Surface Engineering of Nanomaterials
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Lecture - 22
Size Dependency in Nanostructures of Nanocoatings

Hello, today we are going to discuss our new lecture on Size Dependency in Nanostructure of Nanocoatings. So, the main aim of this particular lecture or maybe some next subsequent lectures is that how the nano particle size is actually creating some advantages for the coating purposes. The thing is that when we are talking about the nano composites or nanotechnology or maybe that small nano particles, always we are talking that of nano.

So, nano is nothing but the 10 to the power minus 9e meter, so maybe earlier days or maybe the past times when people who are using these kind of particles maybe that one is into the micro size, but in this particular lecture or maybe next subsequent lecture we are going to show that when the same materials we are using into the nanometer range that properties of these particular composites or maybe the coatings is totally changed.

So, first before going to see that what is going on inside the matrix just let us take a note that what is the role of size in nanotechnology.

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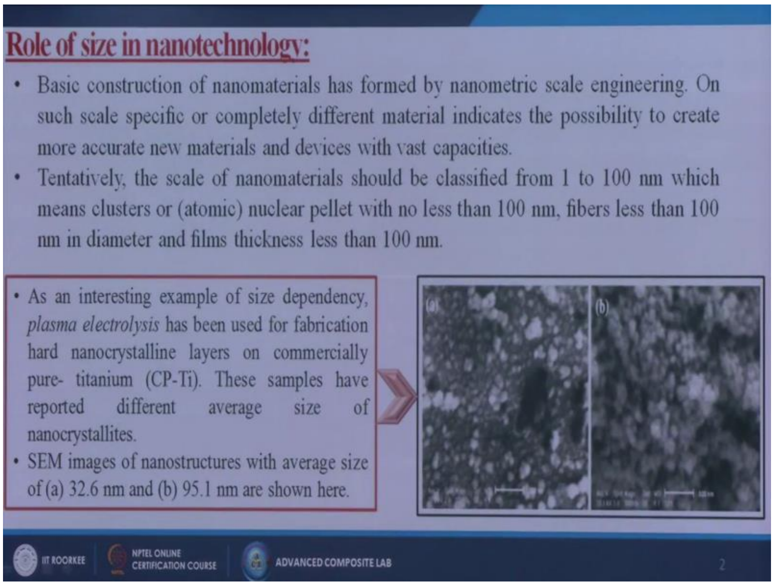

Role of size in nanotechnology:

- Basic construction of nanomaterials has formed by nanometric scale engineering. On such scale specific or completely different material indicates the possibility to create more accurate new materials and devices with vast capacities.
- Tentatively, the scale of nanomaterials should be classified from 1 to 100 nm which means clusters or (atomic) nuclear pellet with no less than 100 nm, fibers less than 100 nm in diameter and films thickness less than 100 nm.

- As an interesting example of size dependency, *plasma electrolysis* has been used for fabrication hard nanocrystalline layers on commercially pure- titanium (CP-Ti). These samples have reported different average size of nanocrystallites.
- SEM images of nanostructures with average size of (a) 32.6 nm and (b) 95.1 nm are shown here.

So, the basic construction of nano materials has formed by nanometric scale engineering. So as I told already whatever the particles we are going to use, the size of that particles is 10 to the power minus 9 meter. So, generally the particles on an average diameter of 1 nanometer to 100 nanometer; we are calling it as a nanomaterials or maybe the nano particles. So, that size particles actually we are going to use for this particular purposes or may be for these particular applications.

So, on such scale specific are completely different material indicates the possibility to create more accurate new materials and devices with the vast capacities. In our last or maybe the past few slides or maybe lectures also we have seen that when we are changing the particle size from macro to micro or maybe some micro to nano, the same properties is changing hell and heaven.

So, here also we are going to give some examples like the scale of nanomaterials would be classified from 1 to 100 nanometer, what I have already discussed which means cluster or atomic nuclear palette with no less than 100 nanometer fibers less than 100 nanometer in diameter and flame thickness less than 100 nanometer. So, whatever the particles I am going to use or maybe whatever the fibers or maybe whatever the pellets I am going to use, the size or maybe the diameter of that particular nanoparticles is less than 100 nanometer.

So as an interesting example of the size dependency, plasma electrolysis has been used for fabrication hard nanocrystalline layers on commercially pure titanium. These samples have reported different average size of nanocrystallites. So, when you are talking about the properties generally that properties is depends upon the two things, first one is known as the particle size of that particular nano particles and what is the coating thickness. So, first one is known as the crystallite size of these nano particles and the second one is known as the coating thickness of that particular material onto the substrate itself.

So, based on these two diameter or maybe the size only that nano composite property and nano composite is showing different kind of properties. So, here this is also an example, so these samples have reported different average size of nanocrystalline. So, from this particular figure we can show that SEM image of nano structures with average size is having 32.6 nanometer crystallite size and here the crystallite size is little bit bigger which is 95.1 nanometer.

So, in this particular case we can see that these materials crystallize size or maybe the nano particle size and these materials; the crystallized size or maybe the nano particle size is totally different and in future I am quite sure that they are going to give the different properties in terms of their crystallite size.

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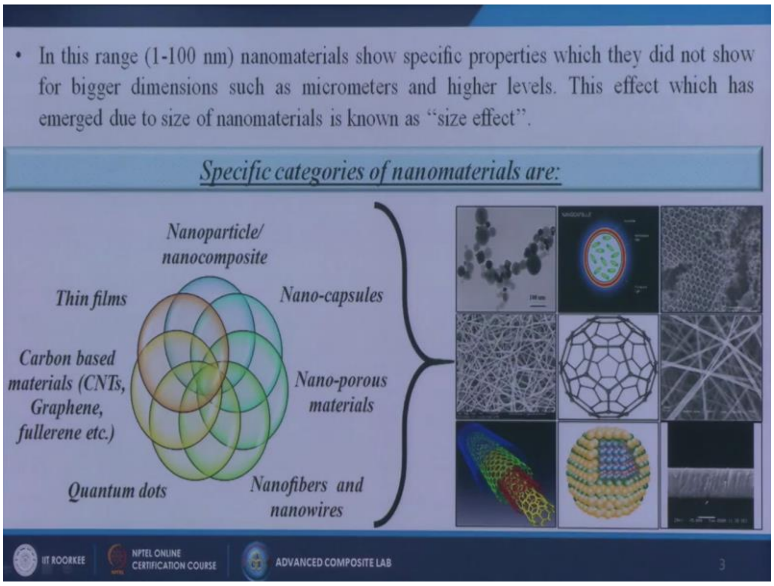

- In this range (1-100 nm) nanomaterials show specific properties which they did not show for bigger dimensions such as micrometers and higher levels. This effect which has emerged due to size of nanomaterials is known as "size effect".

Specific categories of nanomaterials are:

Nanoparticle/ nanocomposite

Nano-capsules

Nano-porous materials

Nanofibers and nanowires

Quantum dots

Carbon based materials (CNTs, Graphene, fullerene etc.)

