Fundamentals of Micro and Nanofabrication
Prof. Sushobhan Avasthi
Centre for Nano Science and Engineering
Indian Institute of Science, Bengaluru

Lecture - 16
Chemical Vapor Deposition: Basics

This lecture is a part of the ongoing module on additive processing. We are going to talk about some of the basics of chemical vapor deposition. What is CVD? As the name suggests, CVD is a deposition of material on a substrate using chemistry.

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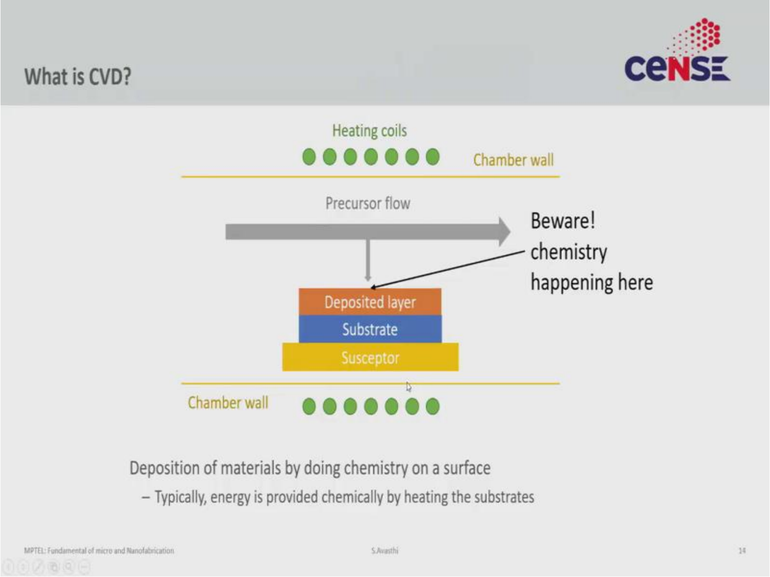

What is CVD?

Deposition of materials by doing chemistry on a surface

- Typically, energy is provided chemically by heating the substrates

This is a very simplified abstraction. You have a chamber that encloses the vapor. You provide some amount of energy to the system, typically, thermally as represented here by the heating coils. It can also be radiative energy. The precursor is a chemical that causes deposition on the substrate. Typically, it is a one or two-component chemical that reacts to form the material that you want to deposit. At any given time, you have some amount of deposited film thickness and the chemical reaction happens on top of this deposited layer. This deposited layer, for mechanical as well as other reasons, requires a substrate. It can be a wafer or any other substrate that we have discussed before. This whole assembly sits on a susceptor that holds the wafer while the deposition is going on. There are certain characteristics a susceptor must have, you can guess that cleanliness is one of them, but there are a few others. In very general terms, these are various components of a typical chemical vapor deposition system.

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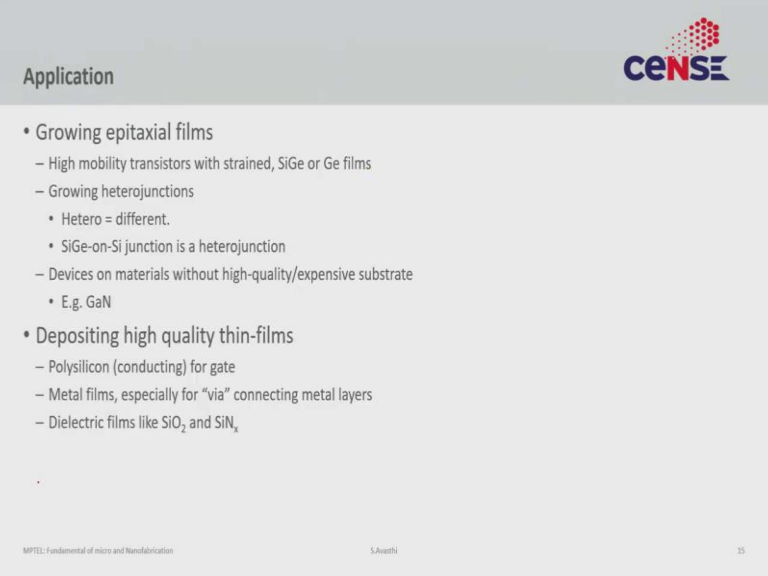

