Carbon Materials and Manufacturing

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Lecture - 01
Introduction to Materials and Manufacturing

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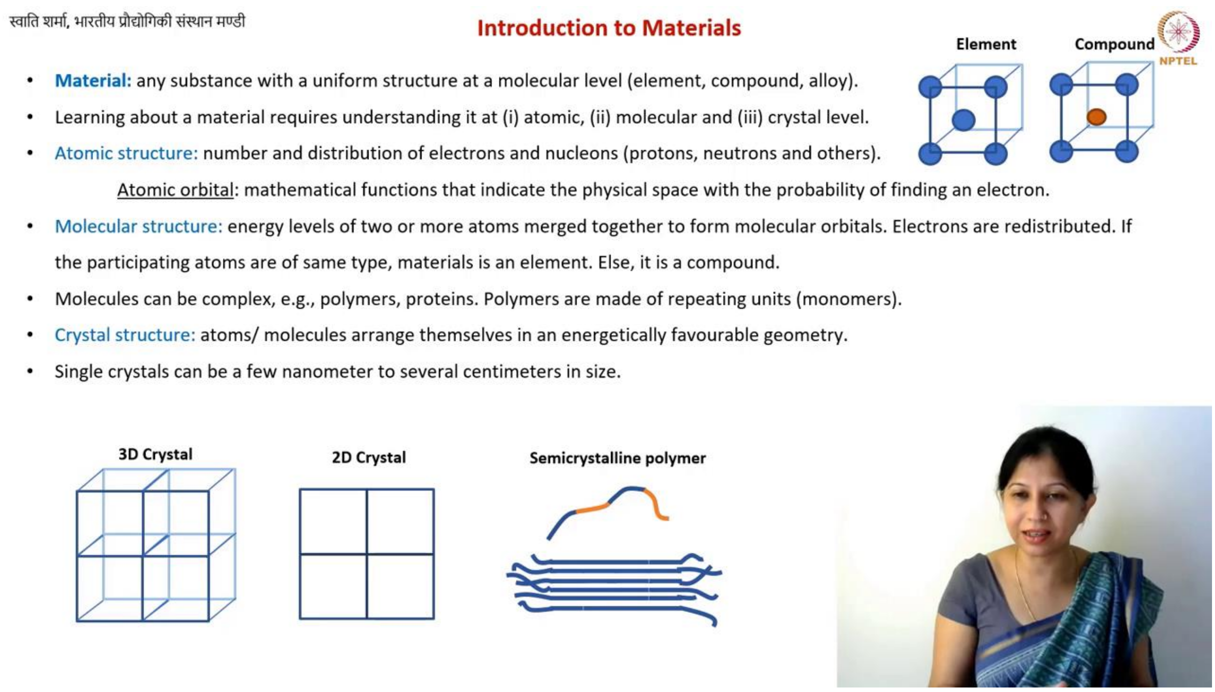

Hello everyone. Welcome to the first lecture of Carbon Materials and Manufacturing. Now, before we start talking about carbon materials specifically, in this lecture I am going to discuss briefly about what materials are? And what are the properties of the materials that we need to know before we start thinking of manufacturing something?

What is manufacturing? Manufacturing is just making something and for making something you need to know certain fundamental properties of the material. What are these properties? Let us take an example of an iron material, cast iron or any kind of iron steel. Now, you want to make some shape out of it, and you want to perform casting. Now, what do you need to know when you perform casting?

You need to know what is the melting point of your material? What kind of crystal structure does it have? Will there be any phase transition change in the crystal structure when you heat it to a very high temperature? If it is a steel, then what kind of steel is it? What is the hardness of the steel? What kind of defects do you have?

So, all of these things you need to know. And you need to know the properties of the material, in order to understand the application.

Do you know why you are making certain structures using iron? Maybe because of its mechanical strength, maybe because of its electrical conductivity, may be because of certain other properties. So, all these things you need to know and how do we learn about these properties?

