Chemistry and Physics of Surfaces and Interfaces

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Lecture - 40
Summary

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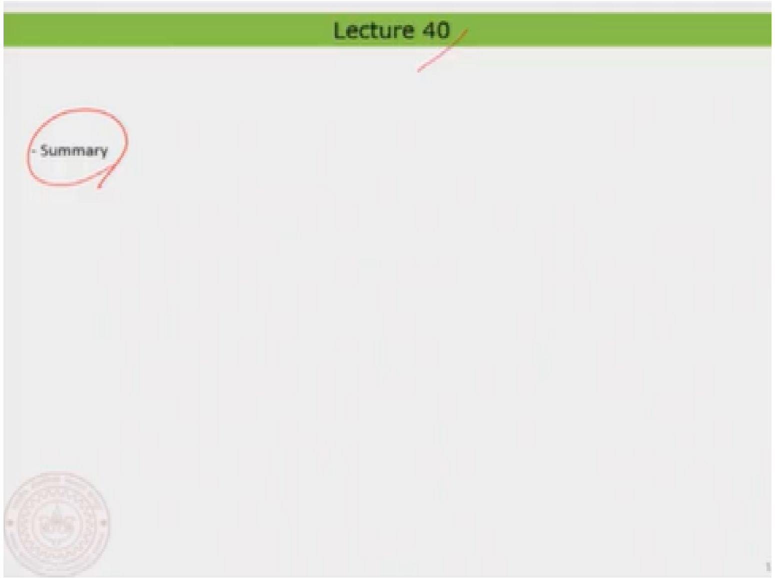

Lecture 40

- Summary

Hello everyone, welcome back to lecture number 40. Well, this is the concluding lecture, so therefore we are going to take a summary of what we have done throughout in this course. So, what I am going to basically do is just go through one more time the most important events that happened in the lecture and then would like to conclude the lecture. So, what we have started was basically just looking at the structure the microscopic structure of the surface. And I also told you this is extremely important because now over the time what you have seen is a structure of the surface which decides everything that you want to do with the surface its reactivity its property its electronic property its chemical nature everything is basically just decided by the structure of the surface.

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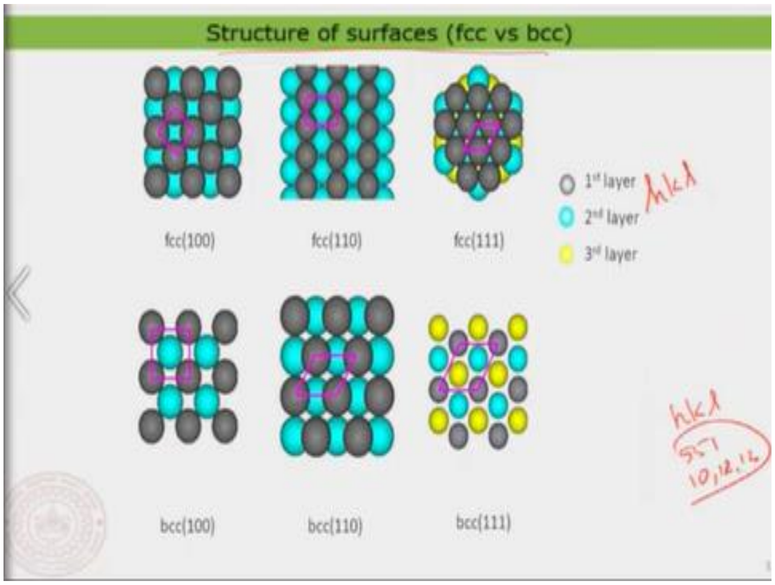

Structure of surfaces (fcc vs bcc)

So, therefore we have actually just spent quite some time on looking at the structure of surfaces and we were focusing mostly on the fcc and bcc type of crystals, but it is not an issue you can now use this understanding in actually working out problems also related to other surfaces of your choice. So, what we have actually just done is also to basically name surfaces and the name was always related to the hkl indexed or the so, called miller index of a surface. Or a plane given of a crystal and then we basically just named according to the plane through which we cut the surface then we basically just name according to the plane through which we cut the surface. So, that is basically what we have done and then we have also seen that depending on the type of the or the structure or the type of the miller index, so being 100 or 110 or 111 surface they are going to get basically different shape. And also, in the previous lecture you have also seen that this is also quite decisive in thinking about the reactivity of the surface there we have learnt for example 110 and the 100 surfaces are much more stronger in terms of their absorption compared to a 111 surface. But well when you look at the bcc 111 surface you see it is quite different that is also something you need to keep it in mind that what is the type of crystal that you are looking at.

