Chemistry and Physics of Surfaces and Interfaces

Prof. Thiruvancheril G Gopakumar
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 04
Reconstruction of Surfaces

So, hello everyone, welcome back to lecture 4 and in this lecture what we are going to do is to look at the high index surface.

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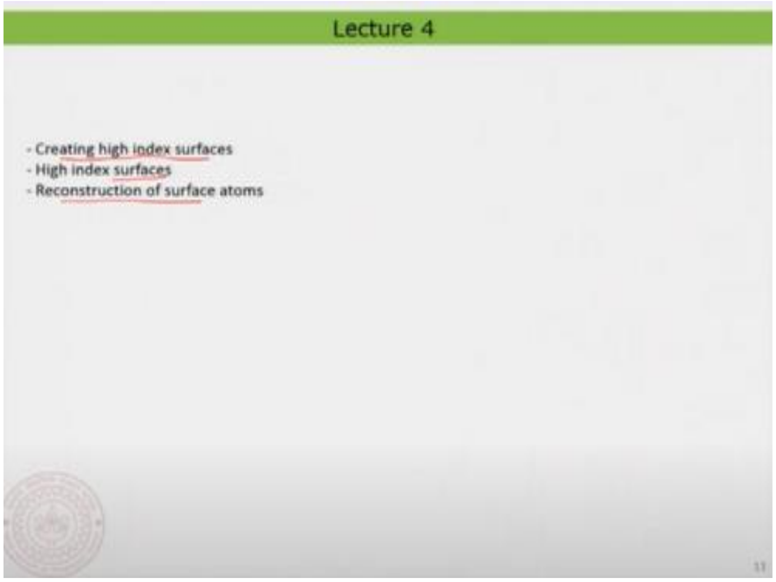

Lecture 4

- Creating high index surfaces
- High index surfaces
- Reconstruction of surface atoms

So, far in the last lecture what we have seen was basically surfaces with low index that basically means like the surface is like 100, 111 or 111, 110 and so on. And today I am going to show you basically surfaces with higher miller indexes and these are actually very interesting surfaces as you will see. And I will quickly show you one simple example of how to create a high index surface and then we will also finally look at something called reconstruction of the surfaces.

So, the surfaces that I have created or the planes that we have created in the last class were actually all unreconstructed. That means a very idealized situation, that is not the case, so things actually just reconstruct on the surface and that is also something we are going to familiarize in this class. Well, let us try to create a high index surface. So, you have already seen how to create a surface using a unit cell. So, what I am going to do now is to show you creating a larger or basically creating a high index surface.

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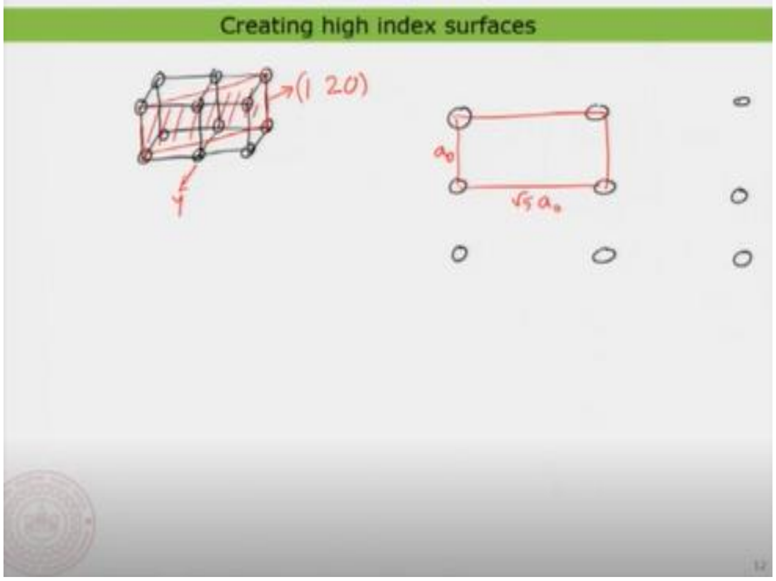