Now, think about carbon. The very fundamental thing about carbon, something very important for this entire course, is that carbon is not one unique material. Even though, it is an element, it’s a unique element, it’s atomic structure remains the same. But you have several different carbon materials, and that is because the definition of materials itself is a very general definition. Any element or any alloy or any compound can be called a material as long as you have a uniform structure at a molecular level, this means that if you take two samples of the same material, you should be able to get the same properties and that is when you call it a material. And especially when it comes to manufacturing techniques, then the material term is used in a very broad way, everything is called material, anything tangible is material for manufacturing purposes. So, carbon can be called a material, but the point is that carbon can have various crystal structures, it can also have some mixed crystal structures, or you probably know about hybridization. I know that in the high school textbooks, you learn very fundamental things about hybridization. And when I was in high school, I only learnt about graphite and diamond, but I understand that now they have also included a short write up on fullerenes. This is very good, now we already know that we are familiar with the materials and then we are going to build upon that, but anyway I am going to discuss some very fundamental aspects.

The point is that based on these hybridization states, carbon can take different physical forms. And you can also do different manufacturing processes. For example, you can make fibres out of it or you can make nano-scale materials out of it. In fact, many of you when you took this course, you must be thinking only in terms of carbon nanomaterials. The first carbon material nowadays that comes to people’s mind is graphene, then you also think about carbon nanotubes and then you might think about fullerenes. These are the carbon materials that are very extensively studied nowadays. For research purposes, they are very important, but for industrial purposes and for manufacturing purposes still the good old fashioned, carbon materials like graphite, glass-like carbons and activated carbons remain very important. So, we need to know about all these materials. And what we need to know is, how can we change the properties of these materials? Can we also design a new carbon material? Can you come up with the new carbon materials?

The answer is yes if you understand your material at atomic, molecular and crystal level. So, the carbon atom remains the same in all carbon materials, irrespective of what is the scale at which you are using it or at which you are manufacturing it.

Carbon atoms and their properties remain the same, what is different is the molecule, and then accordingly the crystal structure may differ. What is a molecule? When you have a lot of atoms together and they form bonds, and then that is how we get a larger unit that is more stable. In the case of carbon, you can have massive sheets like molecules, or you can have sphere-like molecules, you must have heard of C_{60} which is the buckminsterfullerene.

In the case of carbon, these molecules can also be very interesting, and you know that crystal structure is determined by the hybridization states and the shape of the orbitals. We are going to discuss all these things. But the point is that you can have completely different properties, just because of this hybridization. And because of this slight change in the crystal structure, you can have very different mechanical properties. Like a certain carbon form will have a slip plane and another carbon form will not, in both cases you can have very different mechanical properties. Once you understand the carbon atom, then you understand carbon at a molecular level like what kind of molecules are possible and energetically favourable. And then of course, based on that, then you understand the crystal structures. So, these are the things that we learn about not just carbon, but any material when we talk about manufacturing processes.

What is an atomic structure? Very simple you know that there is an atom, it contains electrons and a nucleus that has protons and neutrons. There are many atomic models, for example, you must have learned about Bohr’s model, where you have everything spherical and circular and then you have electrons orbiting around the nucleus. That is a very good representation for an easy explanation especially in school, but that is not correct. So, that is also one thing you need to forget about these models, where electrons are orbiting around a certain circular path that is not the case.

What is an atomic orbital? Orbital is just a region in space where you have the highest probability of finding an electron, these are basically probability distributions. We mathematically derive the shapes of these orbitals by solving the Schrodinger equation for hydrogen atom. We just take a single electron system i.e. hydrogen atom, because that is the easy way of solving the Schrodinger equation. And then based on that we derived shapes, where you can find the electron. There is no real concept of the path that the electron will take. In the case of electron, it is here and after some time it is here, and then it is here and then it is here, we just really do not know how it reached from one place to another place.

We do not know anything about the path of the electron, we also do not know anything about the shape of the electron, it can be just some crazy shape we have no idea about it. In fact, if you are more interested in these topics, then you can probably go through some of the NPTEL lectures on quantum mechanics. But the point is that electrons are just probability distribution functions i.e. atomic orbital.

Now, we will also talk a little bit more about the orbitals when we'll talk about hybridization. Because the easy way of understanding hybridization is when you understand the orbital first. And especially in the case of carbon, because you may have some strange hybridization states which are sp^X, we are also going to learn about them.

