Nanoelectronics: Devices and Materials
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Lecture - 41
Characterisation of nanomaterials

Hello. We today come to the final session of segment three of the course on Nanoelectronics Device Fabrication and Characterization.

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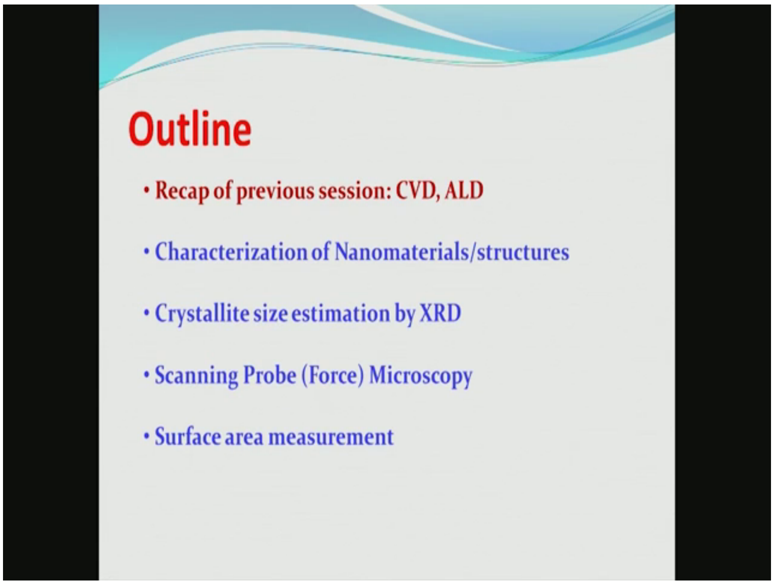

Outline

- Recap of previous session: CVD, ALD
- Characterization of Nanomaterials/structures
- Crystallite size estimation by XRD
- Scanning Probe (Force) Microscopy
- Surface area measurement

What we did does time was to continue with some of the aspects of CVD, and then we came to the atomic layer deposition as a technique for making very fine layers and nanostructures. What we will do today is to go through the characterization of nano materials and structures. We will deal with the crystallite size determination by XRD, scanning probe microscopy for examination of nanostructure surfaces, and if time permits also deal with surface area measurement of nanostructures.

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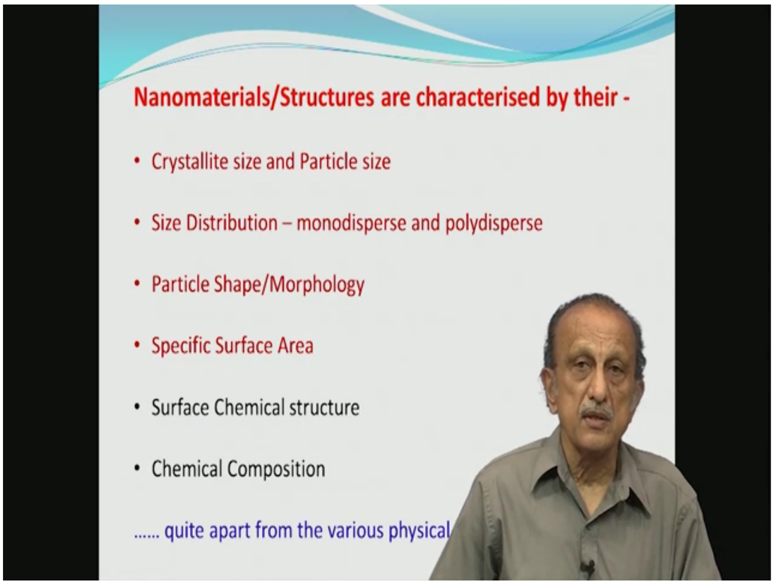

Nanomaterials/Structures are characterised by their -

- Crystallite size and Particle size
- Size Distribution – monodisperse and polydisperse
- Particle Shape/Morphology
- Specific Surface Area
- Surface Chemical structure
- Chemical Composition

...... quite apart from the various physical

Now, nanomaterials and structures are characterized by their crystallite size in particle size, by the size distribution that is whether the distribution is monodisperse or polydisperse, by particle shape and morphology, by the specific surface area which we shall come to later of these nanomaterials surface chemical structure, and chemical composition of course. All these are characterization ways of nanomaterials quite apart from the detailed physical properties, which are characteristic of nanomaterials. So, we deal with characterization of the structure and size and so forth.

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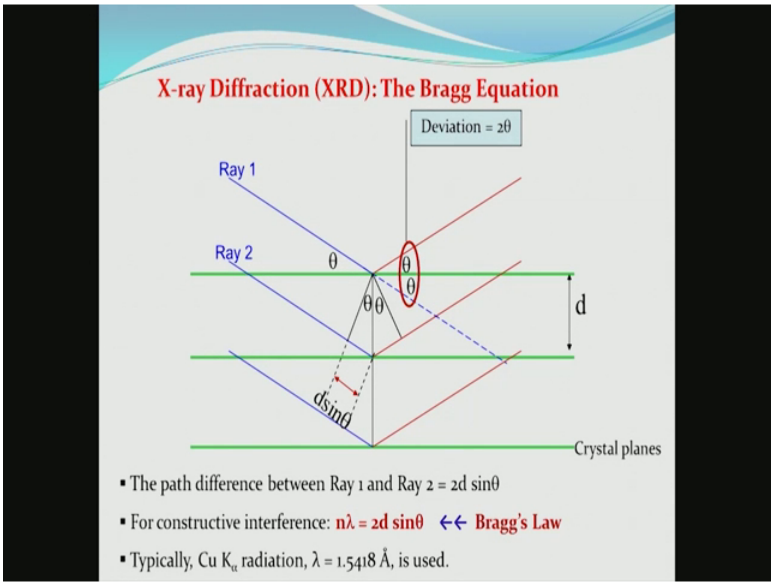

X-ray Diffraction (XRD): The Bragg Equation

- The path difference between Ray 1 and Ray 2 = 2d sinθ
- For constructive interference: $n\lambda = 2d \sin\theta$ ←← Bragg's Law
- Typically, Cu K_α radiation, $\lambda = 1.5418$ Å, is used.

Now, I believe that all of you are familiar with external diffraction you would have learned about the Bragg equation. So, what a diagram indicates is the diagram through which the Bragg law, the well known Bragg law of n lambda is equal to 2d sin theta is derived.

So, you have crystal planes that are present represented by these green lines. So, you have parallel crystal planes between which the distance is d separation is d. And x-rays come in and get scattered from the surface, so you have ray 1 and ray 2. And if and then the path difference between them as shown here by this simple trigonometric equation over here the path difference is 2d sin theta. And if 2d sin theta is equal to n lambda where lm n is the is an integer, and lambda is the wavelength the x-rays incident upon this sample, then you get constructive interference are n lambda is equal to 2d sin theta for those values of theta; which means that you get diffraction peaks at these values of theta.

Typically the wavelength of x-rays that is used is copper K alpha lines of which the wave length is 1.5418 angstroms.

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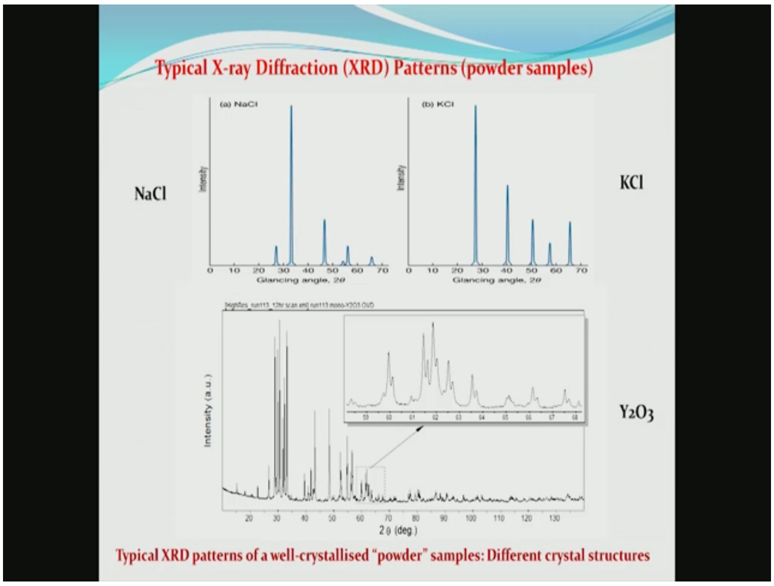

Typical X-ray Diffraction (XRD) Patterns (powder samples)

Typical XRD patterns of a well-crystallised “powder” samples: Different crystal structures

Now, what is shown here is a typical diffraction pattern for a crystalline material sodium chloride and potassium chloride; two well known, compounds which have cubic structure.

So, what you see here or x-ray diffraction patterns in which 2 theta is plotted on the x axis, and the intensity of the x-rays that are scattered for diffracted from the sample is shown on the y axis. So, this is a typical x-ray diffraction pattern. What you see is a small number of lines, and that is characteristic of a highly symmetric structure such as the cubic structure. By contrast what you see below is the x-ray diffraction pattern of yttrium oxide a monoclinic structure yttrium oxide and you can see that it is considerably more complicated with many more lines in the same plot of intensity versus 2 theta as in the case of these 2 chlorides.

Now, what the inset shows is an expanded plot of intensity versus 2 theta over here. So what is evident from this? More evident in this lower graph than in the upper one is that each one of these lines so, to speak each one of these peaks is reasonably broad it is not a sharp line with a very sharp value of theta. In other words there is a certain width to these x-ray diffraction peaks.

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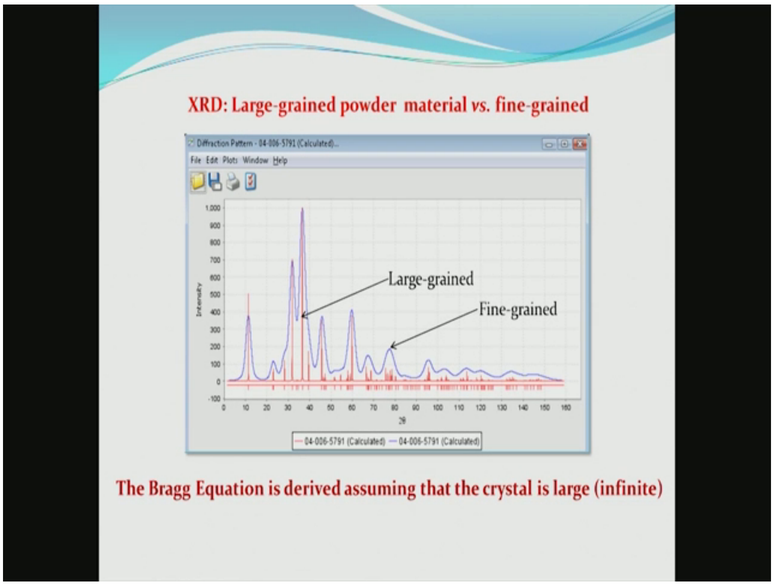

XRD: Large-grained powder material vs. fine-grained

The Bragg Equation is derived assuming that the crystal is large (infinite)

Now, what is shown here is the simulation of the x-ray diffraction pattern of a powder material so, called powder material that is fine material powder in material in the form of a powder crystalline material in the power of form of a powder. So, what is shown in these red lines here is these are these simulated x-ray diffraction pattern of a certain material, this is calculated. And you can see that when there is a large grain material as here you can get very sharp lines, and the blue line represents the same material where the particle size of the crystal size is smaller.

So, the large grain material gives us sharp lines represented by these red ones over here, and the same material when its crystal size is small the same powder material gives us these broader peaks. So this is really a simulation, but we can see from actual experimentation that we will show that will come to that later. So, what is important to note here at this stage is that the Bragg equation: n lambda is equal to 2 sin theta is derived assuming that the crystal is large or effectively infinite.

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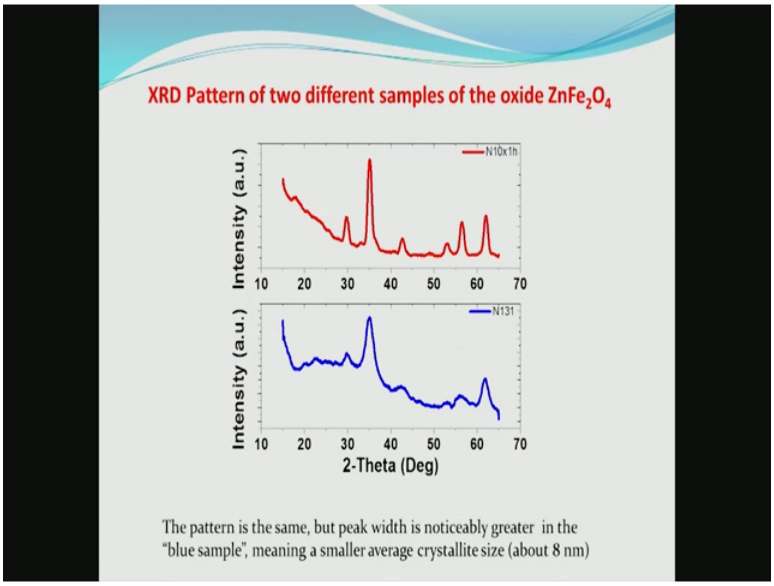

XRD Pattern of two different samples of the oxide $ZnFe_2O_4$

The pattern is the same, but peak width is noticeably greater in the "blue sample", meaning a smaller average crystallite size (about 8 nm)

Now, what is shown here; are the x-ray diffraction patterns of two different samples of a material ZnFe 2 O 4 a zinc ferrite. So what is up above is a relatively a large crystallite size material, and what is below is the same material with a grain size or a crystallite size as small as about 8 nanometers. So, you can see readily from here that the peak width is smaller in the case of larger grains or larger crystallites, and larger in the case of smaller crystallites.

So, there is a direct dependence of the peak width of x-ray diffraction patterns on the average size of the crystals that comprise the sample.

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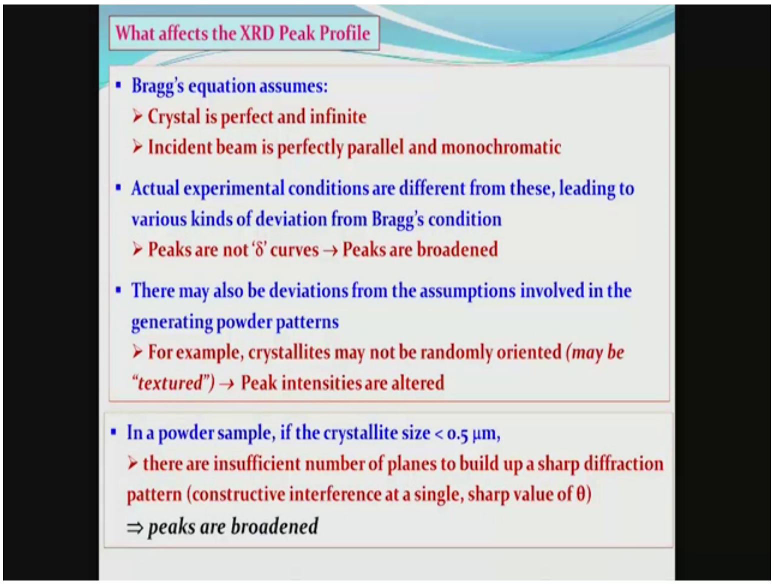

What affects the XRD Peak Profile

- Bragg's equation assumes:
  - Crystal is perfect and infinite
  - Incident beam is perfectly parallel and monochromatic
- Actual experimental conditions are different from these, leading to various kinds of deviation from Bragg's condition
  - Peaks are not 'δ' curves → Peaks are broadened
- There may also be deviations from the assumptions involved in the generating powder patterns
  - For example, crystallites may not be randomly oriented *(may be "textured")* → Peak intensities are altered

- In a powder sample, if the crystallite size < 0.5 μm,
  - there are insufficient number of planes to build up a sharp diffraction pattern (constructive interference at a single, sharp value of θ)

  ⇒ *peaks are broadened*

Now, what really determines affects the XRD peak profile? As I said Braggs equation assumes; the derivation assumes that the crystal is perfect and infinite, and that the incident beam is perfectly parallel and monochromatic. The actual experimental conditions are usually different from these leading to various kinds of deviation from the Braggs condition.

So, peaks are a not delta curve that is peaks are not sharp as over here, indicated by the red lines over here, so peaks are not delta curves. Therefore, the peaks are broadened from these delta curves. There may also be deviations from the assumptions involved in generating the patterns for example, is assumed that all the crystals small crystals are comprised about a sample, have random orientations among them random crystallographic orientations among them in, so called texture samples this condition is not satisfied and therefore, Braggs conditions are not properly satisfied in these so, textured samples.

Now, in a powder sample if the average crystallite size will come to how to measure that later, if the average crystallized size is less than about half a micrometer, then it turns out that there are insufficient number of planes remember the diagram I showed you earlier of planes parallel planes in deriving the lobby deriving the Braggs condition. That number of planes is not sufficient to give a sharp value that is a peek at as single short value of theta. So, peaks are broadened.

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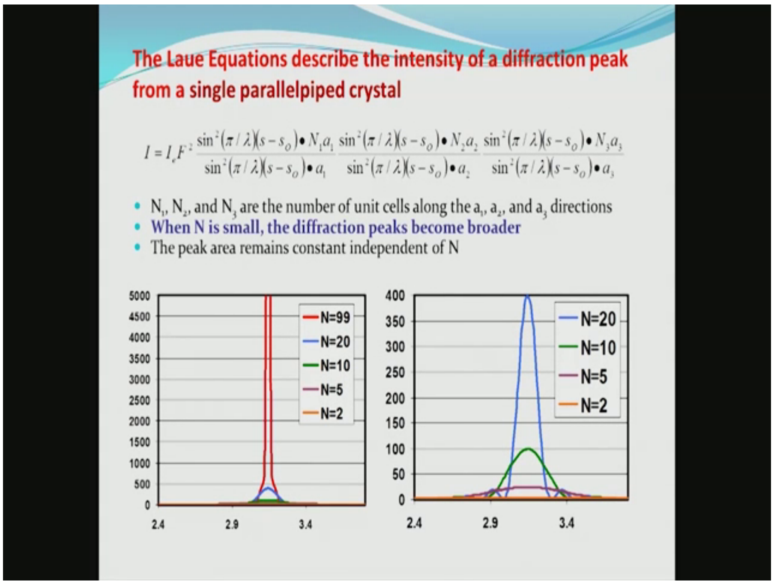

The Laue Equations describe the intensity of a diffraction peak from a single parallelpiped crystal

$$I = I_e F^2 \frac{\sin^2(\pi/\lambda)(s-s_o)\bullet N_1 a_1}{\sin^2(\pi/\lambda)(s-s_o)\bullet a_1} \frac{\sin^2(\pi/\lambda)(s-s_o)\bullet N_2 a_2}{\sin^2(\pi/\lambda)(s-s_o)\bullet a_2} \frac{\sin^2(\pi/\lambda)(s-s_o)\bullet N_3 a_3}{\sin^2(\pi/\lambda)(s-s_o)\bullet a_3}$$

- N_1, N_2, and N_3 are the number of unit cells along the a_1, a_2, and a_3 directions
- **When N is small, the diffraction peaks become broader**
- The peak area remains constant independent of N

Now, the Laue equations in x-ray diffraction describe the intensity of the diffraction peak as a function of the number of planes involved in the particular crystal. That is you take a three dimensional crystal, and if there are n one planes in one direction N 2 in the other and N 3 in the third one, then the intensity is now from this equation shown to be proportional to the product of N 1, N 2 and N 3, when n is small the diffraction peaks becomes peaks become broader, but the peak area remains independent of N, what is shown now is the simulation of how the intensity of the peaks varies with the number of planes N as in the above equation.

So, what you see here is that if N is equal to 5 for example, as shown in the graph then the peak is really very broad, when you come N comes to 99 for example, you get a much sharper peak. So, when N is infinite then this will become a sharp delta type delta function type line. So, the Laue equation predicts that one should have broader peaks if the number of plays involved in the diffraction is small.