Creating high index surfaces

So, for that we would need two unit cell instead of one like what we have done in the last class. So, here I have one unit cell and basically the corner atoms being just marked by these open black circles, but to do the high index surfaces you would require to add basically more unit cells to the figure. So, otherwise it would not be practically possible for you to do, so you have to add more unit cells like this. And depending on how higher the index is you have to basically add more and more unit cells so that you can create the surface clearly. So, now what I want to do is, I want to create basically a surface which is going through these atoms. So, this is a primitive unit cell and going through these atoms. So, that means it is basically cutting through the middle of y axis. So, you can basically see here along the y axis the unit cell is being cut two times so that means the intercept along the y axis is two times but along the x axis it is 1 and this plane is actually parallel to the z axis therefore the intercept is actually infinity in that. So, that means your miller index of this plane is going to be 120, so that is the plane. Of course, this is not a very high index surface but just for the understanding of the practically how to do this I have just shown this but one can actually create as you will see in the slides there are much higher index surfaces you can create. Now let us do this so now basically just take those corner atoms. So, we can basically go back and take the corner atom. So, now the interesting thing is that the corner atoms are actually much far apart compared to the one we have basically created in the last class that means the low index surface. Now you see that the unit cell of this surface is again a rectangle, so that is basically it and this particular case the unit cell along this is actually a_0 and along this direction it is basically root 5 a_0.

So, a_0 is basically the bulk lattice and you can already see that the unit cell is much larger in certain directions depending on the index that you have added. So, this is quite an interesting surface as you would expect clearly in this case the packing density of the surface is much much lower than any of the surfaces that we have seen in the previous class. So, the interesting aspect about creating high index surfaces is that if you want to create more reactive surfaces you need to basically create these kinds of high index surfaces. The high index means the reactivity is increasing or the roughness is increasing as the roughness increases the reactivity of the surface increases. So, that is basically the fact about the catalytic effect of the surfaces.

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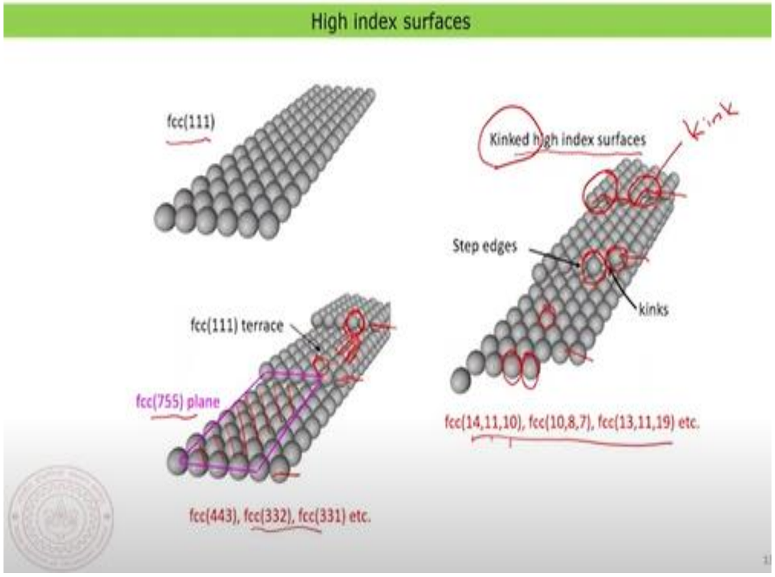

