

**Nanostructures and Nanomaterials: Characterization and Properties**

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**Lecture - 6**

**Introduction to Nanomaterials (C1)**

(Refer Slide Time: 00:19)

- Overview of fundamental concepts (continued)
- Traversing across lengthscales: A demagnetized sample of Fe (Iron)
- Introduction to Nano-terminology (Nanoscience, nanotechnology, nanomaterials, nano-manufacturing, nanoparticle, nanocrystal, nanostructure)

So, we shall consider one more example wherein we traverse across length scales, and see some interesting effects in terms of the properties of a material.

(Refer Slide Time: 00:35)

Change of properties across length scales: Fe sample which has not been magnetized

Atomic level ( $\text{\AA}$ )  $\rightarrow$  Domain level ( $\sim$  few  $\mu\text{m}$ )  $\rightarrow$  Material level ( $\text{cm}$ )

Consider a magnetic material (E.g. Fe, Ni) below the Curie temperature (but  $T > 0\text{K}$ ), where it is ferromagnetic in nature. In this condition the atomic magnetic moments try to align, but thermal effects lead to partial disordering. This takes place within regions in the sample called domains which are typically of micrometer size. The configuration of the domains is in such manner so as to reduce the magnetostatic energy. This arrangement of domains, wherein they are not preferentially aligned, leads to *no* net magnetization of the sample. Hence the story as we traverse length scales is:

Atomic magnetic moments ( $m_{\text{atomic}}$ )

- $\rightarrow$  Less magnetization in a domain than the number of atomic moments (domain) (say if  $n$  atoms are there, then the net magnetic moment within a domain  $\neq n \times m_{\text{atomic}}$ , turns out to be less than  $n \times m_{\text{atomic}}$ )
- $\rightarrow$  No net magnetization at the sample level.

The case which has been considered here is an iron sample which has not been magnetized. In other words an ironed sample which does not behave like a permanent magnet microscopically, so what are the length scales we are going to traverse in this problem, it is going to be the atomic level. To be more precise, even the sub atomic level which is of the order angstroms and below we will travel to something known as a domain level, which could be a few micrometer to something below that as well.

Finally, we look at the level of the entire sample, which could be of the order of centimeters, now a typical iron sample is actually poly crystalline. This actually in fact complicates the issues which we are considering with respect to the magnetism of a sample. Now, let us consider a magnetic material and iron is the example chosen in the current example and we are below the curie temperature and below the curie temperature. We know that the material behaves like a ferro magnet and when you heat the material above the curie temperature, it becomes a paramagnet.

Therefore, we are talking about the ferromagnetic condition of the iron sample in this condition, the atomic magnetic movements try to align within region called the single domain. This tendency of alignment is actually fighting constantly against the thermal disordering effects which is always present.

Now, what is the origin of this magnetic movement in an iron sample if you take a single atom of iron, there are three possible origins of what might you call the net magnetic

movement. One is to the electron spin, one is to the orbital motion of the electrons around the nucleus and here we are considering what we may call a classical view point to magnetism. Finally, there is also a nuclear spin which can give rise to magnetism, but typically nuclear spin is ignored in the systems because the nucleus is much more massive than the electron.

Therefore, as the mass comes in the denominator in the calculation of the magnetic movement you typically ignore the magnetic movement arising from the nuclear spin. Typically, therefore, there are two contributions which are prominent when you are talking about magnetic contributions which are the electron spin and orbital motions of electron, but this for a single iron atom. Now, when we try to make an iron crystal, then it might so happen that the orbital motion could be quenched. In other words, the contribution which is coming from the orbital to the magnetization, net magnetization of the sample could be ignored could be less.

Therefore, prominent contribution could come from the electron spin, therefore every atom makes a contribution to the crystal in terms of its magnetic movement and this magnetic movement is constantly fighting against the thermal disordering. In other words, the magnetic movement in neighboring iron atoms want to align themselves and that is why this is termed as a ferromagnetic material, but there is misalignment or the tendency for the alignment to be lost because of temperature. Typically, what we observe is that there is magnetic movement within a domain, but though that is less than the number of actual participating atoms in terms of the number.

Now, what happens when we consider the region beyond a domain, that means when I cross to a domain to a next domain then there is something known as a domain wall. If you look at a domain wall as shown in the picture below the magnetization vectors or the spin vectors actually go from one orientation to another orientation. Therefore, the region of the domain wall is a region which is in some sense not ordered either to the domain which is on the left, which is can be called domain one or in the orientation which is to the domain two.

The kind of wall which is being shown here is called a blocked wall and in thin film there are other wall which are which are possible which are called Neel walls. Therefore, if you look at the size of the domain wall itself it is typically of the order of a few

hundred atomic diameters and it is a nano structure in itself, though we have not yet gone to the level defining all the nano structures possible nano structures. Now, this tells me that though there is an inherent tendency for iron to magnetize, but magnetic alignment is not perfect due to thermal disordering.

Furthermore, this ordering within a domain is broken when we traverse from one domain to the other and the two domains are connected by a two wall. Here, actually the magnetization vectors rotate from one orientation to other and in this as in the case of block wall shown it actually rotates out of the plane to create these two differently ordered domains. Now, what happens when you look at the sample level at the sample level actually there is no magnetization at all. This happens, because there are multiple, these sample is actually split domains and there are sort of what do we call schematic diagram is shown here in the picture on the right hand side.

There is one domain which is pointing which has a net magnetization in the upward direction one in the downward direction other in the upward direction and there are these closure domains which actually close the magnetic loops. The purpose of doing so is that the overall magneto-static energy of the sample is reduced when the sample is actually split into domains and therefore, this domain structure leads to an overall no lack of magnetic movement at the sample level. So, what is that we are gaining by going across these various length scales, there is an inherent tendency for atomic magnetic movements coming from three sources two of which being electron spin and orbital motion of electrons which are important.

When iron forms a crystal the orbital motion or the orbital contribution, typically gets quenched a lot. Therefore, the main contribution comes from the electron spin alone that means there is a loss of magnetic movement right at that scale, the next scale is a scale of the domain formation. Therefore, within a magnetic domain these magnetization vectors of all iron atoms are aligned and therefore there is a net magnetization at the level of the domain. If you look at the sample level, again the magnetization is completely lost or there is no net magnetization at the sample level because the sample wants to reduce the magneto static energy.

Therefore, we see that the there are properties which fluctuate as you go from various from the various very small length scale starting from the angstrom length scale to length

scale of the material and when you are doing. So, we also encounter structures and properties which are at the nano scale like the case of the domain wall we considered in the current sample. So, the important lesson we learn from considering these examples is that we cannot reside at a single length scale to understand the properties of a material.

(Refer Slide Time: 07:24)

Going from an atom to a component: Fe to Gear-Wheel

In this example there will be a synthesis of concepts which have been presented before. It will also become amply clear as to how different lengthscales 'talk' to each other to determine a property. Let the component be a gear wheel, which requires good surface hardness and abrasion resistance, along with good toughness (for shock resistance). For simplicity assume that it is made of plain carbon steel (alloy of Fe and 0.1-2.0%C). The Fe atom has a propensity for metallic bonding which ensures good ductility, thermal conductivity etc.; but, is soft compared to (say) a covalently bonded material (e.g. diamond). This 'softness' is also directly related to the metallic bond, which leads to a low Peierls stress. This ductility further helps in improving the microstructural level properties like tolerance to cracks (high fracture toughness). Sharp crack tips (e.g. in window pane glass), lead to high stress amplification (high stress intensity factor), which results in much lower stresses for causing fracture. But, when a crack tip gets blunted due to plastic deformation, it reduces the stress amplification and enhances the toughness of the material. The ease of deformation and good tolerance to cracks implies good ductility in a material. This available ductility is useful in the deep drawing forming of the component (such as making long-form containers).