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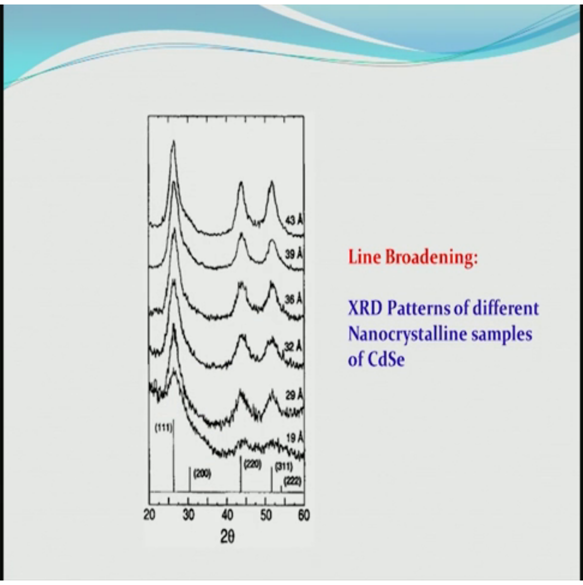

Line Broadening:

XRD Patterns of different Nanocrystalline samples of CdSe

Now, this is shown here this line broadening as it is called is shown here, in the case of cadmium selenide which is an important semiconductor actually quantum dots are made out of this as we described in a in an earlier session. So, when cadmium selenide is prepared with different average crystal sizes, as shown here this x-ray diffraction pattern becomes sharper and sharper, at the low end where the crystal size is only 19 angstroms are about 2 nanometers, then you can see that the peaks are very broad as the particle size or crystal size approaches 50 angstroms or 5 nanometers you can see that these peaks are becoming considerably sharper. So, this is an illustration of the broadening of x-ray diffraction peaks due to crystal size.

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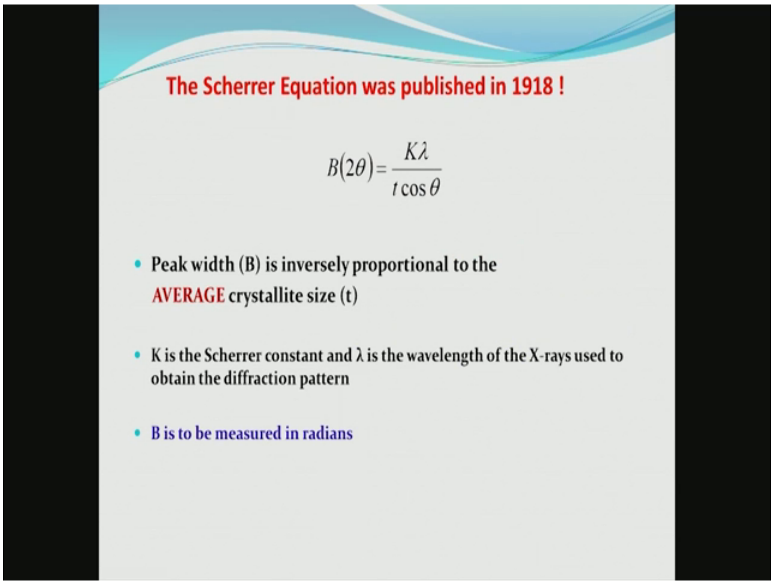

The Scherrer Equation was published in 1918 !

$$B(2\theta) = \frac{K\lambda}{t\cos\theta}$$

- Peak width (B) is inversely proportional to the AVERAGE crystallite size (t)
- K is the Scherrer constant and λ is the wavelength of the X-rays used to obtain the diffraction pattern
- B is to be measured in radians

Now, Paul Scherrer derived as long ago as 1918 a formula called is Scherrer formula which relates the width of the peak to the thickness or the size of the crystals, t is the size of the crystal. So, this is known as the Scherrer formula, B is the width of the peak K is a so called Scherrer constant, lambda is the x-ray wavelengths, and theta is the angle involved in x-ray diffraction from the pattern.

So if you know lambda which is the incident x-ray wavelength, if you know theta and the b that is the width of the peak, then you can measure t which is the size of the crystal that is represented by the x-ray diffraction pattern. So, what this shows is that the peak width b is inversely proportional to the average crystallite size let us remember that, when we use x-ray diffraction of a powder material a crystalline powder material, what we get is really the data for all the entire ensemble of the crystals in the powder, and therefore what we get through such a formula is the average crystallite size.

Now, K is the so called Scherrer constant which depends on the crystal symmetry, and will come to that shortly and it is important to note that B is to be measured in radians.

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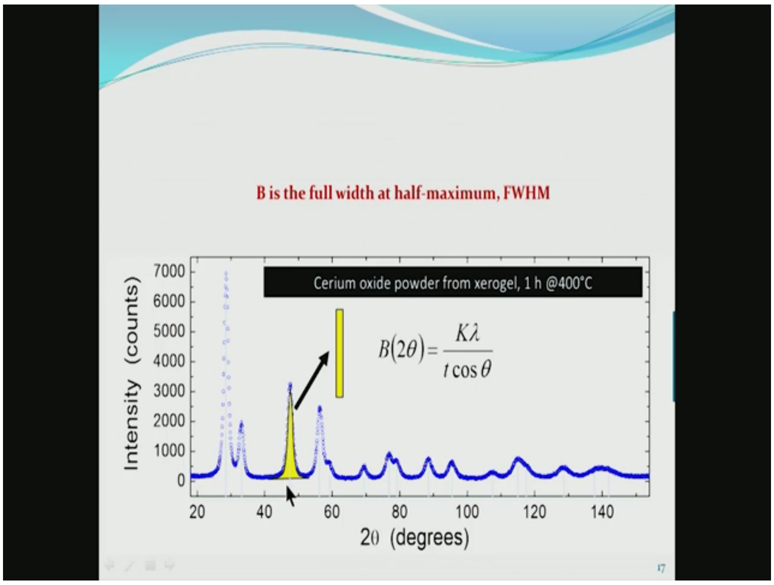

B is the full width at half-maximum, FWHM

$$B(2\theta) = \frac{K\lambda}{t\cos\theta}$$

Now, what is shown here is the x-ray diffraction pattern of cerium oxide, and as I said here see this is a peek over here that is now highlighted in the yellow in yellow. And we measure the peak width, and then full width at half maximum B is so called full width at half maximum. So, here is the peak width take half of that, at half maximum, then that is a full width at half maximum. So, that B is related to the thickness of the rather the size of the crystals t as I said just a while ago.

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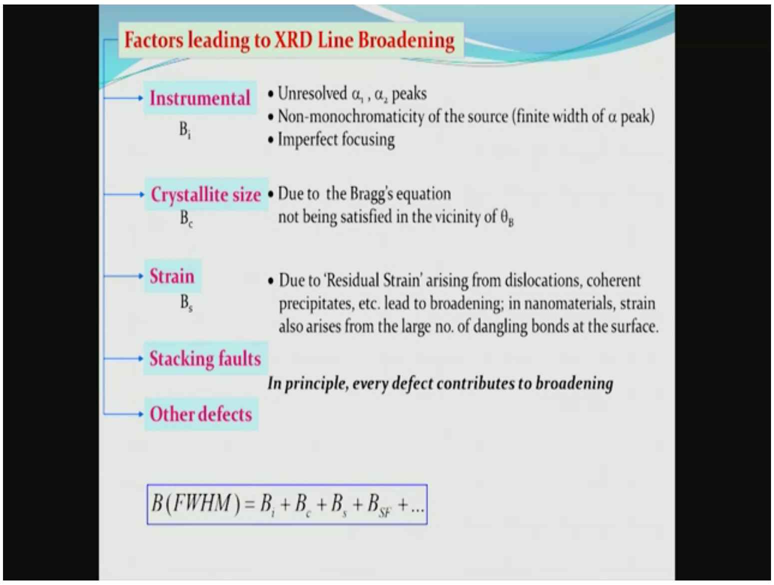

Factors leading to XRD Line Broadening

- Instrumental B_i
  - Unresolved α_1, α_2 peaks
  - Non-monochromaticity of the source (finite width of α peak)
  - Imperfect focusing
- Crystallite size B_c
  - Due to the Bragg's equation not being satisfied in the vicinity of θ_B
- Strain B_s
  - Due to 'Residual Strain' arising from dislocations, coherent precipitates, etc. lead to broadening; in nanomaterials, strain also arises from the large no. of dangling bonds at the surface.
- Stacking faults
- Other defects

In principle, every defect contributes to broadening

$$\boxed{B(FWHM) = B_i + B_c + B_s + B_{SF} + \ldots}$$

Now, it turns out that there are several factors leading to x-ray line broadening not just the size of the crystals, there is the so called instrumental broadening, which is due to unresolved K alpha 1 and K alpha 2 peaks, which is the incident x-ray radiation. If the radiation is not monochromatic perfectly monochromatic, then there is the so called instrumental broadening out of that.

And also factors like imperfect focusing of the x-ray beam on the sample. So, these are instrumental and one assumes that, one can eliminate these are minimize these things through experimental effort. Crystallite size this is due to the Bragg equation which I just described Bragg equation not being satisfied fully because of the small size the crystals that I just explained.

So there is a broadening B of c due to that B of I due to the instrument, and we assume that B of I can be reduced to 0. In addition there is a broadening due to strain in the crystals, this is due to so called residual strain that arises from dislocations coherent precipitates etcetera lead leading to broadening, and in nanomaterials especially strain also arises from the large number of dangling bonds at the surface. Remember in nanomaterials as we learned in an earlier class the surface area is very large and therefore, really you have a large number of dangling bonds at the surface, which means that there is a strain in the material due to in completion of these bonds therefore, there is a contribution B of s to the x-ray line broadening because of the strain.

Stacking faults and other defects it turns out that you can say that in principle every defect contributes to broadening. So, in the end the full width at half maximum of an x-ray diffraction peak B is some of broadening due to instrumental effects broadening due to crystallite size, due to strain, and stacking faults and so on. So, the measured width of the x-ray diffraction peak has a contribution from each of these.

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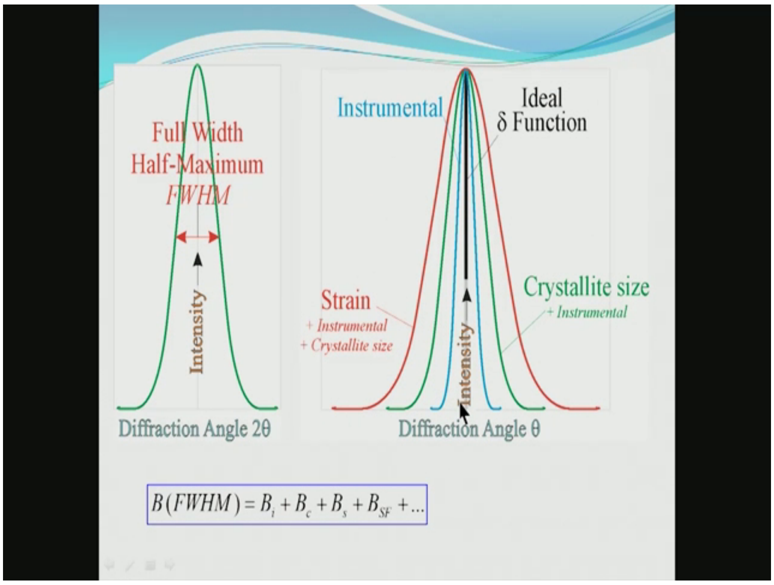

$$B(FWHM) = B_i + B_c + B_s + B_{SF} + \ldots$$

Now, let us look at this FWHM actually shown over here, and what we see is that it is a sum of broadening due to crystallite size, due to instrumental factors, and due to strain and if none of this was present, then you would get this black line over here which is an ideal debt of a delta function therefore, the full width at half maximum B is the sum of contributions from these various factors that we just mentioned.

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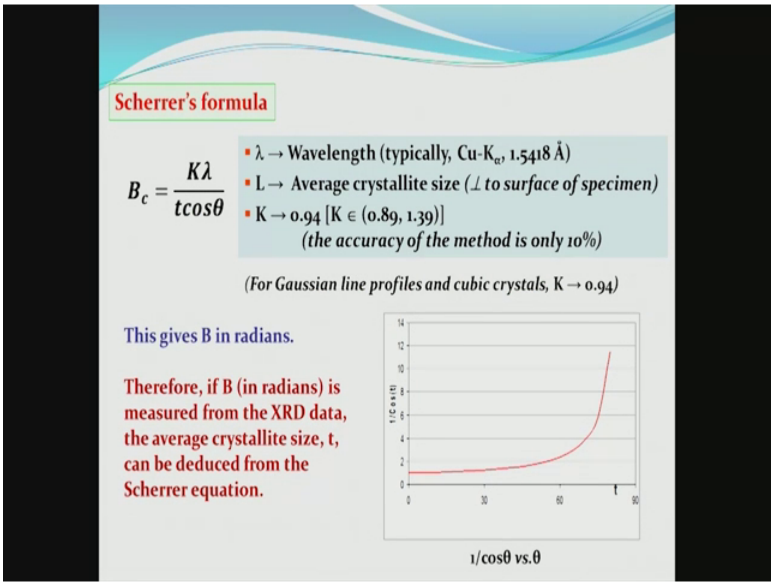

Scherrer's formula

$$B_c = \frac{K\lambda}{t\cos\theta}$$

- λ → Wavelength (typically, Cu-K_α, 1.5418 Å)
- L → Average crystallite size (⊥ to surface of specimen)
- K → 0.94 [K ∈ (0.89, 1.39)]
  (the accuracy of the method is only 10%)

(For Gaussian line profiles and cubic crystals, K → 0.94)

This gives B in radians.

Therefore, if B (in radians) is measured from the XRD data, the average crystallite size, t, can be deduced from the Scherrer equation.

Now, coming back to Scherrer's formula what it describes is B of c which is due to crystallite size B of c is equal to K lambda over t cos theta, where K is a Scherrer's constant, and its value is equal to 0.94 for cubic materials, it varies from 0.89 to 1.39, and it is to consider K to be equal to 1 approximately.

Now t is the average crystallite size, and lambda is the wavelength. Now what is shown in this graph look at this equation again B of c is proportional to 1 over cosine theta therefore, if we plot one over cosine theta over verses theta, you see this sharp increase as theta approaches 90. And therefore, in general we should be in this region where theta is relatively small and there is no sharp increase in theta 1 over cosine theta as shown here.

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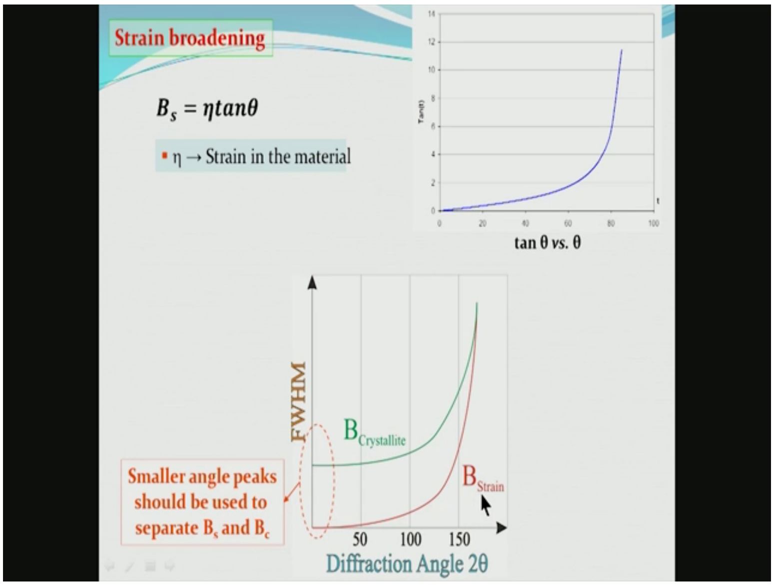

Strain broadening

$B_s = \eta tan\theta$

- η → Strain in the material

Smaller angle peaks should be used to separate B_s and B_c

Now, it can be shown that the broadening due to strain can be is given by B of s equal to eta tan theta where eta is strain in the material. Again we show here a graph of tan theta versus theta to see how this B s varies with theta, and you can see that as tan theta as theta approaches 90 tan theta goes to infinity there is a sharp increase in tan theta over here.

Now what we what is shown here is a variation of the FWHM as a function of theta. This brown graph shows the variation of the B due to strain, and the green graph shows the variation of B that is due to crystallite size with respect to theta, and one can see that at small angles at small angle small values of 2 theta there is a significant separation of B c and B s. And therefore, one should use low angle x-ray diffraction peaks to separate the contribution for from crystallite size and from strain effects.

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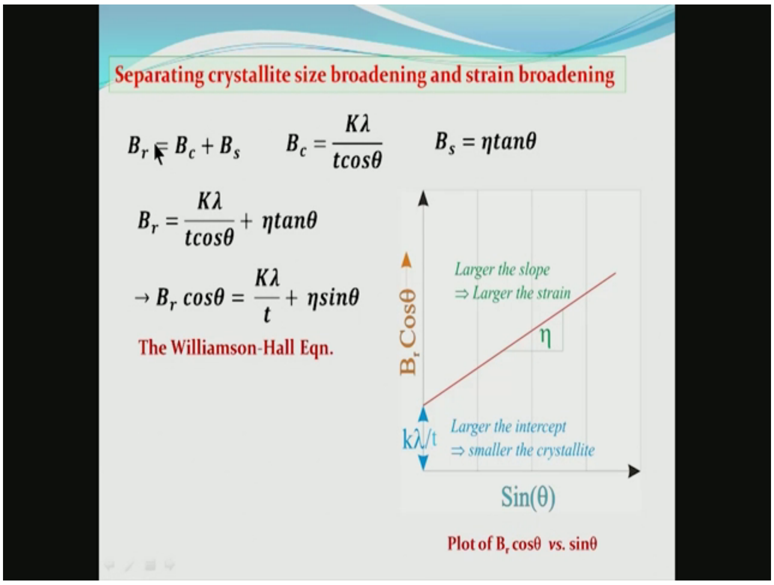

Separating crystallite size broadening and strain broadening

$B_r = B_c + B_s$ $B_c = \frac{K\lambda}{t\cos\theta}$ $B_s = \eta\tan\theta$

$$B_r = \frac{K\lambda}{t\cos\theta} + \eta\tan\theta$$

$$\rightarrow B_r\cos\theta = \frac{K\lambda}{t} + \eta\sin\theta$$

The Williamson-Hall Eqn.

Plot of $B_r \cos\theta$ vs. $\sin\theta$

Now, how do we actually separate crystallite size broadening from strain broadening, now remember the total broadening used to due to is the sum of crystallite broadening and strain broadening. So, B r is equal to B c plus B s, B c is equal to K lambda by t cosine theta, B s is equal to eta tan theta as we have seen before.

Therefore, B r is given by a sum of these two terms. And you can rewrite it in this form as B r into cosine theta is equal to K lambda by t plus eta sin theta this is known as the Williamson hall equation. So, if one plots B r cosine theta B r being the measured full width at half maximum, which is the sum of B c and B s.

So, if one plots B r that is the total width of the peak, cosine theta versus sin theta, then what one gets from the slope of a line, you will get a straight line and the slope of the line gives us the strain in the material, and the intercept gives us the K lambda by t from which one can derive the value of t which is the average crystallite size, so the larger the intercept this smaller the crystallite size.