High index surfaces

So, let us have a look at a few examples of high index surfaces. And also let us have a look at a certain important aspects of features of high index surfaces. So, what is its difference compared to normal low index surface? But I am showing here first is actually an fcc 111 surface and you can see here very large infinite terrace as we have already seen in the previous slides. Now when we create high index surface you have already seen how to create a high index surface. Now, the interesting aspects of the high index surface that, I am showing here as an example is 755 plane of fcc and you see here the plane is basically this one and the plane as you can see here basically bridges between several atoms along a given directions and that actually comes from this high miller in this number. Now the interesting thing is that the high indexes surface most of them will be appearing or will be having terrace edges. That is the first important thing and then you will also have certain areas as you can see here; simple terraces. So, in this case it is particularly an fcc 111 terrace that you are seeing that regions are going to be much flatter but in between you will get these kinds of step edges. Now you can create many high index surfaces and a typical example I am showing here are those surfaces where you can clearly create step edges. But now what is interesting or what is the significance of a surface having step edges. As we have already discussed earlier that whenever you have step edges you basically going to end up in atoms that are having low coordination compared to the atoms that are on the surface, of course you can see here on an fcc 111 surface the coordination is basically very high but the atoms that are actually at the step edges are going to have lower coordination. And immediately when you have lower coordination it is going to be the surface with or the atoms which are having higher reactivity. So, that is the interesting aspect. That means as and when you create a high index surface you are ideally creating surfaces that are more reactive in nature or more roughness in nature. So, now let us also have a few more interesting examples. So, now these are actually high index surfaces that are not only just having step edges which are also having kinks a particular example. So, these are a few index surfaces and here, please note that the index is basically now very large it is 14, 11 and 10 and that is the reason why in this notation we have basically used a comma to separate the miller indices. So, that is common when you get a two-digit number ideally. So, now you have this high index surface with kinks you definitely have step edges as you have seen in the previous case. But in addition to that, now we also have these kinds of kinks, so this part is basically known as a kink or that is a few atoms basically just bending at a step edge. So, now you see when you create these kinds of surfaces you are not only just creating step edges you are also creating basically kinks. So, now the interesting aspect is the atom already on the step edge here like you have seen in the case of fcc 755 is already a low coordinated atom. But now you see here the atom here at the edge of a kink which is definitely much more low coordinated than that one at this temperature. So, this means that when you create basically kinked high index surfaces you are ideally creating surfaces with a lot of atoms having lower coordination or surfaces in general you are creating rough surfaces which is ideally meaning that you are creating a reactive surface. Well, these kinds of surfaces are also nowadays highly available commercially and therefore one can basically just purchase them and then you can basically use them in understanding reactivity of different kind of surfaces where you can particularly focus on the reactivity of molecules or catalysis on surface atoms on step edge atoms and kinked atoms and so on. So, this is a step edge atom this is a kink atom and so on.

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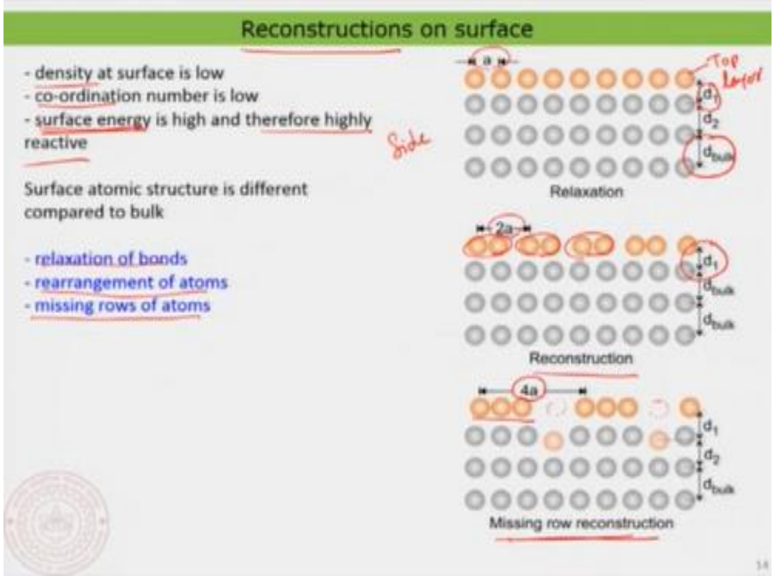