Application

- Growing epitaxial films
  - High mobility transistors with strained, SiGe or Ge films
  - Growing heterojunctions
    - Hetero = different.
    - SiGe-on-Si junction is a heterojunction
  - Devices on materials without high-quality/expensive substrate
    - E.g. GaN
- Depositing high quality thin-films
  - Polysilicon (conducting) for gate
  - Metal films, especially for “via” connecting metal layers
  - Dielectric films like SiO_2 and SiN_x

In general, CVD is used to deposit a very high-quality film that has very low contamination, can be epitaxial, and often single crystalline. Because of all these advantages, they are perfect to grow device grade semiconducting materials. Epitaxy refers to growing single crystalline material on top of an existing single crystalline material. Silicon epitaxy on silicon substrate means growing a silicon single crystalline layer on top of a single crystalline silicon substrate. The deposited layer is perfectly lattice-matched with the underlying silicon. If the orientation is perfect, there are large grains with no or very few grain boundaries, it is an epitaxial growth.

There are several applications. High mobility transistors that are commonplace in modern CMOS fabrication can also be grown using CVD. Heterojunctions or the junctions of two different materials as germanium on silicon or titanium dioxide on silicon may be considered a heterojunction. A great advantage of epitaxial films is that you can start with a native substrate and deposit a different material. Gallium nitride is often grown on sapphire, silicon or sometimes silicon carbide substrates. This is especially useful for materials that are either very hard or expensive to grow in a single crystalline form or in case if you just want to make a heterostructure, where the native substrate is different. You can also do hetero-epitaxy on the native substrate to enhance the characteristics of the device or to get some new functionality. Such heterogeneous integration is becoming important in modern fabrication.

We also use CVD to grow high-quality thin films not necessarily crystalline or epitaxial. A good example is the polysilicon electrode deposited on top of the gate in CMOS. In some cases, even metal films are deposited with CVDs especially if the high aspect ratio holes need to be filled. The third and a very important application of CVD is the deposition of dielectrics, often on top of the metal, sometimes directly on native substrates. Silicon nitride and silicon oxide are commonly grown with CVD.

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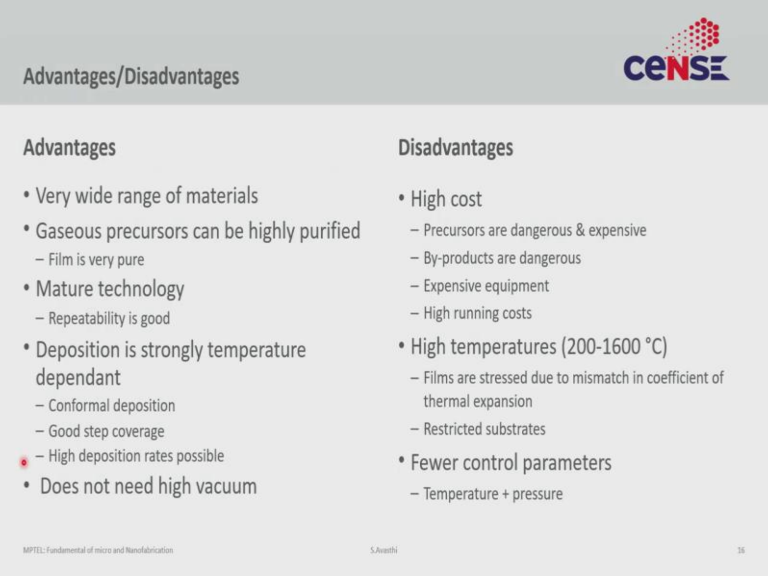

Advantages/Disadvantages

Advantages

- Very wide range of materials
- Gaseous precursors can be highly purified
  - Film is very pure
- Mature technology
  - Repeatability is good
- Deposition is strongly temperature dependant
  - Conformal deposition
  - Good step coverage
  - High deposition rates possible
- Does not need high vacuum

Disadvantages

- High cost
  - Precursors are dangerous & expensive
  - By-products are dangerous
  - Expensive equipment
  - High running costs
- High temperatures (200-1600 °C)
  - Films are stressed due to mismatch in coefficient of thermal expansion
  - Restricted substrates
- Fewer control parameters
  - Temperature + pressure

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There are advantages or disadvantages to any technique; CVD is no exception. One of the advantages is the ability to CVD a very wide range of materials. This ability is only limited by your ability to provide a suitable precursor. Chemists have figured out ways of converting virtually every element that we know into a CVD precursor. A lot of high quality and silicon-based CVD is often done using gaseous precursors. This provides an added advantage that gaseous precursors can be highly purified. With liquid, it is hard to get purity better than 99.9 % or 99.99 %, but gaseous precursors with purity better than 99.9999 % are available. CVD is are very mature technology; people have been doing it for a very long time, even in commercial production as far back as the 1980s or earlier. Maturity means a lot of institutional knowledge and know-how. I will show you some examples.