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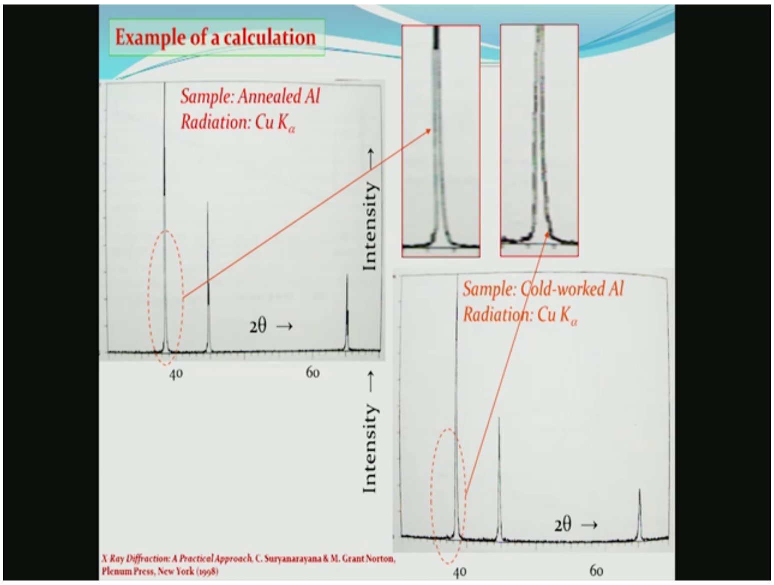

Example of a calculation

X Ray Diffraction: A Practical Approach, C. Suryanarayana & M. Grant Norton, Plenum Press, New York (1998)

So, we show here examples of an actual set of samples, so here is an annealed sample of aluminum, and here is a so called cold worked sample of aluminum. You can see that the peak width that is the width of peaks corresponding peaks is greater in the case of the cold worth aluminum sample, than in the case of an annealed aluminum sample annealing usually removes defects.

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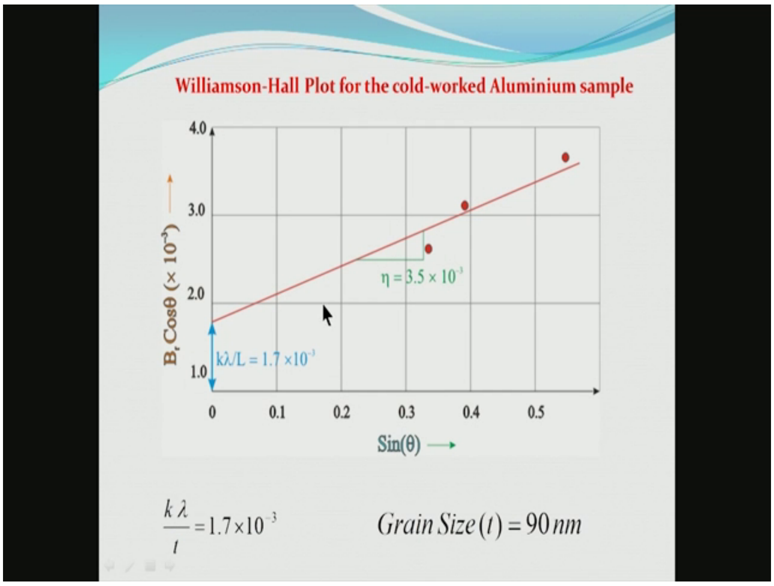

Williamson-Hall Plot for the cold-worked Aluminium sample

$$\frac{k\lambda}{t} = 1.7 \times 10^{-3} \qquad Grain\ Size\,(t) = 90\,nm$$

So, using this data a graph has been plotted, with this is the Williamson hall plot for the cold worked aluminum sample, and this is B r cosine theta verses sin theta, and as I said there is an interceptor over here, the intercept is related to the size of the crystals. It is actually t not L, I am sorry for the mistake in the graph here it is actually t.

So, t gives us the average crystallite size and from this graph one can derive that the grain size of the average crystallite size is 90 nanometers. Now it is also it is important having learned how to calculate how to experimentally determine the average crystallite size remember it is an average.

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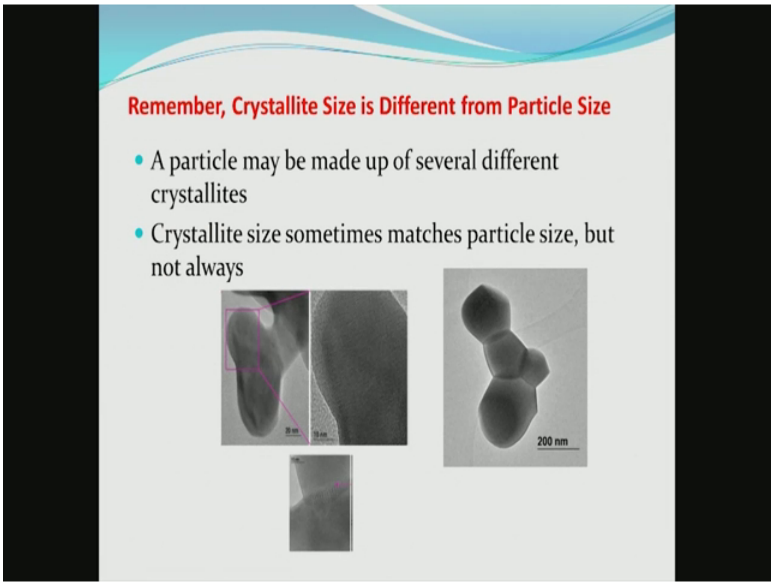

Remember, Crystallite Size is Different from Particle Size

- A particle may be made up of several different crystallites
- Crystallite size sometimes matches particle size, but not always

It is important to remember in the context that crystallite size is different from particle size, because particles can be formed by the agglomeration of crystallites. Therefore, electron microscopy can help us what are shown here, as our transmission electron microscopy images showing how crystals or particles are formed through crystals agglomerating with one another.

And therefore, it is important to make sure that what we get in the end is the average crystallite size, and not the particle size. And electron microscopy is often useful in making sure that what we get is the crystallite size and not the particle size due to agglomeration.

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Crystallite Size Distribution

- Is the crystallite size narrowly or broadly distributed?
- Is the crystallite size unimodal (monodisperse)? or multimodal (polydisperse)?
- XRD is poorly designed to facilitate the analysis of crystallites with a broad or multimodal size distribution
- Electron Microscopy is generally needed to examine size distribution - SEM and TEM

Another factor is crystallite size distribution. Is the size distribution narrow or is it broad, easy christ size distribution unimodal or monodisperse or is it multimodal or polydisperse. Now it turns out that while it is possible to use the profile shape of XRD peaks to get some information on size distribution of particles in XRD sample, it turns out that XRD is poorly designed to facilitate the analysis of crystallites, with a broad or a multi modal size distribution. Electron microscopy is generally needed to examine size distribution,; namely SEM scanning electron microscopy and transmission electron microscopy.

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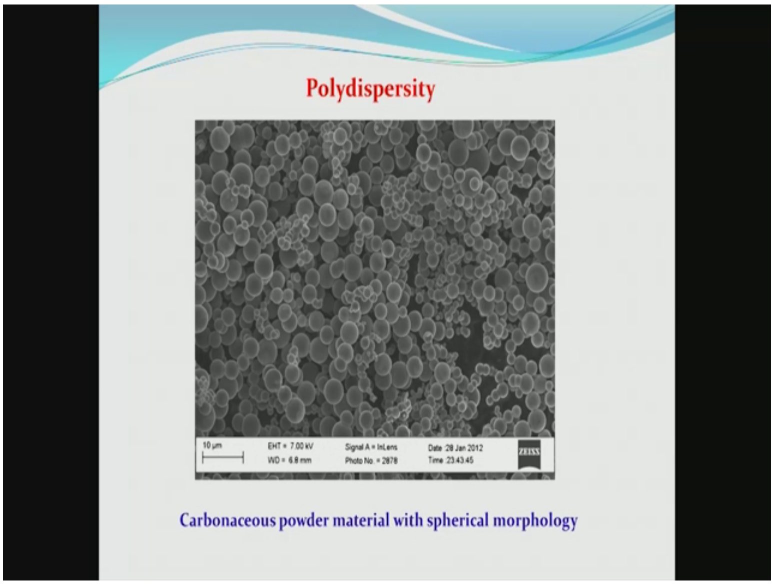

Polydispersity

Carbonaceous powder material with spherical morphology

Now, let us look at an image of a polydisperse sample, these are not crystals these are actually spheres prepared by a certain CVD process, but what I want to do note is that there is a considerable distribution in the size of these spheres. So, this indicates polydispersity there is a considerable distribution in the sizes.

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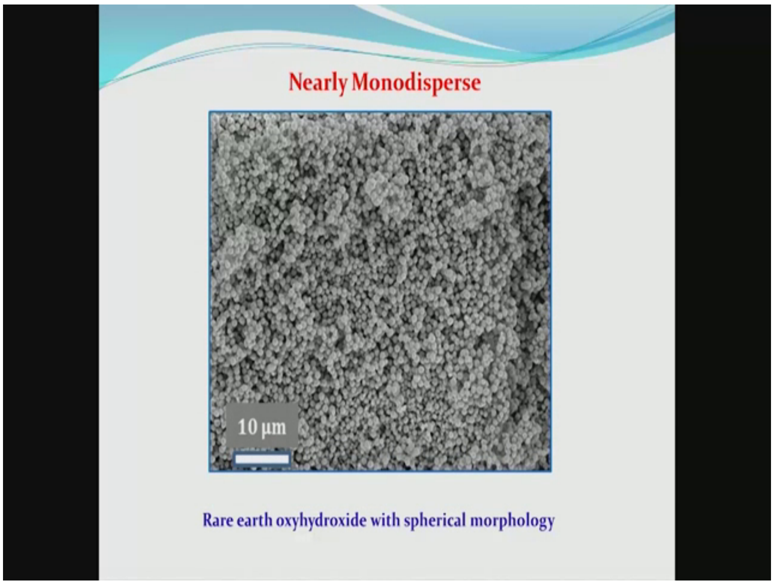

Nearly Monodisperse

Rare earth oxyhydroxide with spherical morphology

Contrast that with a nearly monodisperse sample it turns out that this is a rare earth hydroxide with a spherical morphology, and what you can see here is that there is a relatively narrow distribution of the diameter of these diameters of these spheres. So, you have a nearly monodisperse sample. So, I want simply to point out that it is necessary often to result to electron microscopy to ensure that what you have is mono dispersity a polydispersity.

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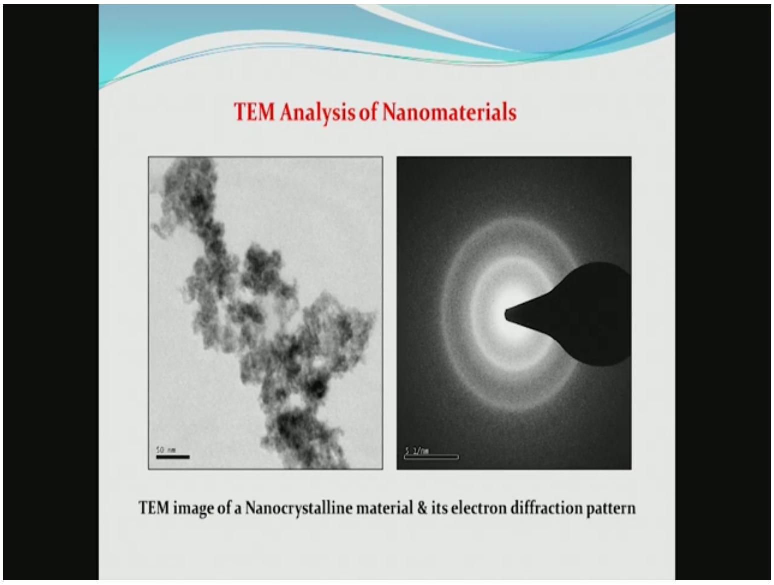

TEM Analysis of Nanomaterials

TEM image of a Nanocrystalline material & its electron diffraction pattern

These TEM analyses have a very small size that is of a sample where the crystallite size is very small, and the electron diffraction pattern indicates that what you have is really is a poorly crystalline sample. As you can see from the transmission electron image of this sample, you can see that the average size now this is in the range of a few nanometers.

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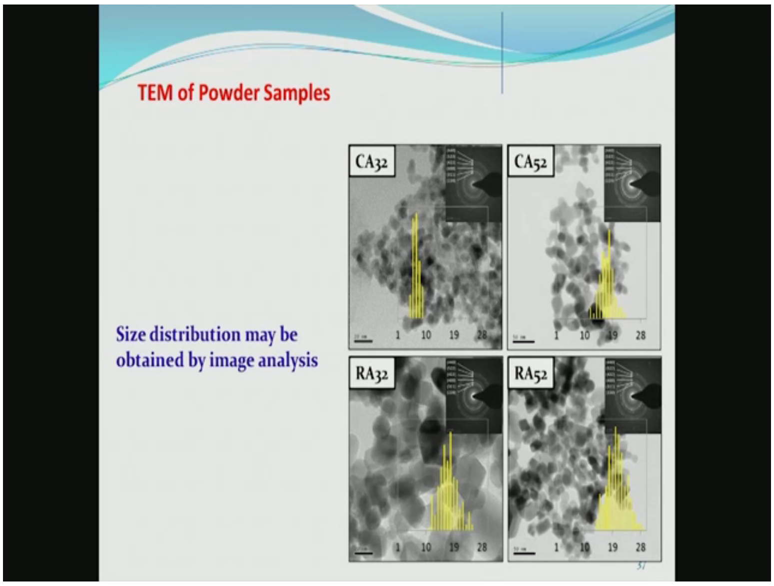

TEM of Powder Samples

Size distribution may be obtained by image analysis

Now, it is possible to use transmission electron microscopy, obtaining images of these particles and using image analysis one can determine the size distribution. So, in this case what is shown here in each case is by counting the number of crystals different sizes one can plot histograms are shown here, to show whether it is a relatively narrow distribution here, as in this graph or relatively broad distribution as over here. So, electron microscopy is often necessary to make sure that one has a proper distribution one can discern describe the distribution properly.

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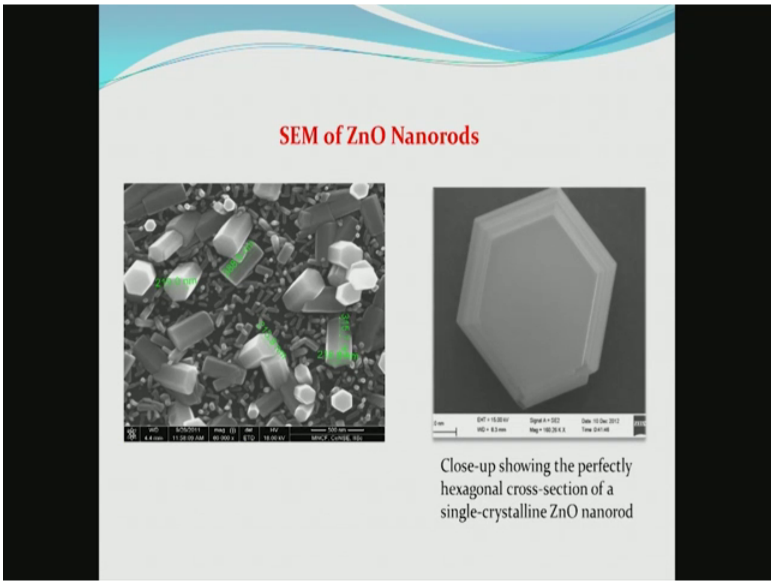

SEM of ZnO Nanorods

Close-up showing the perfectly hexagonal cross-section of a single-crystalline ZnO nanorod

As I mentioned earlier the shape of the crystals is also important, that is a part of the characterization what I what I shown here or nanorods of zinc oxide. And one can see here over here these are nanorods, and this is the front view of a nanorod, you can see that they have hexagonal cross sections characteristic of the crystal structure of the (Refer Time: 25:05) site phase of zinc oxide.

Now this is a close up of a nanorod over here, one of these over here and what you can see is the perfect hexagonal shape of the crystal in the car in cross section. So, this illustrates that one can have very perfect morphologies or very perfect faceting of nanocrystals.

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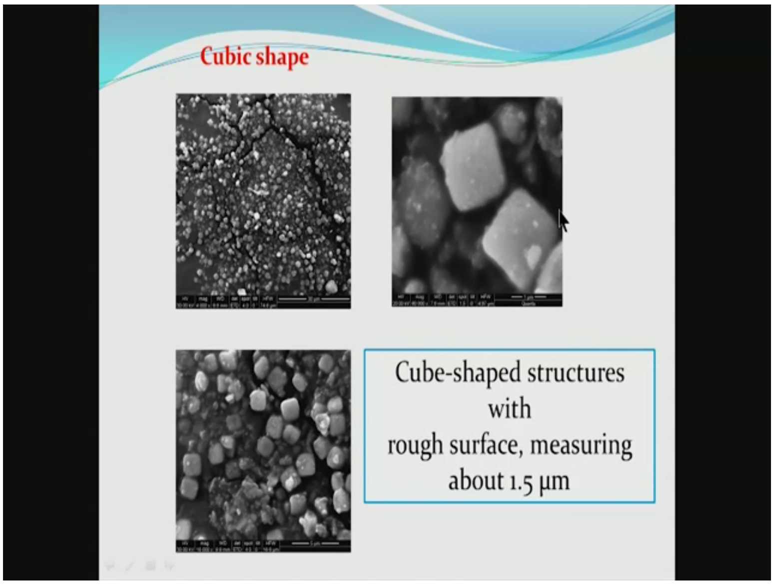

Cubic shape

Cube-shaped structures with rough surface, measuring about 1.5 μm

What are shown here are cubes; nano cubes, you can see that is a sharp distinction from that one so, you can you really see that the crystal symmetry of the underlying material which is actually a rare earth oxide. The crystal symmetry of a cubic rare earth oxide not reflected perfectly well in the nanocrystals of the material grown under certain conditions.

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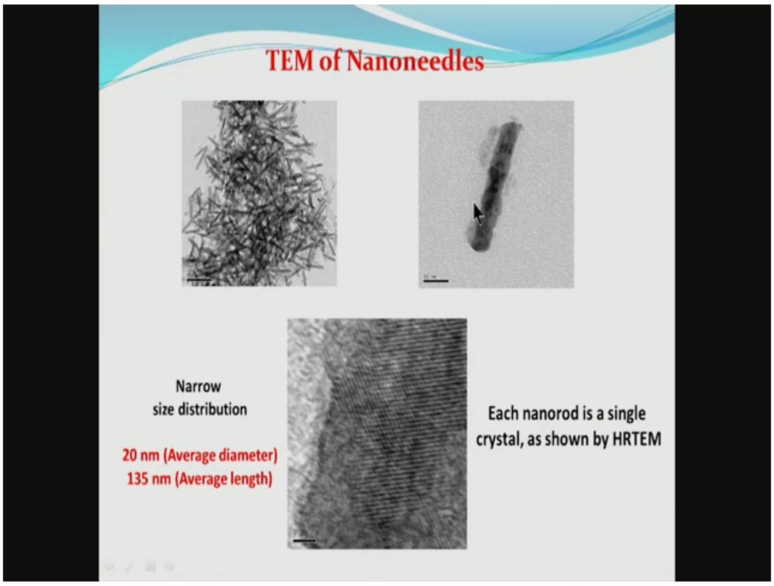

TEM of Nanoneedles

Narrow size distribution

20 nm (Average diameter)
135 nm (Average length)

Each nanorod is a single crystal, as shown by HRTEM

In contrast with the hexagonal and the cubic shapes one can have nano needles. So, these are TEM images of some needles prepared by a solution process, and you can see that these are extremely tiny needles essentially the aspect ratio is very high. So, they are very thin in diameter small in diameter and pretty long, and it turns out that there is a narrow distribution is a fairly monodisperse size of these things. 20 nanometers is the average diameter 135 nanometers is the average length and each of these as shown by this high resolution TEM image over here, each one of these is a single crystal.

So, these three these different shapes illustrate that electron microscopy is important in understanding the you know in examining and understanding the shape of these crystals, which is very again very important one of the ways of characterizing nanomaterials.

