

**Indian Institute of Technology
Kanpur**

**NP-TEL
National Programme
on
Technology Enhance Learning**

**Course Title
Advanced Characterization Techniques**

Lecture-28

**by...
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Hello everyone in today's class on advanced characterization technique we are going to talk about a new characterization technique.

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Module content	
a.	Introduction to X-Rays and Review of basic diffraction theory
b.	Small Angle X-ray Scattering (SAXS)
c.	Grazing Incidence Small Angle X-ray Scattering (GISAXS)
d.	Low Energy Electron Diffraction (LEED)
e.	Reflection High Energy Electron Diffraction (RHEED)
f.	Extended X-ray Absorption Fine Structure (EXAFS)
g.	Surface Extended/Near Edge X-Ray Absorption Fine Structure (SEXAFS/NEXAFS)
h.	Properties of neutron radiation and neutron sources
i.	Small angle neutron scattering (SANS)

Known as increasing incidence small-angle x-ray scattering in the last class we have studied small angle x-ray scattering and we understood that how small angle scattering can help us about the distribution of sizes as well as shape of different particles and precipitates in a variety of materials we also know that with the improve our increase in nano research going on in

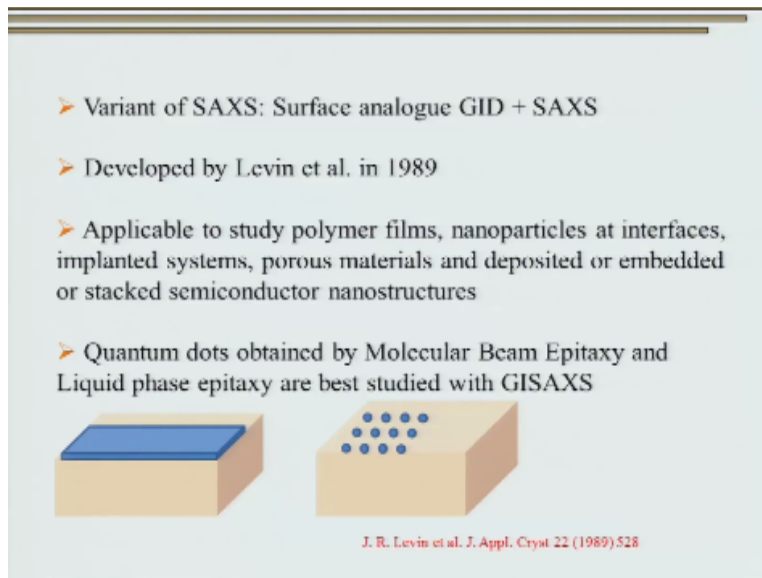
nanotechnology there is a lot of need for a characterization technique that can be used to characterize small scale sizes and shapes on the surface right and for that we need to use a technique which is essentially known as grazing incidence small-angle x-ray scattering.

Now if you remember we had talked about grazing incidence while we talked about the normal x-ray diffraction so that you can have either a normal incidence where in the x-ray beam is incident on your sample in a reflection or in the transmission mode while in case of grazing incidence the beam is almost parallel and makes a very small angle with the sample under consideration the most important point that I would like to emphasize here onwards and that is why I am sticking on this particular slide is that what all techniques you are going to talk from here on in the course of this lectures is that are pretty sophisticated techniques.

And these are not the techniques which essentially are available you know in laboratory and like you just pick up pick up your sample and take your sample all day there to do the characterization instead these are very sophisticated techniques and it is expected that you understand these techniques and get an exposure to these techniques and then carry out your preliminary characterization using laboratory scale x-ray diffraction and other characterization tools.

And then you go to this advanced characterization techniques in order to solve your problem of importance so let us start talking about grazing incidence small-angle scattering in the present class.

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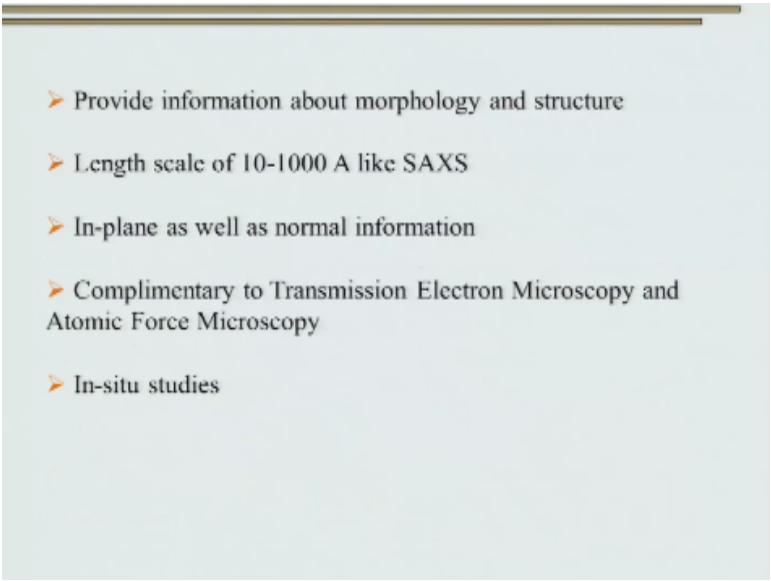
So as I had already mentioned grazing incidence small angle x-ray scattering is a variant of small-angle x-ray scattering but it is used extensively for carrying out characterization on the surface it has it was developed by Levin et al in 1989 so you can realize that this technique is not something that is pretty old in fact that there have been less than 15 years this technique has evolved however the development in this technique has been tremendous in the last 15 odd years.

And this technique is used extensively in almost all centered on sources all over the world because it is essentially applicable to study polymer films nano particle search interfaces implanted systems porous materials and deposited embedded or stacked semiconductor nanostructures so you can see the tremendous implication that GISAXS offers for characterization not only pertaining to semiconductor materials characterization but also for surface related issues.

Like surface chemistry as well as catalysis another important aspect that has been investigated extensively using GISAXS has been quantum dots which have been obtained by state of the art processing techniques like molecular beam Epitaxy and liquid beam Epitaxy the most important part and the biggest advantage that GISAXS offers is that we can really monitor the evolution of size shape and morphology as well as the distribution on the plane or a 2d distribution why the deposition is occurring.

So this way it offers us a tool to constantly monitor the evolution of these quantities nanoscopic structures and the ability to play with the processing parameters or rather the deposition parameters to control the size shape and morphology of the quantum or rather the nanoscopic entities to be processed.

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- Provide information about morphology and structure
 - Length scale of 10-1000 Å like SAXS
 - In-plane as well as normal information
 - Complimentary to Transmission Electron Microscopy and Atomic Force Microscopy
 - In-situ studies

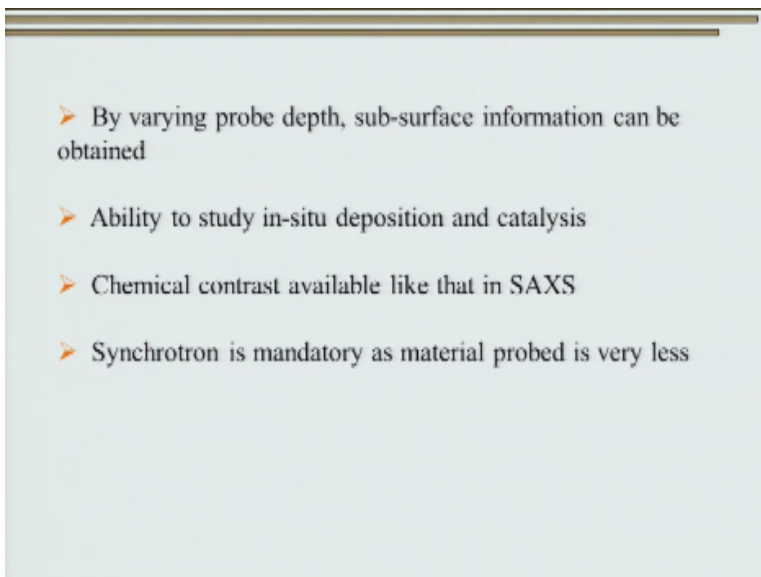
So not only does GISAXS provide information about the morphology it also gives us information about the structure of the material we would not be talking much about the structure part but I am just trying to touch upon this aspect just to let you know that GISAXS can give us some information about the chemical structure as well as the morphological structure of the material it gives us information in the same length scale as that of SAXS ranging from about 10-1000 Å.

In addition it can give us information about in plane since grazing incidence x-ray small-angle x-ray scattering essentially is a surface characterization technique it gives us information not only in the plane but also out of the plane or normal to the plane which is very important for doing what is known as x-ray reflectivity and like I had already mentioned in the last class small-angle x-ray scattering is complementary to say characterization techniques like SEM TM and atomic force microscopy.

