Fundamentals of Micro and Nanofabrication

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Lecture - 22
Atomic Layer Deposition Contd

We discussed Atomic Layer Deposition in the last lecture. We looked at the basis, the main USP of ALD, and the mechanism behind layer by layer growth. In this lecture, we shall get into more details like the deposition window, some nucleation aspects, and advanced features such as plasma-enhanced ALD.

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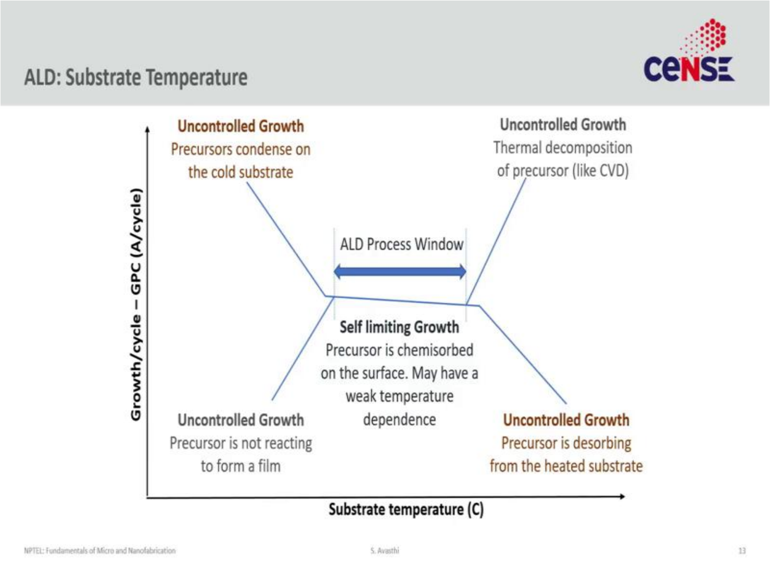

ALD: Substrate Temperature

The substrate temperature is one of the parameters that you control during the deposition that we have not discussed. It has a huge effect on ALD and must be optimized for a recipe. The figure shows various things that can happen as you change the substrate temperature. You want to do the ALD in a window where the growth is self-limiting, somewhere in the middle of the graph. Because, in the self-limiting growth window, by and large, the growth per cycle is independent of the substrate temperature.

When you start or design a new recipe, you do not know what that window is. With the new precursors, you must run some tests and optimization cycles to extract the window.

As you do the ALD growth at various substrate temperatures, you would see nonlinear growth at lower temperatures and higher temperatures.

At lower temperatures, the precursor can condense on the cold substrate just like mist condenses in the winter morning on the leaves. It is different from adsorption or chemisorption. The condensed layer can be arbitrarily thick. Let's say water is one of the components and it condenses on the substrate. When you send component A which reacts with water, you would form a lot of material, but that would be a CVD-like reaction because it is not self-limiting. So, your growth per cycle will be larger. You will get more growth, but that would be non-uniform, and that is not good.

The other reason for nonlinear growth versus #cycle at lower temperatures is that the precursors do not react. ALD assumes that component A reacts with component B, but that requires a certain amount of reaction rate. Reaction rates are often limited by temperature. At very low temperatures, the two components might not react. In that case, you get a lower growth rate than what you assumed, and that too is undesirable, as it is not self-limiting.

At high temperatures, some of the precursors can decompose. ALD assumes that precursor A reacts with precursor B to form the material that you want. But precursor A alone usually doesn't deposit the desired material. Any organic precursor or any chemical precursor will have some decomposition temperature. And if the substrate temperature is higher than that, you get a film of the decomposed constituents, which may or may not even be the material you want to deposit. So, you will get some growth, but that is like CVD from a pyrolysis reaction. If you flow silane at 1000^oC substrate temperature, silane will break and form silicon, but that is not ALD.

Precursor desorption is another nonlinearity that happens at higher temperatures. Till now, we have assumed that the precursors are chemisorbed and neglected the desorption. That makes chemisorption a one-way reaction, but everything has a limit. If you heat the substrate enough, you may provide enough energy to get over the chemisorption hump and the precursor desorbs. In that case, again, you don't have a self-limiting layer. Subsequent component B will have nothing to react with and you will have slower but uncontrolled growth. It would not be repeatable or consistent. So, it would be outside the

ALD window. Which of these cases occur depends upon the precursors and the chemistry.