It is not just necessary it is not just enough to conclude everything based on just the type of plane it is also important to consider what is the type of crystal you are looking at whether it is an fcc or whether it is a bcc and so on. Then we also have looked at many different type of surface formation and then we also have talked about so called stepped surfaces, when we used higher miller indexes so when hkl values are bigger like in the order of 551 or 10, 12, 12 and so on. So, we have looked at a few examples when the miller index is high, then we have also seen that those surfaces could actually be also more corrugated. So, that means the surface roughness, so the corrugation is also going to be dependent on the surfaces, well that is what we have done.

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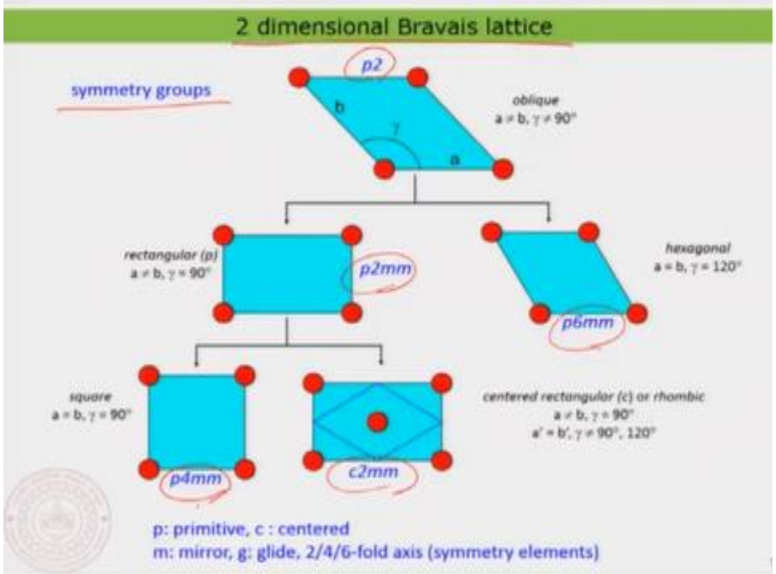

2 dimensional Bravais lattice

p: primitive, c : centered
m: mirror, g: glide, 2/4/6-fold axis (symmetry elements)

And then we also have looked at the typical Bravais lattice what we are interested is the two-dimensional Bravais lattice. So, we have said it is typically five everything that you want to address the symmetry of the surface can basically be just put under these five symmetry groups p2, p2 mm, p6 mm, c2 mm and p4 mm. So, they are basically just nothing but the obliqued rectangular hexagonal square and centred rectangular. So, these are the point groups where the number is basically representing the symmetry so it is a twofold sixfold fourfold and so on. And m and m these are actually representing the number of mirror planes, and the c is basically representing whether you have something in the middle of the unit cell, and that is called centred and p depict basically the primitive cell. So, that is basically something we have done.

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Reconstructions on surface

- density at surface is low
- co-ordination number is low
- surface energy is high and therefore highly reactive

Surface atomic structure is different compared to bulk

- relaxation of bonds
- rearrangement of atoms
- missing rows of atoms

Now then we also have said that well although we can basically just look at an ideal surface as we just cut a surface from the bulk. It is not necessary that you are going to get the surface as it is like you predict, there is something called reconstruction on surface. Things are actually not simply stable because you have low coordination on the surface. So, the number of coordination’s so if I would draw a line here you directly see I have 4 coordination for the bulk. But you can see here I have basically 3 coordination. So, that means it is actually having something known as dangling bonds or lower coordination site. So, whenever there is a low coordination the surface energy is very high and therefore the surface atoms start to move around. Most of the time what they do is actually they pair up in order to increase the strength of interaction and also, they sometime get retracted towards the bulk. So, that the strength of the interaction at the surface is actually increased, but you also sometime get something called a missing row reconstruction. So, we looked at that particularly in the case of 110 surfaces, we have also looked at two examples then we see basically they can also have missing row reconstruction. So, ideally having more atoms coming together and the most unstable atom that would come here which is basically not present there. So, that is what ideally happening so that is also something we have looked at.

