Chemical Engineering Principle of CVD Processes
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Module-3
Lecture 24
CVD Applications: CVD of nano-Structured Films

Good morning and welcome to this lecture in our course on chemical engineering principles of CVD process. As I mentioned in the last lecture we are going to discuss how CVD relates to nano technology. As you know nano materials are increasingly found everywhere they have certain unique properties that are very advantages whether you are trying to take, they are trying to (()) (0:43) reactivity or their surface area or their hardness characteristics for their melting point differences.

Each nano particle has a certain specific characteristic that makes it very attractive for certain applications. For example nano sensors are used increasingly to study the presence of trace amounts of materials, (()) (1:08) for trillion amount of materials in various environments starting from that atmosphere to the human body. Nano drug delivery is another emerging application where timed release of medicines is possible by encapsulating them in a nano carrier.

Now for chemical engineers nano catalyst have huge potential in terms of being able to drive up the available area for promoting surface reactions by several orders of magnitude and of course nano devices in general particularly the MEMS and NEMS devices. Micro electromechanical devices, nano electromechanical devices which combine the functionalities about the electrical as well as the mechanical functionalities of nano materials are also finding (()) (2:02) application everywhere.

So given the fact that nano materials are in great demand there is huge amount of interest on how to actually make nano materials? If you look at nano in general is still what I would call in the science realm rather than technology realm I mean it just has not, the production of nano material is not scale to such an extent that it has penetrated deep to our everyday life except in occasional products like, you know, cosmetics or topical creams or things like that.

So what is holding it up? Well, the fact is nano materials are difficult to make, now if you look at nano technology and overall there are really 3 important steps to it, the first is the synthesis slash assembly of nano materials, the second is the characterization, with nano materials you constantly have to characterize the product to make sure that it is coming out the way you want it and so the characterization is the other important technology and the third one is manufacturing and processing, particularly the processing aspect.

You know, one of the difficulties with nano materials again is the tendency to agglomerate even if you make nano materials and at the time of production can ensure nano dimensionality, you let the particles, you know, just stay in suspension for a while they stick back together and become larger dimensions. So the post processing of nano materials after they have been synthesised is another important challenge.

The fundamental to all this is again modelling, unless you can capture the theory of what is happening, how are nano materials being formed? How do you characterize that stability over time? How you characterize their ability to perform certain operations that they are intended for? Unless you can model all this and develop a predictive ability you are really not going to be able to either control the process or optimise the process.

You are kind of going to be at the mercy of, you know, day-to-day variability's in the process or in the purity of the materials or in operating conditions and so on. So the challenges are really twofold, one is to develop a manufacturing process that is sufficiently scalable, you want to be able to make tons of nano materials per day not a few grams for lab use and the second is to be able to model this Manufacturing processes with sufficient rigour where we have some predictive ability over what we are going to see at the end of the process.

So given these constraints chemical vapor deposition is actually emerged as an attractive tool to make nano materials because it satisfies both this conditions, it is scalable and it is simulatable. Now the other approaches to making nano materials essentially though we can classify them in 2 ways bottom up and top down. The top-down methodology basically take larger particles and break them down into finer particles.

So you take micron sized particles and like crushing or grinding or sonication or whatever method you will reduce the size to nano dimensions. So that is only one way to go and it has its pluses and minuses, the other way to go is to build up the nano materials from bottom up which means start with atoms or molecules and keep attaching them to each other until you get the particular product that you are looking for.

CVD is obviously bottom-up process but there are other techniques particularly the molecular self-assembly techniques using which you can essentially make designer product, you have the ability now with certain nano dimensional tools where you can actually manipulate atoms and place them in certain configurations, so that you get exactly the structure that you are looking for. These products are also called Langmuir Blodgett films or molecular self-assembled films and they have this distinct characteristic that you have absolute control over the structure as well as the morphology of the product.

So they work great, problem not scalable I mean this is wonderful for, you know, making a few milligrams of material for lab use but it is not a product, it is not the method that is going to give you large amount of nano dimension material. The next best thing is CVD where you essentially deposit the film on the surface but what you try to do is, do not let the film grow to a size larger than few nanometres.