Thin films

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So, in this range generally 1 to 100 nanometer when we are using this kind of materials nanomaterial so specific properties whether which they did not show for bigger dimensions such as micrometers and higher levels. So, as I told already the same material, the same substance if we are using in a bigger particle size or maybe the crystallite size of that particular particle is bigger then it will show something different properties, but if we reduce the size of that particular crystallite, it will show some better properties.

So, this effect which has emerged due to the size of nanomaterials is known as the size effect. So when you are dealing with the different sides of that particular nanomaterial, the technology is known as the size effect of that particular case. So, here are the some examples, so it is a broad examples because there are n number of examples or n number of materials we are trying to prepare by which we are getting different properties. Here we have tried to give certain kind of nanoparticles or maybe the nano fillers or maybe the nano materials which we are using in our day to day life, which are you are using for the industrial purpose or maybe some kind of electronic purpose, optical purpose, biomedical application purpose or maybe any other purpose.

So, here it is like a list of example that where or maybe how or maybe what type of nano materials or maybe the nano particles we are going to use. So, here we are using that materials in the nano particles on maybe the nano composites then nano capsules, nano porous materials, nanofibers and nanowires, quantum dots, carbon based materials like carbon nanotubes, graphene fullerene, etcetera and the thin flame. The same thing into the pictorial view we have given over here, so here we are giving the picture of some kind of porous materials then we are giving the picture of some kind of fibers then some kind of wears then we are giving the thin flames then we are giving the picture of carbon nanotubes then we are giving some kind of carbon dots; somewhere we are giving some kind of microcapsules type of things. So, here these all are the plenty of examples by which we can use this kind of material in our day to day life.

So here before going to start; just let us know that how many sizes are available or maybe how many dimensions are available for using this kind of nano materials for our requirement.

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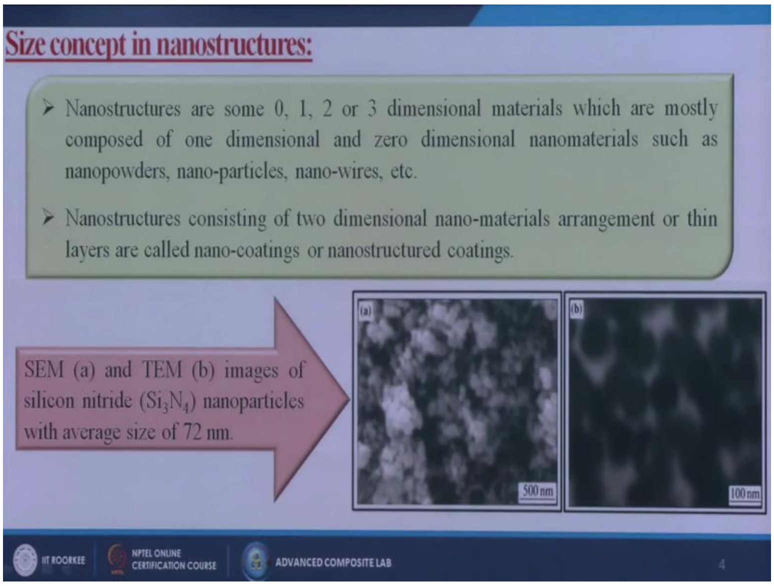

Size concept in nanostructures:

- Nanostructures are some 0, 1, 2 or 3 dimensional materials which are mostly composed of one dimensional and zero dimensional nanomaterials such as nanopowders, nano-particles, nano-wires, etc.
- Nanostructures consisting of two dimensional nano-materials arrangement or thin layers are called nano-coatings or nanostructured coatings.

SEM (a) and TEM (b) images of silicon nitride (Si_3N_4) nanoparticles with average size of 72 nm.

So, nano structures are some 0, 1, 2 or 3 dimensional materials which are mostly composed of 1 dimensional and 0 dimension nano materials such as nanopowders, nano-particles, nano-wears. So when we are talking about any nano particles, the nomenclature of that nano particle is known as maybe the 1 d, 0 d, 2 d, 3 d like that. So, that d actually they there by two method actually we can get the informations or maybe we can put the nomenclature of that particular nanoparticles; one is the confinement and unconfinement and another one is called the size means x and x is y axis and the z axis.

So, nano structures consisting of two dimensional nanomaterials arrangement or thin layers are called the nano coatings or maybe the nano structured coatings because here maximum times we are using the film onto the substrate itself that is why we are calling it as a 2 d or maybe the two dimensional nanomaterials or maybe the 2 d two dimension and nanomaterials coating.

So, here this is also a beautiful example of Si2N4 that means, silicon nitride, so left hand side it is showing the scanning electron microscope image and the right hand side it is showing the transmission electron microscope image, where we can see that average particle size of that silicon nitride is 72 nanometer range. In the next also we are trying to discuss about the size dependency in nano structure in terms of some kind of particle size and thickness of the nano coatings.

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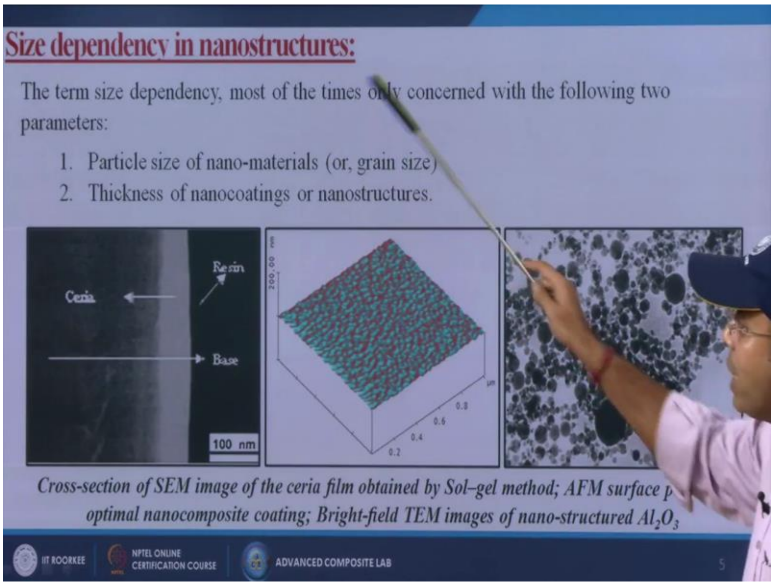

Size dependency in nanostructures:

The term size dependency, most of the times only concerned with the following two parameters:

1. Particle size of nano-materials (or, grain size)
2. Thickness of nanocoatings or nanostructures.

Cross-section of SEM image of the ceria film obtained by Sol–gel method; AFM surface p optimal nanocomposite coating; Bright-field TEM images of nano-structured Al_2O_3

Already I have told you that term size dependency most of the times only concerned with the following two parameters, one is the particle size of the nano materials or maybe the grain size or maybe the crystallites site and the second one is that thickness of nano coatings or the nano structures; that is how much layer may be a single layer, may be a multiple layer; I am trying to put onto my substrate or may be that onto our materials.