Now, we come to the molecular structure, what is a molecular structure? When you have two or more atoms coming together and they are forming a bond, why do they form a bond? They basically merge their energy levels; orbitals are energy levels. They merge them and they form something known as hybrid energy level. And if they form this hybrid energy level, they do come together and give them a more stable state that is the reason you form a bond. Because you have a more stable overall geometry. And that is why it's not necessarily just two atoms, it can be more than two or it can be 60 atoms also, if that is what gives it a more stable geometry, then you can have these bonds and then you can form molecules.

Now, of course, you know what are elements and what are alloys and what are compounds? Here this is a crystal structure (refer to slide at 10:18) of one element and this is a crystal structure of one compound.

Now coming to the third level that is the crystal structure, it is how the atoms are organized when they form a molecule, it is typically not one single molecule. There may be millions of such molecules and then this entire molecular geometry somehow needs to organize itself again to get an overall stable energetically favourable geometry. Everybody wants to minimize their energy, you want to sleep, sleeping is when you are in your minimum energy state. You are not really very sad, you are not happy, you are not angry, you do not have any emotions, you know that is your minimum energy state and that is what everybody wants to get.

And similarly, the molecules, crystal structures and every chemical structure also want to attain the minimum energy state. And that is what we also call thermodynamically favourable state, and that is the direction it takes. So, it organizes itself. All the atoms and molecules would arrange themselves in such a way that they try to get that minimum energy state. And sometimes that is why you will have these repeating units and very regular structures, which you would call crystal structures. And interestingly there are certain classes of crystal structures that can explain or accommodate pretty much all the elements or all the materials arrangement. These are called crystal structures.

Now, crystals are always 3D crystals, whenever we talk about crystal structure what comes to our mind is a cube because we have the face centred, cubic structures and base centred cubic structures and so on. What often comes to our mind is something that is 3D. Even when we talk about a hexagonal crystal, we are thinking in the in 3D right, but it's not always the case. Let's say here I have drawn a crystal; there you have lots of cubes stacked on top of each other. So, you get a 3D geometry, but if I just remove one layer the one that is shown with the darker color (refer to slide at 12:36). If I just remove this one layer, then that becomes my 2D crystal.

Crystal is nothing, but an arrangement where you have repeating units, you can also have that in 2 dimensions. These are the kinds of materials that are called layered structures and these kinds of crystals are known as 2D crystals.

Now, you can also have a third thing which is known as semi-crystallinity. Now, it gets a little more complicated. It's a mixture of crystalline and non-crystalline materials, something called semi-crystal. For example, you have polymers, you know that they contain these chain-like structures, some polymers may contain sheet-like structures as well. And occasionally you know some part of them has this certain type of layered arrangement. But you see, on both sides of this figure, I have made the crystal geometry, both sides are then random. So, certain parts in the material will have crystal structure or certain arrangement and these crystallites, the little parts, where you have the arrangement, you will call them crystallites and these crystallites; however, in the bulk material, they are randomly oriented. Not all crystallites are arranged on top of each other, then these crystallites are randomly oriented. These kinds of materials are known as semi-crystalline materials.

Now, a single crystal can be just a few nanometers long in terms of size or sometimes, you can even have several centimetres long single crystals, for example, when you manufacture silicon, you have single crystals that are several centimetres long. You can have crystals with or without defects, you can have crystals that are small which are large. And different crystal structures are what basically determine the properties of a certain material at least when it comes to the manufacturability of that material.