In other words you should have certain checks and balances in your deposition process for certain features on your surface which will ensure that the product once it is deposited is not become a continuous film over many millimetres or even many micro-meters but somehow it is curtailed after it grows to few nanometres. Now there are couple of ways in which you can do this.

One way is to deposit the material using CVD and essentially provide certain energetic barriers on the film which prevents the surface migration from happening make it difficult for the atoms to keep jumping from one space to the other and this can be done by crystalline orientation it can be done by providing radiation of surface energy on the surface there are different ways you can do this which essentially focuses on preventing the surface migration of surface diffusion of the deposited molecules to form a continuous film.

The other way is to do something in the gas phase, as we have discussed earlier you can turn a CVD reactor into an aerosol reactor by allowing heterogeneous nucleation to take place. So you try to form nano dimensional particles in the gas phase and again freeze the process, so that these particles do not keep growing to larger sizes and then direct these nano dimensional particles to deposit on the surface, so that you essentially form these discrete nano particles on the surface. So these are methods essentially using CVD and also what is known as CVS chemical vapor synthesis reactors to make nano dimensional product.

Now in terms of again modelling and simulation of such reactors to make nano products, there is something we discussed in one of the earlier lectures. Modelling of any CVD system requires multiscale modelling, right? There is the so-called macroscopic system which then breaks down into the mesoscopic system which then breaks down into the molecular system. When we talk about nano materials you essentially add another layer of complexity because now you have to have a model essentially at atomic level which will capture how the growth is curtailed to discrete particles rather than a continuous film?

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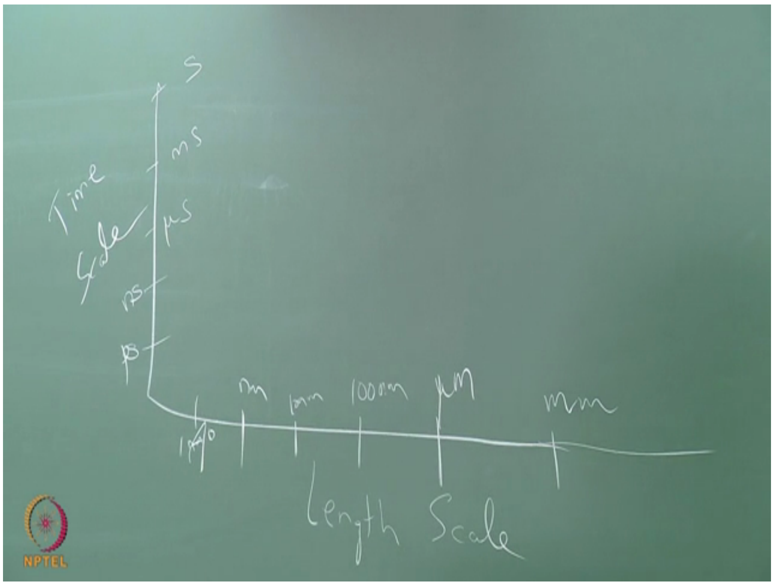

So you add one more element to the model, in fact another way to look at what we have discussed in that class is to plot your, let say your length scale to a timescale on the y-axis. So the length scale can start from let say 1 angstrom nanometre, 10 nanometres, 100 nanometres, micro-meter and then lets a millimetre and similarly on the timescale you can start with picoseconds timescale, nano second, microsecond, millisecond, second and so on. So this is kind of your modelling space.

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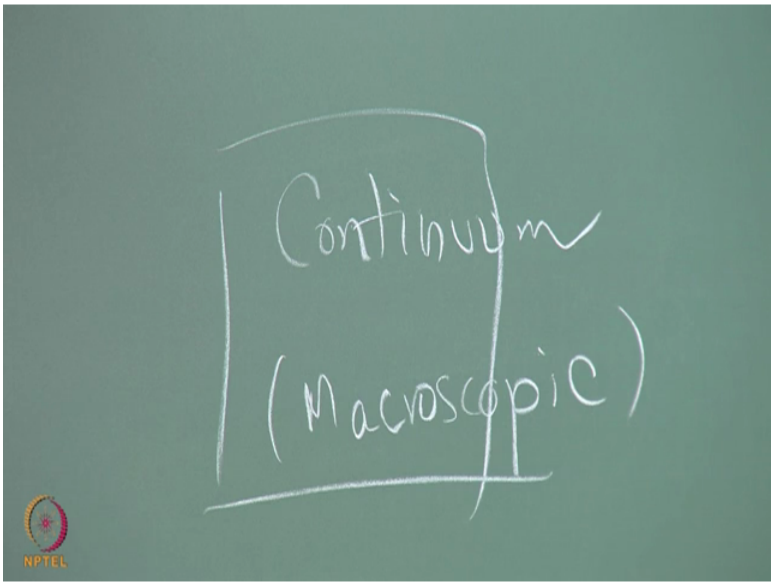

