Optical Sensors
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Lecture - 13
Plasmons – IV
Surface Plasmon: Field Enhancement, SPR Sensors, Sensitivity, Extra ordinary Transmission

Welcome to the 13th lecture of Optical Sensors course. In the last lecture, we discussed the intensity and phase modulation techniques. Also, we discussed the N-layer model to simulate plasmonic structures and not only plasmonic structures, but also multilayer optical structures. And, then we saw that why we require a particular thickness of the plasmonic film to have optimum SPR excitation.

Today, we will discuss what are Field Enhancements in surface plasmons and how we use SPR as sensors. We will discuss what are the sensitivity attributes in angular and spectral interrogation and then, if time permits, we will briefly discuss the field of Extraordinary Transmission, that is also a plasmonic phenomenon and it is very interesting. What happens to the field is that when you shine light on an interface and when you excite surface plasmons, the field at the interface also gets enhanced.

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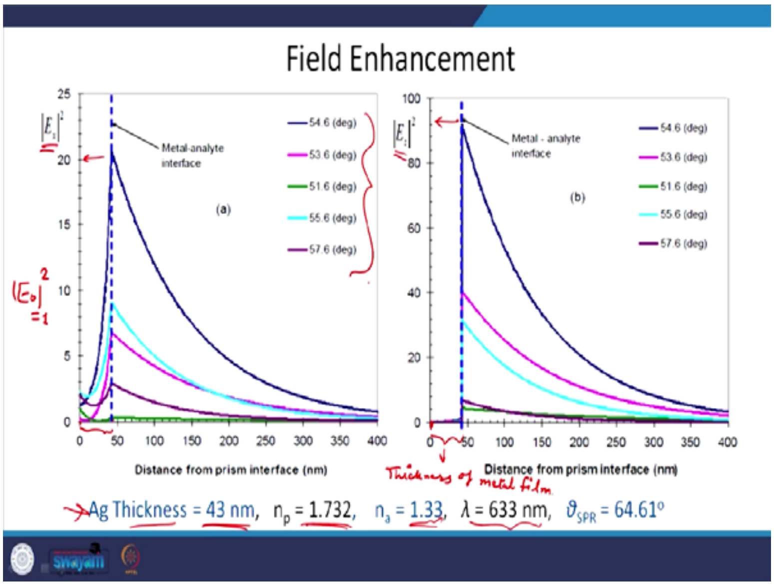

For example, here I have plotted the E x and E z components of the electromagnetic field for plasmons and this is the case from the prism interface. This is the thickness of the film here - this is thickness of the metal film and this is the interface for prism and metal. So, what you see here is that for incident value of E 0 is equal to 1 - E 0 mod square equal to 1; you will have about say 20 times or sometimes even 80 or 100 times of field that was incident at the interface; so, that is something very interesting.

It means plasmons behave like nano concentrators. I mean, they are nano sized films and they are concentrating all the light at the interface; also, you see that in x it is decaying exponentially. If you start from the metal and analyte interface, what you see is that inside the metal it decays very fast, while in the dielectric medium it decays slowly. You can see the penetration depth is - if you take 1 by e value, here you will have around 200 - 250 nanometers of the penetration depth; similarly, it happens with E z also.

Here, these are the parameters - silver thickness is around 43 nanometers, prism refractive index is 1.73, analyte refractive index is 1.33. Analyte is water in this case. The wavelength of the incident laser is around 633 nanometers and theta SPR - the Surface Plasmon Resonance is occurring at 64.61 degree. So, you see that this is the angle of incidence from the prism side.

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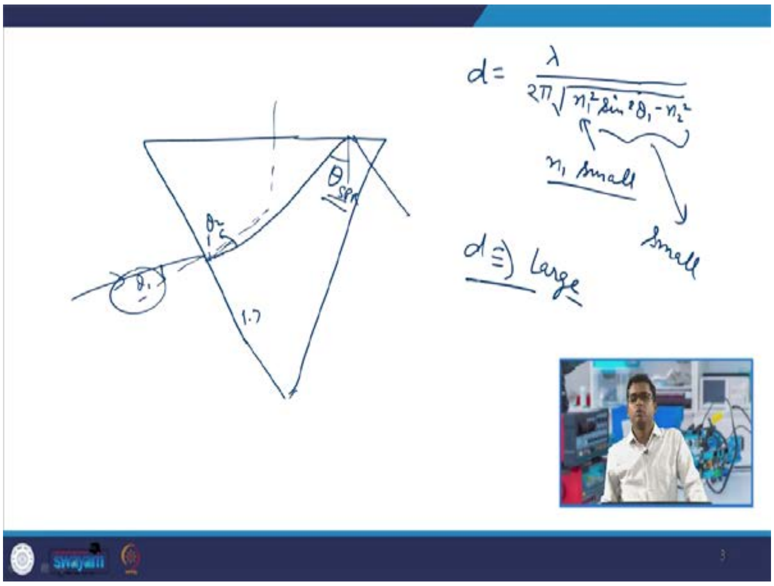

Mind it! When you are doing this measurement, basically, it is like this. There is an interface here. Suppose, you incident at an angle theta 1 here, it will be - since it is from air to prism 1.7, it will move towards the normal - that will hit here; somewhere here. I am a bit poor in drawing; this is theta 2. This angle will be larger even from theta 1; so, this is the actual angle theta. So, we are talking about this theta.

This is the theta from the prism side - this is theta SPR which is happening here at this interface. So, you are measuring basically theta SPR; so, at theta SPR this theta 1 will be different - it is not that theta, ok. What you see here is that for this angle you have maximum enhancement; that means, that you are at resonance, ok. So, when you are at resonance, you will have maximum enhancement of the electric field and that is because of surface plasmons.

