Nanoelectronics: Devices and Materials
Prof. S. A. Shivashankar
Centre for Nano Science and Engineering
Indian Institute of Science, Bangalore

Lecture – 40
Atomic layer deposition (ALD)

Hello, this is the next session in the course on Nanoelectronic Device Fabrication and Characterization.

(Refer Slide Time: 00:29)

Nanoelectronics Device Fabrication and Characterization

- Segment 3
- S.A. Shivashankar
- Centre for Nano Science and Engineering (CeNSE) IISc, Bangalore

What we did last time was to learn about Carbon nanotubes and the CVD process.

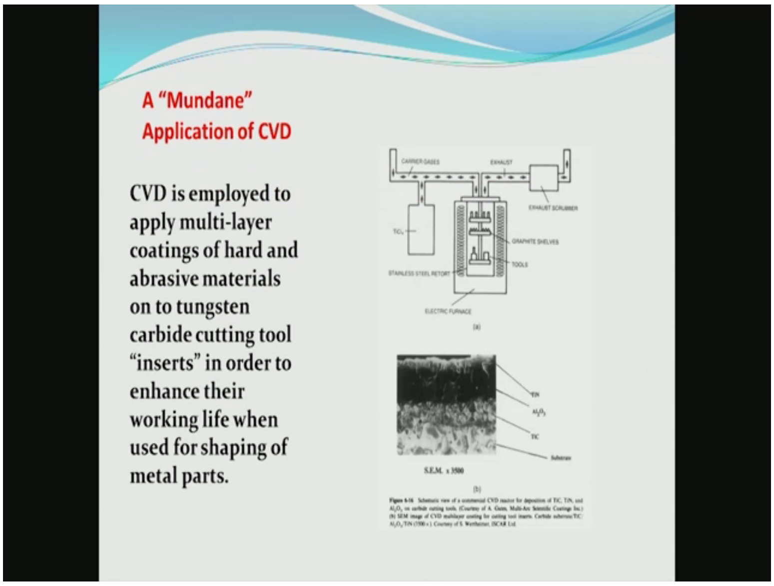
(Refer Slide Time: 00:32)

Outline

- Recap of previous session: CNTs, CVD
- CVD (continued)
- Atomic Layer Deposition (ALD)
- Examples of Nanostructures from ALD

What we will do today is to continue a bit more about the CVD process, and then we come to Atomic Layer Deposition or ALD and then look at examples of nanostructures that are obtained from ALD.

(Refer Slide Time: 00:51)

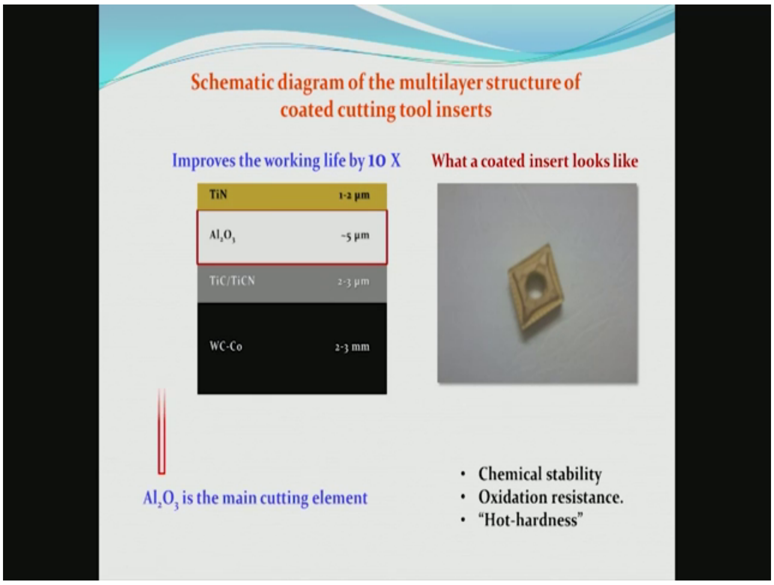


A "Mundane" Application of CVD

CVD is employed to apply multi-layer coatings of hard and abrasive materials on to tungsten carbide cutting tool "inserts" in order to enhance their working life when used for shaping of metal parts.

Now at the end of the class last time, I pointed out that there is a "Mundane" application of the chemical vapour deposition process in making cutting tool bits that is coating on cutting tool bits for the machine shop.

(Refer Slide Time: 01:07)



Schematic diagram of the multilayer structure of coated cutting tool inserts

Improves the working life by 10 X

TiN	1-2 µm
Al_2O_3	~5 µm
TiC/TiCN	2-3 µm
WC-Co	2-3 mm

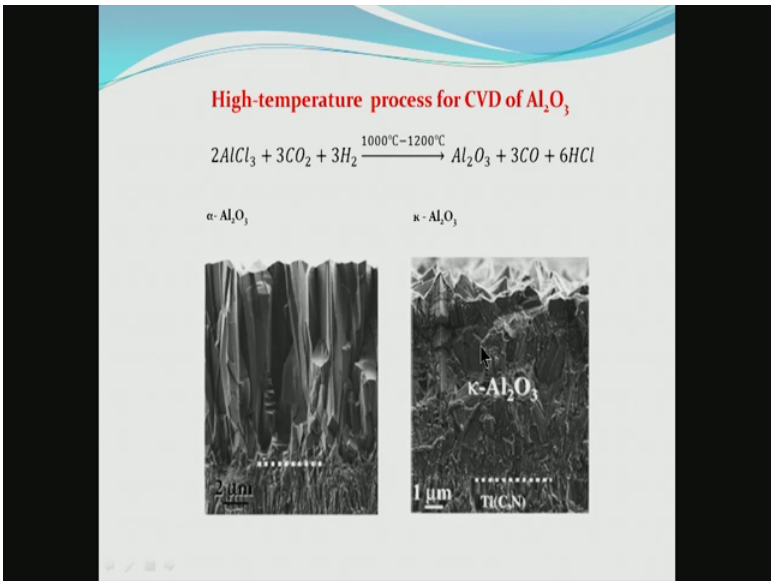
Al_2O_3 is the main cutting element

What a coated insert looks like

- Chemical stability
- Oxidation resistance.
- "Hot-hardness"

What they look like or this is a typical cutting tool bit for cutting for example, high speed steel and what it consists of at the last layer is a coating of till nitride which gives it is golden globe, beneath that is a layer of aluminum oxide measuring about 5 micrometers, beneath that is a titanium carbonitrate coating all of this sitting on top of several millimeters of a tungsten, carbide, cobalt substrate which really is a total cutting tool. This aluminum oxide layer at the top actually enhances the lifetime of this cutting tool by a factor of as much as 10.

(Refer Slide Time: 01:52)



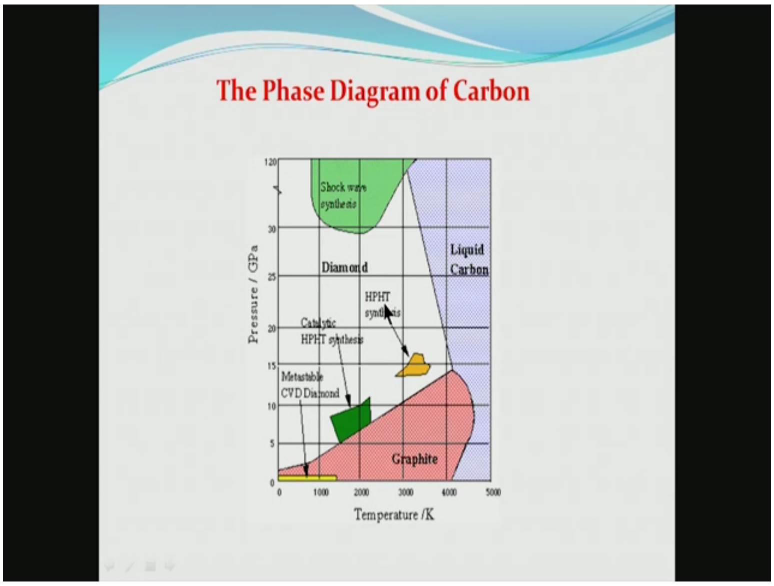
High-temperature process for CVD of Al_2O_3

$$2AlCl_3 + 3CO_2 + 3H_2 \xrightarrow{1000℃-1200℃} Al_2O_3 + 3CO + 6HCl$$

Now the reason it happens, is because of the teeth that you can see here these are aluminum oxide crystals that are essentially vertical or perpendicular to the substrate thin long needles in the alpha Al2 O3 phase of aluminum oxide, on the right side is the kappa alumina phase which can also we obtained all of these by a CVD process that uses aluminum trichloride as the precursor along with carbon dioxide and hydrogen and a temperature at which this works is about 1000 degrees and more and the result is obtaining Al2 O3 coatings on the substrates.

Now, what I want you to look at is that these are very thin long needles of Al2O3 crystals are Al2O3, which have the cutting force necessary for cutting high speed steel and these are very thin in terms of nanometers although they are long several micrometers long. On the other hand the kappa alumina phase which can also be obtained by the same process under slightly different conditions is also a hard material for cutting metals and that consists of essentially nanometric grains of kappa alumina which is an orthorhombic phase of aluminum oxide. I want to point out that this is a very effective cutting material kappa alumina and the nanometric nature of it gives it additional mechanical advantage.

(Refer Slide Time: 03:20)

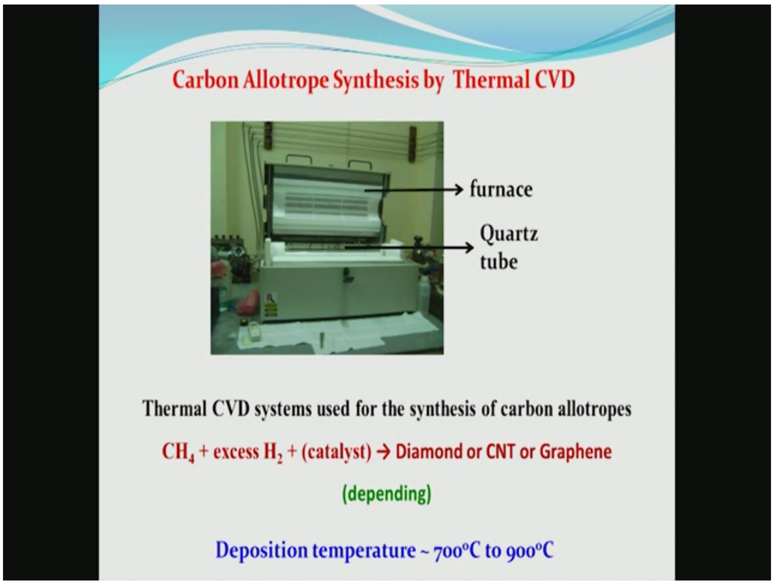


The Phase Diagram of Carbon

Now we come to look at a phase diagram of carbon which is the equilibrium phase diagram of carbon where pressure is plotted on the y axis and temperature on the x axis and different forms of carbon allotropes of carbon are plotted on this graph. Now what I wanted to see is that diamond is a high pressure high temperature phase of carbon that is under equilibrium you need high pressure and high temperature to obtain diamond otherwise it is mostly graphite. But at this lower end corner over here is a region where the CVD process is capable of producing diamond instead of at high pressure and high temperature these had a much lower temperature and much lower pressure.

So, CVD has the capability to produce metastable diamond under these conditions and it is actually a process that is used today in producing films of diamond for various purposes including a breading.

(Refer Slide Time: 04:14)



Carbon Allotrope Synthesis by Thermal CVD

Thermal CVD systems used for the synthesis of carbon allotropes

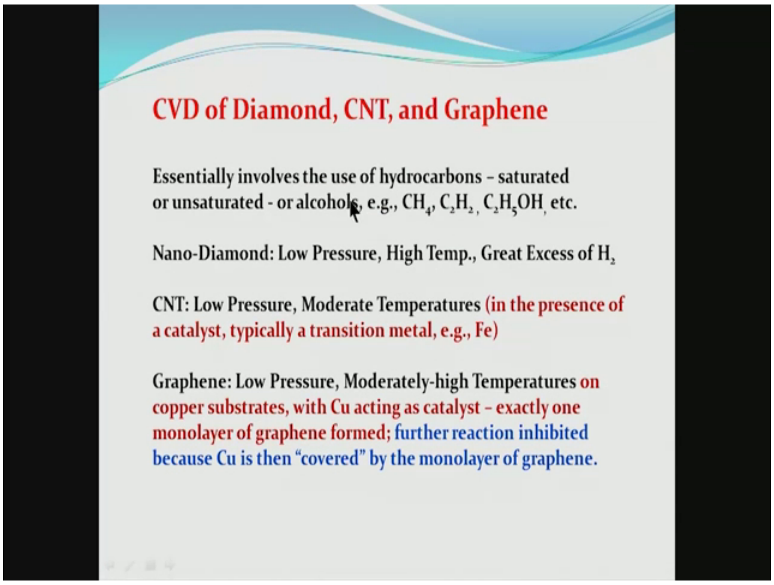
CH_4 + excess H_2 + (catalyst) → Diamond or CNT or Graphene

(depending)

Deposition temperature ~ 700°C to 900°C

Now, this is the kind of a chamber CVD process chamber, in which such depositions can be done actually carbon allotropes can be synthesis by thermal CVD, different carbon allotropes by which I mean diamond, Graphene and carbon nanotubes. So, these are different allotropes and all of that requires a hydrocarbon and excess of hydrogen in the chamber and typical a catalyst especially for a carbon nanotubes and graphene it requires a catalyst and a deposition temperatures typically a range some 700 to 900 degrees are slightly about. So, the same thermal CVD process is capable of giving us different allotropes of carbon.

