Surface Engineering of Nanomaterials

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Lecture - 29
Thin Film Deposition through Gas Phase Techniques

Hello, today we are going start our new lecture on Thin Film Depositions through Gas Phase Techniques. If you remember that in my last previous lectures also, we have discussed about some gas phase techniques, but here in this particular lecture, we are going to discus some advanced gas phase techniques which we are going to use for the modifications for the surface.

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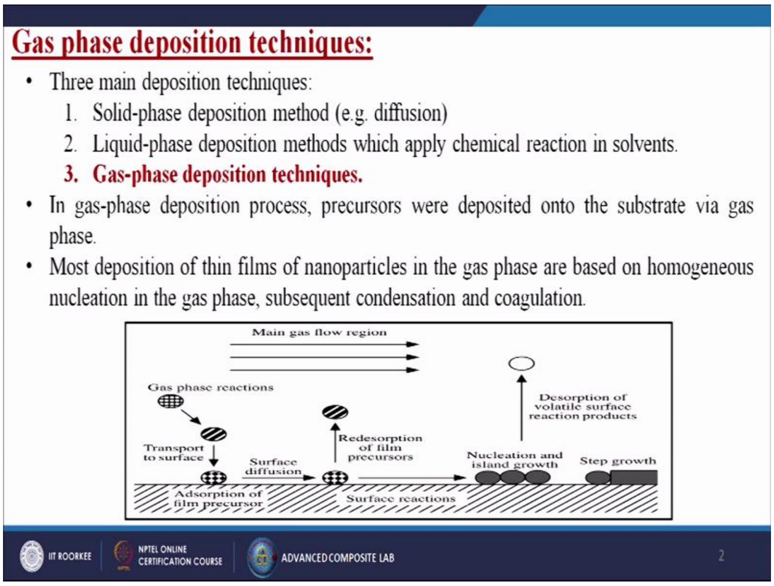

Gas phase deposition techniques:

- Three main deposition techniques:
  1. Solid-phase deposition method (e.g. diffusion)
  2. Liquid-phase deposition methods which apply chemical reaction in solvents.
  3. **Gas-phase deposition techniques.**
- In gas-phase deposition process, precursors were deposited onto the substrate via gas phase.
- Most deposition of thin films of nanoparticles in the gas phase are based on homogeneous nucleation in the gas phase, subsequent condensation and coagulation.

First before going to start, just we have to know little bit about the gas phase deposition techniques. So, as we know that there are several types of deposition techniques which is called the solid deposition techniques where generally solid phase deposition methods, we are going to use like the diffusion process, then we are having that liquid phase deposition method which apply chemical reactions in the solvents and when you are talking about the gas diffusions means we are doing these kind of modifications into the gas phase itself.

In gas phase deposition process, precursors were deposited onto the substrate via gas phase. So, first I am having that precursor or maybe the target materials then I am having the substrate materials. So, I have to heat it or maybe some other means I have to create some kind of vapor or maybe the gas then that vapor or gas will directly go and it will deposit on to the material surface.

The most depositions of thin film of nanoparticles in the gas phase are based on homogeneous nucleation in the gas phase subsequent condensations and the coagulations. So, generally this is the standard method by which we are doing the gas phase depositions. So, from this particular case, we can understand that we are having that thin films, we are flowing the gas on top of that. So, from that gas phase, the molecules is coming then first the adsorption of this film precursor is taking place onto these once then, some kind of volatile gas, it is removing from that particular substrate and then the pure molecules is attaching with the surface then they are doing the reactions then nucleations of the growth is taking place and some kind of volatile surface or maybe toxic gas, it is removing directly coming out from the material surface and by one layer to one layer step growth mechanism by step growth mechanisms the film deposition is taking place.

Now we have to discuss about that as several types of classifications of the gas phase techniques. So, as I already told there are several types of techniques generally we are following.

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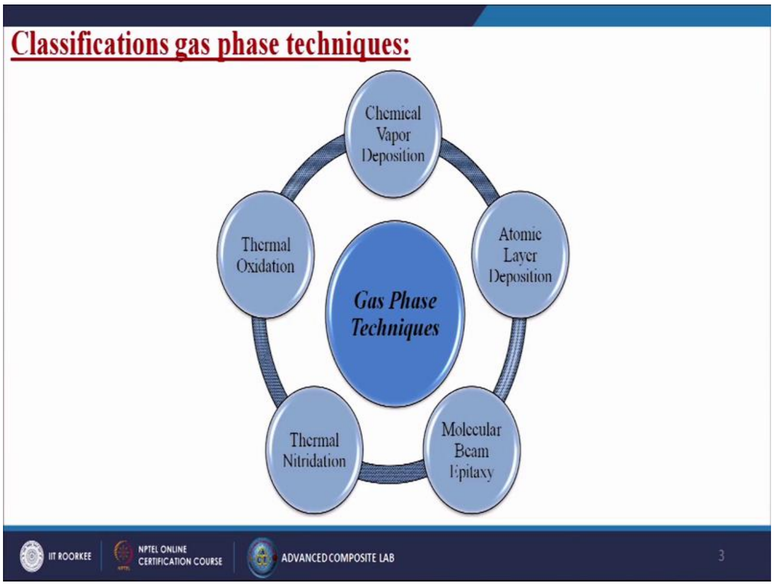

Classifications gas phase techniques:

Gas Phase Techniques

Chemical Vapor Deposition

Atomic Layer Deposition

Molecular Beam Epitaxy

Thermal Nitridation

Thermal Oxidation

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One is called the chemical vapor depositions, in short form generally we are calling it as a CVD process then, atomic layer depositions, ALD process, molecular beam epitaxy, MBE process, thermal nitridations, TN process, thermal oxidations is TO process. So, there are more or less 5 different methods by which we can do the gas phase modifications of nanomaterials.

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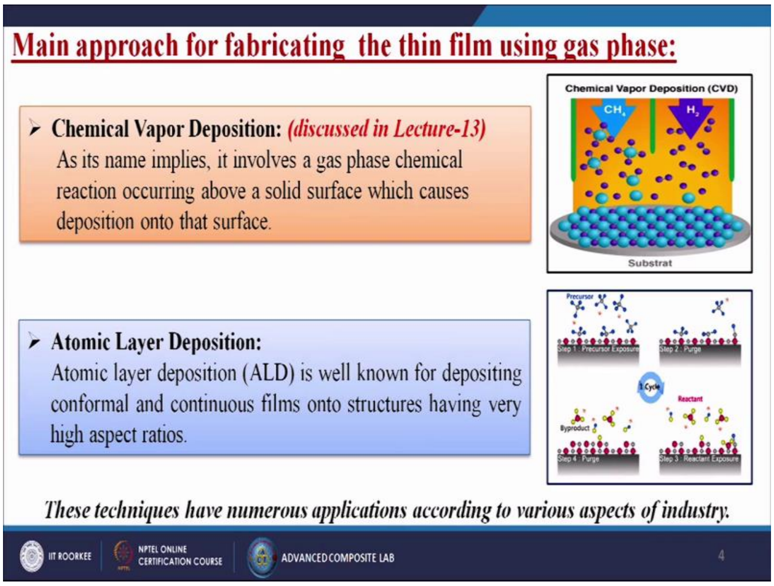

Main approach for fabricating the thin film using gas phase:

- **Chemical Vapor Deposition:** *(discussed in Lecture-13)*
  As its name implies, it involves a gas phase chemical reaction occurring above a solid surface which causes deposition onto that surface.