Similarly GISAXS is also complementary to something like SEM and atomic force microscopy at the same time as we discussed in the last course or the last slide we figure out that GISAXS is

absolutely essential and absolutely state of the art when it comes to studying in situ studies on deposition of various materials.

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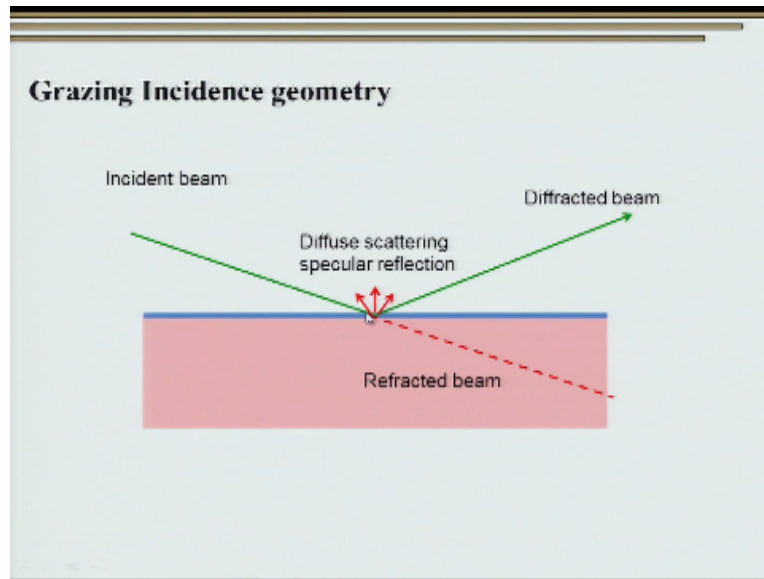
The best part about GISAXS is that simply by bearing the probe depth the depth to which the x-rays are penetrating we can study subsurface information we can obtain significantly important subsurface information using GISAXS this is particularly important for studying subsurface damage caused during say something like implantation the others an important aspect which is very important which is very peculiar to GISAXS is the ability to study in situ deposition and catalysis at the same time like we had discussed in the last class.

That small-angle x-ray scattering also provides us if not directly in an indirect way the chemical contrast between different phases we can also use GISAXS and separate out chemically distinct entities in GISAXS however having said that I hope you appreciate that in grazing incidence small-angle scattering x-ray scattering the entire diffraction is occurring from a very small volume of material and since the volume of material is very small the kind of intensity that we are going to get is also going to be very low and therefore we need a synchrotron source which gives us very high brilliance and intensity to obtain good amount of data using grazing incidence small-angle x-ray scattering.

In the last class we had discussed that for small-angle scattering synchrotron is essentially good I but however you can always do small-angle x-ray scattering using say a rotating anode or a

microphone costume however in order to do grazing incidence small-angle scattering it is almost always better to use a synchrotron source as the result of results obtained will be of high fidelity using a synchrotron source.

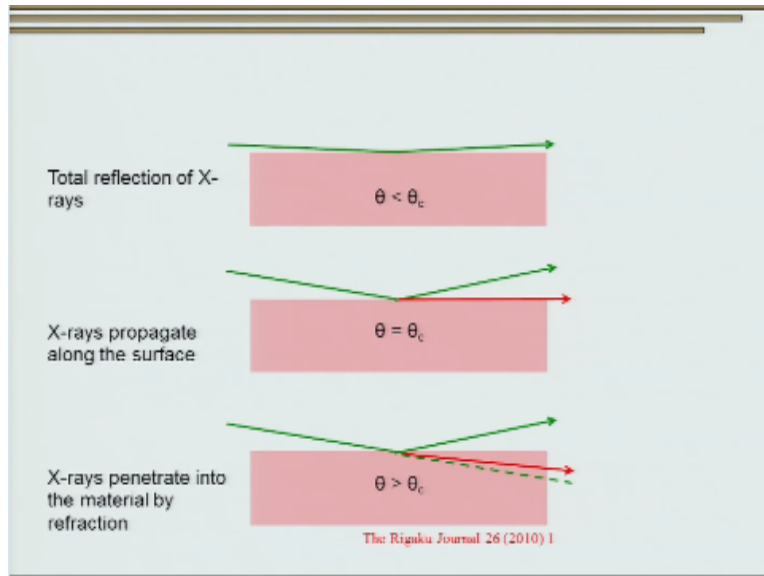
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So let us first try to understand what exactly or how really it works out in case of grazing incidence in diffraction so let us look at the grazing incidence geometry first so if you look at the grazing incidence geometry here I have shown or thin film deposited over the substrate here you can see I have kind of exaggerated this incident angle say θ_i and you can see how the incident beam on the substrate gets diffracted at the same time since it is incident on the sample at a very small angle we do get a diffuse scattering or due to specular reflection.

And this is if you can imagine it is going mostly perpendicular or at an angle away from the substrate plane at the same time we also have a refracted beam which is going over here now I hope you appreciate depending on the incident angle we can have various situations this is what is depicted in the next slide.

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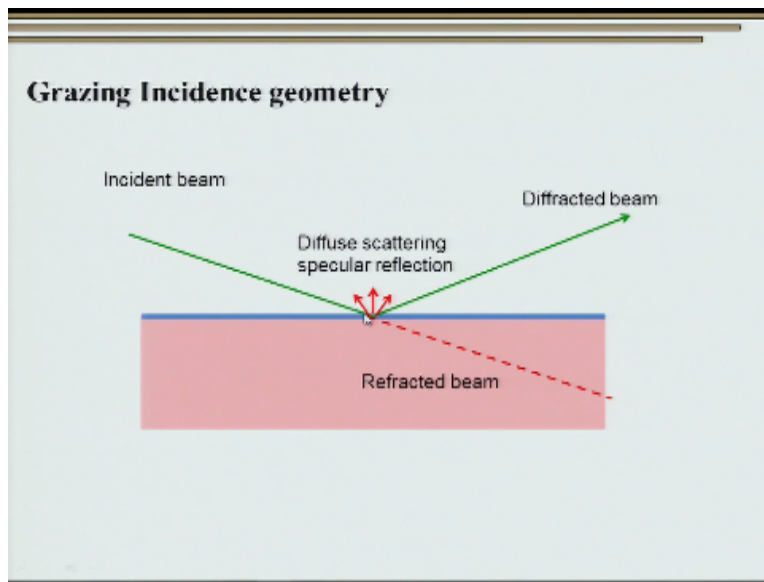


Here in it is shown that for a angle θ incident angle θ which is less than a particular critical value which will be described in the next graph or next image you see there is no refracted beam at the same time there is no beam along the surface, so there is just an incident beam we just bounce this off from the surface of the substrate so this is what happens below the critical limit which is the θ critical or θ_c in case of any substrate or any material however when you increase the θ incident which is over here you see that at a particular angle you do get a diffracted or reflected beam.

But in addition to that you get another refracted beam we just travels parallel to the surface of the substrate so this the angle at which this particular phenomena occurs is known as the critical angle this essentially ensures that if your θ is less than θ_c you do not get any beam that gets refracted however at $\theta = \theta_c$ you do get a condition where you your view does not get refracted but in fact it runs parallel to the substrate surface.

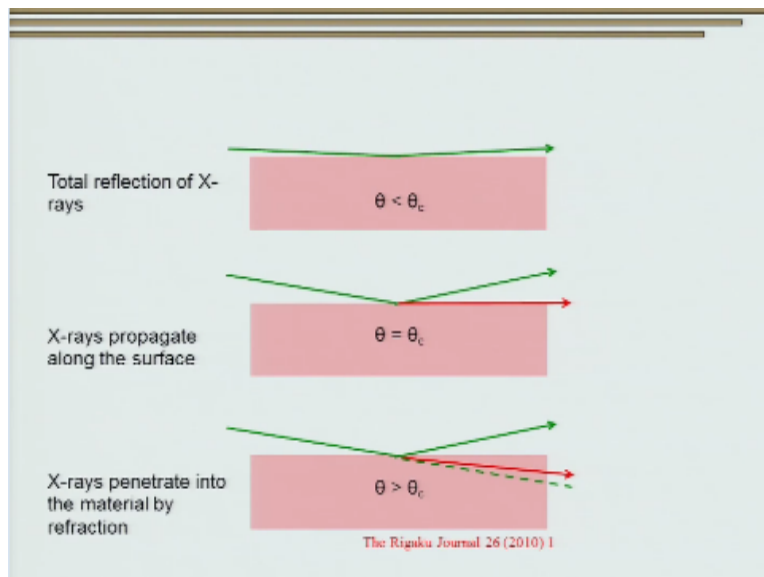
Now you can imagine that if you are at $\theta = \theta_c$ you are going to get some information of the surface what all you are having on the surface at the same time when you have angle which is more than θ which is more than the critical angle you do c that you will get a refracted beam also so now you can imagine by just that by just changing the incident angle we can get a lot of information from the substrate imagine now let us go to the previous slide and look at a realistic situation.

