Nanostructures and Nanomaterials: Characterization and Properties

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Lecture - 07
Introduction to Nano materials (C1)

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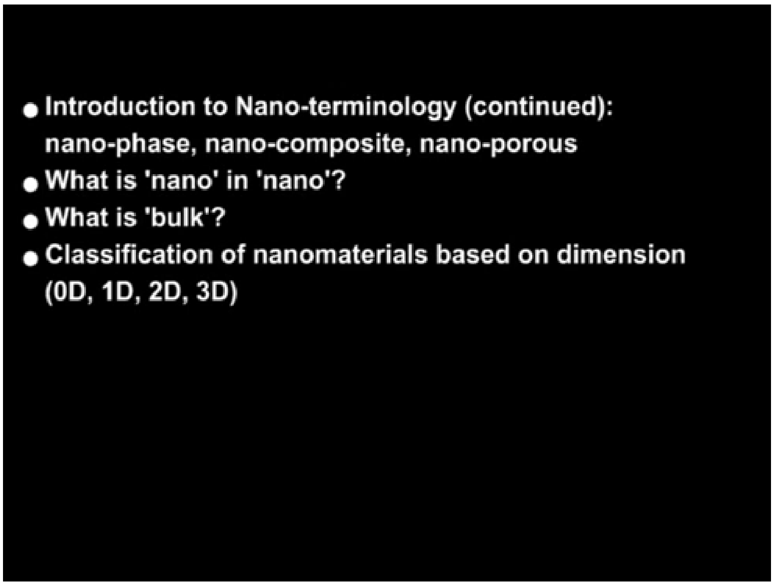

The next important term, is the class of Nano phase materials, and the phase which is being referred could be based on atomic order.

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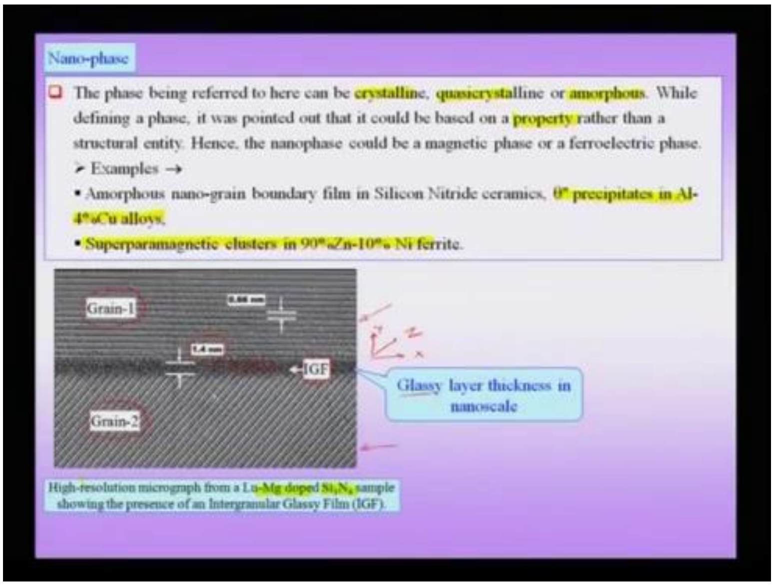

In which case I would have terms like crystalline, quasi crystalline or amorphous Nano phases, or it could be based on a property rather than a structural entity. And when I am talking about a property, I would be referring for instance to a magnetic phase, a ferroelectric phase or a conducting phase, which could be in the Nano scale.

One example of such a Nano phase material is shown here, which is a very interesting example, in which you see a sample of silicon nitride, which is actually a lutetium magnesium doped silicon nitride ceramic. And in this ceramic, there are two parts which are, which have lattice fringes, which are the, what we might call the crystalline green.

So, this is the crystalline green, this is another crystalline green here. Between the two crystalline greens, is a different kind of contrast which is seen in a high resolution lattice fringe image in a transmission electron micro graph. And you can see that this kind of contrast actually comes from a glassy material. The word glassy has been used instead of the word glass because, the structure of this what you might call the inter granular glassy film, is slightly different form that of the bulk glass which is typically found.

And this differences is precisely coming because of the Nano scale confinement between the two grains, which is the grain 1, which is the crystalline grain of silicon nitride, and a grain 2 which is another crystalline grain of silicon nitrite. So therefore, it is the phase which is in between which is of course, as we shall see later will be called a 1 dimensional Nano material, or which is been constrained 1 dimension.

Therefore, there are 2 dimensions which are bulk, and in an alternate classification, you could call it a 2 dimensional Nano material is about 1.4 Nano meters stick. And the other 2 dimensions. Of course, it behaves it is pretty long, that means if I am talking about this is the x axis, it is pretty large, the axis going inside which is the z axis also pretty large, only in the y dimension this is Nano scale, it is about 1.4 Nano meter.

Now, there are other examples, like for instance the theta double prime precipitate, in an aluminum copper, 4 percent copper alloy, which is been aged that means, you do as we have seen before you take a aluminum copper 4 percent copper alloy, solutionize it at high temperature, quench it to retain a super saturated solid solution. And then when you age this alloy, you actually get initially a GP zone, which itself a Nano structure, or a Nano phase, which is a copper rich zone in a aluminum copper matrix, then you get these theta double prime and theta states.

And in the initial stages of their growth, these are actually in the Nano scale. You could also have as I pointed out, a classification based on a property and you could have super paramagnetic clusters in an 90 percent zinc, 10 percent nickel ferrite. Therefore, when I am talking to summarize this slide, when I am talking about a Nano phase, this phase could be a phase defined based on a structural entity, like a quasi-crystalline and amorphous, it could be based on a property like in the case of a ferroelectric material or a ferromagnetic material, and as we shall see later that, this phase can be Nano in 1 dimension, 2 dimension or 3 dimension. The example of 3 dimensionally confined clusters, are the super para magnetic clusters, in nickel 10 percent nickel ferrites. Now, some of the details of some of these phases, like super para magnetic phases and the amorphous green mount, which you have seen here, we consider in detail later. But for now it is important to note that, the definition of Nano crystallinity or Nano ness is based on a phase.

And therefore, here we are not actually considering the geometry, like I would consider in the case of a Nano structure. So, there is the importance to geometry given here is less, it is importance is given to the formation of a particular kind of phase. Now, we can proceed to other examples or other classifications and other terms. One of the important ones is a Nano composite. Now, we have seen that there is a class of monolithic materials, and the class of hybrids. Sometimes the word hybrids is used synonymously with composites, but we have to be care full that composites actually speaking a sub class of the hybrids. And we have seen some examples of hybrids like before.

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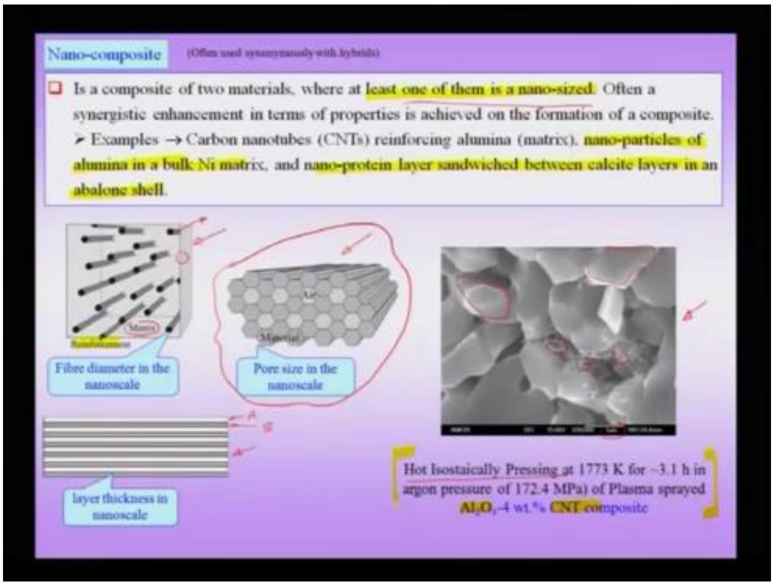

Like for instance the example on the left hand side, where we have a fiber reinforced. Composite or a kind of lattice structure, which is a composite or a combination of a pore and that is material and where, or we could have certain laminates. So, these are examples of what we may called hybrids. And when I am talking about a Nano composite, I am actually referring to one of these or at least one of these components being in the Nano scale.

So of course, all the components could be in Nano scale, but typically at least one of them has to be Nano sized, for us to call this composite a Nano composite. The reason of course, we have, we found these composites are hybrids is because, we get a synergistic effect on in terms of properties. And therefore, I have enhance properties of course, the property being talked about is a specific property in a given context, but in general we have an enhancement in a specific property.

And therefore, we have these hybrids, which we engineer. In the case of Nano composites of course, I could have, for instance suppose I am talking about a reinforcement phase, which is in the Nano scale. So now, in this whole composite, the matrix could be a bulk phase, which is the matrix here. The reinforcement could be in the Nano scale. So, we have an example of such a real example of that, on the right hand side you see here. You see that this is actually a hot iso-statically pressed sample, and in this sample, you have a carbon Nano tube reinforcement.