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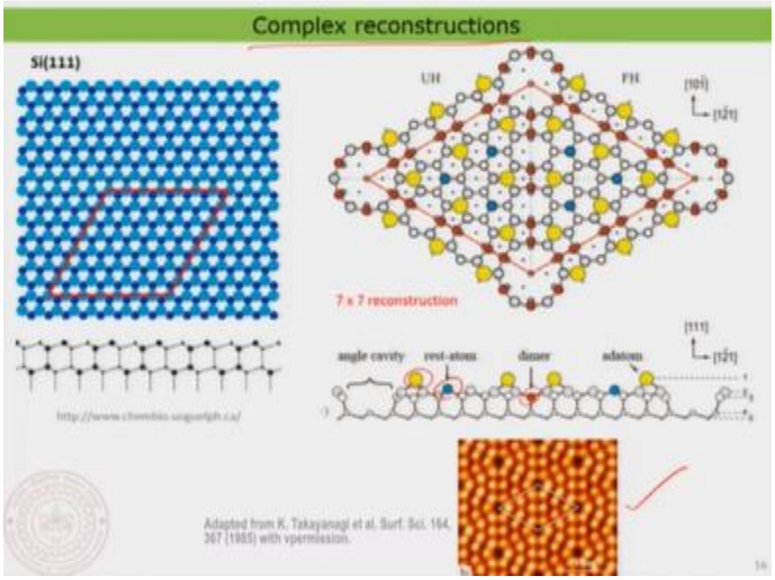

Complex reconstructions

http://www.chembio.uoguelph.ca/

Adapted from K. Takayanagi et al. Surf. Sci. 164, 367 (1985) with vpermission.

And then we looked at particularly a few very complex reconstructions. Although it was looking very complex in the beginning of the lecture later, we have understood the philosophy of reconstruction is very simple that surface always wants to minimize the number of surface atoms. That is the philosophy of the reconstruction. So, always the surface depending on the material structure whatsoever the surface would decide by itself you cannot basically decide what reconstruction you want to have. So, that is basically why surface is always the choice of evil and not of the goat. So, you see basically that the surface is basically deciding, how many number of surface atoms it should have like particularly in the case of a silicon 111 7 by 7 reconstruction you ideally end up in just 12 surface atoms instead of the expected 46 or 48 something calculation we have done that time. So, you can see basically it is reduced by about 25% is just remaining.

Every atom is basically moved into the bulk or they rearrange in a way that you get a lot of interesting type of atom. So, then we said like we have this so-called ad atom, rust atom, dimer atom and so on. The philosophy is still to increase the coordination and minimize the number of surface atoms on the surface. Well, so this example particularly we have focused a lot. So, we have also seen indeed the microscopic structure as you see here in STM. We have looked at the microscopic structure; we have also looked at the electronic structure particularly of this kind of a surface.

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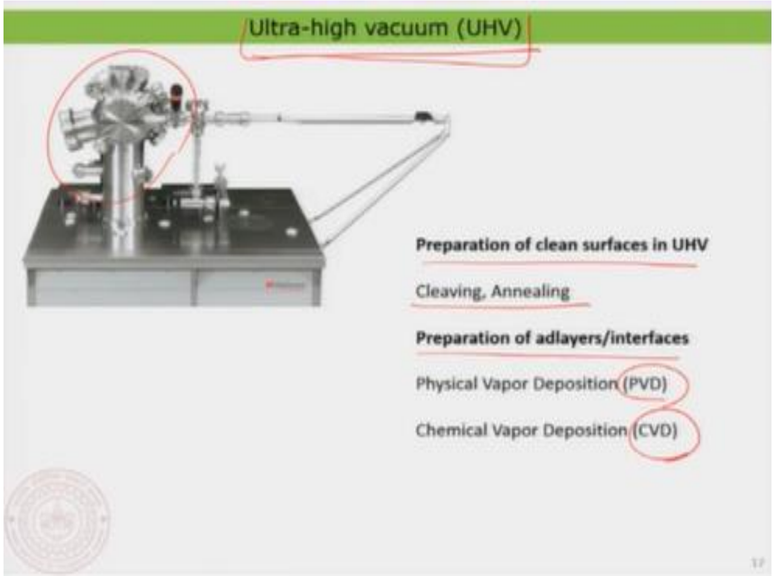

Ultra-high vacuum (UHV)

Preparation of clean surfaces in UHV

Cleaving, Annealing

Preparation of adlayers/interfaces

Physical Vapor Deposition (PVD)

Chemical Vapor Deposition (CVD)