Reconstructions on surface

- 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, let us have a look at one very important thing which is known as a reconstruction of the surface. So far, the surfaces that I have showed you are all ideal unreconstructed surfaces. But this is not possible. So, any surface that you create is going to get actually reconstructed in order to actually stabilize their surface energy. So, why is it actually necessary for the surface to do this reconstruction and all surfaces believe it that they are all going to be reconstructed. So, you would obviously say that compared to the bulk the atoms on the surface are having low coordination and also the density of the atoms on the surface are actually much less compared to the one in the bulk. This is very obvious by just looking at different surfaces. So, the problem is now due to the fact that they are low coordinated and the density is low. Now the surface energy is actually just shooting up. The surface energy is very high due to the fact that you have low coordination. So, since the surface energy is very high every surface is going to be reactive ideally, but as I already told you within these surfaces the one with the high roughness that actually means atoms with much lesser density and atoms with much lesser coordination number are going to be the one which is much more reactive. So, that means every surface that you create is going to do some kind of rearrangement on the surface or some kind of reconstruction on the surface in order to minimize the surface energy, so this is the main point. Now how does the surface do it? The surface does it by relaxing bonds. That means like by if this would be the typical size of the two atoms but they would basically be coming closer or they would be going out or they would be just changing their position and things like that. So, you would relax the bonds or you rearrange the atoms within the surface or you would also do something very interesting called missing row atoms. So, like you would try the surface try to skip actually one of the rows or by just displacing it is strange to understand but let me show you some examples that you are going to understand. So, now let us have a schematic look about how this would happen. So, this what you are seeing is actually the side view of a bulk crystal where this is actually the top layer. This is the top layer and these are actually the gray atoms are actually the one which is in the bulk. Now, what the first thing the surface do or every surface does is actually the top most layer is much more close to the second layer. So, that means the distance between the top layer and the second layer is always lower than that compared to the bulk. So, this is something which is the simple relaxation of the atoms within the surface. So, this is what the first thing it does or the atoms can actually be slightly rearranged and that is exactly what you are seeing here the atoms on the surface are getting paired to each other. So, when they get paired ideally what it does the surface atoms has actually come closer. So, now of course by doing this they actually just reduce the surface energy. In addition, they will also just reduce the relaxation along the bulk direction. This is typically known as reconstruction where you basically rearrange the atoms on the surface. Now the interesting thing here you have to note, now the periodicity of the surface is not anymore a, this is actually 2a because 22 atoms are actually making a pair. And therefore, the periodicity of the surface is going to be 2a in this case compared to an ideal case where it is just a. Now you can also have something called missing row reconstruction. The missing row reconstruction is very interesting where more atoms are actually coming closer as you would see here, three atoms are coming closer and they are forming actually some kind of a group. And once you actually just put three atoms together, immediately one of the atoms here, which was originally there started to feel actually isolated and that atom would miss or it would maybe move into the bulk or it may actually just rearrange into somewhere else and so on. So, originally atoms which was present in this one would just miss from the surface and this is basically known as the missing row reconstruction. Now, you can see in this particular given example the periodicity is actually now grown to 4a. So, that means the surface atoms are actually having a much higher periodic distances compared to the ideal one which is a. So, this would be called as a 2 times reconstruction compared to the original or this would be called as a 4 times reconstruction compared to the surface and so on. Now let us have a look at a few typical examples to understand this more clearly.

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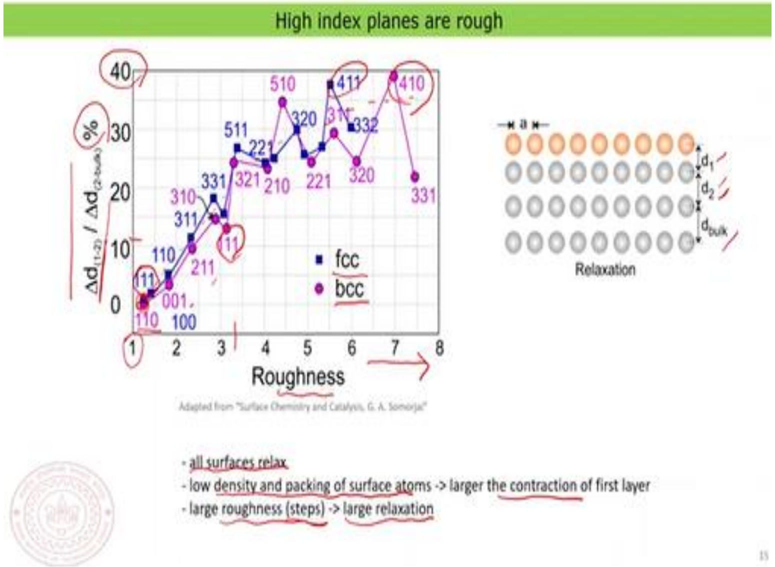
High index planes are rough

Adapted from "Surface Chemistry and Catalysis, G. A. Somorjai"

- all surfaces relax
- low density and packing of surface atoms -> larger the contraction of first layer
- large roughness (steps) -> large relaxation