- **Atomic Layer Deposition:**
  Atomic layer deposition (ALD) is well known for depositing conformal and continuous films onto structures having very high aspect ratios.

These techniques have numerous applications according to various aspects of industry.

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First let us know that what is the chemical vapor deposition; that means, main approach for fabricating the thin film using the gas phase. So as I already discussed that chemical vapor deposition that we have already discussed in our last lectures means lecture number 13 as its name implies, it involves a gas phase chemical reactions occurring about solid surface which cusses deposition onto the surface. So, if you remember that here we are using different kind of vapors that suppose the vapor of vapor of hydrogen then there going and they are reacting on the substrate and they are forming a new material on top of that. So, by this here the generally we are following some kind of chemical reactions. So, that is why it is known as the chemical vapor deposition process.

Next we are going to discuss about the atomic layer deposition process. So, atomic layer deposition is also well known for depositing conformal and continuous films onto structures having very high aspect ratios. So, here also we are taking different kind of precursors. So, either we can take a single precursors, we can take multiple precursor then they will react each other, then they will from some kind of molecules, then that molecules can directly go inside the substrate itself or maybe they can make a layer by layer on to the surface side. So, by this one we are doing the atomic layer depositions of these particular molecules or maybe the atoms.

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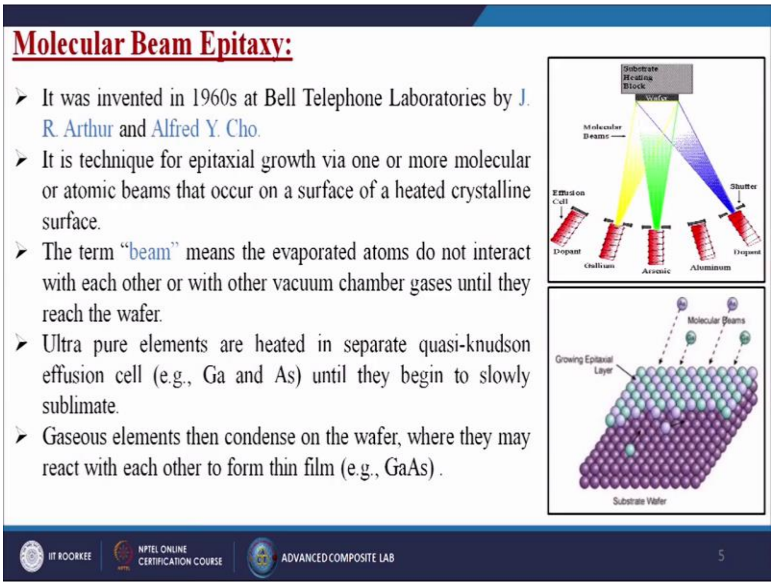

Molecular Beam Epitaxy:

- It was invented in 1960s at Bell Telephone Laboratories by J. R. Arthur and Alfred Y. Cho.
- It is technique for epitaxial growth via one or more molecular or atomic beams that occur on a surface of a heated crystalline surface.
- The term "beam" means the evaporated atoms do not interact with each other or with other vacuum chamber gases until they reach the wafer.
- Ultra pure elements are heated in separate quasi-knudson effusion cell (e.g., Ga and As) until they begin to slowly sublimate.
- Gaseous elements then condense on the wafer, where they may react with each other to form thin film (e.g., GaAs).

Then next one is that molecular beam epitaxy, it is also a one kind of gas phase deposition methods, before going to start about the molecular beam epitaxy, just let us know that what is it actually? So, it was invented in the year 1960s at bell telephone laboratories by J R Arthur and the Alfred Y Cho. So, from the year you can understand that it is not the new one method, it is little bit the older method, but still this is the good method which we can follow.

It is technique for epitaxial growth via one or more molecular or atomic beams that occurs on a surface of a heated crystalline surface. So, generally we are taking it as a heated crystallize surface then top up that we are growing the layer by layer techniques, we are doing the modifications by layer by layer techniques and that is known as the epitaxy film.

Here the term beams means the evaporated atoms do not interact with each other or with other vacuum chamber gases until they reach the wafer. Ultra pure elements are heated in separate quasi Knudsen effusion cells like gallium and arsenic until they begin to slowly sublimate gaseous elements then condense on the wafer, where they may react with each other to form thin film. So, from this particular figure, we can understand that here we are having the substrate then we are having the dopant, gallium, arsenic, aluminum and the dopant itself. So, here this is one kind of gun. So, I am having the substrate air from where dopant is coming then it is giving a layer onto the substrate then gallium is coming, it is giving a layer on to the substrate then arsenic is coming, it is giving a layer on the substrate. So, any kind of combinations of the surface we can do by this kind of molecular beam epitaxy.

And here from this particular figure you can understand that first we have given the arsenic film over there then we are putting the gallium film over there. So, growing the epitaxial layer one by layer, it is forming and then when they are reaching onto the substrate then only they can react with each other, but when we are along them to go up to the substrate a before that they are not reacting each other that is the beauty of this particular techniques.

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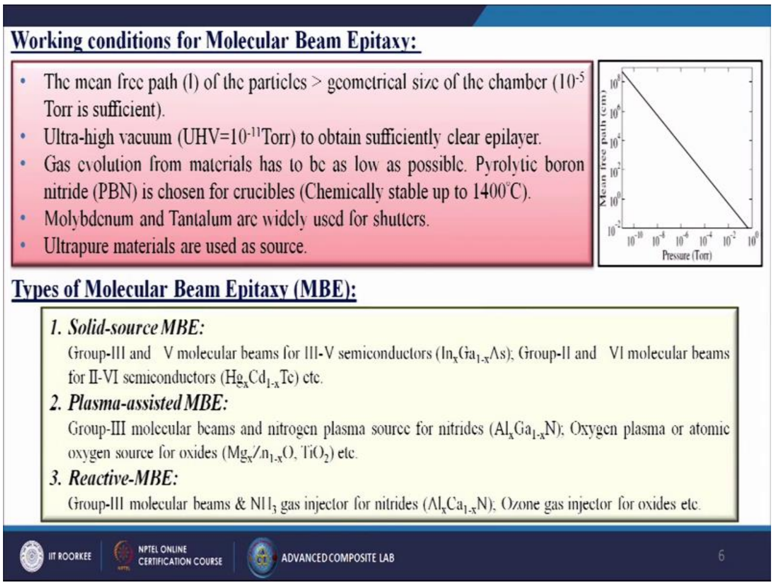

Working conditions for Molecular Beam Epitaxy:

- The mean free path (l) of the particles > geometrical size of the chamber (10^{-5} Torr is sufficient).
- Ultra-high vacuum (UHV=10^{-11}Torr) to obtain sufficiently clear epilayer.
- Gas evolution from materials has to be as low as possible. Pyrolytic boron nitride (PBN) is chosen for crucibles (Chemically stable up to 1400°C).
- Molybdenum and Tantalum are widely used for shutters.
- Ultrapure materials are used as source.

