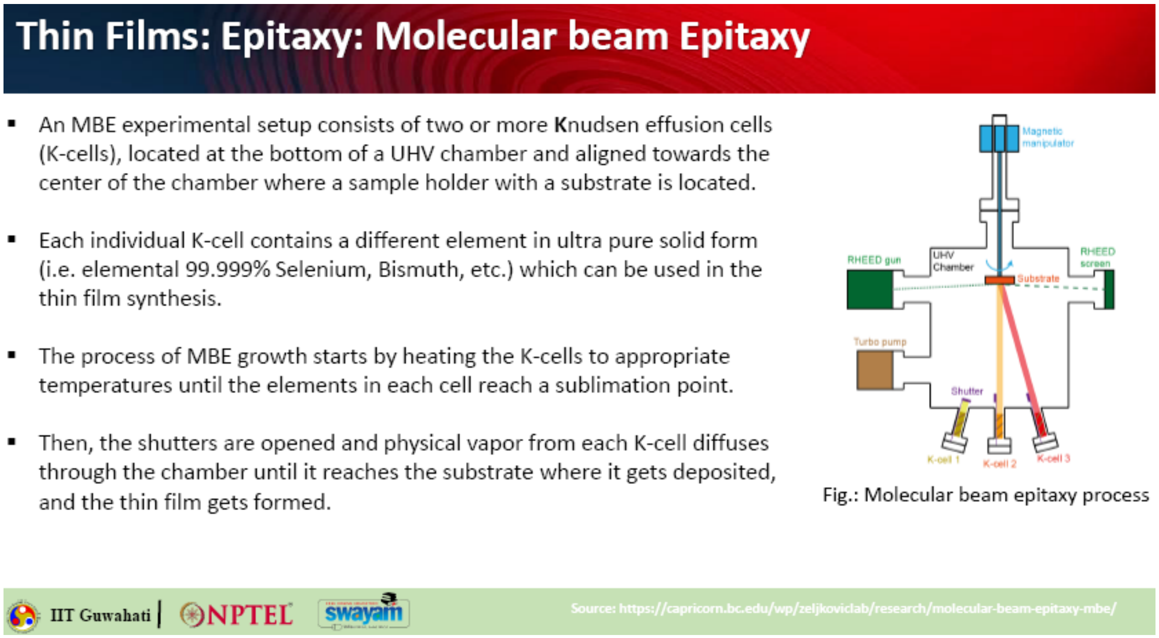
Source: https://capricorn.bc.edu/wp/zeljkoviclab/research/molecular-beam-epitaxy-mbe/

So, remember that MBE is considered to be one of the cleanest, but also one of the most technically challenging and demanding process because this MBE growth takes place in ultra-high vacuum environment. So, this is the chamber which is a ultra high vacuum UHV chamber.



## Thin Films: Epitaxy: Molecular beam Epitaxy

- An MBE experimental setup consists of two or more **K**nudsen effusion cells (K-cells), located at the bottom of a UHV chamber and aligned towards the center of the chamber where a sample holder with a substrate is located.
- Each individual K-cell contains a different element in ultra pure solid form (i.e. elemental 99.999% Selenium, Bismuth, etc.) which can be used in the thin film synthesis.
- The process of MBE growth starts by heating the K-cells to appropriate temperatures until the elements in each cell reach a sublimation point.
- Then, the shutters are opened and physical vapor from each K-cell diffuses through the chamber until it reaches the substrate where it gets deposited, and the thin film gets formed.

Fig.: Molecular beam epitaxy process

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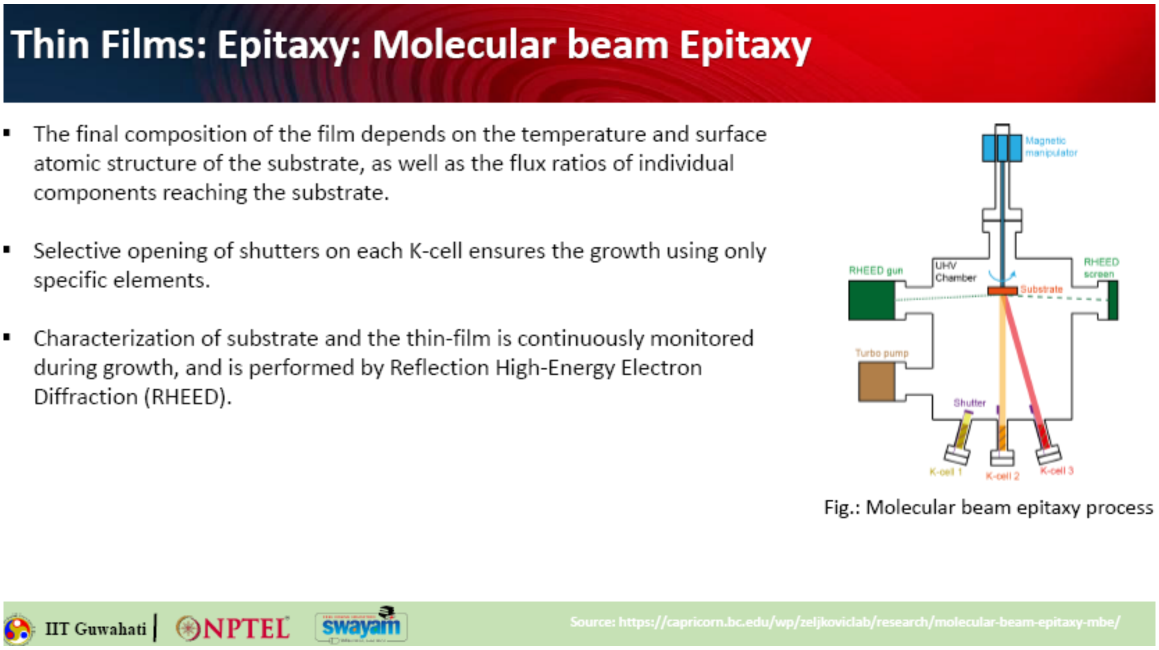
Source: https://capricorn.bc.edu/wp/zeljkoviclab/research/molecular-beam-epitaxy-mbe/