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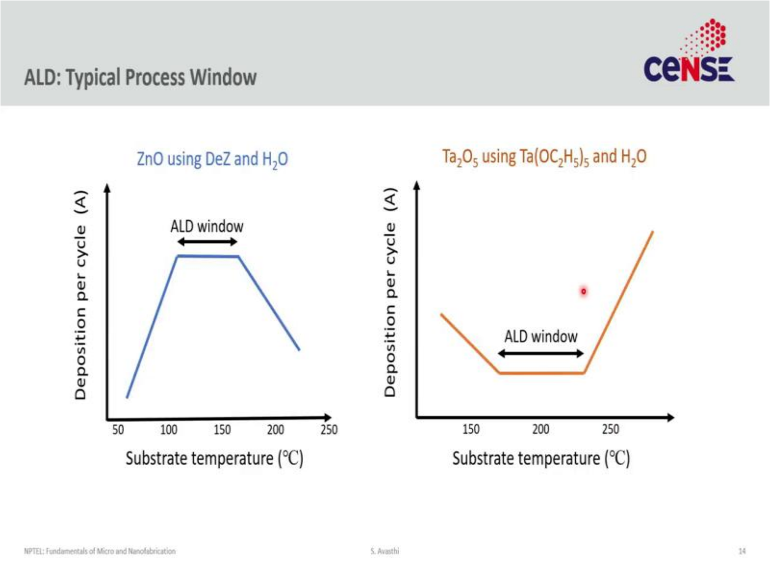

ALD: Typical Process Window

For example, diethylzinc and water react to form zinc oxide. It shows the ALD window with a slow reaction rate on the left and desorption on the right. On the other hand, tantalum oxide formed using tantalum ethoxide and water has a very different ALD growth vs temperature, with condensation on the left and pyrolysis on the right. The goal in every case is to find this flat region, where you can do your reactions.

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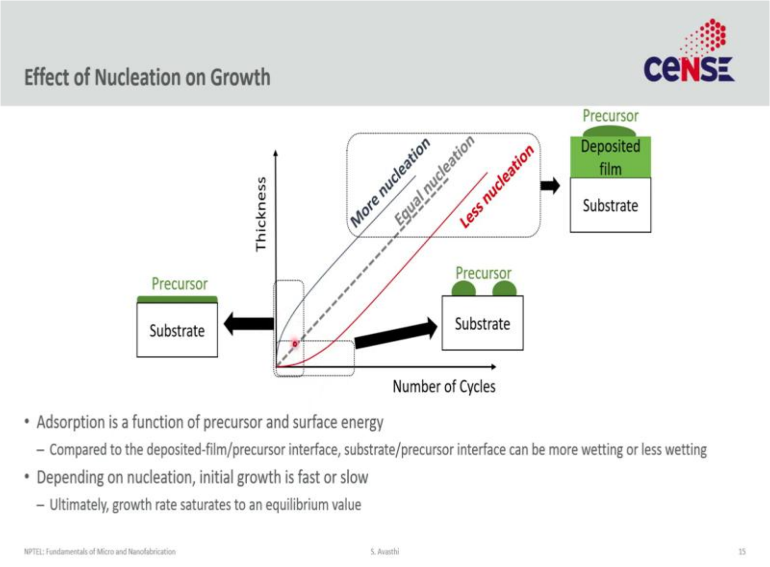

Effect of Nucleation on Growth

- Adsorption is a function of precursor and surface energy
  - Compared to the deposited-film/precursor interface, substrate/precursor interface can be more wetting or less wetting
- Depending on nucleation, initial growth is fast or slow
  - Ultimately, growth rate saturates to an equilibrium value

We discussed nucleation in CVD. We shall not go into that much detail in ALD, but certain nonidealities occur that must be explored. We assume that in ALD, the thickness versus the number of cycles is linear. In the example of TMA and water, it is exactly linear. That is this dotted line of equal nucleation. You might have an enhanced or suppressed growth initially. However, the thickness as a function of the number of cycles is usually linear at higher numbers. What is the cause of this initial nonideality? In cases where there is less nucleation, what might be happening is that the precursor does not stick to the surface because of higher surface energy and hence, contact angle. The precursor would sit as globules, not as an adsorbed film. In that case, the growth rate will be lesser because the self-limiting film is not as widespread.