Types of Molecular Beam Epitaxy (MBE):

1. ***Solid-source MBE:***
   Group-III and V molecular beams for III-V semiconductors ($In_xGa_{1-x}As$); Group-II and VI molecular beams for II-VI semiconductors ($Hg_xCd_{1-x}Te$) etc.
2. ***Plasma-assisted MBE:***
   Group-III molecular beams and nitrogen plasma source for nitrides ($Al_xGa_{1-x}N$); Oxygen plasma or atomic oxygen source for oxides ($Mg_xZn_{1-x}O$, TiO_2) etc.
3. ***Reactive-MBE:***
   Group-III molecular beams & NH_3 gas injector for nitrides ($Al_xCa_{1-x}N$); Ozone gas injector for oxides etc.

Now we have to know, what are the working conditions for the molecular beam epitaxy? So, the mean free path of the particles should be more than the geometrical size of the chamber 10 to the power minus 5 Torr is sufficient, yes it is quite natural, suppose I am having that substrate in this particular range and if my molecules pre sample path is less than that. So, what will happen at the time of vapor or maybe the gas it will not directly reach on to the vapor itself. So, it mean path should be more than the distance in between the target material and to the on the substrate material.

Next ultra high vacuum generally UHV is equal to 10 to the power minus 11 Torr, we are telling it to obtain sufficiently clear epilayer; gas evolutions from materials has to be as low as possible pyrolytic boron nitride PBN is chosen for crucibles chemically stable up to 1400 degree centigrade; molybdenum and tantalum are widely used for shutters; ultrapure materials are used as source.

These all are the working conditions for these particular techniques. Now we are going to discuses that there are the also the classifications in between the molecular beam epitaxy methods, what are those? First one is called the solid source MBE. So, group III and V molecular beams for III to V semiconductors just a combinations of indium, gallium and arsenic group II and VI molecular beams for group II to VI semiconductors like GgCd and tellurium, etcetera. Plasma assisted molecular beam epitaxy, group III molecular beams and nitrogen plasma source for nitrides is a combination of aluminum, gallium and the nitrogen, oxygen plasma or atomic oxygen source for oxides; that means, magnesium, zinc, oxygen, zinc oxide or maybe the and the titanium dioxide. Reactive MBE: group III molecular beams and ammonia gas injector for nitrides like aluminum, calcium and nitrogen, ozone gas injector for oxides. So, that is the thing is that how what is the target and what is the gas phase I am going to use actually.

If my target material is totally solid then it is known as a solid beam epitaxy or maybe that solid molecular beam epitaxy, if we are using that materials into the plasma form then it is called the plasma assistant MBE and if we are using certain kind of materials then when it will touch with the wafer it will react or maybe before when we are agitating that materials maybe they can react and they can form a new materials so that is its why it is called the reactive molecular beam epitaxy.

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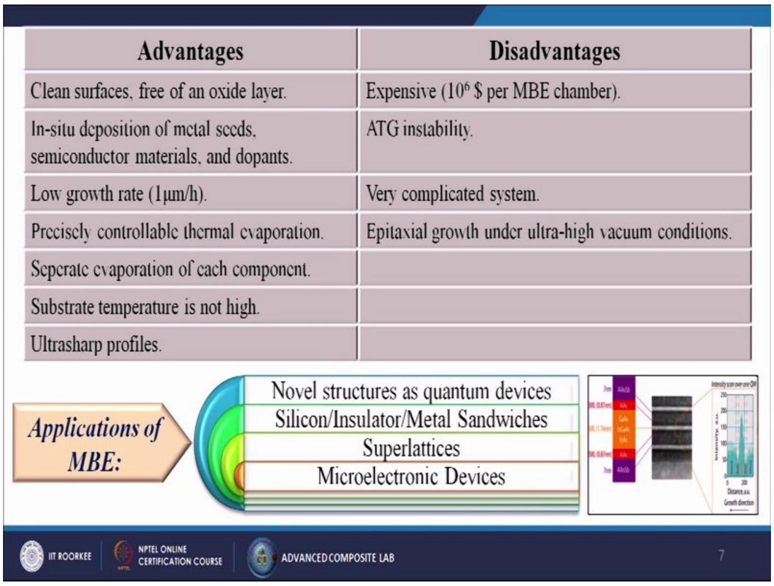

Advantages	Disadvantages
Clean surfaces, free of an oxide layer.	Expensive (10^6 $ per MBE chamber).
In-situ deposition of metal seeds, semiconductor materials, and dopants.	ATG instability.
Low growth rate (1µm/h).	Very complicated system.
Precisely controllable thermal evaporation.	Epitaxial growth under ultra-high vacuum conditions.
Seperate evaporation of each component.	
Substrate temperature is not high.	
Ultrasharp profiles.	

Applications of MBE:

Novel structures as quantum devices

Silicon/Insulator/Metal Sandwiches

Superlattices

Microelectronic Devices

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Now we have to know that what are the advantages and disadvantages of this particular process. So, advantages is that we need the clean surface, free of an oxide layer otherwise whatever those material we generating when that will deposit on to that substrate itself, it will not do the proper adhesions. So, after certain time that layer may come out from the substrate itself.

In-situ depositions of metal seeds semiconductor materials and that dopants, low growth rate, precisely controllable thermal evaporations, separate evaporations of each component, substrate temperature is not high, ultra sharp profiles, these all are the advantages for this particular techniques, but of course, there is certain kind of disadvantages too. First of all, it is very vey expansive process, then very complicated systems, epitaxial growth under ultra high vacuum conditions. So, these all are the different types of disadvantages of this particular process.

Applications, generally we can make some kind of novel structures as quantum devices, silicon, insulator, metal sandwiches, super lattices, microelectronic devices. So, main mainly the application is all the electronic best applications, but some other applications also we can do this kind of coatings.

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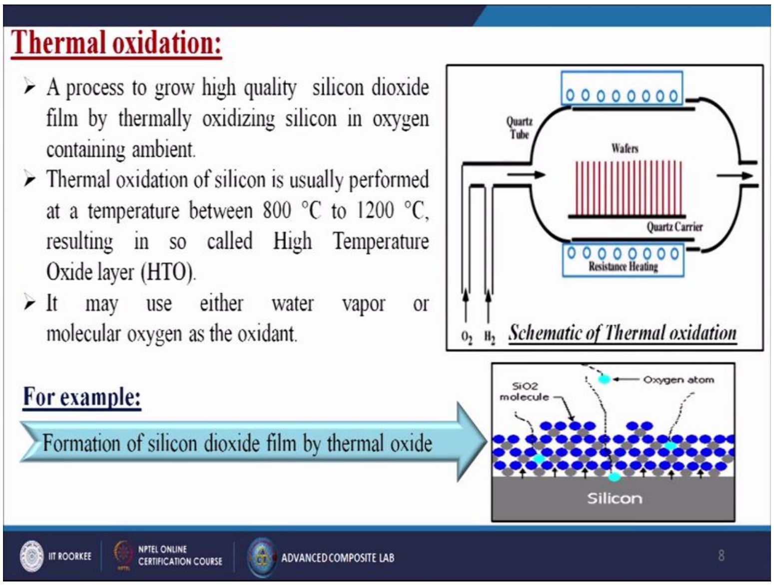

Thermal oxidation:

- A process to grow high quality silicon dioxide film by thermally oxidizing silicon in oxygen containing ambient.
- Thermal oxidation of silicon is usually performed at a temperature between 800 °C to 1200 °C, resulting in so called High Temperature Oxide layer (HTO).
- It may use either water vapor or molecular oxygen as the oxidant.