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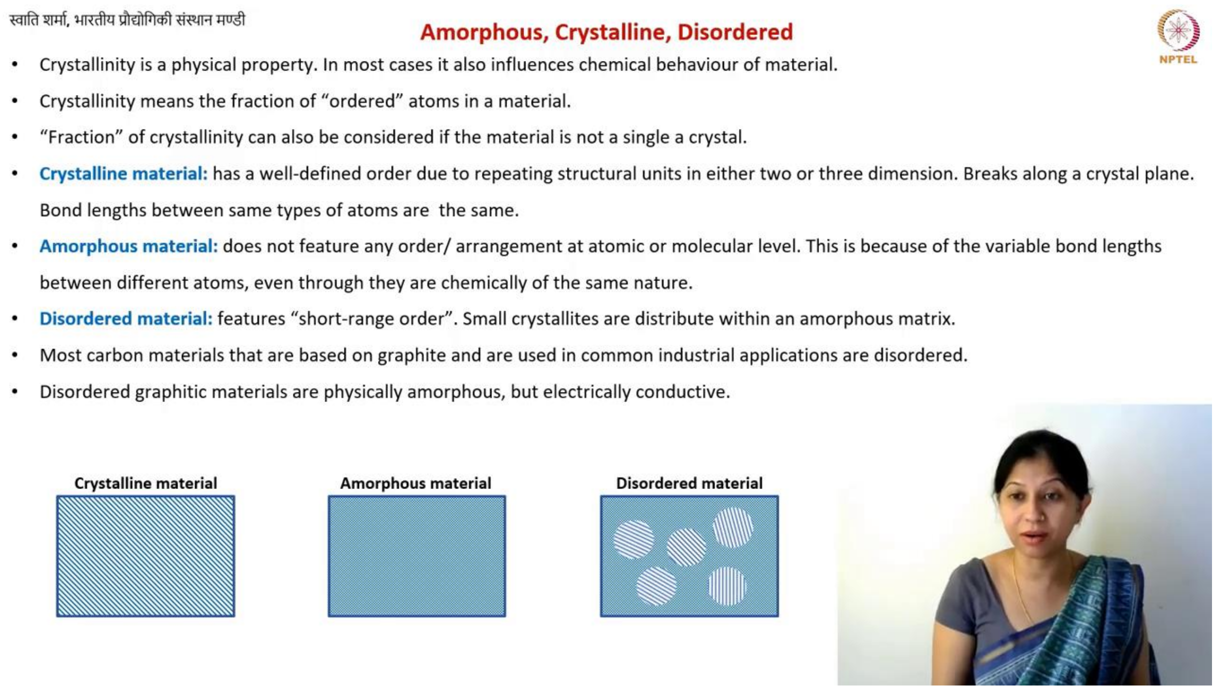

So, we talked about crystal structure, but what are the things that are not crystalline? Are they always amorphous? Whenever you learn about crystalline materials, you learn these are some materials that are crystalline with a nice order and the other materials are amorphous.

If I ask you how to define an amorphous material? That is not easy, you would think it is very easy, but it is not. Because, you can say that something that shatters on breaking is amorphous, but that is not completely correct. So amorphous, and crystalline you know, but disordered you do not.

Is crystallinity first of all a physical property? Yes and no, it is a physical property, because it determines a lot of physicochemical properties of the material, but as such, it is an arrangement. You can say this is a physical arrangement of atoms. But that physical arrangement is defined, by the chemical properties of the material, by the attractive forces that the atoms have with each other and by the nature of bonding. So, it is both a chemical and physical property, but it influences the chemical behaviour of a material, it influences the electrical thermal also, it is a behaviour of the material. As such, you can say it is a physical arrangement. It is a physical property, but everything is guided by the crystal structure of a material. This means that you have a certain order crystallinity means; you have a certain order in the material.

Sometimes you say that this material has a certain fraction of crystallinity. What is crystallinity? Crystallinity means the property that you have that you are a crystal, that is your crystallinity. But now certain materials may not be completely crystalline, they may not be a single crystal. Single crystal, you know large scale single crystals, are relatively rare, even in nature when you mine something large material. But what you can have is partial crystallinity or a certain fraction of the material, which is ordered like you also saw in the case of semi-crystalline materials.

You can have this kind of order in elemental materials not just in polymers. In the case of a semi-crystalline polymer, you saw that there are chain-like molecules, but you do not necessarily have chain-like molecules to have fractional crystallinity. So, some part of your material is crystalline, and the rest is, what is it? Well. Let us just call it non-crystalline. The term amorphous needs to be used very carefully.

Now, crystalline material has a well-defined order. Let us see here (refer slide), here I have shown a picture. What is this picture? There are these lines. What are these lines? These lines are basically planes, these are crystal planes. this is like a cross-section of your crystal. And these lines are going into the computer screen. So, they are like planes.