In CVD, the thickness is strongly dependent on temperature. That is not very surprising, because chemical reactions are often strongly dependent on temperature as given by the

Arrhenius relation. The consequence of strong temperature dependence is that CVD often tends to be conformal. Conformality means uniform deposition on the underlying topology. If the reaction is only dependent on temperature and substrate independent, then as long as you maintain the temperature uniformity, the deposition would also be uniform. It would not care about the topology underneath and coat everything uniformly.

You can get very high deposition rates if you can figure out how to transport a lot of precursor onto the substrate. Also, it does not need a high vacuum. A vacuum can come in several grades, with pressure in the range 1 mbar, 10^{-6} mbar, or 10^{-9} mbar. The higher the grade of vacuum you need, the more expensive it becomes to build and maintain that equipment and in general, lower the throughput because it takes some amount of time to get to that vacuum. Higher the vacuum, harder it is and longer it takes to get there.

CVD is done around 1 mtorr 1 torr or a few torr ranges, which is not a very low pressure and can easily be achieved by typical rotary pumps. So, that is an advantage. The disadvantage of CVD is it is costly compared to physical vapor deposition which we shall discuss in the next module. CVD is more expensive partly because the precursors are dangerous and expensive chemicals. In order to purify the precursors, a lot of the material gets lost, so they also can be very expensive. Running cost tends to be high because in order to do CVD safely and in a repeatable fashion, a lot of supporting infrastructure is required; you need exhausts, scrubbers, very good gas cabinets, gas detectors, and as the technique is a little complex, you need very highly skilled workers. And all of these add to the operational cost of a CVD equipment.

The other disadvantage is that high-quality CVD, especially epitaxial CVD often requires high temperatures. High is a relative word, but typically for silicon, you need $T > 700\text{-}800^{o}C$. This has consequences on cost and also on the stress that develops in the film. Once you deposit a film at those high temperatures and cool it down, it can have some residual stress which can cause problems. This is especially important if the lattice is mismatched or if the film that you are trying to grow does not like to nucleate on the surface. High temperature also shortens the list of substrates that can be used. Steel may not be a very good substrate for CVD, because steel has iron and iron will diffuse at high temperatures and contaminate the film that you are trying to grow (at high temperatures). So, your substrates must be non-contaminating and able to withstand the temperature. You cannot do CVD at $700\text{-}800^{o}C$ on a plastic substrate. Even substrates like glass may not be able to withstand that temperature, so that reduces your options. And lastly, CVD is often a thermodynamically limited process, rarely kinetically limited process. That allows you only two parameters to control the reaction; pressure and temperature. Other than these two, you do not have a lever to control the reaction and hence, the properties of the eventual film. On the other hand, with physical vapor deposition, say sputtering, you have access to bias voltages, temperature, pressure, stoichiometry, and different type of targets, etc… In that way, CVD is a little restrictive and the flip side of that is it’s relatively easy to control and repeat which some of the PVD processes tend not to be.

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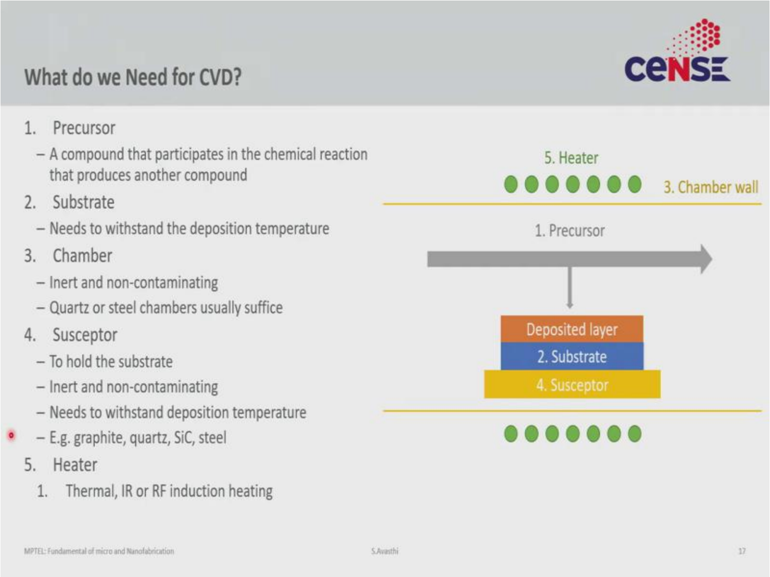