(Refer Slide Time: 04:59)



CVD of Diamond, CNT, and Graphene

Essentially involves the use of hydrocarbons - saturated or unsaturated - or alcohols, e.g., CH_4, C_2H_2, C_2H_5OH etc.

Nano-Diamond: Low Pressure, High Temp., Great Excess of H_2

CNT: Low Pressure, Moderate Temperatures (in the presence of a catalyst, typically a transition metal, e.g., Fe)

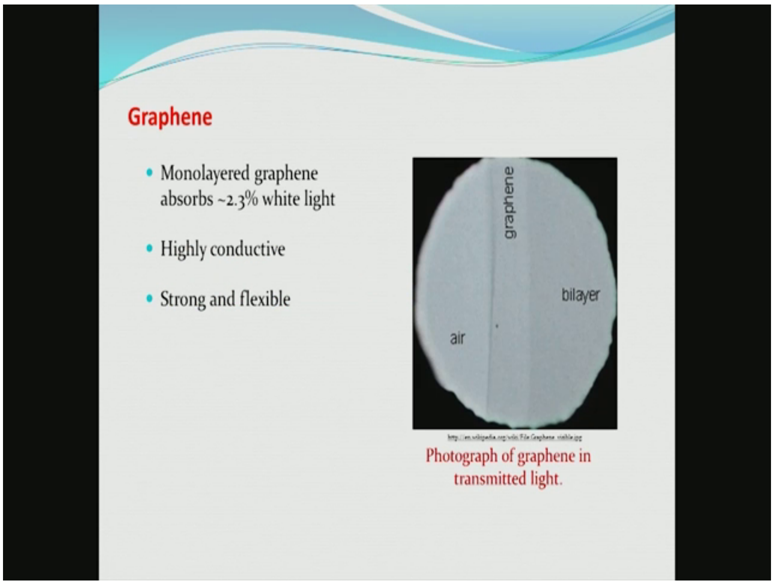
Graphene: Low Pressure, Moderately-high Temperatures on copper substrates, with Cu acting as catalyst - exactly one monolayer of graphene formed; further reaction inhibited because Cu is then "covered" by the monolayer of graphene.

Now, let us look at that a little bit more, it involves the use of hydrocarbons saturated or unsaturated like methane, acetylene, ethyl alcohol and so on. And nano matric diamond that is diamond films which have grains of diamond in the nano metric range can be produced at low pressure and high temperature in great excess of hydrogen by the CVD process.

Now, carbon nanotubes called for low pressure and moderate temperatures and the presence of a catalyst especially a transition metal like iron, nanometer crystals of iron as the catalyst.

Graphene which is a more recently discovered allotrope of carbon which is the single layer of graphite, carbon atoms requires low pressure moderately high temperatures and especially on copper substrates. For example, with copper acting as a catalyst exactly one layer of graphene can be deposited on copper by see the CVD process and further reaction is inhibited because copper is then completely covered by a monolayer of grapheme. Therefore, using a copper substrate and the CVD process is very efficient in giving us a Monolayer of graphene on which a lot of work has been done recently.

(Refer Slide Time: 06:15)



Graphene

- Monolayered graphene absorbs ~2.3% white light
- Highly conductive
- Strong and flexible

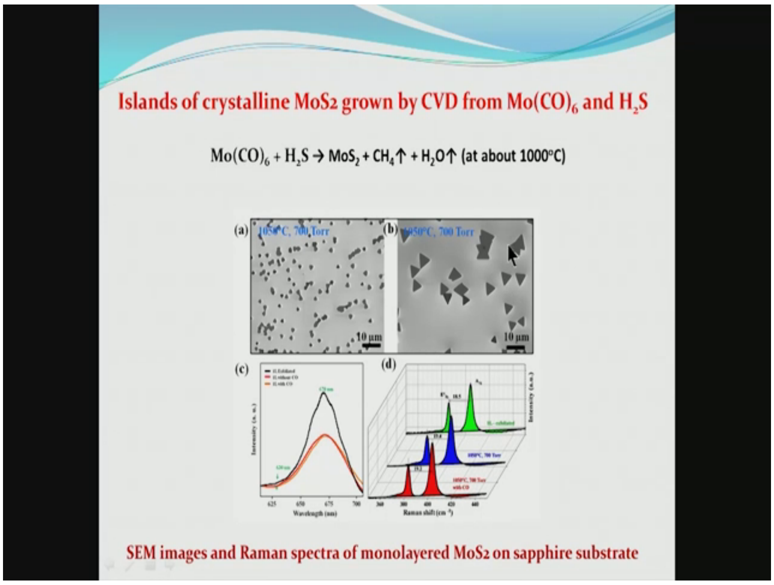
http://en.wikipedia.org/wiki/File:Graphene_visible.jpg

Photograph of graphene in transmitted light.

Now, Graphene what we are looking at is a photograph of a graphene layer produced by CVD in transmitted light. In the middle you are seeing a monolayer of graphene and you are able to see that because graphene monolayer of graphene absorbs 2.3 percent of white light and therefore one is able to see graphene and then next to that is a bilayer of graphene, 2 layers of graphite on top of each other so that is a bilayer of graphene. So, these are produced rather readily now by this CVD process.

Now CVD is turns out is also an ideal process for layered or 2 dimensional transition metal dichalcogenides like MoS 2. All of these have become a range in the research field today following the discovery of graphene is a monolayer of carbon. Similarly, MoS 2 one can get a monolayer of MoS 2 which is a transition metal disulfide.

(Refer Slide Time: 07:14)



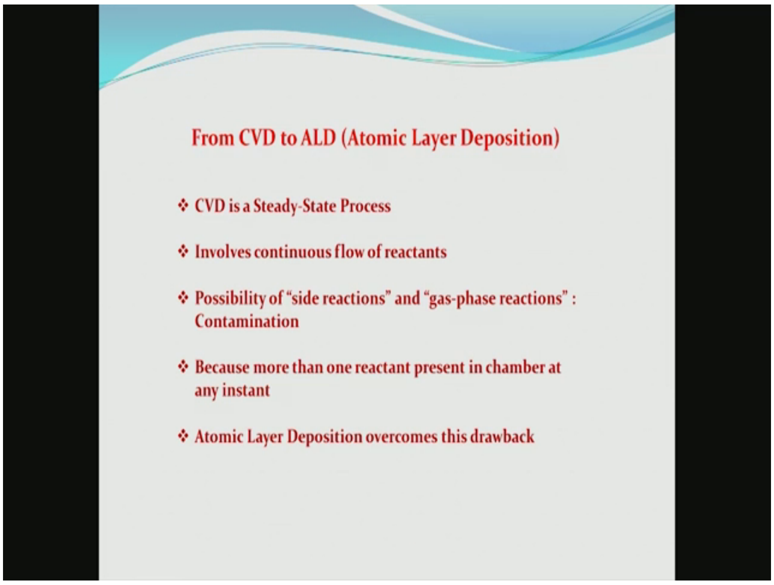
Islands of crystalline MoS2 grown by CVD from Mo(CO)$_6$ and H$_2$S

$Mo(CO)_6 + H_2S \rightarrow MoS_2 + CH_4\uparrow + H_2O\uparrow$ (at about 1000°C)

SEM images and Raman spectra of monolayered MoS2 on sapphire substrate

Now, these can be obtained by the CVD process, for example using molybdenum hexacarbonyl has one precursor, along with hydrogen sulfide and under the ideal right conditions of CVD of high temperature and high pressure and low pressure, one gets molybdenum disulfide as the product, and what you see in this SEM micrographs, are monolayer pieces of very well shaped triangular shaped MoS 2 layers and what you see below or Raman spectra of these monolayers, which can be interpreted to tell us whether it is a single layer mono double layer and so on and these happened to be single monolayer molybdenum disulfide layers.

(Refer Slide Time: 08:01)

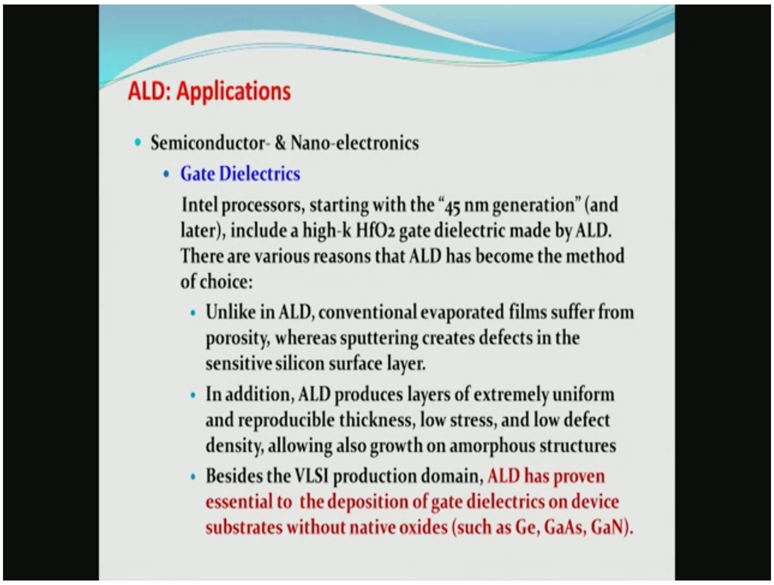


From CVD to ALD (Atomic Layer Deposition)

- CVD is a Steady-State Process
- Involves continuous flow of reactants
- Possibility of "side reactions" and "gas-phase reactions" : Contamination
- Because more than one reactant present in chamber at any instant
- Atomic Layer Deposition overcomes this drawback

Now, we now move from CVD of which we have learned some capabilities, from CVD to atomic layer deposition or ALD. And before you go we recognizes a CVD is a steady state process, it involves continuous flow of reactance and therefore, there is a possibility of side reactions are undesired reactions or gas-phase reactions which can produce by products which can contaminate these films that one is obtained, interested in obtaining that is because more than one reactant is present in the chamber at any instant. Atomic layer deposition is design to overcome this particular drawback.

(Refer Slide Time: 08:41)



ALD: Applications

- Semiconductor- & Nano-electronics
  - Gate Dielectrics

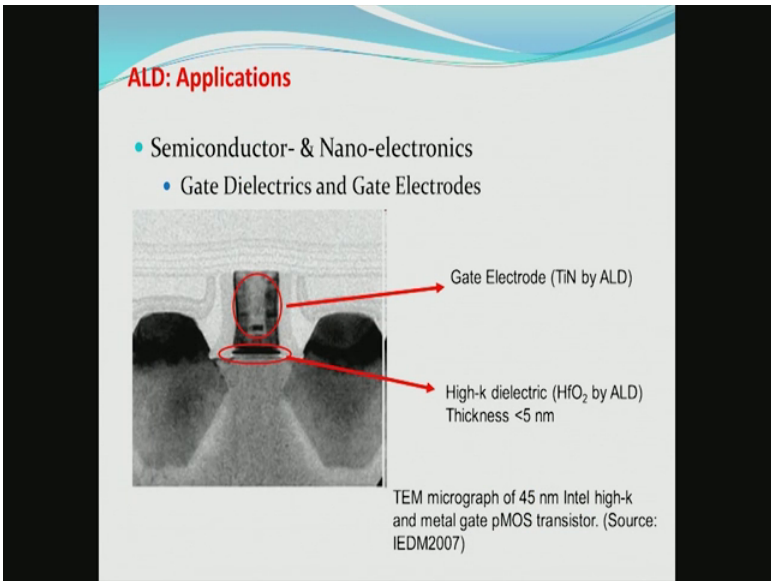
    Intel processors, starting with the "45 nm generation" (and later), include a high-k HfO_2 gate dielectric made by ALD. There are various reasons that ALD has become the method of choice:

    - Unlike in ALD, conventional evaporated films suffer from porosity, whereas sputtering creates defects in the sensitive silicon surface layer.
    - In addition, ALD produces layers of extremely uniform and reproducible thickness, low stress, and low defect density, allowing also growth on amorphous structures
    - Besides the VLSI production domain, ALD has proven essential to the deposition of gate dielectrics on device substrates without native oxides (such as Ge, GaAs, GaN).

Atomic layer deposition is already a well developed technology with applications in semiconductors nano electronics. In particular, in the deposition of Gate Dieelectrics in the more recent versions of CMOS technology, Intel processors starting some starting with the 45 nanometer generation and later include the a thin layer of hafnium oxide so called high k dielectric or a dielectric with a large dielectric constant, that is deposited by atomic deposition.

There are various reasons that are ALD has become a choice for this purpose because unlike ALD, conventional evaporation and sputtering give rise to porosity, which is undesirable in very thin dielectric layers and therefore non porous layers are required. In addition, ALD produces layers of extremely uniform and reproducible thickness, low stress, and low defect density, allowing for growth on amorphous substrate also. Furthermore, besides VLSI production, ALD has proven essential to the deposition of gate dielectrics on device substrates without native oxide such as germanium, gallium arsenide, and gallium nitride.