Continuum

(Macroscopic)

So when you look at a CVD system for making nano materials you can actually sub divide it into 4 regions. The region that is characterized by the longest length scales and the longest timescales is the continuum regime or the macroscopic regime. So this describes what is happening in the bulk of the reactor, how the reactance are getting fed to the reactor? How they are getting distributed in the reactor? How the products are flowing out of the reactor? How the velocity gradients are happening? How the temperature gradients are being set up and so on? And this is what again we described using continuum equations, conservation laws, constitutive relationships and so on.

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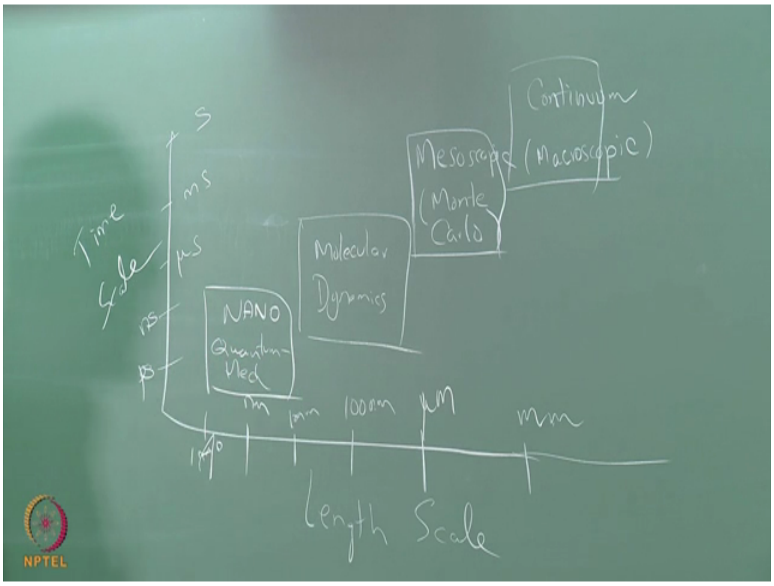

Now the second scale here which essentially starts in the submicron region and extends till tens or hundreds of micron is called the mesoscopic region also known as the Monte Carlo regime for simulation and then there is the next region which is called the molecular dynamics regime and then comes the regime that is unique to nano materials it is basically a quantum mechanical regime which is characterized by for example the Schrödinger equation.

So how do these things again (()) (12:55) each other? When you start talking about nano materials, again at its smallest level we are talking about the assembly of a few atoms to make a sensible structure at that length scale and at that timescale we are really talking about the interaction of electrons with atoms. The atoms are actually responding to a feel that they set up by the quantum Electronics that are present in the system. Essentially the wave nature of matter comes into play.

So you have to go back to your I guess it was your first semester physics or second semester physics where you are studying quantum mechanics and quantum dynamics to remember how we used to describe the motion of electrons and very very fine particles such as atoms in the Earth's electromagnetic field and that is really the level of detail that you need to get into at that level.

What you really care about is the electron density at each location in the reactor and on the surface. What is the gas phase composition in terms of ions and electrons that are present in the system? How are interacting with the atoms that are present in the gas phase as well as on the surface? How are they either aiding or inhibiting the motion of these atoms, again both in the gas phase as well as on the surface.

What role are they playing in either promoting that attachment of these atoms to make larger molecules or in preventing the migration and attachment of these atoms to keep them at atomic level? So the focus is really at that level, we are trying to look at how atoms and molecules are interacting with each other and with the electrons and ions that are present in the system.

