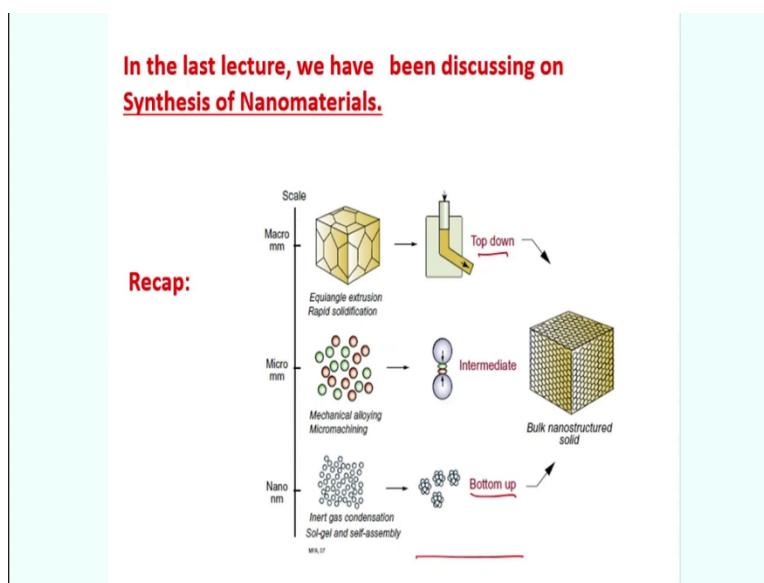


Nanomaterials and their Properties
Prof. Krishanu Biswas
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Indian Institute of Technology, Kanpur

Lecture - 16
Synthesis Routes of Nanomaterials (II)

Students, we are going to start the lecture number 16 ok. So, this lecture will be again primarily devoted on the Synthesis of Nanomaterials. As you know synthesis of nanomaterial is not part of your syllabus, but we have been talking about different types of nanomaterials and their applications, their properties. So, I thought it is pertinent for you to know a bit about synthesis where this is connected with shape, size and also the various properties.

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In the last lecture, we have been we have discussed quite a lot of different synthesis routes and techniques of nanomaterials. And in order to recap this diagram which I have used on this slide you can see that that is very crucial. As you know there are two ways of preparing nanomaterials it is top down, bottom up that is what we call it, and it is easy to remember. Top opposite word

down, bottom opposite word up, is very funny is it not? So, you if you want to go down these size, we start with the big one big size, right.

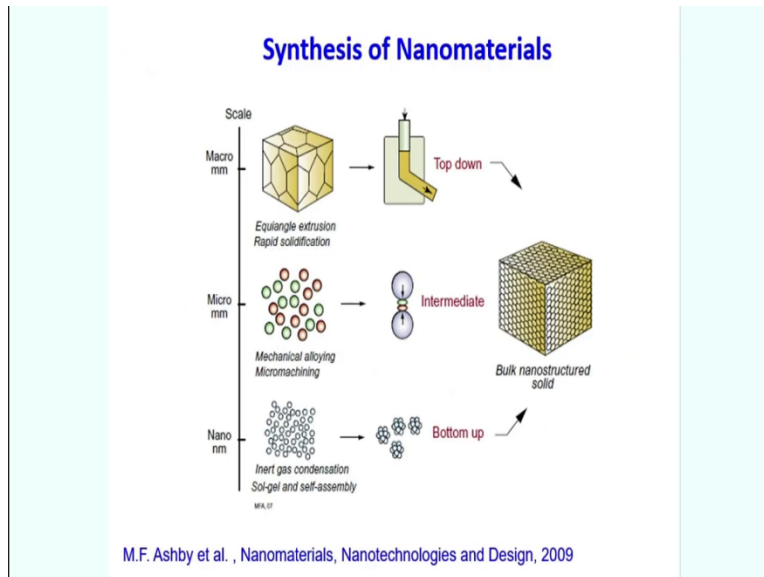
So, you start with the material with the grain size crystallized size bigger than 100 nanometers. It can be as big as possible it can millimeter size also. Then you start breaking it down, ok that is very destructive method, but you can break it down and metallization famous for that ok to break down things to nanoscale. Other way of looking at it is to start with atoms and then allow them to self-assemble, allow them to form clusters and then build nanostructures, right.

So, this is normally used in chemical synthesis routes, and this can lead you to produce control size and shape. Well, both the techniques have plus and minuses, but both are equally important. One can also have intermediate things like micro machining which we will discuss today or mechanical alloying in which you can start with mixture of different elements or different pieces and then allow them to allow them to atomically mixed and form an alloy.

So, all these things especially the bottom up and the micro alloying or micro machining technique will ready lead to production of powder as you know or particles and if you want to generate or if you want to prepare bulk nanostructure materials what you need to do is basically you need to use some consolidation technique or some kind of a sintering route technique to synthetic.

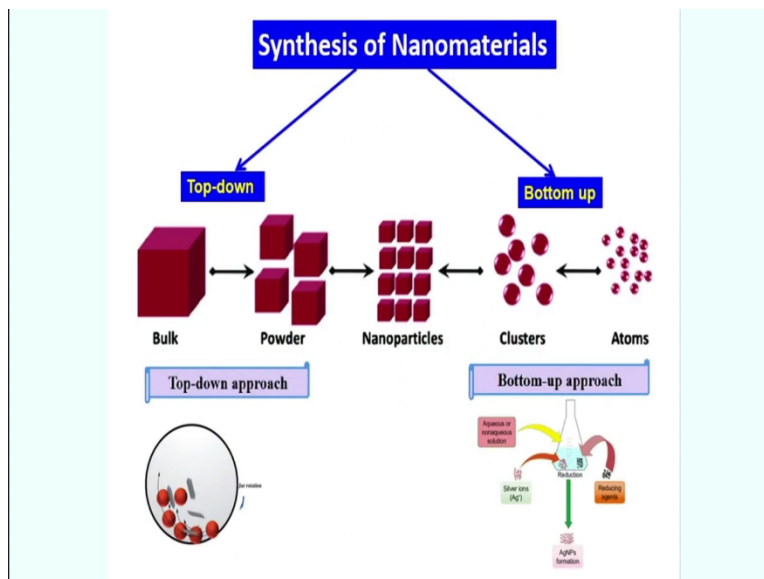
So, in case of top down, it basically you get a starting material with big one you can get a bulk material only the grain size will be severely reduced, fine.

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So, that is the important aspect we should remember when you are talking about these techniques, ok. This is again the same slide which I am showing you in a bigger way. I have been showing this slide for you last two – three lectures because this is a very important one for you to remember.

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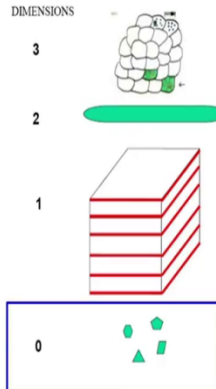


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Synthesis of Nanomaterials

0D Nanomaterials

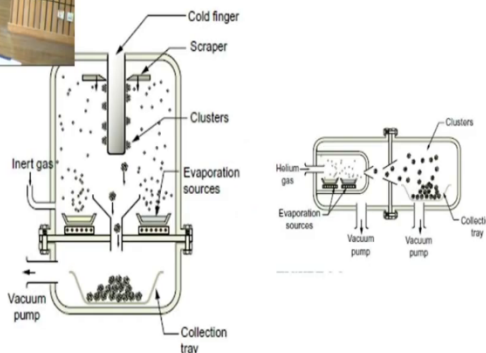


Well, as you know this is again the same thing to show you that how top down and bottom-up approach looks like and then we started with production of zero dimension nanomaterials; zero dimension means all the sizes in every direction x, y, z are the nanometric domain or nanometric scale; that means, this form 1 to 100 nanometers, correct?