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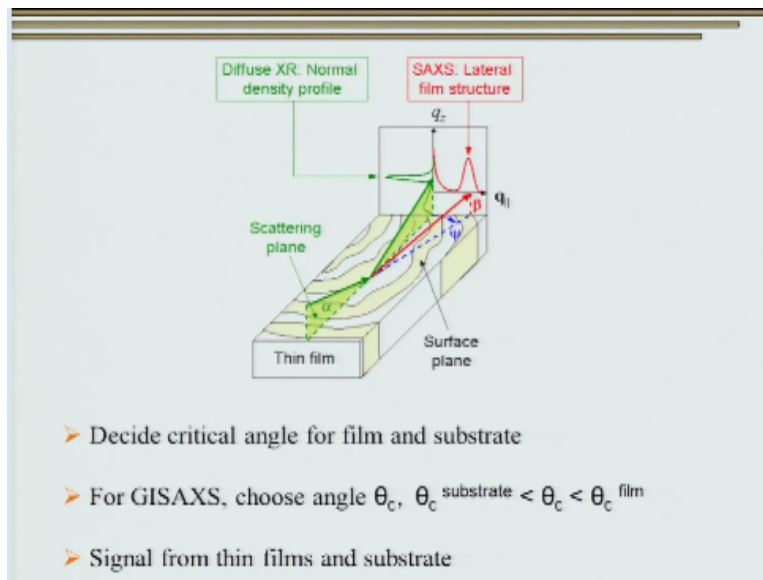
Wherein we not only have a substrate but also we have a thin film or say something like a quantum dots different morphology or say nano particles which are deposited on the surface of this substrate so you can imagine that by choosing a proper combination or rather a proper value of θ we can get different conditions.

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And obtain a lot of information which is pertaining to within the surface or normal to the surface or subsurface in grazing incidence geometry now this particular point is exploited extensively while doing grazing incidence small-angle x-ray scattering.

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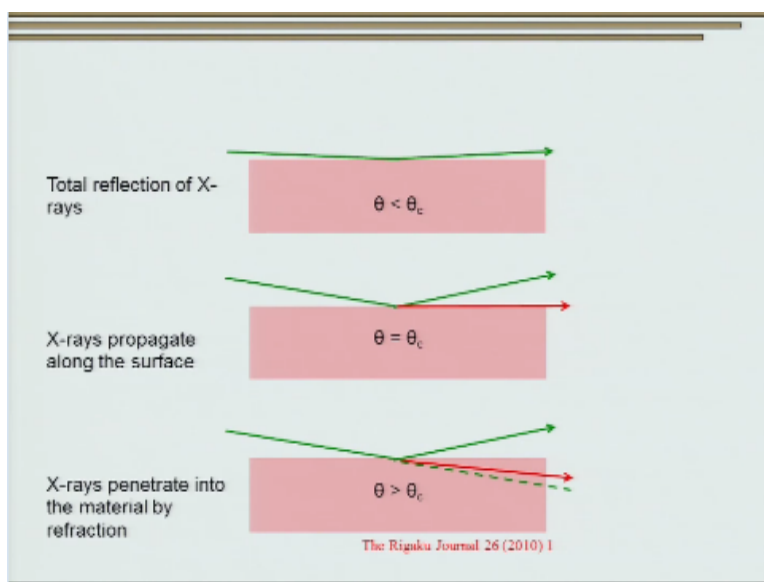
So in this figure we have shown how exactly a thin film is deposited on a substrate and how when a high intensity x ray is incident at and at a particular angle say α it gets reflected at a particular angle α_f which is not shown over here but we will have a look at it later and there is another angle Ω which is or rather ψ in which there is in plane diffraction or rather in in-plane are in plane diffraction so you can see that there is one condition where there is out of plane and in the other case there is a diffraction within the plane which is along the direction parallel to the surface of the substrate and therefore the scattering vector is given by q_{parallel} while the normal vector the scattering vector in the direction normal to the substrate plane is given by q_z .

Now how do we choose a critical angle for doing a grazing incidence small-angle x-ray scattering on a film deposit on a substrate so I hope you appreciate that we can have two critical angles over here one for your film or nanoscopic particles that are deposited on the surface and other for the substrate itself so we choose depending on what kind of information we need

obviously we are more interested when we are studying say a thin film or the nanoscopic deposited particles.

We are more interested in the in these particles and therefore we want all the information the diffraction information from these particles so we want that we do get some information from a we get maximum information from these particles therefore I hope you appreciate that when θ has to be greater than the θ critical from or θ critical of the particles or of the thin film now this is very essential to ensure that my x-rays get refracted let us go back to the previous slide and have a look.

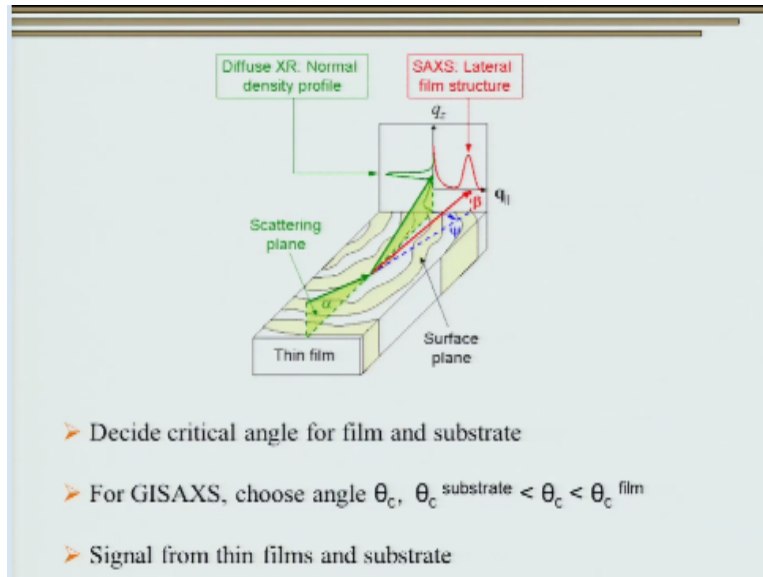
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So if my film if my $\theta > \theta_c$ of the particles this will ensure that my x-ray is passing through the particle and this can give me a lot of information about the structure as well as morphology of the particles however or thin film for that matter however if my θ_c is higher than that of the θ critical for substrate then my information what I am getting for the nanoscopic part nanoscopic entity either a thin film or a particle will also contain some information of the due to substrate refraction.

This is something that I want to avoid since my area of interest is only the nanoscopic film or the particles therefore I have to choose a critical angle for my thin film or nano particle on a substrate assembly such that the angle lies in between the θ critical of the substrate and that of the film.

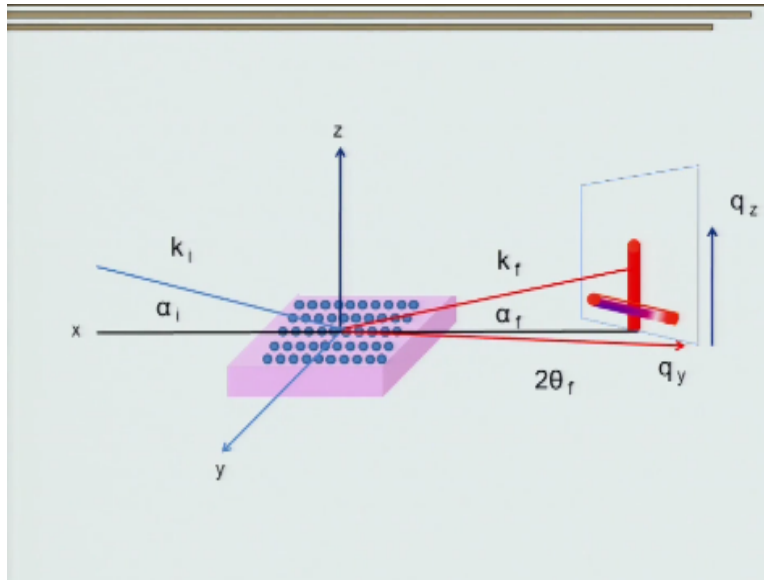
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Okay so that I get some signal from the rather most of my signal is coming from the thin film as well as I get some signal from the substrate but if there is no refraction occurring in the substrate now this is also very important if at all say I am doing implantation studies you know what happens during implantation during implantation we have heavy metal ions or heavy ions colliding with a surf with the substrate so you can imagine that there will be a lot of damage costs in the substrate depending on the energy of the ions.