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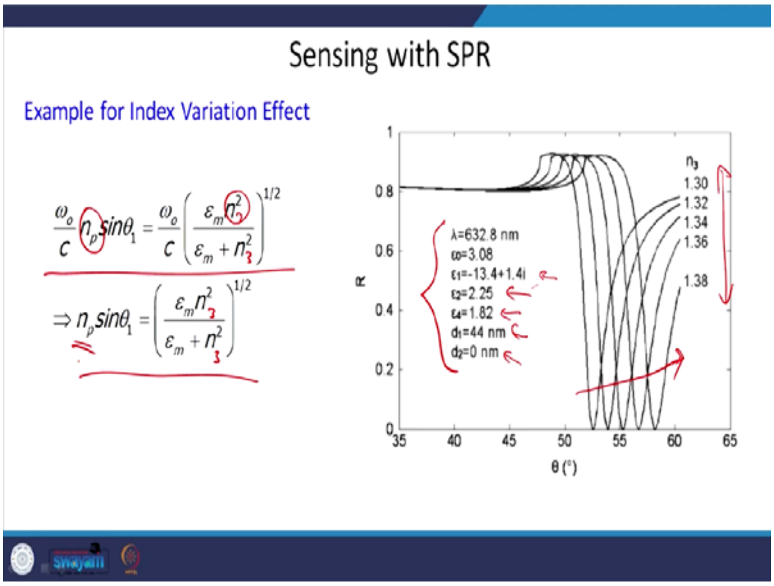

What happens with the SPR sensing? We already discussed that a bit. We have simulated this kind of structure - you know, you have multi-layer structure: you have d 1, d 2. And, then epsilon 1, epsilon 2, epsilon 3, epsilon 4, epsilon 0 all this and you see that with an increase in the refractive index value, there is a shift in resonance. We remember that the surface plasmon excitation condition was given by this. This was the refractive index of the prism.

This is the refractive index of the medium here, here it will be n 3 in this particular case and if you can out cancel omega 0 by c, then you end up with this term. So, we will come to this and we will see what it means. When you arrive to this condition, only then you will have a surface plasmon resonance and when you change the value of n - here n 3, you have to change theta 1 if you are keeping the n p fixed. That is how you measure the change in theta.

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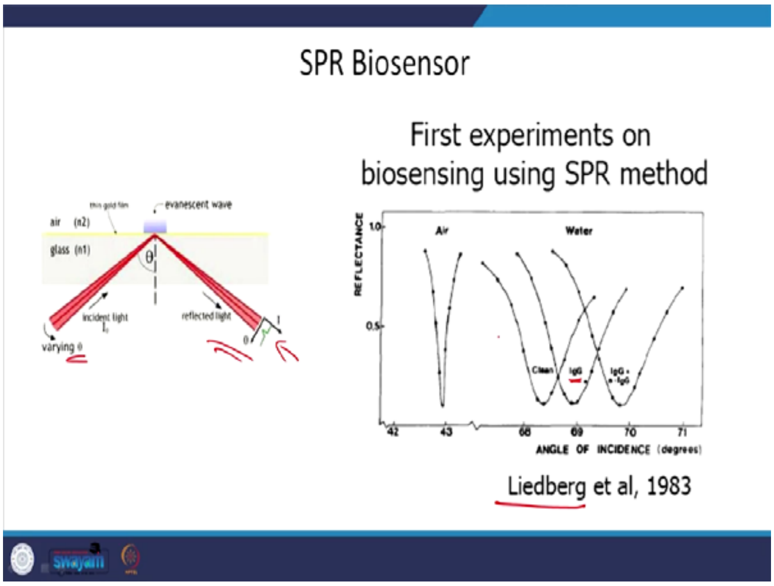

The first experiments on bio-sensing using SPR were done by Bo Liedberg - He is a leader in this. And what he did actually is that he had evanescent wave from the air glass interface and this evanescent wave probes the biological sample. So, while varying theta in the incident light, you measure the reflected light and then from there you conclude the resonance angle, that is what he did. And, you can see that for immunoglobulin G - two different samples, he had two different resonances. This was the first report on bio sensing using SPR, ok.

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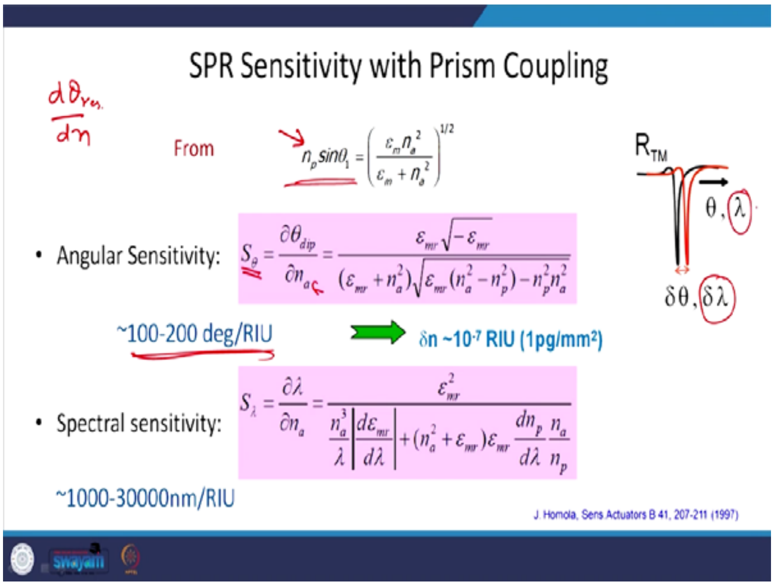

What happens to the sensitivity? Again, I come to this same expression and if you are doing the angular interrogation what we do is that - d theta by d n; now here we have put n a for the analyte. So, it will be d theta by d na - theta resonance actually - at resonance what will be the angle. To calculate the angular sensitivity, what to do is that you differentiate it with respect to n. So, it will be like d theta by d n and you end up this relation.