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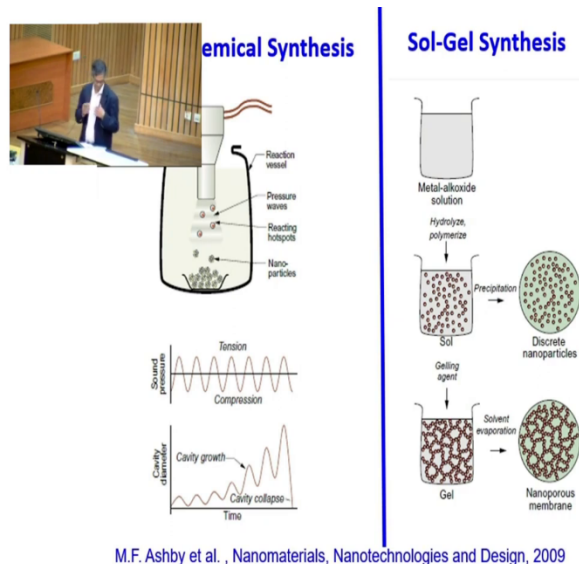


Inert Gas Condensation



And, then we discussed about few techniques like at inert gas condensation which is the first technique, then it has two different variations ok of using the gas how the gas can be used; inert gas can be used for preparation of agglomeration feed nanoparticles.

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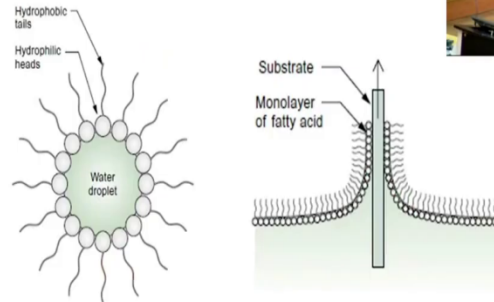


M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

Then, yes, in the last lecture I talked about sonochemical techniques and then I talked about something about sol-gel – how they are important; sonochemical is very important because it allows you to prepare a large quantity of nano powders. Sol-gel is very controlled technique; you can easily create this combination of sol-gel to prepare nanoparticles, ok.

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Molecular self-assembly



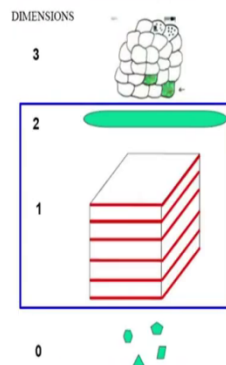
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And, obviously, the important one is which is very recent and which is not yet fully realized it potentially is full not fully realize is the self-assembly by which you can create micelle like structures and then form nanoparticles, am I clear?

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Synthesis of Nanomaterials

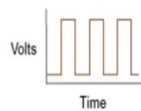
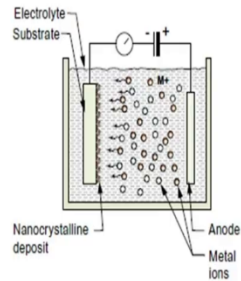
1D-2D Nanomaterials



Then you talked about a bit about one or 2D nanomaterials in which one or two dimensions of nano in x, y, z will be nanometric domain.

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Electro-deposition

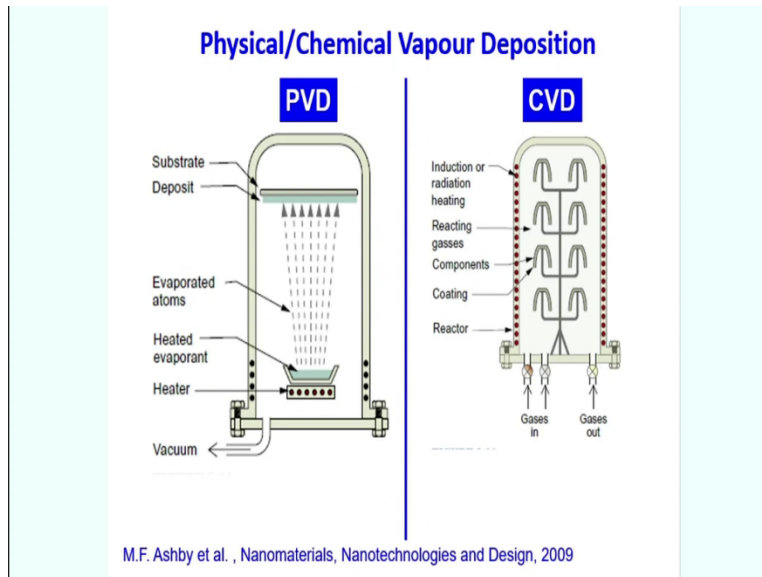


Pulsed Electro-deposition

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And, we can basically do one dimension by electro deposition thin films ok pulsed electro deposition is what is used, ok. It is not standard electro deposition or pulsed electro deposition. So pulsed electro deposition is quite widely used.

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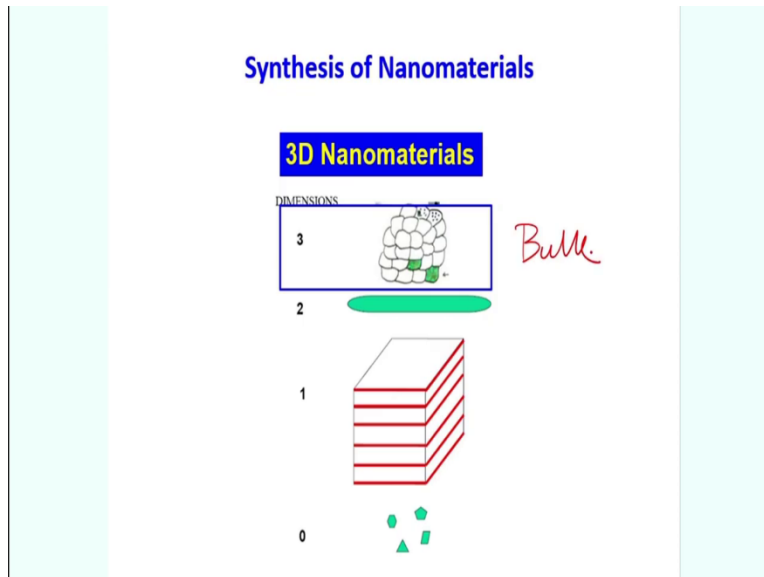


Now, we can obviously, use thin film deposition techniques like physical vapour deposition or chemical vapour deposition to create all kinds of you know 2D or sorry, basically 2D or 1D nanostructures, correct. 2D and 1D difference only differs only in terms of this thickness is nanocrystalline; if thickness is not also nanocrystalline grains can be nanocrystalline ok.

Yeah, I have already discussed about it, but you know compared to PVD, CVD small versatile. Because you can create different kinds of nanomaterials PVD is serial restricted because of evaporation or you know sputtering ability of the system to prepare vapour phase, but PV CVD is basically based on decomposition of the gases or the precursor.