Schematic of Thermal oxidation

For example:

Formation of silicon dioxide film by thermal oxide

Next one is called the thermal oxidation process. So, in the name itself thermal oxidation means we are using certain kind of heat energy to agitate the materials and by which we are doing the coating. So, what is the definition? A process to grow high quality silicon dioxide film by thermally oxidizing silicon in oxygen containing ambient, so simply we are taking the silicon wafers over there, then we are heating that silicon wafers in to the oxygen environment so that the silicon atoms and the oxygen they can react each other and they can form the silicon dioxide and that silicon dioxide directly we can deposit onto our substrate.

Thermal oxidation of silicon is usually performed at a temperature between 800 degree centigrade to 1200 degree centigrade resulting in so called high temperature oxide layer HTO, it may be used either water vapor or molecular oxygen as the oxidant, either we can put the oxygen gas over there or maybe some kind of water vapor we can put inside the chamber itself and hear hydrogen is nothing but the carrier gas so for examples, formation of the silicon dioxide film by the thermal oxide layer.

Here we are having that oxygen atoms, we are having that SiO 2 molecules then is SiO 2 molecules to getting reacted with the oxygens and they are forming the silicon dioxide on the subtract itself. So, oxides are grown by generally by 3 methods, we can generate this oxide into on to the substrate itself.

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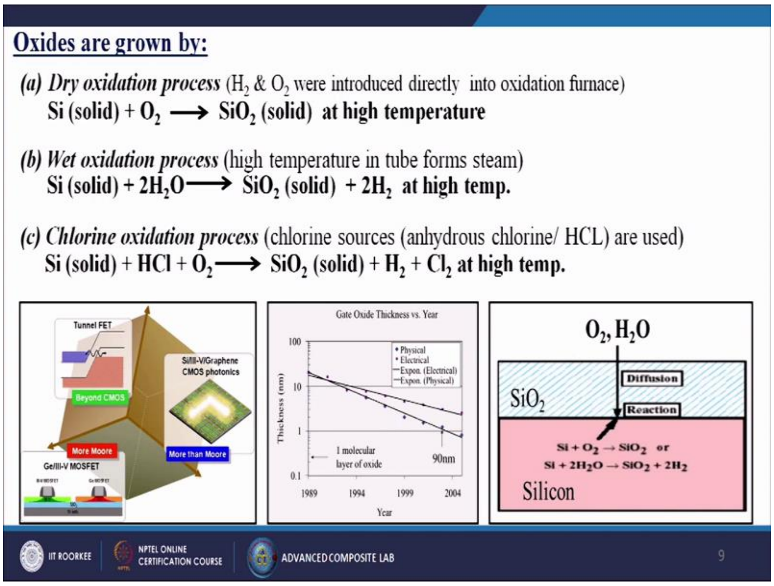

Oxides are grown by:

(a) Dry oxidation process (H_2 & O_2 were introduced directly into oxidation furnace)

Si (solid) + O_2 $\longrightarrow$ SiO_2 (solid) at high temperature

(b) Wet oxidation process (high temperature in tube forms steam)

Si (solid) + $2H_2O$ $\longrightarrow$ SiO_2 (solid) + $2H_2$ at high temp.

(c) Chlorine oxidation process (chlorine sources (anhydrous chlorine/ HCL) are used)

Si (solid) + HCl + O_2 $\longrightarrow$ SiO_2 (solid) + H_2 + Cl_2 at high temp.

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First one is called the dry oxidation process where generally hydrogen oxygen were introduced directly into the oxidation furnace. So, the reactions looks like this silicon is into the solid form plus oxygen, it is forming the silicon dioxide at the high temperature wet oxidation process. So, here the oxygen we are using as a gas and that is the dry one, but when you are talking about the wet oxidation process generally we are using the water vapor over there. So, high temperature in 2 forms streams, so what is the reaction? Silicon solid plus 2 water is equal to it is forming the silicon dioxide solid form and 2 hydrogen gas at high temperature, but when you are talking about the chlorine oxidation process, simply we are replacing the water vapors and instead of that we are putting the hydro chloride gas inside it.

Then the reaction is coming like that silicon plus HCl plus oxygen forming silicon dioxide plus hydrogen plus chlorine at high temperature. So, these all are the different process by which we can do the thermal oxidations. So, from this particular figure, you can understand that we are using this kind of techniques for the electronic purposes like MOSFET, like CMOS, like FET, some kind of graphene CMOS photonics, there are all the lots of applications where we are using the this kind of thermal oxidation process. Here one is the examples that where if we go for the year to year like 1989 to 2004, the thickness of the materials, how we are reaching in to the nanoscale size means the growth of that layer is very very fine on to the substrate itself.

And here this is the reactions which I was talking about. So, we are the silicon surface, then they silicon it is generating the Si ions and then we are adding some kind of oxygen gas and the water vapor or maybe the simple hydrogen gas they are reacting each other and there are forming the silicon dioxide layer on top of the vapor or maybe the substrate.

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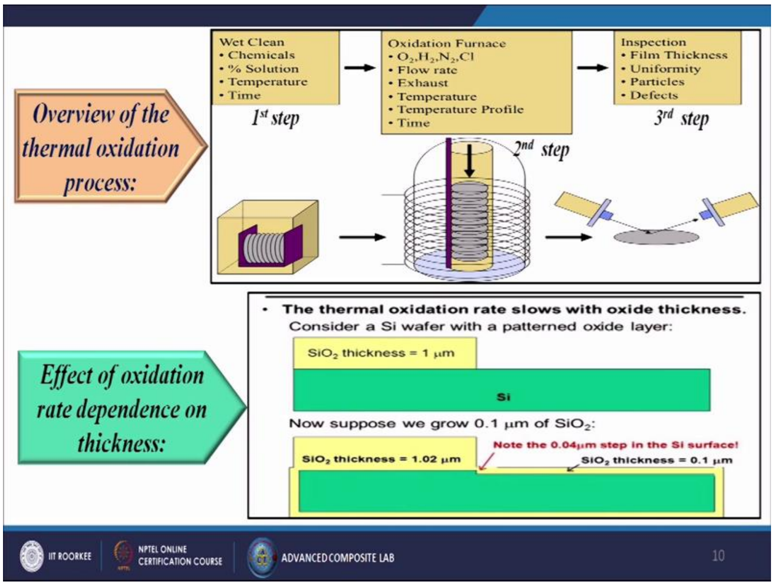

Overview of the thermal oxidation process:

Wet Clean
- Chemicals
- % Solution
- Temperature
- Time

1st step

Oxidation Furnace
- O_2, H_2, N_2, Cl
- Flow rate
- Exhaust
- Temperature
- Temperature Profile
- Time

2nd step

Inspection
- Film Thickness
- Uniformity
- Particles
- Defects

3rd step

Effect of oxidation rate dependence on thickness:

- **The thermal oxidation rate slows with oxide thickness.**

Consider a Si wafer with a patterned oxide layer:

Now suppose we grow 0.1 μm of SiO_2:

Here this is the overview of the thermal oxidation process. So, first step generally we are wet clean by chemical process, by solutions, by temperature or by time. So, we have to clean the surface itself then we have to put the material into the oxidation furnace in the atmosphere of oxygens, hydrogens, maybe nitrogens or maybe chlorine, fluoride we have to maintain, exhaust we have to keep it, then we have the options to increase or decrease the temperature because maybe some times depending upon the temperature various chemical reactions is taking place and then we have to keep the time over there.