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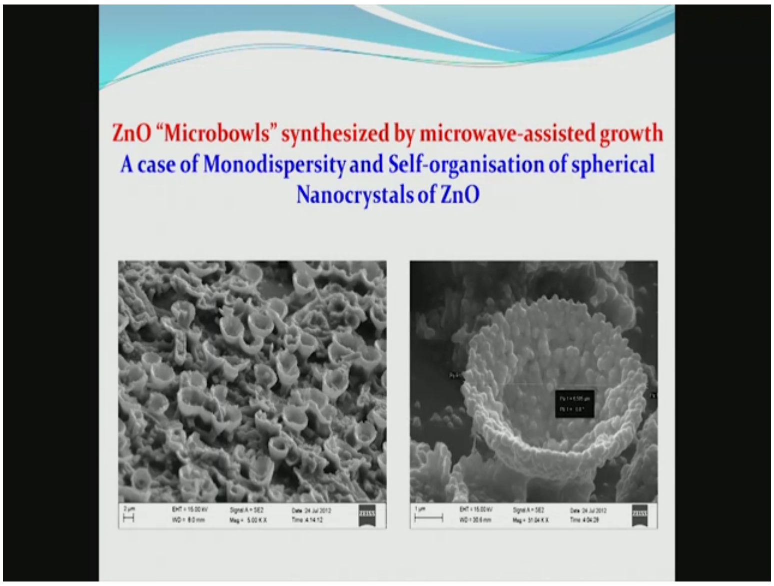

ZnO “Microbowls” synthesized by microwave-assisted growth
A case of Monodispersity and Self-organisation of spherical Nanocrystals of ZnO

We come back to zinc oxide here, what are shown here also called zinc oxide nano bowls synthesized by a assisted growth process that we have described in an earlier session. And you can see that you really have small tiny bowls made of zinc oxide, upon close examination what we can; one can see is that, each one of these is made of spherical nanocrystals there is a so called self organization of spherical nanocrystals of zinc oxide into these micro bowls.

So, that is known as orient and aggregation which we have no time to go into, but it done what can see here is that, electron microscopy is very important in describing the shape and size and face sitting in crystalline materials on the nano scale.

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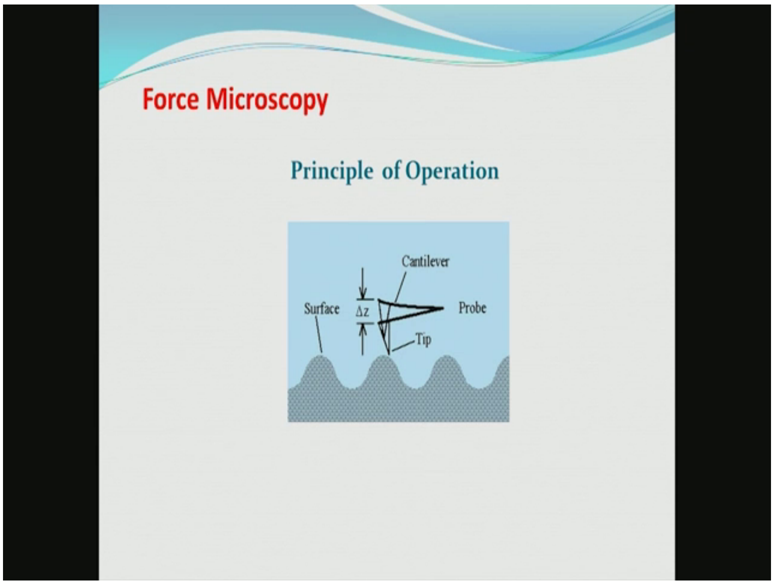

Force Microscopy

Principle of Operation

Now, we come to force microscopy. Force microscopy as described by atomic force microscopy AFM you are probably familiar with AFM as a technique, now what is the principle of operation of this.

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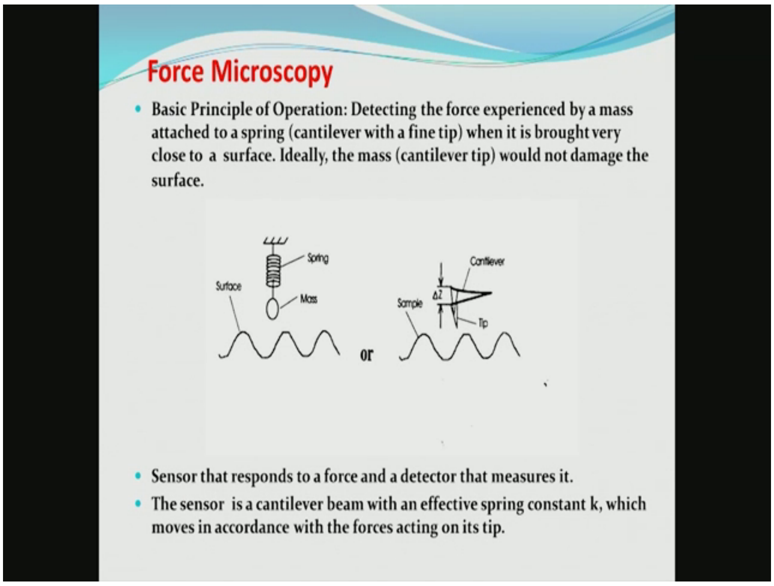

Force Microscopy

- Basic Principle of Operation: Detecting the force experienced by a mass attached to a spring (cantilever with a fine tip) when it is brought very close to a surface. Ideally, the mass (cantilever tip) would not damage the surface.

- Sensor that responds to a force and a detector that measures it.
- The sensor is a cantilever beam with an effective spring constant k, which moves in accordance with the forces acting on its tip.

The basic principle is detection of the force experienced by a mass attached to a spring that is a cantilever with a fine tip, when it is brought very close to a surface. Ideally the mass would not damage the surface when it is brought very close to it. So, these are cartoons that show, so we can describe this mass as attached to a spring and this cantilever which is now representing this mass attached to a spring is now brought very close to an undulating surface over here.

Now, consider this as a sensor this sensor responds to a force; that is the force, that it experience when it comes close to the surface will come to that shortly, and a detector that measures this force. The sensor is a cantilever with an effective spring constant k and this sensor moves in accordance with the forces acting on the tip of this cantilever.

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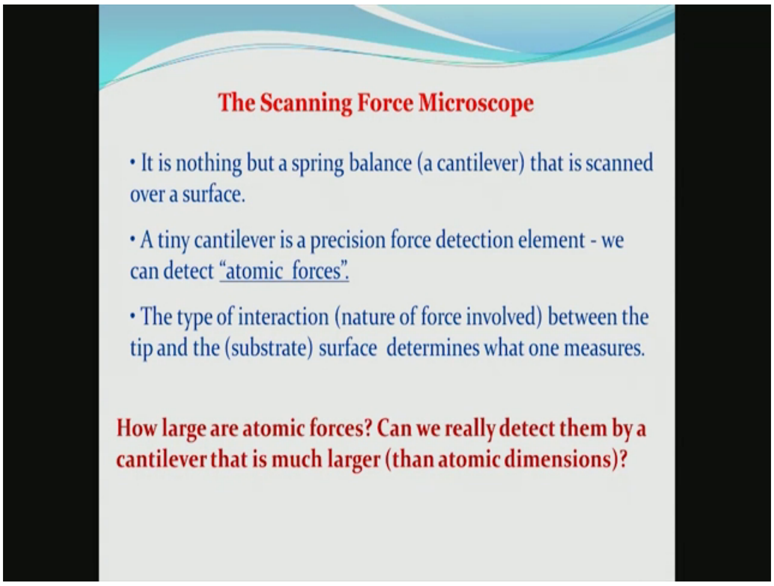

The Scanning Force Microscope

- It is nothing but a spring balance (a cantilever) that is scanned over a surface.
- A tiny cantilever is a precision force detection element - we can detect "atomic forces".
- The type of interaction (nature of force involved) between the tip and the (substrate) surface determines what one measures.

How large are atomic forces? Can we really detect them by a cantilever that is much larger (than atomic dimensions)?

So, the scanning force microscope is nothing but a spring balance or a cantilever that is scanned over a surface. A tiny cantilever is a precision force detection element, and we one can detect with them atomic forces, the type of the interaction that is the nature of the force involved between the tip and the surface over which it is scanned, the type of the interaction involved between the tip and the substrate or the surface determines what when one measures as we shall see shortly. How large are atomic forces, can we really detect them by a cantilever that is much larger, than atomic dimensions let us examine that.

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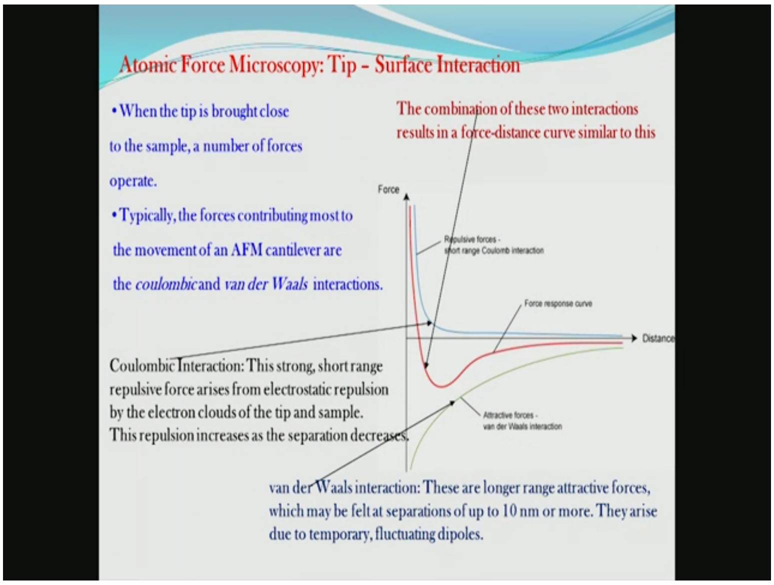

Atomic Force Microscopy: Tip – Surface Interaction

- When the tip is brought close to the sample, a number of forces operate.
- Typically, the forces contributing most to the movement of an AFM cantilever are the *coulombic* and *van der Waals* interactions.

The combination of these two interactions results in a force-distance curve similar to this

Coulombic Interaction: This strong, short range repulsive force arises from electrostatic repulsion by the electron clouds of the tip and sample. This repulsion increases as the separation decreases.

van der Waals interaction: These are longer range attractive forces, which may be felt at separations of up to 10 nm or more. They arise due to temporary, fluctuating dipoles.

Now, when you bring it find tip close your surface as we have just discussed, what one must consider is the so called tip surface interaction. A number of forces operate when such a tip is brought very close to a surface, most importantly the forces that contribute to the movement of this cantilever that affect this cantilever or coulombic forces and van der Waals interactions.

Now, coulombic interaction as you shown here in this what is shown here is the force versus distance that is the separation between the tip and the surface. So, this blue curve over here shows that the show force is repulsive, and increases sharply when the separation is small. So, this is the columbic repulsion it is a short range interaction and the repulsive force arises from the repulsion between the electron clouds, within the tip, and within the sample surface or the sample surface.

This separation increases rep this repulsion force increases rapidly when the separation is reduced, this green curve here shows is represents an attractive force it is a van dar Waals interaction, these are longer range attractive forces, as you can see from the graph it ranges up to about 10 nanometers or so, and this is due to the attraction between temporary fluctuating dipoles that are in the tip and in the sample.

So, when these columbic and van der Waals forces summed what you get is the resultant force that is shown in red over here, this resultant force which is attractive except when the separation is very small when it becomes repulsive.

So the combination of these two interactions results in the force distance curve that is shown here, so this is a force distance curve force separation curve. So, this is the kind of force separation curve that is involved in a cantilever tip being brought close to a surface as in an atomic force microscope.

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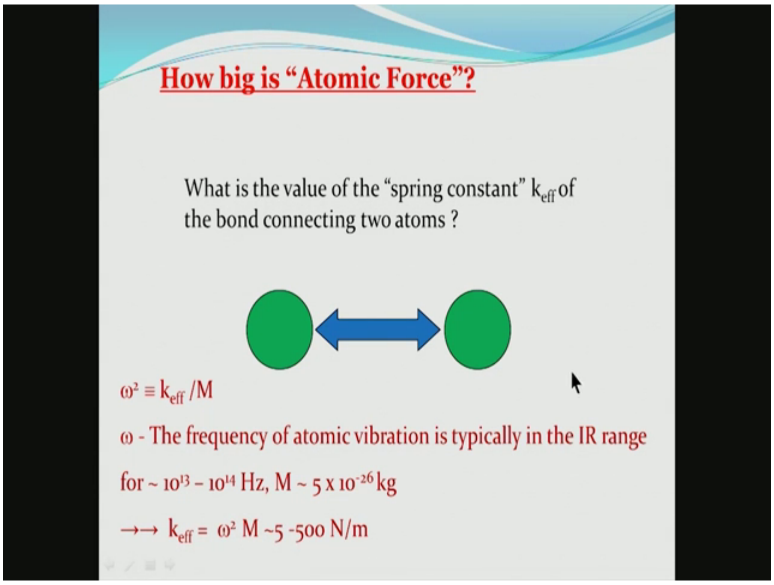

How big is "Atomic Force"?

What is the value of the "spring constant" k_{eff} of the bond connecting two atoms ?

$\omega^2 \equiv k_{eff}/M$

ω - The frequency of atomic vibration is typically in the IR range

for ~ $10^{13} - 10^{14}$ Hz, M ~ 5×10^{-26} kg

→→ $k_{eff} = \omega^2 M$ ~5 -500 N/m

Now, how big is the atomic force what are the numbers, what is the value of the spring constant k of the bond that connects two atoms, there is a bond that connects two atoms this the atomic bonds and we know atoms vibrate, and therefore we know that there is a spring like behavior that results from this atomic binding.

Now, it turns out that the frequency of atomic vibration, as measured by spectroscopy is in the infrared range that is of the order of 10 to the power 13 to 10 to the power of 14 hertz. And the mass of atoms can be taken to be about 5 into 10 to the minus 26 kilograms therefore, from the equation omega square is equal to k divided by M which is the ordinary simple harmonic motion equation, then we can deduce that the k, k effective for the atomic bond is of the order of 5 to 500 Newton's per meter depending on the actual frequency, omega can be different and therefore, there is a range of values for k which is 5 to 500 nano Newton's per meter.

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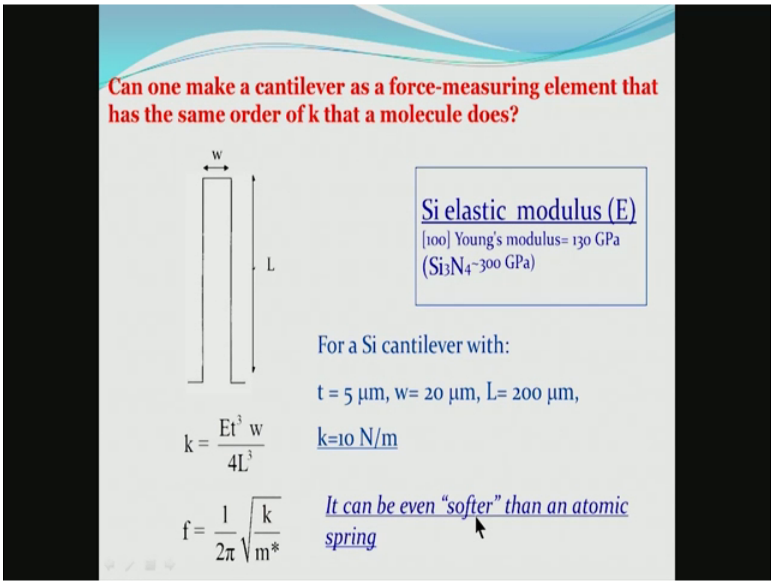

Can one make a cantilever as a force-measuring element that has the same order of k that a molecule does?

$$k = \frac{Et^3 w}{4L^3}$$

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}}$$

Si elastic modulus (E)
[100] Young's modulus= 130 GPa
(Si_3N_4~300 GPa)

For a Si cantilever with:

t = 5 µm, w= 20 µm, L= 200 µm,

k=10 N/m

It can be even "softer" than an atomic spring

Now, can one make a cantilever as a force measuring element that are the same order of k as in the as a molecule does, as then atom as two atoms do. As we have seen just now it is between 5 and 509 Newton's per meter can we make a cantilever with a spring constant of that magnitude. Now, what are shown here are standard results from the calculation of vibrating frequency of cantilevers, and if you have a cantilever whose length is L width is W and thickness is t then k value is given by this well known equation where e is the Young's modulus.

So, let us consider silicon; silicon, has a Young's modulus of 130 GP a, when we consider the 100 plane, which is common in semiconductor fabrication silicon nitride has a greater Young's modulus 300 GP a. Now suppose we had a silicon cantilever with a thickness of 5 micrometers width of 20 micrometers and length of 200 micrometers, then from this formula we can deduce that k is 10 Newton's per meter, well within the range of values actually at the lower end of the range of values which you have just derived for the spring constant of the bond between two atoms.

So, it turns out that by making a cantilever that is sufficiently small with a material that is with a material like silicon, then we can have spring constants that are capable of measuring atomic forces. So, it turns out that these kinds of cantilevers can even be softer, so to speak with a smaller value of k than atomic than an atomic spring.

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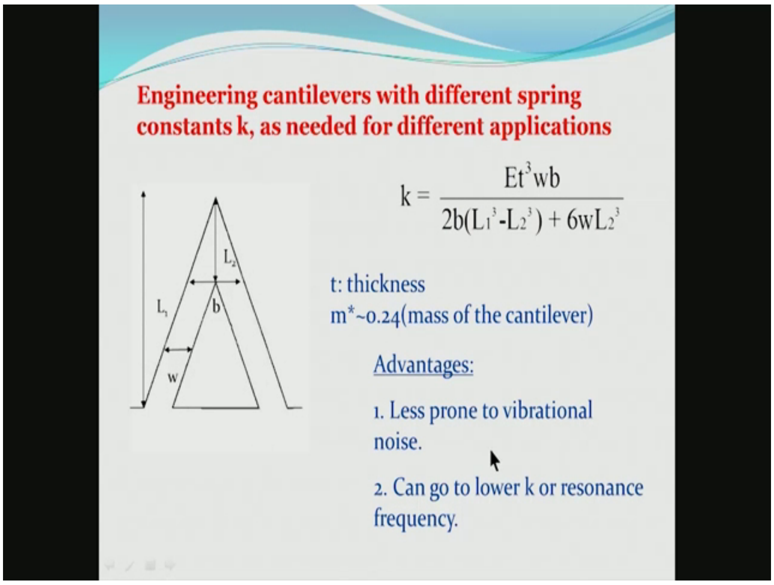

Engineering cantilevers with different spring constants k, as needed for different applications

$$k = \frac{Et^3wb}{2b(L_1^3 - L_2^3) + 6wL_2^3}$$

t: thickness

$m^* \sim 0.24$(mass of the cantilever)

Advantages:

1. Less prone to vibrational noise.
2. Can go to lower k or resonance frequency.

Now, it is possible to engineer cantilevers with the different spring constants needed for different applications, now that is because the shape and the exact details size of these cantilevers can be engineered what is shown here is the engineering of a tip of this shape over here over here, as shown here triangular tip. And the k of this is given by this formula where w b and t have usual meanings, that are shown over here and t is the thickness of this one, and m star that is in this formula over here is the rather the m star of this is 0.24 times the mass of the cantilever.

Now, the advantages of having a shape like this is that it is less prone to vibrational noise, and get can go to lower k or resonance frequency, then the rectangular cantilever that we encountered earlier.

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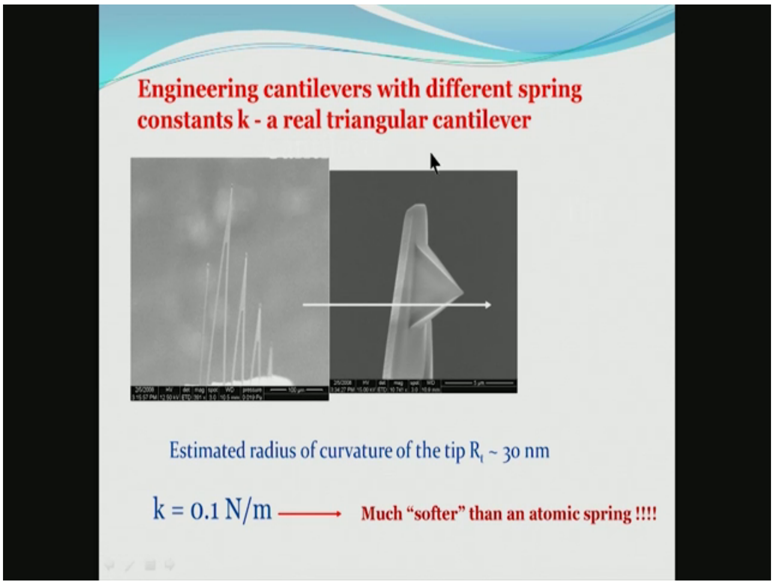

Engineering cantilevers with different spring constants k - a real triangular cantilever

Estimated radius of curvature of the tip $R_t \sim 30$ nm

$k = 0.1$ N/m ⟶ **Much "softer" than an atomic spring !!!!**

So, you can look at these shapes over here that are produced by fine lithography, you can see these very sharp tips or of radius approximately 30 nanometers at this edge. And it turns out that the k of such a tip can be as little as 0.1 and Newton's per meter, which is much softer than in that of the atomic spring. So, one can see that by engineering the shape of these cantilevers it is possible to measure extremely small forces. So, the cantilever is the key.