So, this is a ceramic alumina which has been reinforced with carbon Nano tubes. Of course, the reason for doing such a reinforcement is because, typically ceramic submittal, they have a low fracture toughness, and when you reinforce it with carbon Nano tubes, the toughness of the material increases. So, in this sample you can see that the carbon Nano tube, just here you can certain regions where there are carbon Nano tubes you can see here. These are typically multi valve carbon Nano tubes, which is now reinforcing by matrix, which is now poly crystalline alumina.

So, you can see the different grains, this is for instance one grain of alumina, this is another grain of alumina we can see here. And therefore, the carbon Nano tube is which is the Nano scale in this Nano scale structure in this whole composite is actually reinforcing alumina. The alumina grain size if you look at, it is typically of the order of microns.

So therefore, the alumina is not Nano structured, it is only the carbon in the or the carbon Nano tube in the reinforcement, which is Nano structured. And of course, this satisfies our condition for us to call it a Nano composite because at one of the phases at least, it is in the Nano scale. In any of the other examples for instance a composite like these, we will specifically take up a lattice structure in the coming slide, in which you have a, what you might call a composite or a hybrid of air and material.

And in this case again at least one of the two has to be either the air phase, which is the pore phase or the material has to be in the Nano scale, and we will take up an example soon. In a laminate like this for instance, you can see that there are two components, for this let me call the bright component a, and the dark component b. It could, so happen that a and b both are Nano scale, or at least one of a and b have to be Nano scale for us to call it a Nano composite.

We could also have reinforcements like Nano particles of alumina in a nickel matrix, we could have Nano protein layer sandwiched between calcite layers in an abalone shell. So, these are all examples of what you may call Nano hybrids or Nano composites. And of course, we already know the clear difference between, what is a hybrid and which subclass of these hybrids should be called composites.

So, let me summarize this slide, that when you work with hybrids we get certain important benefits. In the case of Nano materials, if one of the phases happens to be in a

Nano scale, not only we get the usual benefit we expect to get from a composite, but dis benefit could be highly enhanced. And in the case of a composite at least, one of the entities has to be in the Nano scale, it could so be possible that all the entities are more than one entities in the Nano scale. And Nano composites are a very important from the point of view of applications and the enhancement in the properties.

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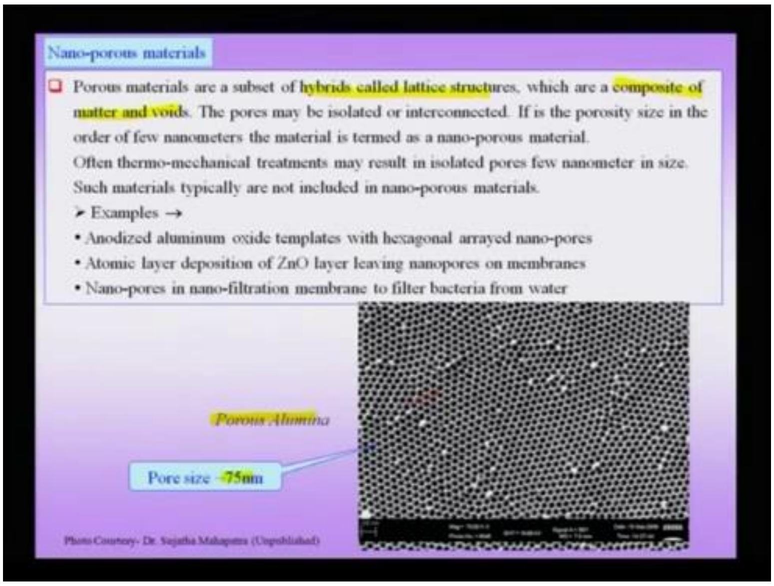

So, one such example was considered here which is now an alumina 4 weight percent, carbon Nano tube composite, which has gives us good fracture toughness. We had talked about a composite of air and material, which we called a lattice structure and of course, we had already differentiated this kind of lattice structure form the lattice structure in the context of crystallography. And these hybrids or these hybrids which are lattice structures, are a composite of matter and voids.

And in the example as you can see below here, this is now porous alumina, wherein the pore size of the order of 75 Nano meter, but if you look at the inter connects between the pores, that is also of the Nano scale. Because, now my pore size which is here these are my pores here the black things are my pores, this is in the Nano scale, but additionally they inter connects for instance, there is material between the two pores, that is also in the Nano scale.

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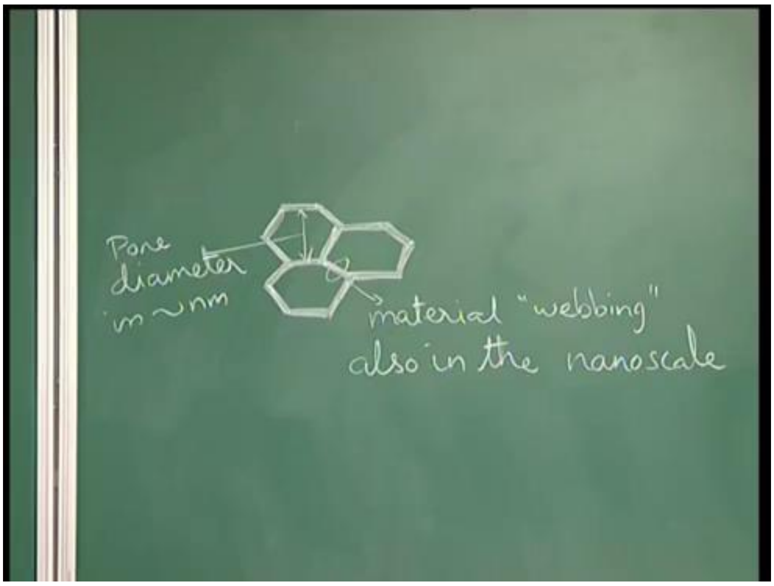

So, let me draw this in a little expanded fashion in the board. So, I have approximately hexagonal pores, and this pore diameter, it is pore diameter in the Nano scale, but actually it inter connects between the two, like this regime.

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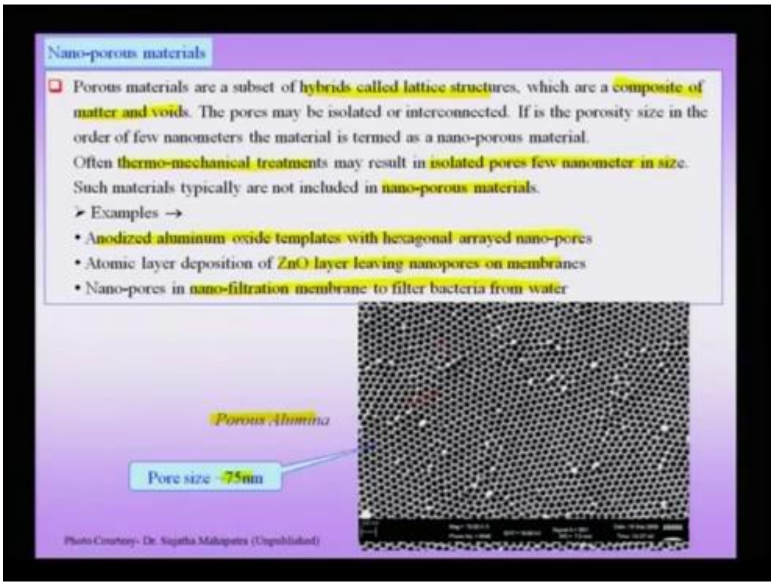

So, these kinds of materials wherein you have a pore and material, we can also, we use for certain very special purposes like for Nano filtration membrane to actually filter out bacteria, from water. They may have other interesting uses where, in the pore can actually be filled with other kind of metals and other kind of things and of course, when you fill it to the metal, that would now be a composite with the metal with alumina and can no longer be called a lattice structure.

Typically, one class of materials we exclude form this definition, and that class of materials typically of course, we may want to if intentionally done it can also be included in the definition, is the fact that when you do a thermo mechanical treatment, sometimes if you isolated pores may occur. So, this is actually a defect in a larger material, it is not being engineered to put these small pores in the material and typically, we do not include these pores into a Nano porous material.

If you take a irradiated material and then unyeild it often the vacancy is present in the irradiated material may come together to give a small void, which could be a Nano void. This presence of these Nano voids can alter the properties of the bulk material especially, if you are talking about a nuclear component wherein actually if there is component is actually being irradiated continuously.

But these class of materials may not be called Nano porous materials because it has not been engineered to put those pores in place. It has been coincidently coming because of the what do we call irradiation treatment, or certain kind of thermo mechanical treatment. But most of the structures like suppose, I am talking about zinc oxide layer having Nano pores or membranes or I am talking about the example which we construct below here, which is anodized aluminum oxide templates with hexagonal arrayed Nano pores.

These are all definitely Nano porous materials, and as we shall see later that of course, there could be some pores which are in the Nano scale some pores could be larger in size, but and therefore, such a material can with out and hierarchical arrangement of pores, when we talking about Nano materials and Nano structures and the Nano science there are very many additional terms which are pervaded in to literature. We are not going to each one of those in detail at present, but we have to remember that these additional terms can be understood in the background of all the terms you have described so far. Some of these terms I am listing here.