Then last one is called the inspections where we can check the film thickness uniformity particles and if there is any defects on to the substrate or not, whether the coating is homogenous or heterogeneous or not or maybe that layer thickness is continues throw out the surface or not.

Then effect of oxidation rates depends on the thickness. So, this is one kind of literature review results, what we have found that the thermal oxidation rates slows with oxide thickness consider a silicon vapor with a patterned oxide layer. SiO 2 thickness is generally 1 micrometer then silicon. Now suppose we grow 0.1 micrometer of silicon dioxide silicon dioxide, thickness will be at the time 1.02 micrometer and here the silicon dioxide thickness will be 0.1 micrometer. Note that: the 0.04 micrometer step in the silicon surface.

As the oxide layer formations will be increasing and increasing so, automatically by normal logic that silicon whatever is coming from the slain or maybe the vapor that quantity will be less. So, automatically the reaction will be also reduced. So, automatically the oxide formation will be going to be decreased. So, then the thickness growth thickness is also will be into the decreasing manner.

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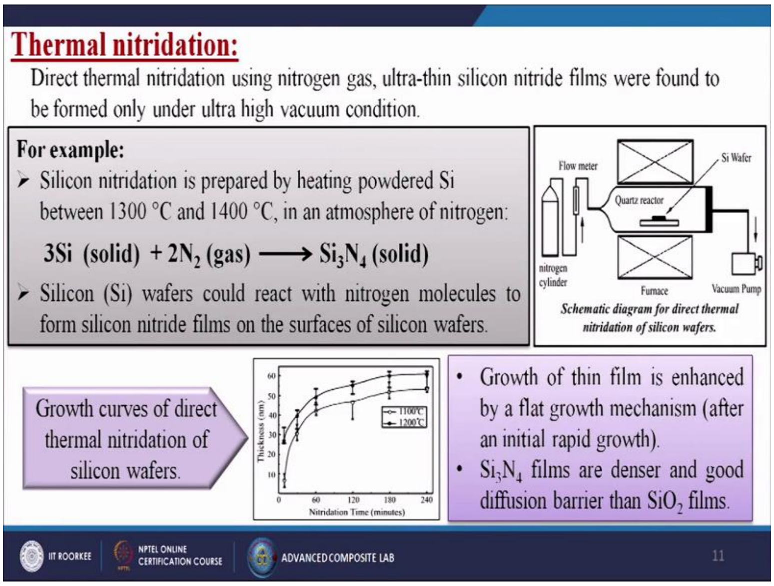

Thermal nitridation:

Direct thermal nitridation using nitrogen gas, ultra-thin silicon nitride films were found to be formed only under ultra high vacuum condition.

For example:

- Silicon nitridation is prepared by heating powdered Si between 1300 °C and 1400 °C, in an atmosphere of nitrogen:

$$3Si\ (solid) + 2N_2\ (gas) \longrightarrow Si_3N_4\ (solid)$$

- Silicon (Si) wafers could react with nitrogen molecules to form silicon nitride films on the surfaces of silicon wafers.

Schematic diagram for direct thermal nitridation of silicon wafers.

Growth curves of direct thermal nitridation of silicon wafers.

- Growth of thin film is enhanced by a flat growth mechanism (after an initial rapid growth).
- Si_3N_4 films are denser and good diffusion barrier than SiO_2 films.

Next one is called the thermal nitridation process. So, direct thermal nitration using nitrogen gas, ultra thin silicon nitride films were to be formed only under ultra high vacuum conditions. So, here generally we are doing the nitridation process, last lecture we are discussing about the oxidation process here we are doing in to the nitrogen atmosphere itself.

Here how we are doing? We are taking the silicon nitridation is prepared by heating powdered silicon between 1300 degree centigrade to 1400 degree centigrade in an atmosphere of nitrogen, just here we are replacing the oxygen gas, we are replacing the hydrogen gas and we are introducing the nitrogen gas that is why this process is known as the thermal nitridation process.

Here we are taking the silicon then with the nitrogen and we are forming the silicon nitride materials. So, silicon wafers could react with nitrogen molecules to form silicon nitride films on the surface of silicon wafers. So, here this is the schematic diagram of direct thermal nitridations of silicon wafers. So, we are having the nitrogen cylinder then we are having some flow minute flow meter by which we can control the flow of that particular nitrogen inside the chamber itself then we are having that silicon wafer, simply that nitrogen is going into the quartz reactor then we are keeping it into the fun vacuum pump so that inside is the vacuum then we are putting the whole reactor on to the furnace so that we can increase or decrease the heat on the substrate then the nitrogen is reacting with that surface and they are forming the silicon nitride. This is the fair growth curve for the direct thermal nitridations of silicon wafers.

So, if we increase the nitridation times, it minutes automatically we can see that thickness is also increasing. So, here we have seen that at 2 temperatures, how the growth mechanism is taking place? One is called the 1100 degree centigrade; another one is called the 1200 degree centigrade. So, growth or thin films enhanced by a flat growth mechanism after an initial rapid growth. So, simply if we keep that experiment for a longer time. So, automatically our thickness of that coating will be automatically increased and then silicon nitride films are denser and good diffusion barriers than the silicon oxide films this is the added advantage for the thermal nitridations over thermal oxidation process.

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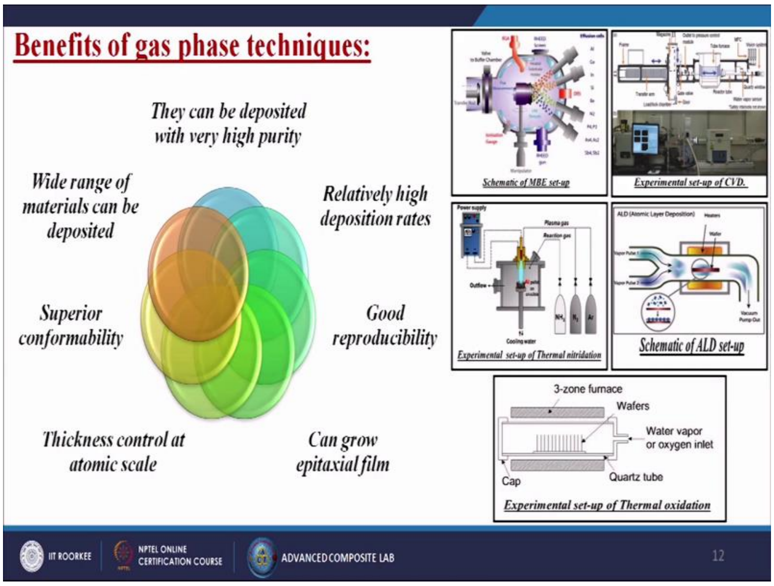

Benefits of gas phase techniques:

They can be deposited with very high purity

Wide range of materials can be deposited

Relatively high deposition rates

Superior conformability

Good reproducibility

Thickness control at atomic scale

Can grow epitaxial film

Benefits of the gas phase techniques. So, there are lots of benefits, generally we can get it by this technique itself, what are those? First one is called that they can be deposited with very high purity. So, here the incorporations of the impurity is very very less then relatively high deposition rates because it is control level it depends upon the gas flow rate, it depends upon the target materials, it depends upon the how much energy I am putting onto the target material. So, it is totally under control.