The Gear wheel

The slide includes three images: a 3D rendering of a gear wheel, a cross-sectional view of a gear showing its internal structure, and a stress-strain graph with a yield strength of 1.42 GPa.

We will consider one more important example here where in we go from an iron crystal on an iron sample to the entire component which is the gear wheel. So, not only are we now talking about material length scale, but we are also talking about the length scale of an entire component. We will see how these various length scale talk to each other and how certain property is not only arising, but also can be engineered for a particular application as in the case of gear wheel.

So, what does a gear wheel require, a gear wheel requires good surface hardness, it requires good aberration resistance, it also needs good toughness. That means it needs to be shock resistant, it needs to absorb energy when certain energy is imposed on it in the form of an impact or a contact.

Therefore, if my gear wheel has to have all these properties, then it has to be engineered in certain way the way the engineering is done is that the gear wheel is machined. Of course, you can see that there is certain geometry out here and this gear wheel is made in certain geometry and what is done is that the surface of the gear wheel is actually preferentially imposed with more carbon than the interior. So, we have a sample of a

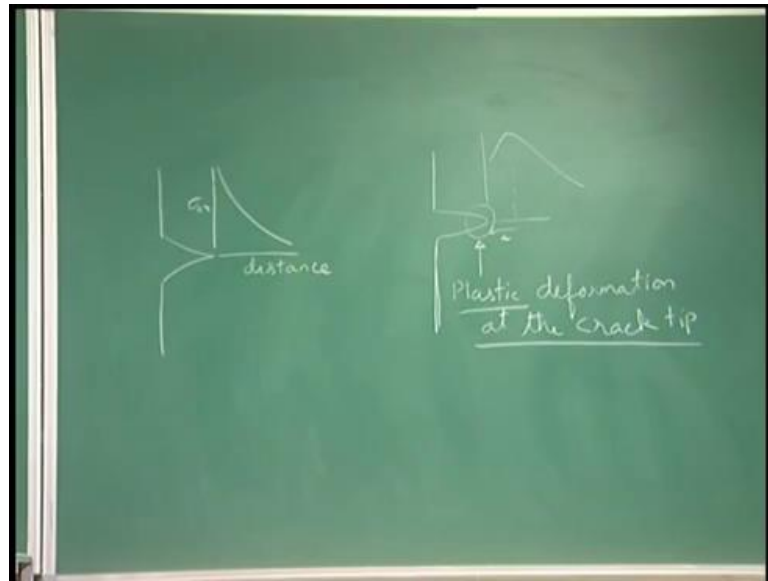
gear wheel on which we impose a carburizing medium and the carburizing medium, in fact lets carbon diffuse into the sample.

So, this is for instance the distance inside the surface and this is the percentage of carbon and with increasing time which is shown by the arrow, you see that more and more of carbon is actually diffusing into the sample. Therefore, we are preferentially increasing the carbon content of the surface the reason for this is that when I started the base composition. For instance iron with about 0.12 percent carbon or 0.2 percent carbon that material has good fracture toughness or it has good toughness.

So, what does this toughness property implied, it implies that the material will fail only after it absorbs a lot of energy. Now, often this toughness is also can be thought of as a product of ductility and into the strength, it is the area under the curve if not tested under impact in attention, it can be thought of the area under the stress strain diagram. Now, why does a material which is never going to deform so much because if this component actually deforms by even a few microns, then its machine will start changing with respect to the remaining gear components in the assembly.

Therefore, any change of the order of millimeter is unacceptable as far as the gear assembly goes therefore, the tolerance being so high, why do I require this kind of ductility in a material. We know that the material is never going to deform that much the reason lies in a length scale, which is much smaller and this can be understood as follows.

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Suppose, I am talking at a crack tip and we have already seen a crack tip in a material and during manufacturing, it is unavoidable that there are some micro cracks present in a material. Therefore, this crack tip we have seen already has very high stress concentration, so this is my  $\sigma_x$  for instance and with distance such a sharp crack is actually extremely deleterious to the material and can lead to the failure of the material. If the material of sufficient ductility and it has got sufficient toughness, what would happen is that the crack tip would actually blunt instead of being a sharp crack tip. It will end up being a blunt crack tip and this would imply that the crack tip stresses do not become very sharp.

In fact the crack tip stresses reaches at maximum at a certain distance from the crack tip, so a brittle or a sharp crack a sharp crack is typically found in a brittle material. The crack tip traces tend to become very large and in fact in mathematical form, they become singular, but in the case of a ductile material the crack tip is blunted. Therefore, the crack tip stresses are reduced and in fact the crack tips may not occur right at the crack, but at a certain distance on the crack this kind of a blunting of crack tip requires. This plastic deformation is what is required for this plastic deformation that we require the ductility in the material.

Therefore, to understand the need for this ductility, we actually have to go down to the crack tip level and to understand the plastic deformation, which is occurring at the crack

tip. Therefore, to summarize a gear wheel needs to have good surface hardness, it needs good aberration resistance and also needs good toughness the reason for toughness. We have seen now and the way the good surface toughness is achieved as I pointed out is by actually imposing a higher amount of carbon on the surface.

The total treatment actually consists of not only putting this carbon, but and this carbon is typically put at a high temperature. Then later on the sample is quenched from the high temperature, so that face known as the martinsite face actually forms which gives it the required surface hardness.

(Refer Slide Time: 12:41)

**Going from an atom to a component: Fe to Gear Wheel**

In this example there will be a synthesis of concepts which have been presented before. It will also become amply clear as to how different length scales 'talk' to each other to determine a property. Let the component be a gear wheel, which requires good surface hardness and abrasion resistance; along with good toughness (for shock resistance). For simplicity assume that it is made of plain carbon steel (alloy of Fe and 0.1-2.0% C). The Fe atom has a propensity for metallic bonding which ensures good ductility, thermal conductivity etc.; but, is soft compared to (say) a covalently bonded material (e.g. diamond). This 'softness' is also directly related to the metallic bond, which leads to a low Peierls stress. This ductility further helps in improving the microstructural level properties like tolerance to cracks (high fracture toughness). Sharp crack tips (e.g. in window pane glass), lead to high stress amplification (high stress intensity factor), which results in much lower stresses for causing fracture. But, when a crack tip gets blunted due to plastic deformation, it reduces the stress amplification and enhances the toughness of the material. The ease of deformation and good tolerance to cracks implies good ductility in a material. This available ductility is useful in the deep drawing forming of the component (such as making long-form containers).

The Gear wheel

The diagram shows a gear wheel, a cross-section of a gear wheel with a crack, and a stress-strain graph. The graph plots stress (σ) on the y-axis (0 to 0.8) against strain (ε) on the x-axis (0 to 1.4). It shows a yield point at approximately (0.1, 0.2) and a peak at approximately (0.2, 0.6). A red line indicates a crack path through the material, and a yellow shaded region highlights the area of plastic deformation.

Now, if you want to start from the bonding level of the iron, so we know that iron has a propensity for metallic bonding which ensures good ductility good thermal conductivity etcetera, which happens to be good in the case of a component like this. Then, it does not over heat and it actually heat tends to be dissipated away, but it is soft as compared to say equivalently bonded material like diamond. Now, this softness is directly related to the metallic bond which leads to low Peierls stress, Peierls stress being the inherent lattice friction for the motion of a dislocation.