(Refer Slide Time: 10:01)



ALD: Applications

- Semiconductor- & Nano-electronics
  - Gate Dielectrics and Gate Electrodes

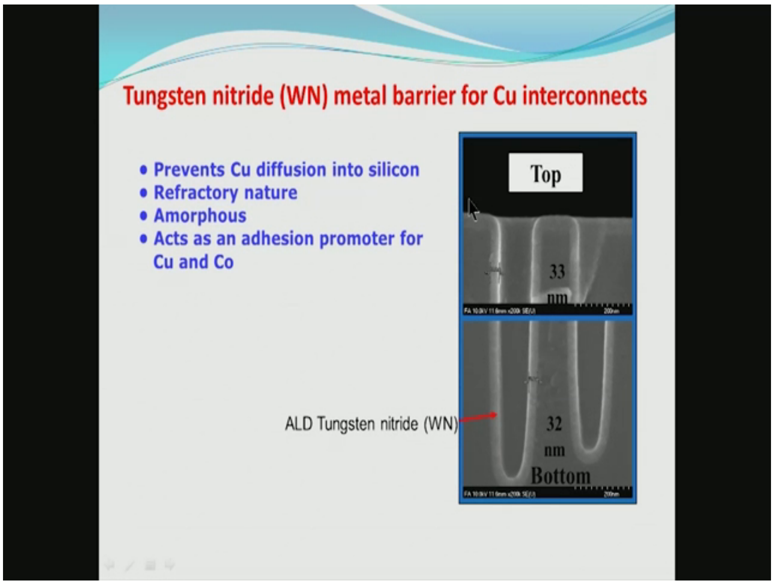
Gate Electrode (TiN by ALD)

High-k dielectric (HfO_2 by ALD)
Thickness <5 nm

TEM micrograph of 45 nm Intel high-k and metal gate pMOS transistor. (Source: IEDM2007)

What is shown here in the micrograph is a structure that is obtained that is part of these Intel technology, where the high k dielectric Hf O 2 of thickness less than 5 nanometers is deposited by ALD and then the gate electrode is titanium nitride also deposited by ALD.

(Refer Slide Time: 10:32)



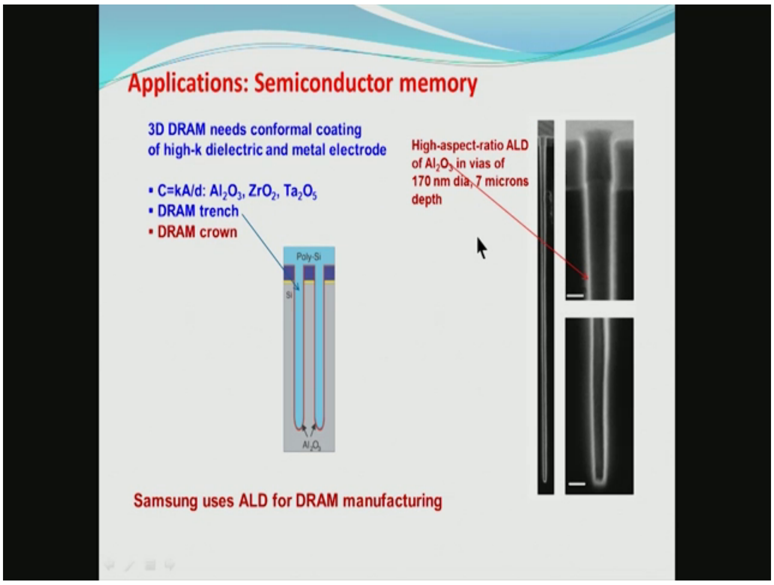
Tungsten nitride (WN) metal barrier for Cu interconnects

- Prevents Cu diffusion into silicon
- Refractory nature
- Amorphous
- Acts as an adhesion promoter for Cu and Co

ALD Tungsten nitride (WN)

These next micrograph shows the capability of ALD in really producing conformal coverage of very high aspect ratio features that are common in today’s VLSI devices. So, what is shown here is a thin layer of tungsten nitride, that is covering this deep trench and that is insulating copper which is the metalizing layer from silicon. Copper diffuses rapidly into silicon affecting device performance and therefore the tungsten nitride is used as a diffusion barrier, very thin diffusion barrier that is now covering this very deep trench in a very conformal fashion only ALD can do this.

(Refer Slide Time: 11:08)



Applications: Semiconductor memory

3D DRAM needs conformal coating of high-k dielectric and metal electrode

- C=kA/d: Al_2O_3, ZrO_2, Ta_2O_5
- DRAM trench
- DRAM crown

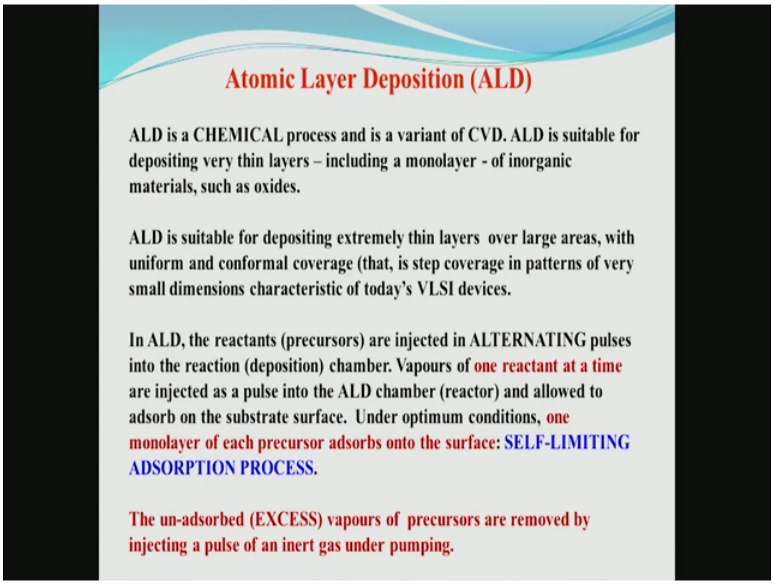
High-aspect-ratio ALD of Al_2O_3 in vias of 170 nm dia, 7 microns depth

Samsung uses ALD for DRAM manufacturing

ALD is also used in DRAM manufacturing for example, by a Samsung and what is shown here is a structure again with a deep trench, so this is so called DRAM trench where one has a layer of atomic layer of aluminum oxide that now separates silicon from copper.

So, therefore, ALD is capable of covering very fine features conformally, that is those features are present in today’s VLSI devices. What is ALD? We have shown examples what is ALD?

(Refer Slide Time: 11:41)



Atomic Layer Deposition (ALD)

ALD is a CHEMICAL process and is a variant of CVD. ALD is suitable for depositing very thin layers – including a monolayer - of inorganic materials, such as oxides.

ALD is suitable for depositing extremely thin layers over large areas, with uniform and conformal coverage (that, is step coverage in patterns of very small dimensions characteristic of today's VLSI devices.

In ALD, the reactants (precursors) are injected in ALTERNATING pulses into the reaction (deposition) chamber. Vapours of one reactant at a time are injected as a pulse into the ALD chamber (reactor) and allowed to adsorb on the substrate surface. Under optimum conditions, one monolayer of each precursor adsorbs onto the surface: SELF-LIMITING ADSORPTION PROCESS.

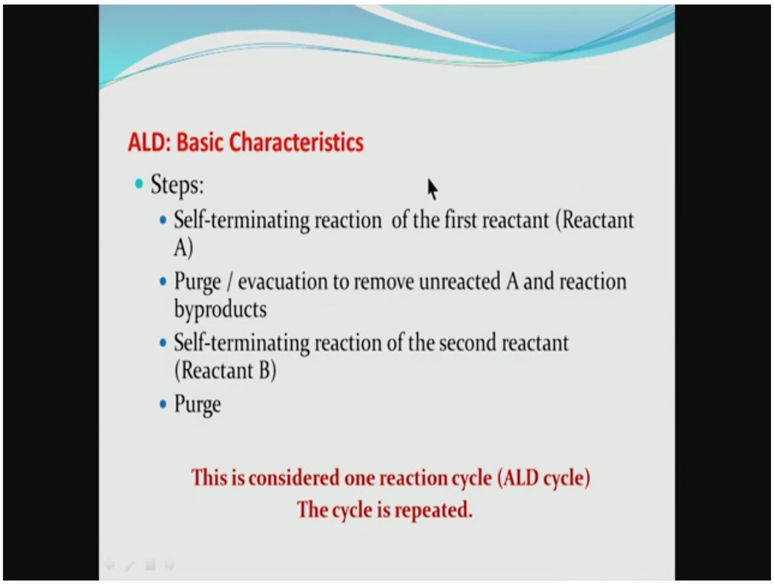
The un-adsorbed (EXCESS) vapours of precursors are removed by injecting a pulse of an inert gas under pumping.

ALD may be defined as "film deposition technique based on sequentially use of self terminating gas solid reactions. So, the operative thing is sequential use of self terminating gas solid reactions". As I said in CVD there is a continuous flow of all the reactants involved whereas, in ALD by contrast there is a sequential flow of or pulsing of reactants into the deposition chamber.

ALD is a chemical process and is a variant of CVD actually because chemical reactions or involved and ALD as I said is suitable for depositing very thin layers including a monolayer of inorganic materials, such as oxides. ALD is suitable for depositing extremely thin layers over large areas, so one advantage is that it is capable of producing very thin uniform layers on substrate as large as 300 millimeters, which is today used in VLSI manufacture.

In ALD, reactants are injected alternating pulses into the reaction chamber and vapors of one reactant at a time are injected in as a pulse, and allowed to adsorb on the substrate surface. Under optimum conditions one monolayer of each precursor adsorbs onto the surface resulting in a self limiting adsorption process it depends on a self limiting adsorption process; the unabsorbed or excess vapours because we only require a monolayer or removed by injecting a pulse of inert gas and by pumping.

(Refer Slide Time: 13:22)



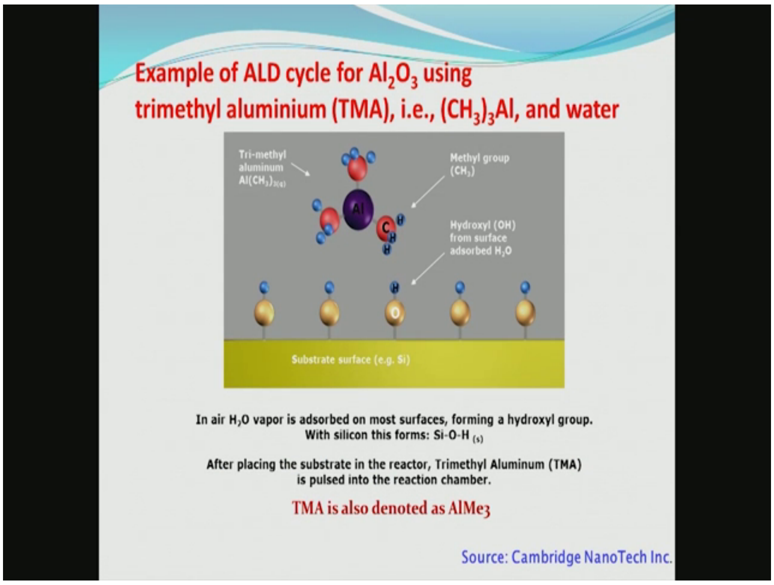
ALD: Basic Characteristics

- Steps:
  - Self-terminating reaction of the first reactant (Reactant A)
  - Purge / evacuation to remove unreacted A and reaction byproducts
  - Self-terminating reaction of the second reactant (Reactant B)
  - Purge

This is considered one reaction cycle (ALD cycle)
The cycle is repeated.

Now the basic steps of basic characteristics of ALD, involves steps of self terminating reaction of first reactant: Reactant A. a purge or a evacuation to remove unreacted A material and the byproducts, then inject a self terminating reaction of second the reactant, Reactant B and then another purge. So, together these 4 steps consider or considered to forum one ALD cycle and this cycle is repeated depending on the thickness of the material that one requires.

(Refer Slide Time: 13:59)



Example of ALD cycle for Al_2O_3 using trimethyl aluminium (TMA), i.e., $(CH_3)_3Al$, and water

In air H_2O vapor is adsorbed on most surfaces, forming a hydroxyl group.
With silicon this forms: Si-O-H $_{(s)}$

After placing the substrate in the reactor, Trimethyl Aluminum (TMA) is pulsed into the reaction chamber.

TMA is also denoted as $AlMe_3$

Source: Cambridge NanoTech Inc.

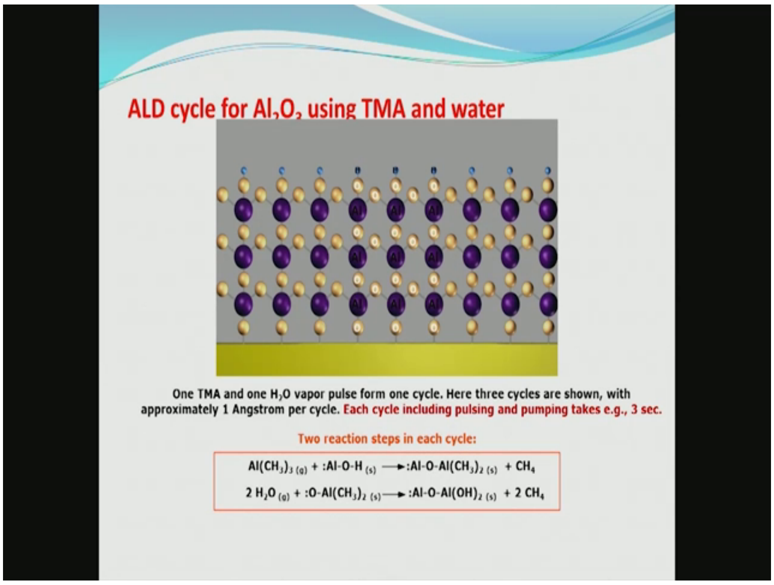
It can be illustrated very well by the example of aluminium oxide deposited by Al2 O3 using Trimethyl-aluminium or CH 3 tries Al and water as a 2 precursors. So, what is shown in this cartoon is a substrate such as silicon on top of which typically there is a hydroxyl group unless the pressure is very low, but CVD and ALD has done not at very low pressures and therefore one can expect these O-H hydroxyl groups to be present on the silicon surface.