And then we have learned something called Ultra high vacuum, because I told you this ultra-high vacuum is something quite important in surface science, because we want to understand the surface. At microscopic level it is important to prepare something very clean, otherwise we are going to end up in understanding something which is extremely difficult. So, like any surface that you take is quite complex. So, therefore it is quite important that we prepare a clean atomically flat or atomically precise surface so, that we know what we are really doing it. So, therefore we said that ultra-high vacuum is basically an important component in surface science and we have learned how to prepare or how to generate vacuum and this is a typical example. And using that ultra-high vacuum or most of the example that we have discussed was actually in ultra-high vacuum. But of course, we have also seen that we can prepare interfaces even outside in terms of the applications and things likes you cannot all the time afford ultra-high vacuum technology. Therefore, there are also techniques where you can actually prepare things in ambient condition. So, that is another aspect of it, but if you want to study the surface in a microscopic level in an atomic precision then ultra-high vacuum is actually kind of an important component.

So, then using that ultra-high vacuum, we have learned about the different methodologies that you can use for cleaning the surfaces by just simple cleaving, annealing, sputtering and so on. Then we have also learned that how to prepare adlayer or interfaces. So, we have learned mainly two different types of methods one is a physical vapour deposition, on the other one was basically a chemical vapour deposition. So, both methods have its own advantage and disadvantage, so chemical vapor deposition is something that you can think about when you want to prepare something much more bulkier or much more larger scale. But physical vapor deposition is a bit more expensive because most of the time this is done in an ultra-high vacuum or in a high vacuum chamber. Therefore, these techniques are more expensive but of course this is very, very important if you want to generate something with a low impurity and high precision and so on.

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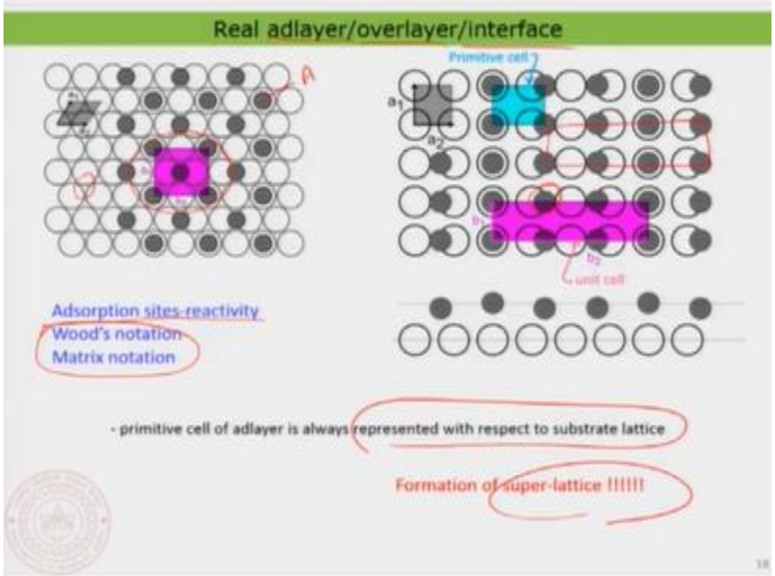

Real adlayer/overlayer/interface

Adsorption sites-reactivity
Wood's notation
Matrix notation

- primitive cell of adlayer is always represented with respect to substrate lattice

Formation of super-lattice !!!!!!

What we have done is? We have started looking at the microscopic structure of adlayer or overlayer or interface. They are all the same so people call it in in different names then what we have particularly looked at was the adsorption sites and the relative reactivity. So, we have already talked about that whenever an adsorbate goes, they will always try to go on a so-called hollow side because it has the highest coordination number possible. And then once you have the adsorbate. So this is basically the adsorbate. that is ticking on the surface and then based on the arrangement of the adsorbate on the surface, we can basically just define the unit cell and that unit cell also comes under the same two-dimensional Bravais lattice, and looking at that we could also just name or so called the nomenclature of the adlayer was also done using two different methodologies woods notation or matrix notation.