And, if you put roughly the values for epsilon m r, which is the real part of the metal dielectric function and n p is the, again, prism refractive index, n a is the refractive index of the analyte, then you get about 100 to 200 degree per RIU; that is a huge sensitivity. So, it can detect basically delta n values about 10 to power minus 7 refractive index unit, which is about 1 picogram per millimeter square - very small! Other way of doing that was measuring change in lambda. What you to do is that you calculate spectral sensitivity.

It will be like d lambda by d n a and you end up with this relation. And, the sensitivity comes about 30000 nanometer per RIU. Can you believe it!! - unprecedented sensitivity. You can go 10 to power minus 7, 10 to power minus 8, 8th decimal place of the refractive index value - it can measure this change; 7th or 8th decimal place – it is very sensitive. So, if you have a sensor surface, where a molecule comes and attaches on it -

even if it makes say difference at the 6th or 7th decimal place of the refractive index, it can be detected using SPR - that is what we are doing.

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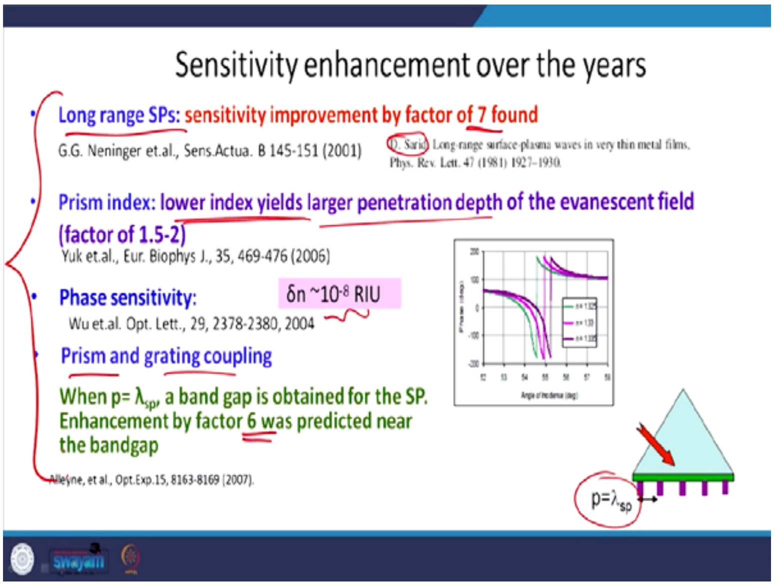

So, people have tried to enhance the sensitivity further and over the years. Now, someone, who was, actually, Dror Sarid, who reported long range surface plasmons and improved the sensitivity by a factor of 7. If you decrease the index of prism, basically, the penetration index becomes larger. So, you can have evanescent field more, which means that you can increase the sensitivity by a factor of 2.

Again, I told you that phase sensitivity is very high, and it can detect changes about 10 to the power minus 8 RIU. If you remember the phase curves, they were like this and since this is very sharp, any small change can also be measured. That is why, it has very high sensitivity. Then there is another report using prism and grating coupling and in this kind of configuration, what you have - that you use a grating and, you shine from the prism side. When the p is equal to lambda sp, a band gap is obtained and enhancement factor of 6 was predicted near the band gap. There are a few reports where people try to enhance the sensitivity by using different configurations and interrogation techniques. Here prism index thing - if you remember, d was equal to lambda upon 2 pi under root n 1 square sin square theta 1 minus n 2 square.

If n 1 is small, then what will happen? This difference - this will be small; d will be large. So, if the prism refractive index is small, you will have large penetration. Large penetration means the interaction volume is large; when interaction volume is large the sensitivity is large - that is how you correlate these, ok.

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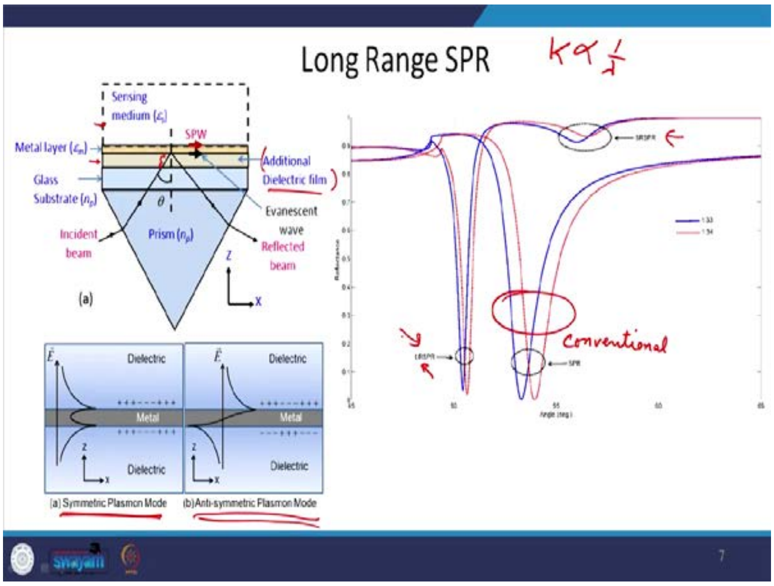

What happens in long range SPR? Why is it highly sensitive? What kind of configuration it is? Let us see what it has. In a Kretschmann configuration what we had is that, we had a metal layer directly on the glass substrate or prism, but here you add additional dialectic film between the glass plate or maybe prism and the metal layer. So, what it does actually is that, since the wave vector is getting enhanced by the prism and this is very thin layer, it does not make any difference to excite surface plasmons at both the interfaces.