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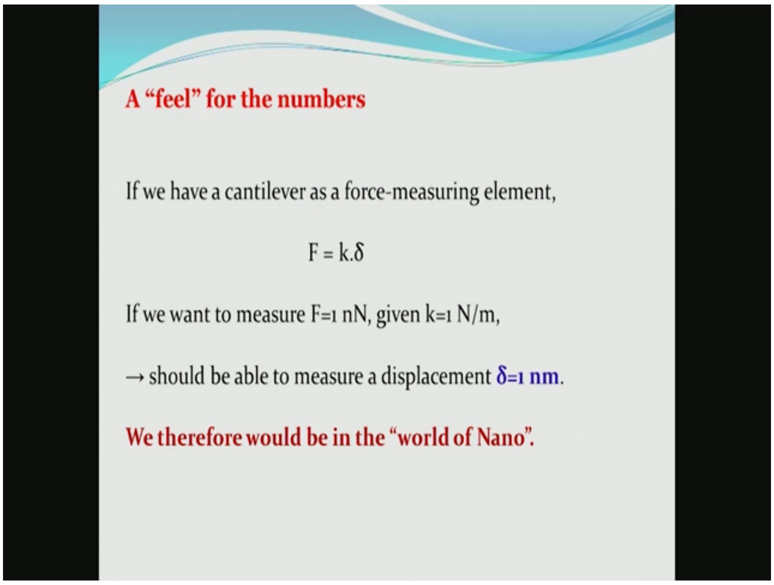

A "feel" for the numbers

If we have a cantilever as a force-measuring element,

$$F = k.\delta$$

If we want to measure F=1 nN, given k=1 N/m,

→ should be able to measure a displacement **δ=1 nm**.

We therefore would be in the "world of Nano".

So, let us get a feel for the numbers, if we have a cantilever as a force measuring element then F is equal to k into delta, force is equal to spring constant multiplied by the displacement, so this is just this simple harmonic relationship, this is a simple harmonic vibrator.

Now if we want to measure a force of 1 nano Newton and if you have a cantilever with k is equal to 1 Newton per meter, then from this equation we can easily see that we should be able to measure a displacement of delta of one nanometer; that means that we are in the world of nano. So, what this set of simple calculations show is that it is possible to make springs of very fine spring constant very small spring constant capable of measuring atomic forces, and displacements that are again in the nanometer range of interest in nano materials and structures.

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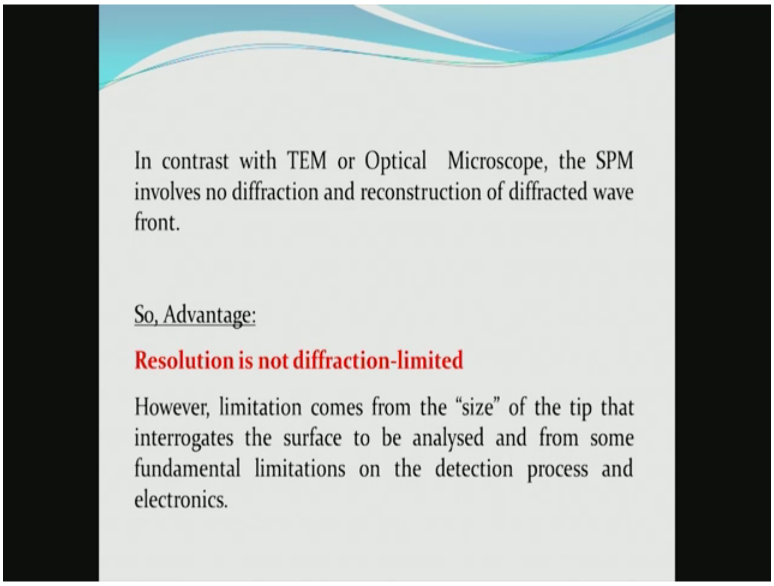

In contrast with TEM or Optical Microscope, the SPM involves no diffraction and reconstruction of diffracted wave front.

So, Advantage:

Resolution is not diffraction-limited

However, limitation comes from the "size" of the tip that interrogates the surface to be analysed and from some fundamental limitations on the detection process and electronics.

Now, in contrast with transmission electron microscopy where electrons are used and therefore, the wavelength of electrons is important or optical microscopy where light is used again wavelength is important, scanning probe microscopy involves no diffraction a reconstruction or diffracted wave fronts.

Therefore, resolution is not diffraction limited as in the case of either transmission electron microscopy or optical microscopy; however, limitations come from that is limitations in scanning probe microscopy come from the size of the tip, that interrogates the surface, and from some fundamental limitations on the detection process and electronics namely electronic noise.

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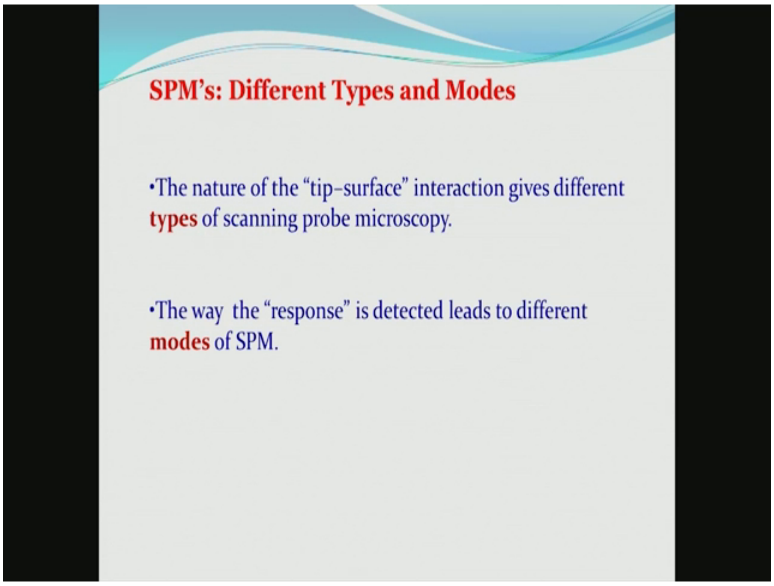

SPM's: Different Types and Modes

- The nature of the "tip-surface" interaction gives different **types** of scanning probe microscopy.
- The way the "response" is detected leads to different **modes** of SPM.

Now, if SPM's are scanning probe microscopes have different types and modes. The nature of the tip surface interaction gives us different types of scanning probe microscopy. The way the response is detected leads to different modes of SPM, so let us review these briefly.

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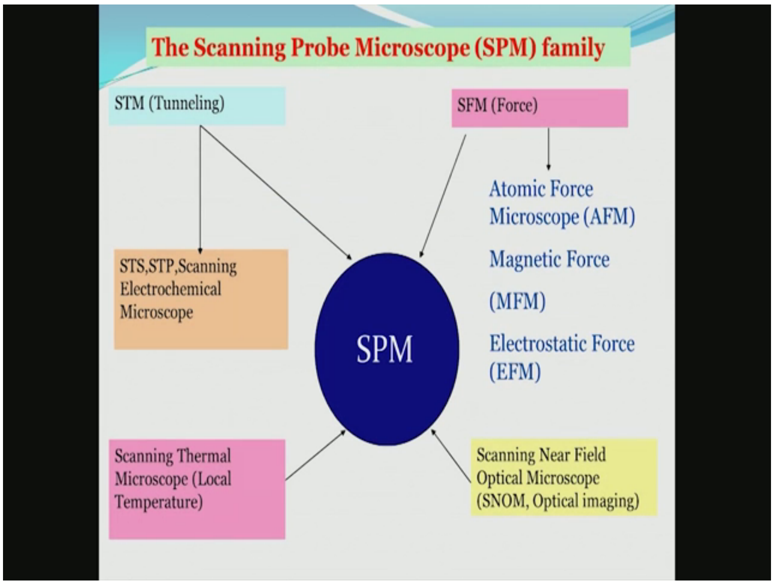

The Scanning Probe Microscope (SPM) family

STM (Tunneling)

STS,STP,Scanning Electrochemical Microscope

SFM (Force)

Atomic Force Microscope (AFM)

Magnetic Force (MFM)

Electrostatic Force (EFM)

SPM

Scanning Thermal Microscope (Local Temperature)

Scanning Near Field Optical Microscope (SNOM, Optical imaging)

So what is shown here is the range in the scanning probe microscope family, the original one scanning tunneling microscope from which actually eventually AFM was born. So, you have scanning tunneling microscope, you have electrochemical microscope which actually can make measurements of this kind in solution medium, scanning thermal microscope where imaging of temperature is done local temperatures done.

Most importantly the scanning force microscope, so it is your atomic form it can be the atomic force microscope, as we have just seen it can be a magnetic force microscope, if one can detect the magnetic interactions at the surface for example, or it can be electrostatic force microscopy AFM or in a different sense scanning near field optical microscope or SNOM for optical imaging.

So, what in other words scanning probe microscopy is a very versatile technique, if one is considering force microscopy, then these are the varieties over here as shown here, another one is PSO electric force microscope or PFM that is not shown here. So, force microscopy has varieties, and it is capable of measuring forces on every fine scale on the surface of a sample. Now one important aspect or one common factor in all these surface probe microscope or scanning probe microscopes is that they interrogate the surface. So, the information you get is of the surface of a material not the interior, but in nanomaterials as we have learned surface is very important. And therefore, in examining nanomaterial structures atomic force microscopy for example, is an extremely useful technique.

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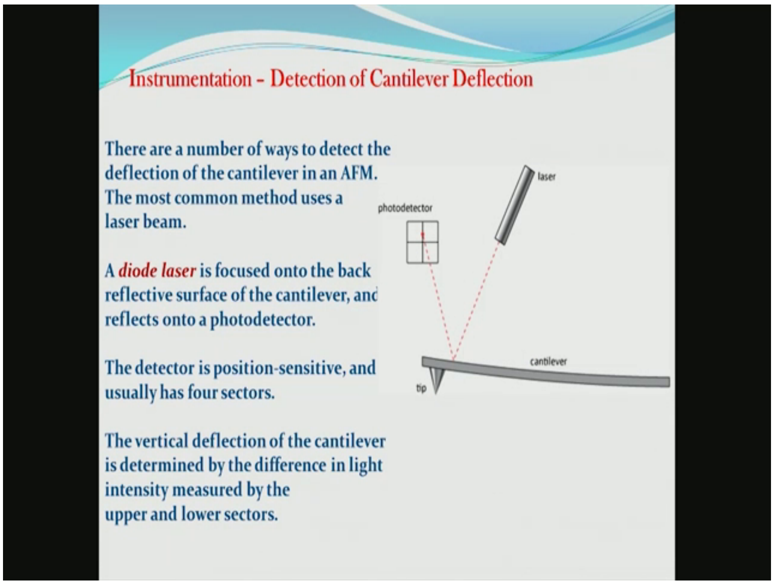

Instrumentation - Detection of Cantilever Deflection

There are a number of ways to detect the deflection of the cantilever in an AFM. The most common method uses a laser beam.

A *diode laser* is focused onto the back reflective surface of the cantilever, anc reflects onto a photodetector.

The detector is position-sensitive, and usually has four sectors.

The vertical deflection of the cantilever is determined by the difference in light intensity measured by the upper and lower sectors.

What is the instrumentation involved one has to measure the displacement of a cantilever as it scans a surface. So, how the displacement is measured is shown here, a laser is incident on the back surface of a cantilever which are fine tip as shown as shown here, this is reflective also so, this light is reflected onto a photo detector as shown here which is usually it has four quadrants.

And the detective is position sensitive and therefore, it is possible to measure small displacements because the light beam laser beam then falls at different parts of the photo detector and therefore, by following the reflected beam into the photo detector, and deducing the meaning of the position of the reflected beam on the photo detector it is possible to measure extremely small displacements in the nanometer range. So, this is the technique instrumentation involved.

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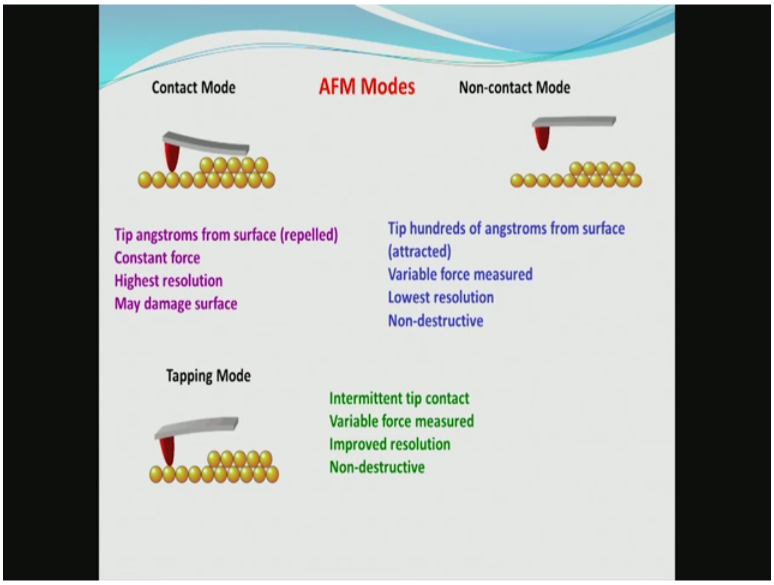

AFM Modes

Contact Mode

Tip angstroms from surface (repelled)
Constant force
Highest resolution
May damage surface

Non-contact Mode

Tip hundreds of angstroms from surface (attracted)
Variable force measured
Lowest resolution
Non-destructive

Tapping Mode

Intermittent tip contact
Variable force measured
Improved resolution
Non-destructive

So what I shown here a three different modes shown in animation, so have the contact mode which is self descriptive, you have the noncontact mode, you have the so called tapping mode. So, these are three different modes in which the AFM is operated in contact noncontact or in the tapping modes.

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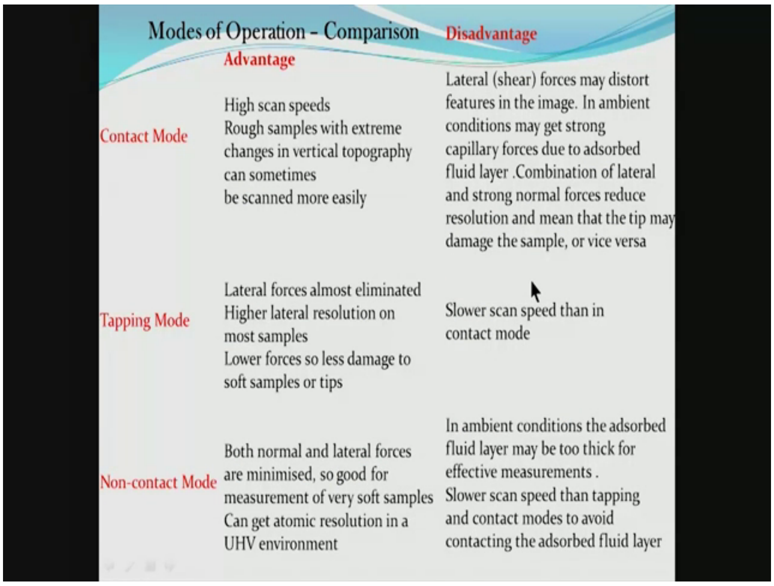

Modes of Operation - Comparison

	Advantage	Disadvantage
Contact Mode	High scan speeds Rough samples with extreme changes in vertical topography can sometimes be scanned more easily	Lateral (shear) forces may distort features in the image. In ambient conditions may get strong capillary forces due to adsorbed fluid layer .Combination of lateral and strong normal forces reduce resolution and mean that the tip may damage the sample, or vice versa
Tapping Mode	Lateral forces almost eliminated Higher lateral resolution on most samples Lower forces so less damage to soft samples or tips	Slower scan speed than in contact mode
Non-contact Mode	Both normal and lateral forces are minimised, so good for measurement of very soft samples Can get atomic resolution in a UHV environment	In ambient conditions the adsorbed fluid layer may be too thick for effective measurements . Slower scan speed than tapping and contact modes to avoid contacting the adsorbed fluid layer

There are advantages and disadvantages to different modes the contact mode is where the tip is in contact with the surface which is which it is measuring, that allows high speed scans, and rough samples with extreme changes in vertical topography can be scanned more easily because it tip is in contact, but this is a disadvantage is that the lateral shear forces may distort the image and so on.

In the tapping mode the lateral forces are almost eliminated, but the speed is lower than in the case of the contact mode, in the noncontact mode lateral forces as well as normal forces are minimized. So, it is very good for measuring very soft samples, and if you have an ultrahigh vacuum environment it is possible to get atomic resolution images of the surface using the noncontact mode.

Now, the atomic force microscope is typically used in the ambient, and in ambient conditions the absorbed fluid layer for example, moisture in their ambient may be too thick for effective measurements and therefore, the resolution is reduced because as their absorbed film layer when the AFM is used in the ambient.

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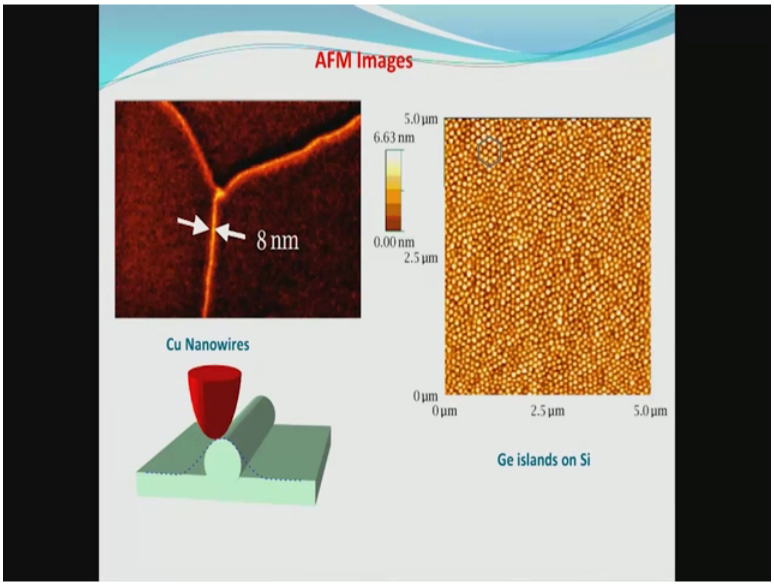

AFM Images

Cu Nanowires

Ge islands on Si

So the some images over here, images of a cup of copper nanowires a very small diameter, and images of islands or germanium deposited on silicon. So, you can see that it is possible to measure extremely fine topographies and extremely small sizes on the surface.

