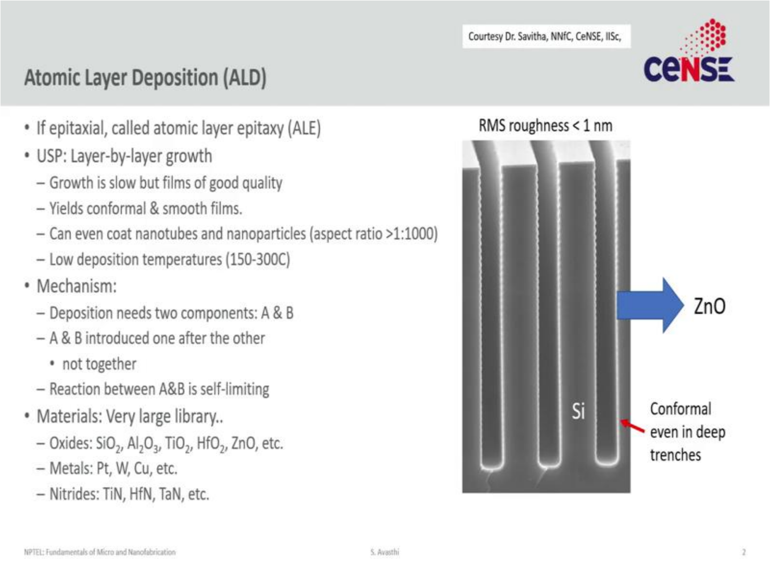
Fundamentals of Micro and Nanofabrication

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

Lecture – 21
Atomic Layer Deposition

In this lecture, we shall continue the module on additive processing. We have discussed chemical vapor deposition. We will spend a lecture on atomic layer deposition, which is a form of chemical vapors deposition, but the details are significantly different. So, it is worth learning about it in a separate lecture.

(Refer Slide Time: 00:57)



Courtesy Dr. Savitha, NNfC, CeNSE, IISc,

Atomic Layer Deposition (ALD)

- If epitaxial, called atomic layer epitaxy (ALE)
- USP: Layer-by-layer growth
  - Growth is slow but films of good quality
  - Yields conformal & smooth films.
  - Can even coat nanotubes and nanoparticles (aspect ratio >1:1000)
  - Low deposition temperatures (150-300C)
- Mechanism:
  - Deposition needs two components: A & B
  - A & B introduced one after the other
    - not together
  - Reaction between A&B is self-limiting
- Materials: Very large library..
  - Oxides: SiO_2, Al_2O_3, TiO_2, HfO_2, ZnO, etc.
  - Metals: Pt, W, Cu, etc.
  - Nitrides: TiN, HfN, TaN, etc.

NPTEL: Fundamentals of Micro and Nanofabrication S. Avasthi 2

Atomic layer deposition (ALD), as the name suggests, is layer by layer growth. In this extreme case, that layer can be a monolayer thick. The idea is that you make the film by literally adding one atomic layer on the other. The great advantage of atomic layer deposition is that it leads to extremely smooth and conformal films.

In the figure on the right, we have very deep trenches etched into silicon. We will learn how to etch these deep trenches by deep reactive ion etching when we talk about subtractive processing. Notice two things. One, the aspect ratio of this trench is very high; it is very narrow, but also very deep. Another thing is, the way etching happens, it leaves a little roughness or wriggles on the surface. On top of that wriggle, you see a white layer.

That white layer is zinc oxide that has been deposited using ALD. It follows the topology of the underlying silicon pretty exactly. The roughness that you can see on the top is less than a nanometer and it is conformal even very deep below. The thickness that you see at the bottom, at the side, and at the top is essentially the same.