What do we Need for CVD?

1. Precursor
   - A compound that participates in the chemical reaction that produces another compound
2. Substrate
   - Needs to withstand the deposition temperature
3. Chamber
   - Inert and non-contaminating
   - Quartz or steel chambers usually suffice
4. Susceptor
   - To hold the substrate
   - Inert and non-contaminating
   - Needs to withstand deposition temperature
   - E.g. graphite, quartz, SiC, steel
5. Heater
   1. Thermal, IR or RF induction heating

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What do we need for CVD? We need a precursor, a compound that participates in the chemical reaction and produces the material that we want to deposit. Then we need a substrate that can withstand high temperatures, a chamber that is non-contaminating or inert. In general, quartz or steel chamber suffice; steel in those cases where the chamber does not heat up and quartz where it does. We need a susceptor to hold the substrate. It must also be inert and non-contaminating and withstand the deposition temperatures because it is always going to be at almost the same temperature as the vapor. Often, this is graphite, quartz, silicon carbide. In cases where the temperature is relatively low, say atomic layer deposition, it can be steel, but not for ultra-pure or high-temperature applications. Finally, we need a heater. This can be a nichrome wire for thermal contact heating or infrared radiation which heats in a non-contact fashion. It can also be an RF induction heater similar to an induction oven that you may have in your home.

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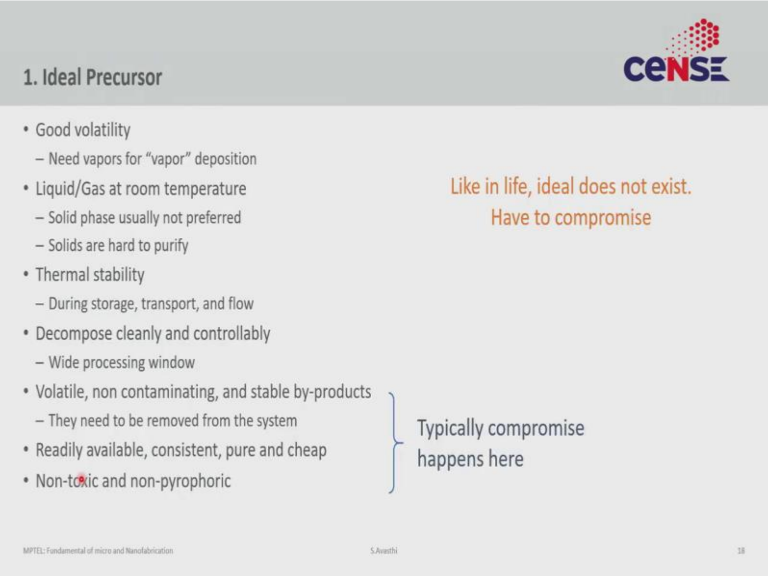

1. Ideal Precursor

- Good volatility
  - Need vapors for "vapor" deposition
- Liquid/Gas at room temperature
  - Solid phase usually not preferred
  - Solids are hard to purify
- Thermal stability
  - During storage, transport, and flow
- Decompose cleanly and controllably
  - Wide processing window
- Volatile, non contaminating, and stable by-products
  - They need to be removed from the system
- Readily available, consistent, pure and cheap
- Non-toxic and non-pyrophoric

Like in life, ideal does not exist.
Have to compromise

Typically compromise happens here

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Let's talk about precursors first. An ideal precursor is volatile because chemical vapor deposition is done best in the vapor form. While there have been, in the recent past, some techniques developed for liquid precursors like mist CVD or nozzle based CVDs, by and large, traditional CVD has always used gaseous precursors. For cases where the precursor is a liquid, you can still use them by vaporizing it into a vapor form and then using those vapors. You still need volatile precursors that you can convert to vapors.