Then good reproducibility; that means, if the same sample I am doing it today and if the same sample it I can do it tomorrow also whatever the properties in terms of thickness layer homogenizations everything it will be almost same. So, that is why it can reproduce the same results in future also can grow the epitaxial film by layer by layer method it can grow onto the substrate itself. Thickness control at atomic scale auto already I have discussed that thickness control is very very controllable by these methods superior conformability and the wide range of materials can be deposited more or less any materials which can we can put into directly into the vapor or gas phase that material can be easily taken out and can be used for this particular purpose.

Here these all are the schematic diagram already what we have discussed till now. So, schematic of MBE setup then experimental setup of the chemical vapor deposition process schematic presentations of the atomic layer deposition setup experimental setup of the thermal nitridation process and the last one is the experimental setup of thermal oxidation process. So, it is giving you a more or less the glimpse about the whole lecture.

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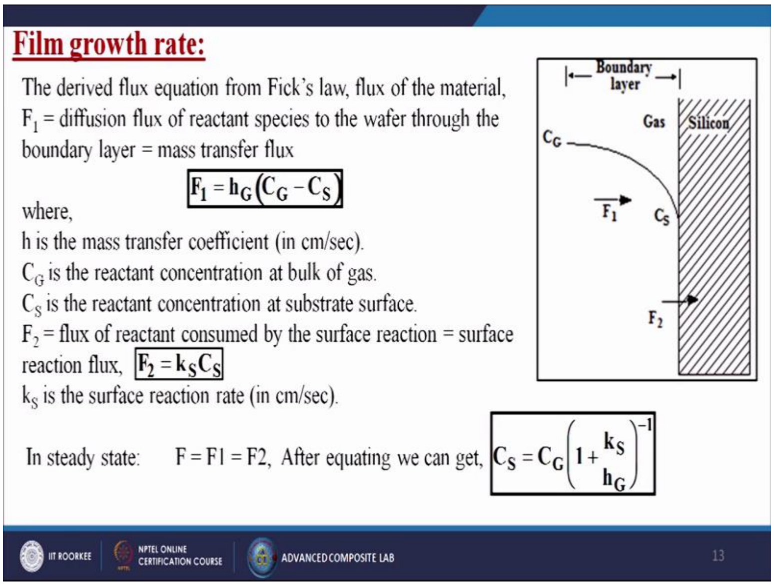

Film growth rate:

The derived flux equation from Fick's law, flux of the material, F_1 = diffusion flux of reactant species to the wafer through the boundary layer = mass transfer flux

$$\boxed{F_1 = h_G(C_G - C_S)}$$

where,

h is the mass transfer coefficient (in cm/sec).

C_G is the reactant concentration at bulk of gas.

C_S is the reactant concentration at substrate surface.

F_2 = flux of reactant consumed by the surface reaction = surface reaction flux, $\boxed{F_2 = k_S C_S}$

k_S is the surface reaction rate (in cm/sec).

In steady state: F = F1 = F2, After equating we can get, $\boxed{C_S = C_G\left(1+\frac{k_S}{h_G}\right)^{-1}}$

Then we have to discuss because till now we are discussing about the different deposition techniques. Now we are discussing that how the film is forming onto the substrate itself. So, the derived flux equations from the Fick's law flux of the material F one diffusion flux of reactant species to the wafer through the boundary layer is equal to mass transfer flux. So, here we are having that silicon on top of that we are doing the coating. So, this is called the boundary layer by which we can grow the film onto this wafer itself.

The famous equations calling it as a Fick's law that is F 1 is equal to H g, in the first bracket C G minus C S. So, where H is the mass transfer coefficient in centimeter per second, C G is the reactant concentrations at bulk of gas, C S is the reactant concentrations at substrate surface, F 2 flux of reactant consumed by the surface reactions, surface reaction flux F 2 is equal to k S into C S - where k is the surface reactions rate in centimeter per second in steady state if F equal to F 1 is equal to F 2 after equating, we can get C S is equal to C G into 1 plus k S by H g to the power minus 1.

By applying this law, we can easily get the film growth rate of that onto the substrate itself and before going to know that the film growth rate, we have to know all these values. So, simply we have to take all these values we have to keep put into these all these equations and automatically we can get the film growth rate. So, depending upon that we can increase or decrease the gases flow rate or maybe that energy what we are applying for the target itself. So, there are lots of input parameters by which we can easily control the film growth rate on to the substrate itself.

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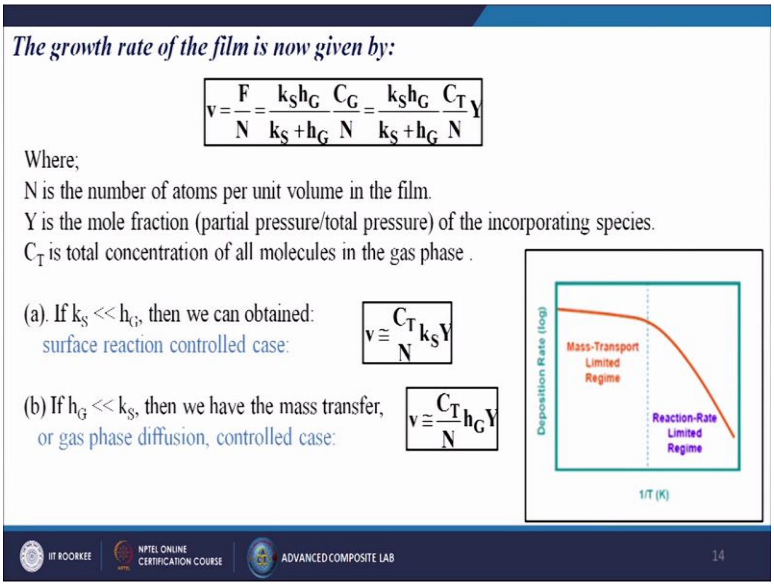

The growth rate of the film is now given by:

$$\boxed{v = \frac{F}{N} = \frac{k_S h_G}{k_S + h_G}\frac{C_G}{N} = \frac{k_S h_G}{k_S + h_G}\frac{C_T}{N}Y}$$

Where;
N is the number of atoms per unit volume in the film.
Y is the mole fraction (partial pressure/total pressure) of the incorporating species.
C_T is total concentration of all molecules in the gas phase .

(a). If $k_S << h_G$, then we can obtained:
surface reaction controlled case:

$$\boxed{v \cong \frac{C_T}{N} k_S Y}$$

(b) If $h_G << k_S$, then we have the mass transfer,
or gas phase diffusion, controlled case:

$$\boxed{v \cong \frac{C_T}{N} h_G Y}$$

Now, the growth rate of the film is now given by the equations is called the v is equal to F by N which is nothing, but the k S into h G divided by k S plus h G into C G by N is nothing but the case h G C T Y by k S plus h G into N where N is the number of atoms per unit volume in the film itself, Y is the mole fractions partial pressure by total pressure of the incorporating species is C T is the total concentration of all molecules in the gas phases. So, if that k S is lesser than the h G then we can obtain surface reaction controlled case that is v is equal to C T by N k S Y, if h G is less than the case then we have the mass transfer or gas phase deposition controlled case where v more or less equal to CT by N into A G Y. So, this is the equations over there.