So, in this slide what I would like to show you is basically a semi quantitative measure of roughness of different surfaces as a function of relaxation of different surface to bulk layers in different types of surfaces. Now the roughness one is basically representing the fcc 111 surface as we have already seen in the previous lectures that the fcc 111 surface is considered or is the lowest rough surface. Therefore, we are taking the fcc 111 surface as the lowest roughness surface and whose roughness is 1. And then as the index increases basically the roughness also increases along the scale. Now, this roughness of different surfaces is plotted against the difference between the lattice distances between the first and second layer and between the second and bulk lattice is basically plotted along the y axis and that is given in percentage basically. So, 0% in this case basically meaning that there is no relaxation. So, ideally the 111 surface will have the lowest relaxation and that is basically our starting point for both bcc and fcc you can see our starting point is basically around 0. Now you notice particularly for fcc that the fcc 111 surface has the lowest roughness and the lowest relaxation of the surface atom with respect to the bulk. But now, in general you can see that the roughness is increasing in this manner with respect to the index of the surfaces and that is actually the same for both fcc and bcc. But what has to be particularly noted is that you can notice that your fcc 111 surface has the lowest roughness. But when it comes to the bcc 111 surface you notice that it has a much higher roughness and also has a higher relaxation of the surface atom. That is also something what we have actually summarized in our previous lecture that the bcc 111 surface is definitely a higher roughness surface compared to the fcc 111 surface and it is also noted therefore the bcc 110 surface is the lowest rough surface in the case of bcc. But then it is the 001 surface and then 211 surface and so on. Of course, in this diagram not all surfaces are included. One can basically do this exercise by taking any type of surface you like. But what I would like to show you here in a summary is that in general the roughness increases, the relaxation increases. And also, it is basically showing you that all surfaces are relaxing and when the surface having the lowest density packing of the surface atoms then you will have the larger contraction of the first layer and if the large roughness is basically also related to the larger number of steps, and the larger number of kinks that is actually what we have discussed in these high index surfaces you can actually see that the relaxation actually goes in the order of about 40%. So, this is quite a lot compared to the bulk lattice. So, whenever you have surfaces with steps and kinks you will have very very large relaxation also associated to that. That is also what we have basically seen that in the high index surfaces in general, we have very high relaxation or very high reactivity therefore also associated. And that is also the point here whenever you have basically a higher roughness or points which are actually in this range is basically representing higher reactivity of the surfaces.

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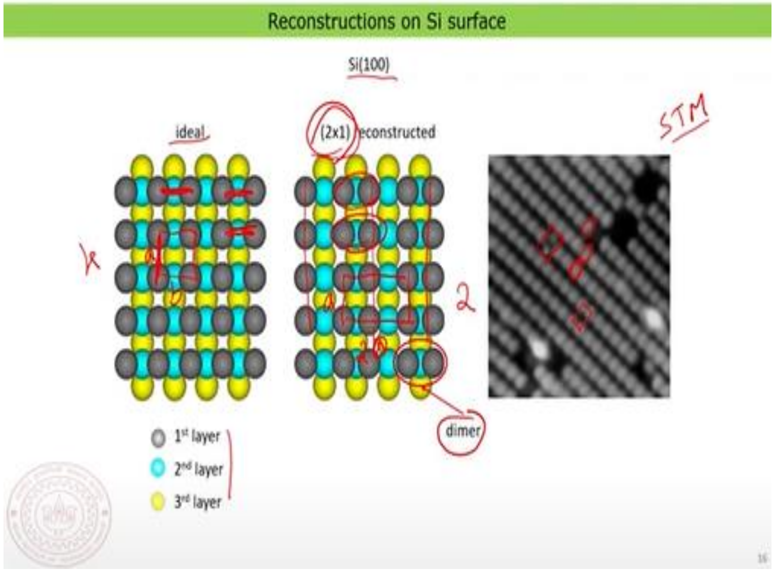

Reconstructions on Si surface

Si(100)