And this damage can vary depending on the depth right the distance from the surface so if you want to study the subsurface damage that is occurring due to implantation you can always play with the incident angle the θ so that we get information from different terms so this is one parameter which is used routinely to control the information the extent of information that we are getting during greasing incidents small-angle x-ray scattering. So the entity that I was showing like how exactly it looks.

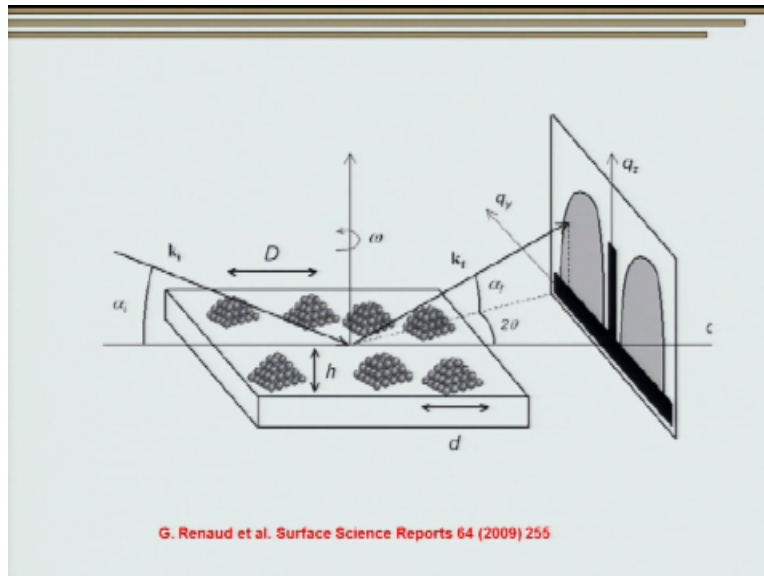
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So this time around I have drawn a set of a bunch of rather small nanoparticles on a substrate so we have the beam incident at α_i and the wave vector corresponding to k_i this gets scattered at k_f the deflection the scattering vector is k_f while the angle here is α_f at the same time this is normal the scattering here is out of the plane at the same time there is going to be some scattering which is going to be in plane and this is shown over here which corresponds to this scattering vector q_y and angle of $2\theta_f$ right.

So we have these two scattering vectors q_z and q_y one out of the plane and q_y which is in the plane right so we get information all the information related so you know that q_y and q_z will be in the reciprocal space right but q_y will contain all the information corresponding to what is happening in the two dimensions while q_z or q_z will consider all the information in the reciprocal space in the direction normal to the surface of the substrate.

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So I have another schematic which is shown over here borrowed from a very nice review paper which have extensively followed by Renaults et al so this shows essentially the realistic picture of what exactly is happening during GISAXS so you have the incident beam and you see all these nanoscopic things means we are really talking about very small dimensions means GISAXS is used to essentially proved very small dimensions of the order of few nanometers so the structure is essentially similar to like this and this essentially shows what kind of events that you can expect during GISAXS.

And what kind of signals that you can get here again it is shown you can see that this sample rotation is provided about Ω just to improve the statistics and this is how and we can have no down the value over here no down the pattern the scattering pattern as a function of Ω .

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➤ Incident X-rays at α_i are scattered along k_f in the direction $(2\theta_f, \alpha_f)$

➤ Corresponding scattering wave vector is

$$q_{x,y,z} = \frac{2\pi}{\lambda} \begin{bmatrix} \cos(\alpha_f) \cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f) \sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}$$

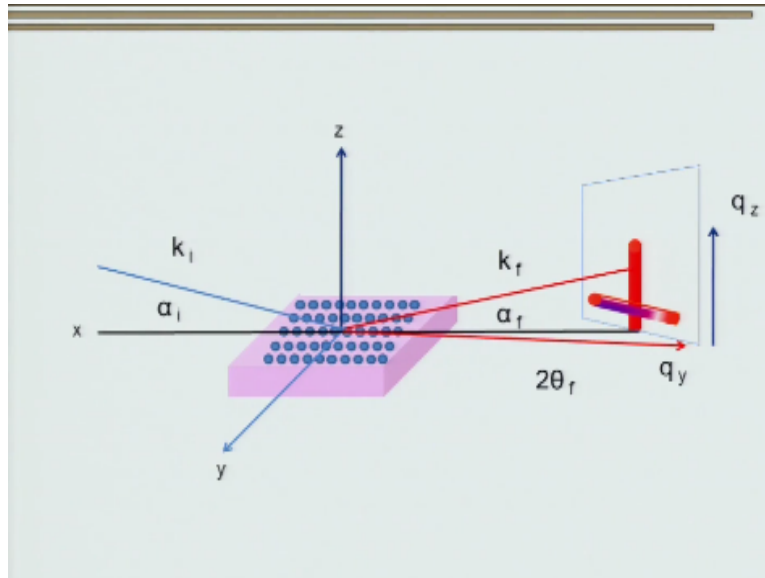
➤ Sample detector distance 1-4 m

➤ Distance may be as high as 12 m for GIUSAXS

Okay so let us now go into and understand try to just touch upon the physics of grazing incidence a small angle x-ray scattering well I would like to mention that it is a pretty involved subject and I am not going to touch upon all the details of you know the scattering or diffraction theory associated with grazing incidence small-angle x-ray scattering but what we are going to try and do is just to get a feel for things and see how the kind of knowledge that we have gained while deriving structure factor for normal diffraction as well as we derived what are known as the form factors right.

In the last class how these can be extended to understand how does grazing incidence small-angle x-ray scattering works so you know that incident x-rays are at α I are scattered along k_f in the direction $2\theta_f$ and α_f .

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Right like if you go back to the your slide you see that you know there is this k_r and there is two θ_f which is a cave in the direction $\theta\alpha_f$ and which is out of the plane as well as in the plane it is reflected at $2\theta_f$ right.

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➤ Incident X-rays at α_i are scattered along k_f in the direction $(2\theta_f, \alpha_f)$

➤ Corresponding scattering wave vector is

$$q_{x,y,z} = \frac{2\pi}{\lambda} \begin{bmatrix} \cos(\alpha_f) \cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f) \sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}$$

➤ Sample detector distance 1-4 m

➤ Distance may be as high as 12 m for GIUSAXS

So this is what is given over here you can always define a corresponding scattering wave vector using the geometry as $q_{xyz} = 2\pi / \lambda$ and this particular matrix remember this is in 3d now if you remember in small-angle x-ray scattering we also had a term which was a q what we got was $4\pi / \lambda$ and there was a $\sin \theta$ term if I remember it correctly.

Now you I hope you appreciate that we talked about this in small-angle x-ray scattering right like the angles we are talking about are going to be very small and since the angles are going to be very small in order to detect these very small angles the sample to the detector distance has to be very large therefore we looked that you know even in small angle x-ray scattering this distance was as large as 1 meter now when we are talking about the grazing incident scattering the same rule applies.

And we have a sample detector distance as large as 1 to 4 meters so this is quite cute however if you go to even what is known as grazing incidence ultra small-angle x-ray scattering where the diffraction occurs are at very small angle less than certainly one degree you see the distance can be as large as 1 to 12 meters but this is only possible or rather only used when we are using a synchrotron light source.

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- Scattering intensity in lateral direction

$$I(\vec{q}) = \langle |F|^2 S(\vec{q}_\perp) \rangle$$

- S is the total interference function
 - Describes spatial arrangement of objects on surface
 - Lateral correlation
 - Fourier transform of shape function of object
- $$F(\vec{q}) = \int_V \exp(i\vec{q} \cdot \vec{r}) d^3r$$
- Conventionally use Born approximation of kinematic scattering

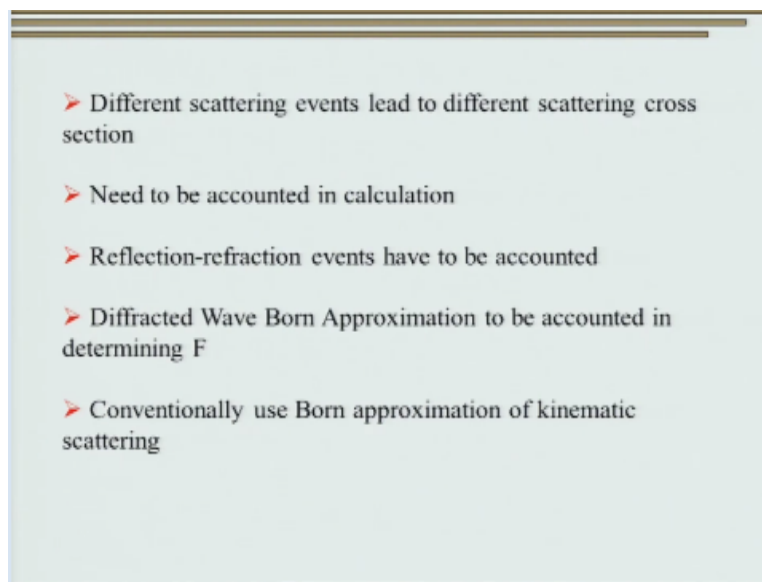
So you know that T scattering intensity in the lateral direction what all intensity that we are getting can be given is I_q and this I_q is related to the form factor F which is nothing but which still carries the information of the shape of the sample in the reciprocal space and your S_q which is known as the interference function this in fact is very similar to or to what is what we studied what is known as structure factor now this I hope you appreciate and understand that here we are talking only about to be structures.