So, an experimental setup as you can see here it consists of two or more Knudsen efficient efficient cells or you can say them as K cells which are located at the bottom of this ultra high vacuum chamber and they are aligned towards the center of the chamber like this ok where the sample holder with a substrate. So, this is the sample holder where the substrate is actually located. Now, each individual K cells they contain different elements in ultra-pure solid form. So, when you say ultra pure the purity is typically 99.999 percent ok. So, what kind of materials like selenium, bismuth ok they are used in the thin film synthesis. Now, how it works the process of MBE growth starts by heating this K cells to appropriate temperature until the elements in each cell reach a sublimation point ok. And then the shutters over here as you can see the shutters this is open shutter open shutter and this is a closed shutter. So, these shutters are then open and the physical vapor from each K cell diffuses through the chamber until it reaches the substrate and get deposited and this is how thin films are being formed. Now remember that for more uniform growth substrate can be continuously rotated at low rotation speed.



## Thin Films: Epitaxy: Molecular beam Epitaxy

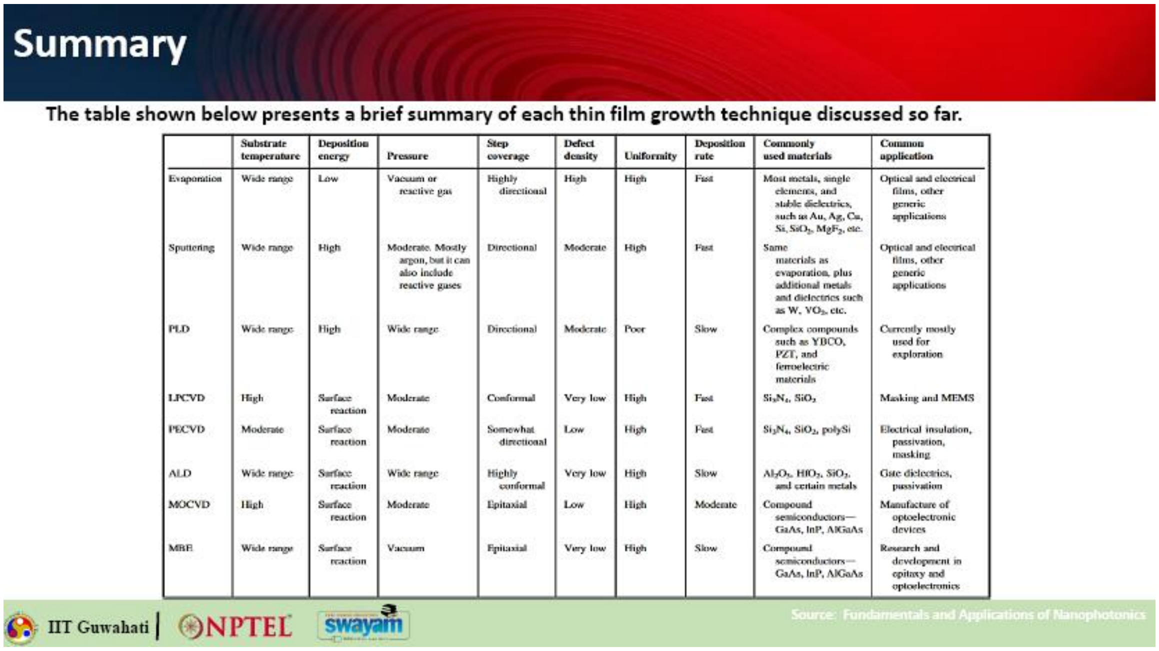
- The final composition of the film depends on the temperature and surface atomic structure of the substrate, as well as the flux ratios of individual components reaching the substrate.
- Selective opening of shutters on each K-cell ensures the growth using only specific elements.
- Characterization of substrate and the thin-film is continuously monitored during growth, and is performed by Reflection High-Energy Electron Diffraction (RHEED).