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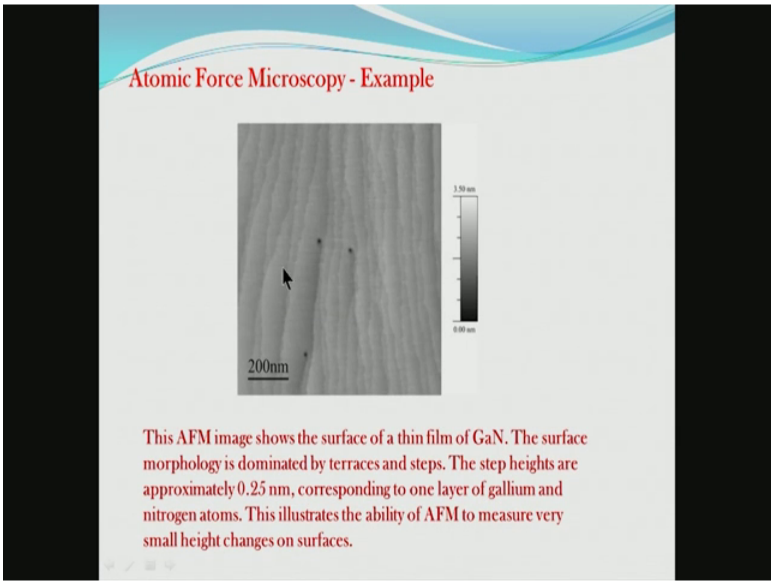

Atomic Force Microscopy - Example

This AFM image shows the surface of a thin film of GaN. The surface morphology is dominated by terraces and steps. The step heights are approximately 0.25 nm, corresponding to one layer of gallium and nitrogen atoms. This illustrates the ability of AFM to measure very small height changes on surfaces.

What is shown here is an AFM image of the surface of a thin film of gallium nitride, now the surface morphology is dominated by terraces and steps as you can see here, the step heights are typically about 0.25 nanometers corresponding to one layer of gallium or nitrogen atoms. So, this image illustrates the ability of AFM to measure small height differences on surfaces, surface topography in other words.

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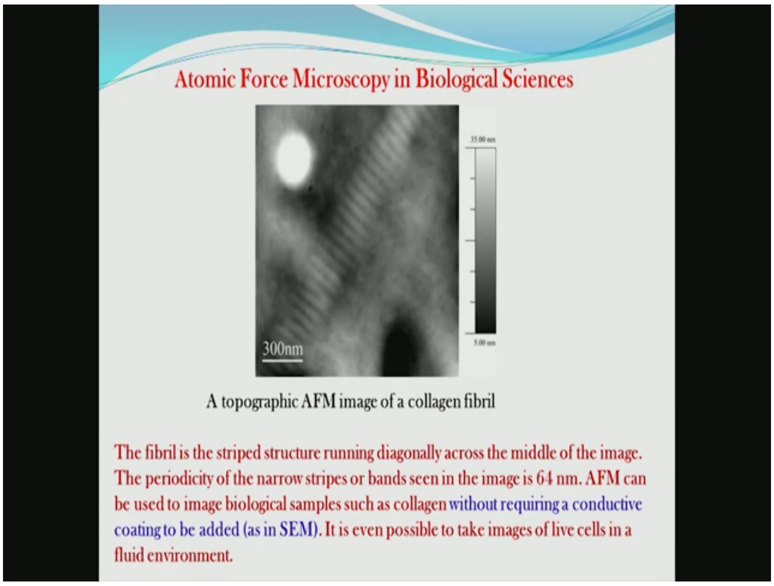

Atomic Force Microscopy in Biological Sciences

A topographic AFM image of a collagen fibril

The fibril is the striped structure running diagonally across the middle of the image. The periodicity of the narrow stripes or bands seen in the image is 64 nm. AFM can be used to image biological samples such as collagen without requiring a conductive coating to be added (as in SEM). It is even possible to take images of live cells in a fluid environment.

Atomic force microscopy in biological sciences, atomic force microscopy has found extensive applications biological sciences, where the samples are of a different kind.

Now what we must remember is that if you want to image biological samples by scanning electron microscopy it is usually necessary to deposit a contact metallic layer, because biological samples are typically non conducting and therefore, electrons there or you get because of the charging effect you get poor images by electron microscopy therefore, a conductive metallic layer has to be deposited on biological samples, when they are examined by sem.

The great advantage of atomic force microscopy is that no such conductive layer needs to be deposited on a biological sample to be examined by AFM. So, what is shown here is a fibril, so you can see this type structures over here. So, this is a collagen fibril imaged by atomic five point force microscopy, so I can see the fine structure of these fibrils on the nanometer scale obtained through atomic force microscopy, it is even possible to take images of live cells in a fluid environment through AFM .

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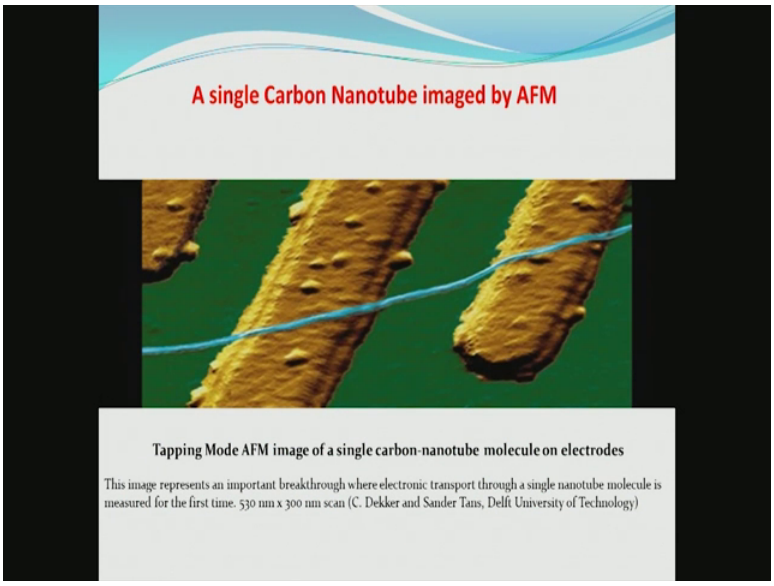

A single Carbon Nanotube imaged by AFM

Tapping Mode AFM image of a single carbon-nanotube molecule on electrodes

This image represents an important breakthrough where electronic transport through a single nanotube molecule is measured for the first time. 530 nm x 300 nm scan (C. Dekker and Sander Tans, Delft University of Technology)

What is shown here is the image of a single carbon nanotube; single carbon nanotubes, which is lying on two electrodes these are metal electrodes, so what is being done here is to make measurements of the electrical conductivity of a single carbon nanotube, and what this shows is the imaging of this single carbon nanotubes that is contacting two electrode lines over here. This again shows the capability of atomic force microscopy.

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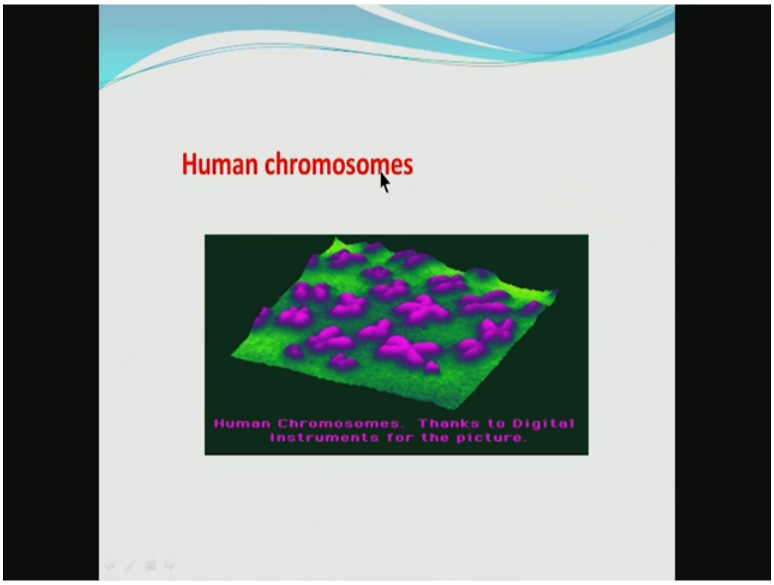

Human chromosomes

Human Chromosomes. Thanks to Digital Instruments for the picture.

I mentioned biological samples so, what are imaged here are human chromosomes through AFM.

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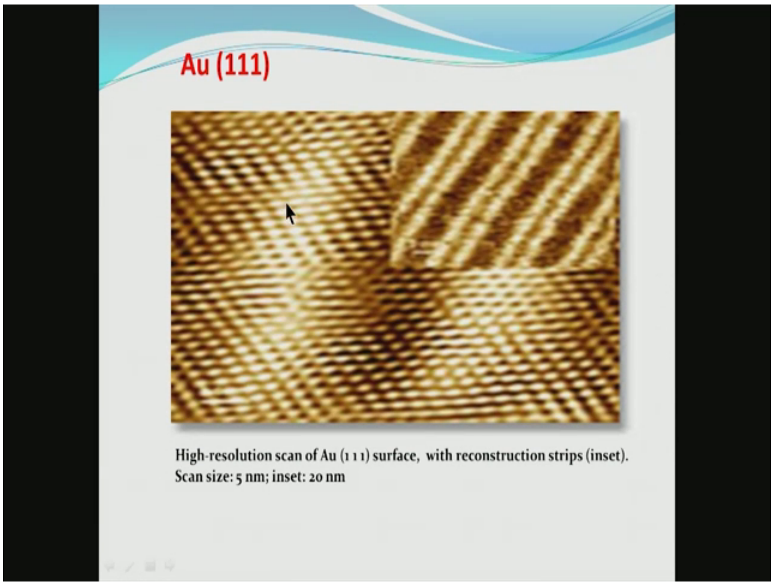

Au (111)

High-resolution scan of Au (1 1 1) surface, with reconstruction strips (inset). Scan size: 5 nm; inset: 20 nm

Finally, we have the imaging at high resolution of a gold single crystal that is the 111 phase of the gold single crystal. You can see the high resolution, that one can obtain by atomic force microscopy this is done in a high vacuum and you can see that these stripes over seen over here is due to reconstruction of the surface of the single crystal of gold.

So, what we have seen is that scanning probe microscopy is a very versatile technique of which atomic force microscopy is a very important branch, and by designing cantilevers in such a way as to have very small or soft spring constants, it is possible to measure extremely small forces and to image surfaces very precisely especially in ultrahigh vacuum. And it is also possible to image biological samples using atomic force microscopy.

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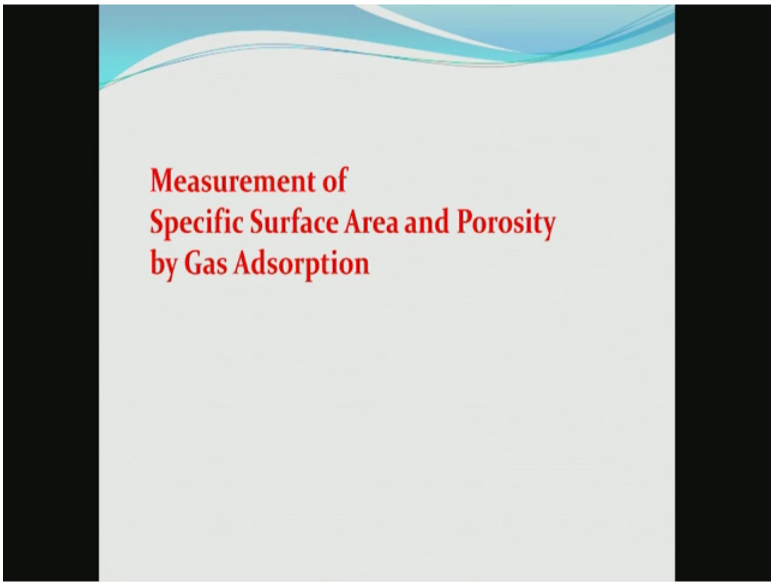

Measurement of
Specific Surface Area and Porosity
by Gas Adsorption

Finally, we come to the analysis of another aspect a nanomaterials namely to measure the specific surface area and the porosity by gas adsorption.

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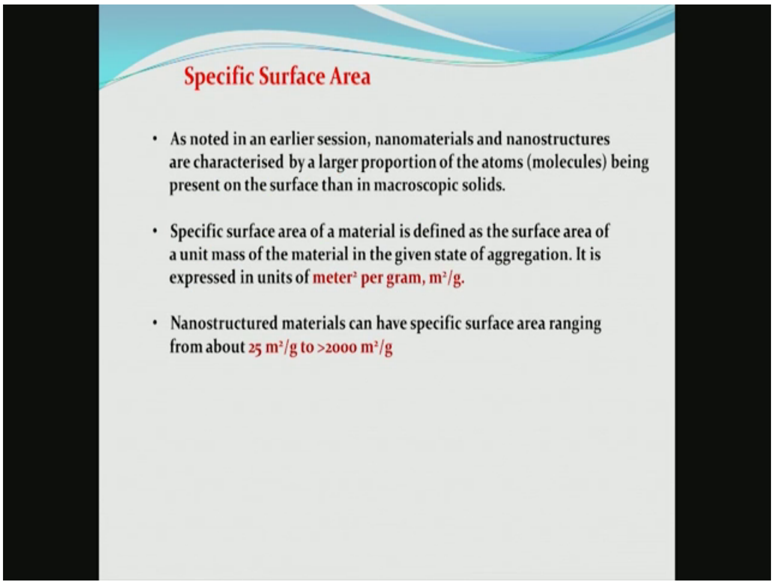

Specific Surface Area

- As noted in an earlier session, nanomaterials and nanostructures are characterised by a larger proportion of the atoms (molecules) being present on the surface than in macroscopic solids.
- Specific surface area of a material is defined as the surface area of a unit mass of the material in the given state of aggregation. It is expressed in units of meter^2 per gram, m^2/g.
- Nanostructured materials can have specific surface area ranging from about 25 m^2/g to >2000 m^2/g

Now, specific surface area as we have noted in an earlier session nanomaterials and nanostructures are characterized by a larger proportion of the atoms or molecules being on the surface, that is larger fraction than in macroscopic materials. So, surfaces of nanomaterials are important, and the surface area of nanomaterials is larger, than the surface area of the same material that is in a macroscopic size. The specific surface area of a material is defined as a surface area of a unit mass of the material in the given state of aggregation it is expressed in units of meter square per gram.

Nanostructured materials because of the small size can have large specific surface areas ranging from about 25 meters per meter square per gram to even more than 2000 meter square per gram as in the case of graphing sheets for example, which is a single layer of carbon atoms. So, this specific area is very large.

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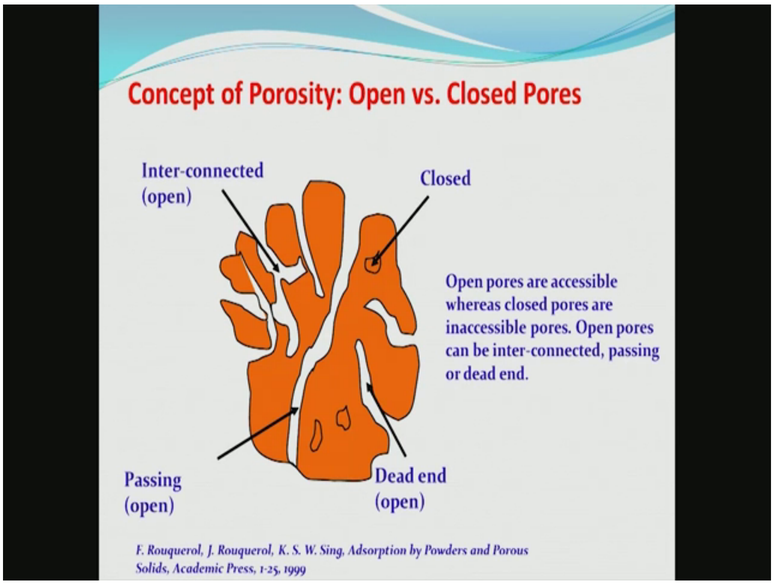

Concept of Porosity: Open vs. Closed Pores

Open pores are accessible whereas closed pores are inaccessible pores. Open pores can be inter-connected, passing or dead end.

F. Rouquerol, J. Rouquerol, K. S. W. Sing, Adsorption by Powders and Porous Solids, Academic Press, 1-25, 1999

Porosity we all understand what porosity means, so what is shown here is the different kinds of pores that may be present in a material.

So, you have open passing pores that is connecting one end the material, one end the particle to another end, this is straight through you have interconnected pores as shown in this part of the diagram on over here, you have dead end, but open pores over here, you also have completely closed pores that is these are hollows within the sample and therefore, they are inaccessible but all these other kinds of pores are accessible to a vapor phase.

So, nanostructures are typically characterized not only by a large surface area, but nanostructured powder material can be characterized also by porosity of these different types and therefore, their behavior can be understood by measuring the extent of these pores and the size of these pores.

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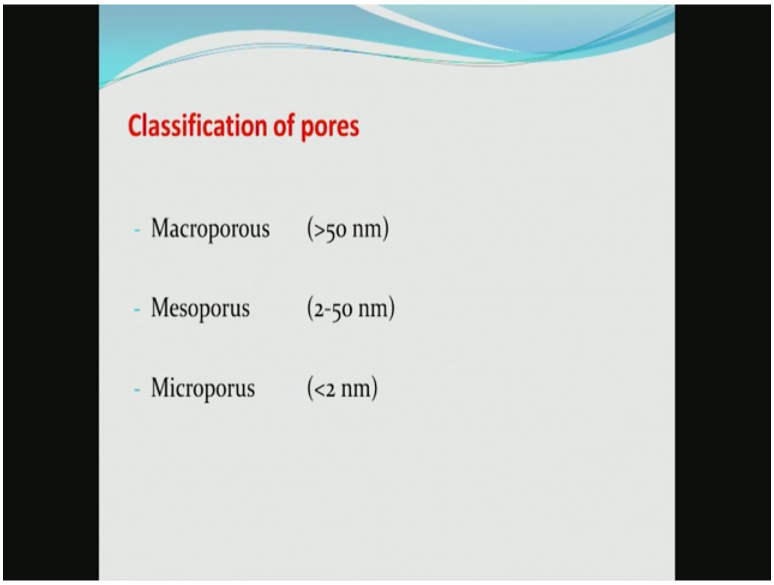

Classification of pores

- Macroporous (>50 nm)
- Mesoporus (2-50 nm)
- Microporus (<2 nm)

There is a classification of pores that we need to note. If the pore size is greater than 50 nanometers we call the material macroporous, if the pores on the average are between 2 and 50 nanometers they are mesoporous. And if the pore size is smaller than two nanometers they are classified as microporous.

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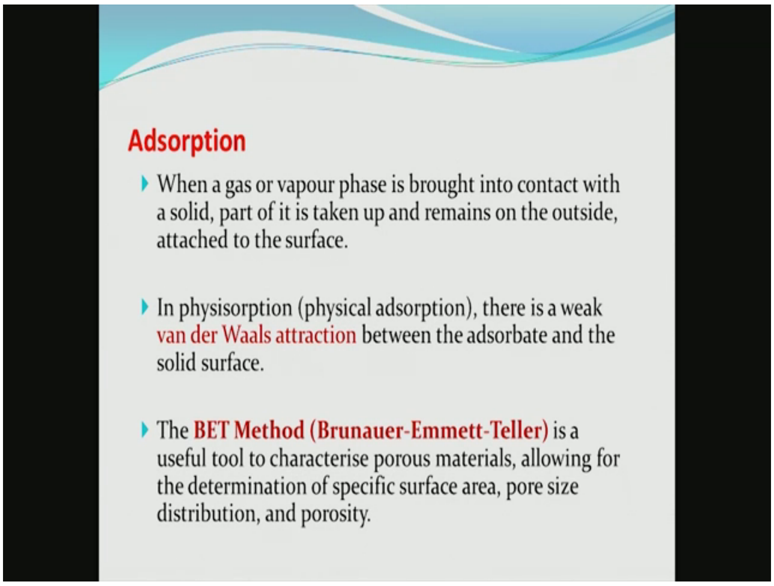

Adsorption

- When a gas or vapour phase is brought into contact with a solid, part of it is taken up and remains on the outside, attached to the surface.
- In physisorption (physical adsorption), there is a weak van der Waals attraction between the adsorbate and the solid surface.
- The **BET Method (Brunauer-Emmett-Teller)** is a useful tool to characterise porous materials, allowing for the determination of specific surface area, pore size distribution, and porosity.

Now I mentioned adsorption, gas adsorption as a way to measure specific surface area and porosity. When a gas or a vapor phase is brought into contact with the solid part of this vapor is taken up and remains on the outside attached to the surface of the solid, we call that adsorption.