So, Trimethyl Aluminium is shown here in this diagram and trimethyl aluminium comes in as a vapor and what happens when that occurs is that a reaction occurs where by the hydrogen that is over here then gets attached to one of the methyl groups producing methane which escapes as vapor and now you have what you now have is a an aluminum oxygen bond and then dangling CH 3 groups on this particular molecule. And when the entire substrate is covered what you know have is a uniform layer of this aluminum oxide precursors over here this is not aluminum oxide yet, but you have these dangling bonds of trimethyl aluminum in the right now it is dimethyl aluminum and methane escapes and therefore what you now have is a uniform layer of this particular structure.

Now, at this stage water is introduced as water vapour. so this is HOH that comes in and when that happens then what happens is that this hydrogen now attaches to the itself to oxygen over here and there is oxygen that bridges 2 aluminum atoms. And therefore what you now have is oxygen bridges and hydroxyl surface groups that are formed now and when this particular step is complete what you now have is a uniform layer that used that has hydroxyl groups and then oxygen aluminum oxygen bridges.

So, if this process continued therefore one builds up these aluminum oxide layers. So, each cycle is under ideal conditions capable of giving us one such layer and if this repeat cycle as repeat at one has this uniform layer uniform aluminum oxide film of the desired thickness that is a function of the number of cycles ALD cycles.

(Refer Slide Time: 16:37)



ALD cycle for Al_2O_3 using TMA and water

One TMA and one H_2O vapor pulse form one cycle. Here three cycles are shown, with approximately 1 Angstrom per cycle. Each cycle including pulsing and pumping takes e.g., 3 sec.

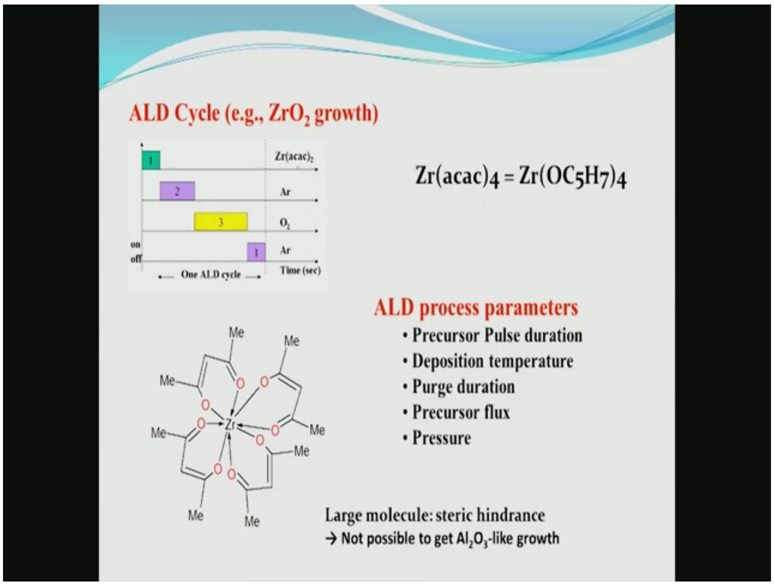
Two reaction steps in each cycle:

$Al(CH_3)_{3\,(g)} + :Al\text{-}O\text{-}H_{(s)} \longrightarrow :Al\text{-}O\text{-}Al(CH_3)_{2\,(s)} + CH_4$

$2\,H_2O_{(g)} + :O\text{-}Al(CH_3)_{2\,(s)} \longrightarrow :Al\text{-}O\text{-}Al(OH)_{2\,(s)} + 2\,CH_4$

Now, that is a very good example of the ALD process, but aluminum oxide has very good precursors namely trimethyl aluminum which is very suitable for the ALD process.

(Refer Slide Time: 16:45)



ALD Cycle (e.g., ZrO_2 growth)

$Zr(acac)_4 = Zr(OC_5H_7)_4$

ALD process parameters

- Precursor Pulse duration
- Deposition temperature
- Purge duration
- Precursor flux
- Pressure

Large molecule: steric hindrance

→ Not possible to get Al_2O_3-like growth

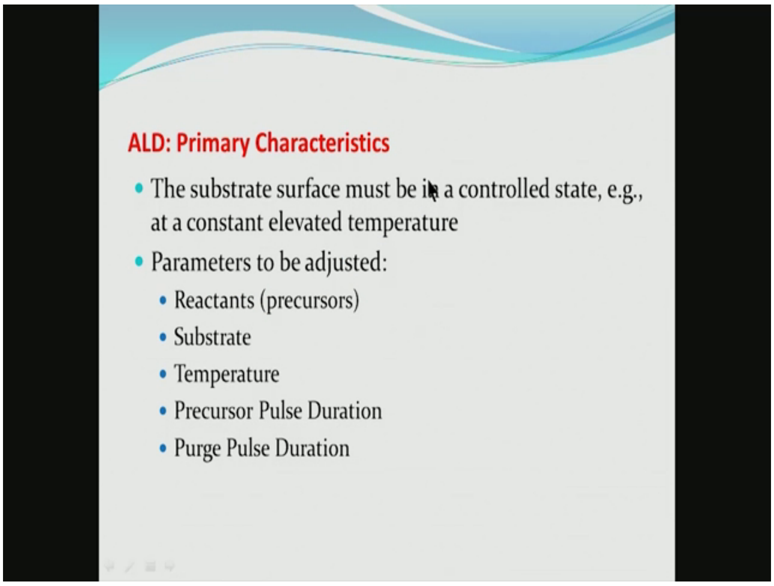
If you want to do zirconium oxide for example, which is a zirconium oxide is a high k dielectric if you want to do zirconium oxide for example you do not really have such a conveniently structured molecule what you have is zirconium acetylacetonate of which this structure you shown here now this is much less suitable for the ALD process as we shall see later.

Now, what are the process parameters for ALD; it is the precursor pulse duration, substrate deposition temperature, substrate temperature, purge duration, pressure all these together for different parameters that control the ALD process. The chemical nature of the precursors themselves of course is fundamental.

Now, what is shown here is a schematic of the what we are going to see next is an ALD cycle, a typical cycle lasts only a few seconds a total cycle and that is illustrated in this particular animation as you will see ok.

So, what we will see is the completion of 4 parts of the cycle and one cycle therefore is repeated to get the desired thickness of whatever film we are interested in. So, thickness is proportional to the total number of ALD cycles so that is the primary metric we have for measuring the thickness or controlling the process.

(Refer Slide Time: 18:35)



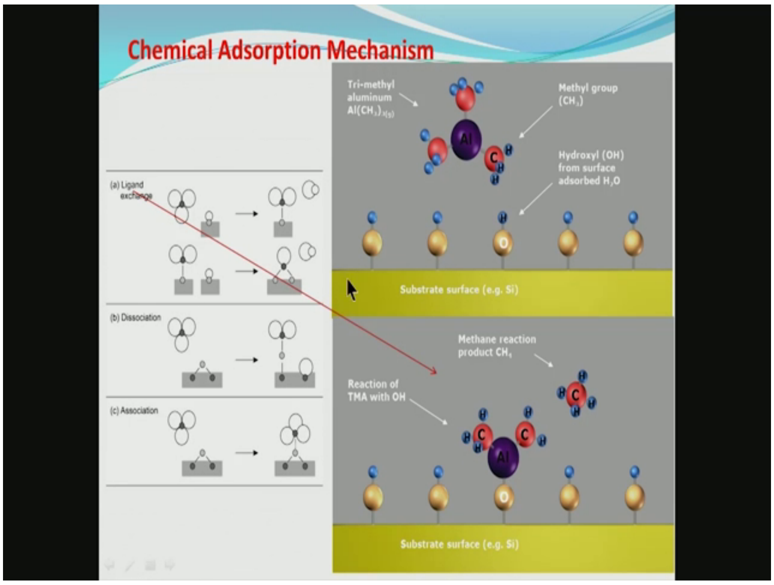
ALD: Primary Characteristics

- The substrate surface must be in a controlled state, e.g., at a constant elevated temperature
- Parameters to be adjusted:
  - Reactants (precursors)
  - Substrate
  - Temperature
  - Precursor Pulse Duration
  - Purge Pulse Duration

Now, what are the requirements or characteristics of the ALD process, the substrate surface must be in a controlled state for example at a constant elevated temperature. The parameters to be adjusted are the reactants, the chemical nature of the reactants or the precursors, the substrate itself, the nature of the substrate, substrate temperature, precursor pulse duration and purge pulse duration. All these variables that are specific to a particular process that is the right choice of these parameters has to be done for the deposition of a particular process particular material by ALD.

Now what ALD involves is the chemical adsorption or the adsorption of the precursors on the surface actually both physical and chemical adsorption are involved in a ALD process in a typical ALD process. So, what you have is precursors coming and landing on the substrate and adsorbing on the substrate.

(Refer Slide Time: 19:46)

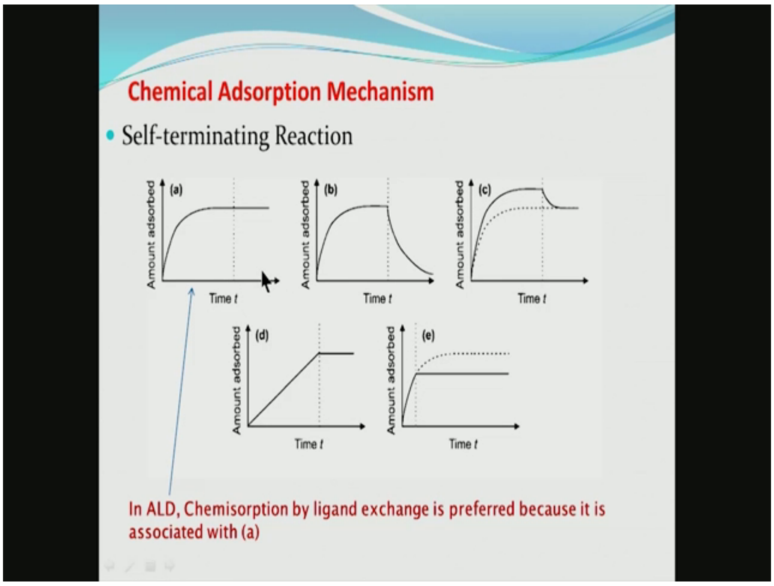

Chemical Adsorption Mechanism

Now, there are different kinds of adsorption mechanisms are chemical processes that involved, when the next precursor comes in that is you have one layer and the next precursor comes in what can happen is Ligand exchange. So, a part of the molecule that comes in then exchanges a part of the molecule that is already adsorbed and that is called ligand exchange and therefore what you are left now is with this kind of a layer as in the case of aluminum oxide or you can have dissociation.

So, if the incoming molecule or incoming precursor molecule dissociates and therefore you have a different kind of as chemical circumstances on the substrate or it can be association, the incoming molecule then gets associated with what is already on the substrate and you have an association so these are different cases.

Now what we saw in the case of aluminum oxide represents ligand exchange that is we now have CH 3 trice Al and then O HOH or water molecule and what we know instead get is out of that a methane molecule and then the dangling bonds of tri methane aluminum on the surface so this is a case of ligand exchange and it turns out that ligand exchange of the sort is more suitable to obtain uniform layers with the ALD process. Now, as I said ALD involves a self terminating surface reaction of an adsorption process.

(Refer Slide Time: 21:16)



Chemical Adsorption Mechanism

- Self-terminating Reaction

In ALD, Chemisorption by ligand exchange is preferred because it is associated with (a)

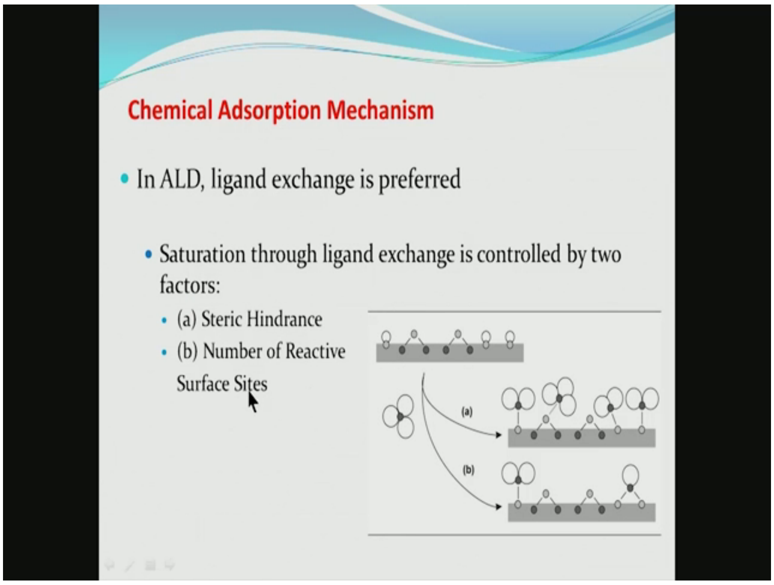
Now it is possible to consider different kinds of self terminating reactions what I have shown here or the amount of adsorbed material as a function of time in 5 different types of adsorption. So, what we now have here is a quick saturation and a complete saturation. Now in the second one in b what you have is saturation but then again desorption and so on.