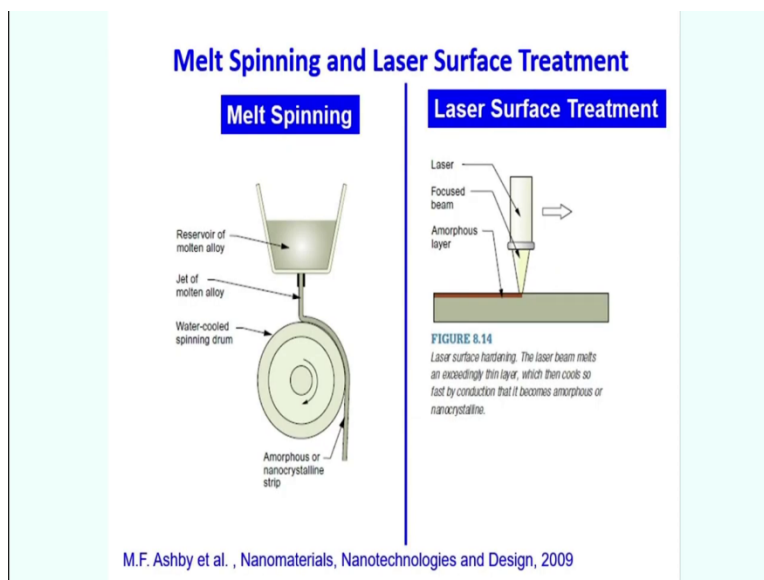
So, is precursor and decomposition of precursor can be done or aided by using laser or plasma or even you can do it by creating low melting temperature, low forming temperature material like some kind of an organic compound can be prepared right of the pieces which you want to deposited as a thin film.

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3D ones are the one which have been discussing. 3D means none of the dimensions are nano crystalline, but they are bulk actually. So, 3D nanomaterials they are mostly a bulk nanomaterials ok.

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So, they can be prepared starting from liquid route like when start with a liquid and spin it out in the forms of thin ribbons by put putting the liquid or by allow the liquid to fall onto a water cooled rotating copper drum. This will lead to rapid solidification of the liquid on the this copper drum or basically it is a copper wheel and then it can be that the grain size can be very small.

But, again the thickness of this ribbons are very small; very small in the sense of 25 to 40 micron and there are a few variation of these route in which actually thickness can go up to maximum hundred micron, but that is also 0.1 millimeter that is not very thick. So, we cannot really call this a bulk, but you know these are very important for transfer micros applications.

Many of the transfer micros requires a combination of amorphous and nanocrystalline phase, ok and some of these alloys are widely used now for you to understand that they are actually having very good soft magnetic properties. So therefore, these routes is, i have been discussing, ok.

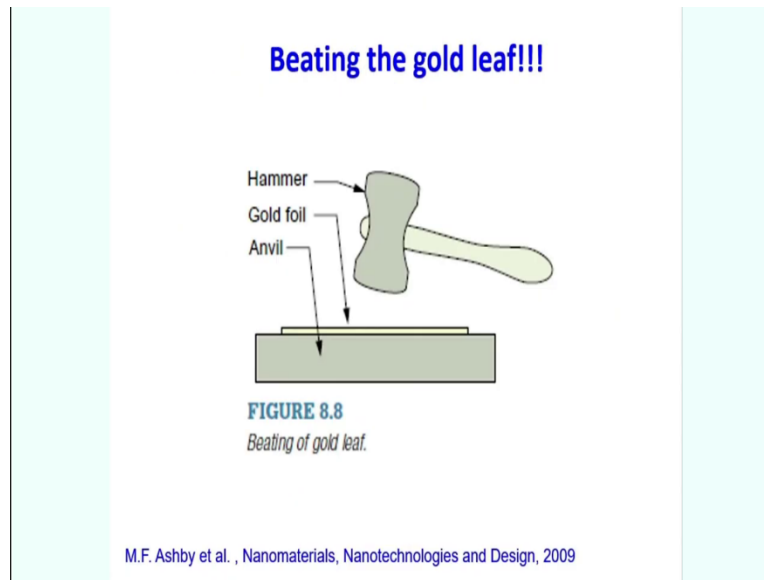
So, again I let me tell you that in this route you have a pool of liquid kept in reservoir and then allow this pool of liquid to fall on or you can force eject through this orifice at the bottom of this reservoir using argon gas and once its liquid comes out it falls on a copper drum or kind of a copper wheel.

And, this leads to rapid solidification of this and as the copper is rotating at a high speed of the rpm of 2000 to 3000 rotations revolution per minutes because of that high rotation speed the thickness of the ribbon is very small and width is large. So therefore, heat transfer is very rapid from these liquid to the copper drum and this leads to very nanocrystalline grain formations.

Well, can we can do this on a surface of a substrate or surface of a something by using a laser beam you can melt this very small thin layer of the substrate by using the laser beam. And this will allow formation of a thin liquid on the top of a solid surface and because of formation of the thin liquid and solid surface what is going to happen? This again heat transfer will be very fast and solidification will happen rapidly and the grain structure will be nanocrystalline.

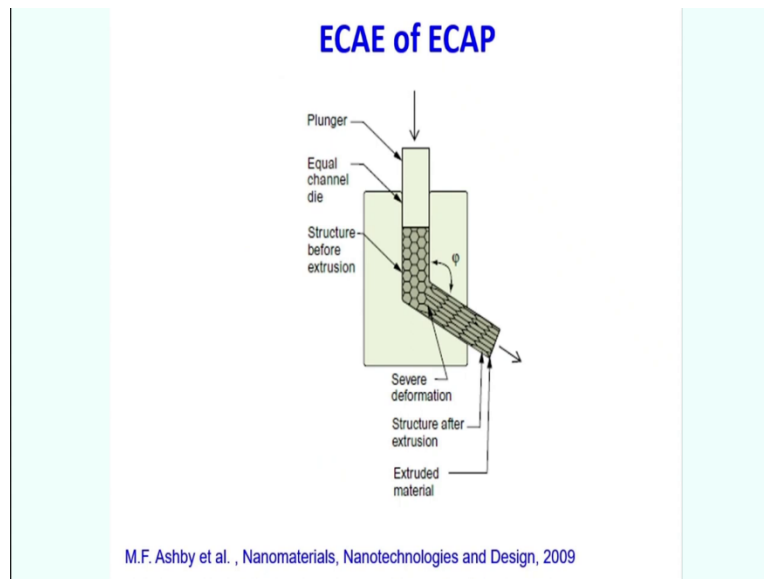
You can also form amorphous layers by this way by proper controlling of compositions. And, then heat it up and then nano parts will transform to the crystalline phases and thus you can form nanocrystalline grains. So, there are many variation of these routes possible.

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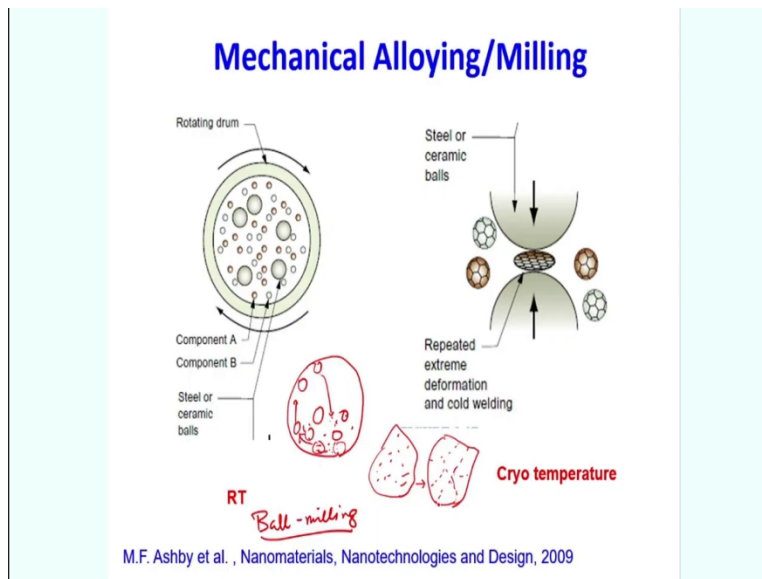
Well, the then I discussed about the beating the gold leaf which is very old technique in which you can take a gold leaf and beat it beat it beat it till it becomes very thin, ok. As you beat it the grains of gold will get severely deformed and the dislocation inside the grains will align and form nanocrystalline grains. I have discussed a lot and not go back it.