So, here all of the different kind of characterization techniques by which we can prove that how much thickness we obtained after doing the coating on to the substrate itself or maybe the what is the surface roughness or maybe the surface properties we are getting or maybe that how the nanoparticles actually looks like on to the substrate itself. So, here first one is that cross section of scanning electron microscope image of the ceria flame obtained by solider methods. So, here we can see that this is our base materials then the ceria flame has been formed on to the substrate itself then in between that we are having some resins, so resins is acting as a binder over there; so which is actually enhancing the adsorption properties in between the substrate and in between the coatings so by which that ceria flames is stick with the best materials.

Here this one is called the AFM or maybe Atomic Force Microscopy image, so in which atomic force microscopy surface profile optimal nanocomposites coating by which we can see that what is the surface roughness of that particular material or maybe sometimes we can measure the particle size of that particular nanoparticles too and the third one is called the bright field transmission electron microscope images of the nano structure alumina. So, here also we can see that just getting the dimension of these kind of nanoparticles are non fillers easily we can calculate what is the average size of alumina has been present in the matrix itself.

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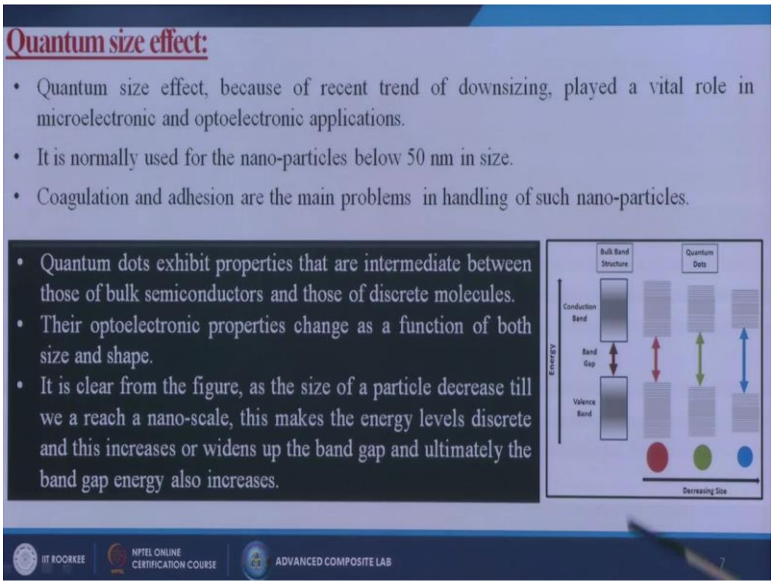

Quantum size effect:

- Quantum size effect, because of recent trend of downsizing, played a vital role in microelectronic and optoelectronic applications.
- It is normally used for the nano-particles below 50 nm in size.
- Coagulation and adhesion are the main problems in handling of such nano-particles.

- Quantum dots exhibit properties that are intermediate between those of bulk semiconductors and those of discrete molecules.
- Their optoelectronic properties change as a function of both size and shape.
- It is clear from the figure, as the size of a particle decrease till we a reach a nano-scale, this makes the energy levels discrete and this increases or widens up the band gap and ultimately the band gap energy also increases.

Next we are trying to discuss about the quantum size effect, so quantum size effect in respect of the size dependency of that particular nanoparticles. So, quantum size effect because of recent trend of downsizing played a vital role in micro electronics and optoelectronics applications. It is normally used for the nano particles below 50 nanometer in size, so when you are talking about the nano material or maybe the nano particles generally the scale is ranging from 1 to 100 nanometer, but when you are talking about the quantum size that is well below than the nanometer range; that means, it is below than the 50 nanometer range.

So, it is normally used for nanoparticles below 50 nanometer in size, coagulation and additions are the main problem in handling of such nanoparticles is of course, because when I am preparing my nanoparticles or maybe when I am making my nanoparticles more smaller and smaller, the surface area of that nanoparticles is increasing; not only that its aspect ratio is also increasing. So due to that there is a chance of agglomerations, all the nanoparticles is trying to stick together so that is known as the agglomeration and or maybe sometimes it is known as the coagulation and also the additions because they are so thin; they can stick with each other and then it is very difficult to make them separate.

So, these are all the problems when we are dealing this kind of nanoparticles into the very very small diameter. So, here also we are trying to give on classical example that quantum dots exhibits properties that are intermediate between those of bulk semiconductors and those of discrete molecules. Their optoelectronic properties change as a function of both sides and shape, it is clear from the figure as the size of a particle decrease; so you can see from this particular graph that size of that particular quantum dot is decreasing. So, when the size is decreasing automatically the band gap is increasing, so that is a very very good promising materials for the semiconductor industry.

So, then what again it is giving that it is clear from the figure, as the size of particle decrease till we reach a nano scale, this makes the energy levels discrete and this increases or widens up the band gap and ultimately the band gap energy also increases. So nowadays what we are trying to do, we are trying to use this kind of quantum dots materials; this is also a wonderful material from the carbon groups, so that materials actually we are trying to make it into the small small size. So, we are trying to make those materials into the smaller size so that it can give the maximum band gap so that we can get the maximum semiconducting properties from that particular filler itself.

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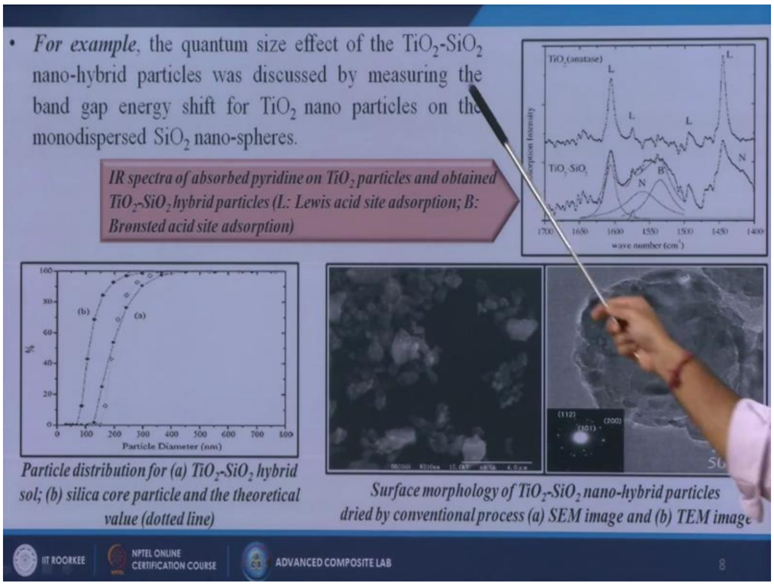

- *For example*, the quantum size effect of the TiO_2-SiO_2 nano-hybrid particles was discussed by measuring the band gap energy shift for TiO_2 nano particles on the monodispersed SiO_2 nano-spheres.