Fig.: Molecular beam epitaxy process

Source: https://capricorn.bc.edu/wp/zeljkoviclab/research/molecular-beam-epitaxy-mbe/

So, when I say low rotation speed is typically 1 or 2 rpm ok and by utilizing a stepper motor which can be attached to this magnetic manipulator. So, this is how in this form it can be slowly rotated and the electrons which come from this reed gun ok. So, this is electron diffraction gun. So, you can see that it actually incident electron at a very low angle and you can get the defected electron and you can observe the pattern here. And this pattern can actually reveal the quality of the film that is being developed and also you can measure the film thickness starting from single monolayer ok.

So, as I told this particular characterization is done by using reflection high energy electron deflection that is RHEED ok. So, in this particular method the final composition of the film will depend on the temperature and the surface atomic structure of the substrate as well as it will also depend on the flux ratio of individual components which are reaching the substrate. So, this is how you can mix things up and get a thin film of a particular composite material. Selective opening of the structures shutters of each K cell they will ensure growth using only specific elements. So, you can also do one by one kind of just by opening the shutters you can do one layer first and then the next layer and so on.



## Summary

The table shown below presents a brief summary of each thin film growth technique discussed so far.

| | Substrate temperature | Deposition energy | Pressure | Step coverage | Defect density | Uniformity | Deposition rate | Commonly used materials | Common application |
|---|---|---|---|---|---|---|---|---|---|
| Evaporation | Wide range | Low | Vacuum or reactive gas | Highly directional | High | High | Fast | Most metals, single elements, and stable dielectrics, such as Au, Ag, Cu, Si, $SiO_2$, $MgF_2$, etc. | Optical and electrical films, other generic applications |
| Sputtering | Wide range | High | Moderate. Mostly argon, but it can also include reactive gases | Directional | Moderate | High | Fast | Same materials as evaporation, plus additional metals and dielectrics such as W, $VO_2$, etc. | Optical and electrical films, other generic applications |
| PLD | Wide range | High | Wide range | Directional | Moderate | Poor | Slow | Complex compounds such as YBCO, PZT, and ferroelectric materials | Currently mostly used for exploration |
| LPCVD | High | Surface reaction | Moderate | Conformal | Very low | High | Fast | $Si_3N_4$, $SiO_2$ | Masking and MEMS |
| PECVD | Moderate | Surface reaction | Moderate | Somewhat directional | Low | High | Fast | $Si_3N_4$, $SiO_2$, polySi | Electrical insulation, passivation, masking |
| ALD | Wide range | Surface reaction | Wide range | Highly conformal | Very low | High | Slow | $Al_2O_3$, $HfO_2$, $SiO_2$, and certain metals | Gate dielectrics, passivation |
| MOCVD | High | Surface reaction | Moderate | Epitaxial | Low | High | Moderate | Compound semiconductors—GaAs, InP, AlGaAs | Manufacture of optoelectronic devices |
| MBE | Wide range | Surface reaction | Vacuum | Epitaxial | Very low | High | Slow | Compound semiconductors—GaAs, InP, AlGaAs | Research and development in epitaxy and optoelectronics |

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Source: Fundamentals and Applications of Nanophotonics

And you can characterize the thin film that is getting generated by this RHEED method ok. So, this particular table sums up all the techniques that we have studied till now. So, you can see the methods are being mentioned here. So, evaporation sputtering, pulsed laser deposition, low power CVD plasma enhanced CVD, ALD, MOCVD, and MBE and you can see the parameters on which they are discussed. So, you have substrate temperature deposition energy pressure step coverage defect density uniformity deposition rate and the materials that are used and what are the different applications.

So, this actually gives you a very good idea. And what is important to see here that all these methods more or less are very very uniform other than pulsed laser deposition that does not give a very good uniformity. And you can see that this is pulsed laser deposition is also slow and these are first evaporation and sputtering are first deposition method these are physical methods. In chemical methods LPCVD and PECVD are first methods ok. And you can also see the substrate temperature in this case you can have a wide range in case of physical method in LPCVD it should be high PECVD it should be moderate.

And these are the materials that can be used. So, when you talk about MBE these are typically compound semiconductors like gallium arsenide, indium phosphide and aluminum gallium arsenide. MOCVD you can again use the similar kind of compound semiconductors. Atomic layer deposition is useful for alumina, hafnium oxide, silicon dioxide and certain metals okay. Then silicon dioxide can be also deposited by low pressure CVD or plasma enhanced CVD okay.

Polysilicon can be done by PECVD ok. Pulsed laser deposition can do complex compounds as we mentioned though it is poor or slow, but this method only allows to develop this kind of complex compounds like PZT YBCO and other ferroelectric materials and so on. So, these are the different applications. So, optical thin films as you can see evaporation and sputtering they are the most commonly used for making thin films that can be used for photonics application ok. Then MOCVD they can manufacture optoelectronic devices and MBE they are also in the useful for research and development in epitaxy and other optoelectronics components. So, this particular chart should actually give you a complete overview of the different processes in thin film growth and what are their pros and cons and what are their applications.

So, with that thank you for your attention and we will stop here and in the next lecture we will look into the methods of lithography and pattern transfer of how to make a particular pattern on your for your device. And if you have got any queries regarding this lecture you can always drop an email to the similar address mentioning MOOC on the subject line. Thank you.