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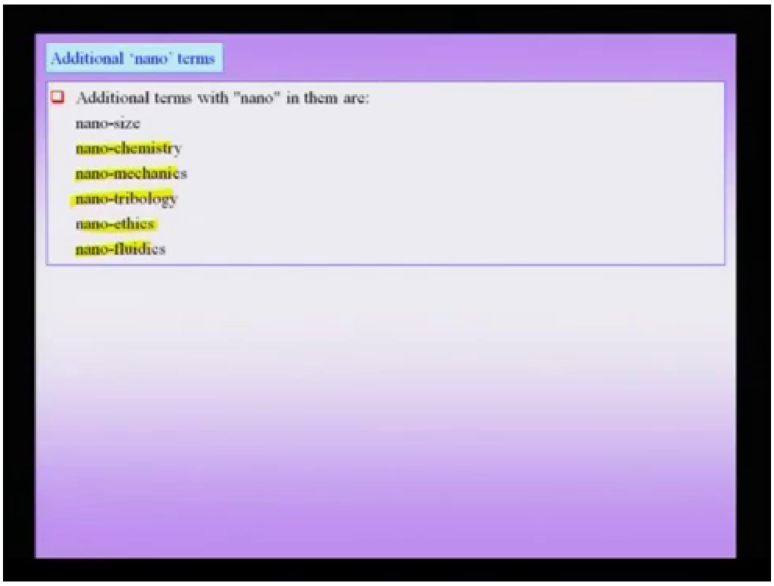

For example, Nano-chemistry, Nano-mechanics, Nano-tribology we will also talk a little bit more later about this which is the feed of Nano-ethics, Nano-fluidics etcetera. The reason for emergence of these fields and therefore, dedicated books, hand books. And journals to these fields is a kind of interesting effects and phenomenon, which come about when we study material and processes and various kind of scientific disciplines at the Nano scale.

And this is being some of the thrust reason why Nano science and Nano technology has grown over the years. We have considered of course, a small set of some of these things which can be Nano, but often we may not explicitly be stating them in a material. But in terms of their actual effect some of the other things also could be Nano, but we may we may or may not want to classify them as Nano material.

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For instance, cracks in a material could be Nano sized, which we can call Nano cracks. We could have actually surface steps in materials which could be Nano size. Some of the surface steps you see here and this is it could be Nano size for this is in hot iso-statically pressed alumina. And in this hot iso-statically pressed alumina you can see there are lot of surface roughness and surface steps and the step size could be of the order of Nano meters.

In modern tool, which is of very important form the determination of mechanical behavior of Nano material is a tool of Nano indentation, and the tool is very important because suppose I have a Nano material. For instance I could be having a Nano film on a substrate.

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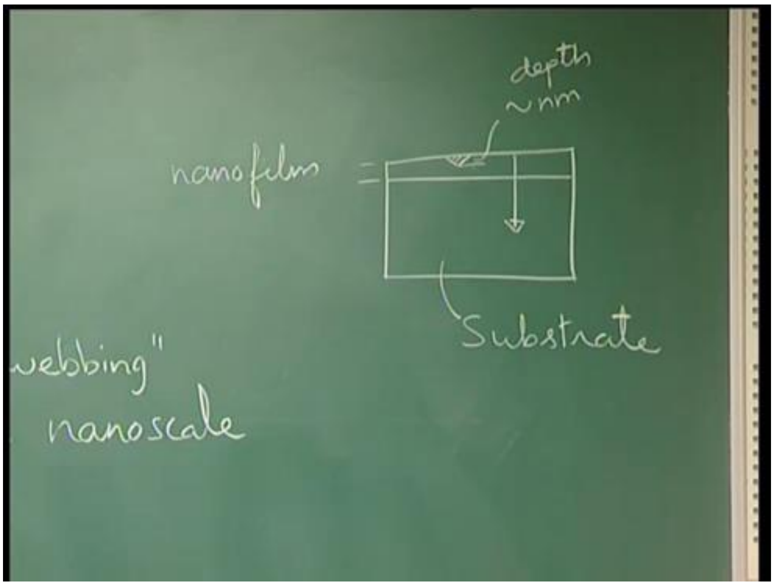

Now, suppose I want to determine the properties of the Nano film selectively, without actually taking into account, the substrate effects. In such a case the indentation obviously cannot pervade too much into the depth. So typically, I would like to keep my indentation less than half the distance of the thickness of the film therefore, I cannot use my bulk in indenter. Suppose, I put a bulk indenter it may actually penetrate my sample in to the lot of depth which, could be of the order of microns and therefore, I will actually not be sampling only the Nano film.

Additionally I cannot make a tensile placement that easily from my Nano film or use one of the standard test like a fracture toughness testing only by studying making actually a large specimen therefore, now I am restricted because, of the volume of material and the geometrical configuration of the material to do a test which is now my Nano indentation. And here the depth of the indentation is typically of the order of Nano meter.

Hence, often in Nano materials the testing technique is very much altered with respect to the bulk testing techniques, and often we have to come up with new standards for testing these materials and in this example which we have considered here we are talking about Nano indentation.

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And in a Nano indentation which has been shown here, we can clearly see that the of course, the diameter of the indentation of the dimension of the indentation on the surface is large, but the depth which is shown in the scale here is of the order of Nano meter.

Therefore, you have a indentation depth which is of the order of Nano meter and this is as I pointed out very important powerful tool in the study of Nano structures, Nano films Nano phase materials, etcetera. Another interesting example is shown here, which is now a zigzag spiral structure made of MgF 2 on glass slide, by a technique known as electron bean deposition. In this technique you can see that these are now MgF 2 spiral like structures or zigzag structures, which are growing, each individual entity can actually be referred to a Nano structure.

So, if I am isolating this individual entity here, this itself is a Nano structure because, it has a very specific geometry and its geometry happens to be in the Nano scale of course, as a hole now this combination can be called a Nano material now, and I may use some of the techniques like for instance, I could if this were not MgF 2, but carbon Nano tubes aligned grown then I could actually do a compression test on the cylinder, which is grown from such a align growth

And therefore, this is a very nice example of a totally different kind of a Nano structure as from what we have seen before and also, an aligned kind of a structure where in there is a what you might call, a co-relation in the way the various, what you call structures are grown. By changing the deposition condition, and the way the angle to which the deposition is done, and the angle at which the sub state is rotated we can get very many interesting structures using this technique. And this is just one of the examples which we have shown here.

So, when you are entering the Nano world, there are very many more things which can be Nano. We will deal with some of them as we go along, but it is important to note that, some of these are by choice, like for instance when you are doing a Nano indentation, or we are growing a layer like this, the zigzag spiral layer. But sometimes it is just co-incidental that you may have a crack in a material which is Nano sized, and you may want to call it a Nano crack. Because, now it is confined within for instance a certain phase, which is of the Nano scale dimension or you could have a coincidental Nano surface steps, which one we think that actually has not been engineered to be...

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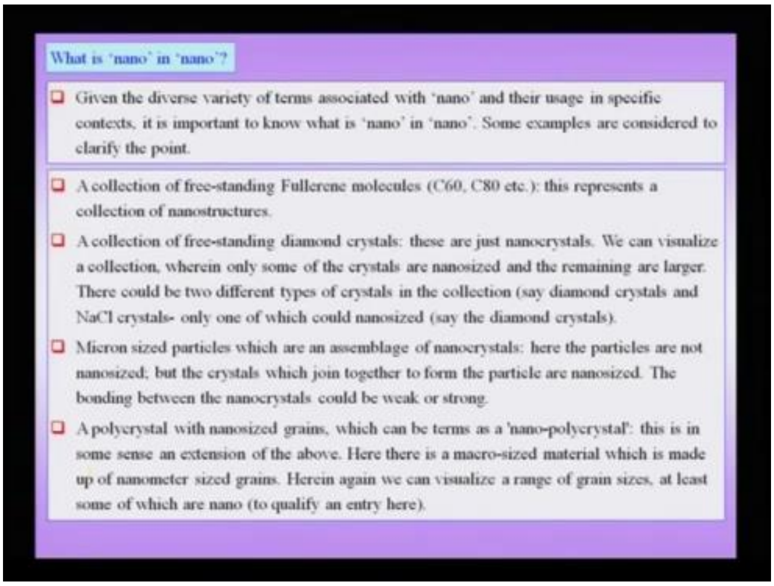

Before we have exposed ourselves to quite a few Nano terms now, and we have to be a little careful in understanding what is Nano in Nano. We are seeing for instance, in a previous example.

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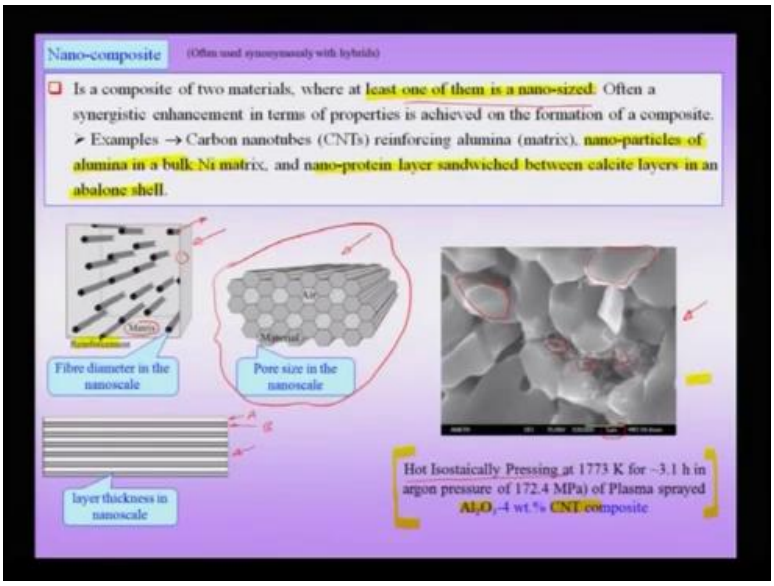

That in this sample everything is not Nano, for instance if I am talking about this Nano composite, everything is not nano. It is only a specific entity in the structure which is nano. And do the properties of this material deviate from that of the bulk material? Is another question which we may want to ask.