Here this is the mass transfer in limited regime and this is the reaction rate limited regime in terms of temperature and this one is the diffusion rate in the logarithmic form. So, here first the mass transport is taking place then slowly slowly the reaction rate is going down. So, by these equations we can easily understand that what is the thin film growth rate onto the substrate itself.

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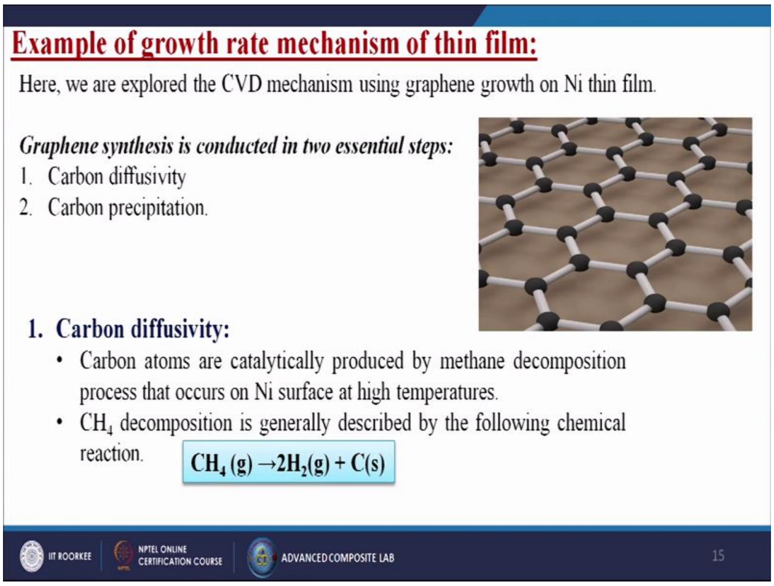

Example of growth rate mechanism of thin film:

Here, we are explored the CVD mechanism using graphene growth on Ni thin film.

Graphene synthesis is conducted in two essential steps:

1. Carbon diffusivity
2. Carbon precipitation.

1. Carbon diffusivity:

- Carbon atoms are catalytically produced by methane decomposition process that occurs on Ni surface at high temperatures.
- CH_4 decomposition is generally described by the following chemical reaction.

$$CH_4\,(g) \rightarrow 2H_2(g) + C(s)$$

Here we are giving one example of the growth rate mechanisms of thin films by the CVD methods means chemical vapor deposition methods. So, here we are explored the CVD mechanisms using graphene growth on nickel thin film. So, graphene synthesis is conducted in 2 essential steps, one is called the carbon diffusivity methods, another one is called that carbon precipitation methods.

First one is called the carbon diffusivity methods. So, carbon atoms are catalytically produced by methane decomposition process that occurs on nickel surface at high temperatures methane composed decomposition is generally described by the following chemical reactions. Methane into the gas form it is divided into the hydrogen and into the carbon so that carbonate it is creating some kind of layer then which is forming the graphene.

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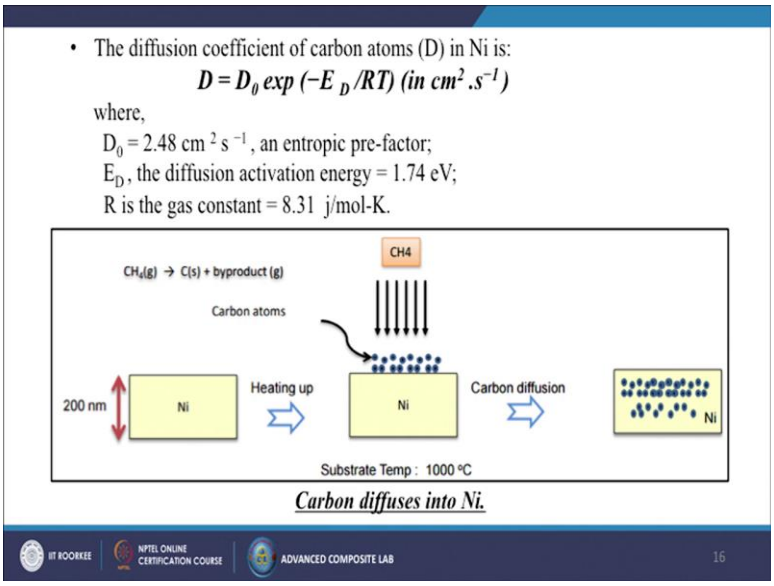

- The diffusion coefficient of carbon atoms (D) in Ni is:

$$D = D_0 \exp(-E_D/RT)\ (\text{in } cm^2.s^{-1})$$

where,
$D_0 = 2.48\ cm^2\ s^{-1}$, an entropic pre-factor;
E_D, the diffusion activation energy = 1.74 eV;
R is the gas constant = 8.31 j/mol-K.

Carbon diffuses into Ni.

The diffusion coefficient of carbon atoms in nickel is D equal to D 0 exponential mine into minus E D by RT in centimeter square per second where D 0 is nothing but the 2.4248 centimeter square per second and entropic pre factor E D is the diffusion activation energy that is 1.74 electron volt, R is the gas constant that equal to 8.1 joule per mole Kelvin. So, by knowing this one we can easily calculate the diffusion of coefficient of the carbon atoms.

Here this is the whole schematic diagram that how we are following the graphene. So, we are having that nickel. So, which is having that 200 nanometer thickness, we are heating that materials then simply we are purging the methane gas inside the chamber. So, when these methane gas is coming with the nickel simple, it is forming some kind of carbon atoms on to the substrate itself then these carbon atoms is going inside the nickel wafer or maybe that substrate onto the nickel wafer itself.

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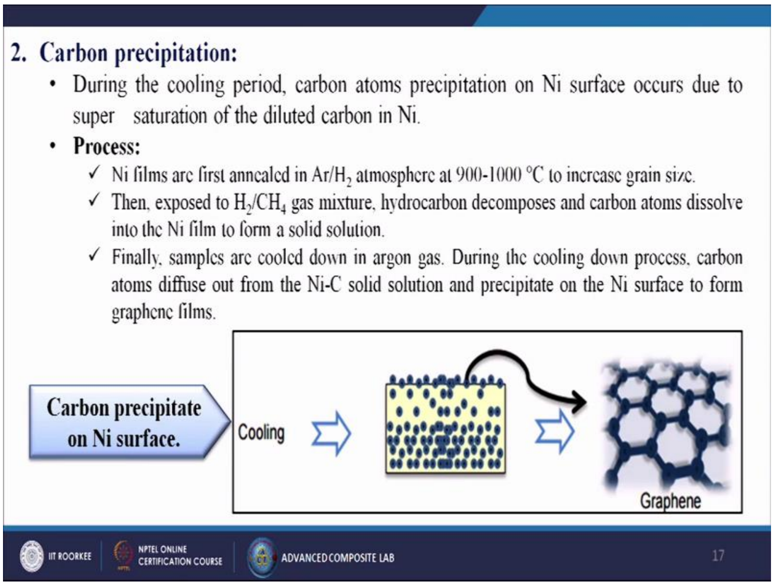

2. Carbon precipitation:

- During the cooling period, carbon atoms precipitation on Ni surface occurs due to super saturation of the diluted carbon in Ni.
- **Process:**
  - ✓ Ni films are first annealed in Ar/H_2 atmosphere at 900-1000 °C to increase grain size.
  - ✓ Then, exposed to H_2/CH_4 gas mixture, hydrocarbon decomposes and carbon atoms dissolve into the Ni film to form a solid solution.
  - ✓ Finally, samples are cooled down in argon gas. During the cooling down process, carbon atoms diffuse out from the Ni-C solid solution and precipitate on the Ni surface to form graphene films.