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And, then one variation of this route is called equal channel angular extrusion or equal channel angular processing route in which you can actually pass this hot solid through an equal channel die which is angular and because of this angle and because of equal channel the grains will undergo huge deformations and lead to deformation of nanocrystalline grains again because of dislocation aspects ok.

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Now, you know there are few routes which are also important one is this mechanical alloying or milling, ok. In mechanical milling this is known as also ball milling popularly ok all of you know that it can be done at room temperature or cryo temperature or it can be done even in high temperature. But nanocrystalline materials normally prepared by mechanical milling at room temperature or cryogenic temperature.

So, what is done here? So, you know in mechanical milling you charge powder and powder means it can be powder mixture or it can be single powder depending on how what you want. You want to alloy it, then you have to put powder mixture. If you want a single crystalline single component material, then you can put directly into that, ok. So, you charge this material along with the several line number of balls into a rotating drum ok.

So, because of these charging action and the rotation of these drum the balls actually go up and then fall. Basically, if you rotate it hard, then now what will happen? If you consider this is the drum in which the powders and the balls are there these are the powders and these are the balls, ok. Now, as the ball goes above like this then it falls ok. So, as it falls it falls on the surface bottom surface of these bottom wall all these drum.

Because of the bottom wall falling of such a large distance the huge amount of energy is transferred because of the collision of this ball along with these bottoms or the of the drum actually and this will lead to huge energy generation. And, if any powder particles entrap between this ball and this drum, they will undergo severe plastic deformation. Again, something like ECEP or ok that is what happens or beating the gold.

So, this is very very common in mechanical alloying. This is known as a planetary motion. As you see the every ball as it rotates it is initially grinds these powders like this suppose this ball is moving again so, this ball is moving again like this again it goes up and falls. So, as the drum rotates this action happens repeatedly. So, because of repeated action of that that the powder particles are repeatedly deformed. As the powder particles are repeatedly deformed the large number of dislocations is generated.

Again, same thing happens the dislocations of the grain if there is a grain and if you generate large number of dislocations like this the dislocations will increase energy system and finally, because to reduce the energy system the dislocations will align in small angle grain boundaries ok. And that is how one big grain will become small grains and if you keep on doing that finally, you will form a nanocrystalline grains. That is exactly happens in mechanical alloying.

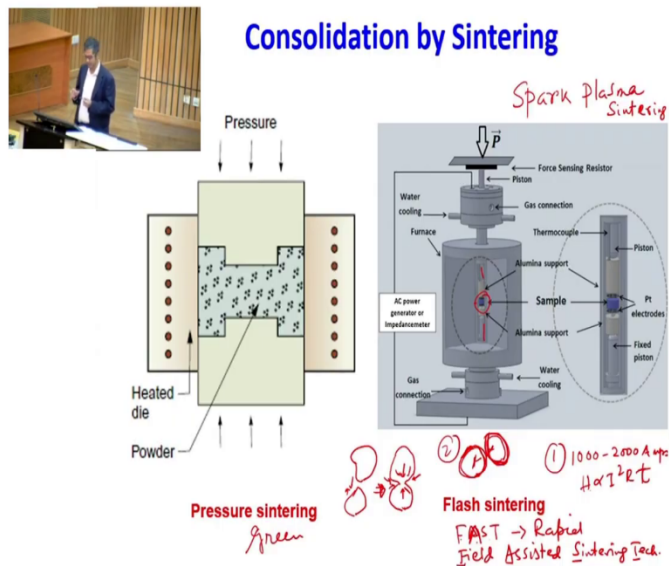
You can do same thing in low temperature, but that advantage of low temperature is that if you cool it down to liquid nitrogen temperature there will be more texture than deformation because most of the material will become brittle at liquid nitrogen temperature except few things like stainless steel, aluminum, copper most will become. And because of that a fractioning will be happening rapidly.

So, material undergo rapid fracture and because of that particle size will also reduce. At the same time deformation will not be completely zero, there will be some deformation will also be happening deformation will be much restricted in case of low temperature ball milling compared to room temperature, but this will indeed will happen and same kind of phenomenal like I discussed here, the grains will also fragmented.

So, here you have two things happening one is rapid fracturing that will lead to breakage of the particles and also in addition you have deformation; deformation will lead to dislocation generation or defect generation and this defect can also lead to nano crystallization of the grains. So, this is a very routine technique used by the metallurgist to prepare nanocrystalline material. But, nonetheless, this leads to production of powder, ok.

So, at the end of the mechanical milling you what you get is a powder and this powder cannot be used in many applications this requires to be consolidated or sintered and that is why you need to use judiciously the sintering operation, ok.

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So, how it is done? You know sintering is normally done in a furnace, but if you do not do sintering properly, ok. Let me first tell you what is sintering? Sintering is nothing, but consolidating the powder particles. So, because of the action of temperature and pressure during sintering the particles will join each other due to diffusional mass transport. So, particles will form necks as you deform them particle will form a small neck and this neck will slowly go grow and then finally, this will join, ok. That is what happens.

So, mass transport will happen like this, like this from surface in the bulk because of the curvature change also as I have discussed right the defect density or the vacancy concentration will vary depending on the negative or positive curvature whether they can be concave or convex curvatures. And nonetheless many such aspects will be operating at these necks at the neck of the powders.

So, therefore, you can apply pressure and temperature to allow the faster mass transport and then create a situation in which these particles will join and then form a single material; this is something which is known as sintering, ok. But you know if you use a normal sintering route that is what is known as a pressure sintering in which the powder particles are compacted using a die actually; a die means you can put this powder particle inside a die and then apply force to form some kind of a green compacted.

Green compact means green compact green means it does not have much strength. So, you can actually do that you can put this powder particle inside in a die, die has a cylindrical cavity or square cavity and then using punch you can apply force into it. As you apply force the particle will loosely bond it, but nonetheless it will form a green compact.

And, then you can put this into the furnace at higher temperature diffusion will happen and then join, but as you putting in the furnace of the high temperature for long time it will require diffusion is slow, right. So, because of that the particles will grow or grain size will increase. So, therefore, such a kind of techniques will not be good enough to retain the nanocrystalline grain size.

And that is why literally very you know last 20 years several fast sintering techniques have come, ok. By FAST means the two things first one is fast is rapid and another one is the field assisted sintering ok. So, one is fast is rapid other one is known as a field assisted sintering technique. So, fast field assisted means you apply electric field, right. So, what is done here? Please try to concentrate. What is done is very simple. You have a system in which you have two graphite rods are present, ok.

And you can actually put the sample in between the two graphite rods this is what the sample is this is two graphite rods with some aluminum support and then you can apply pressure and the current. And current will be very high something of the order of 1000 to 2000 amperes; that is the level of current we apply 1000 to 2000 amps. So, as you know the voltage will be very low 2 to 3 volts because current and voltage is when you multiply properly you get a power, right.