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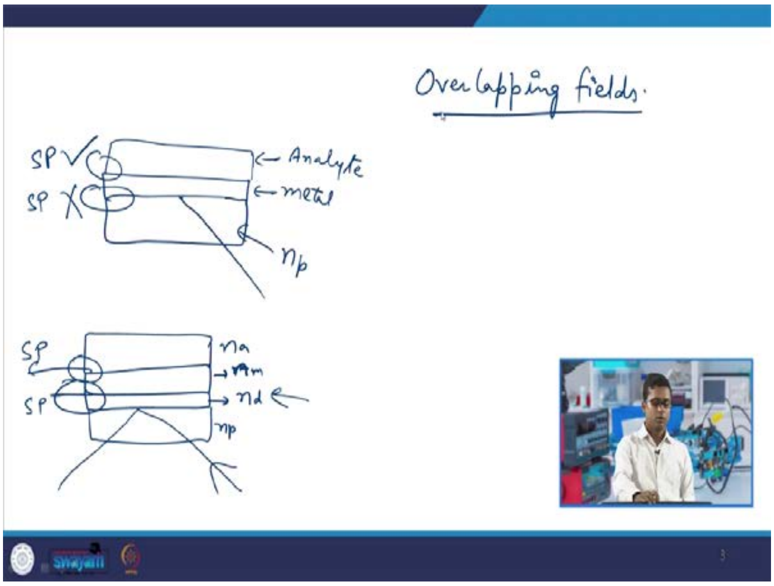

So, if you remember - when we are considering the prism configuration here, let us say that we had only 3 layers; so, you have one layer, then metal. It was n p layer, this was metal and this was analyte. You remember, that light coming from this could not excite surface plasmons here -no. It could excite surface plasmons only here. Here you have SP, here you do not have SP. Now, what I have? I have this layer and again a layer, now here I have n p, here I have n dielectric then n m and then n a; n p is the prism.

There is now additional dielectric layer. This is the refractive index of the metal n m and n a is the analyte. So, the wave vector here is getting enhanced, but it is exciting surface plasmons at this interface, here also SP and here also SP. So, now you have two surface plasmon modes. What will they do? Because, they are very close, they will have overlapping fields. If you consider a symmetric case, like IMI case - like you have a dielectric here, you have a dielectric here also.

So, you can consider it like this, if their electric fields are super imposing in phase, then you will have symmetric plasmon mode. If they are interfering out of phase, you will have antisymmetric plasmon mode. So, now, you have two plasmomic modes and then they super impose and give you two new plasmomic modes - those are called super modes, plasmonic super modes. So, you will have either symmetric mode or anti-symmetric mode.

When you have symmetric mode, it will have enhanced electrometric field at the interface. The wave vectors are adding in phase; so, you will have larger wave vector than the SPR for symmetric case. And, anti-symmetry case - you will have smaller wave-vector. k is proportional to 1 by lambda - wave vector. So, if one has larger wave vector; that means, they have smaller wavelength.

That is why here, what I have shown is the conventional SPR - this one, this one is long range SPR and this one is called short range SPR. So, when you add an additional layer between the prism and the metal, you will have two plasmonic modes; plasmonic super modes - one will lead to long range surface plasmon resonance, other one will have short range surface plasmon resonance and, they have different sensitivities also.

I told you that at larger lambda, it will have larger penetration depth. That is not the case here; long range SPR has larger penetration depth. It travels to large distance, it has larger sensitivity, it is all beautiful and short range SPR has shorter penetration depth and small sensitivity. If you want to detect a bigger analyte you use long range SPR, if you want to detect a smaller analyte, short range SPR. There are other techniques also to improve the sensitivity and that is nearly guided wave SPR. It was first reported by Atef Shalabney and Ibrahim Abdul Halim in Optics Letters 2012.

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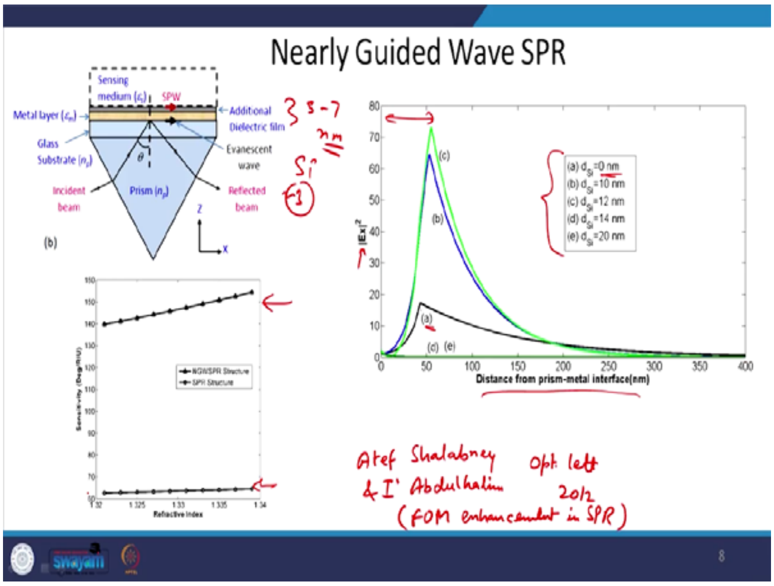

You can see the Figure of Merit enhancement - FOM enhancement and SPR, something like this. What they did actually is that on top of the metal layer they put additional dielectric layer. So now, they did not embed it in the middle, they put it on the top and its thickness is only few nanometers say 5 to 7 nanometer and it has high refractive index. They chose silicon, which has around 3 refractive index. So, what they saw is that you have this surface plasmons, if you add a thick layer there - what happens?

If you added thick layer of dielectric film on the metal film, it will excite surface plasmons and that can under suitable conditions be guided into that dielectric layer. That will be guidance surface plasmons. But here, since it is only 5 to 7 nanometers 10 of nanometers, you cannot say that it is guided SPR, that is why they called it nearly guided SPR. It is not actually guided, but somehow it enhances the electromagnetic field because, there are back and forth reflections here - of the light; so, it is getting to enhance the electromagnetic fields.