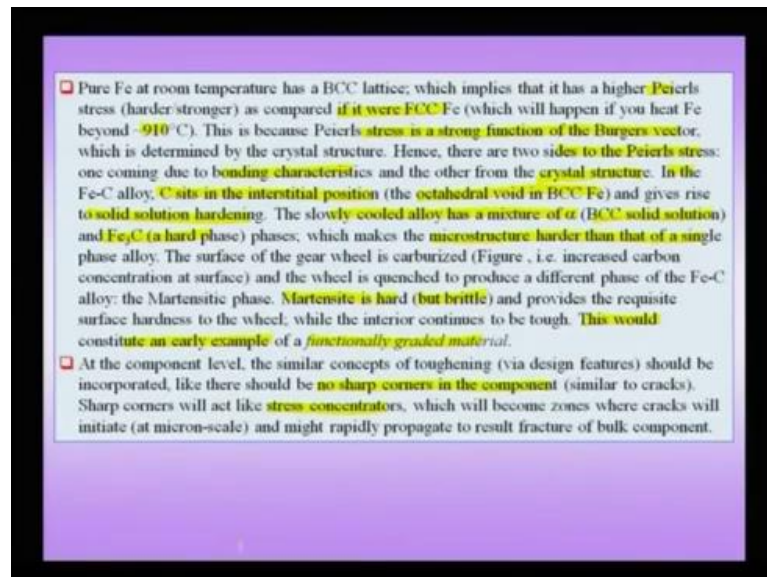
This ductility further helps in improving micro structural level properties like tolerance to crack, which we have just now seen and this leads to high fracture toughness, sharp crack as we saw lead to high stress amplification. That should be avoided in a real component and therefore, we by making a material making this out material like a ductile



material like iron with a low Peierls stress as compared to material like diamond which has high Peierls stress. We can actually achieve this toughness; the easy of deformation and good tolerance to crack symbolize good ductility in a material.

This available ductility can be actually used in actually making the component from the metallic components. Now, if we reside at this lens scale of the component, we already see that there are certain important design parameters, which will come into play, but also we are also going to the micro structural level wherein we are seeing the surface is actually martensitic. We found martensite on the surface of the gear wheel and below this we have a mixed micro structure which actually gives us the good toughness.

(Refer Slide Time: 14:19)



Now, though iron has a low Peierls stress as compare to other ceramic materials, but it has a much higher Peierls stress as compared to a material, which it were an FCC form of iron which is found at high temperatures. This Peierls stress is a strong function of a burgers vector and also of the kind of bonding which is present in the material.

So, we have two sides to the Peierls stress one coming due to the bonding characteristics and other from the crystal structure the crystal structure of course determines the burgers vector and the burgers vector sits in the exponential. When it comes to the Peierls stress, now we said that we are starting with a base material, which consists of an allow of iron and carbon the carbon actually sits in the interstitial position. That means now I 7 have to

focus this at the level of the individual crystal level or the individual unit cell level and typically in the octahedral void in BCC iron.

This gives rise to solid solution hardening, in other words a material which is a pure iron vis a vis a material with carbon dissolved in it. We notice that the carbon dissolved material is actually harder and the slowly cooled mixture consists of alpha which is BCC solid solution and  $\text{Fe}_3\text{C}$ , which is a hard phase an orthorhombic hard face. Therefore, this micro structure of a combination of alpha and  $\text{Fe}_3\text{C}$  is harder micro structure, which is called a polytic micro structure. The important hardness does not alone from the solid solution level or the micro structure consisting of  $\text{Fe}_3\text{C}$  or the alpha phase, but actually it is coming from formation of martinsite on the surface which is hard, but unfortunately it is brittle.

Actually, by now actually engineering, the composition or engineering the heat treatment I make sure that the martinsite actually forms on the surface the interior has a more slow experience, actually a slower cooling rate. It would have a polytic kind of a micro structure or a alpha and  $\text{Fe}_3\text{C}$  combination of the phases and this would give it a good requisite toughness at the inside of the material. Therefore, this kind an example of the gear wheel is an what you might call a example of classic example of a functionally graded material.

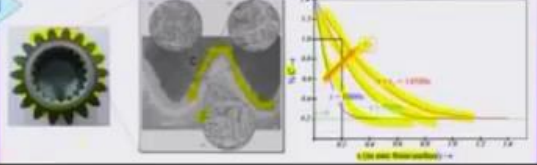
Here, each part of the component has a different kind of a property, which suits the need of that region of the component. However, we should not forget the usual good design practices, we need to flow when you are actually designing the component. That means no sharp corner should be present in the component because there sharp components at the microscopic level act like cracks at the microscopic level. This will lead to stress amplification, which would be zones wherein failures can initiate.

(Refer Slide Time: 16:54)

Going from an atom to a component: Fe to Gear Wheel

In this example there will be a synthesis of concepts which have been presented before. It will also become amply clear as to how different length scales 'talk' to each other to determine a property. Let the component be a gear wheel, which requires good surface hardness and abrasion resistance, along with good toughness (for shock resistance). For simplicity assume that it is made of plain carbon steel (alloy of Fe and 0.1-2.0 %C). The Fe atom has a propensity for metallic bonding which ensures good ductility, thermal conductivity etc.; but, is soft compared to (say) a covalently bonded material (e.g. diamond). This 'softness' is also directly related to the metallic bond, which leads to a low Peierls stress. This ductility further helps in improving the microstructural level properties like tolerance to cracks (high fracture toughness). Sharp crack tips (e.g. in window pane glass), lead to high stress amplification (high stress intensity factor), which results in much lower stresses for causing fracture. But, when a crack tip gets blunted due to plastic deformation, it reduces the stress amplification and enhances the toughness of the material. The ease of deformation and good tolerance to cracks implies good ductility in a material. This available ductility is useful in the deep drawing forming of the component (such as making long-form containers).

The Gear wheel



So, to summarize the consideration of the gear wheel we see that when we want to understand the properties. Also, when we want to understand how a component has to be designed, we have to traverse from the atomic length scale to the crystal length scale to the length scale of the entire component. We need to follow certain sound engineering practices including the avoidance of sharp corners providing a smooth surface finish. So, there is no aberration taking place at the surface etcetera the level of the other end of the spectrum.

We know that the carbon which is present in the starting material of iron is actually giving rise to solid solution hardening and further in cold slowly cooled sample this carbon can form a Fe<sub>3</sub>C phase along with the alpha phase. This kind of micro structure gives it further hardening up and above that present in a pure iron sample or even a solid solution sample. Now, we go further and we actually engineer the component putting in more carbon on the surface by what is a process known as case carburizing. In case carburizing we surface the carbon slowly diffuses in the sample and the surface content of carbon increases.

Therefore, when you quench the sample from high temperatures, wherein the carburizing treatment is favorable to be conducted. At the high temperatures, the solubility of as we noticed that the iron is in gamma form which can actually dissolve more carbon than the alpha form. Therefore, we dissolve more carbon into the iron sample and then quench it

to produce the martensitic phase and the martensitic phase is very hard. This gives it a good what you might call the good aberration resistance and good surface scratch resistance.

Therefore, we see that if you want to consider a property or design a component, then we have to traverse from length scale from the where the interstitial atom of carbon sits to the scale of the entire component. We can actually not only engineer the component, but actually engineer the micro structure by doing a suitable heat treatment. So, this is another nice example, wherein we are traversing multiple length scales to understand the properties.