This is a crystal, you see this is a very nice order, you have lines with well defined, you know the distance between them, so this is your crystal. Now, the second type of material is an amorphous material. As I said the definitions of amorphous that you have learned basically, they all shatter on breaking, well a lot of things can shatter on breaking. Even if you have a polycrystalline structure, polycrystalline means you have a lot of crystals, the material has very high crystallinity, which may be more than 90 percent, but each crystallite is very small and they are randomly organized. They are not one crystal, they are not exactly on top of another crystal or not exactly in the same direction, you can have very random directions of your crystallites. Even these materials will physically break, if you drop it, it will shatter, it will not break according to a crystal plane which is the property of crystalline material. You know that the metals which are crystalline, have a certain plane if you break it, they will break along that plane. So does amorphous material, so how do you define amorphous materials? Amorphous materials basically have variable bond lengths between any pair of atoms. This is the formal definition in which you have completely random bond lengths. If I have 1000 carbon atoms, then carbon 1 and 2 have certain bond length, 2 and 3 have something else, 3 and 4 have something else and so on. Maybe some have the same bond length, for example, carbon number 1,2 and carbon number 67, 68 also have the same bond lengths. But overall what you get is a range of bond lengths, then you call it an amorphous material. So, there is no order whatsoever.

If you take a picture of an amorphous material, I do not know if it's very clear from here, but what you see is like a grey area. You do not really see because you know when you take pictures at this scale you are using electron microscopy. So, you get this kind of random picture, where you cannot really differentiate what you cannot say. This is where my atoms are and this is where they are not, so this is an amorphous material.

Now, what is the third type of material? Disordered materials? Disordered as the name itself suggests they are not ordered. They are definitely not crystalline. But what you have is a short-range order. What does it mean? You have crystallites, but they are very shorts. There is an order, but only for some time only for a very small distance. This is called a short-range order. So, you have crystallites distributed through the material. And they have a certain order, that you may increase for example, by increasing the heat treatment temperature. We will come to it, for carbon materials this is very important. So, you see in this picture, I have taken the picture from the crystal picture and the amorphous picture, this is like a mixture of the two. So, you have tiny little crystallites distributed inside an amorphous matrix. And these crystallites may or may not be attached to each other.

If you somehow by tuning the manufacturing process, if you can keep on increasing the size of these crystallites at some point, they will touch each other, then you call it a percolation point. Percolation means you know when you have this network formation inside a material. Once you have the network, what is going to happen is, you are going to have electrical conductivity in the material. But it is not the case with all crystal structures, for example, diamond is crystalline, but it is still an insulator, but typically for many metals if you have a crystalline structure and if you do have free electrons for electrical conductivity, if it is crystalline, then it will have higher electrical conductivity because you know there is a nice path for the electron to flow.

But, in the case of amorphous, you will not have that kind of electrical conductivity. Disordered materials will be somewhere in between, especially when they have this percolation, when they have a network of these tiny crystallites, then electrons can find a path, electrons can propagate. You will have electrical conductivity, maybe also thermal conductivity, and other properties. But, if you drop that material, it’s going to shatter on breaking. So, you do not call it crystalline, but just because it shatters you also do not call it amorphous. You need to understand the material at its atomic and molecular level and crystalline level to say that this is neither amorphous nor crystalline; this is a disordered material. And a lot of bulk industrial carbons, are disordered materials.

I think this is my personal opinion in the case of carbon, if you do not know the exact structure microstructure of the material, then just rather use the term disordered rather than amorphous because carbon almost always has certain short-range order, well we will come to it. Most of the carbon materials that are based on graphite, I mean that you have sp2 hybridization, at least to some extent, not all the atoms are sp2 hybridized, but you do have sp2. This is a primary hybridization state in your material in that case I will call it graphite-like material or sp2 carbon materials. Most of these sp2 carbon materials if are not perfect graphite, in that case, they are often physically amorphous.