Now, let me show you a few particular examples, so this is actually a silicon 100 surface. So, the silicon 100 surface is not an fcc surface, it is a diamond lattice, but this actually comes in the family of fcc. But now this is basically the ideal silicon 100 surface and of course as expected for the 100 surface you can see basically it has actually a square unit cell and that is basically meaning the symmetry of the surface is four-fold. And the different colors here actually represent the different layers. So, the first layer is basically the gray and that is basically showing you that the atoms are arranged in a fourfold symmetric manner and that is what we would expect. But now interesting thing that you notice is that the distance between the atoms are basically very large and therefore the atoms at the different locations are feeling a very very low coordination. And therefore, in reality what happens is that the silicon 100 surface get reconstructed by compressing or by moving these atoms closer to each other. So, the adjacent two atoms would basically come closer and they bind together and form something called as a dimer. Now ideally, what you see is that due form kind of a dimer rows along the 100 lattice. So, therefore when you have more dimers formed each of these dimers are basically feeling much more stable because their coordination has increased. Now something also, you can notice that this the atom are actually forming or arranging like this and therefore this would represent the unit cell of the lattice and therefore along one of the directions it is 2 times a and if you would have taken basically this as a and b then you would basically find that this distance is basically 2b and this is basically a. And that is the reason why you call this as a two by one reconstruction; where the two by one is actually a simple notation to show that this reconstruction is actually two times a larger lattice compared to the ideal one and one time along the other direction compared to the ideal. That is also a very common notation that one uses basically for representing the reconstructed surface. Now, let me also show you a scanning tunneling microscopy image, so of course we will see in detail the microscope. With this image you can basically see the atomic arrangement of the surface and now here, these bright lobes are nothing but the dimer of silica. Now you can see here that the symmetry of the surface is basically represented by this rectangle as you see here and that means it is basically a two-fold symmetric surface. And each of them are as dimerize as I have told you, but you can also see in some locations that the atoms have not dimerized so where each atom is basically nothing but a silicon atom. So, this is just by chance it actually happened. So, this is a particular example. So, of course depending on the type of surface we have we can have different types of reconstruction so we will see a few more in the next slide.

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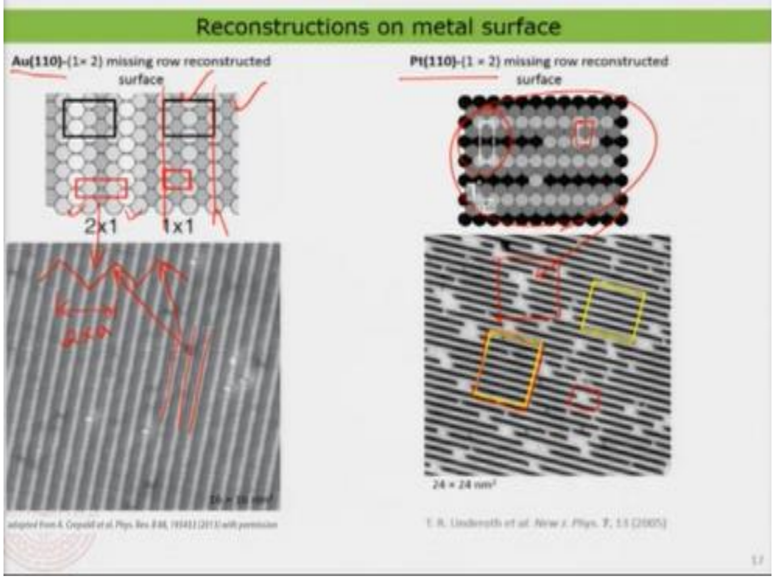

We can also now have a look at a different type of surface called a gold 110 surface and its one by two missing row reconstruction. So, this is the typical unit cell of the gold 110 surface and that you have already familiarized in our previous lecture and now what is going to happen to actually just reconstruct the surface. The surface what it does is actually it misses these adjacent rows and these rows are basically existing and the adjacent rows on the top layer is basically missing. Now, what happens is that you can see now that these rows are basically existing and the row which was in between here which was basically here is actually missing now. So, this is called a missing row reconstruction. So, now you can see after the reconstruction the surface is extremely corrugated it would look like a wedge surface. So, the side view of this would be basically something like this an extremely wedge surface. And this distance is two times of the a and that is why it is actually called as a one by two or two by one reconstruction in whichever way you want to put it. And we can actually have a look at the STM image of the surface and now you can see this is basically the reconstructed surface and that actually corresponds to this top of the wedges. So, that is basically it and now this is nicely reconstructed and you can see almost everything on the surface is completely reconstructed. You can also look at a different example which is platinum 110 surface that is also a face ended cubic unit cell. There also it is typically observes this kind of missing row reconstruction and you can see this would be the most ideal 110 surface, but after reconstruction this is going to be the unit cell and that is the reason why it is known as the one by two reconstruction. So, this region you can see the one with the yellow mark. You can see it is clearly the completely reconstructed part but in between these regions, where you can see atoms are not fully reconstructed there is still some of the rows which are still present. So, that is why you can compare this image is a kind representation of some of the regions like this, where you can see that some regions have the atoms and some of the other regions where atoms are basically missing.