Therefore, we have to specifically ask ourselves what is Nano in Nano because a Nano prefix may often be attached to the entire material. We may call it a Nano material, but everything within the Nano material may not be nano, and it requires little bit of attention to see what is nano, and what kind of properties behave specially which is ((Refer Time: 20:47)) specific classification.

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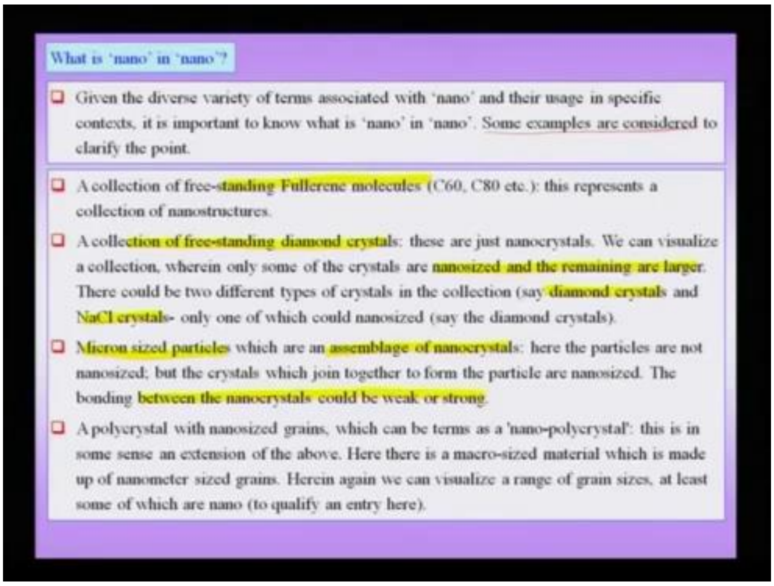

So, let us take up a few of those and some examples we are considering here to see clarify the point that what can be Nano in nano. A collection of free standing fullerene molecules is of course, each one of those molecules is a Nano structure, and in this case each one of those entities in the collection is also a Nano structure therefore, this is a very simple thing to identify what is Nano there.

We could have a collection of free standing diamond crystals, these are all just Nano crystals and in this crystal we can visualize a collection in which some crystals are Nano size and remaining are larger. Therefore, now you might have a bimodal distribution of sizes where, in some are in the Nano scale, some are in microns size, some could even be larger. And for instances we could have a collection of two different types of crystals where diamond crystals, and sodium chloride crystals where, in the diamond crystals are in the Nano size.

And the sodium chloride crystals are larger in size, and we should be clearly we should be very clear that which is the crystal, which is Nano size. Because, often in such a mixture or such a, aggregate the specific property may be arising only from one of the two entities in the collection. We can also visualize micron size particles, which are an assemblage of Nano crystals.

That means now, my particle is not Nano sized, but the particle itself consists of sub units which are Nano crystals or of course, there could also be other kind of we have seen that Nano crystals separated by a Nano amorphous kind of phase, so that is another possibility. And the bonding of course, between the Nano crystals could be weak or strong, like in the example we had considered here.

Suppose, I were to test the fracture toughness of such a material or try to do an impact is typically one finds it. The crack would tent to propagate through the grassy layer or suppose I where subjecting this silicon nitrite to creep test, then I would notice that the creep typically occurs by grain boundary sliding where in the glassy phase softens, and actually you have a slide.

Therefore, when it comes to deformation of this material, it is not just the large volume of fraction of material which is the crystalline grains which is determining the behavior of the material, but it is a small volume of fraction of this Nano size regime between the grains which is actually going to dominate the response of the material. Therefore, you have to be absolutely clear even though the volume fraction of a Nano phase or the volume fraction of the Nano crystal may be very small, it is effect on properties could be extremely large.

An extension of these kind of the concept of collection Nano particles in the case of a poly crystal with Nano size grains, here of course. The whole crystal could be of the order of millimeters, you could have a large poly crystal like our microscopic copper wire, but the grain size could be of the order of Nano meters. And typically you will be talking about 10 Nano meters to 50 nanometers, to even up to 100 Nano meters. And we shall see later that what are the techniques by which such kind of a, what you call a Nano structured poly crystal may be produced, I can name a few for instance for now.

For instance high pressure torsion or severe plastics deformation techniques like equi channel angular pressing, but we could also end up producing a Nano poly crystal, in which not all the grains are in the Nano size. There could be a again a bimodal distribution of grain sizes or a larger distribution of grain sizes in which we could have an extending.

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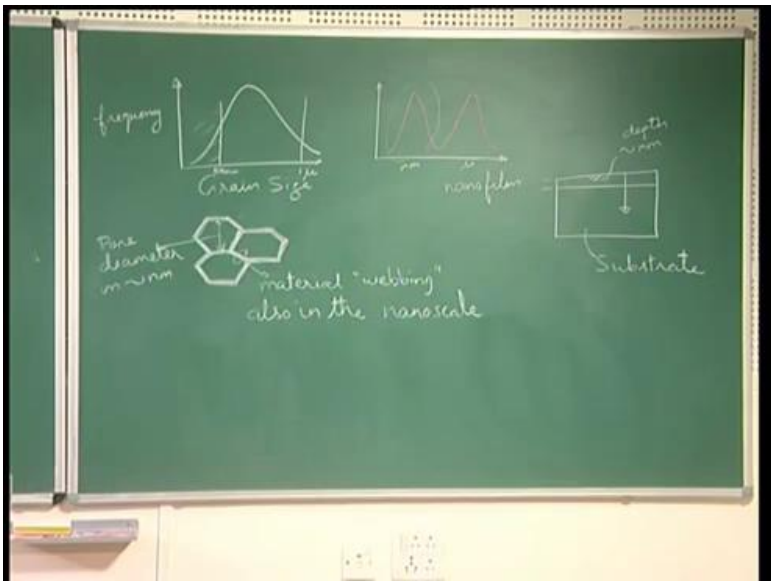

So, if I am plotting my frequency verses grain size, and we have some distribution like this where in, this could be of course, for instance 100 Nano meters and it could extend all the way up to say for instance a micron. So, only these crystals are typically in a Nano scale regime which are lying here, but if the processing condition is very dis drastically different form the one I am describing here, you may end up even producing a bimodal distribution where in, the crystals belonging to this could be in the Nano meter ratio, while this could be in the micro scale.

Therefore, again when I am talking about a Nano poly crystal, I have to be clear that what is the component, which is in the Nano scale and here is the grain size. And not that, all the grains need to be in the Nano crystalline regime, it could be only a small fraction of the grains, which are actually in the Nano crystalline regime, or it could be that we end up because of the processing condition into a bimodal distribution. Wherein one set of grains could be in the Nano crystalline regime. And it could so happen if I am talking about a multi-phase material, then one of the phases which is now in this distribution regime, which is now my distribution regime in the left.

So this could typically be one of the phases, and this could be the distribution which is coming from phase b, so all these are possibilities, and as long as I understand that which entity in this collection is in the Nano scale I am pretty much safe because, I know now that if I am talking about certain enhancement in properties or change in properties where is that coming from.

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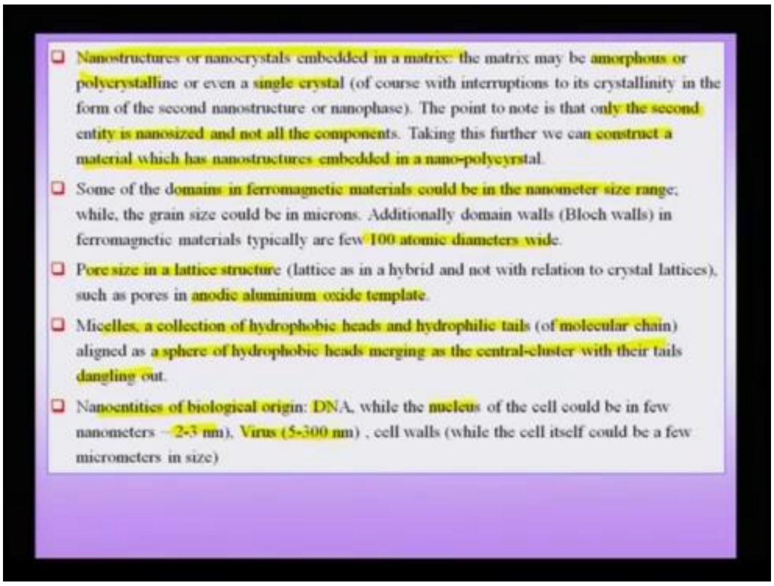

We can also, we have already considered this, we talked about the case of Nano structures or Nano crystals embedded in a matrix. The matrix itself may be amorphous or could be poly crystalline or could even be a single crystal. So these are possibilities for the matrix, and the second embedded phase, could be the Nano phase for instance, the only the second entity is Nano sized and not all the components. We can also think of a construct of a material which is Nano structured embedded in a Nano poly crystal as we had visualized earlier.