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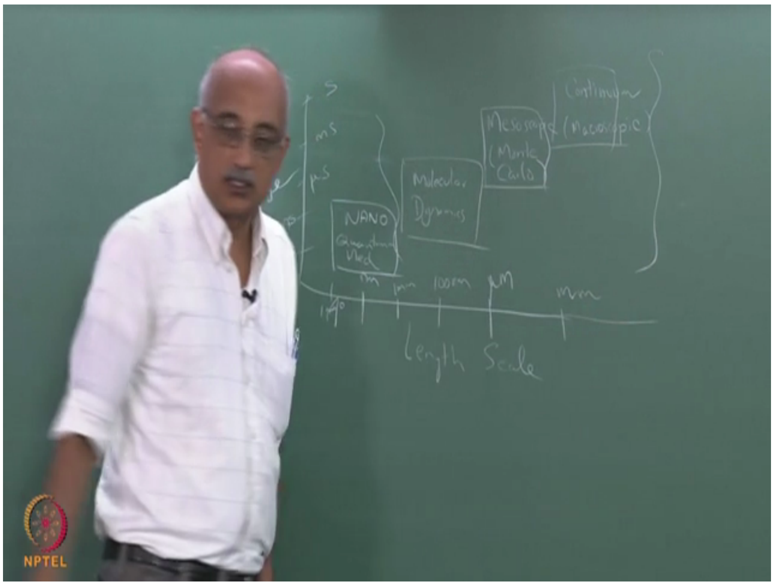

So when you go from these 3 length scales we essentially discussed in the earlier lecture, molecular dynamics range, again what we assumed there is that the kinetics of motion of the molecules is the rate limiting factor. So in this range in the molecular dynamics range as the name suggests it is not studying the dynamics of individual molecules, you model a molecule as a very small particle, so you essentially apply the Newton's equation of motion, you look at the force on the particle relate that to the acceleration of the particle for a given mass.

The force itself is a result of various potential energies that are present in the system starting with intermolecular potentials and so for example the Van der waals potential plays a role all the electrostatic forces, the contact potential forces between the particle and the surface, all these molecular as well as electrical forces play a role particularly in this regime.

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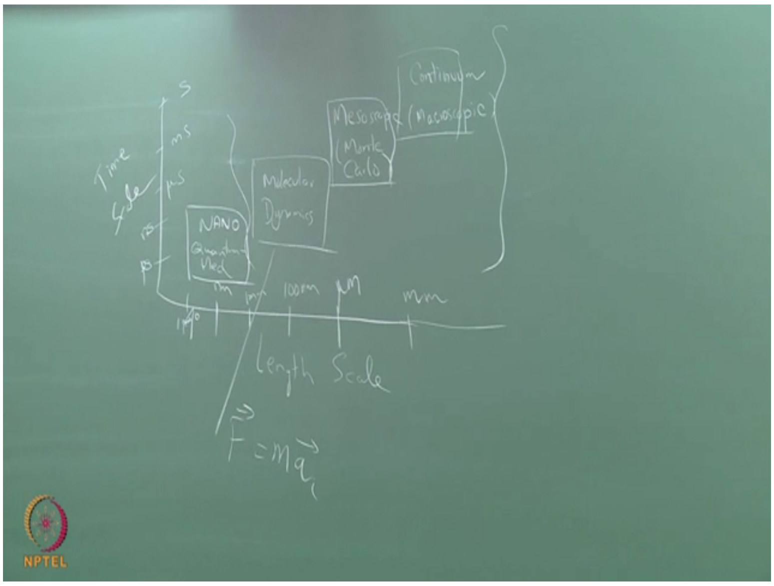

So you essentially characterize the acceleration of that atom or molecule for fine particle i on the basis of all the forces that it experiences and essentially solve the equations of motion for discrete particles. Again what you are doing is modelling molecules as particles and essentially assuming that the motion is deterministically decided by the Newtonian mechanics of the system. For example if 2 atoms collide you look at it as a hot body collision when you use conservation of momentum principles to see how they are going to move in the field and so on.