Now, it is time for us to actually jump into the world of nano materials and let us start with a few basic definitions, because often in the world of nano, there are single definition could have multiple meanings, we have many terms which come into play. In the process, we need to understand how various properties arise in the case of nano materials, nano structures and various other nano terms, which we shall be soon introducing ourselves to, so what are the nano terms which we need to learn?

(Refer Slide Time: 19:45)

**Introduction to Terminology**

- Before we proceed to the exciting realm of the nano-worlds, it is necessary to learn the definition of a few important terms in this context. (The hyphens in the terms may not be used in many places).

**Nano-**

- In day-to-day terminology, the term 'nano' is quite often loosely used. Nano is just a prefix to define a factor of  $10^{-9}$ .  
The term nano, by itself, is not a measure of length, mass, or time and hence should be used as a prefix to standard units. E.g. nanograms would mean  $10^{-9}$ g, nanohertz will mean  $10^{-9}$  Hz, and so on.  
In the context of nanomaterials it denotes the size range between 1-100 nano-meters.  $\rightarrow 300-400 \text{ nm}$ 
  - Literally  $\rightarrow$  a factor of  $10^{-9}$  (usually  $10^{-9}$  m).
  - Practically  $\rightarrow$  the range of sizes from 1-100 nanometers (nm).

- The most important aspect of "nano-" is the appearance of interesting properties (often unexpected), which are absent in their bulk counterparts.

So, let us start with the most basic the word nano itself, in day to day terminology, the word nano is quite of loosely used. We should be careful with the use of the word in multiple context, simply speaking nano is just a prefix to define a factor of 10 power minus 9. In other words, the term nano itself is not a measure of length mass or time and hence should be used as a prefix to standard unit like we can have nano grams, we can

have nano meters, we can have nano Hertz or any one of the standard units like nanopascals. So, it essentially tells us that we are 9 orders of magnitude lower than the unit which is being mentioned in the context of nano materials.

Typically, the word nano implies the size range between 1 and 100 nanometers, though there is nothing hard and fast for this size range, but typically in usual accepted terminology, we are referring to size range of 1 to 100 nanometers. Often, this is I say pointed out not hard and fast rule and often we will notice that if a material is of the order of even, for instance tending towards about 300 or 400 nanometers. Then, such a material should actually be called sub micrometer, it is often sometimes included in the regime of nano materials. So, even though when we are saying nanometer, we actually should mean  $10^9$  meter, but sometimes we extend to  $10^7$  meter and even larger sizes.

Essentially, we understand the importance of the definition lies with respect to the properties. In other words, if there is an property arising, which is special, which is nice, which is interesting, then the use of nano actually makes sense in our context. If it is just a prefix for definition of a scale, then it is important to consider the word nano, but it is not that exciting for us to consider what this nano actually can give us new prospects. So, what we are considering here is that the appearance of interesting properties, especially which are absent in there bulk counterparts.

So, often we have a certain accentuation of the properties as we go down to the nano scale, but if there are new properties new phenomenon and new kind of structures arising when you go down to nano scale. That makes our study of nano materials nano structures more, worthwhile and also opens to the door for application for these kinds of materials into our kind of technology, which we will define soon as nano technology.

So, to summarize this slide nano is just a prefix to a certain standard unit, but typically in the context to nano materials, we imply that there is a certain length scale in the problem which is 1 to 100 nanometers or sometimes slightly larger than that also. So, there are two important terms, which we will come across, one is a word called nano material, another word which is called nano structure.

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**Nano-material**

- ❑ The term 'nano-material' usually implies that **one or more of the components** (entities) which make up the material are nanosized. These components could be **grains, nanotubes, nanospheres** etc.
- Examples
  - **Nanocrystalline copper**: the material itself is 'bulk', but is made up of **grains which are nano-sized**.
  - A crystal made up of **SiO<sub>2</sub> nanospheres** (the nanospheres may themselves be **amorphous**)
- ❑ This is to be contrasted with **free-standing nano-structures**.

**Nano-entity**

- ❑ Anything 'nano'. Used as general term, where **specificity is being avoided**.

Now, what is the technical difference between nano structure and nano material is very important for us note. So, let us start with the definition of nano material when say a material, we actually can visualize a certain kind of a tangible amount of matter in a nano material. We typically do not imply that the material is in itself in a nano scale, what we imply is that there is a material of tangible size. There is some component which could be one or more components in a material, which is what makes up this material is of nano scale.

So, it is not essential that every component of this material is in the nano scale, it is not essential that there is only just one component in the nano scale, but typically one or more components is in the nano scale. This is what is finally giving us important set of properties, which we are interested, these components could be for instance grains in a poly crystal. For instance, this could be nano tubes, which have been grown in align fashion there could be nano spheres etcetera. This form of material and that material can be called a nano material often the word nano material is also used in more liberal or a relaxed fashion.

Here, in various other kinds of things like nano structures are also called nano material, but as long as we understand the context in which the terminology is being used. It is absolutely perfect for us, example of nano materials would be nano crystalline copper, in this case, the copper sample is itself not nano sized, what is nano sized is the grains from

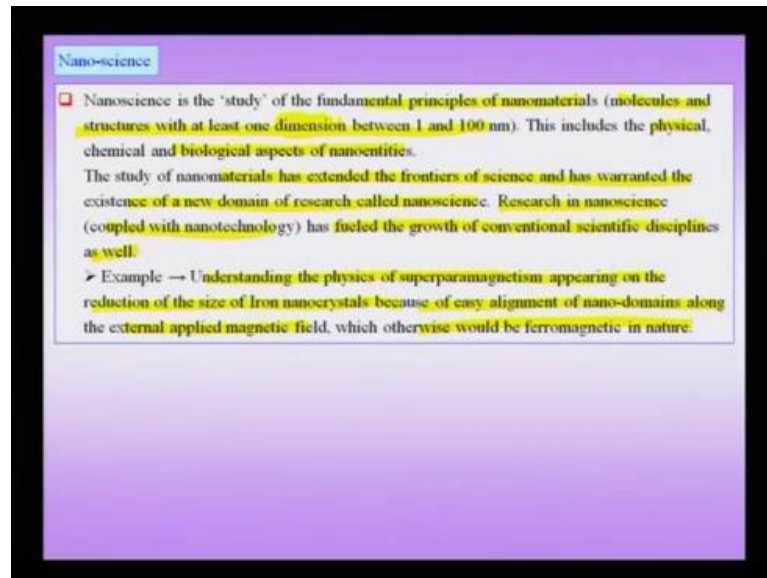
which this nano or nano poly crystalline sample is made of. So, it has to be absolutely clear that in this case the sample is definitely a bulk sample, it could be out of centimeters, it could be at least millimeters, but definitely a tangible amount of sample and what is nano in this sample is the grain size.

Therefore, it is absolutely clear a crystal can also be made out of silicon nano spheres and the nano spheres themselves may be amorphous actually are typically amorphous, but we are not referring to the silicon nano spheres as a nano material. We are referring to the assemblage of this, which is giving rise to the entire material, which we call a nano material. Now, we have to clearly distinguish this nano material from the free standing nano structures, which we will soon discover. What are these free standing nano structures, what kind of geometries can they have, we will soon understand when we delve into deeper.