So, there are different kinds of reactions that can happen on the surface in the ALD process what is desirable is, in ALD chemisorption by the ligand exchange is preferred because it provides us with this rapid saturation and stable saturation as in the figure a over here.

Now, as I said in ALD ligand exchange is preferred and saturation through ligand exchange as in the case of aluminum oxide is controlled by two factors namely: Steric Hindrance and by the number of reactive sites present on the substrate. Now what is Steric Hindrance? Now to have an idea of what is steric hindrance we go over here and look at what zirconium oxide, zirconium acetylacetonate looks like. What you have here is a large molecule the central part represents the precursor namely precursor 2 Zro 2 which is what is desired, but there are many methyl groups that surround the central part of the molecule and these I have to be removed.

But when this molecule adsorbs on the surface then these methyl groups which have to removed cover a lot of area. So when they are gone what you are left with is a much smaller area that this covered by the desired zirconium oxide species and therefore when the next molecule comes here there is a significant amount of void between this Zro 2 entity and the neighboring Z ro 2 entity after the reaction takes place. Therefore the coverage is much less than one mono layer after one cycle and therefore this is called steric hindrance of the process.

(Refer Slide Time: 23:32)



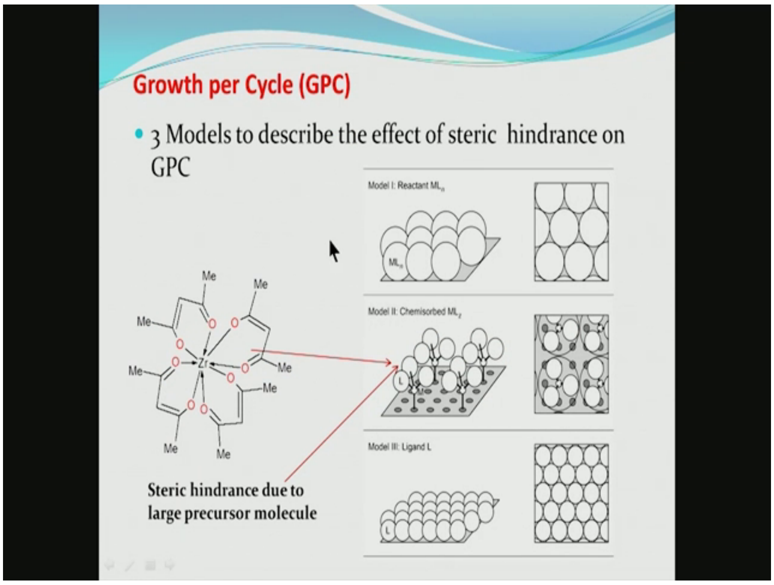
Chemical Adsorption Mechanism

- In ALD, ligand exchange is preferred
  - Saturation through ligand exchange is controlled by two factors:
    - (a) Steric Hindrance
    - (b) Number of Reactive Surface Sites

Now coming back to the steric hindrance case, you can have ligand exchange controlled by 2 factors namely, steric hindrance and the number of reactive sites as shown in this cartoon. Now one parameter that is important is growth per cycle that is the unit that is used in ALD to describe different ALD processes. What is the amount of growth that takes place per ALD cycle.

Now the ideal of course would be to grow one mono layer per cycle, but this does not usually occur due to steric hindrance as I pointed out. Now there are 3 models to describe the effect of steric hindrance on growth per cycle.

(Refer Slide Time: 24:22)



Growth per Cycle (GPC)

- 3 Models to describe the effect of steric hindrance on GPC

Steric hindrance due to large precursor molecule

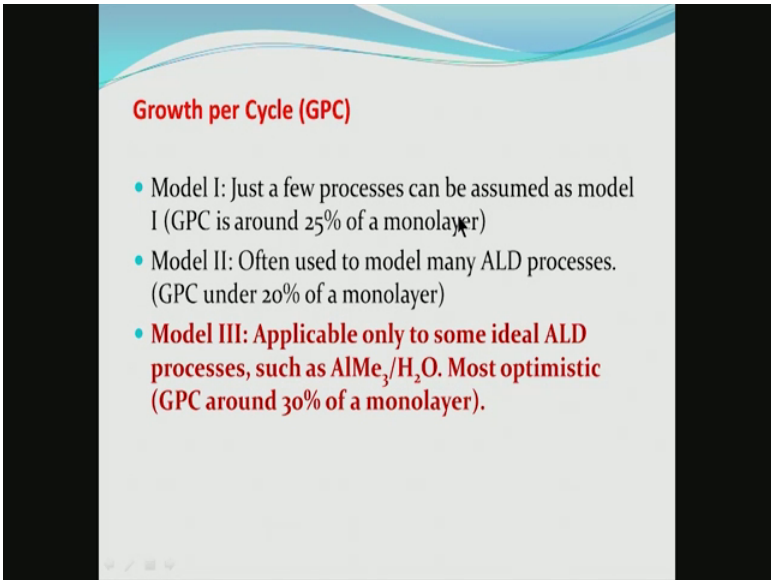
So, what I shown here are 3 different kinds of situations that can arise when we use different kinds of precursors. Now what is shown at the top or model 1 shows a ligand that is rather large in size physical size and therefore when reactions occur there is a significant amount of void that is left on the substrate.

The model 2 is chemisorbed large molecule over here and when that happens as the adjoining figure shows there is a significant amount of void much more than in the case of model 1, a significant amount of void on the substrate as in the case of the zirconium acetylacetonate that I mentioned a while ago.

So, this cannot lead to a complete coverage in one cycle. Now model 3 is the 1, where the size of the ligand molecule here is small and therefore you now have a coverage of the substrate that has much less void than in model 1. Therefore what is ideal for atomic layer deposition is model 3 where you can approach a significantly greater degree of coverage of the substrate per cycle. Now let us look at the numbers.

Now, as I said the case of Al2 O3 using tri methyl aluminum in water is represents this kind of a situation is represented by this kind of a situation where you now have a significant of amount of coverage per cycle. Now the zirconium acetylacetonate, as I already told you represents this kind of a case where there is a large amount of void and therefore, the percentage coverage of the substrate per cycle is bound to be less than in the case of model 3.

(Refer Slide Time: 26:35)



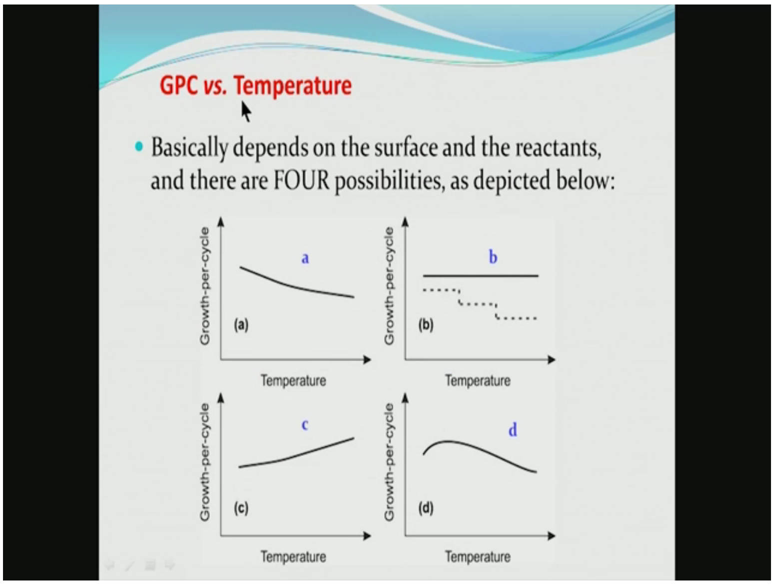
Growth per Cycle (GPC)

- Model I: Just a few processes can be assumed as model I (GPC is around 25% of a monolayer)
- Model II: Often used to model many ALD processes. (GPC under 20% of a monolayer)
- **Model III: Applicable only to some ideal ALD processes, such as $AlMe_3/H_2O$. Most optimistic (GPC around 30% of a monolayer).**

Now, in model 1 which is where I have shown these large ligand molecules, just a few processes can be assumed as model 1. There are not many examples of that and when that is used at 25 percent of a mono layer is formed per cycle only about a quarter of the substrates surface is covered per cycle, the case of zirconium oxide for example would be such a case when zirconium acetylacetonate is used as the precursor.

Model 2 which is where we have these chemisorbed ligands over here is often used to model the ALD process and the percentage coverage is less than 20 percent of a monolayer in such a case large ligand, large void space. Model 3 which is where we have shown these small ligand molecules covering the substrate pretty at a low porosity. Then is applicable to some ideal ALD processes such as, tri methyl aluminum and water and this is the most optimistic one whereby the growth per cycle is about 30 percent of monolayer approximately one-third of the monolayer.

(Refer Slide Time: 27:52)

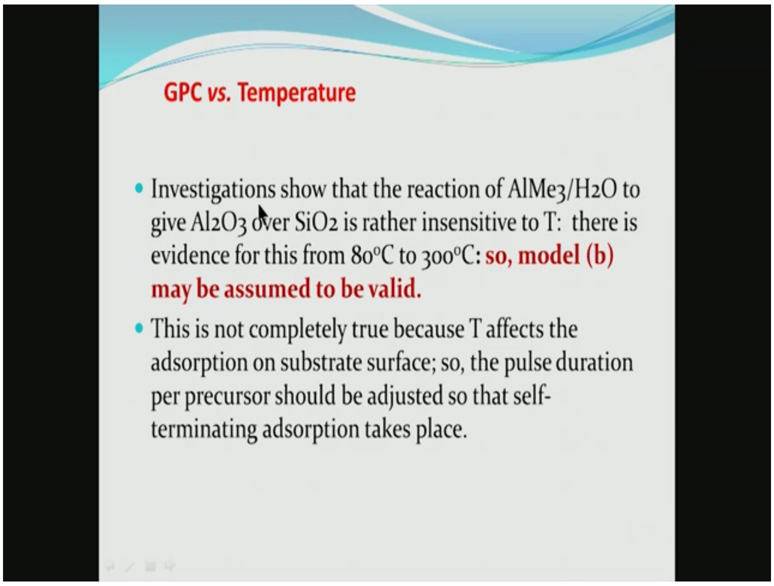


GPC *vs.* Temperature

- Basically depends on the surface and the reactants, and there are FOUR possibilities, as depicted below:

Now how about the growth per cycle and it is dependence on temperature, how does a temperature of the substrate play a role in all these things. Now we have 4 different kinds of variation, one is where the growth per cycle reduces as the temperatures increased, in case b the growth per cycle is independent of temperature and you can really see that such a process where temperature is not a factor would be really desirable in a particle process. Growth per cycle would increase with temperature and growth per cycle in d behaves in an odd way increases then decreases as a function of temperature.

(Refer Slide Time: 28:46)



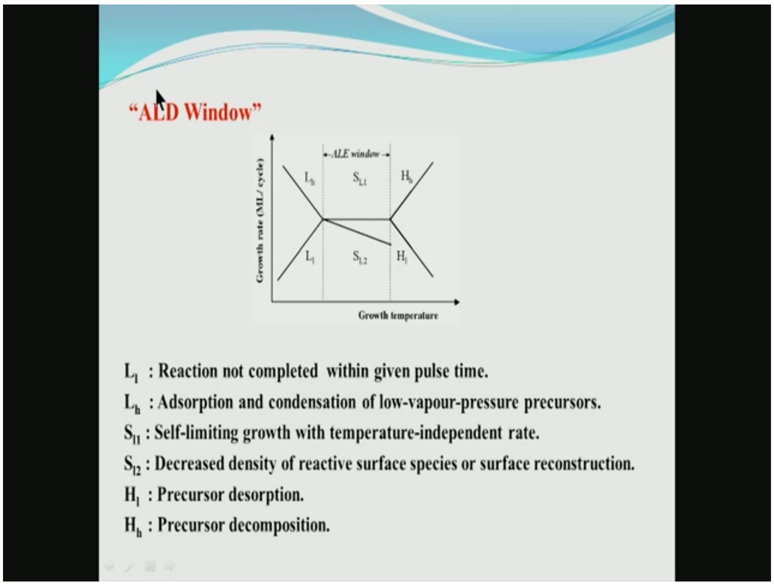
GPC *vs.* Temperature

- Investigations show that the reaction of $AlMe_3/H_2O$ to give Al_2O_3 over SiO_2 is rather insensitive to T: there is evidence for this from 80°C to 300°C: **so, model (b) may be assumed to be valid.**
- This is not completely true because T affects the adsorption on substrate surface; so, the pulse duration per precursor should be adjusted so that self-terminating adsorption takes place.

Now, investigations show that the reaction of trimethyl aluminum with water to give Al 2 O3 on silicon oxide surfaces is rather insensitive to temperature that is it behaves more like b over here where the growth per cycle is independent of the substrate temperature. But this is not completely true because the temperature affects the adsorption and the substrate surface and therefore the pulse duration pulse precursor should be adjusted so that self-terminating adsorption reaction takes place.

So, nevertheless aluminum oxide using tri methyl aluminum and water represents a very good process that describes a temperature independent growth per cycle. Now there is something known as the “ALD window”, Atomic Layer Deposition window that is shown over here.

(Refer Slide Time: 29:34)



“ALD Window”

L_l : Reaction not completed within given pulse time.
L_h : Adsorption and condensation of low-vapour-pressure precursors.
S_{l1} : Self-limiting growth with temperature-independent rate.
S_{l2} : Decreased density of reactive surface species or surface reconstruction.
H_l : Precursor desorption.
H_h : Precursor decomposition.