Matrix notation is more mathematical representation a more correct representation which includes even the symmetry of the adlayer and so on. But then we also said well, it is not necessary that all the time atoms are actually sticking at the same preferred position, you can also have atoms that are sticking at odd positions like this. So, then what we have seen is that over a larger area so they are going to make something known as a super lattice. This is actually just something that we have learnt that variety of adsorption site for the adsorbates. But you can basically see at the end of the day there is always a unit cell that defines the adsorbate adlayer and that unit cell is always represented with respect to the substrate lattice. And that is why we call in this particular case this as the unit cell. So, you can also just call this as the unit cell that is no problem because you need to have always the corner atoms of the unit cell to be at the identical adsorption site. Then you can basically define the unit cell and this would be just the primitive cell. But that is not really representing the entire thing because the surface is always included particularly in the interface. So, therefore you need to represent everything using the surface lattice as well. So, that is what we have learned basically.

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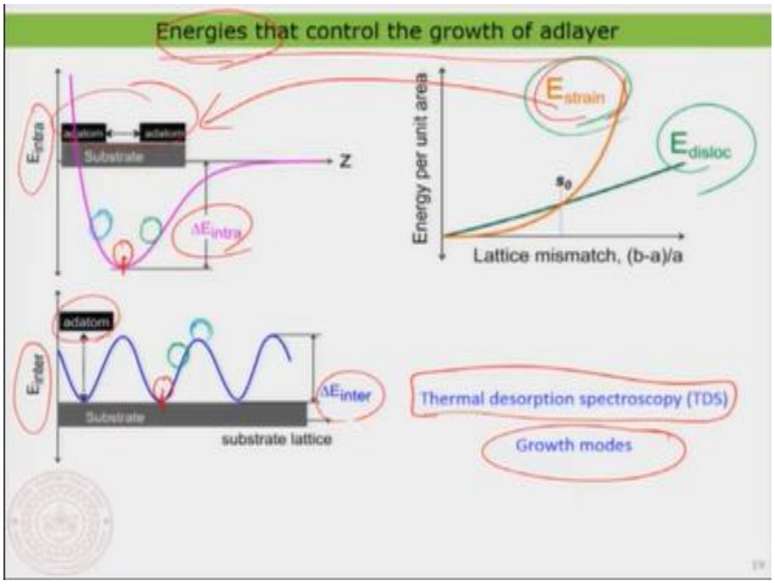

Energies that control the growth of adlayer

Thermal desorption spectroscopy (TDS)

Growth modes

And then we have looked at the most important thing, so that is the energies or the energetics of the adsorption itself. We said when the adsorbate is actually having a very, very low concentration then we need to only worry about the interaction of the adsorbate atom, or it is also the same for molecules we have also seen that that the adsorbate atom and the surface interaction. So, at lower coverage it is only enough to understand everything in terms of the adsorbate surface interaction. You do not need to worry about the so called at adsorbate-adsorbate interaction. But as the coverage increases there is one more component coming that is basically the adsorbate-adsorbate interaction and then we finally said that the total adsorption energy is going to depend on both these parameters called the E intra and E inter. So, this is actually a term that we have used it is not necessary that you have to always follow this particular term. You can choose any terminology as you like and then we said that this so, called difference in energy the sum of these two energies are basically going to decide, what is the total adsorption energy of the adsorbate on the surface. But then we also said that it is not necessary that all the time that adsorbate, adsorbate atom interaction is coming at the minima here and also the adsorbed surface interaction is coming at the minima here.

It is not necessary that you always have the adsorbed sitting here, but you can also have adsorbate sitting at different location like adsorbate can sit here for example adsorbate can sit here or at some it can sit here or at some it can sit here and so on. So, it is basically let me just use a slightly different colour so you can have at adsorbate sitting here, adsorbate sitting here. Then you can have adsorbate sitting here and you can have adsorbate sitting here. So, it is always the different possible combinations that you have to take into account and then you clearly see that there is always a minimum value for both of them. But then you see that sometime it is basically positively affecting one value and in some other hand it is basically negatively affecting depending on where in the potential energy diagram the atoms are adsorbing. So, that means of course the total potential energy surface that is given to the adatom or molecule to adsorb on the surface. And it actually has a big choice and that actually going to be important particularly when you go to a higher coverage. So, that is something what you have to also see because you will suddenly find that you might need to press the items together in order to accommodate more items. So, sometime you would find that the atoms are actually just stretched apart than the normal equilibrium distance and so on. So, that is also where we have actually just learnt two more important components known as the E strain and E dislocation. This is particularly important when you consider the growth of adlayer and the growth of multi-layer typically. So, there for example we need to consider all the time. Of course, I told you that e strain is really related to this one, so they are kind of connected basically but as the coverage increases or as the layer thickness increases.