In a case where the precursor sticks to the substrate a little too well, it might form a very low contact angle film on top of the substrate, leading to more nucleation than you expect. When I say less or more nucleation or contact angle, I am comparing to the case of the precursor on top of that deposited film. Once you deposit a little bit of the desired film, in all those cases, the contact angle will be the same. However, in the beginning, the precursor doesn’t see the deposited film, but the substrate. The contact angle on the substrate might be different, and that explains these initial nonidealities.

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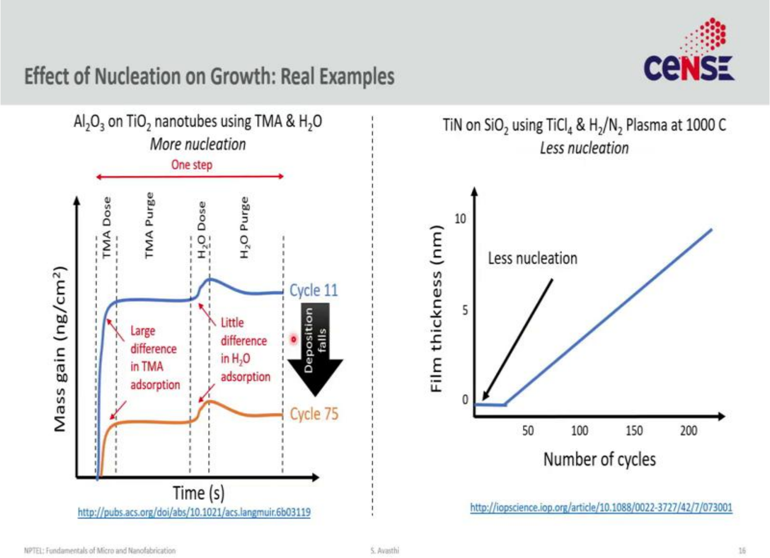

Effect of Nucleation on Growth: Real Examples

Al_2O_3 on TiO_2 nanotubes using TMA & H_2O

More nucleation

http://pubs.acs.org/doi/abs/10.1021/acs.langmuir.6b03119

TiN on SiO_2 using $TiCl_4$ & H_2/N_2 Plasma at 1000 C

Less nucleation

http://iopscience.iop.org/article/10.1088/0022-3727/42/7/073001

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S. Avasthi

16

Here are two such examples; One with more nucleation, and one, less. The figure on the left is the mass gain as a function of the time curve. The orange curve represents the basic TMA reacting with water to form aluminum oxide. But, if you do this reaction on titanium dioxide (coated) substrate, TMA has an enhanced adhesion to the titanium dioxide surface. In cycle 11, which is one of the initial cycles, you gain more mass than what you expect. The mass gain is larger, and most of this difference is not in water. Water is absorbed roughly the same. Most of the difference is in the mass gain of the TMA. As you keep depositing longer and longer, that difference goes away. For example, as you get to cycle 75, you reach a steady growth rate after an initial enhanced rate.

The other example is titanium nitride deposition on silicon dioxide using this chemistry at 1000°C; If you look at the film thickness as a function of the number of cycles, initially you would see almost nothing, and think that there is no growth. But if you wait for some time, ultimately the nuclei form, and once you get a film of titanium nitride, from that point, you start nucleating normally, and you see linear growth. These sorts of nonidealities can occur. These references go into details of both these things.