Carbon precipitate on Ni surface.

Carbon another process is known as the carbon precipitation process. So, where during the cooling period carbon atoms precipitation on nickel surface occurs due to super saturations of the diluted carbon in the nickel metals.

Process: nickel films are most fast annealed in argon hydrogen atmosphere at 900 to 1000 degree centigrade to increase the grain size then exposed to hydrogen and methane gas mixture hydrocarbon decomposes and carbon atoms dissolves into the nickel film to form a solid solutions. Finally, samples are cooled down in argon gas during the cooling down process carbon atoms diffuse out from the nickel carbon solid solutions and precipitate on the nickel surface to form the graphene films.

Actually the thing is that first we are taking the nickel substrate, then we are purging the methane gas, then some kind of atoms it is forming, it is going inside the nickel materials then when we are cooling that material simply that molecules is nickel carbon molecules, it is directly coming and then carbon is substrating or maybe the graphene is depositing on to the nickel surface itself. Here the carbon precipitates on nickel surface while cooling. So, whatever the nickel carbon atoms or carbon atoms it went inside. So, simply it is coming and it is depositing onto the surface of that nickel form nickel substrate and then it is forming the graphene structure over there.

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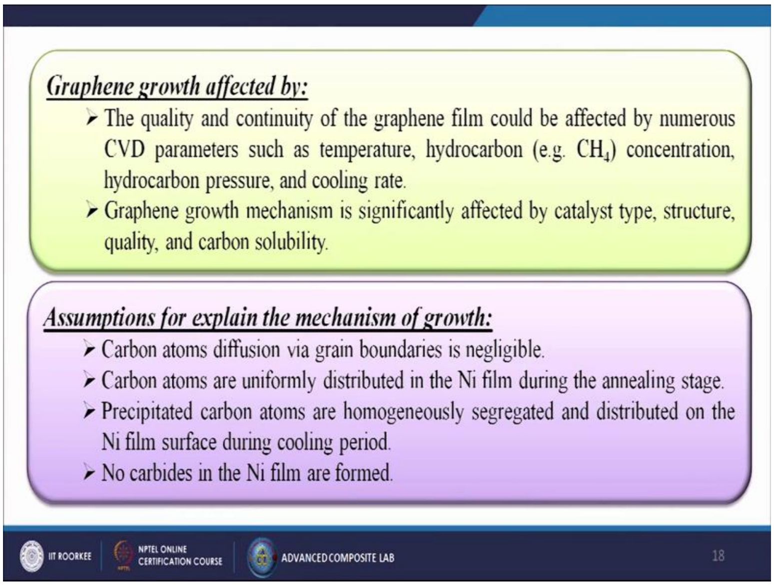

Graphene growth affected by:

- The quality and continuity of the graphene film could be affected by numerous CVD parameters such as temperature, hydrocarbon (e.g. CH_4) concentration, hydrocarbon pressure, and cooling rate.
- Graphene growth mechanism is significantly affected by catalyst type, structure, quality, and carbon solubility.

Assumptions for explain the mechanism of growth:

- Carbon atoms diffusion via grain boundaries is negligible.
- Carbon atoms are uniformly distributed in the Ni film during the annealing stage.
- Precipitated carbon atoms are homogeneously segregated and distributed on the Ni film surface during cooling period.
- No carbides in the Ni film are formed.

Graphene growth rate affected by the quality and continuity of the graphene film could be affected by numerous CVD parameters such as temperature hydrocarbon means what is the CH 4 means methane concentrations hydrocarbon pressures and the cooling rate. Graphene growth mechanism is significantly affected by catalyst type structure quality and carbon solid ability. These all are the important input parameters by which we can control the growth rate of the graphene on to the nickel substrate.

Assumptions for explain the mechanism growth: carbon atoms diffusions via grain boundaries is very very negligible, carbon atoms are uniformly distributed in the nickel film during the annealing stage, precipitate carbon atoms are homogeneously segregated and distributed on the nickel film surface during cooling period, no carbides in the nickel films are the forms. So, these all are the different types of assumptions based on the experimental results.

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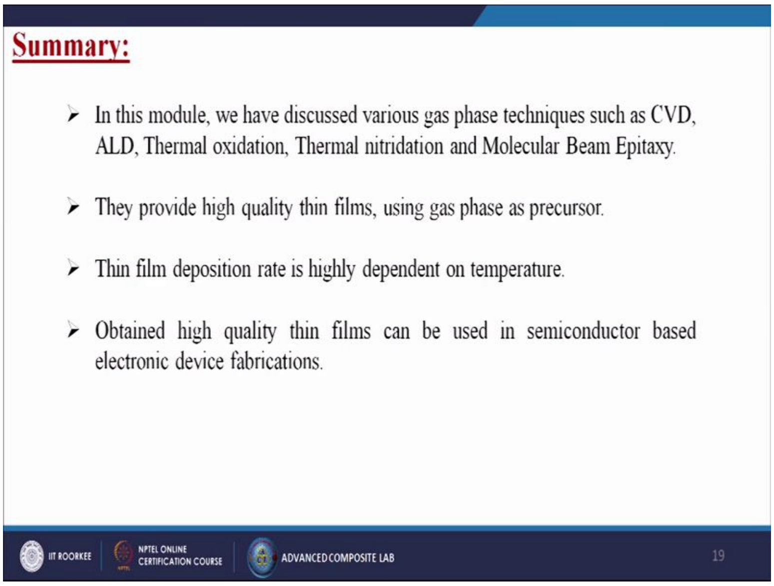

Summary:

- In this module, we have discussed various gas phase techniques such as CVD, ALD, Thermal oxidation, Thermal nitridation and Molecular Beam Epitaxy.
- They provide high quality thin films, using gas phase as precursor.
- Thin film deposition rate is highly dependent on temperature.
- Obtained high quality thin films can be used in semiconductor based electronic device fabrications.

Now we are coming into the conclusions that we have in this particular model, we have discussed various gas phase techniques such as CVD, ALD, thermal oxidation, thermal nitridation and molecular beam epitaxy. Some of the topics like CVD, ALD, we have already discussed in our earlier lecture and in this particular lecture, we have briefly discussed about the thermal nitridation, molecular beam epitaxy, thermal oxidations. They provide high quality thin films using gas phase as a precursor because our main motto of this particular module is to see that how we can deposit the thin film on to the substrate itself. Thin film deposition rate is highly dependent on temperature. Obtained high quality thin films can be used in semiconductor based electronic device fabrications. So, already we have discussed all this in this particular lecture.

Thank you.