This E strain and the E dislocation is going to basically just come into a larger picture inside the system. Now we have also learned that we can basically also understand so effectively it is not possible to understand all these different energy components separately experimentally that is not possible. But theoretically it may be possible, but nonetheless the so-called final adsorption energy can actually be calculated or can be experimentally determined using thermal desorption spectroscopy. So, that is something we have actually just said we can so, called heat the surface and then let the adsorbate to desorb and then using a mass spectrometer you can basically detect the amount of adsorbates coming out of the surface as a function of time you can basically measure that and using that we can actually calculate the adsorption energy. So this is something very commonly used in surface science in order to understand the energies.

That controls the growth of adlayer or in typical the adsorption energy of the adlayers. And then we have also learned that these are the energies that are also going to kind of control the type of growth modes. And particularly for atom like adsorbates, we have seen that there are three different type of growth which is basically one so called layer by layer growth another one which is like an island type of growth and another one which is actually a layer first the so, called wetting layer and then an island formation. So, there were three different types of growth modes and then we have also discussed the factors that controlling these growth modes they are really related to the energies. So, that is also no surprise for sure, and this is basically controlled by the energy. So, that is something that we have also spent quite some time during the lectures and I would encourage you to have a specific understanding on that. Because this is the most important part of the lecture or in general the surface science aspect if you want to consider for the adsorption of atoms and their growth and so on.

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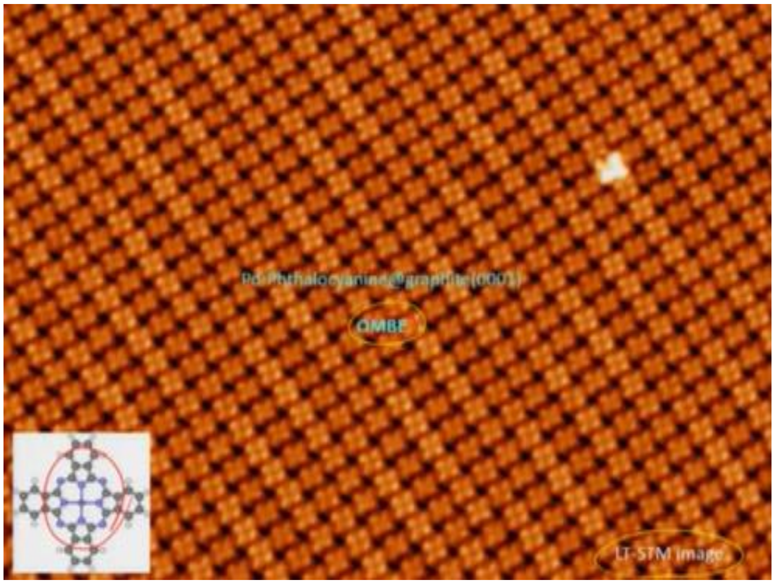

And then what we have also looked was the adsorption of molecular adsorbate. So, this was actually something we have looked at was a phthalocyanine molecule and then I also told that using the same molecular beam epitaxy here. So, using the same molecular beam epitaxy we can actually just perform something known as organic molecular beam epitaxy and then we can prepare this kind of very nice and uniform adlayers of molecules. So, you are not only just can make just one layer, you can of course depending on the coverage you can basically make many, many layers on top of each other. So, but you can of course investigate nicely. And this is a lower temperature scanning tunnelling microscopy image and you can clearly see the molecular adsorbates on the surface. Now when it comes to the molecule, we also said in the energetics there is one important parameter that you have to consider which is actually the; so, called symmetry of the molecule. Because that is something you do not need to consider when you have an adatom or an atom like adsorbates or small atom like molecules. So, we also looked at a few example of carbon monoxide and let us say oxygen or whatsoever there it is not important. But for bigger molecule you can see that this is actually the way the molecules are finally arranging. And then we said that the symmetry of the molecule is quite important. And the symmetry of the molecule is going to quite control the adsorption and also the final adsorption geometry of the final adlayer structure. And then we also said that for the molecule particularly since they are larger the so, called adsorption geometry with respect to surface is quite important. Therefore, there is also possibility of having variety of adsorption geometry with respect to surface.

So, all those additional factors need to be also considered in the case of molecular adsorbates and the outcome basically was that we said that when you work with molecular adsorbates, there is more possible ways that you can basically arrange the atoms on the surface. That is the interesting aspect that we have looked at on the surface.