So, as you increase the current, voltage will drop, but here you need to apply more current, why? Because the current will do two things, one currents will lead to lot of joule heating. What is joule heating? You know if you apply current to material because of resistance the material will heat up and this is known as a joule heating and the amount of heat generated is proportional to I^2RT ; I is the current, R is the resistance and t is the time.

So, therefore, if the current is increasing rapidly and this, I^2 term ok, heat is proportional to I^2RT ; t is the time. So, I^2 . So, if you increase I to 1000 or 2000 amps the heat generation will be very high and this can happen in a very short time also correct. So, this is the first thing first effect of current.

Second effect is that because you are applying a huge current the materials material will have these are powder particles. So, therefore, normally all metallic powder particles there will be oxide layer on the top of the surface of this powder, it is very difficult to avoid that. And nanocrystalline side it will be more prone to have oxidation.

And, because of this oxide layer. So, you have oxide layer in a particle suppose this is the particle ok then you have oxide layer on the top surface, right. This oxide layer is a different electrical conductivity than this metallic layer inside. Because of difference of thermal electrical conductivity, there will be current flow will be varying, ok. It is very simple like ok.

So, if you have two electrodes and if you bring close to each other, it will be sparking. Same thing will happen the current will flow through the grains or to the grain interior to this particle interior very easily because it is metallic. But it cannot flow very nicely through the surface. First

of all surfaces has oxide layer and then between the two particles there is a kind of a resistance, contact resistance, right.

So, because of that between the particles this kind of a spark can happen. What I told you like if you bring two electrodes in direct during welding you see that in the arc welding they bring one electrode on the top of other and there is a arcing happens. This arcing lead to heat generation that is how the welding actually done.

Same thing can happen here also between the two grains, if you apply huge current this is exactly what will happen that will be sparking and sparking will lead to breakage of this oxide layer. As the oxide layer is broken off particles will become cleaner and they can then join nicely. So, these are the two things which can happen during application of current.

Third thing which will happen is the first thing is the joule heating, second thing is this breakage or sparking of the particles, third thing which can happen is because of the electric current there will be electro migration, ok. See, if you apply electric current through material electric field will be prepared. This field will force the atoms to move from one direction to other directions, that is what is known as an electromigration.

So, these three things together can lead to rapid mass transport, ok that is why it is known as a fast rapid mass transport. And, because of this rapid mass transport material will joined very fast without mass in case of grain size. And, one of the you know basic variation of these fast sintering techniques is either spark plasma sintering ok which many of us using in India has several places Spark plasma sintering or flash sintering ok. One can use flash sintering also, it is like a flash ok.

So, these are two variation of this fundamental concepts, ok. So, these fundamental concepts were there in 1950s, but how to fabricated machine this knowledge or this kind of concepts were not they available. Only in 1980s this concept you could realize and few experimental you know sintering machines were prepared. In 1990s, these machines were available in market and many

of the labs have purchased and they are using it for preparation of different sintering components, ok.

So, this is something which is new to you and many of you are not from material science background will find new, but this is widely used. You know many of your functional applications require you start with the powder or preparation of nanocrystalline powder, but then you cannot measure your functional properties like thermoelectric or electrical conductivity or thermal conductivity or even many other properties by using by founding powders.

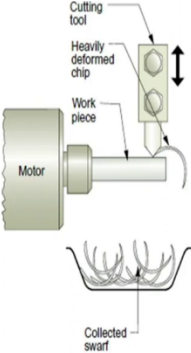
So, you need to seen to these powders. That is why you need to know this route very well, ok. That is something which is very important for you to understand and that is why I am spending so much of time on that. So, you understand, right why you use graphite because graphite has high electrical conductivity ok like copper; copper is electrical conductivity copper is also high melting temperature. Graphite melts are about 3600 degree Celsius.

So, there is no question of current making the graphite melted, but current will flow very easily through the graphite dies. So, that is why our graphite you know rods ok these are graphite rods which are used, but then you have a limitation of applying pressure; graphite cannot hold huge pressure, that is the limitation.

So, one can use tungsten carbide also if you are interested, but then cost increases ok because machining or preparation of tungsten carbide objects is expensive. They require also quite good powder metallurgical you know way of making these tungsten carbide dies and punches. Well, in a nutshell this is a at very advanced technique and now it is widely used to prepare things, ok.

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Micromachining



The diagram illustrates the micromachining process. A motor drives a cutting tool that removes a heavily deformed chip from a work piece. The chip is then collected as swarf. The process is shown in a cross-sectional view.

Machining Method	Materials That Can Be Machined	Feature Size (and Tolerance)	Positional Tolerance	Material Removal Rate, Microns ³ /sec
Micromachining	Metals, polymers	10 microns (2 microns)	3 microns	10,000
Micro electrodischarge machining (EDM)	Any conducting material	10 microns (3 microns)	3 microns	2,500,000
Electron beam machining (EBM)	Any conducting material	5 microns (submicron)	1 micron	100,000
Femto-second laser machining (FLM)	Any material	1 micron (submicron)	Submicron	13,000
Focused ion-beam machining (FIB)	Any material	0.2 microns (0.02 microns)	0.1 microns	0.5

M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

There is another technique which is also we normally ignore is the micromachining, ok. You know micromachining is something which you should know. It is nothing one of the way to torture the materials to prepare nanocrystalline that is what Michael Ashby has written in his book, right.

So, when you look at a machine object, what do you see? You see the technical precisions ok. You see the tolerances, you see the cleanliness, you see, you know the you know different kind of shapes which you can prepared, but what we normally do not look at is the machining leads to lot of chips formation, correct and these chips undergo huge shear induced deformation.

If you have seen how the machine is done you can go to any CNC shops or lathe shops nearby your home or if when you are with IIT, Kanpur you can come to TA 201 or engineering metallurgy lab engineering TA 21 lab actually in the mechanical engineering departments and you can see that you can easily see that this machining are done using very sharp tool.

So, the basically that material is removed machining by shearing action and shearing leads to huge plastic deformation huge, ok. You cannot even imagine how much is the plastic deformation required. So, because of huge plastic deformations chips produced are basically

plastically heavily deformed. Again, this because of heavy deformation the dislocations or the shear bands will form. I know this was something new for many of you who are not from metallurgy backgrounds, but anyway so, you will read about it in the book.

So, if you deform a material heavily ok just like if you take a piece of rod and start hitting it hitting it hitting it hitting it up have you ever done it? If you have not done it you should go to blacksmith ok. Blacksmith does is very routinely. If they want to make an object thinner they will first heat it up and then hit it hard, ok.

How many of you seen bullock carts? You are not seen bullock carts, ok. In earlier days bullock carts used to have hooves made up of wood and then to in order to putting the wood from the during movement on the surface the wood will be you know going to wear and tear because there are everything on the road. You have sharp objects, you will have some holes, you will have something on the surface.

So, because of that hooves will undergo wear and tear and it can even crack also you have to putting that just to put a ring iron ring around this wooden. And this iron ring is basically prepared by taking a strip of iron or steel and then heat it up and hit it, heat first and after taking out from the hot zone then using a hammer you hit just hit the blacksmith does it.

So, once this is hit hard it will deform and then immediately after deformation they will quench it in a water. That is why it become very hard. So, anyway even if it is hitting on something on the surface it will not easily break and the wood inside also be protected I myself was seen when I was a child. So, you must you may not have seen, but if you supposed to see in some places please do watch. So, there deformation is massive ok and it is hot so, deformation can be can lead to huge change of the shape or the size or thickness actually.