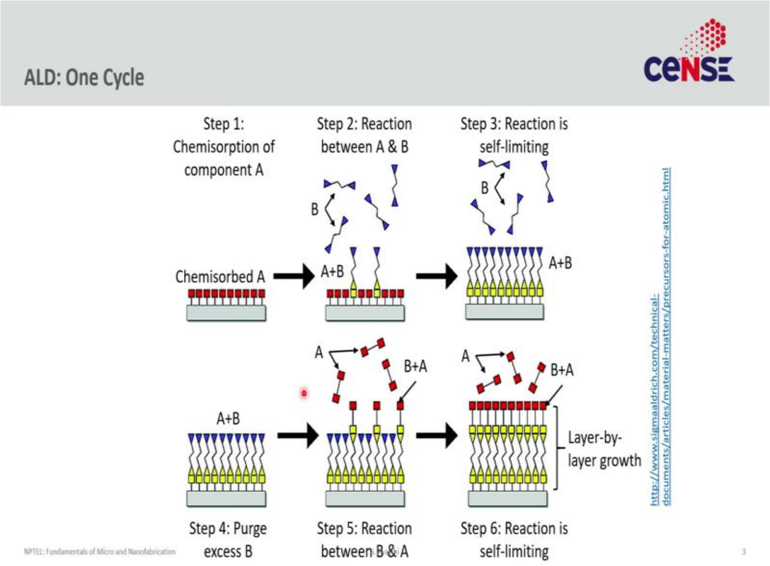
ALD shines in applications that need a very conformal and smooth coating. Typically, the deposition temperatures are low, which is an additional advantage. Especially, if your substrates are plastic, glass, or something other than a silicon wafer. If the film is epitaxial, this process is called atomic layer epitaxy. When ALD was introduced, it was called the atomic layer epitaxy, but later, the atomic layer epitaxy did not become as popular as atomic layer deposition because there was a bigger need for high quality amorphous or polycrystalline films. You can use it for epitaxy, but that is rare.

We shall discuss the ALD mechanism later. It needs at least two components (or steps). In CVD, for a two-component reaction, we flow precursors A and B simultaneously. They react and form the material that you want to deposit. In ALD, we do not flow them together, but one after the other. When precursor A flows, precursor B does not, and vice versa. A or B alone cannot make the materials that you want to deposit, but A and B together can. Also, A and B are self-limiting reactions. They occur at the surface, but not continuously. In CVD, if I keep flowing a precursor for longer and longer, I would get thicker and thicker films. That does not happen in ALD. Once you flow precursor A, you form a certain layer on top that is self-limiting. It does not grow in thickness the longer you flow the gas. Only when you send the precursor B, the chemical reaction completes and you form a (mono) layer of the intended material.

What sort of materials can we deposit using ALD? While the library is very large, oxide deposition is the most popular use of ALD. Aluminum oxide, titanium dioxide, zinc oxide, hafnium oxide, silicon dioxide etcetera. Increasingly these processes are even becoming mass manufacturable, and not just developmental any more. People also deposit metals such as platinum, tungsten, and copper. Lately, people have also started depositing nitrides. Nitrides deposition is a little more complicated because nitrogen is not as reactive. If you remember the lecture on native film growth, we discussed that the growth of a silicon nitride on silicon by flowing nitrogen can not happen because nitrogen is a very stable and inert molecule, and it requires very high temperatures to break nitrogen and forms silicon nitrogen bond. Similarly, growing nitride in nitrogen is not possible. However, just like native nitridation, we can use ammonia, the more reactive form of nitrogen as a precursor. You can also deposit sulfides by substituting water with H_2S. You can even deposit alloys like oxysulfides or oxynitrides. Instead of component A and component B to deposit binary materials, you can have components A, B, and C which allows you to deposit tertiary materials.

We will not get into further details but discuss the simple two-component ALD. The poster child or the base case study that we will use is aluminum oxide.

(Refer Slide Time: 06:47)



ALD: One Cycle

http://www.sigmaaldrich.com/technical-documents/articles/material-matters/precursors-for-atomic.html

NPTEL: Fundamentals of Micro and Nanofabrication

This is what one cycle of ALD looks at the molecular level. You start with a substrate and flow the component A that is designed to chemisorb on top of the substrate to form a self-limiting monolayer. Even if you keep flowing component A, the thickness of this chemisorbed layer does not change because the material A is designed not to stick to itself, or condense, but chemisorb on the substrate. Once the substrate gets completely covered with the monolayer of component A, there is no space for further material to adsorb. Notice the word used is chemisorption, not adsorption. ALD requires chemisorption, which means some chemical interaction needs to occur between the substrate and the component. Once component A is chemisorbed on the surface, you flow the second component of your reaction, in this case, component B. Component B is again designed in a manner that one part of the molecule reacts with the component A.