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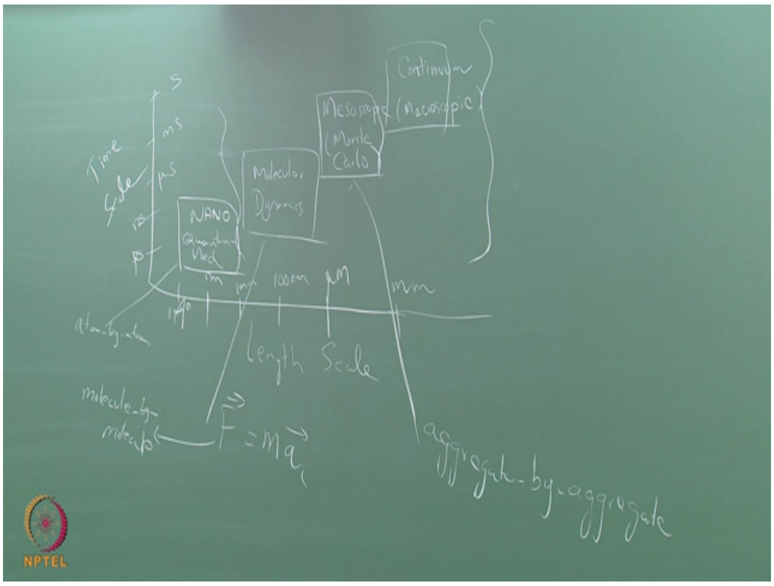

So this is a slightly expanded view, you know, here we are trying to look at atom by atom and here it is more of a, I would call it molecule by molecule the third regime is what we would say is an aggregate by aggregate model. So in this regime you have now formed films for aggregates that are of the order of a few microns and you start trying to understand how these aggregates behave.

So typically this is done using Monte Carlo simulation techniques using probability theory as well because the loss that governed how attachment of individual atoms and molecules to form larger aggregates happens not be deterministic in nature and in the Monte Carlo simulation methods you acknowledge the fact that there is a probabilistic element to it and in fact the solution that you come up with for deposition of the atom or molecule at any time or the size of the molecule at any time is not based upon deterministic principles but on stochastic principles.

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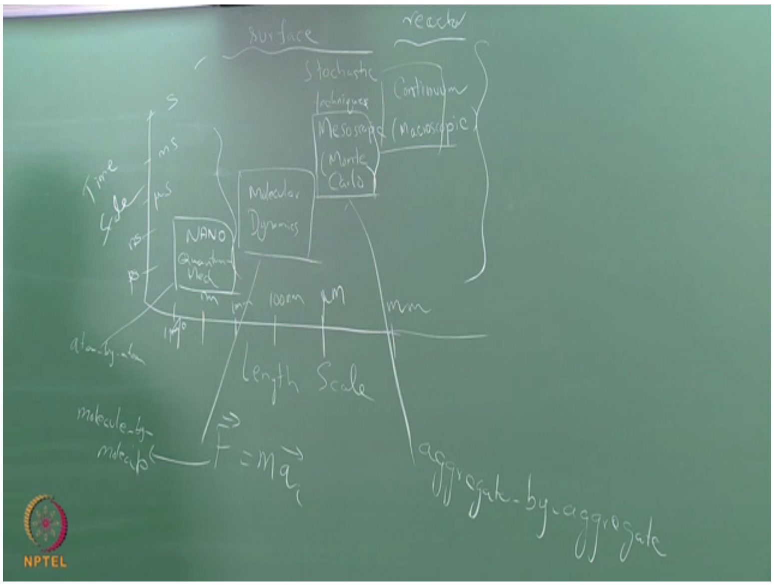

So in this region you are essentially adopting stochastic that needs, again with focus on the substrate or the surface on which this phenomena are happening all and finally you link all these, so the first 3 stages really describe what is happening on the surface or the substrate on which the deposition is happening and you link it to the reactor through your continuum model or macroscopic model. So in terms of scaling this is how we want to look at it.