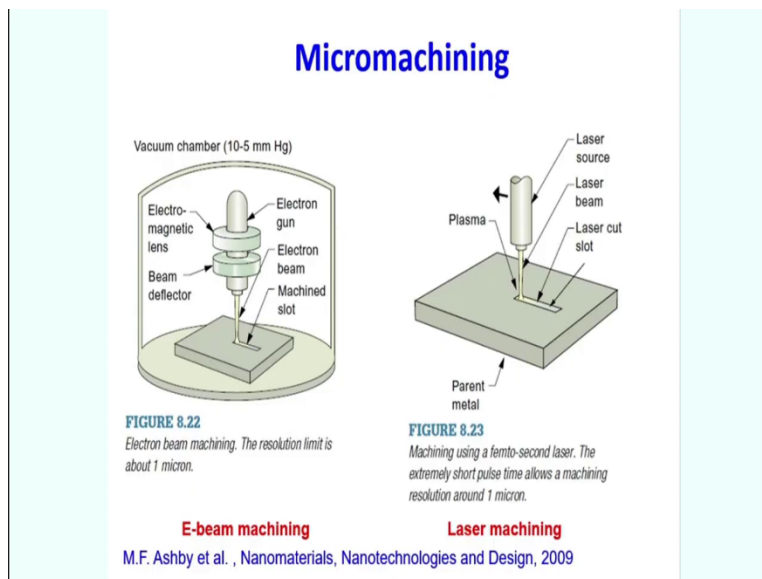
The machining same thing happens you are deforming heavily and this deformation leads to chip generation. This chips actually you know because of that they will undergo huge deformations and then this can lead to nanostructure formations, ok. Later it is the ok so, coarse machining leads to more chip deform chip formations than the fine machine, correct.

So, this chips then can be made powder simply by you know crushing it and then you can sinter it to obtain some kind of a consolidated products that is something which you should know. Well, so, therefore, the consolidation is very very very widely used in this. So, micro machining of there are different kinds of machining methods used you know micro electro digital machining, electron beam machining, femto electrode a second laser beam machining or focused ion beam machining, ok.

So, I will not discuss all of them and each of these has different kinds of feature size and the potential position tolerance ok or material removable plate. So, these are available ok. Some of these can be applied only for metals and polymers, some of this can be applied for every material, but nonetheless this all lead to production of the chips or the materials and this will be having nanocrystalline grains, correct.

So, that is how actually one can produce nanocrystalline material also but remember these are all destructive methods unlike the top bottom up approach this is actually called top down approach.

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Well, another way of doing this is I you know you can create nanostructure by electron beam machining. What is electron beam machining? Well, electron beam or laser beam can be melt

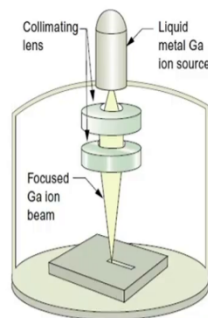
something away and cut something that is what called electron beam machining and you know it the machining the dilution of the machining depends on the beam size. So, electron beam you can reduce the beam size because you can focus electron beam a laser beam to a nice spot and 1 micron, correct.

And, by using femto signal laser you can actually extremely short time pulsed can allow you know rapid solidification of these molten layers. Remember in electron beam machining or laser beam machining you are cutting it off, you are not removing the material by shearing you are simply cutting it off. So, by cutting it off, you are removing the material which are by melting operation by melting it away ok.

So, this thin layer will then solidify rapidly and form nanocrystalline grains ok that is possible. That is not something which is widely used. Now, depending on the what kind of laser you are using is femto-second laser, or 2 second lasers or nanosecond lasers your interaction of the laser beam with the material will change and this will lead to different kinds of nanostructure formation. Nanocrystalline grain size will change depending on the laser beam which you are using, ok.

(Refer Slide Time: 33:10)

Micromachining



Ga⁺

FIGURE 8.24

Focused ion beam machining. The beam is focused to a spot of 5–7 nm diameter, allowing nanoscale shaping.

Focused ion beam machining

Well, also you can use focused ion beam. What is focused ion beam? You can use instead of laser beam or electron beam you can use ion also. One of the important ions is used as gallium. You can take gallium liquid and then apply huge voltage between the input and the outside and then you can create a gallium ion Ga^{+} .

This gallium ions, then can move because of the potential created between two electrodes and then you can generate a beam. So, this beam can focus to very small spot about 5 to 7 nanometers diameter. So, therefore, you can do shipping operation and nanocrystalline sizes because of the beam size is 5 to 7 nanometers you can easily create an object of that dimension a little bit bigger than that.

So, that is how you can create different nanocrystalline objects by using such a kind of a beam, ok. More of these things are available in internet, you can look at it.

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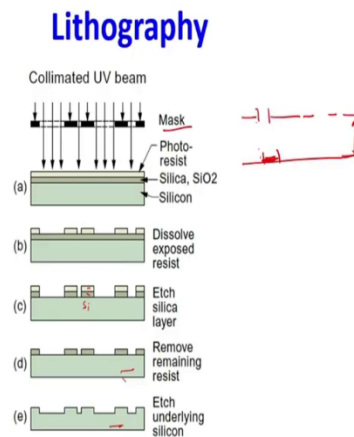


FIGURE 8.25
Photolithography. A beam of UV light activates the

M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

Well, then another technique which is widely used is called lithography. Litho means you know what is the litho means, ok graphy means ok. So, normally what is widely tasting using with a photolithography. What is done here? You take a silicon oxidize the top surface of silicon, it forms silicon dioxide then you apply a photoresist.

Photoresist is the material which will which can easily you know affected by UV or light beam, then you shine the light beam on the photoresist ok using a mask. This is the mask, ok. This mask can be you know put such a height that the image of this mask can be controlled. What I mean to say is that depending on the distance of the mask from the photoresist, the this size can be changed can be controlled ok.

If you are keeping a normal distance this size and this size will be same, but if you are moving it away the size will be reduced, the shadow will be reduced ok by that we can create nanostructures. Nonetheless, does not matter what is the how you do it, but then it you can actually expose, or you can basically what? You can basically expose this past part of the resin in a developer ok just like a photographic. Then what will happen? All these areas which are exposed will be removed because they are reacted with a light and they can be easily removed.

Once they are removed then you can put it into acidic solutions, what will happen? Because of acidic solution the silicon dioxide layer will be etched away. So, what will be behind is? This silicon dioxide layer silicon, silicon dioxide layer and the photoresist ok. So, these then can be used as a pattern to create you know integrated circuits.

Further etching can remove a silicon from the exposed areas creating these channels, resulting nanofeature chips can be then processed further to make electronically active or even use the template for soft lithography, correct. Though concept of photolithography is very simple, but implementation is very complex and expensive.

Mask are to be perfectly aligned with the pattern for the on the offer, silicon are part to be actually perfect single crystals almost defect free this is a silicon ok that has to be perfect and defect free. So, it is very expensive. So, UV light has a length of 250 nanometers. So, that is gives also a limitation of the size which you will create, correct.