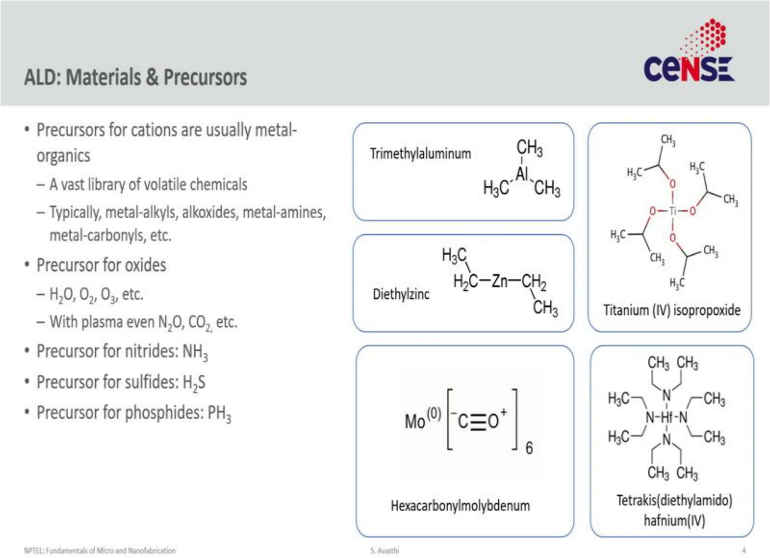
So, it forms this bond which is shaded yellow. As you keep flowing B, this reaction completes and you get a monolayer of component B that covers the surface.

After this step, the surface that had A functional sticking out now has B functional sticking out, but more importantly, you have formed a layer of the reacted species that is both A plus B and this yellow thing is typically the material you want to deposit. If you want to deposit aluminum oxide then this would be the aluminum and oxygen.

Component B is also designed to chemisorb in a self-limiting fashion for the same reason component A is. After that, you purge all the excess B out of your system and introduce the component A again. As there is no B in the gaseous phase, A doesn't react with anything in the gaseous phase, but only with the B functional sticking on the surface. Again, you form these yellow molecules of the material you want to deposit, and the A functional sticks out. After a while, all the sites of B functional would react with A and we get a monolayer of yellow molecules of the desired material and a functionalized monolayer of A. This brings you back to where you started, This is one complete cycle.

In the next cycle, the whole process happens again and you gain one more layer of the yellow stuff that you want to deposit. At a molecular level, this is what ALD tries to do.

(Refer Slide Time: 10:09)



ALD: Materials & Precursors

- Precursors for cations are usually metal-organics
  - A vast library of volatile chemicals
  - Typically, metal-alkyls, alkoxides, metal-amines, metal-carbonyls, etc.
- Precursor for oxides
  - H_2O, O_2, O_3, etc.
  - With plasma even N_2O, CO_2, etc.
- Precursor for nitrides: NH_3
- Precursor for sulfides: H_2S
- Precursor for phosphides: PH_3

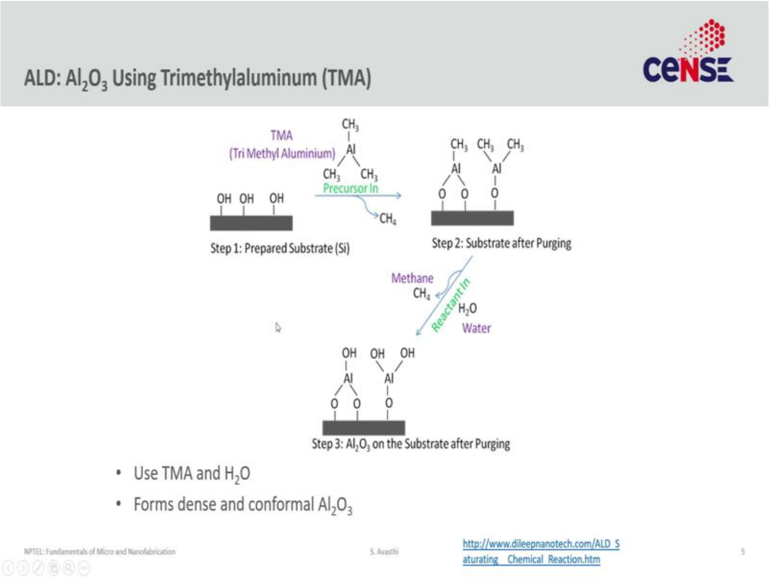
NPTEL: Fundamentals of Micro and Nanofabrication S. Avasthi 4

Let us talk about the materials and precursors often used in ALD. For cations, we typically use metal-organic precursors. There is a vast library of volatile chemicals that we can use, as discussed in CVD. ALD has a larger library.