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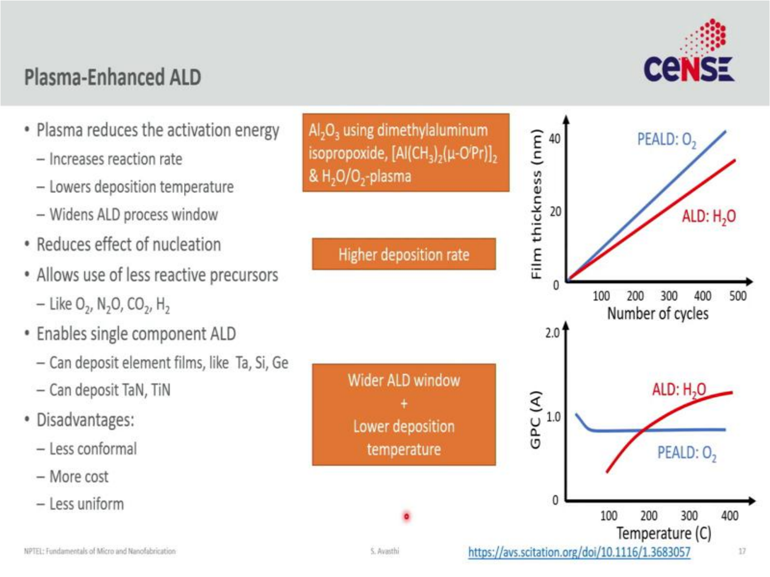

Plasma-Enhanced ALD

- Plasma reduces the activation energy
  - Increases reaction rate
  - Lowers deposition temperature
  - Widens ALD process window
- Reduces effect of nucleation
- Allows use of less reactive precursors
  - Like O_2, N_2O, CO_2, H_2
- Enables single component ALD
  - Can deposit element films, like Ta, Si, Ge
  - Can deposit TaN, TiN
- Disadvantages:
  - Less conformal
  - More cost
  - Less uniform

Al_2O_3 using dimethylaluminum isopropoxide, $[Al(CH_3)_2(\mu\text{-}O^iPr)]_2$ & H_2O/O_2-plasma

Higher deposition rate

Wider ALD window + Lower deposition temperature

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https://avs.scitation.org/doi/10.1116/1.3683057

17

You can solve nucleation and some other issues by using plasma. The plasma-enhanced ALD is a relatively new technique, and the equipment has just started becoming commercially available. The basic idea is simple. Till now, we have discussed thermal ALD, where the reactions are thermally activated, depending on the substrate temperature. If you want to help things along, you can add some energy through other sources, and using plasma is a common technique. Just like plasma-enhanced CVD allowed us to reduce the temperature and enhance the growth rates, plasma-enhanced ALD allows us to reduce the substrate temperature and enhance growth rates.

In this example, we are looking at the growth of aluminum oxide using a new precursor called dimethyl aluminum isopropoxide. If you deposit using water, it is the traditional thermal ALD. If you deposit with oxygen plasma, it is plasma-enhanced ALD. We see that the plasma-enhanced ALD has significantly higher growth than with thermal ALD. The plasma-enhanced ALD often gives us a larger ALD window. Once again, the ALD window is a substrate temperature window where we have self-limiting growth, and hence, the growth rate does not change with temperature. In the ALD of this precursor with water, it does not have a defined ALD window as there is no region where it is very flat. However, once you do it with plasma-enhanced ALD, you get a large deposition window. That is one of the advantages. So much so, that you get a deposition window with almost the same growth rate as high temperature, at very low temperatures. Even near room temperature, you can start getting depositions that you could not get before. Not only do you get a wider window, but that wider window also allows you to do lower temperature depositions at higher deposition rates.

It also allows you to use much less reactive precursors like oxygen, nitrous oxide, or carbon dioxide that are safer and easier to handle. It allows you to deposit single component ALD; for example, metals. We can even deposit nitride. Nitrides tend to be less reactive, so are hard to make using thermal ALD or require very high temperature. In the previous slide, there was an example of using titanium nitride at a very high temperature of 1000^oC. You can significantly reduce that temperature by adding energy through the plasma. The disadvantage is, it is much less conformal. One of the advantages of thermal ALD was because everything was self-limiting, you do not care about the flow of gas, but now you have added plasma.

So, now, you have to worry about the density of the plasma and its uniformity. That muddies the water a little bit and makes it less conformal. It also increases the cost because you now have to design for plasma and RF and DC power supplies. And it also tends to be less uniform. Now that you have added plasma, you have to worry about issues of plasma design that you did not have to before.