What is shown here over here is the growth rate that is the growth per cycle as a function of temperature. What you can see is that there are several regimes where growth is increasing with temperature or decreasing with temperature or constant with temperature.

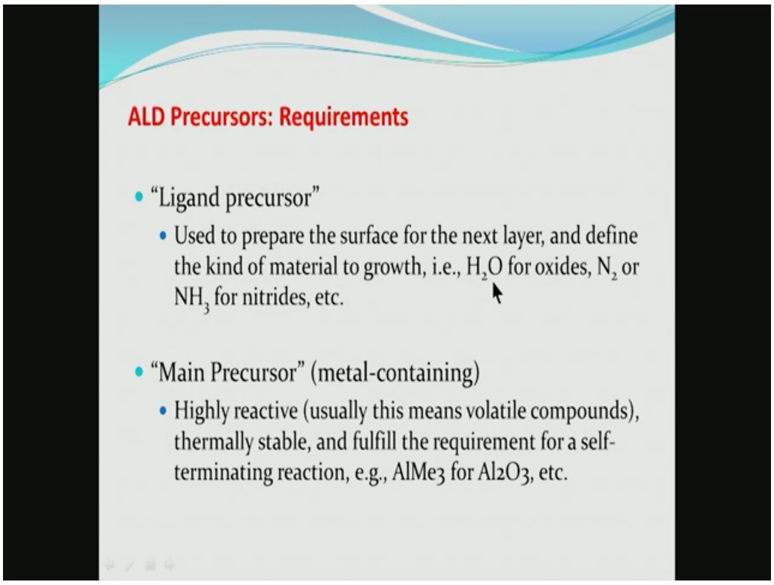
Now, what is shown here in the center is the region what is known as the ALD window, where the temperature is a rather the growth rate is independent of temperature, what happens at low temperature and what happens at high temperature. At low temperature for example in this lower branch the reaction is not completed in the given pulse time and therefore as the temperature increases the reaction rate increases and the growth per cycle increases.

Now, on the upper part of this particular branch what we now have is the reduction in the growth per cycle as a function of increasing temperature. Now what happens is that in this case adsorption and condensation of the precursor takes place without any reaction occurring and therefore actually the growth rate goes down. Now at the high temperature end in this branch of the cycle or in this branch in the curve as a temperature increases desorption takes place rather desorption takes place over here and therefore growth goes down.

Now, over here in this part of the particular diagram if the precursor decomposes as a function of temperature then what we really have is not an ALD process, but a CVD process but growth rate goes up. So, what one wants to have is this kind of a region the ALD window, where the growth rate per cycle or growth per cycle is independent of temperature. And for every pair of ALD reactants one has to examine and identify the ALD window, where the growth is independent of temperature because to have a control process and therefore the number of si number of layers to have that is therefore to determine the number of layers one wants to have to get at given film thickness it is ideal to operate in this ALD window region where the growth rate per cycle is independent of temperature.

Now, what about the precursors? What are the requirements of chemical precursors after all this ALD, is a chemical process. So, what are the requirements of the ALD process, now one can think of describing the 2 precursors by different terminologies ligand precursor. Ligand precursor is used to prepare the surface for the next layer and it defines the kind of material for growth.

(Refer Slide Time: 32:54)



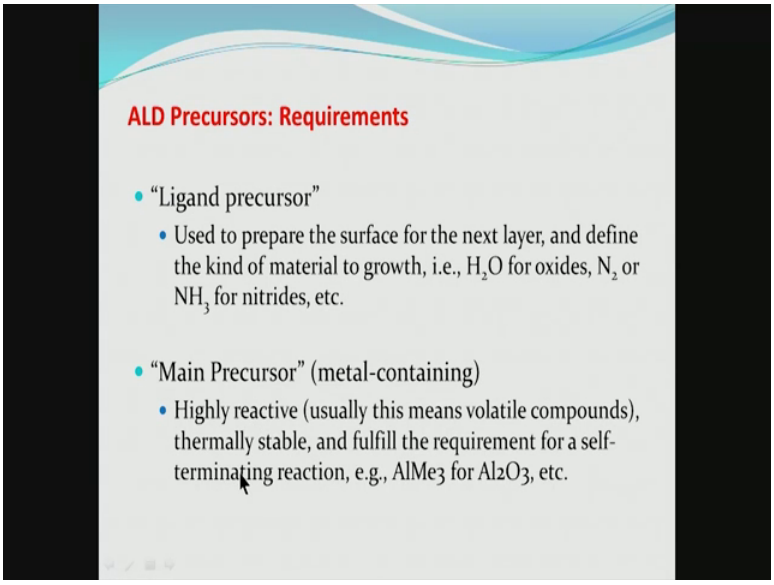
ALD Precursors: Requirements

- "Ligand precursor"
  - Used to prepare the surface for the next layer, and define the kind of material to growth, i.e., H_2O for oxides, N_2 or NH_3 for nitrides, etc.
- "Main Precursor" (metal-containing)
  - Highly reactive (usually this means volatile compounds), thermally stable, and fulfill the requirement for a self-terminating reaction, e.g., $AlMe_3$ for Al_2O_3, etc.

For example water for oxides, nitrogen for nitrates and so on. Remember we came across aluminum oxide we also came across titanium nitride in that Intel device and therefore nitrides are also materials that can be deposited by ALD. So, nitrogen would then be the ligand precursor for forming nitrides just as water is for oxides the so called main precursor is the metal containing precursor.

For example, trimethyl aluminum that we came across and generally one wants to choose a reactive considerably reactive and significantly volatile compound of a given metal as the ALD precursor that is also stable that is it doesn't decompose at the temperature of the substrate therefore it is important to identify the main precursor that is required for the main or the middle precursor that is required for a given process so these precursors have to fulfill requirements for a self terminating reactions such as trimethyl aluminum for Al2 O3 etcetera as we have seen earlier.

(Refer Slide Time: 34:05)

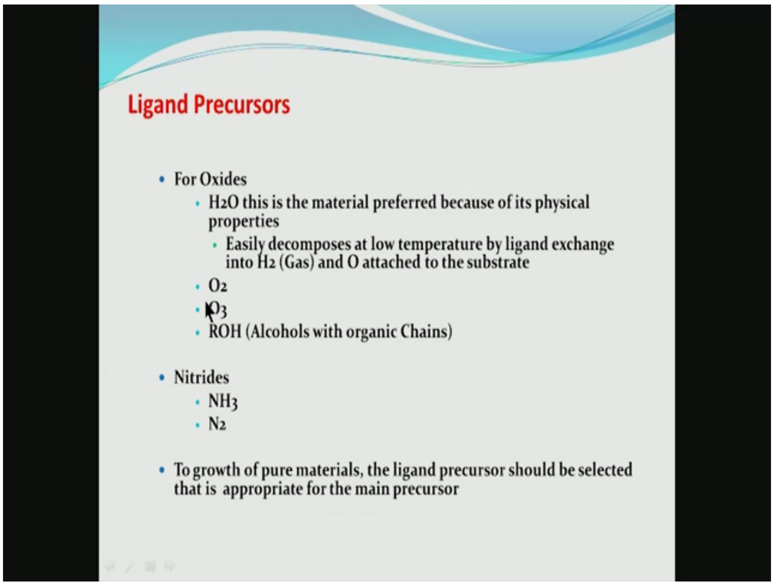


ALD Precursors: Requirements

- "Ligand precursor"
    - Used to prepare the surface for the next layer, and define the kind of material to growth, i.e., H_2O for oxides, N_2 or NH_3 for nitrides, etc.
- "Main Precursor" (metal-containing)
    - Highly reactive (usually this means volatile compounds), thermally stable, and fulfill the requirement for a self-terminating reaction, e.g., $AlMe_3$ for Al_2O_3, etc.

So, these are pretty stringent requirements for identifying ALD reactants for a particular material. Fortunately there is generally speaking is considerable choice of these materials for main precursor for example if one wants to do titanium dioxide layers by ALD, then a compound known as iso titanium isopropoxide is suitable for this purpose and it can be used successfully as the metal containing main precursor for tio 2 deposition

(Refer Slide Time: 34:59)

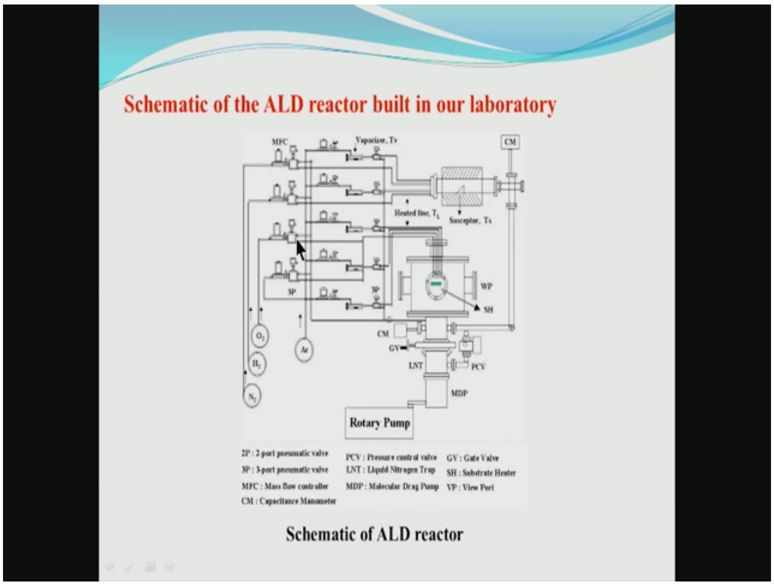


Ligand Precursors

- For Oxides
    - H_2O this is the material preferred because of its physical properties
        - Easily decomposes at low temperature by ligand exchange into H_2 (Gas) and O attached to the substrate
    - O_2
    - O_3
    - ROH (Alcohols with organic Chains)
- Nitrides
    - NH_3
    - N_2
- To growth of pure materials, the ligand precursor should be selected that is appropriate for the main precursor

So, ligand precursors as I already said H 2 O for oxides, it can be oxygen also, sometimes it is advantageous to have ozone because that will be use oxygen radicals which can really speed up reactions, it can also be an alcohol through which one can obtain the hydroxyl group O-H group over here. For nitride silicon precursor would be ammonia and nitrogen and as I said already for the growth of pure materials that is for the deposition of materials that are contamination free then the ligand precursors should be selected that is appropriate for the main precursor so the in other words the choice of precursors is very very important.

(Refer Slide Time: 35:39)



Schematic of the ALD reactor built in our laboratory

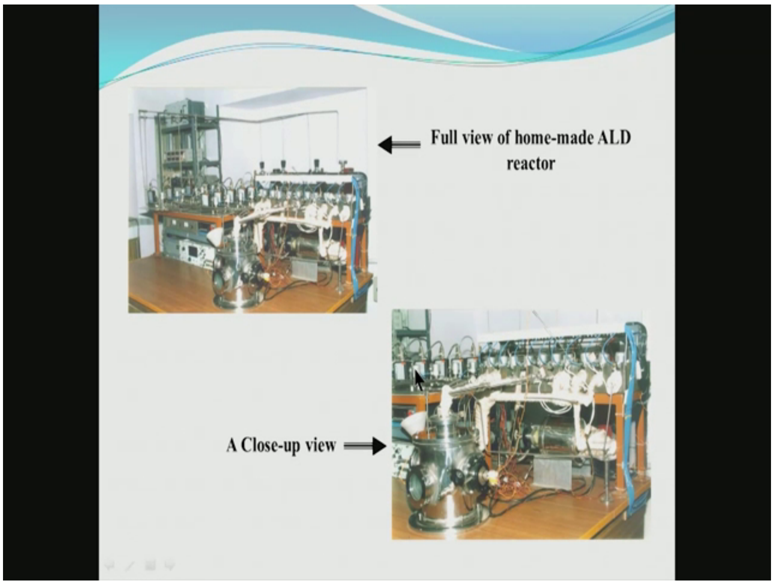
2P : 2-port pneumatic valve
3P : 3-port pneumatic valve
MFC : Mass flow controller
CM : Capacitance Manometer
PCV : Pressure control valve
LNT : Liquid Nitrogen Trap
MDP : Molecular Drag Pump
GV : Gate Valve
SH : Substrate Heater
VP : View Port

Schematic of ALD reactor

What is shown here is a schematic of the ALD reactor, that was built in our laboratory here at the Indian Institute of Science and it is a so called 5 channel reactor that it is possible ideally speaking using this to build a multi layer structure by atomic layer deposition of 5 different components for example 5 different oxides on my it call them laminates of metal oxides. So, this is this as the capacity for doing that.

Now what this one shows is the photograph of this system that of which the schematic shown is here what you see a lot of over here this is a close up.