Typically, the volatile precursors tend to be from the general class of metal alkyls, for example, trimethylaluminum or diethylzinc. They sometimes are alkoxides, for example, titanium isopropoxide, some version of amine, for example, this hafnium precursor, or metal carbonyl. Molybdenum precursor is a molyhexacarbonyl. These sort of precursors tends to be used.

For the anions, it depends on the anion you choose. For oxides, the most common one is water, as water is both volatile at room temperature and is fairly reactive. You can also use oxygen or ozone. Ozone does not store very well, so often has to be made in situ using UV light. If you have access to plasma inside your ALD chamber, you can use even less reactive forms of oxygen, such as nitrous oxide or carbon dioxide. For nitrides, the most common one is ammonia. For sulfides, people use H_2S and for phosphides, lately, people have started using phosphine for gallium or aluminum phosphide.

(Refer Slide Time: 11:41)



ALD: Al_2O_3 Using Trimethylaluminum (TMA)

- Use TMA and H_2O
- Forms dense and conformal Al_2O_3

NPTEL: Fundamentals of Micro and Nanofabrication

S. Avasthi

http://www.dileepnanotech.com/ALD_Saturating_Chemical_Reaction.htm

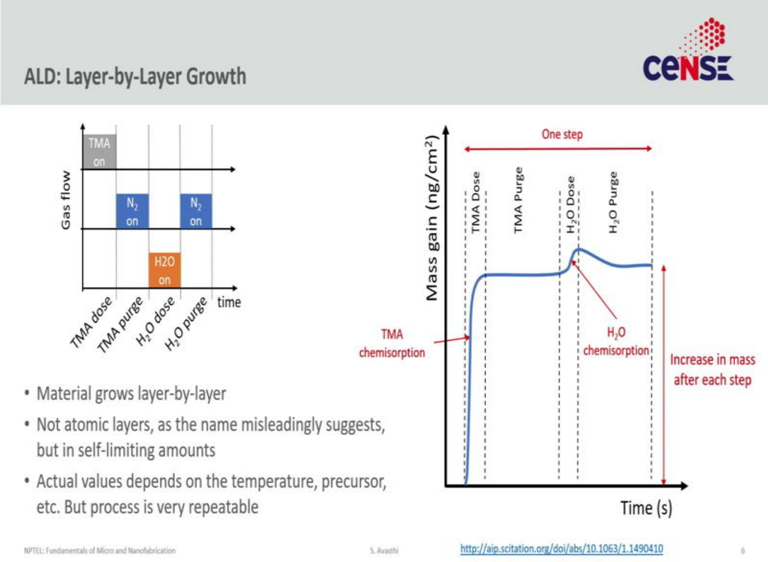
5

Let’s discuss a canonical example - the growth of Al_2O_3 using trimethylaluminum (TMA) which is one of the most ideal ALD reactions. Real, novel or esoteric forms of ALD sometimes deviate from the ideal. Before we start looking at the deviations, we should have an understanding of what simple/ideal ALD looks like.

You start with the substrate primed with OH groups. How do you get these OH? You get them from the end of the last cycle. If your substrate does not start with OH, a common trick is to pulse a lot of water for 10 minutes or so; that pulsed steam on top of the substrate typically creates OH groups on the surface. Then you flow in precursor A which is TMA. The metal alkyl bond is extremely reactive. It reacts with these OH groups because aluminum's affinity to oxygen is very large. You form an Al-O bond and some of these organic groups continue to stick on the aluminum. After that, you flow some inert gas to purge all the excess TMA that has not reacted on the surface.

You started with OH groups and after the purging step, you have this aluminum alkyl group sticking out. Now you flow the second reactant, which in this case is water. The H goes to the CH_3 group and forms methane, and the OH goes to aluminum. Methane is volatile at room temperature, so it floats away and you end up with aluminum OH bond. If the film is thick enough, this Al-OH bond can be dehydrated into the Al-O, forming the aluminum oxide. If you are not ending this chemical reaction here, then this OH reacts with TMA again in the next cycle and you, layer by layer, keep growing aluminum oxide. The reason this is so popular, which is the USP for ALD, is that you grow very conformal and dense films.