So, we have three possibilities when we are talking about a composite, for instance we could have a Nano poly crystal in which there is a Nano scale. For instance a Nano tube reinforcement, we could think of a multi phased poly crystal in which, one of the phases in the Nano scale, and additionally the reinforcement in the Nano scale and many other such possibilities which exist. And we have to absolutely clear here again that, which of that which is being Nano scaled though we may end up using a common nice terminology for this whole kind all these class of materials and call it all Nano materials.

So, we should not get confused that even though we are calling all of them Nano materials, not all this Nano in such a material. Another example would be some domains in a ferromagnetic material could be Nano meter size range, there could be other domains, which are extremely large in the micron scale. But typically we have noted that even in a large domain sized material, we could have domain walls which are typically called the block walls, which are which have a diameter about 100 atomic diameters wide.

And therefore, they are in the Nano scale. So even if we had a ferromagnetic material whose grain size was in microns whose domain size is also in the microns. But we could have these block walls which is the Nano meter lens scale. Additionally of course, we could have for instance surface domains in an ferromagnetic material, which are small in size, but other domains within the bulk of the material could actually be large in size.

Therefore, again in this ferromagnetic material not everything is in the Nano scale. We already seen the example of the pore size in a lattice structure, which is in the Nano scale which was the specific example. We saw the micro graph was the anodic aluminum oxide template, which as I told you can be used to actually do further processing and embed lot of and use them for making metallic Nano wires. So, that is a very nice starting point further processing, but it itself actually said is a Nano porous material.

We could think of micelles, a collection of with a collection of hydrophobic heads, and hydrophilic tails, and this each one of this itself is a molecular chain, and this is aligned as a sphere with a hydrophobic ends merging in a central cluster with their tails dangling out. Because, now suppose I have to disperse these miscalls in to water, then the hydro phobic ends would tend to cluster together, and this cluster could be in the Nano scale.

And of course, the components there are these molecular chains and these molecular chains themselves are of course, could be of the Nano meter length scale. There are many very many entities we already seen biological origin like the DNA, and the nucleus of a cell which could be of the order 2 to 3 Nano meters. The virus for it is many viruses are also in the Nano scale, and people are actually crystallize these viruses and they could be in the Nano scale cell walls could be in the Nano scale, but cell itself is not a Nano scale entity.

Typically, cell is in the what you might call the human beings are pretty large most of the cells, but some entities off sells themselves as we have seen near the cell walls, the DNA etcetera are could be in the Nano scale. And of course, belies abound with many much more, many more examples wherein you have the Nano scale present. And nature has been always been benefiting from the use of Nano scale materials. The Nano scale structures, and various phenomenon, which have very much altered at the Nano scale.

Typically, if you look at a cell wall of an animal cell, it is actually made of a kind of an protein which would actually be like an having an consistency of that of oil or a thick oil, but in the Nano scale this become very viscous and actually can perform the role of a cell wall which now of course, the regulates the entire functioning of the cell.

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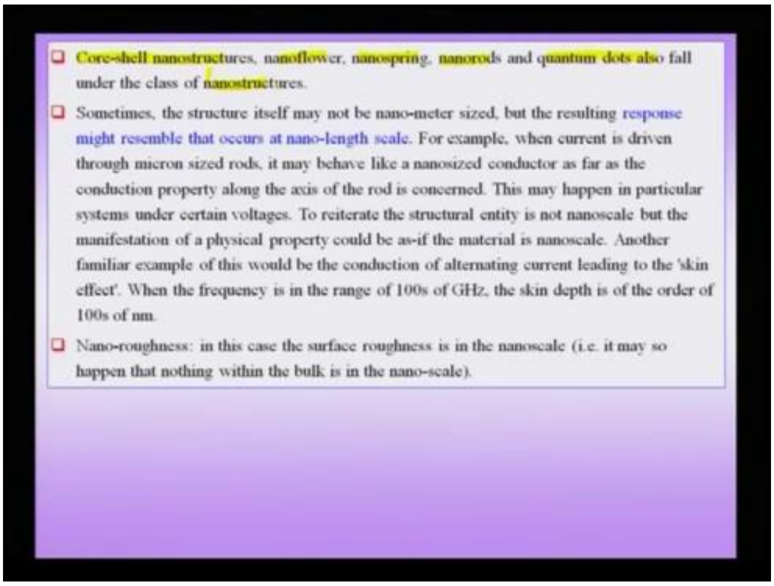

There could be also structures like the core shell Nano structures. And I will draw you one of those, you could have other geometrical entities like Nano flowers, Nano springs, Nano rods, quantum, dots, etcetera, which are also Nano structures and in these things. Of course, all the entities we are talking about could be in a Nano scale in a core shell structure for instance.

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The entire core shell, so this what I call the core and this is my shell and this entire length scale could be of the order of Nano meters. Now of course, the reason for engineering core shells we will see later, but sometimes it is unavoidable because, you have a core of a metal then this metal may get oxidized. Therefore, you have a shell around it and of course, this oxidized core shell structure may itself provide you lot of interesting properties and we will want to study them.

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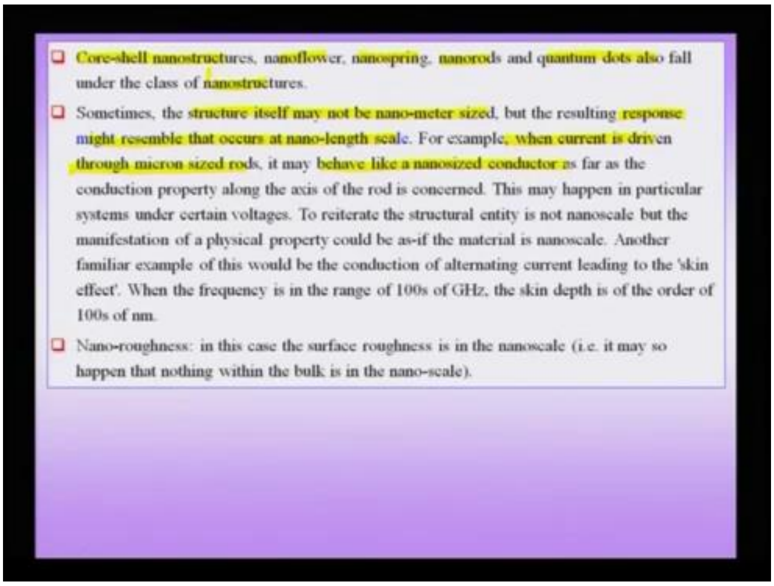

An interesting point to be noted here, we talk about also in the coming slides is the fact that, the structure itself may not be nano-meter sized, important class and it is very different. Now, we are not talking about a Nano structure in the classical sense of the word, that the scale of the structure is not in the Nano scale, but the response of the material, to a certain kind of stimulus could actually be occurring in the Nano scale.

So, this is very different from what we have been talking so far, an example could be when and we will reconsider this example very soon that when current is driven through micron sixed rods, it may behave like a Nano sized conductor. And of course, this is observed for very specific systems and are very specific conditions, when many of the conductors, we are talking about are actually conductors draw a schematic of this process. So, I actually have a micron size conductor.

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But when I am trying to drive form say suppose, let me draw a picture of this in terms this now have a rod, and rod which is now micron sized in which, I am trying to drive current. It so happens now I am looking at this cross section here, and I am trying to drive current through this cross section it ends up some time. The region through which the current tactually passes would be Nano meter sized. And in specific structures the current I am talking about could actually be a ionic current and not an electronic current, and more easily tangible example is the one which we might consider next.

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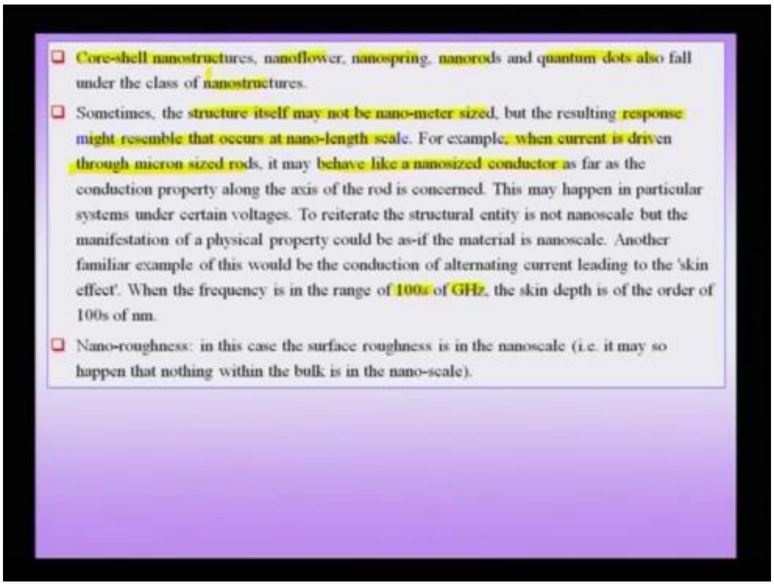

Like for instance suppose, I am driving through a normal conductor, alternating current when I am if I suppose, keep on increasing the frequency, then we know that even when alternating current is not carried throughout the conductor, most of the current density is in the outer region of the conductor which is called the skin of the conductor.