IR spectra of absorbed pyridine on TiO_2 particles and obtained TiO_2-SiO_2 hybrid particles (L: Lewis acid site adsorption; B: Brønsted acid site adsorption)

Particle distribution for (a) TiO_2-SiO_2 hybrid sol; (b) silica core particle and the theoretical value (dotted line)

Surface morphology of TiO_2-SiO_2 nano-hybrid particles dried by conventional process (a) SEM image and (b) TEM image

Next that is also an example, so here the example is that quantum side effect of titanium dioxide, silicon dioxide nano hybrid particles was discussed by measuring the band gap energy shift for titanium dioner particles on the monodispersed silicon dioxide nano spheres. So, here actually the material is the hybrid composites initially we have taken the silicon dioxide fears on top of that we have done the modification by titanium dioxide. So, we have made certain kind of hybrid composites kind of things which we are going to use for some kind of electronic purposes or maybe some kind of other optical purposes.

So, here from this particular figure you can see that we have given some kind of (Refer Time: 14:11) spectra or maybe that Fourier transform infrared spectra. So, in which we can see in the topmost phase that is called the TiO 2 in the antes phase, you know that TiO 2 can stay into the three different form, so (Refer Time: 14:25) is one of the most stable form where we can get or maybe we can put the TiO 2 for a longer time so that it will not decrease its properties.

So, when we are talking about that TiO 2 and this next sample it is showing the TiO 2 Si hybrid composites and from that particular FTR graph, you can see that some graph has been shifted to the left hand side which is showing actually the better entangle entanglement in between the coating materials and in between the substrate materials so that it is showing some kind of better properties how it is showing the better properties, when we are talking about the particle size distribution for TiO 2 SiO 2 hybrid (Refer Time: 15:07) and silica core particles and the theoretical value in the dotted line, we are showing that when we are changing the particle size diameter into the nano level, so automatically some properties is getting increased for that particular case.

The same thing has been proved by the some kind of Fac image and tan image also, here the tan image it is showing that (Refer Time: 15:29) structure of that materials in which we can show in the middle is the SiO 2 silicon dioxide can be easily seen and the outside is surrounded by that TiO 2 materials. So, from that particular figure we can easily show that how the size dependency is affecting onto the semiconductor or maybe the some of the electronics properties.

Then we are trying to discuss that size effect on the thermal conductivity, actually this topic is totally depends upon the size when we are reducing the size of that particular nanoparticles, we are going to see that how the properties is changing or maybe rather we can say that how the property of that particular composite is increasing or maybe it is showing some other extra properties than before.

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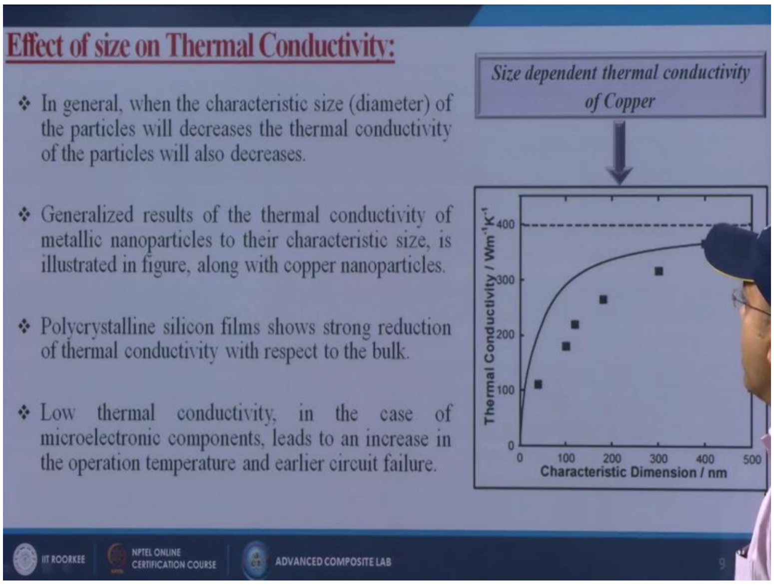

Effect of size on Thermal Conductivity:

- In general, when the characteristic size (diameter) of the particles will decreases the thermal conductivity of the particles will also decreases.
- Generalized results of the thermal conductivity of metallic nanoparticles to their characteristic size, is illustrated in figure, along with copper nanoparticles.
- Polycrystalline silicon films shows strong reduction of thermal conductivity with respect to the bulk.
- Low thermal conductivity, in the case of microelectronic components, leads to an increase in the operation temperature and earlier circuit failure.

Size dependent thermal conductivity of Copper

So here in general when the characteristic size like diameter of the particle will decrease; the thermal conductivity of the particles will also decreases. So, here generalized result of the thermal conductivity of metallic nanoparticles to their characteristic size is illustrated in figure along with the copper nanoparticles. A Polycrystalline silicon film shows strong reduction of thermal conductivity with respect to the bulk. So, you see when we are using this kind of materials and we are using the size of that particular material or may be the shape of that particular material, automatically it is showing the better properties than the before.

Not only that low thermal conductivity, in the case of microelectronic components leads to an increase in the operation temperature and earlier circuit failure. So, when we are reducing the size automatically we are getting the low thermal conductivity in future which is helping us to increase the operation temperature, not only that the earlier circuit failure. So, that the heat energy whatever it is generating at that particular point slowly very quickly it is dissipating, so that; that particular equipment or maybe the circuit or maybe the diode or maybe whatever the electronic part we are going to use, they are not capturing that heat; that means, they are not heated up; up to certain temperature. So, that heat is quickly dissipating; that means, they are cooling down very quick, so that machine fault or maybe that circuit fault may be stopped or maybe rejected.

So, here this is also the thing in where we can see that when we are going to increase the dimensions of that particular nanoparticles, so automatically the thermal conductivity is getting increased so; that means, when we are going to the smaller size then automatically the thermal conductivity of that particular material is getting reduced

Next is called the effect of size and corrosion phenomena, the same thing we can prove for that corrosion property or maybe that corrosion resistant material. So when we are using some kind of nanoparticles, if in the micro size whatever the corrosion properties it is showing if we are trying to reduce its particle size; the corrosion property will be much better or maybe that corrosion resistant property will be much better, the same thing has been shown over here also.

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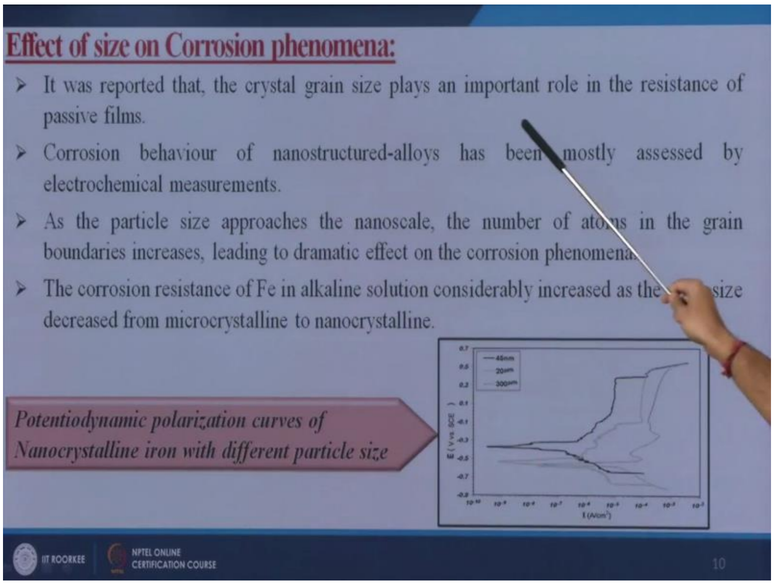

Effect of size on Corrosion phenomena:

- It was reported that, the crystal grain size plays an important role in the resistance of passive films.
- Corrosion behaviour of nanostructured-alloys has been mostly assessed by electrochemical measurements.
- As the particle size approaches the nanoscale, the number of atoms in the grain boundaries increases, leading to dramatic effect on the corrosion phenomena.
- The corrosion resistance of Fe in alkaline solution considerably increased as the size decreased from microcrystalline to nanocrystalline.