So, when I am talking about a nano material, I see that the material is made up of certain components, which are of the nano scale or which has a length scale in the nano meters. Later on, we will ask ourselves this question what is a bulk material, we have been using the term bulk very much. So, we will ask ourselves this question what is a bulk material and what can be nano in a nano material, so these two questions we will again ourselves to clarify the points, which are not clear from this slide

Whenever I am loosely referring to some kind of an object without actually being specific, so sometimes the words nano entity can be used, because then that avoids us being very specific. So, that is very general terms, where in specificity is being avoid and there is something nano in the whole system that is what we are referring to when you are talking about a nano-entity.

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The next important term is nano science, nano science is a study of fundamental principles of nano materials and these could be made up of molecules and structures with one dimension at least which is between 100 nano meter. The concept of dimension based classification we will take up later, but the important thing is that the study of fundamental principles of nano materials is what comprises nano science.

This includes physical chemical and biological aspects of nano entities, the study of nano materials has extended the frontiers of science and has warranted a new domain of research called nano science. In many cases, we actually may not actually observe very drastic new phenomenon, but still the study of whatever properties interesting properties or interesting accentuation of properties. These occurings at the nano scale has warranted us to create a new domain called the nano science research in nano science coupled with nano technology, which we will define soon has fueled the growth of conventional scientific disciplines as well.

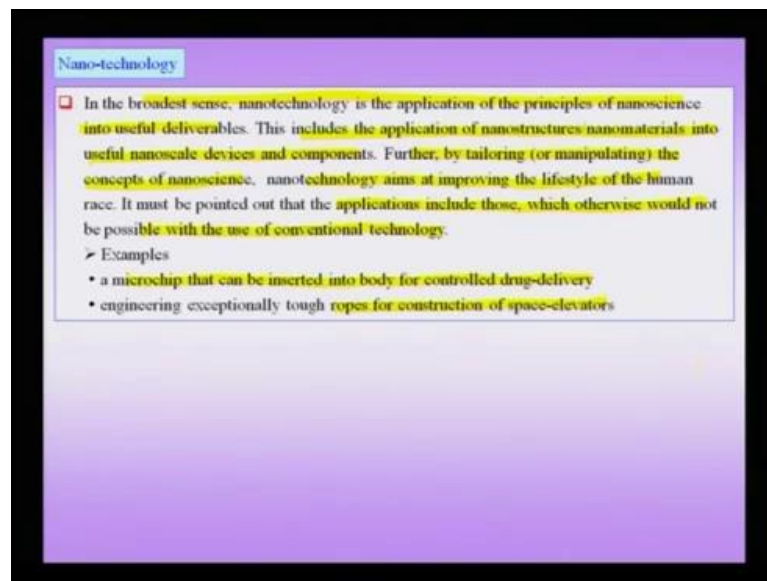
So, not only nano science is a separate discipline by itself, but growth in nano science is helping us actually study the actually conventional kind of materials better. It also has fueled research in other allied areas which are actually not directly related to nano science. For example understanding the physics of super para magnetism appearing on the reduction of size of iron nano crystals, because of easy alignment of nano domains along the external applied magnetic field, which would be ferromagnetic in nature.



So, if here I am studying a phenomenon like super para magnetism as stated here or equivalently I am talking about a phenomenon like giant magnet or resistance, then I would like to know the fundamental principles. For instance I may be talking about spin diffusion length, I may be talking about spin dependent scattering etcetera. So, these fundamental aspects of study of say phenomenon like super para magnetism or a phenomenon like giant magnet or resistance is what would comprise this area of nano science. So, we will again worry about all the kind of properties we have been worrying about in the conventional materials like hardness, we could be talking about mechanical behavior optical transmittivity dielectric constant etcetera.

So, it could be one of those conventional looking parameters, but now we are in the realm of nano science and some of these properties arise. These are very unique to this what we may call nano materials as we saw the case of giant magnet or resistance which has no conventional bulk counterpart.

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Now, nano science of course,, is a study of fundamental aspects, but in the broader sense the nano technologies are application of the principles of nano science into useful deliverables. So, this nano science we have these beautiful properties arising, but we would like to put them to good use like any technology and this application aspect of nano science is what comprises the broad area of nano technology. So, we are not only we are using the principles of nano science to not only make useful products, but also

make useful devices which can actually further even the study of nano science itself. So, that is why the use of nano science can actually help into nano technology can fuel the growth of itself.

This includes the application of nanostructures nano materials into useful nano scale devices and components and these devices could be small devices in the nano scale itself. This could be much larger devices in the micron scale or even larger devices further by tailoring or manipulating the concepts of nano science nano technology aims at improving the lifestyle of the humans. When we actually imply the standard of living of human beings, that is certain tasks and certain kind of issues, which could not be solved for the human race at the level of the macro level.

Here, nano science and nano technology could actually prove extremely useful like for one example would be to insert a micro chip into the body for controlled drug delivery. So, if you have a controlled drug delivery automatically, it implies that we are not going to damage any side tissue the side effect aspects issue is going to be lower the amount of drug needed for the delivery is going be much less. If the chip has sometime delay or time release mechanism, then we are very sure that the drug is only delivered when needed by the tissue. Therefore, when I am putting this nano science into use, it is clear that there are certain benefits, which can arise from arise in the standard of living of human beings.

Of course, towards the end of this chapter, we will also see that all is not green with nano materials. There are obviously serious concerns with the use of nano materials can they be harmful to human beings, can they can cause certain kind of diseases or allergies in human beings which have not been discovered before. So, these aspects also have to be kept in mind, but that is different area of nano ethics and which poses new challenges in terms of the growth of nano science and nano technology, but here we see clearly see that there are benefits. These benefits are going to drive the growth of nano science and nano technologies, so some these applications are those which otherwise would not be possible without the use of conventional.

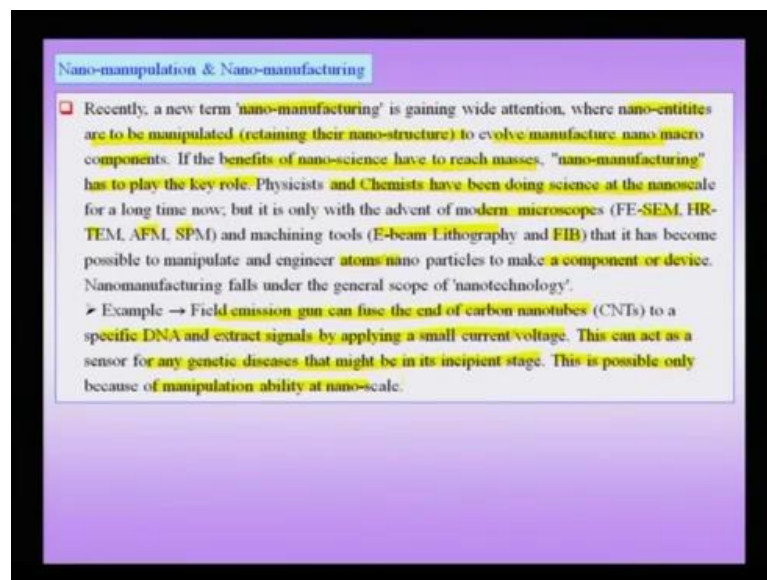
In the case of use of conventional technologies, like for instance I would, I can use some nano structures to make ropes for construction of space elevators, which are extremely strong. So, some of these things may not be possible with the help for with the use of

conventional materials. So, nano technology is application of nano science to useful products and devices useful deliverables, important thing is that some of these deliverables can actually improve the quality or standard of living. Then, nano technology can itself lead to the growth of nano science for instance we can use nano tubes as a probe.