Well, one can look at many different examples, so these are all STM topographs micrographs basically, so we will look at them in detail in the next classes.

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Reconstructions on GaAs surface

Bulk GaAs is Diamond structure

adapted from G. J. de Raad et al. Phys. Rev. B 64, 075314 (2001) with permission

And now finally, I want to show you one interesting example which is a Gallium Arsenide surface. And a Gallium Arsenide surface is also having a diamond structure. But now here, the difference is that the lattice is actually constructed by two different atoms namely you can see the gallium atom and the arsenic atom. So, they are the top view and the side view and the interesting thing once they reconstruct what happens is in the top layer, the Gallium and Arsenide actually pairs up and the Gallium Arsenide comes closer and this is actually the correspondence. So, the gallium and arsenide comes closer than in the bulk and they form basically some kind of a dimer again on the surface. You can have a look at an STM image, so a reference is also given here you can read this article for more details. You can see here again that these bright dots are nothing, but the gallium and arsenide pair in the first layer and you can see in the side view that there is again in the second layer another gallium and arsenide in between so that is the one which you can find in between. So, that means you have the top layer gallium arsenide which is paired and then in between you also have gallium arsenide which is not paired which is actually same as in the bulk as you can see here the distance between the gallium and arsenide are as in the bulk, but in the very top layer this is actually reduced compared to bulk the size of this. So, this is the typical reconstructions that you would find for gallium arsenide and so on. So, now the thing is any surface that you would take they all undergo reconstruction and the main message or the key message of any reconstruction is basically or the surface does it basically to reduce the surface energy and in order to create to minimize the surface energy and also to increase the coordination number of each surface atoms.

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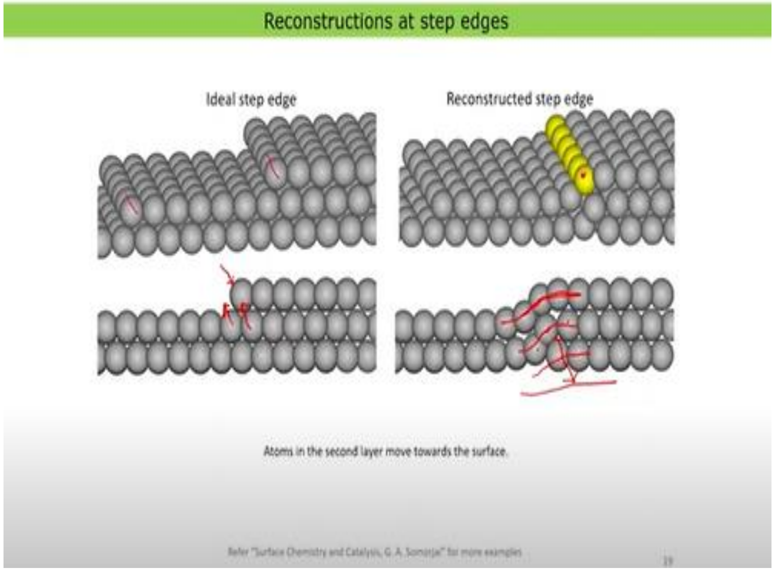

Reconstructions at step edges

Atoms in the second layer move towards the surface.