Potentiodynamic polarization curves of Nanocrystalline iron with different particle size

So, in that some literature it was reported that crystal grain size plays an important role in the resistance or passive films; that means, corrosion behavior of nano structured alloys has been mostly assessed by the electrochemical measurement, as the particle size approaches the nano scale, the number of atoms in the grain boundaries increases leading to dramatic effect on the corrosion phenomena, so this is the basic principle of this particular slide.

The corrosion resistance of iron in alkaline solution considerably increased as the grain size decreased from micro crystalline to the nano crystalline. So, this is very good example that where the size is actually creating some betterment in terms of the corrosion protections. So below is a figure where we are giving that potential dynamic polarization curve of nano crystalline iron with different particle size. So, you can see that we have given the graph in terms of 40 nanometer particle size, 20 micrometer particle size 300 micrometer particle size. So, when we are talking about that smaller particle size you can see the area is much broader; that means the corrosion resistant property of that particular material is tremendously increasing.

Then the same thing we are trying to see in that particular case also that is nothing, but the effect of size on that gas sensitivity. Nowadays you can remember that we are using so many sensors, we are trying to make our all systems in our environment, in our car, in our industry that fully automated. So, in that particular case we are trying to introduce the sensor each and every where. So, when we are making some kind of sensor generally we are talking about the sensitivity of that particular sensor then what is the hysteresis of that particular sensor then what is the reproducibility of that particular sense or maybe what is the longevity of that particular sensor and not only that how fast that sensor can react or maybe that how fast the sensor can work or maybe accept the results that is also the main criteria for this particular gas sensor.

So, when we are trying to use these kinds of nano particles and maybe the small size and nano particles then we can see that the gas sensing properties of those materials is increasing tremendously.

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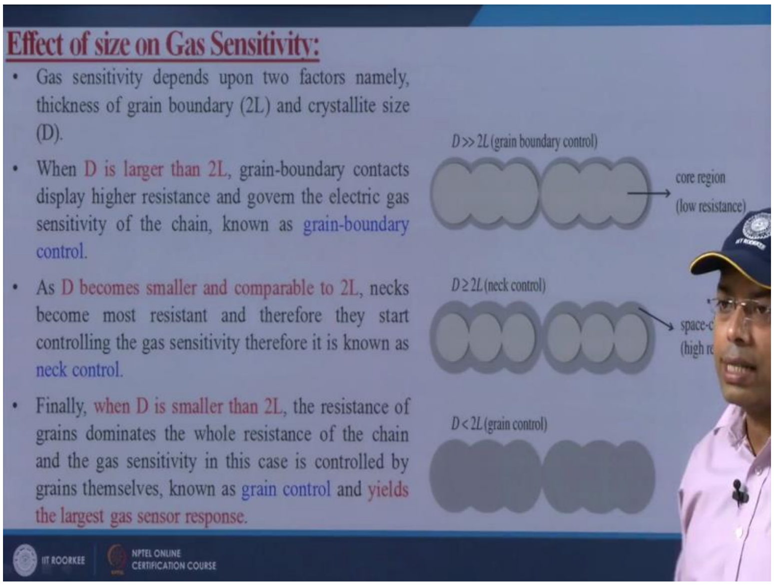

Effect of size on Gas Sensitivity:

- Gas sensitivity depends upon two factors namely, thickness of grain boundary (2L) and crystallite size (D).
- When D is larger than 2L, grain-boundary contacts display higher resistance and govern the electric gas sensitivity of the chain, known as grain-boundary control.
- As D becomes smaller and comparable to 2L, necks become most resistant and therefore they start controlling the gas sensitivity therefore it is known as neck control.
- Finally, when D is smaller than 2L, the resistance of grains dominates the whole resistance of the chain and the gas sensitivity in this case is controlled by grains themselves, known as grain control and yields the largest gas sensor response.

So, gas sensitivity depends upon two factors namely the thickness of the grain boundary that is known as the 2L and the crystallized size which is known as the capital D. So, in this particular figure I am trying to explain that how these different sizes are actually affecting the gas sensing technology.

So, here when D is larger than 2L, here grain boundary contacts display higher resistance and govern the electric gas sensitivity of the chain known as grain boundary control. So, here it is showing the low resistance at that particular point, when D becomes smaller and comparable to 2L, next become most resistant and therefore, they start controlling the gas sensitivity therefore, it is known as neck control. So, here you can see that particle sizes were reducing so the same material is showing the better results than the previous one. So, in that particular case we are observing the high resistance.

Finally, when D is smaller than 2 L, the resistance of grains dominates the whole resistance of the chain and the gas sensitivity in this case is controlled by grains themselves, known as grain control and yields the largest gas sensor response in this particular case. So, the thing is that slowly we are trying to decrease the shape and size of that particular nanoparticle so that we can get the better results in terms of gas sensing properties.

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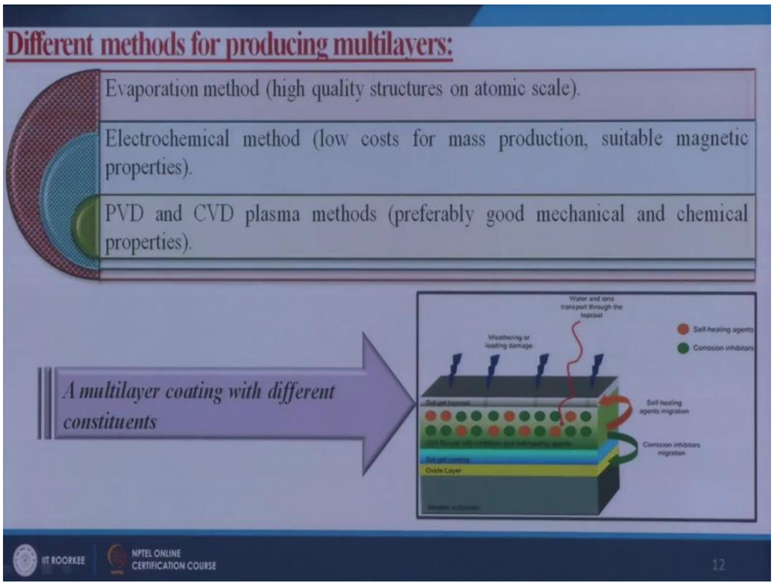

Different methods for producing multilayers:

- Evaporation method (high quality structures on atomic scale).
- Electrochemical method (low costs for mass production, suitable magnetic properties).
- PVD and CVD plasma methods (preferably good mechanical and chemical properties).