(Refer Slide Time: 36:25)

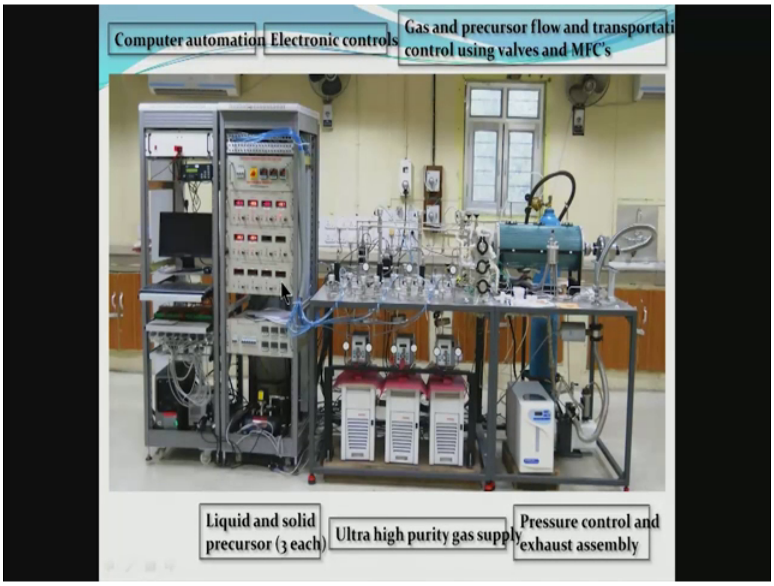


Full view of home-made ALD reactor

A Close-up view

What you see a lot of our pneumatic valves because a significant part of ALD technology, involves fast closing and fast opening pneumatic valves so that precursors can be pulsed into the reactor very quickly so that these total duration of the cycle itself is just a couple of seconds 3 seconds or 5 seconds. So, it is very important to have these high speed valves.

(Refer Slide Time: 36:50)



Computer automation

Electronic controls

Gas and precursor flow and transportati control using valves and MFC's

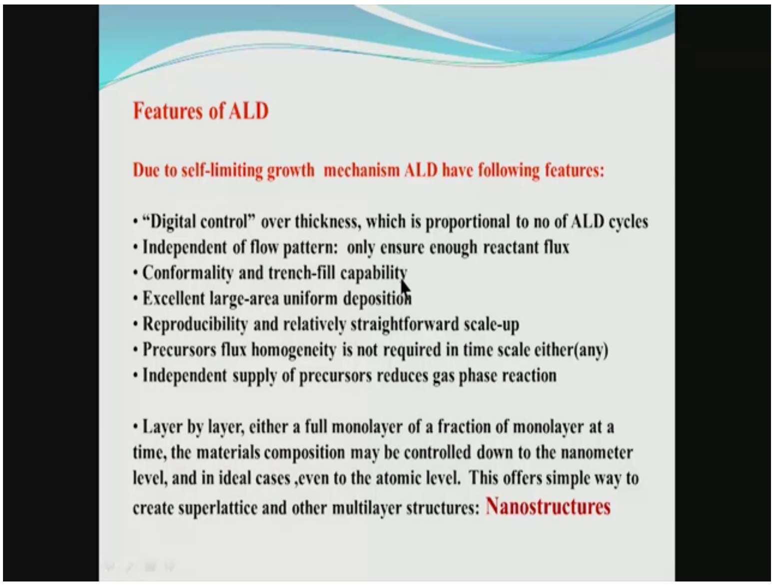
Liquid and solid precursor (3 each)

Ultra high purity gas supply

Pressure control and exhaust assembly

What is shown here is the photograph of a system, that can do both ALD and CVD. So this is the deposition chamber and all of this is valving as I said high speed valve mechanisms for making for switching rapidly between precursors and these are sources where or these are chambers in which precursors are kept at constant temperature so that the dosage in each pulse is exactly the same.

(Refer Slide Time: 37:21)



Features of ALD

Due to self-limiting growth mechanism ALD have following features:

- "Digital control" over thickness, which is proportional to no of ALD cycles
- Independent of flow pattern: only ensure enough reactant flux
- Conformality and trench-fill capability
- Excellent large-area uniform deposition
- Reproducibility and relatively straightforward scale-up
- Precursors flux homogeneity is not required in time scale either(any)
- Independent supply of precursors reduces gas phase reaction

- Layer by layer, either a full monolayer of a fraction of monolayer at a time, the materials composition may be controlled down to the nanometer level, and in ideal cases ,even to the atomic level. This offers simple way to create superlattice and other multilayer structures: Nanostructures

So, what are the features of ALD to summarize: Now due to self limiting growth mechanism ALD has these following features, digital control over thickness which is proportional to the number of ALD cycles as we already mentioned, it is also unlike CVD independent of the flow pattern of precursors, one of the big problems in CVD or at least a an important issue in CVD is the design of the CVD reactor so that the flow is proper in order to obtain a uniform layers of or layers of uniform thickness.

But in ALD, since we are pulsing the precursor there is no flow and therefore all we need to do is to ensure enough of reactants supply through pulsing, conformality and trench-fill capability I have shown already through SEMs earlier of the conformal coverage that ALD is capable of giving and the trench fill capacity that it has got.

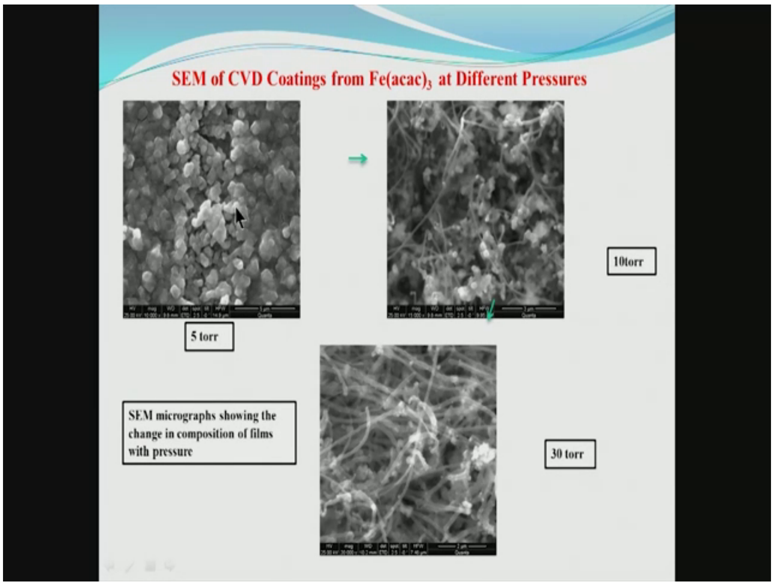
Excellent large area uniform deposition today VLSI circuits are prepared on 300 millimeter substrates and ALD is very suitable for how getting extremely uniform layers of oxide materials and nitrate materials on such substrates. Reproducibility and relatively straightforward scale up that is one can easily scale up from a small substrate to do a large substrate as it has already been done in the VLSI business.

Now because of independent supply of precursors since the precursors are separated in time and space that is two precursors are not in the same chamber in the same at a same time in the chamber at the same time gas phase reactions are reduced or actually eliminated.

So, ALD therefore provides layer by layer growth either a full mono layer or a fraction of monolayer generally a fraction of a monolayer at a time and material composition may be controlled down to the nanometer level and in ideal cases even to the atomic level that is one single layer it is possible to obtain of a given material using the ALD process.

So, this offers a simple way to create super lattice and other multi layer structures also called Nano structures and Nano laminates. Let us look at some of the examples of nano structures and nano materials from CVD and ALD. CVD first what I have shown here are micrographs scanning electron micrographs of a CVD process that uses iron acetylacetonate to produce slightly different materials using pressure as the control. What you have in the left over here top left over here is a process that is conducted at 5 torr relatively low pressure and what we get here it turns out by analysis is iron oxide Fe3 O 4.

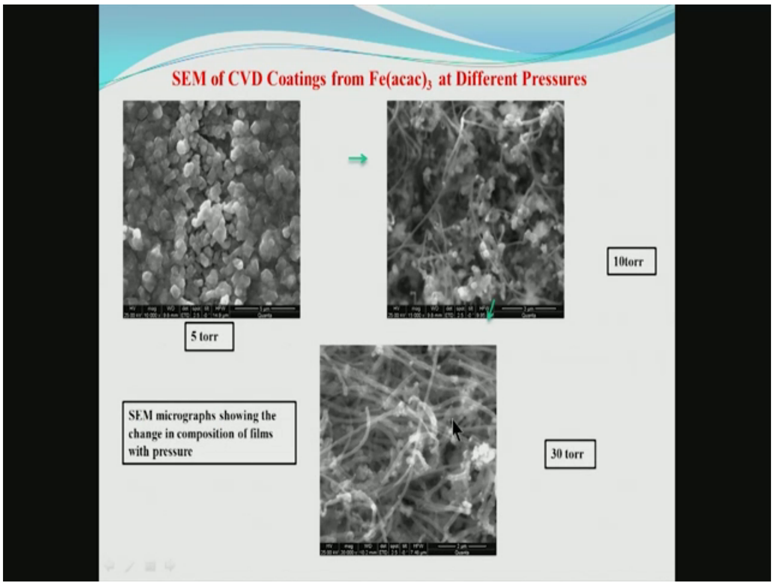
(Refer Slide Time: 40:22)


SEM of CVD Coatings from $Fe(acac)_3$ at Different Pressures

SEM micrographs showing the change in composition of films with pressure

When the pressure is raised to 10 torr, the growth of carbon nanotubes begins simultaneously that is one gets a simultaneous deposition of iron oxide and carbon nanotubes over here. And when the pressure is increased further to 30 torr, then there is a very intimate inter growth of iron oxide and carbon nanotubes which turn out to be multi walled carbon nanotubes.

(Refer Slide Time: 41:18)



SEM of CVD Coatings from Fe(acac)$_3$ at Different Pressures

5 torr

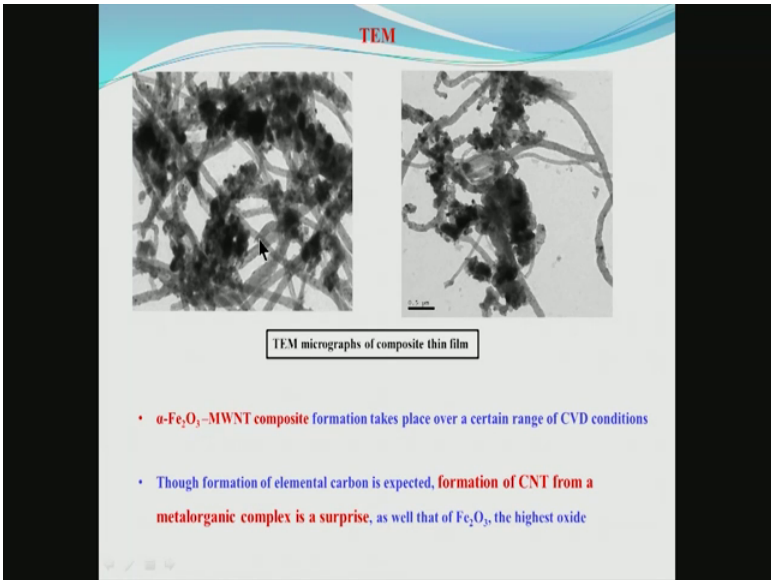
10torr

30 torr

SEM micrographs showing the change in composition of films with pressure

So, this is an example of growing a composite material that contains carbon nanotubes using the CVD process. Now these are transmission electron micrographs of such as film over here as in the bottom so what you see is complete inter growth of iron oxide and carbon nanotubes as you can see here over here.

(Refer Slide Time: 41:31)



TEM

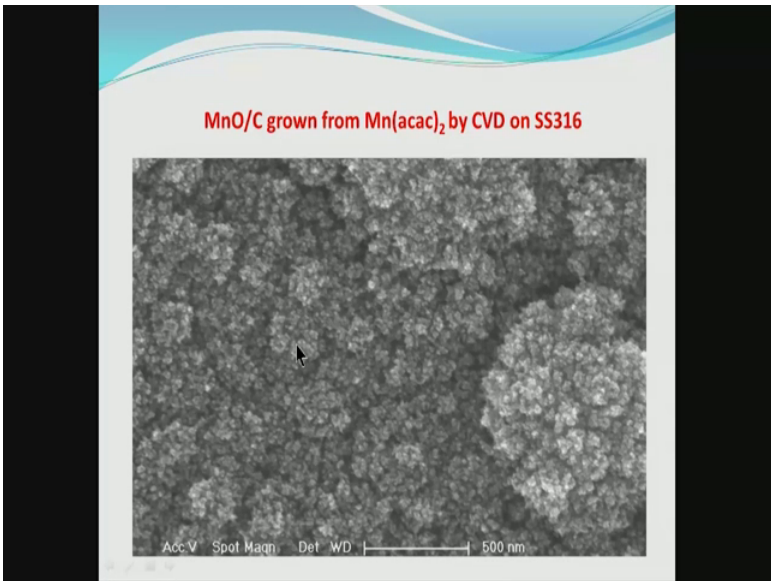
TEM micrographs of composite thin film

- α-Fe_2O_3–MWNT composite formation takes place over a certain range of CVD conditions
- Though formation of elemental carbon is expected, formation of CNT from a metalorganic complex is a surprise, as well that of Fe_2O_3, the highest oxide

So, it turns out also that iron particles are embedded within the carbon nanotubes which actually catalyze the growth of carbon nanotubes in this particular process. Now, what I wanted to say is that here point out here is that what we are using as the precursor here is iron acetylacetonate which is similar in structure to zirconium acetylacetonate which we saw earlier with iron oxygen bonds and then methyl groups on the outer periphery of the molecule.

Now, although carbon nanotubes have been obtained by CVD from various hydrocarbons and alcohols and all that as I have said this turns out to be the first case where carbon nanotubes are obtained from a metal complex where there is a metal oxygen bond, so this is possible by CVD.