Refer "Surface Chemistry and Catalysis, G. A. Somorjai" for more examples

So, now the question is whether reconstruction happens at step edges? Well, we have already seen that the surface is created by a high index surface and there we have already seen that the high index surfaces are ending up with step edges. So, this is a side view of such a high index surface where you can clearly see the step edges. But now of course from a clear side viewpoint so you can basically see that the step edge is basically looking very strict and ideal. But the question is are the step edges always remaining like this in real? But that is not the case in the real case the step edges actually do reconstruct. So, what happens? What happens is simple that the corner or the step edge atom would basically move inward and the atoms which are just below would basically move outward, similarly this atom would also move outward. So, as an effect what you see is that there is a rearrangement of the atoms and then there is a smooth transition happening at the step edges. And of course, a lot of other atoms as you point out here have actually just also kind of followed the reconstruction or the changes that happened at the surface and then eventually as you go to the bulk these changes would basically milden out and then finally you get a smooth lattice, as you would expect in the bulk. So, that means at the step edges there is a clear rearrangement of the atom. So, now due to this rearrangement, what eventually happened it does not anymore look that the atoms at the step edges are having a low coordination as you would expect. But nonetheless of course you can see here that these atoms are more exposed to the reactant atoms and therefore always even when reconstructed the surface with high index surfaces would always remain reactive. But nonetheless the reconstruction would basically reduces their reactivity to a lower extent and therefore the surface would basically remain as a kind of ideal, closer to an ideal surface.

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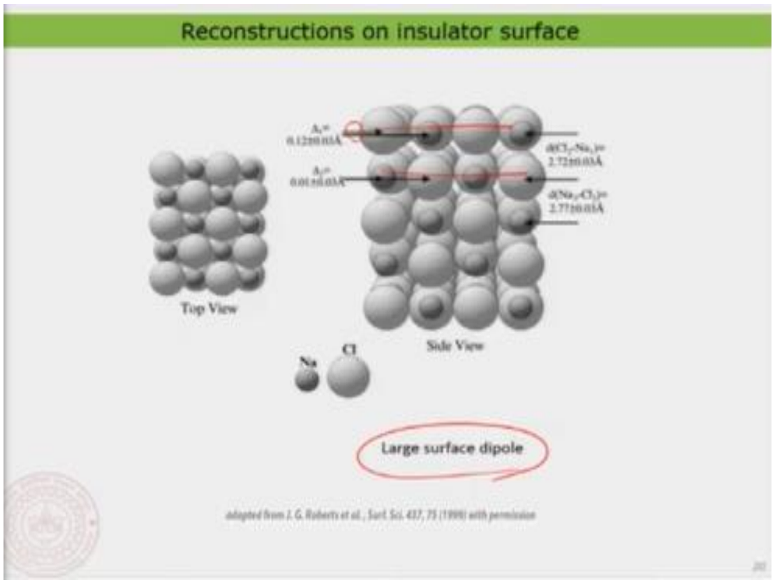

Reconstructions on insulator surface

Large surface dipole

adapted from J. G. Roberts et al., Surf. Sci. 437, 75 (1999) with permission

Now what I also wanted to tell is about insulating surfaces. So, the question is will insulator surfaces reconstruct? Well, normally if I would be asked this question, I would say that it is impossible. The reason is simple because it has a very large surface dipole and usually it is extremely hard to deform insulating material. So, to do something to sodium chloride for example you need to apply very large pressure, very large temperature and so on. So, normally it is known that deforming insulating surfaces or salt is extremely difficult, particularly salt. Now the thing what I want to point out here is that you take for example sodium chloride, and now if you look at the side view and the top view you see the top layer and the second layer there is a very tiny bit of change or relaxation of the top layer towards the surface. That means even for a surface that is actually like having a large dipole you still would find basically relaxation of the top layer. So, this is meaning that any surface that you take the top layer is going to be relaxed. The typical reconstruction that you find in these kind of surfaces particularly in salt you find is just the relaxation of the top layer to the bulk and not the major rearrangement like what we have seen in the case of metals. But for metal and semiconductor is the strongest reconstruction known for it, I will also show you in the next lecture two interesting examples of an extremely specialized reconstruction that you would find in the case of a metal and a semiconductor. But even in general I want to say that reconstructions are ubiquitous on surfaces and then you cannot get any surface which is not reconstructed. Well, with this I would like to conclude this lecture and in the next lecture we would have a look at a certain special reconstruction and also, we would look at a different type of a lattice which is the hexagonal lattice and will try to familiarize creating planes in the hexagonal lattice. Thank you very much you.