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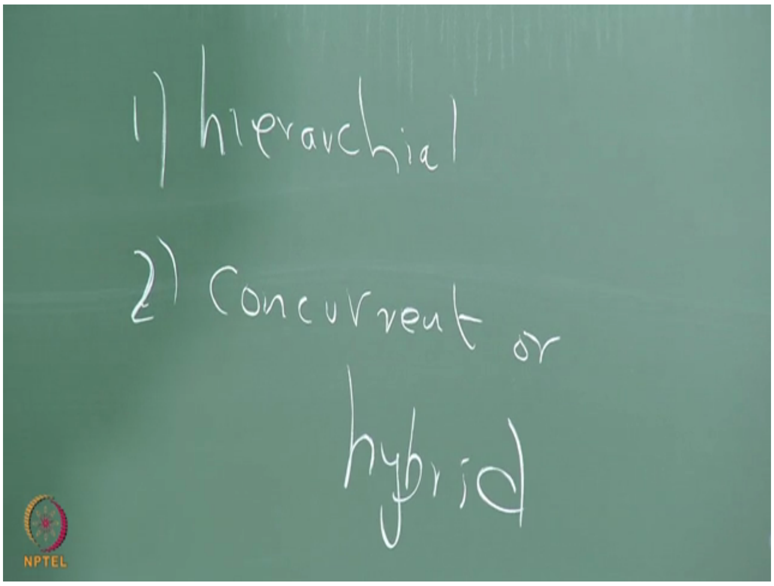

1) hierarchial

2) Concurrent or hybrid

But in terms of actually, let say that you want to predict how a nano sized feature is growing on a substrate? How do you do that? There are really 2 approaches, the first approach is the hierarchical approach and the second approach is called the concurrent or hybrid approach. The hierarchical approach what you do is, you first solve the system at its highest level, you take the output from your simulation at the macroscopic level, feed it to your mesoscopic model and then again take the output from the mesoscopic model feed it to the Monte Carlo simulation take the results from that and feed it down to the nano scale model.

That is called the hierarchical approach because we essentially follow hierarchy of diminishing timescales and length scales. The other approach that can be used is to solve all of them simultaneously. So that you essentially set up an iterative loop then you assume that it is not just a...

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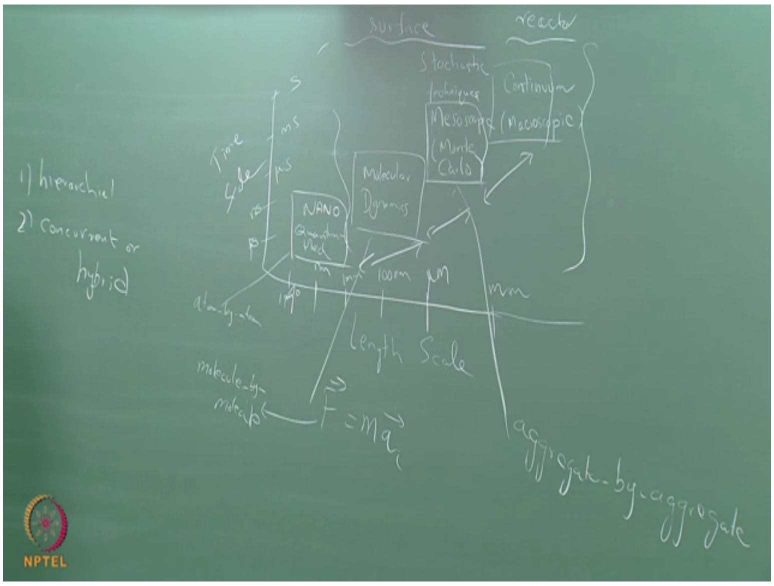

I mean the hierarchical approach basically says it all was this way that you can solve that system first then solve this, solve this and then solve this but in reality that is not necessarily true because what is happening at this level can influence what is happening at this level and so on? So the concurrent model essentially it uses a two-way coupling and makes it into a iterative process where the final closed form solution for the system is obtained after, you know, setting up an iterative loop and obtaining a self consistent set up parameters for the system.