You can see here what you have done is that we have plotted here the electric field component in x direction with the distance from the metal prism interface. Up to 50 - this was the first case with 0 nanometer of silicon. So, this is pure surface plasmon case, you can see that around 20 is the electromagnetic field enhancement. When you add a layer, say, about 10 nanometers you see the blue curve, 12 nanometers is the green one and then again if you increase, it will start decreasing. So, there is an optimum condition for nearly guided SPR and at that optimum condition you will have highly enhanced electromagnetic fields.

It is about 4 times enhancement - more than 4 times enhancement, something like this. About 4 times enhancement is in the electromagnetic field, which improves the sensitivity. Here you can see this curve is for SPR sensitivity and this one is for nearly guided SPR; as you can see that the sensitivity is about 2.5 times high. So, there are two ways: either you have this long range SPR or you can have nearly guided SPR for that purpose.

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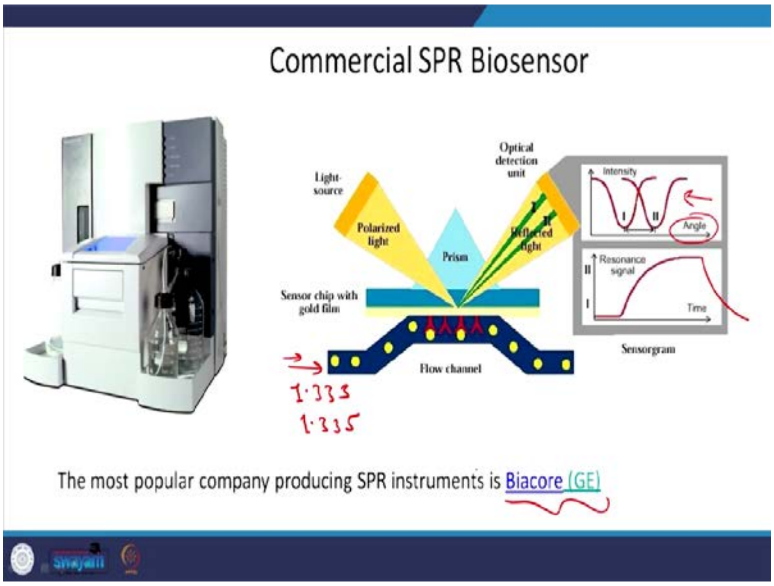

There are other commercial SPR biosensors and in these ones what they do is that, they are doing SPR and then they are do automation to keep on changing the analyte in the flow channel. And, they continuously measure the change in intensity or any other resonance parameters which we discussed earlier and then they make a sensorgram. With time, if you are adding something, say, suppose you had refractive index 1.33, now you added - it became 1.33 3; now it is 335. This small change will get reflected here with time. Now, if you wash it, again it will come down like this - that is how they make a sensorgram.

The most popular company for producing this kind of SPR instruments is Biacore, which is now purchased by GE; so now, it is GE Biacore.

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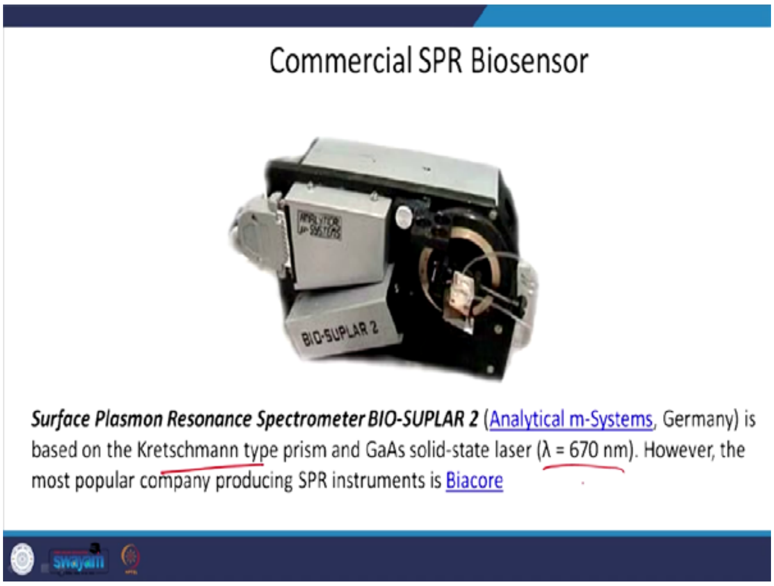

Then there are other companies like one from Germany, where they are again using the Kretschmann configuration and you can see here there are two arms. They are using a solid state laser and it is a relatively cheaper one.

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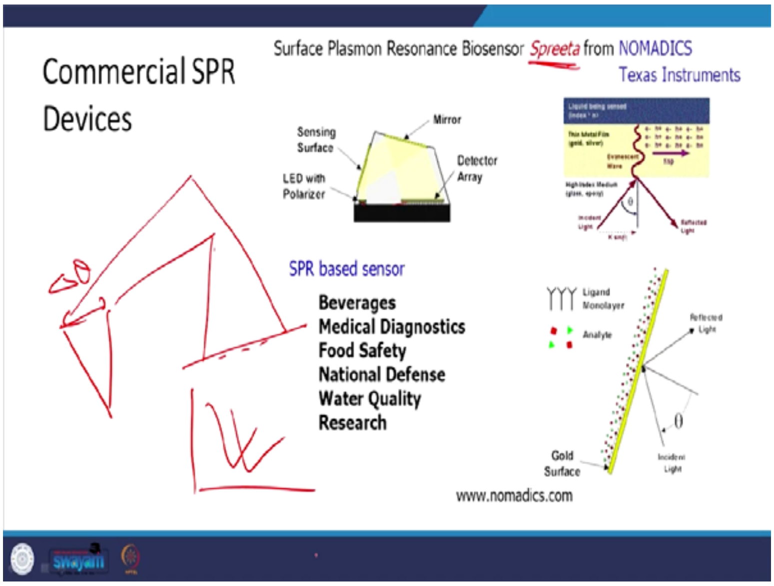

Then there is Spreeta from NOMADICS, where it is all integrated in a box; so, you have a sensing surface here, you have LED with polarizer. So, it basically sends all the angles and then mirror folds all this one and then you have detector array. You are not doing SPR imaging, no SPR imaging here.