As we increase the frequency the skin depth keeps on coming down, and when if you reach very high frequencies of the order of the gigahertz. Of course, maintaining this kind of high frequency current without the current, the conductor becoming a very effective radiator is a challenge in itself, but we are not concerned about that now. So, the point is that suppose, we have a very high current this normal conductor, then you would notice that, when this frequency reaches about gigahertz this skin depth can come down to about a few 100 Nano meters.

Therefore, you can see here the conductor itself is not Nano scale. The frequency of course, is of the order of gigahertz but the effective region through which the electricity is been conducted is of the order of Nano scale. And this is actually the inverse of this kind of a conduction where the core is conducting, here the shell is actually conducting this.

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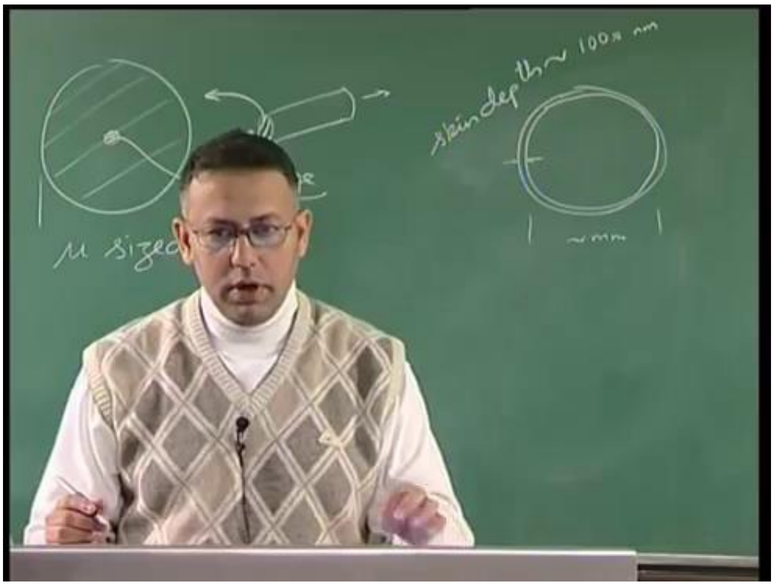

Now, I am talking about alternating current through a conductor, and it could so happen, so effectively of course, this is not to a scale you might notice that this conductor could even be of the order of millimeters, but the region which is now my skin depth, could be of the order of 100s of Nano meters.

So, clearly here, there is no structure in the problem there is the conductor itself we consider is uniform in composition. We consider the grain size to be of the order of microns. Therefore, there is no Nano scale entity involved in the conductor, but the response of the conductor, is as if this material was a small shell which is now of the order of Nano meters or a few 100 Nano meters.

Therefore, these we will take up a little more we will talk a little more about these kind of aspects in the coming slides. But it is very interesting to know that as we are ultimately interested in the properties of the material, which is coming out even if the structure, or the material, or any of the sub components may not be of the Nano scale. But the response of the material could often turn out to be in the Nano scale. And such kind of materials we should of course, classify them separately and also deal with them separately, but also, but keep an eye towards these.

Because, now I do not have to linear my Nano structure, but my response comes out in the Nano scale, another class which we may want to mention here, which we have briefly considered here.

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Suppose, we go back to a few slides and we see the surface, this can be thought of as roughness of the Nano scale. Here of course, this surface roughness has not been engineered to be in a Nano scale. This turn out be in a Nano scale, but it may so happen that we may, we will take a one important example of this kind of surface roughness in a very specific context, but this surface roughness which can be, so this is not the bulk of the material in the Nano scale.

This is not any structure within the material, which is in the Nano scale. It is just a surface roughness, which is nano. And this Nano scale surface roughness, may actually influence the properties of the material in a very profound way.

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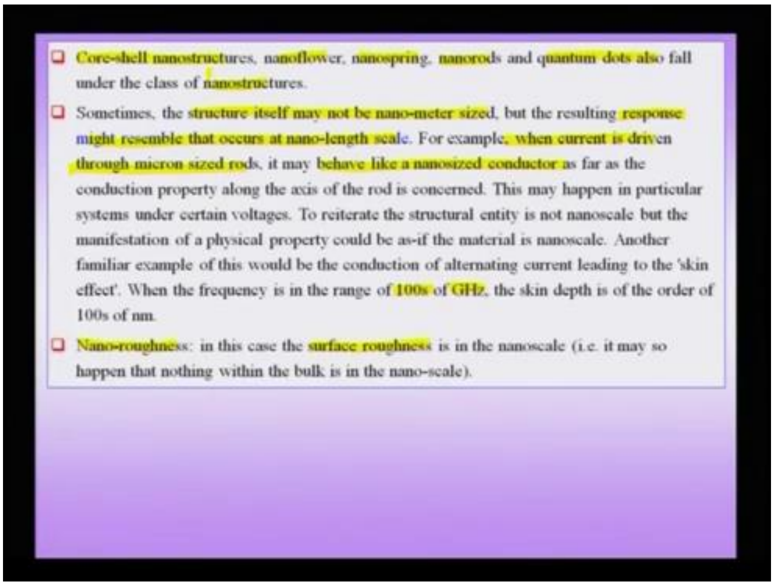

And one such example would actually be for instance the lotus leaf, wherein we get a property known as super hydrophobicity, which we will take up in a little more detail now, and much more detail later.

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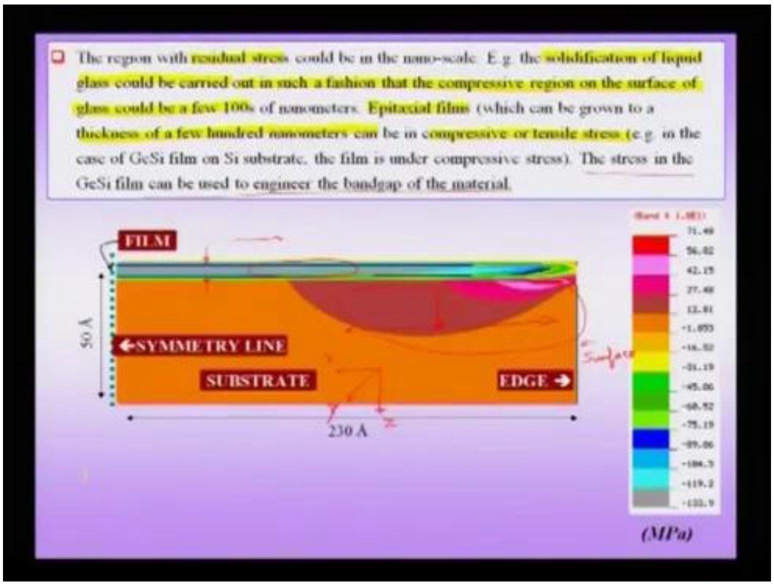

We have already integrated residual stress into the definition of, what you may call the micro structure. And micro structure is what is going to determine my micro structure sensitive properties, therefore I want to engineer my micro structure. If you talk about residual stress, then residual stress itself could be present in a Nano scale. For instance, when I am solidification of liquid glass, could be carried out in such a fashion that the compressive region on the surface of glass could be of the order of few 100s of Nano meters.

Here of course, the glass itself is a microscopic glass of course, the glass could have small clusters the regions, which are slightly crystalline which is called the short range order. But we are not concerned about that, but we are concerned about the fact that the residual stress in the surface is Nano scale. Epitaxial films. And you have seen example of such a thing such an example before could we have a thickness a few 100 Nano meters, and the compressive and tensile regions again therefore, are of the order of Nano meters.

So therefore, this is now for instance a material in which the residual stress is in the Nano scale. The part of the residual stress which is in the film, which is normal films here, is expected to be in a scale because the structural entity itself is in the Nano scale. But suppose I look at my substrate, my substrate is a bulk substrate it could have a thickness of the order of millimeters, but you notice that the effective region of residual stress in the substrate is very limited, and is the order of Nano meters.

The region as you can see will much below the substrate we go down in depth more than say for instance 5 Nano meter or, 10 Nano meter, 20 Nano meter, then there is a residual stress becomes very small in magnitude and therefore my effective region of residual stress in the substrate is of the order of few Nano meters. The film is uniformly strained, that means it is now the residual stress is basically Nano in this dimension. In the other dimension it is not Nano, but if you look at the substrate, substrate is bulk in both structurally bulk in, say for instance could be bulk in all the 3 dimensions.

So suppose, I am talking about the z direction, the x direction in the or the x direction in the y direction, all 3 are bulk, but the effective region of residua stresses is Nano scale in all 3 dimensions. Because, now it does not extend too much from the free surface here, so this is my free surface. It is does not extend too much from the free surface, it does not extend too much in the depth. Of course, the third dimension it can be a little extended. Now we are talking about regions in a material, having residual stress in the Nano scale.

So, and this is clearly not a structural entity. It is as you can see residual stress, it is not one of those classical things we have been, which has talked in textbooks to be are the

Nano scale, but residual stress in the Nano scale can have very profound influence on the properties. For instance the stress in the film can be engineered bandgap in a material.