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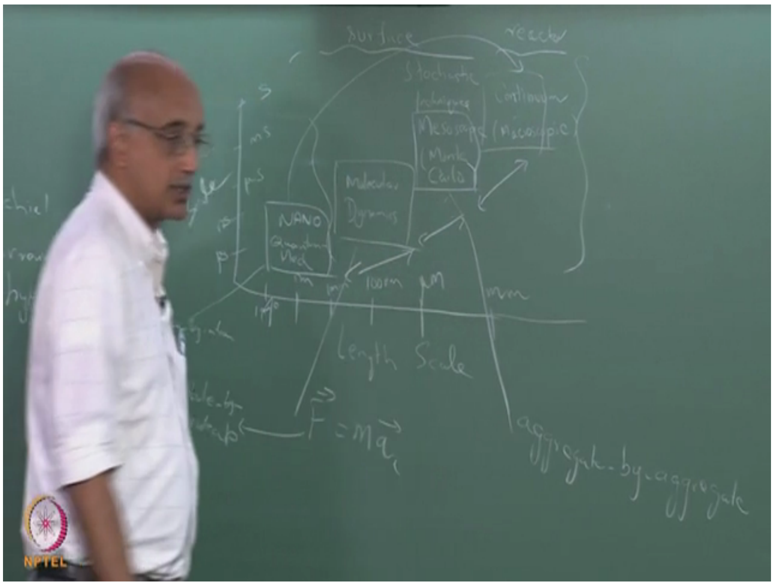

In other words the growth of nano material at the scale cannot violate what is going on at the continuum level. Now is it possible for such couplings to happen I mean can this process influence that process. Well, as an example you know, you can take things like surface roughness. The roughness of the film that you are going on the surface is very much dependent on what is happening at this level?

Because when we talk about the surface roughness or surface asperities you are typically talking about scales that are of the order of sub nanometres, particularly highly polished semiconductor devices and so on. And the presence of even few nano sized particles on a substrate can have a significant influence on the measurable roughness of the surface. It also has an effect on the 3-D profile of the surface.

So if you have a good AFM you can actually see the presence of the nano particles on the surface and you can see how, for example flow around surface is affected even by the presence of these are very small nano sized particles. So certainly at the boundary layer level the presence of even atoms can have an effect and that can feedback up to loop because once the boundary layer gets disturbed and that has an influence on what is happening at the exterior or the mainstream because of the coupling at that level and so this effect can certainly propagate the other way also.

Now regarding pros and cons, obviously the hierarchical model is very simple, simplistic you might say. Basically it splits into 4 different problems and solve them sequentially whereas the concurrent model introduces a much higher level of complexity by insisting that all these equations must be solved simultaneously.

One of the major applications for nanotechnology these days is called the nano tubes. Nano tubes are being used for various purposes, particularly (()) (23:37) they provide huge property enhancements for things like stiffness, elasticity, hardness of materials, conductivity of materials, so there very attractive nano substances to try and make.

Now when you look at this carbon nano tubes and you try to model how they are formed? Clearly the modelling has to start at the nano tube level because it has a certain very distinct shape to it and you have to really have a model that can predict the shape distribution of the nano materials that you deposit. That is really getting down into the nano substance level and then you have to link it to, you know, how you make it happen?

What kind of common source do you provide? What kind of deposition conditions do you provide? Is it even possible to make a carbon nano tube using CVD techniques or do you have to use essentially molecular self-assembly type of methods? So to understand that you really need to be able to do this as well.

Now people have developed models to simulate deposition carbon nano tubes using CVD techniques and these models predominantly tend to be hierarchical in nature. They have really not even tried to deal with the complexity of using a concurrent model for that. Now on the other hand if you look at a silicon film formation. Silicon deposition, you know the first layers of silicon that formed are actually of nano dimensions they can eventually grow to micron dimensions and so on but there are applications increasing in micro-electronics varied other volumes are shrinking while at the same time the functionality is increasing where you are requiring silicon particularly epitaxial silicon of the order of few nanometres.

So when you look at the deposition of epitaxial silicon at the nanoscale, the modelling tends to be more concurrent in nature and one reason for that is, you know, the chemistry of how silicon films are formed quite well understood, it is predominantly an inorganic chemistry, the chemical reaction sequences have been well characterized, well understood and so on. So it is actually possible to try and develop a hybrid model or concurrent model for linking the growth of nano dimensional silicon films on a surface to the reactor conditions.