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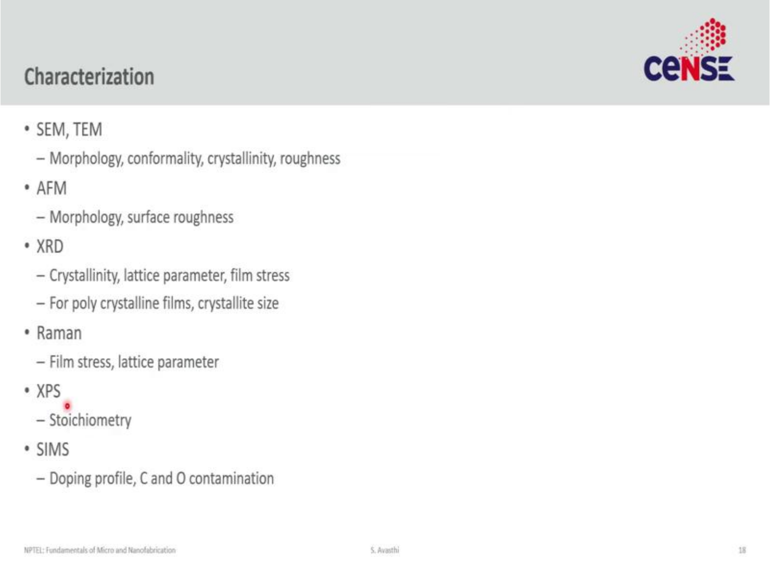

Characterization

- SEM, TEM
  - Morphology, conformality, crystallinity, roughness
- AFM
  - Morphology, surface roughness
- XRD
  - Crystallinity, lattice parameter, film stress
  - For poly crystalline films, crystallite size
- Raman
  - Film stress, lattice parameter
- XPS
  - Stoichiometry
- SIMS
  - Doping profile, C and O contamination

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What characterizations do we do to analyze these films? This is a general list for both CVD and ALD. Typically, people use SEM, TEM to look at morphology, conformality, crystallinity, roughness etcetera, AFM for morphology, and surface roughness. XRD allows you to look at crystallinity, lattice parameter, lattice matching, and the film stress. Raman tells you if you have a substitutional impurity or stress in the film. XPS measures the stoichiometry; If you deposit TiO_2, XPS can tell if it is TiO_2 or TiO_{2+x} or TiO_{2-x}. If you want to look at doping, or carbon/oxygen contamination, you can do SIMS.

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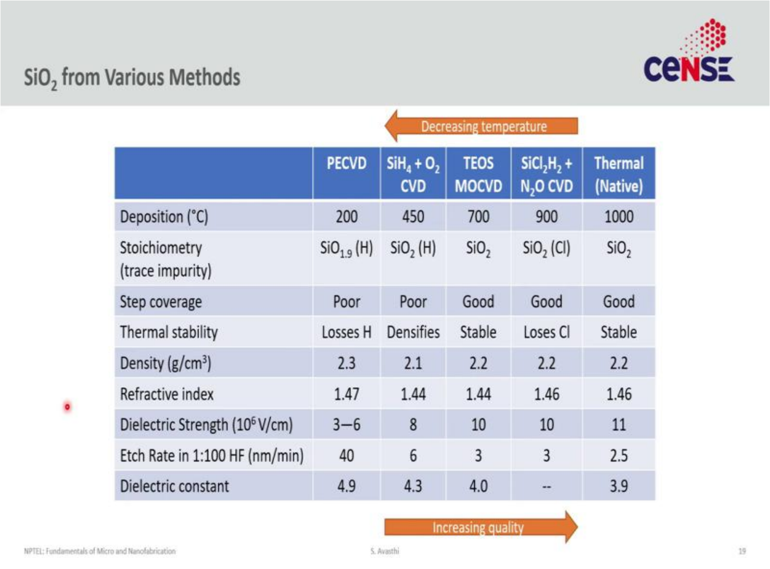