Physisorption means physical adsorption that is these vapors are simply physically sitting without chemically interacting with the surface on which they are sitting; in this case there is a weak van der Waals interaction between the adsorbed vapor or gas and the solid surface on which it is absorbed. The well known bet method standing for brunauer emmett teller is a useful tool to characterize porous materials, and allows for the determination of the specific surface area and the pore size, and the pore size distribution of porous materials.

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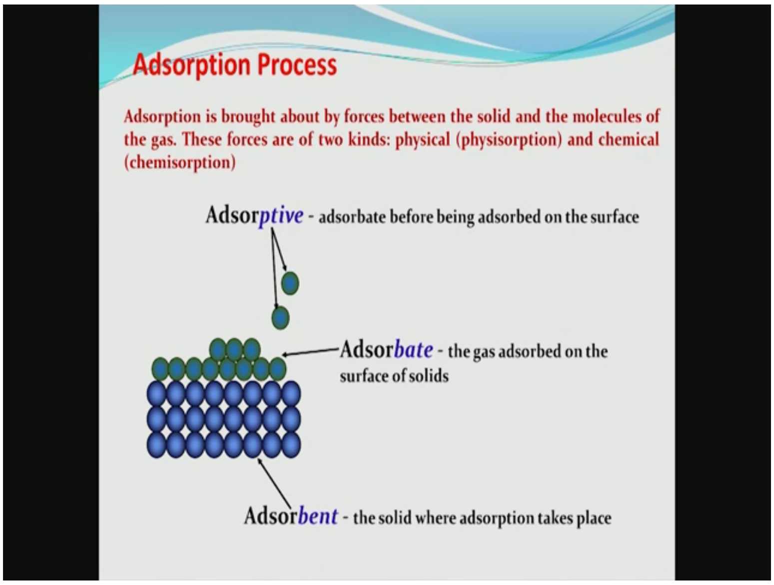

Adsorption Process

Adsorption is brought about by forces between the solid and the molecules of the gas. These forces are of two kinds: physical (physisorption) and chemical (chemisorption)

Adsorptive - adsorbate before being adsorbed on the surface

Adsorbate - the gas adsorbed on the surface of solids

Adsorbent - the solid where adsorption takes place

Now, as I noted already adsorption is brought about by forces between the solid and the molecules of the gas which sit on the solid. There are two kinds of adsorption again to repeat myself physisorption, where there is only a physical contact, but where there is some kind of bonding involved between the molecules that will sit on the surface and the surface. Then it becomes chemisorption we will only be concerned physisorption in what follows.

Terminology is important. So, what you have is a surface over here solid surface on which adsorption takes place therefore, it is called the adsorbent adoptive is the adsorbate material that is the vapor or gas material before it is adsorbed on the surface, when it is adsorbed on the surface it becomes the adsorbate. So, this is gas or vapor adsorbed on the solid surface.

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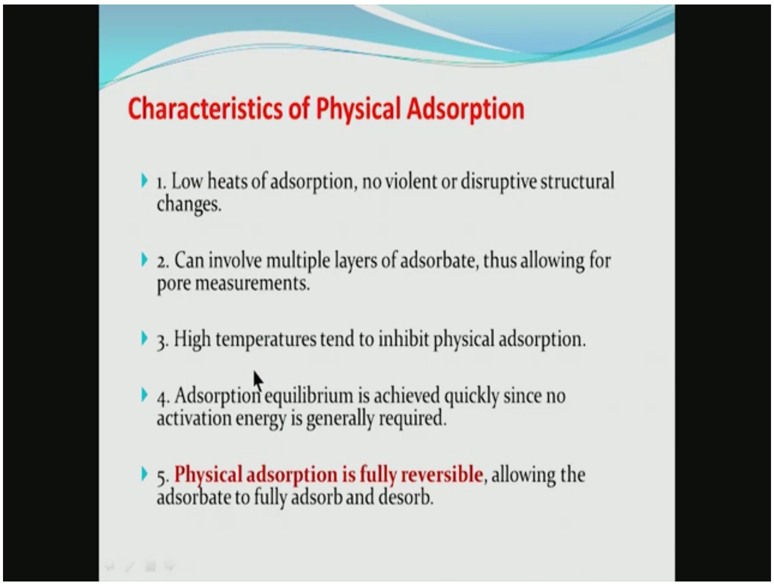

Characteristics of Physical Adsorption

- 1. Low heats of adsorption, no violent or disruptive structural changes.
- 2. Can involve multiple layers of adsorbate, thus allowing for pore measurements.
- 3. High temperatures tend to inhibit physical adsorption.
- 4. Adsorption equilibrium is achieved quickly since no activation energy is generally required.
- 5. **Physical adsorption is fully reversible**, allowing the adsorbate to fully adsorb and desorb.

Now what are the characteristics of physical adsorption; physical adsorption, because there is no chemical bond involved between the adsorbed material or the adsorbate and the surface, it involves low heat of adsorption and no violent or disruptive structural changes of the surface.

It can also involve multiple layers or adsorption that is not just one monolayer sitting on the surface, but multiple monolayers sitting on top of one another. And if you consider a pore we let us go back to that figure if you consider a pore over here, then the pore size may be such that it would take many layers of the molecules of the gas that is absorbed in order to fill the pores.

So, we are talking about being able to measure the pore sizes, if these pores are full and therefore, multi layered absorption is possible. So, the measurement of pores would involve multiple layers of adsorbate high temperatures tend to inhibit physical adsorption as I said the heats of adsorption are low, because there is only van der Waals attraction between the adsorbate and the adsorbent, so high temperatures tend to inhibit physical adsorption; adsorption equilibrium, is achieved rapidly since no activation is generally required. Now, lastly but very importantly physical adsorption is fully reversible, allowing for the adsorbate to fully adsorbent desorb as we will see this is these very important in the methods to measure specific surface area as well as porosity.

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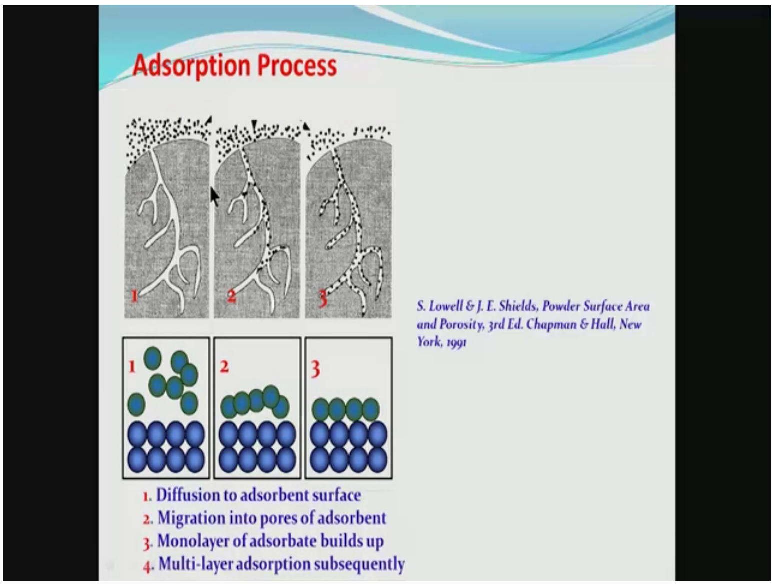

Adsorption Process

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

1. Diffusion to adsorbent surface
2. Migration into pores of adsorbent
3. Monolayer of adsorbate builds up
4. Multi-layer adsorption subsequently

These cartoons illustrate the adsorption process further; the adsorption process involves diffusion of the adsorbent to the adsorbent, adsorbate to the adsorbent surface. So, the they have these molecules of the vapor phase or the gas phase have to diffuse to the absorbent surface, they have to migrate into pore so, the adsorbent a mono layer of the adsorbent has to be formed within these pores around the surface. And multilayer adsorption takes place subsequently. So, this is the adsorption process in a rather simple way of describing it.

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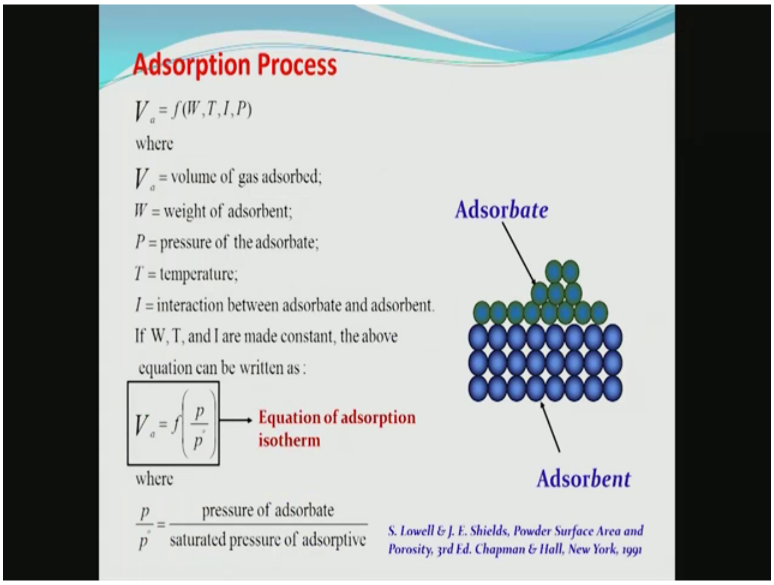

Adsorption Process

$V_a = f(W,T,I,P)$

where

V_a = volume of gas adsorbed;

W = weight of adsorbent;

P = pressure of the adsorbate;

T = temperature;

I = interaction between adsorbate and adsorbent.

If W, T, and I are made constant, the above equation can be written as:

$$\boxed{V_a = f\left(\frac{p}{p^\circ}\right)} \rightarrow$$

Equation of adsorption isotherm

where

$$\frac{p}{p^\circ} = \frac{\text{pressure of adsorbate}}{\text{saturated pressure of adsorptive}}$$

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

Now as one can readily see the volume of the gas or vapor or the adsorbate that is adsorbed onto a surface or into a pore would be a function of the weight of the adsorbent that is how much of the solid that there is, it would depend on the temperature as we noted high temperature actually does not facilitate adsorbed it actually facilitates desorption or temperature is important, it depends on the interaction between the adsorbate and adsorbent. And it depends on the pressure of the adsorbate over here, the how much pressure in the vapor phase is exerted on these surfaces that adsorbs.

So, the volume of the gas adsorbed is a function of all these factors, and if W and T and I are constant, then the above equation can be written as the volume of adsorbent, that is adsorbed is a function of p over p naught; p or p naught is where, p p naught is this saturated pressure of the adsorbent. And p is the pressure at which the actual adsorption is done, that is p naught is the pressure corresponding to saturated adsorption p is the pressure corresponding to any particular level of adsorption. So, the volume of gas adsorbed is a function of p over p naught and this is the equation for a so called adsorption isotherm.

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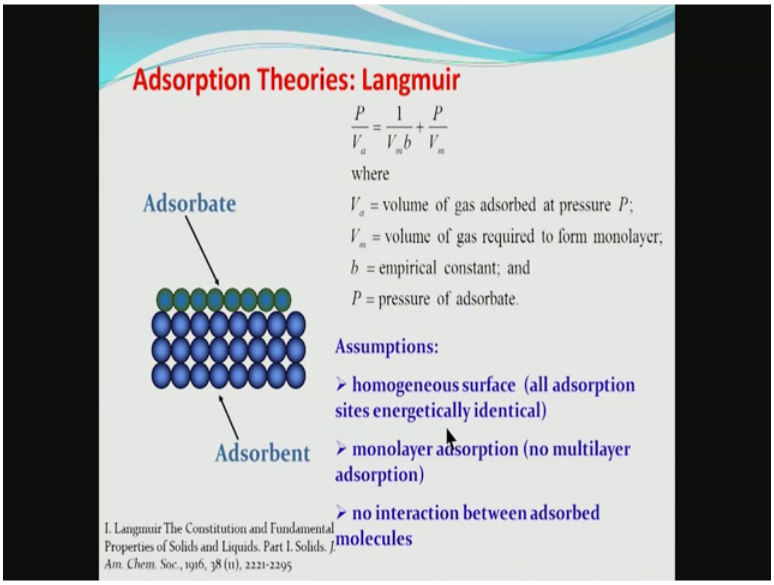

Adsorption Theories: Langmuir

$$\frac{P}{V_a} = \frac{1}{V_m b} + \frac{P}{V_m}$$

where

V_a = volume of gas adsorbed at pressure P;

V_m = volume of gas required to form monolayer;

b = empirical constant; and

P = pressure of adsorbate.

Assumptions:

- **homogeneous surface (all adsorption sites energetically identical)**
- **monolayer adsorption (no multilayer adsorption)**
- **no interaction between adsorbed molecules**

I. Langmuir The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids. *J. Am. Chem. Soc.*, 1916, 38 (11), 2221-2295

So, adsorption isotherm consists of a graph between V and p over p naught. Langmuir described adsorption quantitatively many years ago. So, this is the so called Langmuir absorption equation, and the assumptions are that the surface is homogeneous that is all adsorption sites are energetically equivalent, it also assumes that there is only a monolayer adsorption no multilayer adsorption in this particular treatment. And that there is no interaction between the adsorbed surfaces rather the adsorbed and the adsorbate that is there is no interaction except for van der Waals interaction.

Now, let us look at this equation, V a is the volume of the gas adsorbed at some pressure P, so we have V a corresponding to pressure P V m is the volume of the gas required to form one mono layer of the adsorbate, b is an empirical constant and P is the pressure of the adsorbate. So, this is the Langmuir equation which applies to the adsorption of one single mono layer, but in reality multiple layers is absorbed.

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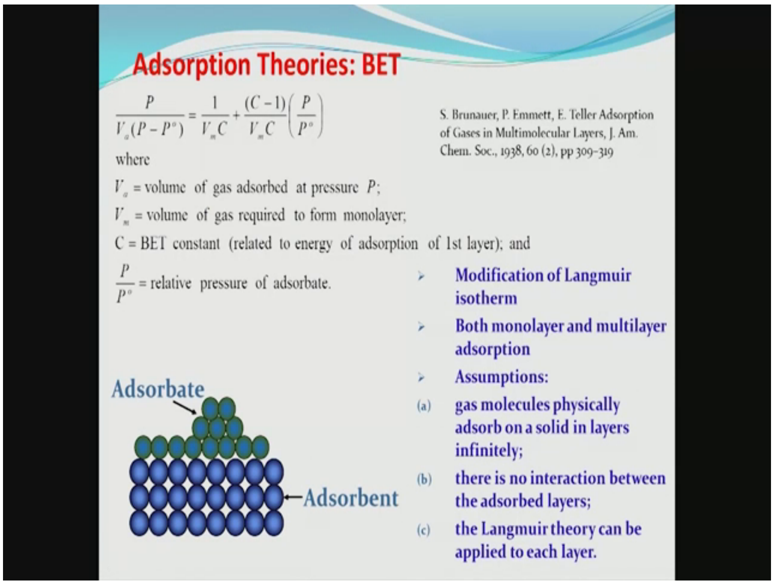

Adsorption Theories: BET

$$\frac{P}{V_a(P-P^\circ)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\left(\frac{P}{P^\circ}\right)$$

where

V_a = volume of gas adsorbed at pressure P;

V_m = volume of gas required to form monolayer;

C = BET constant (related to energy of adsorption of 1st layer); and

$\frac{P}{P^\circ}$ = relative pressure of adsorbate.

S. Brunauer, P. Emmett, E. Teller Adsorption of Gases in Multimolecular Layers, J. Am. Chem. Soc., 1938, 60 (2), pp 309-319

- Modification of Langmuir isotherm
- Both monolayer and multilayer adsorption
- Assumptions:

(a) gas molecules physically adsorb on a solid in layers infinitely;

(b) there is no interaction between the adsorbed layers;

(c) the Langmuir theory can be applied to each layer.

And therefore, what you get is the so called BET equation brunauer emmett teller equation, which takes into account the adsorption of many layers onto a solid surface.

So, in this equation V a is the volume of the gas adsorbed at pressure P, V m is the volume of the gas adsorbed to form mono one monolayer required to form one monolayer c is the so called BET constant which is related to the energy of adsorption of the first layer, and P over P naught is the relative pressure of the adsorbate. As I said P naught corresponds to a saturation level of adsorption and P corresponds to any specific level of adsorption corresponding to that pressure P, and P is related to V a and V a is related to P as in this equation.

So, this one represents the modification of the Langmuir isotherm, both monolayer and multilayer adsorptions are allowed. And the assumptions made in deriving the BET equation is that the gas molecules physically adsorbed on a solid in layers, any number of layers, an infinite number of layers, there is no interaction between adsorbed layers, that is there are different layers of the adsorbed material, they do not interact with one another. And that the Langmuir theory which is applicable to a monolayer can be applied to each layer of the adsorbate of a multilayer adsorption case. So, this is the BET equation which is the basis of experimental measurement or the specific surface area of a material.

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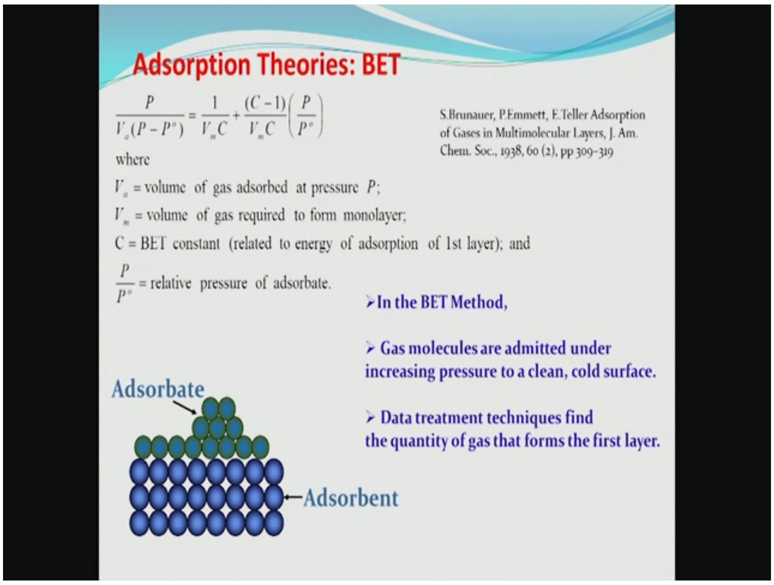

Adsorption Theories: BET

$$\frac{P}{V_a(P-P^\circ)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\left(\frac{P}{P^\circ}\right)$$

where

V_a = volume of gas adsorbed at pressure P;

V_m = volume of gas required to form monolayer;

C = BET constant (related to energy of adsorption of 1st layer); and

$\frac{P}{P^\circ}$ = relative pressure of adsorbate.

S.Brunauer, P.Emmett, E.Teller Adsorption of Gases in Multimolecular Layers, J. Am. Chem. Soc., 1938, 60 (2), pp 309-319

- In the BET Method,
- Gas molecules are admitted under increasing pressure to a clean, cold surface.
- Data treatment techniques find the quantity of gas that forms the first layer.

So, in the b e t method gas molecules are admitted under increasing pressure to a clean cold surface. Cold surface so, that sufficient adsorption takes place as we have said earlier. The heat of low and therefore, elevated temperatures lead to desorption therefore, one takes a cold surface cold clean surface. So in the BET method this is what is done gas molecules are admitted under increasing pressure that is at various pressure, but increasing pressure. So, that saturated adsorption can be achieved, and the adsorption takes place on a clean cold surface.