(Refer Slide Time: 14:19)



ALD: Layer-by-Layer Growth

- Material grows layer-by-layer
- Not atomic layers, as the name misleadingly suggests, but in self-limiting amounts
- Actual values depends on the temperature, precursor, etc. But process is very repeatable

NPTEL: Fundamentals of Micro and Nanofabrication S. Avasthi http://aip.scitation.org/doi/abs/10.1063/1.1490410 6

Let us look into a little more detail on this layer by layer business. To clarify again, we flow the TMA precursor for some time to get a monolayer chemisorbed. The amount of the TMA flown is called dose. Here, you are looking at the gas flow as a function of time. This is followed by a purge cycle. During the purge cycle, all the excess TMA that has not chemisorbed on the surface must be flushed out. You can do this with any inert gas. Nitrogen is most common, so you flow nitrogen for some time to get rid of the excess TMA. Now, the chamber does not have any TMA save for the surfaces which have been covered with a monolayer of TMA. Then you flow component B which is water and wait for this reaction to complete and a monolayer of OH to form on the surface. After that, once again you flow an inert gas to get rid of all the excess water. This is one complete cycle.

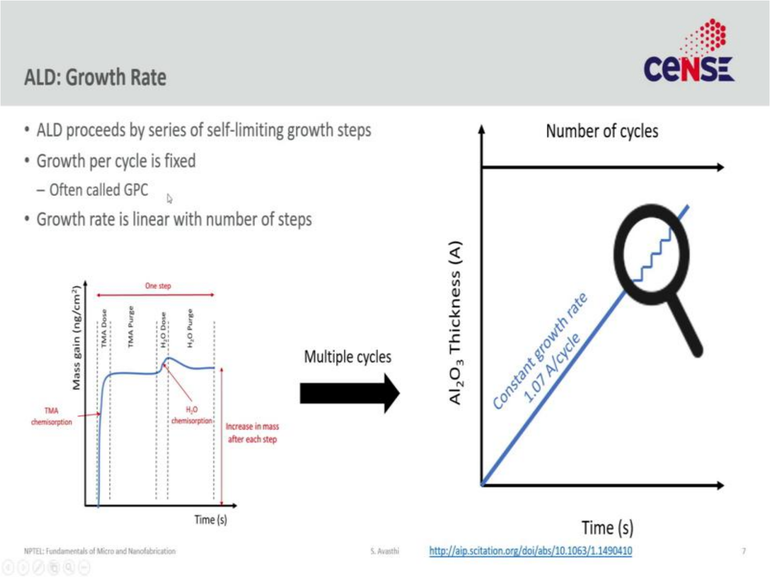
If you stick a quartz crystal in there and look at the mass gain, it tells you a very interesting story. You start from point 0, the TMA dose part. During the TMA dose, you see an increase in the mass because of chemisorption, which is expected. Remember this is a self-limiting reaction, so the mass gain, at some point, flat lines as there is no free surface for TMA to react with or get chemisorbed. After this, there is no point in waiting any further, so you turn off the TMA and do a purge cycle. During the purge cycle, all the excess TMA gets removed, but because this is a chemisorbed process, you do not remove the TMA that is chemisorbed on the surface. Think of it as irreversible adsorption. The material can come in, do a reaction or chemical interaction, but does not have enough energy to get out in the time scales that we are dealing with here. So, the mass does not change and remains flat. When you introduce water, chemisorption happens again, the mass increases, and once you know that the reaction is complete, or flatlining, you turn the water off and do the nitrogen purge.

Interestingly, unlike TMA, you see some drop in the mass. It does not all go away as some water remains, but with time, the amount of water reduces. This is a non-ideality often seen in a lot of precursors. TMA is an excellent precursor. It does not have this nonideality that water does. You would think that the water is chemisorbed on the surface, but that is not the only mechanism at play. Some water could be adsorbed on the surface and adsorption can be reversible. The part of the water that is simply absorbed may desorb while you flow the inert gas. Of course, if it completely desorbs, then it cannot react, but that is not what happens. There is some reactivity between water and

TMA and because of that, a certain amount is chemisorbed (irreversibly) on the surface, and does not come out.

You see some amount of mass gain at the end of one cycle. The mass gain per cycle does not correspond exactly to a monolayer per se. Atomic layer deposition is a slightly poor nomenclature. It seems to suggest that you always have one exact monolayer, which is a little misleading. The better way to think about it is that it is a self-limiting chemisorbed layer. They can be more or less than a monolayer, often less than a monolayer, depending on the temperature of the substrate, and the precursor. Overall, the great news is that the process is very repeatable. Each cycle does essentially the same thing, so, the whole process is extremely repeatable or linear.