Therefore, nano science may grow, so a new phenomenon can be discovered by the use of nano technology itself. Therefore, it is a self, it is a nice positive feedback loop which can lead to a better growth of nano science a closely related term to nano technology is a word nano manipulation or nano manufacturing.

Now, we said that we want to make the nano science to make useful deliverables, this is definitely not possible if you do not have the concepts of nano manipulation or nano manufacturing. Now, we are dealing with material, which is very little or is size very small in size and therefore, there are special ways of handling this material and also special ways of manufacturing using these materials.

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So, in nano manufacturing, nano entities are to be manipulated retaining their nano structure, which is very important. The entire manipulation itself should not alter the material, which we are trying to what you might call manipulate to evolve manufacturing evolve manufacture nano or macro components. So, as I pointed out that the component itself could be actually small or could be big, but we want manipulate these nano

structures and components of nano materials to actually make these components. If the benefits of the nano science has to reach the masses, nano manufacturing has to play a very key role.

Unless you can mass produce some of these using certain new technologies or new manufacturing techniques, we will it will benefits of nano science will not reach the masses, physicists and chemists. If you note have been doing nano, say would do you call nano science or scale science at the nano scale for some time.

Now, it is only with the advent of modern tools like field emission scanning electron micro scoping high resolution transmission electron micro scoping atomic force micro scoping scanning probe micro scoping. Also certain important manufacturing tools like e beam lithography and focused ion beam that has become possible to manipulate and engineer atoms at the atomic levels and sometime at the nano particle level to make a component and device. So, not only that I have my nano structures and nano material components, I am able to manipulate them and finally, leading to the process of nano manufacturing in which we actually produce the entire component.

An example would be the field emission gun can fuse the end of carbon nano tube to a specific DNA and extract signals by applying a small current voltage. This can act as a sensor for genetic disease that might be in its incipient stage, this is possible obviously because of manipulation of the nano scale. So, what I am doing here, I have a very nice example here of an application, wherein I take a carbon nano tube and diffuse its end to DNA by using small amount of voltage current. I extract signal from the DNA and I can actually see from the signal I will deduce if the DNA has some fault. If the DNA has some incipient disease and early detection can actually perhaps lead to even prevention perhaps a cure if not.

Therefore, nano manipulation and nano manufacturing would form an integral part of nanonano technology. If I am going to get the full benefit out of the nano science or the nano, the concepts which I have discovered in the case of nano science, let us now get down to certain specific geometries, certain specific structures. The examples of which typically literature the first of them, we start with is the concept of a nano particle.

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**Nano-particle**

□ A particle with size in the range of 1-100 nm is a nano-particle. It is typically an independent entity which exists in isolation. However, it may be present as a part of a composite. The importance of nanoparticles is not diminished even when they are embedded in a bulk matrix (such as their role in accelerated catalytic conversion) or dispersed in a solution (e.g. in determining the colour of colloidal dispersion of gold nanoparticles in a liquid medium).

- Literally → Single nano-entity which behaves as a complete unit.
- Practically → A nanoparticle can be a single crystal, quasicrystal, polycrystal or even amorphous.
- Examples → particles of amorphous alumina, crystalline gold, AlCuFe icosahedral quasicrystals.

*SiO<sub>2</sub> nano-particles on glass substrate*

The nano-particle may have sub-components

Nano-particle -300 nm in diameter

The slide contains two images. The left image shows a 3D model of spherical SiO<sub>2</sub> nanoparticles on a substrate. The right image is a scanning electron micrograph (SEM) showing a surface with 'Multilayers' and 'Monolayers' of nanoparticles. A scale bar at the bottom of the SEM image indicates 100 nm. Technical data at the bottom of the SEM image includes: Mag: 8.00K X, Photo: 4.00kV, 0.0075um, 100um X 100um, Date: 12 Aug 2011, Time: 18:22:28.

As in the case of definition of any other nano term, what I imply here is there is a particle in the size range of 1 to 10 nano meters and when I am using the word nano particle, I actually not being very specific the kind of particle. I am referring to here the particle itself for instance could be a single crystal and you will see examples of that in coming slides, it could be a poly crystal, it could even be a quasi crystal or even amorphous. One example of amorphous nano particle is shown here, as you can see here each one these spherical entities is a silicon nano particle so the silicon nano particles can assemble in the form a of nano material like this.

In this case, you can see this is in the form of a mono layer or in a case, other cases it could be in the form of multi layers, the size of these particles is in the 300 nano meter regime. That means we have now extended our definitions to be on 300 nano meter regime, which we were residing before. Then, other cases you can actually take up 100 nano meters or 20 nano meters or 30 nano meters particles and arrange them in the form of mono layers. So, when I am referring to a nano particle, I typically think of it as an entity, which exists in isolation even if it exists in assembly as in the picture below at least it is clearly identifiable to be a separate particle.

For instance, it is not a grain in a poly crystal, so that is what when I am saying it is a nano particle it is a free standing entity or at least it can be easily isolated or visualized as free standing entity. However, nano particles may forma part of a composite also may be

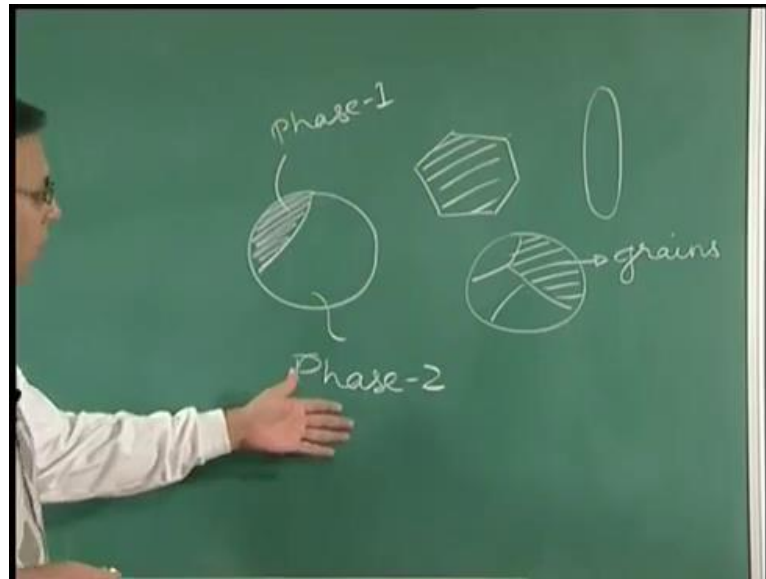
of a larger composite and in this case of course it would assume a new role. It would be called a reinforcement or certain other thing, but nevertheless when I am referring to a nano particle, I assume that it is differently identifiable as a separate entity. The importance of nano particles is not diminished even when they are embedded in a matrix and this is because I am actually expecting certain important properties to arise by putting these nano particles in a certain medium.

If there is no such benefit, then I would not be attempting such a task and therefore, I would expect that there could be some deduction, there could be some amplification in the properties. In some sense, the properties of these nano particles, which are special in some sense is retained when I make a composite out of it. An example of such a role could be the role in accelerated conversion, in fact it may often be that in the presence of a certain catalytic activity may actually increase as seen in the case of gold nano particles. Suppose, I am dispersing this nano particles in a solution, the color comes out from the solution is dependent on the size of the particle.