So what all structures we have in 2d they can have lead to a particular structure factor like you have for simple say FCC or BCC you can do that and in fact we will be going through one example over there but the most important point is so our S_q carries the information about the spatial distribution right while the f carries the information about the shape of the particles right so the actual intensity that we are getting is a combination of these two and we know that this we had studied in the last class itself.

That the shape function what we are having so we can derive shape functions take the Fourier transform because you remember what all in the real space what we are having the particle or your yeah the particle or quantum dot for that matter is going to have a size shape and morphology in real space however you have to appreciate that the entire information is has to be mapped into the reciprocal space and therefore you we had studied that you know your reciprocal space is nothing but a Fourier transform of the real space right.

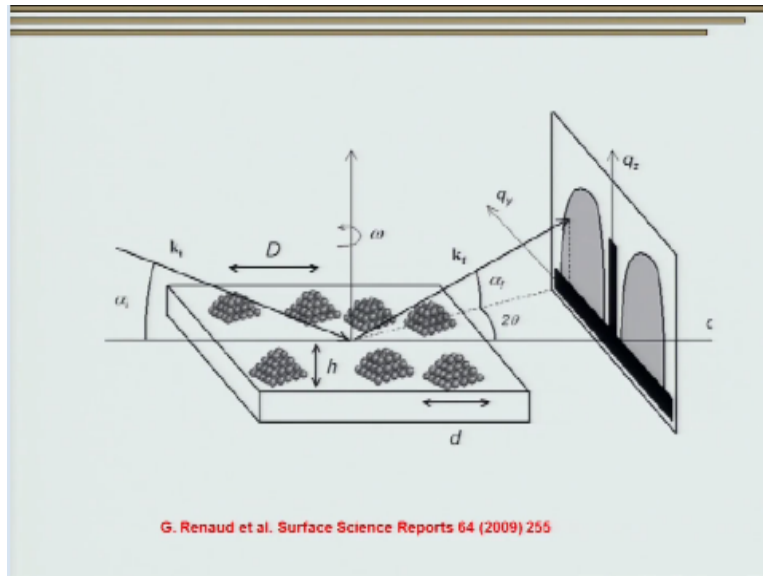
So all this shape size and morphology are going to be modulated in a particular way to obtain a particular Fourier transform so the size shape and morphology that we see in the real space is it is will be if you take a Fourier transform of this size shape you can data corresponding a Fourier transform which corresponds to a particular size shape of the particle in the reciprocal space at the same time when we talk about all these simple transformations you to keep one thing in mind that one thing which you had taken for granted was that all this involved scattering only once And that two kinematic scattering so this is what is known as a born approximation.

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- Different scattering events lead to different scattering cross section
 - Need to be accounted in calculation
 - Reflection-refraction events have to be accounted
 - Diffracted Wave Born Approximation to be accounted in determining F
 - Conventionally use Born approximation of kinematic scattering

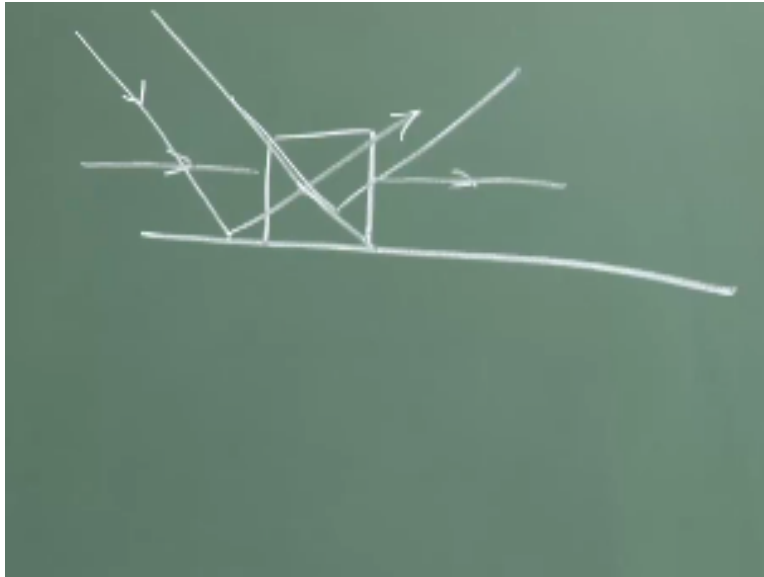
However I hope you appreciate that in GISAXS geometry the Born approximation may not hold true now let me just go back and tell you what exactly is born approximation so if you look at this particular image.

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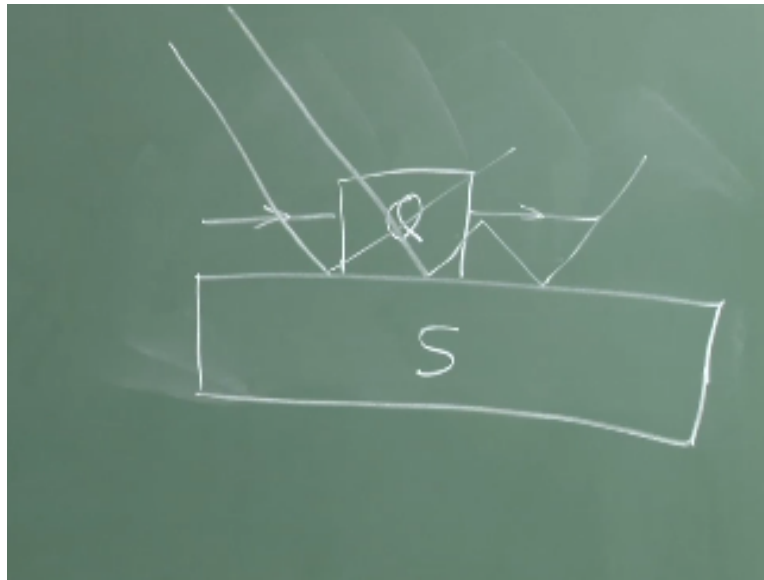
You can see that you know you just have one condition so that is one scattering right from one of these blocks or one of these dots of atoms or a cluster of atoms which we see over here it can be a quantum dot or a nanoparticle however this is not the only case that can be expected like we can have a case wherein let us assume that if you are incident at a different angle you get first reflected from the surface and then you bounce off and you go through this article right there is a distinct probability of this happening let me just go and show you what exactly I mean.

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So let if you go to the surface and we have say something like a pillar over here in case of born approximation we know that you know there is only single scattering while you know that in this kind of a case that is not necessarily true so we can have a situation where your incident x-ray first gets reflected from the substrate and then it gets scattered right and I hope you appreciate that there can be a plenty of other options that can happen right like you can go like this that reflected okay or rather go okay I will just like to put up this off I made a mistake here okay.

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So let us go back and have a look what exactly can happen in this geometry so this is something what we are having so this is a substrate right and say this is my something like a quantum dot so the born approximation essentially talks about single scattering event right single kinematic scattering.

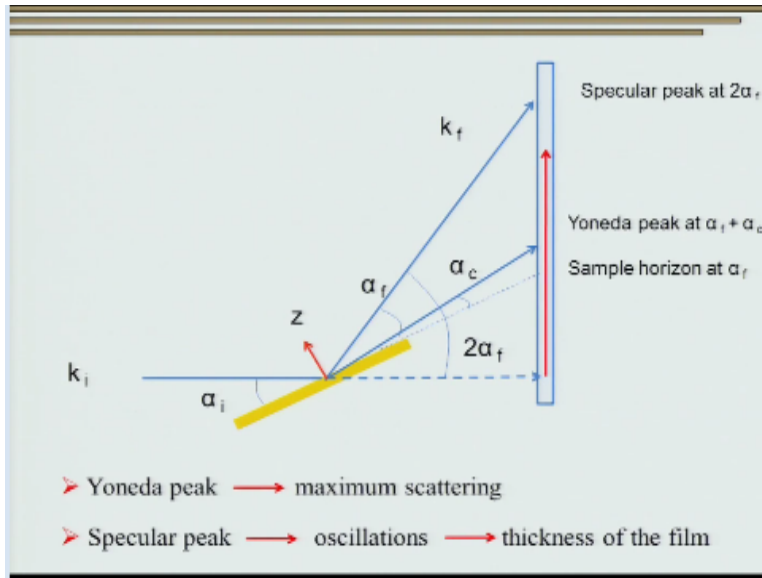
However in this case I hope you appreciate that we can have a situation where the beam gets first reflected right from the substrate and then it gets scattered or it can get scattered through this one right through your substrate and then again get reflected right so all these multiple scattering events can occur in the grazing incidence geometry. Therefore we do not it is generally understood that this normal born approximation of single scattering is not at all a valid and instead we do get different scattering events.