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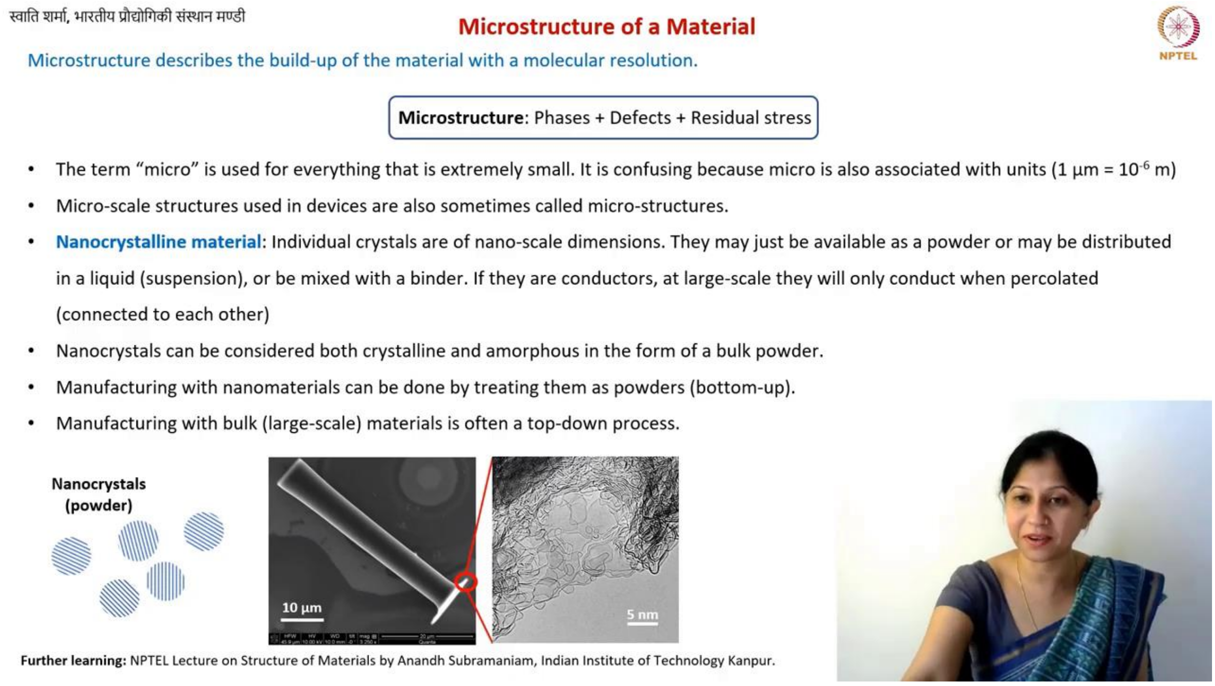

Now, the pictures that I showed you, are schematic diagrams. What do they indicate? What they indicate is the microstructure of a certain material. Microstructure basically would mean how a material looks at a crystal, but this is not the formal definition of microstructure. What do you see in those? You saw the crystalline and amorphous phases. Crystalline and amorphous are phases of the materials. We will also talk about them when we will talk about the phase diagram.

Crystalline amorphous phases you saw, but you also saw how they are associated with each other. You know how much crystallinity you have in a material that you can see when you see that kind of pictures where you see the microstructure of the crystal. If you have certain defects, you can also see the defects. For example: in the case of carbon if you have non-six-membered sheets, then maybe you will not see the individual atoms, but you will see that these are not perfect crystals. There is a certain waviness in those crystals which may have been because of the defects. There is some disordered material in the ordered material also. So, these kinds of things you can see when you see the material at that scale. Then how do you actually define your microstructure in any material? When you can see or you can analyse the phases, the defects, and any residual stress, altogether you call it the microstructure.

Now, this term is a little bit unfortunate because it is called microstructure, now we have very advanced electron microscopy techniques like, we have transmission electron microscopy, for example, you can have very high magnifications, you can see the material very much at the nanoscale, even if you know some very advanced (Refer Time: 26:08) will give you an even atomic-scale image. You can see the pictures of that scale, but you do not call it nanostructure, you still call it a microstructure because the term microstructure was coined when anything that was too small was just called micro. Even now we use the terms like you know micromanagement, micro this and micro that, which basically just means very small scale, same thing for microstructure.

But you need to understand that, when you are talking about the phases, defects, and residual stress, that is how your material's microstructures are defined. If you want to know more about the material in microstructure these very fundamental properties of materials, then I strongly recommend this lecture by Anandh Subramanyam. That is for your further learning because, in this course, we will not be able to talk about all the aspects of materials crystal structure, we will mainly talk about carbon materials.

Now, because microstructure has the term micro in it, sometimes it is also confused with microscale structures. Nowadays we do all this microfabrication and nanofabrication, we make devices even that are extremely small, that are in the microscale, you know microdomain let us say micrometre is 10^{-6} meter. These microscale structures are also sometimes, they can be called micro-structures. Because they are microscale structures but do not get confused. For a material scientist, the microstructure is the phases, defects, and residual stress. But, for a microsystems engineer or somebody who makes microscale devices, then it can also be micro-scale structures.