On the other hand when you are talking about making of carbon, you are typically using a precursor that is Organic in nature and the number of reactions and the reaction sequences are not as well characterized in that class of materials come back to inorganic materials. So even the lack of understanding of the gas phase chemistry per se, it is just too difficult to try and develop a concurrent model.

So what people have tried to do is, develop a simulation model where you predict the formation and growth of the carbon nano tubes and then empirically fit the data to the model and have enough tunable parameters in the model, so that you can try and match your experimental data as closely as possible. Usually these are trainable models where the model will essentially self correct based on the match or mismatch to the actual experimental observation.

So it is more like a neutral network type of a model that people normally use, so it is not as fundamentally based as the models that describe CVD I mean silicon CVD but for practical purposes they do the job. So it is an interesting dichotomy that depending on the nature of the CVD film you can choose either this approach or this approach. I think to some extent it also depends on your computational capabilities and facilities. Because to do this you need a supercomputer, you know high-performance computing, cluster computing all of that is needed whereas this probably do it on your PC these days or a good workstation. So the level of computational details involve is clearly much lower in the hierarchical approach.

Now what are the challenges again in trying to make nano materials in a CVD reactor? I mean if you look at this manner is a very small size but a typical CVD reactor tends to be quite large in terms of its dimension. So that is automatically as mismatch, you know, that you are trying to make very very small materials in a space that is quite large. The problem that introduces is that unless you CVD environment is very tightly controlled, the perturbation somewhere quite remote from the surface on which you are making the nano film then have the significant impact on the quality of the nano product that you are trying to make.

So when you are trying to make a nano material the preferred way to do it, is to have a reactor that just essentially fits around the substrate, trying to minimize the amount of free space. So techniques such as, you know the designer molecule fabrication techniques such as the molecular self-assembly enables you to do that. You can build a control system just around the substrate where you are trying to grow the film and have very precise control over how the film is being formed or how the nano particles are being laid out.

But you really do not have that luxury when you are trying to make larger quantities of nano material. So it is essentially a trade-off, you know, when you are making nano materials can either have extremely well-controlled quality or quantity. It is very difficult to design a reactor in which you can do both. Get 2 tons per day or more of production while still maintaining the precise control over the structure and morphology and other characteristics of the nano material.

This is where the top-down techniques have a certain advantage, particularly if you are not requiring highly complex molecules to be produced for your application for example if we are just doing catalysis. Let say you want to use silicon oxide as your catalyst the main parameters at you are interested in is the surface area. So you can check your micron sized SiO2 particles and fairly quickly reduce size the nano dimensions.

You will not be affecting the crystal structure too much if you do this carefully but at the same time you are not going to be adding any functionality either but if your entire purpose is simply to increase the surface area per unit volume of catalyst material or per unit mass of catalyst material than top-down method works very well. The bottom of method whether it is molecular self-assembly or CVD are required when you have to build for example layer by layer functionality.

If you want to make nano dimensional film where it even at some nano meter levels you require a certain gradiation in the composition of the film or in the structure of the film then you cannot do that using top-down techniques. So you have to use the bottom up techniques and that is why CVD in particular can come in very useful. I mean you can do the same thing with molecular self-assembly what it is going to be much more difficult, much more laborious, time-consuming, expensive and so on.

Whereas with the CVD process we know how to do this, we know how to control the conditions of the reactor to be able to deposit films of known composition and thickness. So it is very easy to do a layer by layer build-up of a nano dimensional film simply by exercising controls so the operating conditions of the reactor and that is the reason why CVD as a technology now increasingly finding use in the synthesis of nano materials.

It is kind of a compromise between the manipulations at atomic level and you know simple top-down type of techniques. It is a methodology that gives you virtually the same level of control as the molecular assembly techniques provide while at the same time minimising the cost and complexity of designing and operating such a reactor. So nano technology and its interaction with CVD is a subject that is really emerging now for a lot of papers that have been written on this subject and you should try to read up and catch up on some of the new things are happening.

I will forward some papers as well to the class, so that you can take a look at them. I think that brings us to the end of CVD applications that I wanted to discuss as part of this course. So we will have one more lecture where I will try to as I said give you an overall picture of what we have covered in this course and get you set up for your final test and so on. So any question on what we have discussed today?

Okay, so I will see you on Monday.