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- Different scattering events lead to different scattering cross section
- Need to be accounted in calculation
- Reflection-refraction events have to be accounted
- Diffracted Wave Born Approximation to be accounted in determining F
- Conventionally use Born approximation of kinematic scattering

That lead to different scattering cross section and therefore there is a need to account for all this in the calculation now this is very complicated and I am not going to touch upon it but this is what is known as or these Corrections considered all these events is accounted for in what is known as diffracted view born approximation and it includes entire examples or entire category of reflection and refraction events that can be that can occur during grazing incidence small-angle x-ray scattering.

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Right so let us again go back and look at the geometries I am and see all the angles what we are talking about are pretty small the α_i α_c or α_f are pretty small but just for the sake of simplicity I have kind of blown them up so that we can appreciate it so you can imagine that what actually is happening again the same image that your sample incident the x rays are incident at the wave vector k_i is incident at a k_i rather incident at an angle α_i .

So what we see is there is a specular peak right now the specular peak as I hope you appreciate gives you a lot of information in the this is all along Z right so this is q_z and this α of that you see that is a long queue wire so this gives you information about the in-plane information right in the reciprocal space while q_z gives you out of plane right so you get what is known as d specular peak.

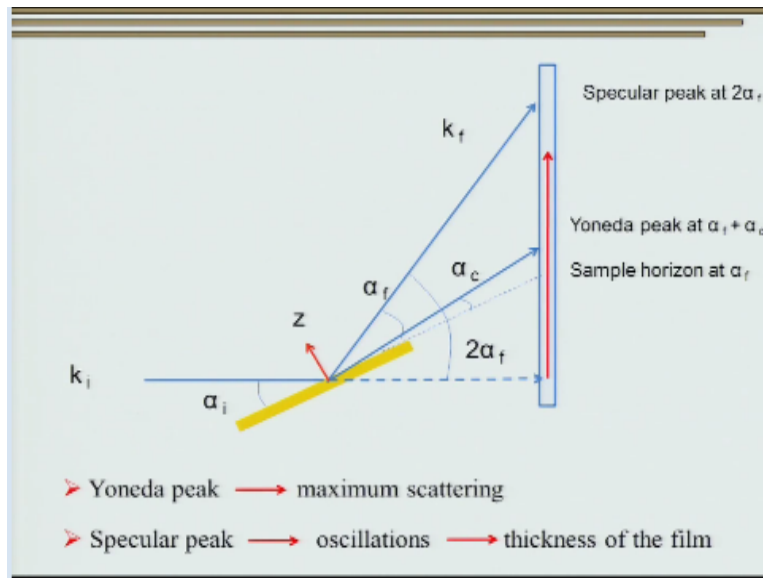
Now this specular peak gives you the information which is normal to the surface of the substrate right or film therefore it can do you information and specular as the name suggests can you information about say something like the thickness of the film right like and this is classically known as x-ray reflectivity while the second fig that you get is essentially what is known as the yoneda peak which gives you the maximum scattering in the Z direction now talking about the specular peak I hope you appreciate that in the form factors calculation we had seen Ahat how we get a lot of bumps right like you get first a valley let me just go and draw it.

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Right so this is something what we had got earlier so this was I versus q and this was correlated with the size of the particle in our small-angle x-ray scattering similarly we can use the specular peak that we are getting to measure say something like the period right if you are having thin film like what is the thickness of individual film so that information can be obtained using a specular peak.

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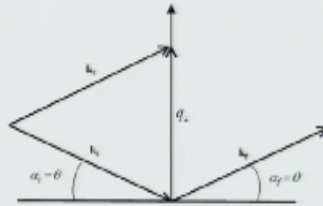
I will talk about in details in the next slide but what I want to want you to remember is that the specular as well as the Yoneda peak okay which occur which show diffraction in the Z Direction gives you a lot of information about in a direction perpendicular to the substrate of the film okay.

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➤ No information on lateral dimension in Specular peak

➤ Best to measure average thickness

➤ Specular X-Ray Reflectivity (XRR) if $2\theta_f = 0$

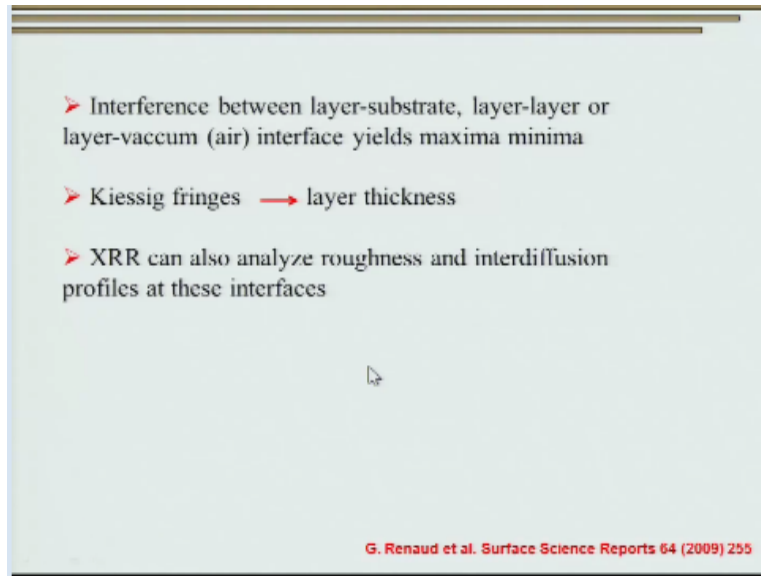


➤ Increase α_i and α_r symmetrically to probe reciprocal space perpendicular to the surface

So in these specular peak there is no information on the lateral surface there is only information for a die along the direction perpendicular to the plane of the substrate and it is best to measure the average thickness of all the particles of average thickness of the film that we are having and this gives rise to a technique known as x-ray reflectivity however I hope you appreciate that if you are interested only in obtaining information perpendicular to the direction or perpendicular to the plane of the substrate you do not really want any information about the plane of the surface.

And there the plane of the substrate and therefore to obtain very good x-ray reflectivity data you have to ensure that there is no scattering in this direction and this gives rise to a particular condition wherein you have $2\theta_f = 0$ so essentially this is achieved using this figure shows a very nice way varying you increase α_n and α_f right symmetrically to probe the reciprocal space perpendicular to the surface and while doing that you have to ensure that your $2\theta_f$ is actually 0 so that all the information that we are getting is only along the Z.

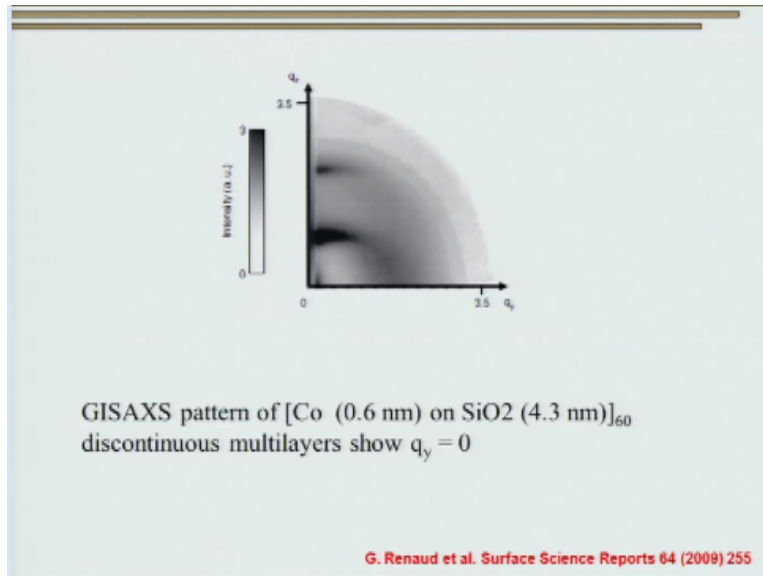
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And this is very important because the interference now why do we get all these speckle Pattern that I showed you this is due to interference between layer and substrate or if there are multi-layer film you get interference between different layers or layer and vacuum if there is only one layer and this gives rise to interference pattern like we have we get during say a young's double slit experiment and this leads to a maxima and minima.