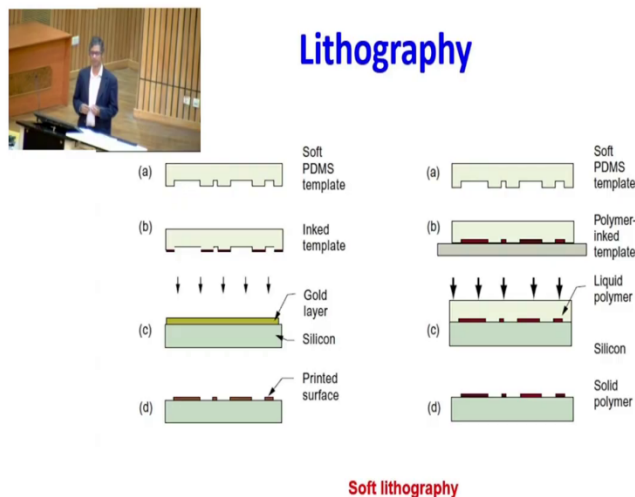
Normally the diffraction limits sets about 100 nanometers, but greater resolution is possible if you use electron beams or X-ray lithography. Electron microlithography pattern is written in a polymer film with a beam of electrons, right. Then, the shorter wavelengths of the electrons allow the features to be much smaller and even as small as about 10 nanometers, and that is how

we can beat the moore'slaw. You can create smaller and smaller size, but we have reached the 10 nanometer limit is very difficult to go down to that.

And, you know because of these resolutions limitations most recent lithography methods make use of many mechanical processes like printing, stamping, molding or embossing instead of protons or electrons, ok. So, there are many such techniques available one is called lithoshop lithography and ok our PDMS kind of stamping methods also available. So, we will not discuss much of that.

But, to in order to say that lithography is one of the very important techniques to create electronic components and these are many variations is possible there are even courses on lithography in IIT Kanpur you one can enroll this course and learn about it. But important aspect is that this can be used to create nanostructures to up to 10 nanometers from photolithography to electron beam lithography depending on whatever use, but it is very expensive technique very very expensive technique and that is why the cost of electronic components is pretty high, ok.

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M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

This is exactly what did I say to you. You can use soft lithography to do that so basically your pattern is a PDMS template, then you can ink template ok you can apply some ink and then put

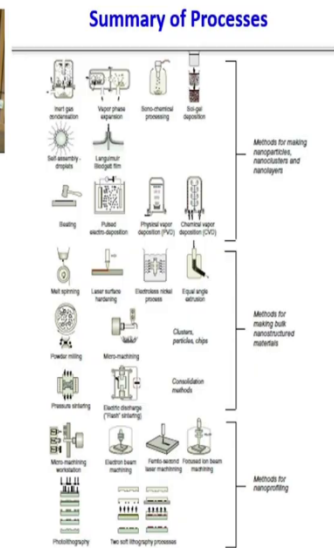
this thing on a gold coated silicon, ok and then what will happen? This whole pattern will be imprinted on the gold and then you can use some kind of a technique to remove the gold layer to create the printed surface and, this is much easier to do that.

And that is how the printed what is called electronics has come into picture ok or flexible electronics have come into picture you can print it, but what you need is the ink here and that ink is the key. Ink has to be a metallic ink because you need conductivity, right. So, therefore, it gives you additional thing. Now, how do you do that? ok.

So, basically you have an electronic lithographed template PDMS template that will have the pattern or reverse pattern of the whatever you want to make ok. This is just the reverse pattern of whatever you want to make and then you apply the ink and then it is pushed onto the gold layer on the top of silicon and create such a kind of printed surface. This is what is done in soft lithography, ok.

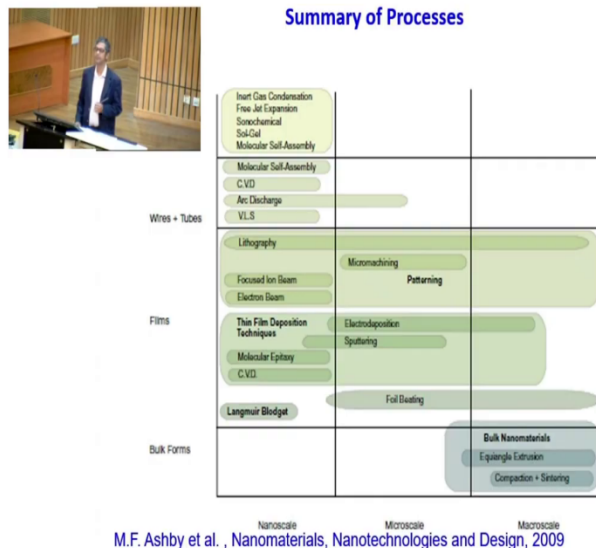
So, that is very something which is widely used now, this little much less expensive compared to the electron beam or optic photolithography techniques, ok.

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So, this is the summary. I do not think you can see everything here ok you can start from a gas condensation method to lithographic techniques. So, here so many ways of preparing nanocrystalline materials which you must remember nicely, ok.

(Refer Slide Time: 40:20)



So, depending on the things if you want to produce particles, you can use inert gas condensations or free jet condensation expansion, sonochemicals, sol-gel or self-assembly. If you want to produce wires and tubes you can go to CVD arc discharge molecular self assembly or if you want to produce thin films also you can use CVD of GVD, ok.

And the bulk pumps can be prepared by using micromachining electric the foil beating or even you know ECAP, compaction sintering, ball milling, correct. So, this is in a nutshell it can lead you to take form different kinds of structures. But depending on the temperatures you can create either mesoscale structure or micron scale structures from nanoscales. Like in sintering if you do not sintering properly grain size can increase rapidly and you can go to microscale structures.

(Refer Slide Time: 41:14)

MECHANICAL PROPERTIES OF MATERIALS

1. Stress-Strain Relationships
2. Hardness
3. Effect of Temperature on Properties
4. Fluid Properties
5. Viscoelastic Behavior of Polymers

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So far, we have learned about synthesis processes of nanomaterials. Now, we are going to start a new topic. We have learned about surface energy thermodynamics, a bit of synthesis process of nanomaterials, we need to now learn about mechanical behavior or basically we are going to start the properties of nanomaterial by mechanical behavior of nanomaterials, right

As you know, mechanical behavior is very important for structural applications, right? Not only that, this also very important for various understanding of how the materials behave at the nanoscale when you apply certain force or you doing some kind of action on the material. And this is equally important for processing also.

So, you know when you talk about mechanical behavior you are talking about few things. Stress-strain relationships, hardness, effect of temperature on mechanical properties, fluid properties, viscoelastic behavior of material mostly polymers, ok. So, basically what I like to do here is a little bit of recap on mechanical behavior first. Reason is very simple.

You are all from different backgrounds some of you are from material, some of you are from physics, some of you are from chemistry and some are from mechanical engineering, many other backgrounds also. So, though hence you may not be exposed to mechanical behavior extensively

in your earlier courses. So, at the beginning let us have some kind of a you know basic understanding of the mechanical behavior properties of materials.

I must accept it is very difficult to do in a small time scale but let us try and understand it. So, the most important aspect of stress strain or mechanical behavior is the stress strain relationships. Most of these things are taken from the book of professor M. P, Groover, Principles of Modern Manufacturing. It is available even online in the in the different websites or it is available in our library also, in fact, but anyway you will be able to get most of the things from my slides.

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MECHANICAL PROPERTIES OF MATERIALS

- Mechanical properties determine a material's behavior when subjected to mechanical stresses
 - Properties include elastic modulus, ductility, hardness, and various measures of strength
- Dilemma: mechanical properties that are desirable to the designer, such as high strength, usually make manufacturing more difficult

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As you know mechanical properties determines a materials behavior when is subjected to stresses; like it includes properties like elastic modulus, ductility, hardness, even various types of measurement of strength and toughness, right. That is what is actually our intended goal. We like to know these properties when you are doing testing of mechanical behavior on the materials.