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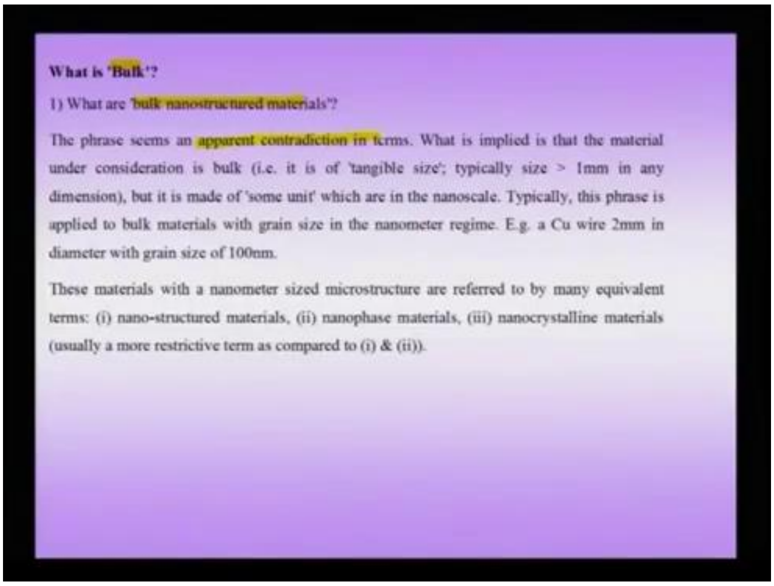

Therefore, this residual stress is very important in terms of the application point of view because now we are using the residuals stress and the resulting strain to actually engineer the bandgap. So, this kind of a definition of a Nano is very different from the definition of Nano based on a structural entity. So, far we have talked a lot about nano, and we have been using the phrase called bulk very frequently.

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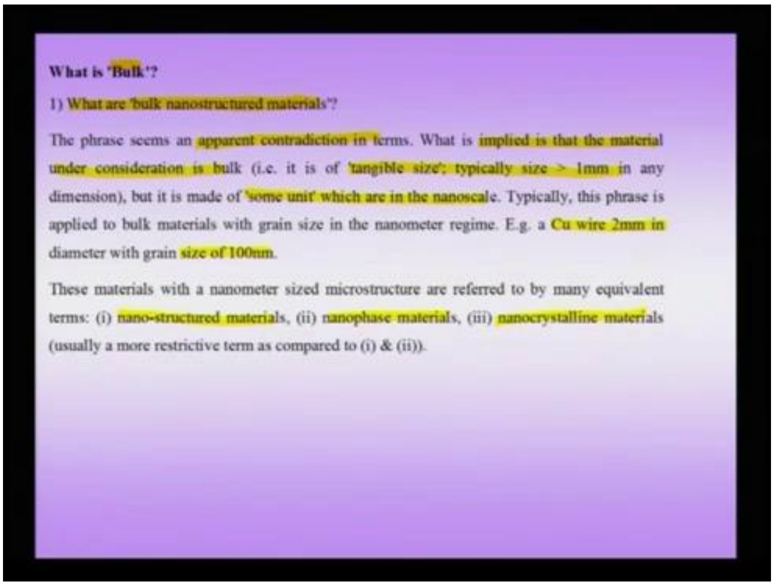

And often you would come across terms, like bulk Nano structured materials. This seems what you might called an oxymoron, wherein we are also bulk we are also talking about Nano in the very same phrase, so what does such a term mean and more importantly what is meant by bulk, what is bulk in bulk, like we asked a question ourselves what is Nano in nano, we have to ask ourselves question what is bulk in bulk. What how do you going to define bulk. And how do we address such kind of quandraticty terms like there are apparent contradiction in the definition like bulk Nano structured material.

So, and the second question we would like to ask ourselves, is that what are bulk properties and this is a very important because if we do not understand what are bulk properties, then we are not going to understand how the properties are going to change when there is a Nano scale confinement, so these two are very inter related questions.

So, let us start with question what are Nano structured materials. What is implied by this phrase is that the material under consideration is bulk, that means it has got a tangible size typically say greater than 1 millimeter, of course, a human eye can has a resolution of about point 1 millimeter therefore, anything more than say point 1 millimeter, we can see. And therefore, we can call it a tangible material, but there is some unit within the material which is in the Nano scale, that is what is implied by calling it a bulk Nano structured material. For instance, we could be consider a copper wire, which is 2 millimeter in diameter whose grain size of the order of 100 Nano meter.

So, this would qualify to be a bulk Nano structure material. And often there are other additional terms by which these bulk Nano structured materials are described. A few of those are Nano structured materials, Nano phase materials, Nano crystalline materials, and all of these when we are using these kind of word materials along with it what we are referring to? It is a fact that actually the end product of all this is a tangible material usually that is the implication, and there is some component within the material which is what you might call Nano structure. A more important question in the context of bulk is, what are bulk properties and we will also take up later on that what is a bulk dimension? So, that another question we will ask ourselves later, but for now we will ask the question what are bulk properties?

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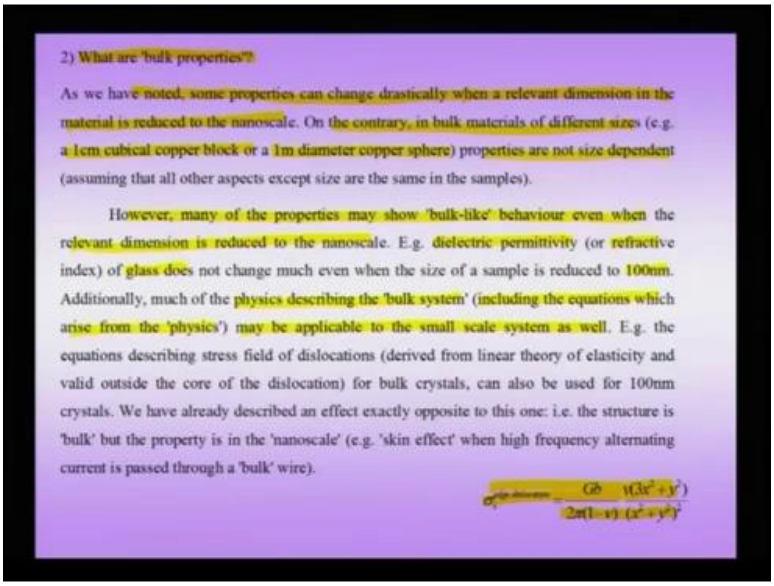

As we have noted some properties can change drastically, when a relevant dimension in the material is reduced to the Nano scale. On the contrary bulk materials of different sizes for instance centimeter cubical copper block or a 1 meter copper sphere, the properties are not size dependent. So what we are talking about as a bulk material now is a material whose properties are not going to change with size.

Suppose, I am measuring the hardness or the tensile strength of a 1 centimeter copper block. I make a specified note of a 1 centimeter copper block, and measure it is tensile strength or the yield strength. I would find that it has a certain value, now I take a much larger material for instance 1 meter copper rod. And then make a tensile specimen in test is used as, it is expected to be very close to what I observe in the case of a 1 centimeter copper specimen.

So, these are all called bulk materials and therefore, the properties do not change as we go even. For instance one or two orders of magnitude in size, but this is not the case, when we go to Nano scale, right, this is why this is what makes study of Nano materials interesting. However we should note that many of the properties, may show bulk like behavior even when the relevant dimension is reduced to a Nano scale.

That means I have gone down structurally to the Nano dimension, I am now completely within the logical definition of what you call a Nano material, but I am not getting any drastic change in properties. Of course, there might be some change in properties, but there is no drastic change in properties which warrens its study in detail. For instance, if I am talking about refractive index or dielectric permittivity, and when glasses show that, when even when you reduce the size of the sample few 100 Nano meters, you notice that the property has not changed much

And therefore, we could be in the Nano scale, but we may not get property which is of the Nano scale or any special property and therefore, we may want to call this a bulk property. So, even though the material is not bulk material, we may want to call it a property as a bulk property and we may want to feed in the, for instance the refractive index, that corresponding to a bulk material. And often we will notice that, the physics describing the bulk system, which includes of course, equations which arise from the physics, may be applicable to the small scale system as well.

So, we may be talking about a very small scale system like an a 5 Nano meter by 5 Nano meter or, may be let us take a little largest size may be a 100 Nano meter by 100 Nano meter. 100 Nano meter plate or a block or a 100 Nano meter by 100 Nano meter by 50 Nano meter plate, and I may well find that the equations, and the physics where very similar to that in the bulk material. One such example could be for instance the stress field of an edge dislocation.

So, I know that my stress field of an edge dislocation in a bulk material of course, this is not my dislocation infinite material, there are similar equations describing the stress field for a finite material. I can take for instance for a finite cylinder, and I take my equation from linear theory of elasticity of bulk materials, and try to apply it for instance to some of the materials which is of the order of 100s of Nano meters. Then, I would notice, the stress field is very accurately describing the equation is very accurately describing, or very closely describing.

These stress field present in the Nano scale material as well therefore, I do not need equations to describe my stress field in a plate which is, or in a block of material which is about a sphere for instance of about 200 Nano meters. I have to keep make sure that do not put my dislocation very close to the surface of this sphere, and as long as I am safe reasonably safely away from the surface of the sphere.