And this interference pattern can be used again remember what information we are getting is in reciprocal space but once we convert it to real space we do get information about say thickness of the film so these are known as Kiessing fringes and this gives us information about the layer thickness having said that not only for you know very homogeneous you know thickness or homogeneous films and we can determine thickness we can also use using a lot of assumptions x-ray reflectivity to analyze roughness as well as inter diffusion profiles in various interfaces.

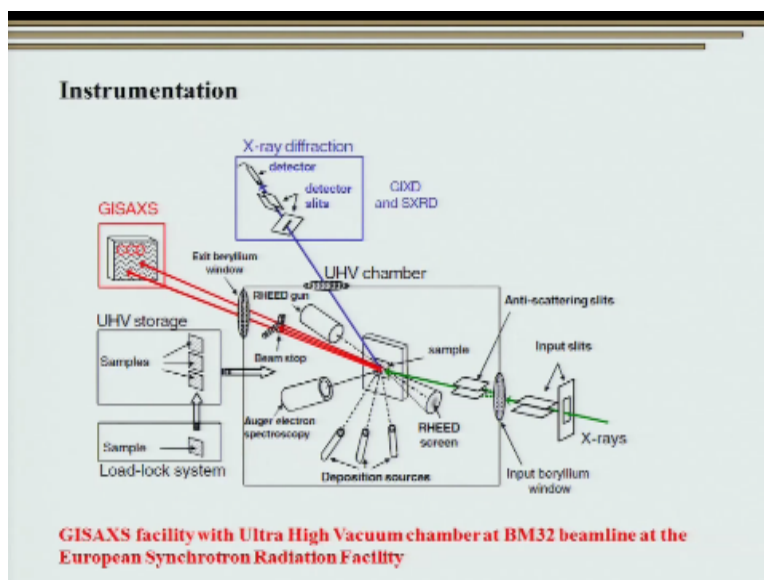
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So cheat or rather experimental result of GISAXS pattern of the cobalt 0.6 nanometer on silica 4.3 nanometer 60 such layers discontinuous multi-layer shows which you see it shows $q_y = 0$ here is q_y but you see your q_s it you see nice Bragg diffraction peaks corresponding to cobalt so you can imagine that how you can use so I am not showing the analysis part over here but using this you see this is in the reciprocal space.

So this will be say something like nano meter inverse so using this we can actually find out what is the period of the film okay, so now let us go and have a look at the instrumentation part update now when we talked about instrumentation of x-rays I hope you know what all is needed but having said that you one thing that needs to be remembered as had already mentioned is that for grazing incidence small-angle x-ray scattering almost always or synchrotron is needed.

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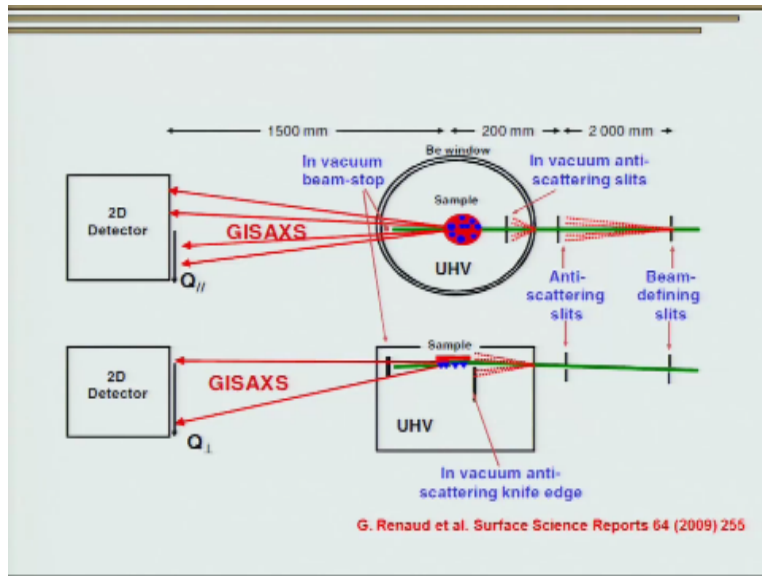


And therefore I am showing a schematic of the grazing incidence small angle x-ray facility with ultra-high vacuum chamber at BM 32 beam line at the European synchrotron radiation faculty so why do we have ultra high vacuum chamber well to utilize grazing incidence small-angle scattering to its optimum now ultra high vacuum chamber actually ensures that we can do a lot of thin film deposition and that is what is shown over here so you can do a lot of deposition sources right and study the evolution of these nano structure will be it nano film or say quantum dots in situ.

And really observe how they are growing how they are growing in vacuum so this assembly essentially shows that from a synchrotron we get a nice coherent parallel array of beam which is incident on your sample and you see over here we have a beam swapper because you know if there is a direct incident beam it can cause damage to our detector and you can see the GISAXS detector is placed right at very small angle to the incident with respect to the sample.

And you see over here we have this normal grazing incidence x-ray diffraction which is at a slightly an angle at a slightly higher angle but you see the incidence over here for your grazing incidence small-angle x-ray scattering is pretty small and this can be figured out as you see there almost in tea they are not in the same light but they make a very small angle with the sample right.

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So this shows another the same thing in a different assembly again note the distance the distance between your sample and the detector is huge and there is a there should be a beryllium window over here so that your X rays can pass and here you see that is almost normal you see how small the angle is ray and you see here you get all the information in plane information over here straight away on your 2D detector while out of plane information is over here to perpendicular right.

This is where you will get your specular pattern and your unit of T so again I am mentioning time and again that all these information these are all exaggerated figures you know these are all happening at a nanoscopic level and see this angle is very small very small and that is why that is the reason essentially why we keep this distance very large right so that we are able to see some difference okay so I hope you appreciate what all is the overall structure of grazing incidence small-angle x-ray scattering system.

And therefore these are not available in laboratories and are available on at various beam lines in a synchrotron source so how do they look like we talked about form factors and all form factors as well as the interference factor right they enter the interference pattern ray so it was rather let us go back and have a look.

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- Scattering intensity in lateral direction

$$I(\vec{q}) = \langle |F|^2 S(q_{\parallel}) \rangle$$

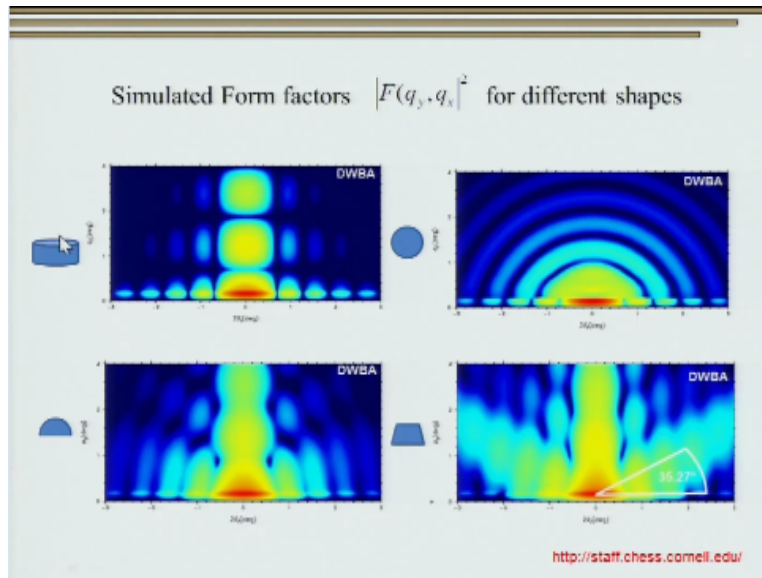
- S is the total interference function
- Describes spatial arrangement of objects on surface
- Lateral correlation
- Fourier transform of shape function of object
- Conventionally use Born approximation of kinematic scattering

$$F(\vec{q}) = \int_V \exp(i\vec{q} \cdot \vec{r}) d^3r$$

So this is your interference function right so we have form factor and we have interference function so let us see now how actually they coincide ray like this we had seen in case of small angle x-ray scattering that if the form factor is different how do we see different diffraction rather a different scattering pattern here in addition to the different scattering pattern we also get information about how those different particles or yeah those different dots are assembled in a 2D along the 2D substrate.

So this is how what we will try to understand so the form factor stuff we know that if you have a particular shape in real space how it can get transformed into the reciprocal space so this is just a simple Fourier transform of the shape under consideration.