(Refer Slide Time: 19:05)



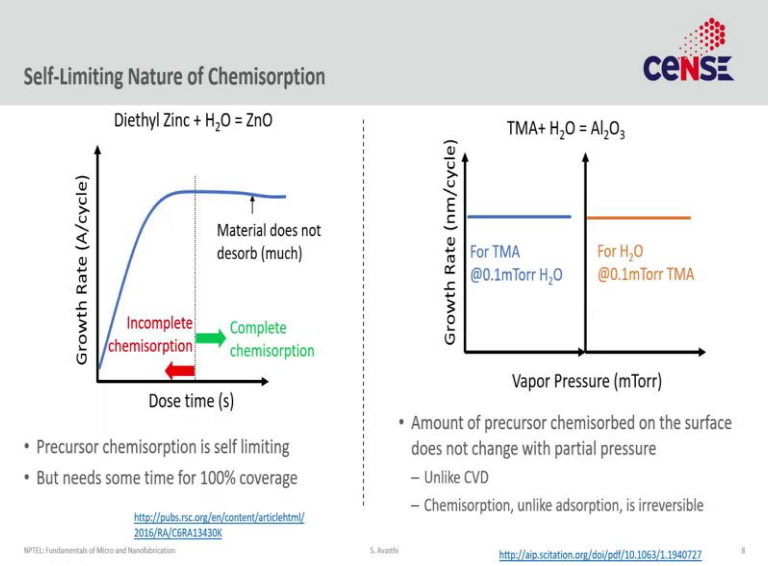
ALD: Growth Rate

- ALD proceeds by series of self-limiting growth steps
- Growth per cycle is fixed
  - Often called GPC
- Growth rate is linear with number of steps

NPTEL: Fundamentals of Micro and Nanofabrication S. Avasthi http://aip.scitation.org/doi/abs/10.1063/1.1490410 7

This is just one step or cycle. If you keep depositing layer after layer, your aluminum oxide thickness will start increasing in a very predictable, linear fashion. In this case, it is 1.07 Å/ cycle. If you zoom, you see the small steps, each of the steps represents one cycle where a little bit of aluminum oxide grows. The thickness that you see in each step is not exactly of a monolayer. It does not have to be, as long as it is repeatable. What you gain in each cycle is called growth per cycle or GPC. We will use this nomenclature.

(Refer Slide Time: 19:59)



Self-Limiting Nature of Chemisorption

- Precursor chemisorption is self limiting
- But needs some time for 100% coverage

http://pubs.rsc.org/en/content/articlehtml/2016/RA/C6RA13430K

- Amount of precursor chemisorbed on the surface does not change with partial pressure
  - Unlike CVD
  - Chemisorption, unlike adsorption, is irreversible