Therefore, we can see that there are the special properties which may be retained when I put this in a certain medium and putting this in a certain medium just could for its preservation or it could be for its isolation. In other words, they do not coagulate or for it could be for other certain other or what you may call even synergistic benefits. Nevertheless, the nano particle has its own entity and its own specific properties, literally when I am using the word nano particle, I assume a single nano entity, which behaves like a complete unit. So, it is a unit by itself and it may have sub-components, that is an important thing which I need to know.

So, there are some examples we can think of, we can think of particles of amorphous alumina, it is an amorphous state, we can think of crystalline gold, which could be a nano particle and it could even be a poly crystal. So, therefore when I am talking about a particle, a nano particle I am not ascribing anything more than a fact that it is a particle.

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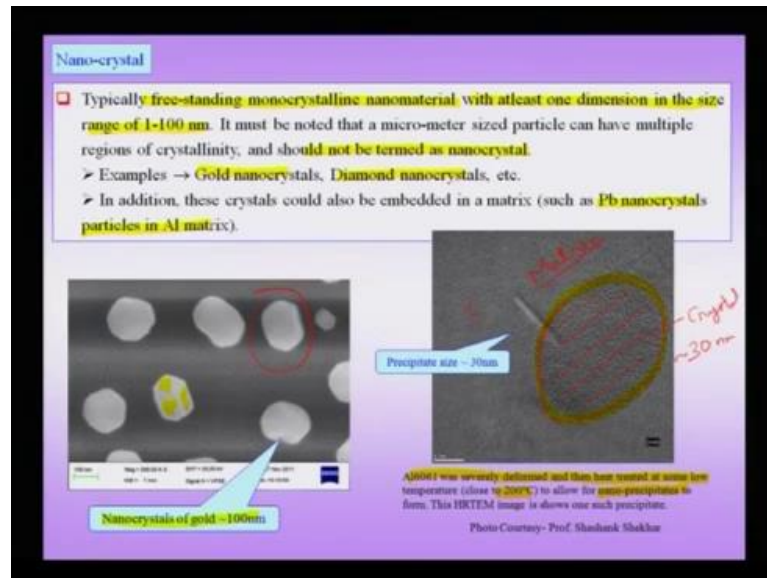


This particle could have its own geometry like could be have faceted faces like it could have a particle which is a Facetted geometry. So, this could be a particle a nano particle could have certain other kind of a shape, it could spherical a nano particle could also have actually components to itself. That means it could be a poly crystal with these being grains, so each one of these is a grain a nano particle. For instance, it could have more than one component, for instance a nano particle could have a spherical nano particle could have one phase here and this could be a different phase and this could be a different phase.

So, there are all these possibilities that I am talking about nano particles and I am not being specific about any of these aspects. In other words, phase one could be crystalline and phase two could be amorphous in a poly crystal, for instance each one of these grains could be randomly oriented, but what I am referring to a nano particle is a fact that this is a particle. It has a certain size, which is in the certain range of 1 to 100 nano meters and in the example here, I considered certain spherical particles of silica, but that is just one example. There could be many other possible examples of such nano particles, one specific class of a nano particle could be a nano crystal.

In other words, here I am being very specific regarding the kind of atomic order in a nano particle and I am saying it is crystalline order, it is not quasi crystalline, it is not amorphous, but it is crystalline order.

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So, one example, is shown here, for instance these are nano crystals of gold and these particles of about 100 nano meters. As you can see that these are free standing gold nano particles, if you look at it more carefully actually, you will observe that these particles have certain nice well developed facets. This is because the anisotropy in the surface energy and therefore, this particle would like to put out those surfaces which will give it a low surface energy and the overall system of the energy is low. So, a nano crystal is typically a free standing mono crystalline nano material with at least dimension the size of 1 to 100 nano meter it must be noted.

So, this concept of at least one dimension we will elaborate a little later during these lectures, but essentially we note that at least one of the dimensions has to be nano meter or 1 to 100 nano meter regime for us to classify it as a nano crystal. So, if we have a poly crystalline particle and this particle as we say could be in nano meter regime, then strictly speaking there should not be termed as a nano crystal.

So, it becomes a nano poly crystal not a nano crystal examples are gold nano crystals diamond nano crystals etcetera sometimes we also refer to nano crystals as I pointed out to those things which are embedded in a matrix. One such example is a case of a precipitate shown here and this is produced in a aluminum 60, 61 alloy, which is being severely deformed and heat treated at some low temperature close to 200 degree celsius to allow for nano precipitates to form. So, we see a region here which is a nano



precipitate, so from these lattice fringes which you can see these lattice fringes lying here, you can see that this region of the precipitate which I will highlight may be here is actually crystalline.

However, this is now embedded in a matrix, so this is my precipitate or a crystal and the size of this crystal is about 30 nano meter and this is embedded in a matrix. In some cases, even this kind of a configuration, wherein the nano crystal is not a free standing nano crystal as in the case of the gold considered here. We might still want to call this nano crystal because it still is an independent identifiable entity of the nano scale regime and it is crystalline and it exists in a matrix. Other such kind of nano crystals have been produced and typical examples good examples of these are lead nano crystals, which are suspended in or has been distributed in aluminum matrix and one of the ways of doing.

So, it is actually taking lead and aluminum and melt spinning the mixture and this gives us tin foils in which lead because lead is typically not soluble in aluminum, but then by doing this fast rapid solidification process. We can actually get lead nano crystals which are distributed in an aluminum matrix, so when I use the word nano crystal, it implies that the material is crystalline the material. Typically, it is a single crystal and typically it is a free standing entity, however in some cases as we just saw the nano crystal could actually be embedded in a matrix and still we may want to call it a nano crystal though it is not free standing if it is embedded in a matrix.

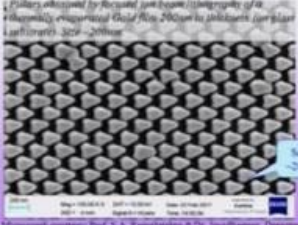
So, there are abundant examples of nano crystalline materials like gold nano crystals, which is typically used for you know catalyses and other important applications, there can be diamond nano crystals, which has nice properties as well and so forth. Now, we come to the next important definition the definition of a nano structure a nano structure has to be differentiated from a nanomaterial and has to be also differentiated from terms we just came across like nano crystals and nano particles. In other kind of similar kind of terminology, which is may sound very close to what is a nano structure, so what is the definitive nano structure and nano material.

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**Nano-structure**

- ❑ Nanostructure is a structural geometrical entity with a distinct shape having at least one of the dimensions in the nanoscale.
- ❑ Nanostructures have a specific geometry.
- ❑ Carbon nanotubes (CNTs), fullerenes, carbon onions, nano-fibers ZnO, and nano-spheres are few of the most common nanostructures. Biology is abound with examples of nanostructures; this includes DNA double helix- structure (size of DNA single strand 2.2-2.6 nm), bacterial cell wall, protein nanolayers in nacre.
- ❑ Examples: Nanosphere, nanopillar, nanocage, fullerene, nanofiber, nanoflake, nanoring, nanobelt, nanobelix, nanobows, nanosphere, nanotube, quantum dot, micelle, nanocone, nanoflower, nanobrushes, etc. (Bloch walls in ferromagnetic materials have a thickness in nanometers).