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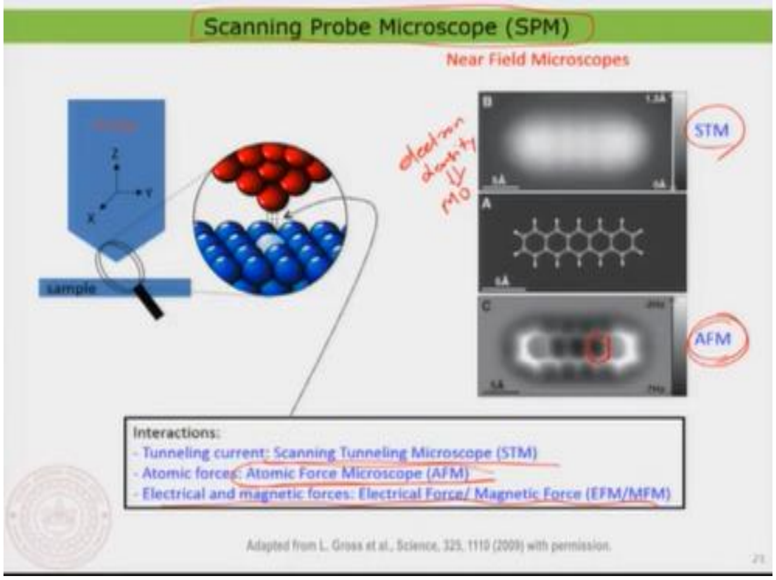

Scanning Probe Microscope (SPM)

Near Field Microscopes

Interactions:
- Tunneling current: Scanning Tunneling Microscope (STM)
- Atomic forces: Atomic Force Microscope (AFM)
- Electrical and magnetic forces: Electrical Force/ Magnetic Force (EFM/MFM)

Adapted from L. Gross et al., Science, 325, 1110 (2009) with permission.

Well then what we have done? Towards the end of the lectures what we have also done was actually familiarizing a few experimental techniques with that we can understand the microscopic structure because it is important that I want to see what is happening on the surface. So, then I need a microscopy and I need a microscopy that actually can reach atomic solution or resolution down to the scale of atoms. So; that I can look at the process that is happening on the surface at an atomic scale. So, this is quite important and that is where we have learned this so, called scanning probe microscopy. It is a general classification there are many scanning probe microscopy, what we have focused was actually the scanning tunnelling microscopy in general known as STM and atomic force microscopy.

And in the atomic force microscopy, we have also seen a two additional variation known as the electrical force microscopy and the magnetic force microscopy. But then when you looked at the STM images, itself it turns out to be that you are not looking at the structure of the adsorbates, you are instead looking at something called the electronic electron density for example. You are looking at the electron density corresponding to a certain molecular orbital. So, that is the interesting thing. So, what you are looking at the electron density near the surface of a given adsorbate of a molecule it was particularly interesting because we have seen that by selectively deciding or selecting the voltage at which you do the experiment you can even basically see the LUMO or HOMO of the molecule. So, this is something you have seen or even the LUMO + 1 or the HOMO - 1 and so on. But in the AFM what we have seen that we can reach ultimate resolution, so this is again the pentacene molecule so we could basically see the nice hexagons of the of the pentacene. So, this is basically beautiful so that we can finally see the molecule as we wished. This is something interesting. We have also seen that this is something to do also with the electron density that is spread on the molecule. So, we are basically looking at something like that, but nonetheless at the end of the day this is actually an image that is giving you the skeleton of the molecule so, this is beautiful. Well, we have also said that this is very specific a very special kind of microscopy that is not something you are going to apply to everything because it is an expensive technique to do because you are doing everything in an ultra-high vacuum using a low temperature STM AFM. And also, everything is done at an extremely molecular level. But when it come to the to the application so looking at the bulk material. so like let us say thin films of more layers and so on or if you want to collectively understand the electronic property of materials then we said well microscopy is good to some extent but then it is also sometime better to go to something like atomic force microscopy because that gives you a little bit more global picture. But you can actually also kind of characterize the microscopic structure, of the surface. But well at the end of the day every technique has its own advantage and disadvantage and scanning tunnelling microscopy and the so called specialized atomic force microscopy was actually the technique that we said can actually go down to atomic resolution and resolve things at this scale.