A multilayer coating with different constituents

Then there are several methods for producing the multi layers, so actually till now we are discussing about the some kind of coating materials which we are using only a single layer or maybe the mono layer onto the substrate itself, but when you are talking about the multi layers, evaporation methods, high quality structures on atomic scale. Electrochemical method; low costs for mass production of suitable magnetic properties PVD and CVD plasma methods; preferably good mechanical and chemical properties.

So when you are talking about the multi layer, from the name itself you can understand that I am having the substrate, on top of that we are putting one layer of one materials then on top of that layer again we are putting a layer of another materials, so like that one by one just we are making a sandwich like structure.

So, a multi layer coating with different conditions is generally looking like this, it is an example where I am having the metallic substrate, on top of that I have put the oxide layer, on top of that I have put some kind of sol-gel coating then I have put some kind of sol-gel with inhibitors and self healing agents which can accept the corrosion inhibitors migrations then on top of that I have put some kind of sol-gel top coat and top of that we are putting some kind of weathering or maybe the loading damage.

So here the main function of this kind of coatings is that, it can show several properties are may be the several vapour better properties than the previous one. So, from this particular material there topmost cover it will not deflect or I mean it will not change into some sunlight or maybe into the rainy season, then we are it is having some kind of self healing agents. So if something some cracks or pores can be taken place on to that particular coating. So automatically they can react together and they can make the chain once again and also it is having that corrosion inhibitors; that means, it can stop that corrosion, so that our substrate material not directly come into the contact with the environment so that its corrosion properties will be diminishing.

Next also we are trying to discuss about this type of hybrid nano fillers in terms of some properties. So, first one is called the coating of TiO 2 layer on the silicon dioxide mono dispersed particles. So in this particular case what we are trying to do; the coating layer thickness of the obtained TiO 2 silicon dioxide hybrid particles were estimated by TEM observations. So here in this case, we are same thing we are trying to make the silicon dioxide microspheres, on top of that we are doing the coating of the titanium dioxide materials. So, the titanium and silicon ratio was changed from 0.1 to 1.0 in order to control the coating layer thickness and the crystallite size.

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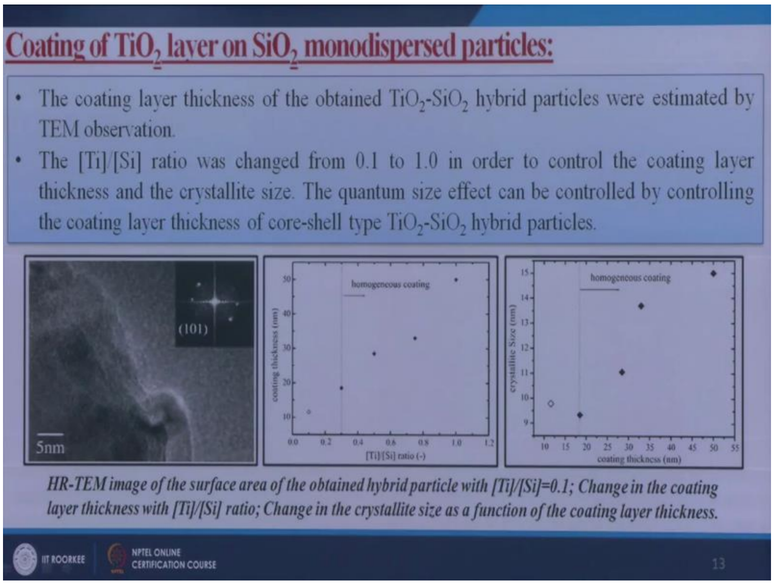

Coating of TiO_2 layer on SiO_2 monodispersed particles:

- The coating layer thickness of the obtained TiO_2-SiO_2 hybrid particles were estimated by TEM observation.
- The [Ti]/[Si] ratio was changed from 0.1 to 1.0 in order to control the coating layer thickness and the crystallite size. The quantum size effect can be controlled by controlling the coating layer thickness of core-shell type TiO_2-SiO_2 hybrid particles.

HR-TEM image of the surface area of the obtained hybrid particle with [Ti]/[Si]=0.1; Change in the coating layer thickness with [Ti]/[Si] ratio; Change in the crystallite size as a function of the coating layer thickness.

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By two methods we can do these kinds of things. Suppose in that particular case what is happening, we are having that titanium dioxide layer; so inside is our silicon dioxide materials and the top of that we are giving the layer of titanium dioxide.

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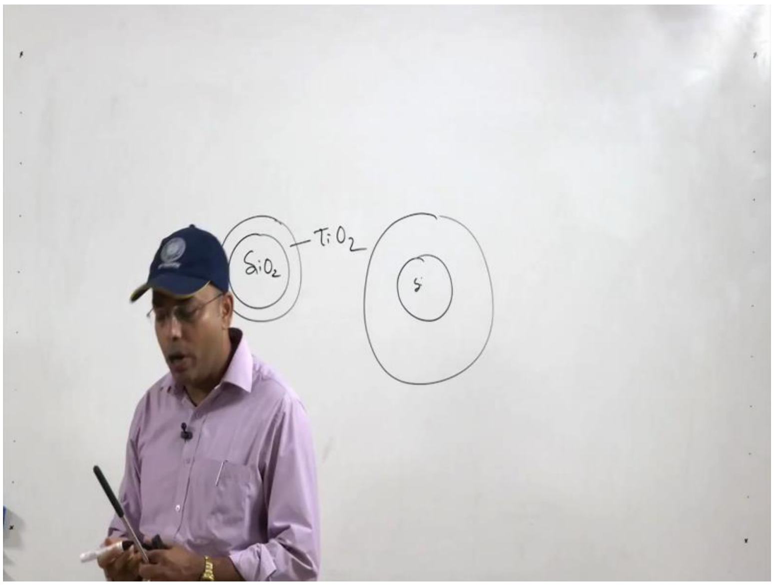

So in this particular case we can do the two things either we can increase the size of this particular silicon dioxide. So, that automatically the titanium dioxide thickness will be reduced that is one way or maybe I can increase the size of the SiO 2 and simultaneously I can increase the size of the TiO 2, so there are two types of ratios can be obtained from that particular case. The same thing has been written over here that 0.1 to 1.0 in order to control the coating layer thickness. So one case I am trying to increase the coating layer thickness, another case I am trying to increase the crystallized size. So, both the cases I can check that whether our material is giving the better properties or not than the previous one.

So, in this particular case we are having a very good high resolution transmission electron microscopy image of the surface area of the obtained hybrid particles with ti oblique; Si is equal to 0.1 ratio. So, where the titanium and silicon ratio is almost 0.1 and next we are trying to change the ratio thickness and then in terms of coating thickness just we are trying to change it from into different value and we can see that how the coating properties is changing. One case we have changed the coating size or maybe that coating thickness, another case we have changed the crystallite size and after that we have seen that how much property or maybe what better properties we are going to get.