*Fracture observed by Atomic Force Microscopy of a thermally evaporated Gold Film. Please to indicate for plate Lecture 3, 201-2010*



Scale ~200nm

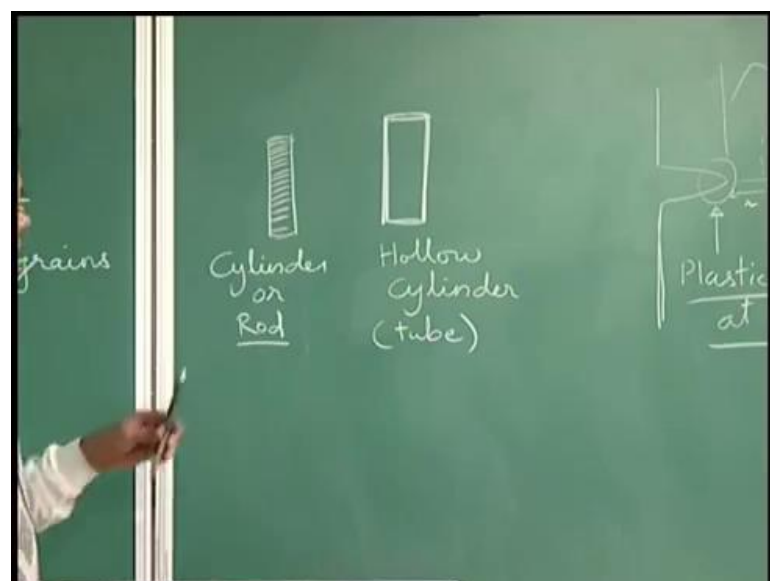
**Carbon Nanotubes**

- 94% pure CNTs
- 40-70nm Outer Dia
- Length 0.5-2µm

*Micrograph courtesy: Prof. S. A. Ramakrishna & Dr. Srivallabha, Department of Physics, I.I.T. Kharagpur*

In the case of a nano structure, we are talking about a structural or geometrical entity with a distinct shape having and this whole entity has at least one dimension in the nano scale and we already said that the nano scale implies 1 to 100 nano meter. So, when I am referring to nano structure, I imply it is a geometrical entity or a structural entity and it has a distinct shape and the shape could be a spiral the shape could be a rod. The shape could be a sphere or any specific shape or that shape should be associated with a certain geometry, which means I have a material carbon.

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Now, I make a structure like this it is a cylindrical structure, the other possibly is that I make a hollow cylinder, of course, a again of a nano meter dimension. Now, I have a hollow cylinder, so this hollow cylinder is like a tube from the external shape, of course they look very similar. This is one kind of a nano structure, because its geometry is different from the geometry of this structure and therefore, these represent two different nano structures. Therefore, when I am talking about nano structures, I have to worry about the geometry and the reason that I need to worry about the geometry is that even the same material in different geometries actually give rise to different properties.

Therefore, nano structures have a specific geometry and that geometry has to be specified whenever you are talking about a certain kind of structure. However, from this example, it should not imply that every kind of structure can be found in every kind of geometry. It is certain structures are only found in certain geometries, for example fullerenes have a certain geometry, I cannot make it in for instance a plate like geometry. It is not possible a fullerene molecule has this geometry, which is it resembles like football and I cannot take a fullerene and make it geometry which is like a plate. Therefore, I have to remember that though I would like to differentiate two different structures.

It is not possible to produce every kind of material or every kind of nano structure in any kind of desirable geometry and this also implies, if there is a structure produced in a certain geometry the properties are very specific.

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**Nano-structure**

- Nanostructure is a structural/geometrical entity with a distinct shape having at least one of the dimensions in the nanoscale.
- Nanostructures have a specific geometry.
- Carbon nanotubes (CNTs), fullerenes, carbon onions, nano-fibers ZnO, and nano-spheres are few of the most common nanostructures. Biology is abound with examples of nanostructures; this includes DNA double helix- structure (size of DNA single strand 2.2-2.6 nm), bacterial cell wall, protein nanolayers in naere.
- Examples: Nanosphere, nanopillar, nanocage, fullerene, nanofiber, nanoflake, nanoring, nanobelt, nanobelix, nanobowls, nanosphere, nanotube, quantum dot, micelle, nanocone, nanoflower, nanobrushes, etc. (Bloch walls in ferromagnetic materials have a thickness in nanometer).

*Pillars obtained by focused ion beam lithography of a... experimentally... Gold Nanopillars in polymer for... (Liu et al., 2007)*

*Carbon Nanotubes*

- 94% pure CNTs
- 40-70nm Outer Dia.
- Length 0.5-2µm

Scale: ~200nm

Scale: 1µm

Micrograph courtesy: Prof. S. A. Ramakrishna & Dr. Venkatesan, Department of Physics, I.I.T. Kharagpur

Here, examples of nano structure include carbon nano tubes, so carbon nano tubes could be single layer carbon nano tubes or single wall carbon nano tubes or multi wall carbon nano tubes. You can see in the picture below here wherein certain carbon nano tubes have been shown and these are typically multiple walled carbon nano tubes. You can see here, so these are all nano tubes and these are multi walled carbon nano tubes fullerenes are other nice examples of nano structures carbons onions which are concentric shells of carbon layers or graffiti like layers.

Then, nano fiber of zinc oxide nano spheres are some of the few common examples of nano structures one nice example of nano structure is shown in figure below, wherein I have certain pillars, which have now grown in a nice crystalline array. If I now consider not the entire crystalline array, but I just worry about one single entity in the crystalline array which forms a mot. If for this crystal and this unit cell for this crystal would be this unit cell, therefore this is now the unit cell of this crystal.

Now, of course this is not a strict crystal in crystal in the strictest sense, but in an average cell would qualify as a crystal, so this structure I see here is a nano structure because now this has got a specific geometry. In other words, at least this one dimension which we are talking about which is visible in this micrograph is of the order of 200 nano meters, which qualifies it to be a nano structure, but the entire crystalline array. Then,

can be thought of nano material and this one single entity which is what now my nano structure in biology is.

We have many more examples of nano structures these include the DNA double helix, the DNA strand is typically 2.2 to 2.6 nano meter in size the bacterial cell wall is another nano structure protein. Nano layers in nacre are other examples of nano structure and in the case of the protein nano layers, it does not exist in isolation. Actually, it exists in combination with other layers, which actually gives nacre the extremely or the a shell it is extreme toughness. Other examples of nano structures are nano spheres and nano pillar nano cage fullerenes nano fiber, nano flakes, nano rings, nano belts, nano helix, nano bows, nano sphere. Of course, repeated here nano tube quantum dots micelles nano cone nano flower and you can see one example which seems like a small nano flower here with four fold kind of a dendrite.

So, nano flowers, nano brushes etcetera, you will see one example in upcoming slide which resembles some kind of a nano brush, we have already seen, we talked about blocked walls. So, block walls in ferromagnetic materials can also be thought of as nano structures because they have a specific geometry they have a specific arrangement of spins within that wall. This is what comprises a magnetic domain wall, which is itself a nano structure in its own, therefore to summarize this slide we come across very many terms when we read literature regarding nano materials. We come across terms which have been described here like the nano flower, nano ring, nano flake etcetera.

When I am talking about this kind of a classification, I am referring to a specific geometry whenever a specific geometry is being referred to the term. I would use for the entity or the nano entity would be a nano structure. So, a nano structure is characterized with specific geometry because this specific geometry would also determine the properties from this kind of geometry. Certain examples are shown via micrograph, we considered like a multi walled carbon tube in the right hand side. We also talked about nano pillars, which are basically made by basically made by focused high photolithography of a thermally operated gold fill. So, this is done by photolithography focused ion beam lithography and therefore you see that each one of these entities is a nano structure.