This precursor must be liquid/gas at room temperature. The solid phase is usually not preferred, though in some cases you can get solids that will sublime at a slightly higher temperature and hence can be used as precursors. Solids, however, even in those cases are a little hard to purify and are often not used. It must be thermally stable. You want your precursor to do the chemical reaction only inside the chamber and not in the tank where it is stored or in the gas lines, where it is being transported or in the pump where the byproducts will go. It should decompose cleanly and controllably. There should be a unique chemical pathway to form a compound. A precursor that can do multiple reactions simultaneously may not be ideal because then you do not have control over what you are forming. You would also prefer a precursor that in one step form the compound you want to deposit and the one that goes through multiple stages of chemical reactions because again, that creates uncontrollable situations.

In general, we want precursors that have a wide deposition window i.e. a wide range of temperatures and pressures where they can do the chemical reaction and deposit material, because that gives the unit process engineer flexibility in coming up with a recipe for an application. They must be non-contaminating and have stable byproducts. In CVD, the chemicals react on the substrate depositing a film and also form some byproducts. Those byproducts must leave. So, they must also be volatile.

A precursor forming precipitates is not a good CVD precursor, because the precipitates have nowhere to go and will just deposit or stay on the substrate and contaminate the film. Also, the byproducts must themselves be non-contaminating. A chemical reaction forming metal particles may not be a very good precursor, because those metal particles may contaminate the semiconducting layer that you are growing. They must be stable and not start secondary or tertiary reactions. Finally, the precursor must be readily available, and hopefully consistent - the performance on day 1 and day 30 should roughly be the same. They should be pure, cheap, non-toxic and non-pyrophoric because those two things tend to increase cost and associated dangers.

In general, it is very hard to satisfy everything. Ideal things rarely exist; we have to compromise. A lot of the precursors compromise on the last two. A lot of precursors are pyrophoric, and/or toxic and a lot of them are very expensive.

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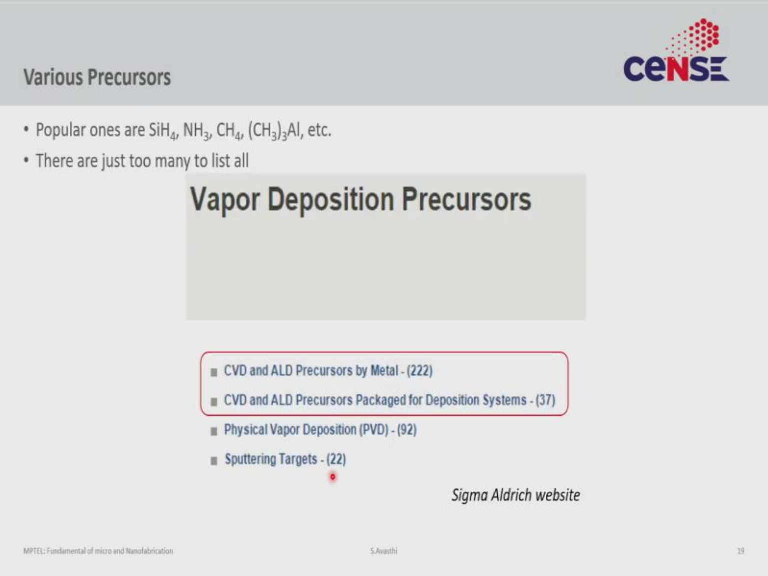

Various Precursors

- Popular ones are SiH_4, NH_3, CH_4, $(CH_3)_3Al$, etc.
- There are just too many to list all

Vapor Deposition Precursors

- CVD and ALD Precursors by Metal - (222)
- CVD and ALD Precursors Packaged for Deposition Systems - (37)
- Physical Vapor Deposition (PVD) - (92)
- Sputtering Targets - (22)

Sigma Aldrich website

A wide variety of precursors are available. I cannot list all of them on this slide or in this lecture; I will just point you to some website. For example, here is a snapshot from the Sigma Aldrich website. You can see about 220 precursors. Given that the periodic table has around 90 useful elements, there are more than 2 or 3 precursors for every element in the periodic table.

In the next lecture, we will go into more details of the CVD mechanism.