So, here we are trying to discuss about some key features of the multi layer coatings. So, when we are talking about the multi layer coating, which includes different pile materials on atomic scale these multi layer coatings are called the super lattice. In my last slide we have maybe last two last slide I have already told you that when on substrate itself, when you are changing the different coating by layer by layer techniques we are calling it as a multi layer coating.

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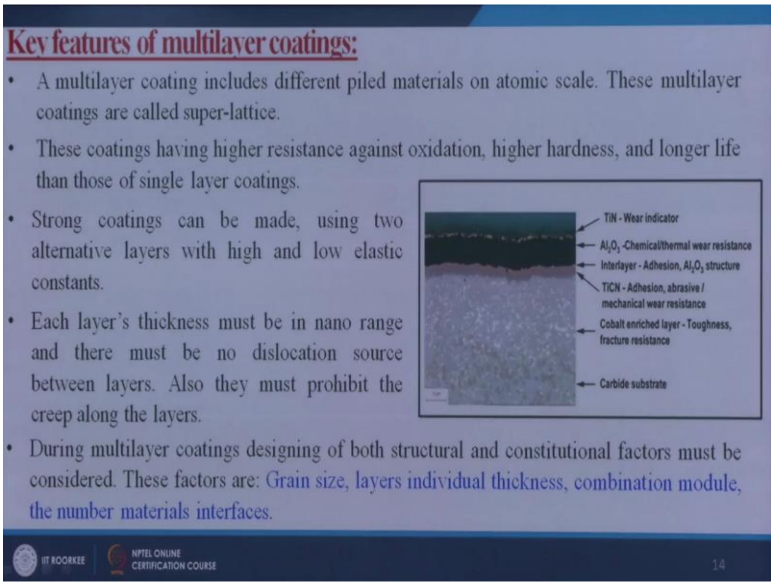

Key features of multilayer coatings:

- A multilayer coating includes different piled materials on atomic scale. These multilayer coatings are called super-lattice.
- These coatings having higher resistance against oxidation, higher hardness, and longer life than those of single layer coatings.
- Strong coatings can be made, using two alternative layers with high and low elastic constants.
- Each layer's thickness must be in nano range and there must be no dislocation source between layers. Also they must prohibit the creep along the layers.
- During multilayer coatings designing of both structural and constitutional factors must be considered. These factors are: Grain size, layers individual thickness, combination module, the number materials interfaces.

So, here that multi layer coating also sometimes known as the super lattice, these coatings having higher resistance against oxidations, higher hardness and longer life than those of single layer coatings and strong coatings can be made using two alternative layers with high and low elastic constants. So, here by these methods may be whatever the coating I am primarily doing that we can protect that coating or maybe we can enhance the properties of that coating or maybe we can add some more harder than the previous one.

So by doing this one, we can get the better properties by doing these kind of multi layer coating. Each layer thickness must be in nano range and there must be no dislocation source between layers also they must prohibit the creep along the layers; that means, when I am using a one lower onto that substrate itself that layer should be stick together that layer should be homogeneously dispersed onto the substrate then I am going to put the second layer and second layer also will stick with that first layer in a very nice manner, it is not like that that may be some places the first layer is totally absent and the second layer is reaching and it is attaching with the substrate, it should not be like that and not only that during multi layer coatings designing a both structural and constitutional factors must be considered, these factors are grains size, layers individual thickness, combination module and the number of materials interfaces.

So, these all are the key important parameters when we are trying to do the multi layer coating on to our substrate. Here is also one very nice examples has been shown that we are having some kind of carbide substrate, on that we are having some cobalt enriched layer which is giving you the toughness and fracture resistance then on top of that we are putting the titanium cyanide materials which is giving you the better additions, averages or maybe the mechanical wear resistance, on top of inter layer we are putting some kind of alumina structure which is actually giving some kind of additions in between the coating materials because sometimes in between the coating materials also we need to put certain kind of binder materials or maybe the addressing materials so that both the coating layer can stick together and they cannot come out very easily or maybe that layer separation should not be taking place.

Then on top of that we are putting some kind of alumina which is giving you the chemical or maybe the thermal wear resistance and top of that the last layer is known as the titanium nitride which is nothing, but the way indicator. So, by applying different materials layer by layer we can get so many properties from a particular material or maybe from a particular sample.

Next what are the improvements generally in physical and mechanical properties through multi layer and multi constrained coatings.

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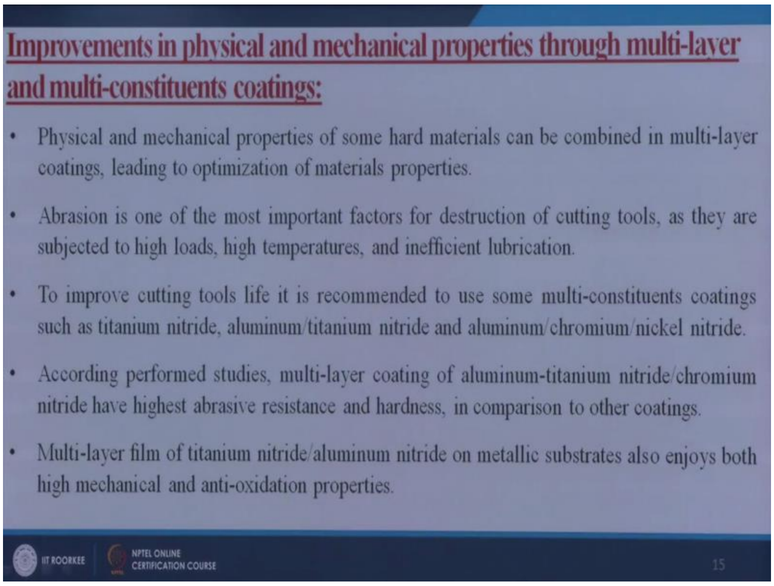

Improvements in physical and mechanical properties through multi-layer and multi-constituents coatings:

- Physical and mechanical properties of some hard materials can be combined in multi-layer coatings, leading to optimization of materials properties.
- Abrasion is one of the most important factors for destruction of cutting tools, as they are subjected to high loads, high temperatures, and inefficient lubrication.
- To improve cutting tools life it is recommended to use some multi-constituents coatings such as titanium nitride, aluminum/titanium nitride and aluminum/chromium/nickel nitride.
- According performed studies, multi-layer coating of aluminum-titanium nitride/chromium nitride have highest abrasive resistance and hardness, in comparison to other coatings.
- Multi-layer film of titanium nitride/aluminum nitride on metallic substrates also enjoys both high mechanical and anti-oxidation properties.

First one is called the physical and mechanical properties of some hard materials can be combined in multi layer coatings leading to optimization of material properties. Yes of course, that actually totally depend upon our requirement, I can put some kind of soft materials on top of that I can put some kind of hard materials, again top of that I can put some kind of soft materials, it totally depends upon our requirement.

Abrasion is one of the most important factors for destruction of cutting tools as they are subjected to high loads, high temperature and the inefficient lubrications. To improve cutting tools life it is recommended to use some multi constituents coatings such as titanium nitride, aluminum titanium nitride, aluminum chromium nickel nitrate because these all are the hardest materials. By (Refer Time: 32:03) if we want to make the cutting tool by this kind of materials, it will be very very expensive not only that maybe after certain time they can break then replacing cost of that particular cutting tool is also too high.