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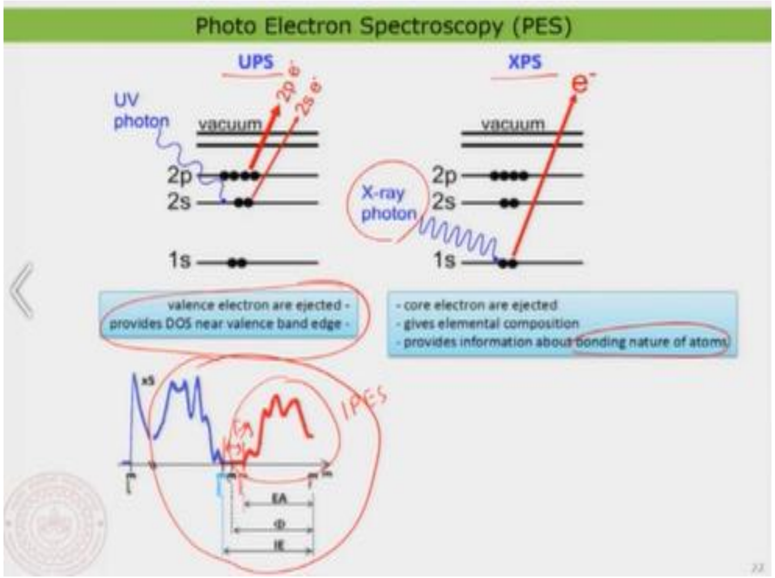

Photo Electron Spectroscopy (PES)

valence electron are ejected -
provides DOS near valence band edge -

- core electron are ejected
- gives elemental composition
- provides information about bonding nature of atoms

Well then, we said well if I am really interested in looking at the global electronic structure, so then I can also just use techniques like ultraviolet photoelectron spectroscopy or X-ray photoelectron spectroscopy. So, these both techniques are working based on the photoelectric effect, where you shine your material with a given photon it could be like a UV photon or X-ray photon then you kick some electrons out of the band or some core level. So, if you are basically removing the electrons from the valence band you can do that using just ultraviolet photons, then what we are going to basically understand is actually the density of state of the valence band. So, this is quite important because I told you we need to know the electronic property particularly near the fermi energy and that is what is deciding the property of the molecules or property of the adsorbates or the surface or whatsoever. That defines really the reactivity the chemical property everything is decided by the electronic structure itself. But then we also looked at something called X-ray photoelectron spectroscopy where you shine actually with a higher energy photon and then you are kicking electrons from the core level which is extremely sensitive to the bonding nature of that atom or the so, called oxidation state of that particular atom or the element that we are looking at.

And we have of course taken a few case studies very specifically and we have actually just seen that we can clearly, clearly understand what is happening or what is the chemical nature of a given element that we are interested in so that is was it. Then I also just showed you that we can combine something called an inverse photoelectron spectroscopy where instead of your shine photon you actually inject electron into the system. And then you look at the photon coming out of it and then you can combine basically those two techniques UPS and inverse photoelectron spectroscopy. and then you can clearly get the complete electronic structure of the surface or interface or thin films or so whatsoever you like. This is quite important because I can basically know the band gap, so this is basically the band gap E G I can note relatively the conduction bandage the valence band edge I know the density of state and so on.

So, this is quite important. So, therefore we have actually just used and we also have used a combination of XPS, AFM, STM and so on in understanding collectively for a few cases to understand clearly how to apply these techniques in general.

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Well with that I come to the acknowledgement, I would like to mention the name of these people who also contributed partly to these lectures Dr Prithwidip Saha, Dr Khushboo Yadav, Dr Vipin Mishra these are also students who graduated from my research group. They have contributed partly to this lecture in terms of the research components that I have used in the lecture and then also my current students Ms Himani Malik, Ms Richa Arjariya, Mr Hariom Birla, Ms Diksha Srivasthava, Mr Sunny Gautam. So, these are my current PhD students who are also helping me in doing this lecture and I also would like to thank the financial support from the department of science and technology. Ministry of electronics and information technology government of India, because their money has been used in doing a lot of research that we do in the lab and those components has been also shared with you in this lecture. And I would also like to finally thank you very much for choosing this particular subject. This is of course an interesting subject which also has quite some fundamental importance and also quite in the modern technology it also has a greater importance. So, therefore I thank you very much for choosing this subject and also thought of popularizing my lecture. I would like to thank you very much for your kind attention. And looking forward to also work with you in the during the tutorial and also during the evaluation time. Thank you very much.