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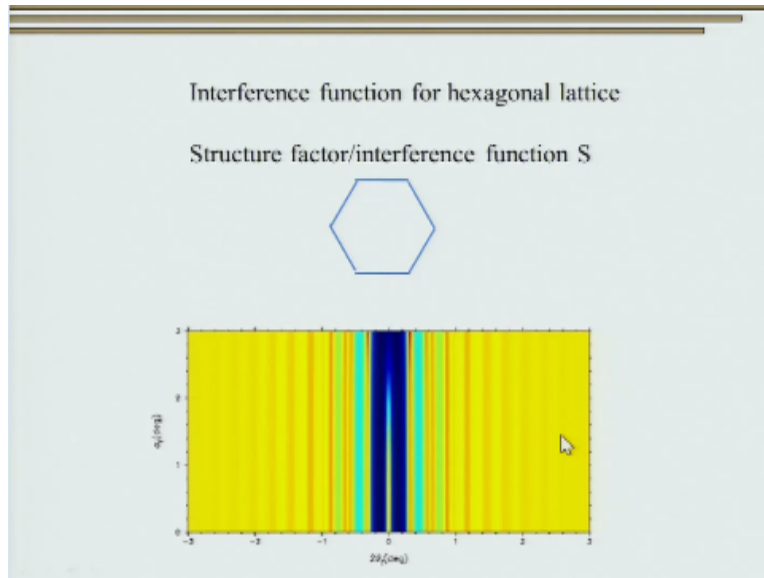


So here if we look in the first figure we see that if we have one a cylindrical shape we do get a particular pattern now I would like to mention that this takes into account the diffracted view born approximation right reflected wave born approximation which accounted for different reflection and refraction conditions so this diffracted wave born approximation ensures that you know this is the kind of pattern that we get now you know that if you are getting this kind of a pattern a particular kind of pattern this can be correlated with the shape of the particle right.

And you see there is a bit of periodicity now this periodicity comes in the reciprocal space because of various multiple scattering events right now if you go and have a spherical shape you do see that we get a completely different kind of figure so see depending on the two shapes right a cylindrical versus a spherical we can get different form factors right in the reciprocal space the same case or similar case is shown for a half sphere as well as for a for a prism.

So here you can see how different it looks and depending on this particular form factor we can find out what is the shape of the particles.

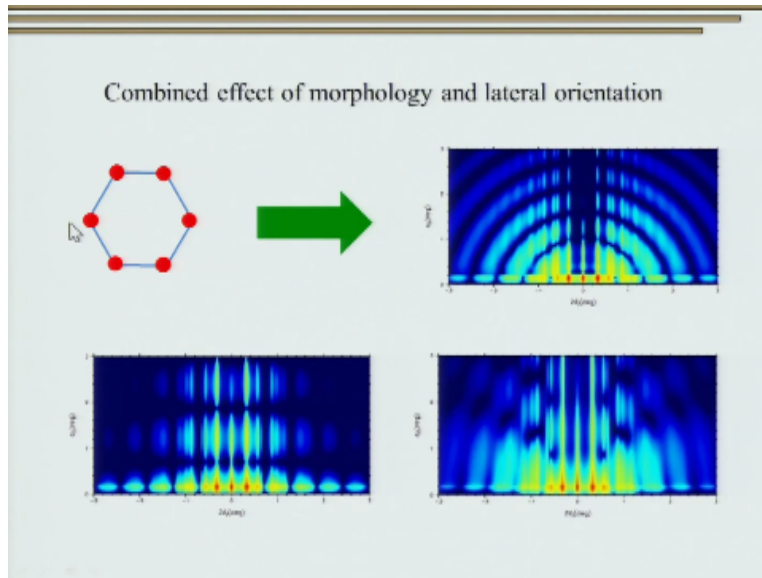
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At the same time I talked about right like how we are keeping the material are the nano particles in 2D and you rise to what is known as the interference function so therefore if you look at a simple exact shape articles that that means in other words the particles are arranged forming a hexagonal lattice we get the variation in along say something like your $\alpha f + 2\theta f$ in this pattern so you do get these fringes now these fringes that we are getting have a particular periodicity because of the hexagonal structure.

Now the actual scattering pattern that we are going to get has is going to be the superposition of this interference function and the form factor right like we had this equation $F(q_y, q_z^2)$ into s right that was your shattering intensity so this is where you see.

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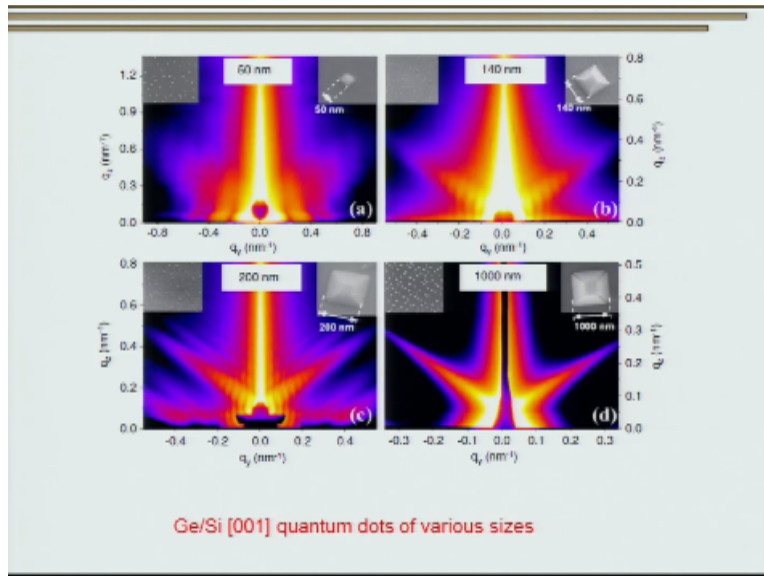


So if I have a hexagonal arrangement of my spherical patterns well I do get a pattern which correspond it to my spherical form factor right leg which we had derived over here so here we have a spherical form factor but the way it is arranged the lattice is hexagonal so therefore there is a superposition of these two things and we do get a very different pattern right.

So now this form factor I hope you appreciate that once you get your experimental pattern what we need to do is we need to assume shapes or make a first guess do simulations and get a good match between the experimental and simulated pattern to comment something about the size and shape of the particle similar in you know information or similar path for now can we try to guess what exactly we are getting.

So I hope you appreciate that we are getting the same period or rather similar yeah it is the same period so this has to be all hexagonal now if you look at this one now this to me looks like so this is what this is superposition of half sphere with the hexagonal one while this is superposition of half sphere the superposition of a prism or with the hexagonal lattice so therefore I hope you appreciate that for the last two scattering patterns particularly for the width and we are having a hexagonal arrangement however of particles however for the first case we are having a half sphere part in our rather a half sphere sitting at all the corners of the hexagon while for the second case which is shown over here we have a prism sitting at all the corners of the hexagon.

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So here again I have chosen one particular example and try to show you how exactly we can see in situ growth of particles so here again we are having the growth of germanium on silicon 001 substrate right so here you see that as the sample or as the quantum dot is growing we do see that there is a change in the scattering pattern and also all these things can be confirmed by doing say AFM or scanning electron microscopy.

So we can see that with the deposition condition we can look at how the you know how the quantum dot is evolving in shape as well as sighs now I would like to emphasize that you know for carrying out a SCM and all it is very difficult you cannot do it we have to stop at each and every stage and then do the sample however grazing incidence small-angle x-ray scattering probably offers the only technique wherein you can monitor you know the evolution of a particular you know the growth of particles or catalysis or chemical reactions occurring at the surface in situ. Right so this is the only technique that gives you real in situ information okay.

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Summary

- GISAXS technique is now well established to characterize morphology of nanoscopic and microscopic materials
- Complete information about nanoparticle sizes, shapes, distribution, faceting and spatial correlation
- In-situ studies offer an excellent platform to study growth, catalysis and self-organization
- Synchrotron radiation is a need
- Compliment results with SEM, AFM

So to summarize I hope you appreciate that grazing incidence is small-angle x-ray scattering technique is now well established to characterize morphology of nanoscopic and to a certain extent microscopic particles for microscopic particles we essentially do not really need a grazing incidence small-angle x-ray scattering.

But for nanoscopic particles this is probably the only technique to give you a lot of information while doing in situ experiments we get complete information about nano particle sizes shapes distribution faceting as well as spatial correlation however I would like to point out that this information is not a you know a straightforward information like diffraction all the information that we are getting is in the diffracted space and then that is that corresponds to the Fourier space right.

The best possibility of GISAXS is the in situ studies they offer an excellent platform to study growth catalysis and self-organization having said that synchrotron radiation is almost necessary I will make a very strong statement and say that you know synchrotron radiation is necessary for doing good quality grazing incidence small-angle x-ray scattering and having done grazing incidence small-angle x-ray scattering it is always a good idea to confirm your results with say other techniques like scanning electron microscopy or scanning tunneling microscopy or AFM.

Having said that grazing incidence small-angle x-ray scattering though not available are routinely offers a very sophisticated tool to study the structure of materials at the nanoscopic scale thank you.

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