But, when there is a attachment of any ligand or mono layer here - basically you are not changing the angle, you already fixed this range of theta - delta theta you fixed it. So, whatever you are getting from here, basically after the mirror you measure on the detector array right, it was changed the band; because of the binding over it, every time the resonance will change, something like this happens.

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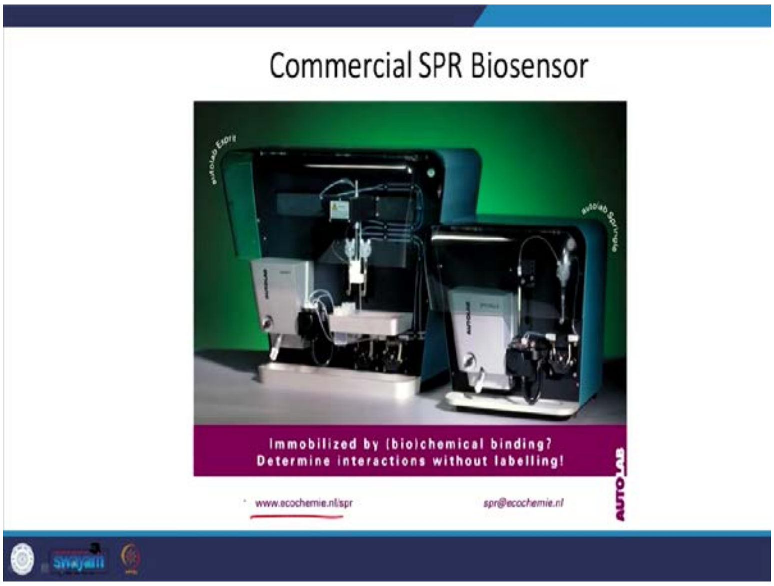

There is another commercial SPR biosensor from Eco Kimi, it is a Netherlands company, and this becomes very costly because, they put lots of automation in it. Doing it, then putting other samples, then washing it; all it is automated. You just put all the samples and it takes care of everything - all the measurements and the correct calibration curve.

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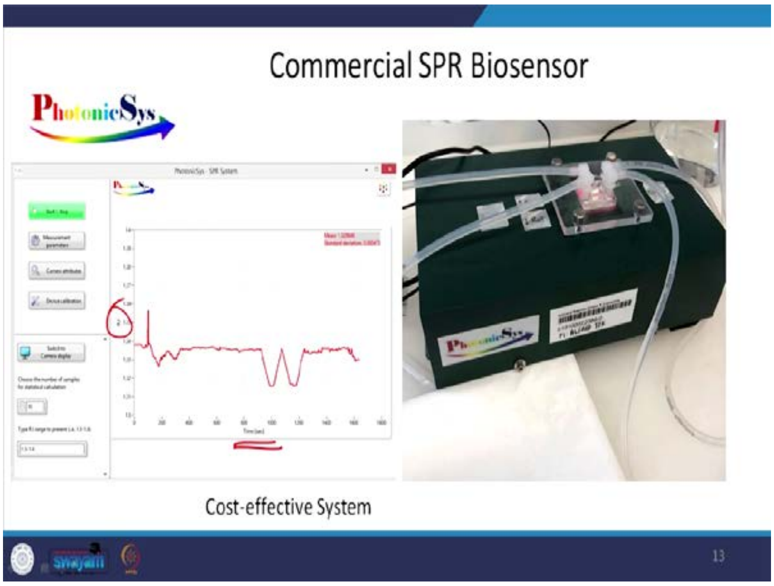

And, this one is a very cost-effective system. It was developed by, again, Professor Abdulhalim in Israel. It is a very cost effective a sensor. You can see here that is a very small and handy and it has a flow sense here. So, you can still use it to monitor the flow of analytes in real time. So, here again it is with time and its measures the refractive index up to 8th decimal place.

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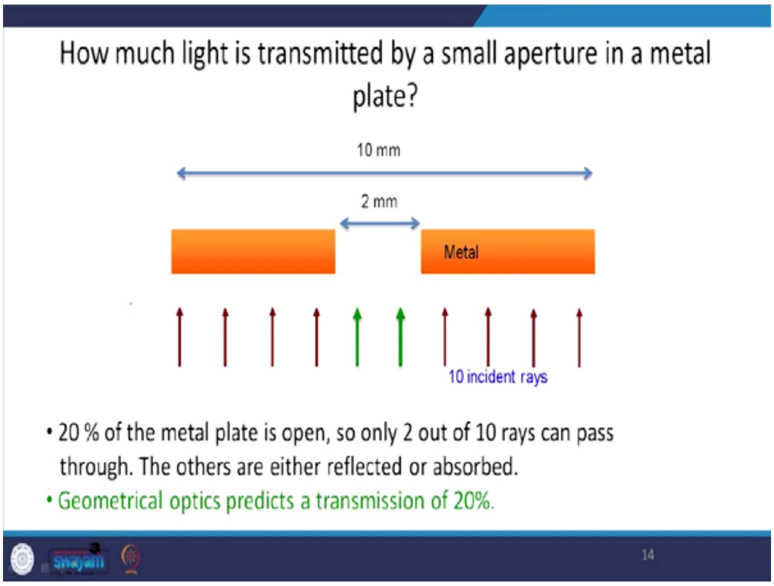

Till now we discussed SPR, how to use it for sensing and what are available commercial SPR bio sensors. Now, let us try to understand what happens when you have a small aperture in metal plate. Suppose I have a big metal plate of 10 millimeters and 2-millimeter hole it is having and if I send 10 rays what will happen that only these two will pass, others will be blocked - is very simple, right! So, only 20 percent of the metal plate is open, 2 out of 10. So, only 20 percent will be transmission - that is what geometrical optics predicts, ok.