SiO_2 from Various Methods

Decreasing temperature

	PECVD	$SiH_4 + O_2$ CVD	TEOS MOCVD	$SiCl_2H_2 + N_2O$ CVD	Thermal (Native)
Deposition (°C)	200	450	700	900	1000
Stoichiometry (trace impurity)	$SiO_{1.9}$ (H)	SiO_2 (H)	SiO_2	SiO_2 (Cl)	SiO_2
Step coverage	Poor	Poor	Good	Good	Good
Thermal stability	Losses H	Densifies	Stable	Loses Cl	Stable
Density (g/cm^3)	2.3	2.1	2.2	2.2	2.2
Refractive index	1.47	1.44	1.44	1.46	1.46
Dielectric Strength (10^6 V/cm)	3—6	8	10	10	11
Etch Rate in 1:100 HF (nm/min)	40	6	3	3	2.5
Dielectric constant	4.9	4.3	4.0	--	3.9

Increasing quality

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This slide summarizes and compares different additive processes that we have discussed using the example of SiO2. You can grow silicon dioxide by thermal oxidation (native oxide growth), CVD where dichlorosilane reacts with nitrous oxide, using TEOS, which is MOCVD, or just silane reacting with oxygen in a simple CVD. You can also do it with plasma-enhanced CVD if you involve plasma. The temperature, as you go from native oxide to a PECVD, reduces, and so does the quality. The highest quality films are formed at the highest temperature, while at the lowest temperatures, you get the lowest quality films.

Stoichiometry also tends to reduce with temperature. You form very stoichiometry films at high temperatures, but not so much at low temperatures. Depending on the chemistry you use, you might have different impurities like chlorine or hydrogen. Step coverage tends to be better when the growth is temperature limited. At high temperatures, you get good step coverage, but when you use things like plasma, you do not.

Thermal stability: thermal oxide is very stable, while PECVD oxide is less stable. Thermal stability is also related to stoichiometry because the film becomes more unstable if it is off-stoichiometric. In general, higher-quality films tend to be denser. Native oxide is very dense, and as you go to CVD, the deposited film is slightly less dense. One exception is the PECVD case, where the density can sometimes be higher. The reason for that is the ion bombardment that makes the film compact and artificially enhances the density. The Refractive index follows the same trend as density. It is a very good proxy to understand what happens to density. Dense films have refractive indices that are closer to the bulk values and lower density films have lower refractive indices. Dielectric strength follows the same trend. Denser, higher quality films tend to have higher dielectric strength than less dense and poor quality films.

The same strength also reflects in the resistance to chemical attack. HF will etch all of these films, but at different rates. The thermal oxide will etch very slowly, PECVD very fast. The closer you are to a high-quality film, the closer the value of dielectric constant will be to the bulk value. Often, because of these impurities like hydrogen or oxygen, the dielectric constant becomes a little higher than the bulk value.

Depending on the application, you select a certain recipe, and that tells you at what temperature you can do the process. There is always this give and take. For lower temperatures and easier processing, you have to compromise on quality. For higher quality films, you need higher temperatures, complicated equipment, cleaning, and recipes. You get what you pay for.

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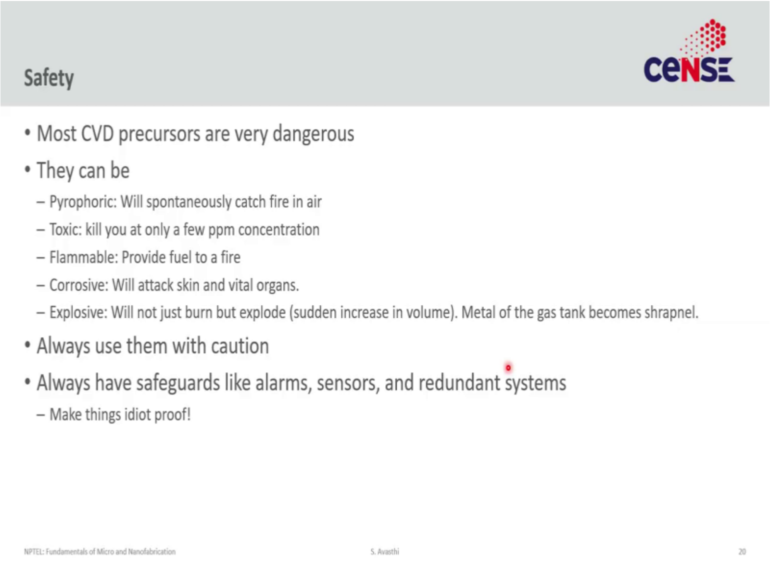