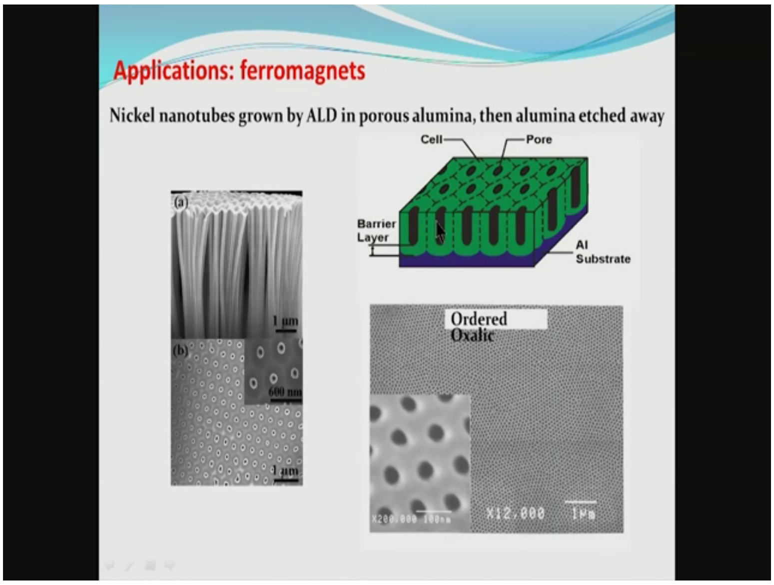
(Refer Slide Time: 42:30)



MnO/C grown from Mn(acac)$_2$ by CVD on SS316

What is shown here is the SEM micrograph, high resolution SEM Micrograph of a composite of manganese oxide and carbon grown from manganese acetylacetonate. Again this compound has manganese oxygen bonds and methyl groups on the periphery of the molecule. So, this is a growth on stainless steel the growth temperatures above 500 degrees rather 700 degrees what you can see is a very porous structure where the particle size is of the order of a few nanometers, tremendous surface area as you can see from here. So it turns out that this material is very good as an electrode for capacitors so called super capacitors.

(Refer Slide Time: 43:14)



Applications: ferromagnets

Nickel nanotubes grown by ALD in porous alumina, then alumina etched away

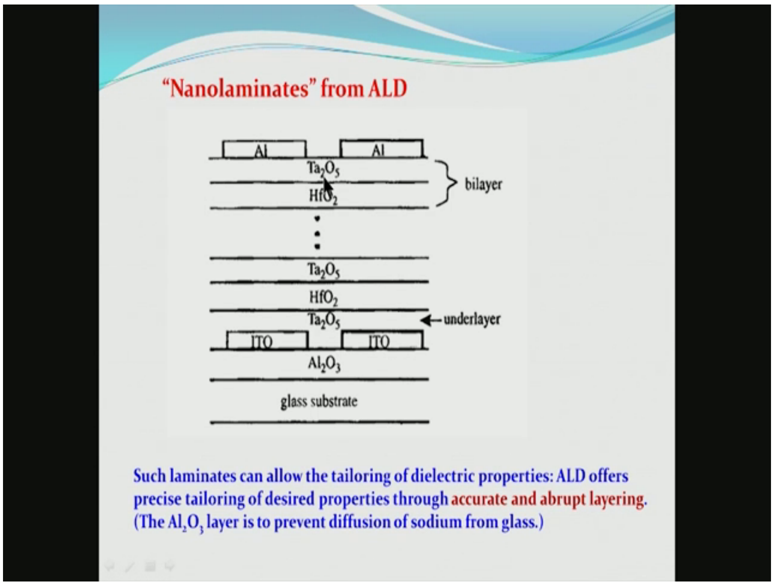
Now, we come to atomic layer deposition using structures that are produced by using anodized alumina to obtain porous alumina porous aluminum oxide so it turns out that by suitable anodization of an aluminum plate it is possible to grow layers of aluminum oxide amorphous aluminum oxide with this kind of an ordered porous structure as you can see here these pores a nanometric in diameter and a few micrometers or so or a few 100 nanometers in depth. So, what you can see here is the uniformity transmission electron micrograph here shows the uniformity of the pores over here on top of this anodize alumina substrate.

So, what these provide are really again as in the case of CMOS circuits, earlier these provide trenches so can these trenches be filled by atomic layer deposition of course, the answer is yes because these the aspect ratio here is not very high. What I forgot to mention earlier when I showed the trench structure in a CMOS device for example, in the DRAM structure ratio that is the ratio of the depth of the trench to the diameter of the trench can be as high as 60. Here is not so high, so it turns out that using the CVD process rather the ALD process it is possible to deposit nickel in these pores of alumina. So, that after the alumina is etched away when the alumina is etched away after the deposition of nickel then what you get are these nanotubes of nickel as you can see here

So, ALD is capable of very nice conformal coverage ceiling of the pores and outer that a very ordered structure of nickel nanotubes nickel being a ferromagnet this can have significant applications. What is shown here is a more complicated structure using porous alumina as before so what is done is of course, to obtain these kind of a porous structure on top 1 alumina plate and then use it as a substrate for film deposition, but in this case it is more complicated so what is done is first a layer of tio 2 is deposited as I mentioned earlier tio 2, can be done using titanium isopropoxide so titanium isopropoxide is done.

Then a layer of aluminum oxide and then filled with another layer of titanium oxide, so what you can see here is these 3 rings represent titanium oxide, aluminum oxide, and titanium oxide again in these ordered pores. So, you can see that is actually as good as very high definition lithography. So, ALD is capable of producing very interesting structures of the sort.

(Refer Slide Time: 46:43)



"Nanolaminates" from ALD

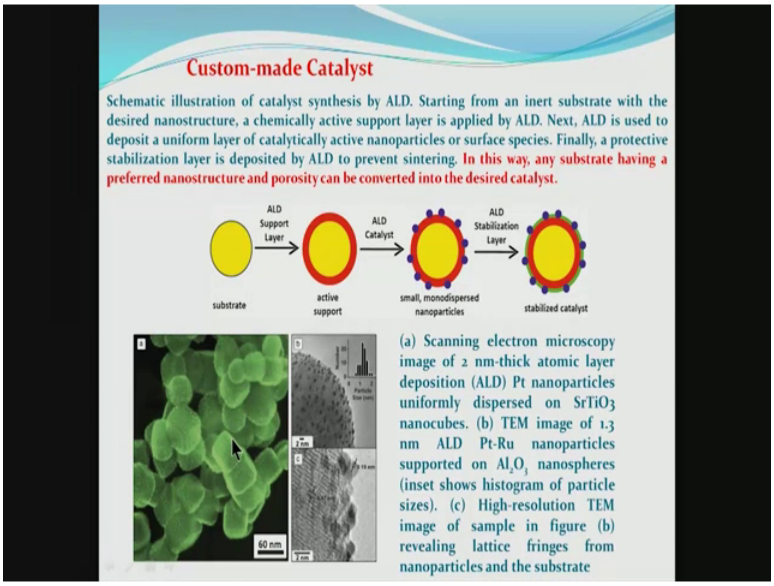
Such laminates can allow the tailoring of dielectric properties: ALD offers precise tailoring of desired properties through accurate and abrupt layering. (The Al_2O_3 layer is to prevent diffusion of sodium from glass.)

Nano laminates I mentioned earlier that it is possible by ALD, to produce multi layered structures. So, what is shown here is a multi layered structure of Ta 2 Ta 2 O5 tantalum oxide in Hf O2 in alternating layers, alternating layers because it turns out that it is possible to control the dielectric properties of such a structure by having these repeated units and controlling the thickness of individual layers.

Therefore, it is possible to Taylor the dielectric properties and it is possible to obtain nano laminates with a desired dielectric constant and desired set of dielectric properties and it also turns out to the ALD is a capable of producing accurate and abrupt layering that is a layer of H f O2 and immediately with very little interface a layer of Ta 2 O5 etcetera, so nano laminates from ALD is possible.

Now, another example so called custom made catalyst. You know catalysis is a very important part of technology and it is possible it turns out using ALD process to design catalysts nano metric design of catalyst, custom made catalyst now. So, what one does is to start with an inert substrate.

(Refer Slide Time: 47:56)



Custom-made Catalyst

Schematic illustration of catalyst synthesis by ALD. Starting from an inert substrate with the desired nanostructure, a chemically active support layer is applied by ALD. Next, ALD is used to deposit a uniform layer of catalytically active nanoparticles or surface species. Finally, a protective stabilization layer is deposited by ALD to prevent sintering. In this way, any substrate having a preferred nanostructure and porosity can be converted into the desired catalyst.

(a) Scanning electron microscopy image of 2 nm-thick atomic layer deposition (ALD) Pt nanoparticles uniformly dispersed on $SrTiO_3$ nanocubes. (b) TEM image of 1.3 nm ALD Pt-Ru nanoparticles supported on Al_2O_3 nanospheres (inset shows histogram of particle sizes). (c) High-resolution TEM image of sample in figure (b) revealing lattice fringes from nanoparticles and the substrate

Let us think of it as some kind of a sphere and that is coated with and so called active support and then the catalysts that we want such as for example platinum is quoted on this you can see that this catalyst is now platinum particles are quoted by ALD and they cover this substrate over here and then ALD is used again to stabilize this thin layer of the catalyst. So, you have 4 steps over here and let us look at an example that illustrates what is being done.

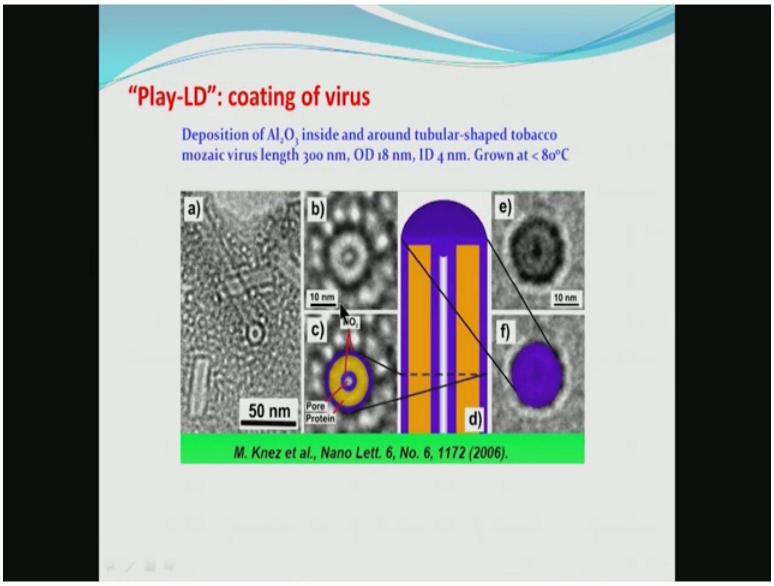
So, what is shown here on the left in green is a high resolution scanning electron micrograph and by the side of it or transmission electron micrograph is the same thing. So, what we have are cubes of strontium titanate, it is possible to obtain nanometric cubes of strontium titanates. Strontium titanate has a cubic structure and therefore the morphology of cubes in nano structures is the natural for earth strontium titanate, although it is not easy to produce them.

And then what is done is using ALD you can see that there are specks, speckles of platinum on top of these cubes. So, these transmission electron micrographs show clearly that there is this tiny platinum particles and therefore very large surface area for them given that they are so tiny and excellent as catalyst. So this TEM micrograph, here actually high resolution hrtm, so called hrtm shows fringes which represent that these platinum particles individual platinum particles are actually single crystalline. So, it is clear from this example that is possible to use ALD to produce custom made catalysts using nano structures.

Finally we can go to an example that may be called a Play-LD, as suppose to ALD play ld one can play with ALD to produce interesting structures. What we have here is deposition of Al 2 O3 and inside and around a tobacco mosaic virus 300 nanometers in length, outer diameter 80 nanometers, inner diameter 4 nanometers all these grown at less than 80 degrees Celsius by ALD.

As I said trimethyl aluminum is a very reactive precursor and trimethyl aluminum when used in combination with water it is possible to or sometimes with ozone it is possible to get reactions that produce Al2 O3 at temperatures as low as eighty degrees, such a low temperature is important because we are dealing with a biological material which is unstable at high temperatures which are typically needed in a ALD.

(Refer Slide Time: 51:13)



"Play-LD": coating of virus

Deposition of Al_2O_3 inside and around tubular-shaped tobacco mozaic virus length 300 nm, OD 18 nm, ID 4 nm. Grown at < 80°C

M. Knez et al., Nano Lett. 6, No. 6, 1172 (2006).

Therefore in this case it is important to conduct the ALD process, at a very low temperature. So, what you can see here is the conformal uniform coverage of these tobacco mosaic virus structure without destroying it because a low temperature has been used.

So, this particular example illustrates both the capability of ALD to produce conformal coverage of nanometric structures, but also ALD is capability with suitable precursors and suitable process engineering to produce oxide coatings aluminum oxide is typically a high temperature oxide, oxide coating at very low temperatures, temperatures as low as that biocompatible with biological materials.

Therefore what we are learned in this particular session is about the ALD process, atomic layer deposition process what we have learned is that it is dependent on self terminating reactions and sequential such self terminating reactions that are repeated in cycles so as to produce layers of great uniformity in thickness as well as layers that cover large substrates and also it is possible to produce multi layered structures and laminates because of the great uniformity that atomic layer deposition provides.

So, ALD therefore because of it is capability to produce these uniform structures because of the capability to produce conformal coverage of very deep trenches in patterns it has become a staple today of CMOS technology and it is used in semiconductor technology widely and it is capable because of it is varies lecture ALD's capable of producing nano structures and nano materials as illustrated by the nano laminates and as illustrated by the custom made nanocatalyst that I just showed you.

Thank you.