The major dilemma although which are which is quite significant is that mechanical properties that are desirable to the designer such as high strength usually make the manufacturing more difficult. Why you are saying this? Because mechanical property and manufacturing they are related.

Many of these manufacturing techniques rely more on the mechanical behavior of the material. Like, if you want to shape a material, you must be thinking how it is important. Well, you know suppose you want to make a blade of fan you know all of you saying that you may have a fans in your home master fans in your home. So, you have seen the blades right how the blades are made have you ever thought about it.

They are made by deforming the slab produced in a continuous casting machine in a steel plant because most of these blades actually made of steels. So, that is why you will say that mechanical properties as per the strength is related to the manufacturing ductility also and manufacturing produce process processes we used in the real life.

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Stress Strain Relationship

- Three types of static stresses to which materials can be subjected:
 1. Tensile - stretching the material
 2. Compressive - squeezing the material
 3. Shear - causing adjacent portions of the material to slide against each other
- Stress-strain curve - basic relationship that describes mechanical properties for all three types


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Well, so, first is the stress-strain relationship. What kind of stresses we apply? First one is the tensile stretching. This is very simple, ok. If we take a material and stretch it, ok. If you take a rod or if you take this thing and stretch it on the both side that is what is the tensile loading. Compression is opposite. Think of a pillar in your home, ok. The load of the roof is on the pillar ok.

So, that is pillar is under compressions compressive stress. So, that is nothing, but squeezing the material. And the third one which is very important is a shear; it is causing adjacent portions of the material to slide against each other, ok. Shear is like this ok you are making sliding over each other.

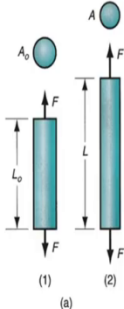
Now, all these kinds of stresses which are existing in the real life are going to make impact on the material behavior, right. So, we need to know the stress strain curves like basic relationship they describe the mechanical properties of all the three types, but for you that is not required to know all of these three. Mostly we will be talking about tensile, ok. Tensile is a stretching of material that is why it dictates the most important mechanical behavior of a many materials.

(Refer Slide Time: 46:28)



Tensile Test

- Most com stress-strz especially metals
- In the test, a force pulls the material, elongating it and reducing its diameter
- (left) Tensile force applied and (right) resulting elongation of material



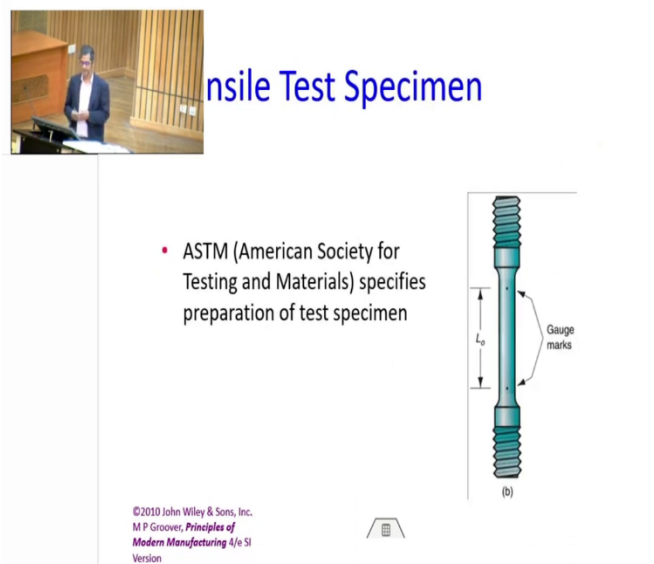
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So, what is done in tensile test? It is more of a stress no is stress is like you take a material and pull it down, but you cannot take any shape and size to pull it up, then your properties will not be reproducible. What is the meaning of reproducibility? Well, I do the test here at Kanpur, you do the test at your home or maybe somebody does the test at in the USA or in France or in Africa or maybe in Japan, what is the guarantee that the properties which you will be getting out of it will be same.

So, in order to maintain that we need to use certain standards. So, standards tensile specimens are used and mostly standard tensile specimens are specific dimensions and specific geometry. So, we will not talk about that how this is important, but in a tensile test the force pulls the material, it elongates and because of elongation the diameter reduces. That is obvious; volume of the material is remaining constant.

So, therefore, if you increase the length, diameter will reduce. Tensile process applied a resulting elongation of most of the materials actually and finally, the material after elongation it fails.

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The slide is titled "Tensile Test Specimen" in blue text. On the left, there is a small photograph of a man in a blue jacket standing in a lecture hall. To the right of the photo is a diagram of a tensile specimen, which is a cylindrical rod with threaded ends. A central section is labeled "Gauge marks" and has a length dimension L_0 indicated by a vertical double-headed arrow. The diagram is labeled "(b)" at the bottom.

- ASTM (American Society for Testing and Materials) specifies preparation of test specimen

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So, the standard specimen looks like this. You can see, these are the grip areas where this specimen is hold and pulled correct and this is the gauge on which most of the measurements are met, decrease of diameter, increase of length ok all these things are made and that is your initial dimension L_0 . Similarly, you can also define initial diameter of the material.

So, this is the standard which is used and we normally use a standard by ASTM American society for testing and materials and this specifies the testing specimens you can actually look at it. It is provided in any book of ASTM standards or even ASM books American society for

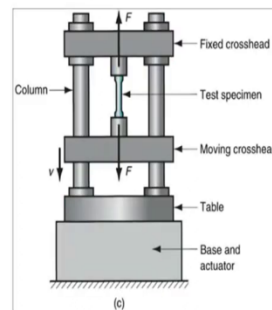
materials these standards are provided. You do not need to bother about that. So, most of the things actually are standardized.

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Tensile Test Setup



- Tensile testing machine



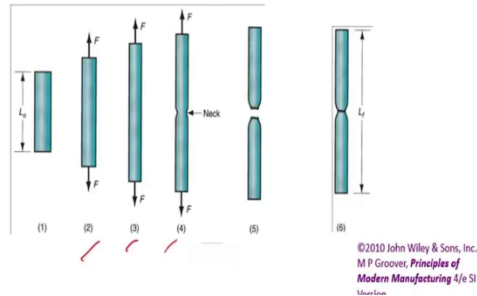
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And, these tests are done in tensile testing machine as you can see this table is loaded and pulled, ok. So, as you pull it the tensile test specimen is elongates and finally, it fractures ok that is what happens. So, load is uniaxial, and you can put all kinds of devices to measure the elongation and all these things.

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Tensile Test Sequence

- (1) no load; (2) uniform elongation and area reduction; (3) maximum load; (4) necking; (5) fracture; (6) putting pieces back together to measure final length



So, in a typical tensile test sequence you can take a specimen of length that is the gauge length of L_0 , pull it using force F , the diameter decreases finally, at one point time the neck develops and because of the neck development most of those elongations actually are concentrated at the neck region and finally, the neck actually ruptures and that is why it breaks sample breaks.

So, ok so, therefore, few things important. Uniform elongation area reductions in number 2, ok number 3 maximum load applied, number 4 actually necking that is where the thin neck forms and then 6 piece putting the pieces back together basically number 5 is basically fracture the samples and number 6 is putting the things back together to measure the elongation total elongations ok.

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Lecture 17

So, that is about the things which completes the lecture 17.