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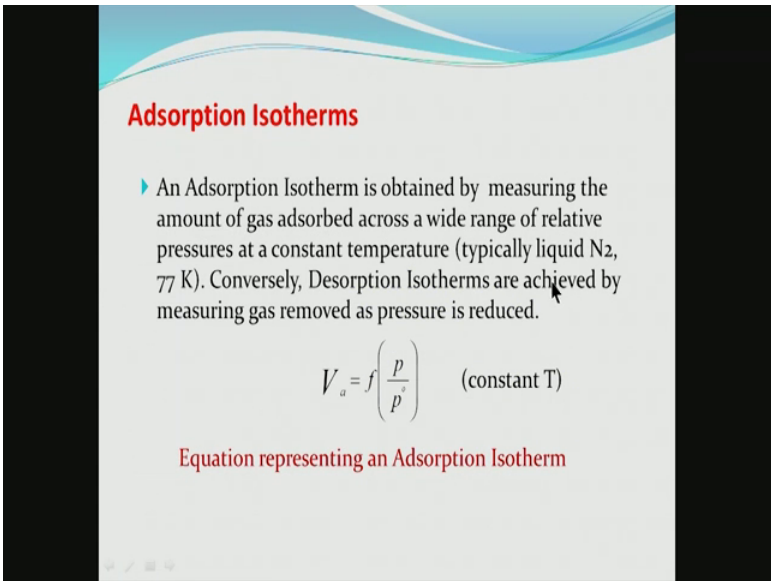

Adsorption Isotherms

- An Adsorption Isotherm is obtained by measuring the amount of gas adsorbed across a wide range of relative pressures at a constant temperature (typically liquid N2, 77 K). Conversely, Desorption Isotherms are achieved by measuring gas removed as pressure is reduced.

$$V_a = f\left(\frac{p}{p^\circ}\right) \qquad \text{(constant T)}$$

Equation representing an Adsorption Isotherm

Now, let us look at adsorption isotherms an adsorption isotherm is obtained by measuring the amount of gas adsorbed, over a wide range of pressures under which adsorption is made to take place, and at a constant temperature which is typically the temperature of liquid nitrogen or 77 K desorption isotherms are achieved by measuring the gas removed as the pressure is reduced, that is in the case of adsorption one goes on increasing the pressure.

So, the isotherm is obtained by measuring the volume of the gas adsorbed as the pressure is increased, and in desorption one reduces the pressure, and one measures the volume of gas that is taken out that has been previously adsorbed that is taken out as the pressure is decreased. So, this equation as we have said earlier represents an adsorption isotherm.

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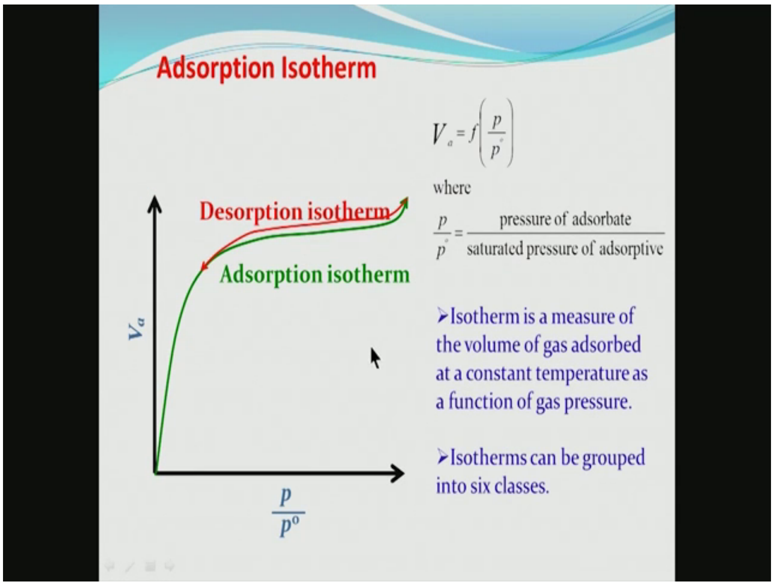

Adsorption Isotherm

$$V_a = f\left(\frac{p}{p^\circ}\right)$$

where

$$\frac{p}{p^\circ} = \frac{\text{pressure of adsorbate}}{\text{saturated pressure of adsorptive}}$$

- Isotherm is a measure of the volume of gas adsorbed at a constant temperature as a function of gas pressure.
- Isotherms can be grouped into six classes.

So, what is shown is at typical adsorption isotherm plotting V a versus P over P naught. So what you can see is an adsorption isotherm, whereby V a increases as the pressure is increased, and desorption as the pressure is decreased represented by this red curve. So, you can see that there is a hysteresis that is there is a separation between the adsorption isotherm, and desorption isotherm. These isotherms can be classified into six classes.

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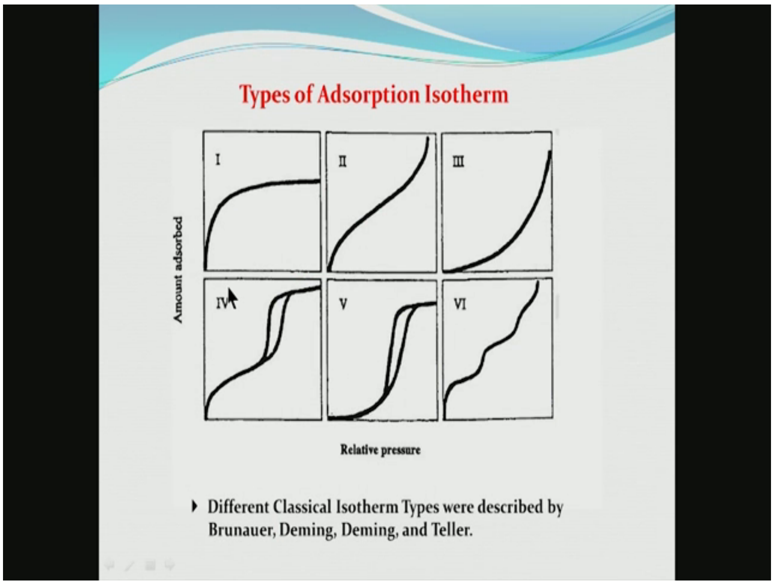

Types of Adsorption Isotherm

- Different Classical Isotherm Types were described by Brunauer, Deming, Deming, and Teller.

So, experimentally it has been observed that different kinds of surface structure lead to different kinds of adsorption isotherms. So, this is type one type two type three four five and six. So, these are what experimentally the known to be different types of adsorption, you can see here that there is hysteresis, he and see here that there hysteresis it also turns out that in type one also there can be hysteresis. This hysteresis occurs because when there are pores present then getting the gas out of the pores as the pressure is deduced causes this hysteresis.

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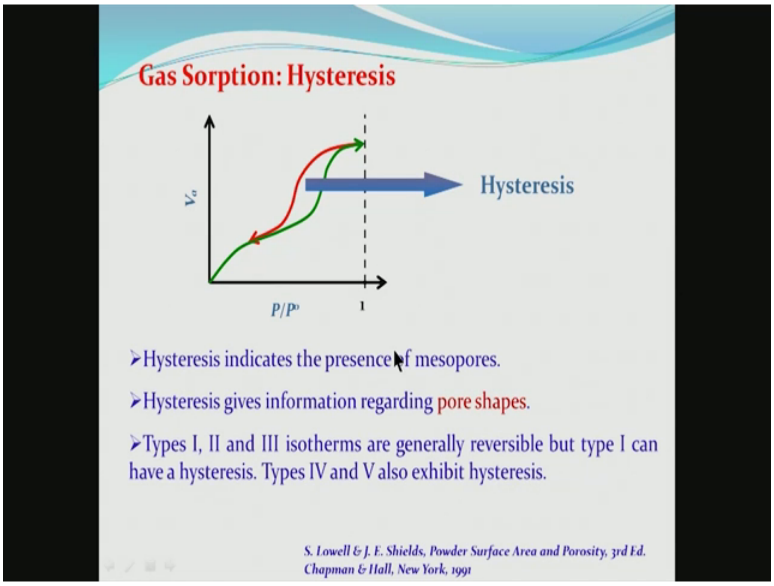

Gas Sorption: Hysteresis

- Hysteresis indicates the presence of mesopores.
- Hysteresis gives information regarding pore shapes.
- Types I, II and III isotherms are generally reversible but type I can have a hysteresis. Types IV and V also exhibit hysteresis.

S. Lowell & J. F. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

So, hysteresis indicates the presence of mesopores, that is pores with dimensions between 2 and 50 nanometers and hysteresis also gives information regarding the pore shapes I will come to that, and isotherms are the type one two and three generally a reversible, but type one and type four and tie five exhibit hysteresis, that is type four and type five exhibit hysteresis type one, also can do that at some in some conditions, but typically type four and type five exhibit hysteresis.

Now, once again the details of the hysteresis that is the shape of this hysteresis uses information regarding the shape of the pores present.

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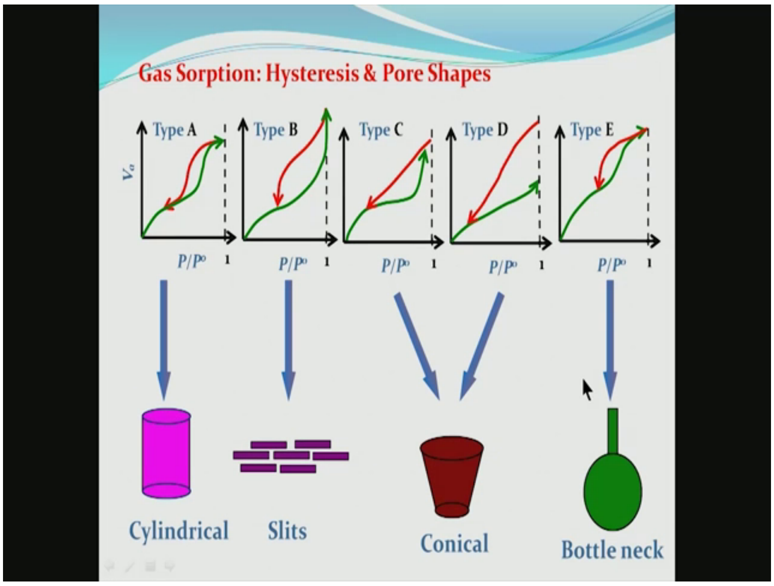

Gas Sorption: Hysteresis & Pore Shapes

So, what this cartoon show is the different kinds of pore shapes and the corresponding differences in the hysteresis so each one is representing hysteresis. So, if you have a cylindrical pores in a solid, then you get this kind of a hysteresis if you have slits it is this kind, if you have conical pores then you get either types here type D. And if there are bottleneck shaped pores then you get type E. So, by experimentally measuring the shape of the desorption, adsorption isotherm then we can deduced the shape of the pores that are present in that particular material.

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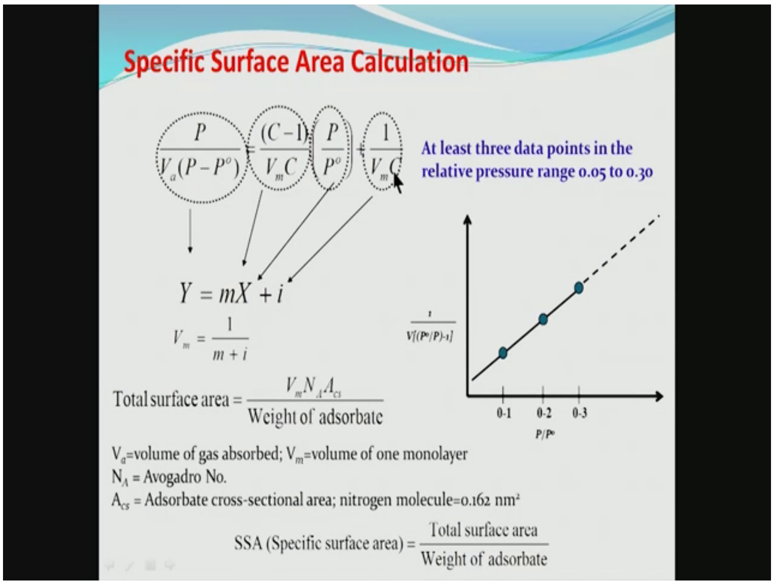

Specific Surface Area Calculation

$$\frac{P}{V_a(P-P^o)} = \frac{(C-1)}{V_m C}\left(\frac{P}{P^o}\right) + \frac{1}{V_m C}$$

$$Y = mX + i$$

$$V_m = \frac{1}{m+i}$$

At least three data points in the relative pressure range 0.05 to 0.30

$$\text{Total surface area} = \frac{V_m N_A A_{cs}}{\text{Weight of adsorbate}}$$

V_a=volume of gas absorbed; V_m=volume of one monolayer

N_A = Avogadro No.

A_{cs} = Adsorbate cross-sectional area; nitrogen molecule=0.162 nm^2

$$\text{SSA (Specific surface area)} = \frac{\text{Total surface area}}{\text{Weight of adsorbate}}$$

Now, coming back to the BET equation, this is the BET equation which can be written in the form of the equation of a straight line Y is equal to m X plus i, and by recasting this equation it is easy to see that if we plot the reciprocal of V into P naught divided by P minus 1, that is P naught divided by P is the relative pressure. So, if you plot V into P naught divided by P minus 1, verses P by P naught which is a relative pressure, then we ought to get a straight line, and from the straight line we can deduced V m which is the volume which is connected to the volume of the gas that has been adsorbed.

So, from this graph we can obtain V m because we know m and i, m is the slope of this line, and i is the intercept. So, we get V m that is the volume of the gas over here, and N a is the Avogadro number A c s is the adsorbate cross sectional area, that is the molecular cross sectional area of the adsorbate which is typically nitrogen. And is therefore, 0.16 to nano meter square.

So, with all this we can deduce that the specific surface area, rather the total surface area is given by this equation over here V m is the volume of gas adsorbed N is the Avogadro number A c s is the adsorbate cross sectional area, divided by the weight of the adsorbate. So that gives us the total surface area.

So, what is what one is measuring is the weight of the adsorbate that is one measures the weight of the sample, before gas is adsorbed and one measures the weight of the sample after the gases are adsorbed at a low temperature. So, that gives us the weight of the adsorbate and therefore, very precise measurement of the weight difference is important so for micro balances are used.

So, by measuring the weight of the adsorbate, and the volume of the adsorbate as derived from the BET equation from this graph BET plot, one can deduce the total surface area and one divides the total surface area by the weight of the adsorbate, which we measure experimentally so therefore, one derives is specific surface area of this sample.

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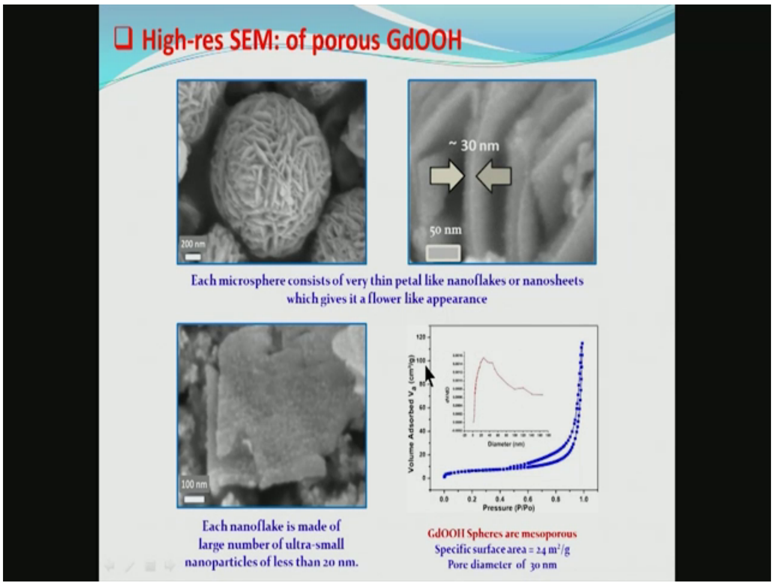

❑ High-res SEM: of porous GdOOH

Each microsphere consists of very thin petal like nanoflakes or nanosheets which gives it a flower like appearance

Each nanoflake is made of large number of ultra-small nanoparticles of less than 20 nm.

GdOOH Spheres are mesoporous
Specific surface area = 24 m^2/g
Pore diameter of 30 nm

So, what are shown here are some examples of samples that are prepared in our lab which have a relatively large surface area and a porous structure, so these are as it turns out these are samples of a rare earth oxy hydroxide g gadolinium oxy hydroxide, you can see the fine pore structure in these things. And these are actually what you might call these are spherical structures with petals in them so to speak.

So, you can see there is a lot of porosity and by using the BET method as we described here the specific surface area measured is about 25 meter sphere grams meter square per gram and you can see the adsorption isotherms. And the desorption isotherms there is a significant hysteresis which indicates porosity, which is evident from the scanning electron micrographs, micrograph and it turns out that by using a plot of this sort over here one can obtain the pore size distribution.

So, what is shown here is the pore size distribution that is the diameter of the pores, and the relative frequency of those diameters present in the pores, so what we see here is that the pore diameter has a peak at about thirty nanometers. So, this is a mesoporous sample with a significant number of pores that are measuring in the order of about 10 nanometers, you can see that corresponds to the SEM image quite well.

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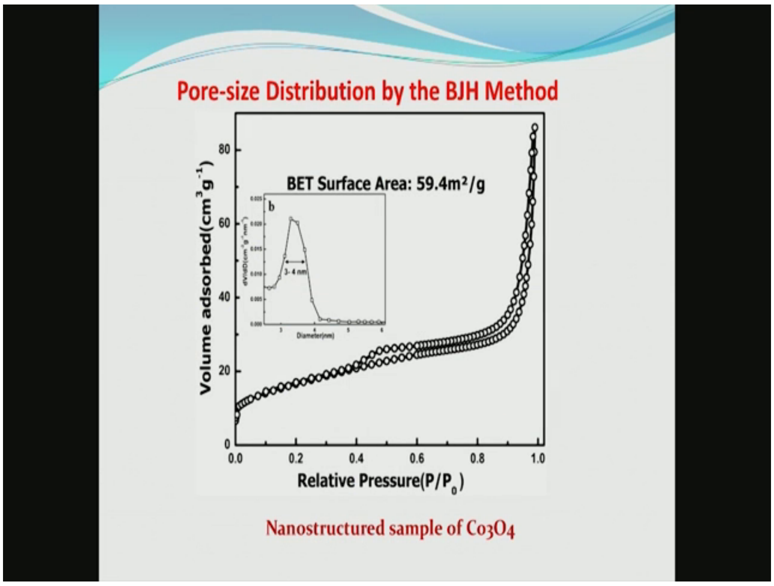

Pore-size Distribution by the BJH Method

BET Surface Area: 59.4m²/g

Nanostructured sample of Co_3O_4

What is shown here is a plot of this kind and this plot is known as a barrett joiner hacienda plot b j h plot over here that is a plot of d v d d versus diameter that is volume derivative of the volume versus the diameter of the pore. So, this graph is known as the b j h plot, so what it is done is to obtain in a desorption adsorption curve for a sample of cobalt oxide Co 3 O 4 which is an important material in electro chemical science, as an electrode material potential electro material for lithium ion batteries.

So, what is shown here though is that in these structures is a significant amount of porosity, the surface area is also large about 60 meters square per gram, and the pore diameters are pretty small three to 4 nanometers, so this is mesoporous technically speaking, but approaching microporous nature very fine pores in this particular sample of cobalt oxide.

So, what we have seen in this session therefore, is a description of the x-ray diffraction technique for measuring the crystallite size, by measuring the broadening of the x-ray diffraction peaks; peaks, and separating the broadening due to strain from the broadening, due to the crystallite size, one can determine the average crystallite size, one uses electron microscopy for detailed distribution of sizes force, microscopy is a very powerful technique to examine the details of the surface of nano structures, and by designing cantilevers with appropriate spring constants even though the cantilever measure in micrometers it is possible to make measurements of displacements of the order nanometers and extremely fine forces at the atomic scale to measure solid samples and even biological samples.

Finally, we have seen that the adsorption of gases or vapors on solid surfaces with a significant degree of porosity and a large surface area, can be adsorption measurements can help us measure the specific surface area, one of the things that I forgot to mention is that this specific surface area is very important in two aspects of the user nanomaterials namely catalytic action, which we dealt with in the last session and also in the sensing action for which nanomaterials are again being investigated heavily.

So, having a large surface areas is very important for sensing action, for catalytic action, and the porosity of these things is capable of telling us how this how materials can be stored in this for example, storage of hydrogen in these pores can be important. Therefore, nanostructured materials can be studied by the techniques of x-ray diffraction, by electron microscopy, by atomic force microscopy or more broadly scanning probe microscopy, and by gas adsorption.

So, that brings us to the close of this segment three of these course Nanofabrication Techniques. And I hope that the segment has been useful to you in telling you giving you an introduction to nanomaterials and nanostructures

Thank you.