Safety

- Most CVD precursors are very dangerous
- They can be
  - Pyrophoric: Will spontaneously catch fire in air
  - Toxic: kill you at only a few ppm concentration
  - Flammable: Provide fuel to a fire
  - Corrosive: Will attack skin and vital organs.
  - Explosive: Will not just burn but explode (sudden increase in volume). Metal of the gas tank becomes shrapnel.
- Always use them with caution
- Always have safeguards like alarms, sensors, and redundant systems
  - Make things idiot proof!

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A couple of slides on safety. This lecture series does not include anything on safety, but CVD is something with which we have to be extremely careful. A lot of CVD precursors are extremely dangerous. They can be toxic, pyrophoric, or lethal. They can cause explosions, can attack the stainless steel, and the containing cylinders. A lot of them are dangerous for both - environment, and personal life and safety.

So, always treat the precursors with extreme caution. If you are new to them, please talk to somebody who has experience in dealing with them. The industry has a lot of standards on how to manage these types of gases and we should follow them. Always have safeguards like alarms and sensors. Have redundancy, and make things idiot-proof. Saying that I will be careful is not a safety standard. Safety standard is assuming that somebody will make a mistake and then having something to prevent that mistake from blowing-up.

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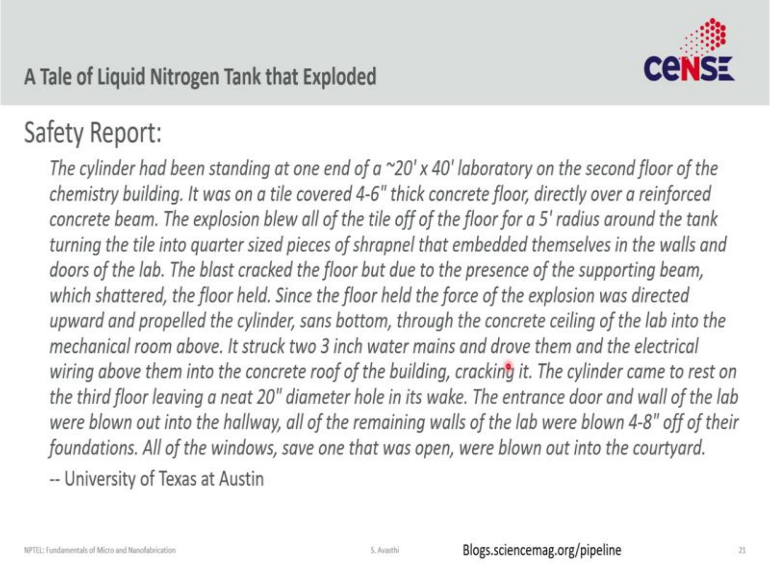

A Tale of Liquid Nitrogen Tank that Exploded

Safety Report:

> *The cylinder had been standing at one end of a ~20' x 40' laboratory on the second floor of the chemistry building. It was on a tile covered 4-6" thick concrete floor, directly over a reinforced concrete beam. The explosion blew all of the tile off of the floor for a 5' radius around the tank turning the tile into quarter sized pieces of shrapnel that embedded themselves in the walls and doors of the lab. The blast cracked the floor but due to the presence of the supporting beam, which shattered, the floor held. Since the floor held the force of the explosion was directed upward and propelled the cylinder, sans bottom, through the concrete ceiling of the lab into the mechanical room above. It struck two 3 inch water mains and drove them and the electrical wiring above them into the concrete roof of the building, cracking it. The cylinder came to rest on the third floor leaving a neat 20" diameter hole in its wake. The entrance door and wall of the lab were blown out into the hallway, all of the remaining walls of the lab were blown 4-8" off of their foundations. All of the windows, save one that was open, were blown out into the courtyard.*
>
> -- University of Texas at Austin

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This is a report of a liquid nitrogen tank that exploded in a lab. Additional details can be found in this blog. Thankfully, nothing bad happened, which is why it is a slightly funny story. But the thing I want to highlight is, in this case, what exploded was a liquid nitrogen tank. Nitrogen is inert. As things go, liquid nitrogen tanks are one of the safest things you can have in a lab, as a lot of CVD precursors and equipment are more dangerous than this. Even then, liquid nitrogen can cause so much damage. Imagine what a CVD precursor can do.