I would notice that my equations which are applicable actually to only to bulk materials, can reasonably give me a good approximation or a good estimate of the stress field in the case of a Nano. And of course, we have already described an effect which is exactly opposite of this one, and what is this effect we are describing here? We are describing a structure which is in the Nano scale, but the property as if it is bulk, the opposite of this would be, a macro scale material, but property in the Nano scale. And that we have already done for instance in the case of a skin effect when very high frequency alternating current is passed through this bulk wire.

So, if I were to summarize this slide that what are bulk properties, the important take home message from this slide is that, I may actually in many cases we doing or trying to study Nano materials. Of course, there are important new effects which may come, important new effects which come purely form the geometry of the Nano material etcetera. But many a times I may notice, that I can actually get away by using the equations, the physics and the properties which are used in bulk materials.

So, and this may be very good approximation, and this in some sense eases my calculations done on these Nano structured materials or the Nano scale materials. And so both are possible, we have bulk material with a Nano scale response, and Nano material with bulk like response. So, these both of these possible and we should of course, be careful with respect to each one of the properties that which property I am having in mind, which property gets drastically changed when I go to the Nano scale, which other property remains bulk like that is of course, I have to keep in mind.

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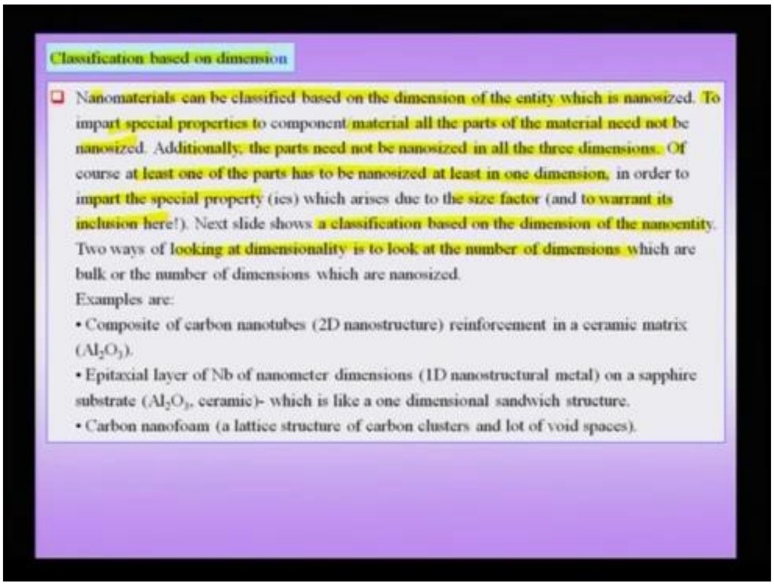

The standard way of classifying Nano materials, and Nano structures, is based on the dimension. So, this is the formal standard way of classifying Nano structures and Nano materials and let thus take up that next. Nano materials are can be classified based on the dimension the entity which is Nano sized. To impart special properties to a component or material, all parts of the material need not be Nano sized. Additionally the parts need not be Nano sized in all 3 dimensions of course, at least one of the parts has to be Nano sized in 1 dimension.

So suppose, I have a material, I have to have at least one part of the whole system, and it has to at least be Nano sized in 1 dimension. In order to impart typically, a special property or at least classify it in to the class we just called Nano structured materials and Nano materials. Otherwise we would not be wanting to include it in a topic like Nano structured materials. The next we will consider the classification based on the dimension of a Nano entity.

There are two ways of looking at dimensionality of a Nano entity, one is either I look at the dimension which is micro sized or the large size or I look at the number of dimensions which are Nano size, So, let me take up the next slide.

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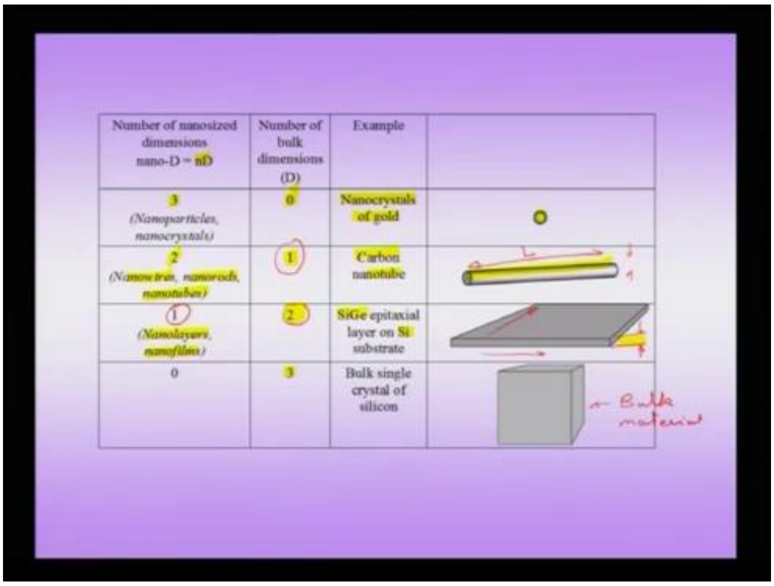

Number of nanosized dimensions nano-D = nD	Number of bulk dimensions (D)	Example	
3 (Nanoparticles, nanocrystals)	0	Nanocrystals of gold	
2 (Nanowires, nanorods, nanotubes)	1	Carbon nanotube	
1 (Nanolayers, nanofilms)	2	SiGe epitaxial layer on Si substrate	
0	3	Bulk single crystal of silicon	

So, for instance suppose have a sphere, which is now the number of bulk dimensions is 0, but it is Nano scale in all 3 dimensions, in a typical classification this would be called the 0 dimensional Nano structure. Though I am calling it as 0 dimensional Nano structure, what is meant is that the number of bulk dimensions is 0, and it is not meant all the Nano dimensions is 0.

So, this is a typical classification, but of course, if somebody specially wants to say that he can say it has got 3 Nano dimensions. If to be very specific that actually he is talking about the number of Nano dimensions, and not about the number of bulk dimensions. An example of this we have already seen like ones in Nano crystals of gold. If I am and there is very small versions of these, for instance some time are called quantum dot, where in you can think of not only that all the 3 dimensions are Nano scaled. But this is typically a lesson about 10 Nano meters such a thing could also be called a quantum dot.

If I am talking about only 1 dimension which is bulk, which can happen in the case of for instance a Nano cylinder. Of course, the geometry could be different from that of a cylinder, it could be a hallow cylinder, it could be a square cross section tube, it could be a square cross section prism, but at least one of the dimension or 1 dimension is bulk the remaining 2 dimensions are in the Nano scales. And based on geometry I could call it Nano y or Nano rods Nano tubes etcetera. And a nice example of this would be the carbon Nano tube. So, here in this case we are talking about.

So, the only Nano dimension, the only bulk dimension is this dimension. A little word of caution is required here, sometimes we may be calling for instance, a carbon Nano tube as a 1 dimensional Nano crystal or a 1 dimensional Nano structure. It may so be that the other dimensions we are talking about, could be a few Nano meters. And therefore, we need to call it a one dimensional Nano structure, but the larger dimension, which is the dimension of the length could also be in the Nano scale.

For instance, it could be length of the carbon Nano tube could be a few 100 Nano meters. It may not be much larger than this it could be 50 Nano meters if it is a short length carbon Nano tube. Even though now in some sense all the 3 dimensions are in the Nano scale. We typically classify under the, what we might call the 1 dimensional Nano structures. We could have further two of the dimensions being bulk, like this example of the plate shown here.

So, this dimension is bulk, and additionally this dimension is bulk, and it is Nano in the third dimension. We already seen examples of this for instance, the epitaxial films we considered with respect to the stresses they are typically having this geometry, wherein only one of the dimensions in the Nano scale and two of the dimensions are bulk. And such a thing would either be called a Nano layer or a Nano film.

Instead of having silicon germanium on silicon, we could rather think of other kind of epitaxial systems like indium, gallium, arsenide on gallium arsenide or thin layers of coatings, which are not coherent with the matrix. But all in all these cases, if one of the dimensions is in the Nano scale, we call it a two dimensional Nano structure. Of course, the other extreme of a 0 dimensional Nano material or a Nano structure, would be a bulk material, which in some sense we can call it a 3 dimensional material, which has actually has no bulk no Nano scale dimension, and this is the other extreme.

And therefore, this is what we call the bulk material. And for now we simplicity, we take an example like a single crystal of silicon which is in the bulk. So, let us summarize what we mean, this because, this is the most standard way of classifying Nano structures is based on the dimension of the Nano structure. And therefore, we could have Nano structures, which has, which is bulk in 0 dimensions bulk in 1 dimension or bulk in 2 dimensions, and correspondingly you will have 3 Nano dimensions, 2 Nano dimensions or 1 Nano dimension.

And therefore, if I at least have 1 Nano dimension in the whole system, then I would be logical in calling it a Nano structure or Nano structured material. When you talk about the dimensionality, a further question needs to be asked that, what is the dimensionality of a system or in other words how many dimensions does an object have? So, again we go back to what you might call real physical perspective on this problem. And this is very important to consider, because often we may have a 3 dimensional object, but the relevant dimensions just may be 2. So, this is an important question we will ask.