So what we are doing; we are trying to use some kind of simple cutting tool made by the high speed steel then we are doing the coating of this kind of materials on the high speed steel or maybe that HSS steel so that material may be some harder material can be cut easily and then when the coating material will be (Refer Time: 32:39) then second times also we can coat the material. So, in a broader manner we can see that cutting tool cost will be reduced not only that the production rate will be very very high. So, according perform studies multi layer coating of aluminum, titanium nitride, chromium nitride have highest abrasive resistance and hardness in comparison to other coatings. Multi layer film of titanium nitride, aluminum nitride on metallic substrate also enjoys both high mechanical and oxidation properties. Not only that it is giving you the some hardness or maybe the toughness to the cutting tool, sometimes it is giving you some kind of high mechanical and oxidation, anti oxidation properties too.

Then we are trying to discuss; what are the advantages of multi layer flames over the single layer, and what are the disadvantages.

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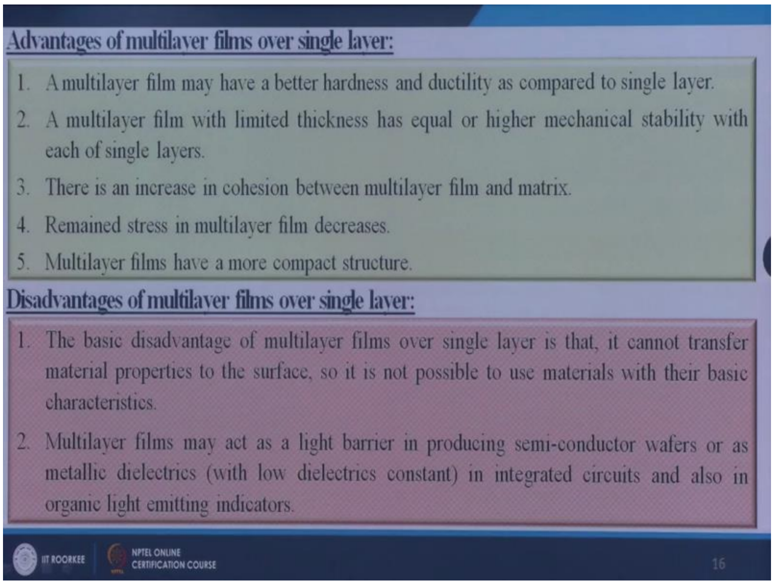

Advantages of multilayer films over single layer:

1. A multilayer film may have a better hardness and ductility as compared to single layer.
2. A multilayer film with limited thickness has equal or higher mechanical stability with each of single layers.
3. There is an increase in cohesion between multilayer film and matrix.
4. Remained stress in multilayer film decreases.
5. Multilayer films have a more compact structure.

Disadvantages of multilayer films over single layer:

1. The basic disadvantage of multilayer films over single layer is that, it cannot transfer material properties to the surface, so it is not possible to use materials with their basic characteristics.
2. Multilayer films may act as a light barrier in producing semi-conductor wafers or as metallic dielectrics (with low dielectrics constant) in integrated circuits and also in organic light emitting indicators.

So when you are talking about the advantages; a multi layer flame may have a better hardness and ductility as compared to single layer. A multi layer flam with limited thickness has equal or higher mechanical capability stability with each of single layers. There is an increase in cohesion between the multilayer film and matrix, remained stress in multilayer film decreases; multilayer films have a more compact structure. So, these all are the added advantage that is why we are going to use that multi layer coatings on to some substrate just to enhance the so many properties at a time.

Then of course there is certain kind of disadvantage otherwise totally the research or maybe the development will be stopped. So what are those disadvantages, the basic disadvantage of multilayer films over single layer is that it cannot transfer material properties to the surface. So, it is not possible to use materials with their basic characteristics that is the biggest disadvantage of this kind of multi layer coating.

Then multi layer films may act as a light barrier in producing semiconductor wafers or and metallic dielectrics, so sometimes it can create certain problem for the electronic purposes. So, that is also one kind of disadvantage for using the multilayer coating on single layer coating.

Then we have to come to the summary, so when we are summarizing this whole lecture first we have discussed about the size which is the size of particles or grain size and thickness of nano structure is a very crucial factor for nano application.

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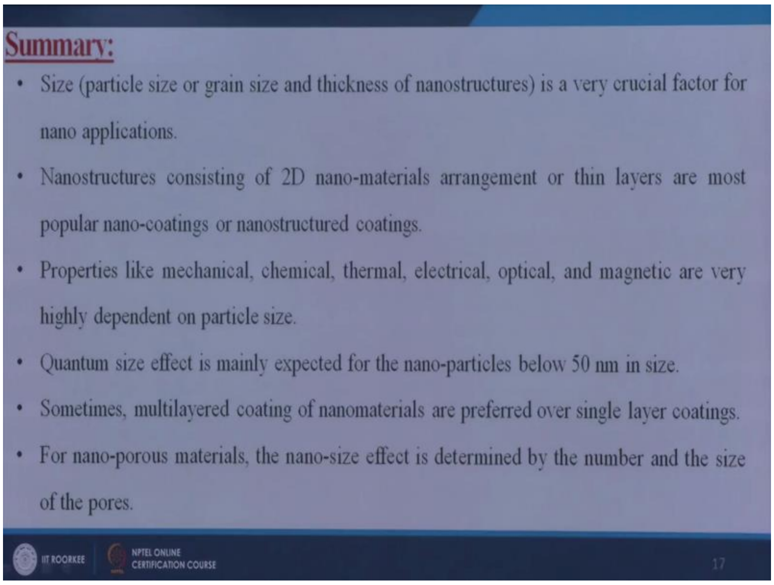

Summary:

- Size (particle size or grain size and thickness of nanostructures) is a very crucial factor for nano applications.
- Nanostructures consisting of 2D nano-materials arrangement or thin layers are most popular nano-coatings or nanostructured coatings.
- Properties like mechanical, chemical, thermal, electrical, optical, and magnetic are very highly dependent on particle size.
- Quantum size effect is mainly expected for the nano-particles below 50 nm in size.
- Sometimes, multilayered coating of nanomaterials are preferred over single layer coatings.
- For nano-porous materials, the nano-size effect is determined by the number and the size of the pores.

So, as I told already the crystallite size and the thickness of that coating are the two most vital parameters for this kind of coating techniques. Then nano structures consisting of 2 d nano materials arrangement or thin layers are most popular nano coatings or nanostructured coatings. Properties like mechanical, chemical, thermal, electrical, optical and magnetic are very highly dependent on particle size. Quantum size effect is mainly expected for the nano-particles below 50 nanometer in range; it is more below than the nanometer scale. Sometimes multilayered coating of nanomaterials are preferred over single layer coatings, for nano porous materials the nano size effect is determined by the number and the size of the pores, so these all are the main key factor of this particular lecture.

Thank you.