The liquid nitrogen cylinder stood at a corner of a 20’ × 40’ laboratory on the second floor of the chemistry building. All cylinders come with some safety valves. Some student or a postdoc, somewhere along the way, might have found one of the safety release valves leaking, and instead was changing it, they would have blocked it. The system continued because it was used often. The pressure never built up to unsafe levels. But someday, after a long time without being used, internally, the liquid nitrogen evaporated. The pressure built up in the tank, and one night, it exploded.

When it exploded, it was on a tile-covered 4” to 6” thick concrete floor, directly over a reinforced concrete beam. The explosion blew all the tiles off the floor in a 5’ radius around the tank, turning them into quarter-sized shrapnel that embedded into the walls and doors of the lab. Imagine if somebody was there inside. The blast cracked the floor, but due to the presence of the supporting beam, which shattered, the floor held.

Since the floor held, the force of the explosion was directed upward and propelled the cylinder, without the bottom, through the concrete ceiling of the lab into the mechanical room above. It struck two 3” water mains, drove them and the electrical wiring above them into the concrete roof of the building, cracking it. The cylinder came to rest on the third floor, leaving a neat 20” diameter hole. The entrance door and the wall of the lab were blown out into the hallway. All of the remaining walls of the lab were blown 4” to 8” off their foundations. All of the windows save for the open one, were blown-out into the courtyard. Just imagine, if this happened not in the dead of the night, where there is nobody in the lab, but in the day! Please exercise extreme caution with CVD.

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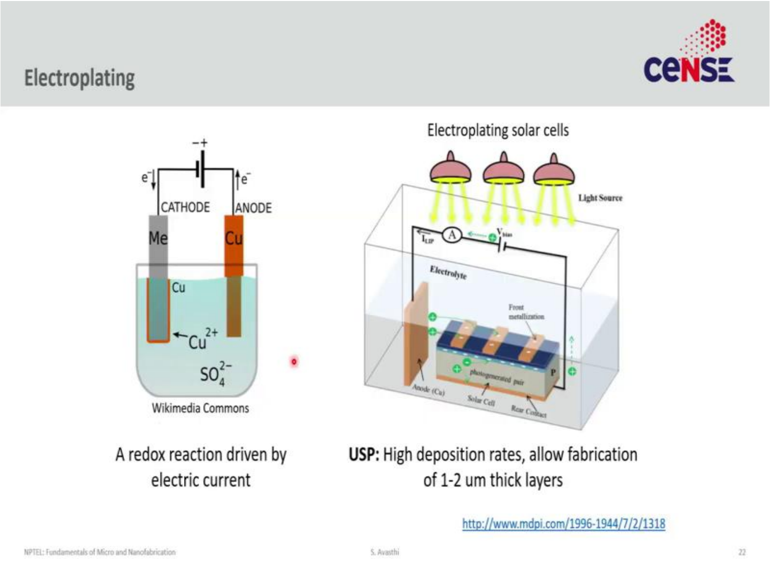

Electroplating

Electroplating solar cells

Wikimedia Commons

A redox reaction driven by electric current

USP: High deposition rates, allow fabrication of 1-2 um thick layers

http://www.mdpi.com/1996-1944/7/2/1318

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Lately, electroplating has become important, especially, for depositing metals such as copper. The basic idea is simple. You take your substrate, put it in an electroplating solution, which is a salt of copper and flow current. Depending on whether it is cathode or anode, you will get a deposition of copper. People have started using this and have even proposed that they should use this for silicon solar cells. Silicon solar cells have a lot of silver that they are trying to replace with copper. We will not go into more detail about electroplating.

This brings us to the end of the module of Chemical Vapour Deposition. Next, we shall talk about Physical Vapour Deposition, which will be the final part of the larger module on additive processing.