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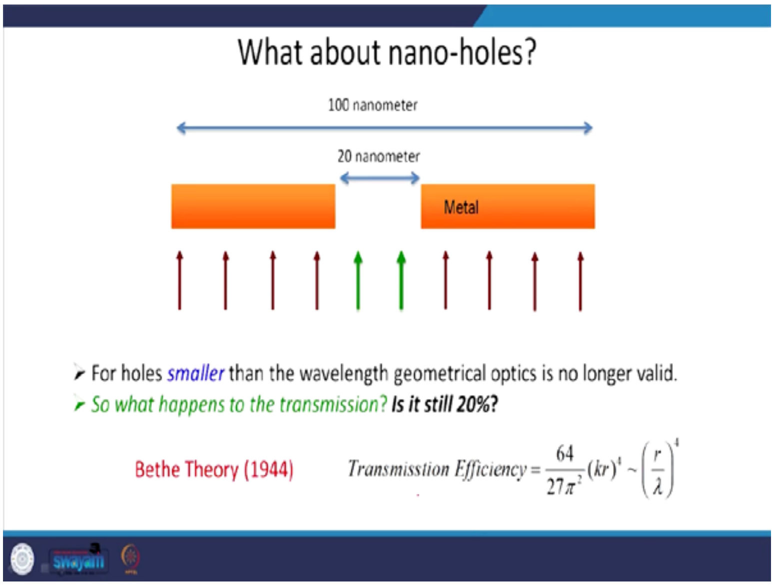

Now, what will happen if I make all this nanometer sized - say about 20 nanometer hole in a 100 nanometer film? Is it still 20 percent? Now, remember we have holes which are smaller than the wavelength of light - 20 nanometer hole. In 1944, Bethe predicted that the transmission efficiency of such kinds of structures is inversely proportional to lambda. So, if you have r much smaller, the transmission efficiency will be 0, practically 0; it has to be 0, that is what he predicted ok.

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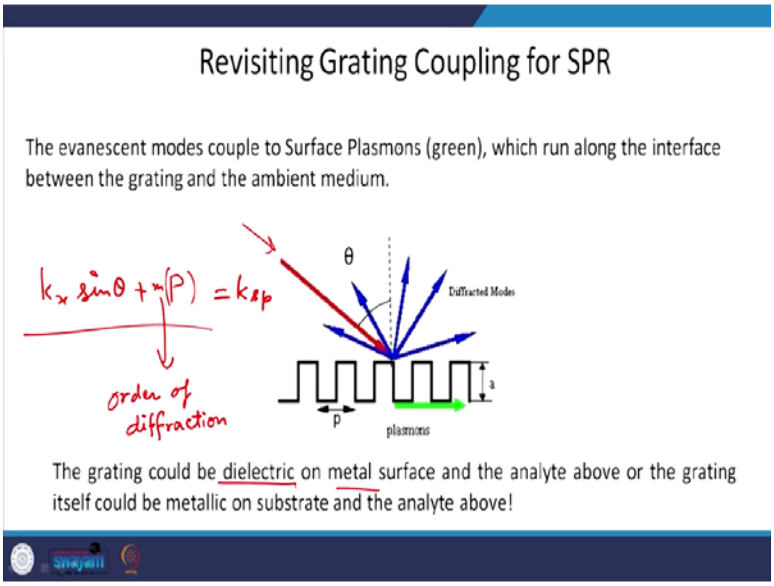

Before we move further, let us revisit what we discussed in grating coupled SPR and what we said - that you have grating kind of a structure. And, you incident at an angle theta, what happens actually - that you have k x sin theta plus, because of this p and orders of m; m is the order of diffraction. When it becomes equal to k sp, for this grating which is dielectric or metal, but the surface has to be metal. If it is a dielectric grating, then it has to be coated with metal.

So, evanescent modes couple to surface plasmons, which run along the interface between the grating and the ambient medium. This is what we discussed earlier and there is something very important - what is that? You see, you have a metal dielectric interface and it supports surface plasmon modes. But, if you want to excite them, you need to increase the wave vector of light incident on it - this interface. And, how you do that?

You do that either by using a prism or you make the structure rough - like grating. So, you induce a roughness in the structure, light incident on it can couple to surface plasmon. There is an equal chance that surface plasmons propagating on a rough structure give back this momentum or wave vector and convert to light. So, it is like this -think of it - light incident on a rough structure gets coupled to surface plasmons; surface plasmons moving on a rough surface can couple back to light by giving momentum back to the structure, ok! This is something which has to be seen.

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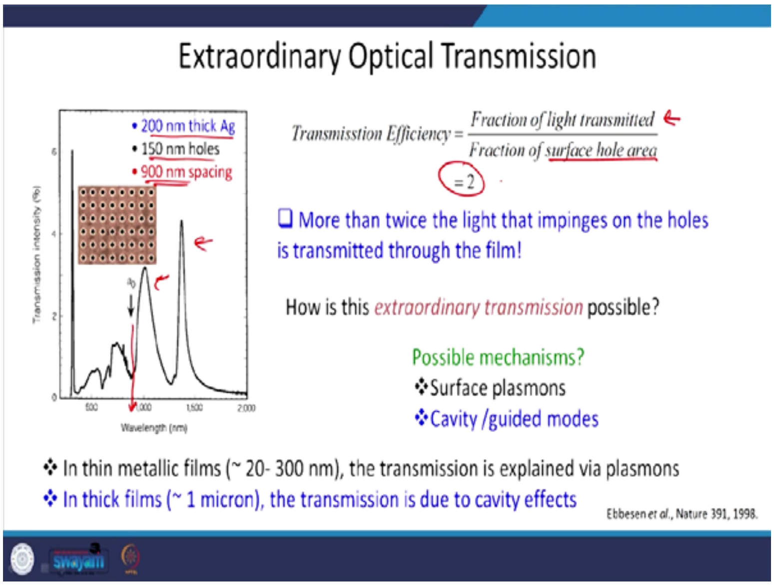

In 1998, Thomas Ebbesen - he said that it is possible to have transmission through nano sized holes. What he did is that he took a film of 200 nanometer thickness of silver with 150 nanometer holes in it and the spacing between them was about 900 nanometers. 150 nanometer is still sub- wavelength hole and he measured the transmission intensity. And you can see that even for the 900 nanometers spacing also, which you call the grating period, even for wavelengths larger than the grating period, he could get transmission.