NPTEL: Fundamentals of Micro and Nanofabrication

S. Avasthi

http://aip.scitation.org/doi/pdf/10.1063/1.1940727

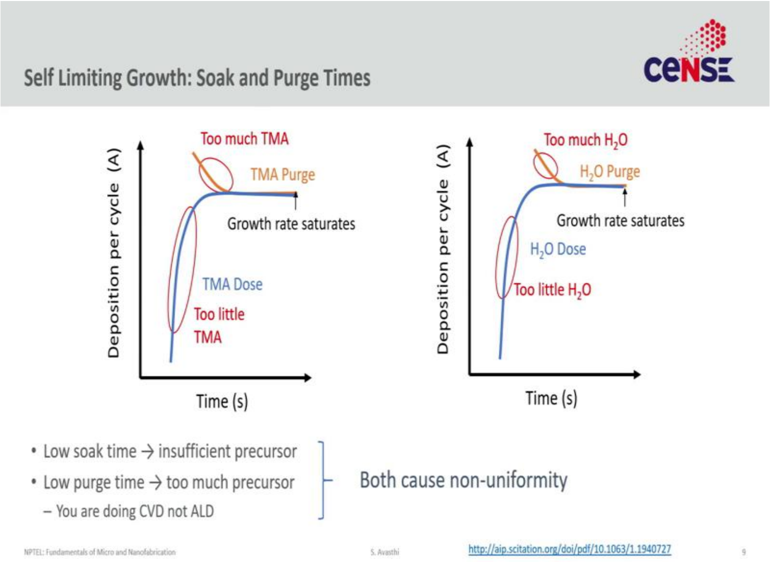
8

Let us talk about this self-limiting nature of chemisorption. For example, diethylzinc and water react to give you zinc oxide. This is a plot of the growth rate per cycle as a function of dose time. It is how long you leave the precursor A, in the case diethyl zinc on. Once again, you start from 0, as the precursor keeps starts chemisorbing on the surface you will see the growth rate increase because you are absorbing more and more of the material. At some point you get to the self-limiting case, where giving it more time would not add more precursor. Before that, you are in the incomplete chemisorption phase. You must give this much amount of dose or pulse time for the precursor to completely chemisorb, otherwise, you get suboptimal growth.

Once you reach this point, you have as good a coverage as you can get; after that, even if you continue to flow the precursor, you do not add any more material, and the growth rate per cycle does not go up much. Also, the material does not desorb, as it is a one-directional reaction. The little bit of change that you do see is some second-order effect that is not important. For more details, you can look at this reference. Understand that chemisorption is its dependence on partial pressure. In the CVD lecture, we repeatedly talked about how partial pressure is one of the key parameters to control the growth rate in CVD, no matter what regime you are in, what type of reactor you. ALD is very different because the reaction is irreversible and self-limiting. The growth rate tends to be fairly independent of the vapor pressure.

Here is an example of TMA and water that we used to form aluminum oxide. If you keep the vapor pressure of water constant at 0.1 millitorrs but change the vapor pressure of TMA, the growth rate will be the same. You can do the reverse where you maintain a 0.1 milliTorr of TMA, but change the partial pressure of water, and once again you do not see any change, very much unlike CVD and this is an important point. The partial pressure of the precursor does not matter much, only its temperature does. In CVD, we went through a lot of pain to maintain nearly uniform flow and partial pressure by using very complicated showerheads, and pressure control systems. ALD tends to be a lot simpler because pressure control is not that big a deal.

(Refer Slide Time: 23:23)



Self Limiting Growth: Soak and Purge Times

- Low soak time → insufficient precursor
- Low purge time → too much precursor
  - You are doing CVD not ALD

Both cause non-uniformity

NPTEL: Fundamentals of Micro and Nanofabrication S. Avasthi http://aip.scitation.org/doi/pdf/10.1063/1.1940727 9

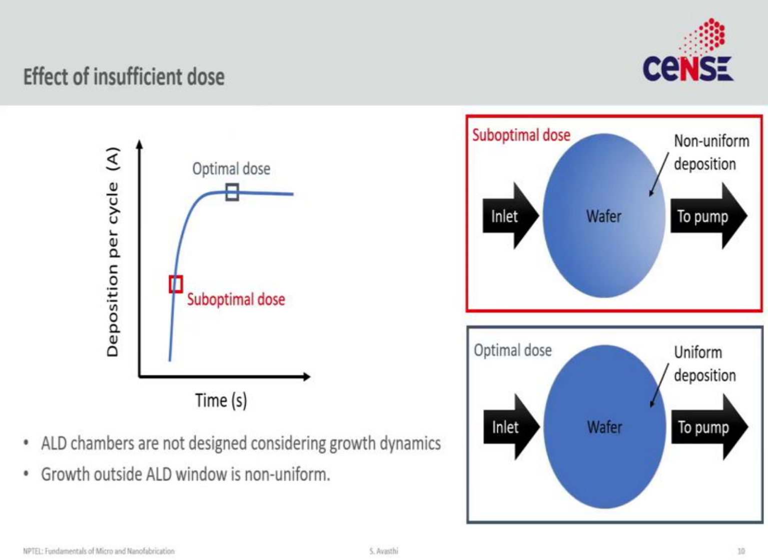
From new precursors A and B, how do you design the recipe of ALD? You need to optimize the 4 parameters that you control. Those are the dose and purge of component A and the dose and purge of component B. You do the deposition and plot the deposition per cycle or growth per cycle of that precursor as a function of dose or pulse time. For very short times, you have incomplete chemisorption and hence, sub-optimal growth rates. Once there is enough time for component A to form a self-limiting layer on top of the substrate, increasing the dose time further does not do anything. The optimal length of the dose cycle should be exactly this time; Any less, you have sub-optimal ALD, any more, you waste time/precursor.