So, what we are going to do in this particular course in order to avoid any confusion when I talk about microscale structures, I am going to use 'micro-structures', dash between micro and structures. Then, we are talking about a device and when I write one single term microstructure, then we are talking about well microstructure.

Now, yet another thing is nanoscale structures or nanomaterials, you must have heard the term nanomaterials. What is so special about nanomaterials? Is not every material, a nanomaterial? Because every material has some nanoscale units which are the fundamental or the building blocks of that material. Everything can be called a nanoscale material.

What is the special thing about these nanoscale materials? Now, let us talk about the crystalline materials that are crystalline at the nanoscale, then they are pretty much like what you had in a disordered carbon material or disordered material that I showed. Except for the fact that they are not inside an amorphous matrix, they are just there, they are just present, here is this image of nanocrystal powder. This is where you see that you have these nanoscale crystal structures, it is important that they are on the nanometer scale. However, each one of them is randomly oriented and in bulk form what you will get is a powder, it can be a 2D crystal, it can be a 3D crystal or any kind of crystalline structure which is very well defined.

When we intentionally design a certain type of crystal or structure at the nanoscale, then we are able to get what we designed, then we call it technology. The fact that we are able to characterize those materials and we are able to utilize the properties of these nanoscale materials for technological applications, that is all together nanotechnology.

So, nanoscience is about understanding the properties of the material at the nanoscale. And nanotechnologies when you utilize these nanoscale materials, let us say nanocrystals for any technological application, for example, making devices, making coatings, making a lot of functional structures and so on.

When you want to when you purchase a bottle of a nanocrystal, then you are going to get a powder. Now, if you look at that powder inside a very high magnification microscope, then you are going to see these nanoscale crystals. Typically when you want to do manufacturing with nanomaterials, you are going to bind them together, you will not use a single nanocrystal of this kind, for a device. You can, there are examples. This is where the research is moving forward like how we can utilize single nanostructures for technological applications.

But, in general, a lot of manufacturing is still done by mixing these nanocrystals or the powders into a binder, buying them and making something out of them. You can still get the functionalities if not all of them, at least a lot of them, the functionalities of your nanomaterial that you designed and prepared. Now, you can consider them as crystalline or amorphous that I leave it up to you. Because you see it is crystalline at the nanoscale, we prepared something that was crystalline. Because it is crystalline it is going to give you the beautiful properties of a crystal, it is going to give you whatever electrical conductivity you want. But in fact, at the nanoscale, the properties become very much more interesting.

Now, you see nanocrystals will not have defects. But large-scale crystals or if you are manufacturing cast iron, the actual manufacturing materials have a lot of defects. But for nanocrystals, the defects will anneal out, the defects will leave the material. The entire crystal is so small that if there are defects, then this makes it a very high energy structure, it will try to minimize its energy and get rid of the defects.

So many properties of the materials change at the nanoscale. And that is why they are very interesting materials. But do you call them crystalline, or you call them amorphous? if I take the bulk powder-like. I said I purchased a bottle of nanopowder or nanomaterial, then I get a powder, then that powder in bulk is amorphous. Amorphous you know physically amorphous that shatters on breaking. If I also mix this nanopowder into a binder. All together that structure will also shatter on breaking. But the properties that they get are from the crystals. So, you can call them crystalline, you can call them amorphous, or you can call them nanocrystals, so better to call them nanomaterials and nanocrystals.

Now, like I said that you can do manufacturing using binding. This is a bottom-up manufacturing approach, it means when you add things one on top of another. You also call it additive technique and top-down approaches. When you remove material from a big block and whatever is the undesired material then you remove that, those are called top-down processes. Often large-scale manufacturing processes are top-down, because you know if you start making things then it is going to take a lot of time. But there are also examples of large-scale bottom-up manufacturing, you would not call it manufacturing, let us say construction when you have a building construction. Then, you have bricks one on top of another, you know that is a bottom-up process. So, also on a large scale, you will have certain bottom-up processes for making things, whether you call them manufacturing or not. But, typically for industrial, you know tool manufacturing and so on, you will use top-down approaches when it comes to large-scale production of something. These are the things we are going to learn about carbon materials from the next lecture onwards. We will talk specifically about carbon.