Suppose you take a plate, where you have 20 holes or so. So, you have a small fraction of light which is falling on these holes. But what he measured is that the fraction of light which gets transmitted through this structure and if you take the fraction of the surface hole area, he got - twice. What it means? It means that the amount of light which is falling on the holes and the amount of light which is coming out of the structure - they are different. The amount of light which is coming out of the whole structure is more than the light falling on the open portion - and that is why he called it extraordinary transmission.

Why is it happening? There can be many possible mechanisms. I am considering only two and giving you the essence of it. It can be either by surface plasmons or cavity or guided mode. So, if you have thick films, say about a micron or so, the transmission is due to cavity effect. So, it becomes Fabry-Perot (Refer Time: 30:19) kind of cavity and the light can get resonantly excited and then it leaves the structure - or thin films of metal about 20 to 300 nano meters.

So, what happens actually that you have very small hole - light, which is incident on this structure, because it has a roughness, it converts into surface plasmons. Surface plasmons now funnel this energy through the holes and then it converts back to light. So, the surface plasmons traveling on this rough surface convert back to the light and that is why you get transmission. And, remember this transmission is always larger than the light falling on the open area. We can use it for sensing.

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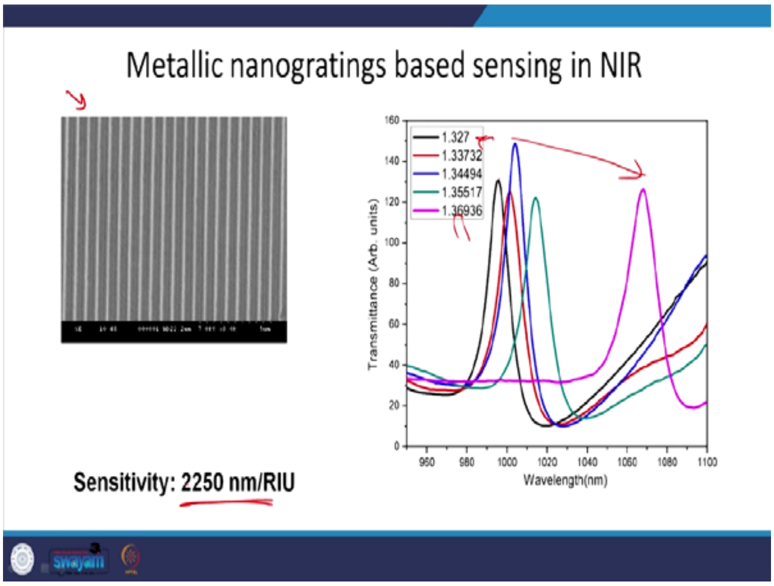

Here we see a picture of a metallic grating and if you change the refractive index of the medium on the top of this grating, you can have different transmission intensities. And, you can see that when you increase the refractive index of the analyte - from the black to pink curve, it shows a red shift. You get a sensitivity of about 2250 nanometer per RIU. So, you can use metallic grating, also metallic nano hole arrays, for sensing applications. This also supports surface plasmons and it is a called a new phenomenon, which is extraordinary transmission.

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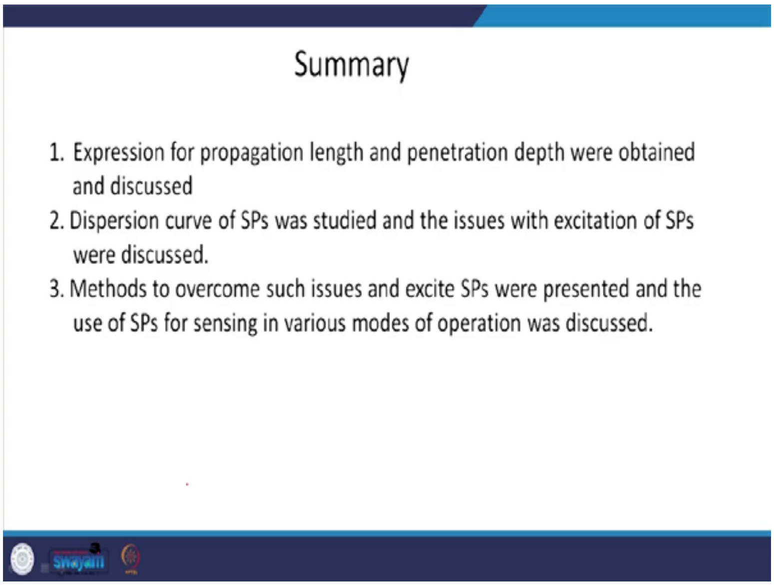

To summarize this talk - today we discussed the electric field enhancements in SPR configurations and also, we discussed - if you want to use SPR for sensing applications or bio sensing applications, what will be the sensitivities. Also, we showed some commercially available biosensors from different companies and then we discussed extraordinary transmission in metallic nano hole, nano grating structures and how to use it for sensing applications. In the next talk, we will be discussing localized surface plasmons resonance.

Thank you.