Similarly, for the purge cycle, you plot the deposition per cycle for various purge times. For very small times, you have excess TMA that hangs out in the chamber and is not absorbed on the surface. This is bad because it can react with the water that you put in the subsequent cycles and do a CVD type reaction, not ALD. You always want ALD to happen on the substrate, not in the gas phase.

If you leave excess TMA, that would enhance your growth rate, but that is not proper ALD. As you increase the purge times, the growth will fall. At some point, there is no excess TMA in the ambient of the chamber, and all the TMA is only present on the substrate. The TMA on the substrate is irreversibly chemisorbed and is not going to come out. What should be the length of the purge cycle? It should be as long as exactly this point; any less, you have excess TMA in the chamber that messes up ALD, any more, you waste time. You can do the same optimization with component B.

You always want to be in the regime where the growth saturates. What happens in these red regions? In the red regions, you often get nonuniformity.

(Refer Slide Time: 26:53)



Effect of insufficient dose

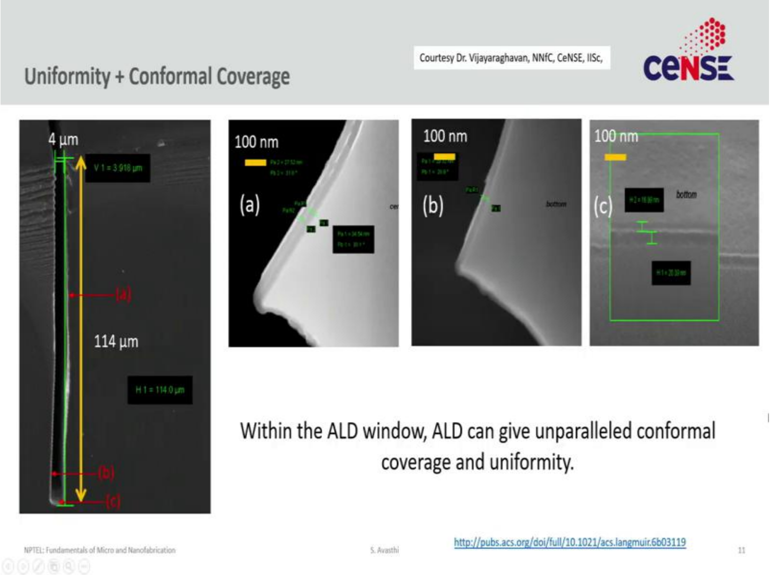
- ALD chambers are not designed considering growth dynamics
- Growth outside ALD window is non-uniform.

NPTEL: Fundamentals of Micro and Nanofabrication S. Avasthi 10

Unlike CVD, ALD chambers are often not designed keeping the gas flow in mind because the reaction does not happen continuously, but in the steps. The assumption is that in every step, you form a self-limiting monolayer in a conformal and uniform fashion. You do not need to worry about gas flow dynamics.

If CVD like growth happens because of excess or deficit precursor, that leads to non-uniformities. Look at a wafer that was processed at a suboptimal dose which is the red square and the one processed at an optimal dose which is the blue square. In the red square, you will see a non-uniform deposition. If you keep it such that the inlet is on the left and the pump on the right, the right side gets lesser deposition than the left because of the lower dose. In the optimal case, there is no non-uniformity.

(Refer Slide Time: 28:25)



Uniformity + Conformal Coverage

Courtesy Dr. Vijayaraghavan, NNfC, CeNSE, IISc,

Within the ALD window, ALD can give unparalleled conformal coverage and uniformity.

NPTEL: Fundamentals of Micro and Nanofabrication

S. Avasthi

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

The USP for ALD is uniformity and conformality. We have seen this slide earlier, but now you can probably appreciate it more. Even in these very deep trench coated with a very thin layer of conformal aluminum oxide or some other material, there is the same thickness on the side, on the top, and bottom. ALD is extremely conformal and uniform. It does not depend upon the gas flow dynamics or patterns, or diffusion. By and large, it is a chemisorption process. All that happens in a higher aspect ratio structure is that the dose time or purge time increases, but you still get the uniform film. Here is an example of a very deep trench. At the cross-sections at points A, B, and C, we see the same thickness of ALD deposited material.

In the next lecture, we will look at more complicated aspects of ALD. For example, the deposition windows, plasma-enhanced ALDs, some aspects of nucleation, etcetera.