Chemistry and Physics of Surfaces and Interfaces
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Lecture - 03
Creating Surfaces from Bulk Lattices

Hello everyone, welcome back to the third lecture of our course and in this course what we are mainly going to discuss is about creating surfaces from bulk lattices.

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Before that, we also need to have a quick idea about the Bravais lattices, which is the one we are going to use in creating surfaces. So, this is basically the three-dimensional Bravais lattice, we just have a quick look at it. And then, we will familiarize with something called Miller indices, which you might have studied already in solid state, we will have a quick look at it. Then, we create using the bulk lattices, we would basically create the surfaces from different types of bulk lattices and then finally, we will also have a look at the atomic structure of different surfaces. And please keep it in mind that in my lecture, I am going to only cover the surfaces of crystalline materials. Therefore, the atomic level understanding is extremely important and, in this course, we will never be covering any amorphous materials.

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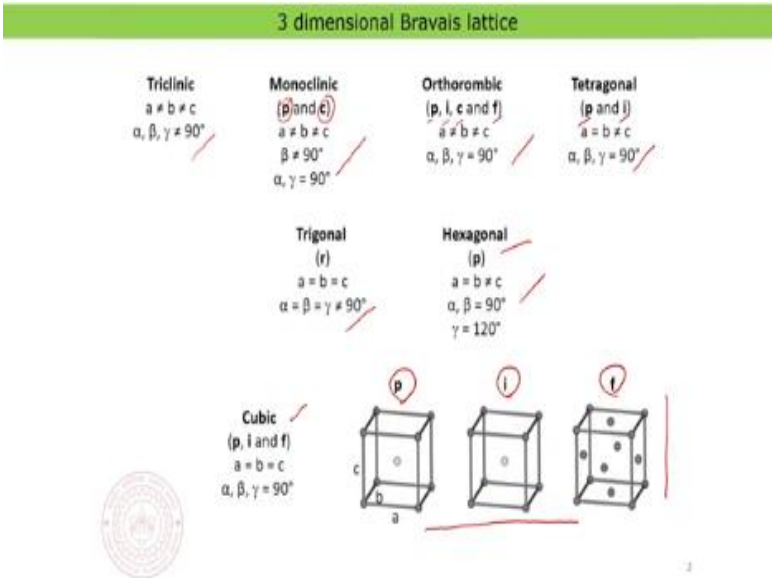

Well, before creating two dimensional lattices, let me introduce to you these three-dimensional Bravais lattices. So, you might have already heard this in solid state chemistry or solid state physics, so typically there are 14 Bravais lattices in which triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic are the different type of crystal packets in which you can see that monoclinic itself has primitive and centered then orthorhombic you have primitive, body centered, centered and face centered, and in tetragonal, you have primitive and body centered and in cubic, you have again primitive body centered and face centered. So, in our lectures, we will be mainly focusing on cubic, and as well as hexagonal crystal lattices. Now, I will show you in the next slide, how to basically create different types of surfaces using these bulk lattices and then, we will basically try to create surfaces from different bulk lattices where we concentrate mostly on the cubic type of crystal packing.

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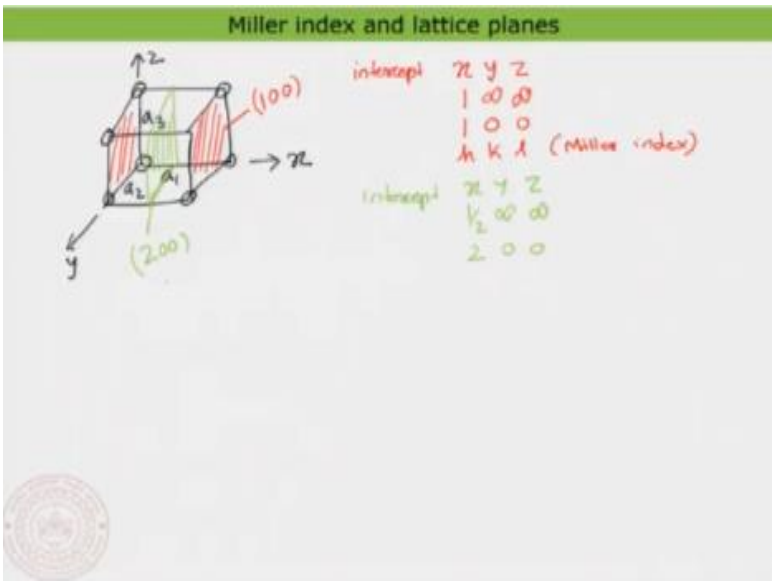

Well, let us have a look at what is Miller index and also the lattice planes. So, when you look at a lattice, there are different ways that the atoms are arranged within the lattice and the way you basically name a given plane of atoms are known as actually or is basically indexed using something known as Miller indices. This is basically named after the scientist who invented Miller and let us have a look at it and then for that we are going to take basically a unit cell, which is a cubic unit cell. I am going to draw a cubic unit cell where the corner atoms are actually placed. So, this is basically a simple cubic and having the corner atoms placed and now this is basically the cubic cell. Now this unit cell has to work out, so we need to basically define the coordinates at which we are working. So basically, I am defining this as my x coordinate, and this as my y coordinate, and this as my z coordinate. Now, this is quite important and this unit cell of the bulk is defined by three unit lattice vectors, namely a_1, a_2, and a_3. These are the three unit lattice vectors, which are basically along the x direction, along the y direction and along the z direction. Now, if I want to create a plane, within this, let us assume that we have a plane which is looking like this which is actually the face of this particular unit cell. Now, how do we basically index this or how do we basically name this and this is what is basically given by the Miller index itself. So, let us have a look, how do we do this? So, along the x axis, this plane so you can also see that this plane is basically the same on both sides and if you continue growing the cell along the x, y and z direction, you are going to meet actually these planes parallel to each other in equal intervals of a_1, $2a_1$, $3a_1$, $4a_1$ and so on. So, now along the x direction, this particular plane has one intercept along the x axis within the unit cell and along the y, you can

see that this plane is basically parallel to the y axis therefore, this plane is never going to intersect actually the a_2. So, therefore your intercept is infinity along the y direction and the same also along the z direction. Now you take the reciprocal of this value, so that is going to give you something called 100 and this is what is actually known as the Miller index of this given plane. So, we can call this plane as 100 planes and normally to represent a plane, so you always put that index in parenthesis, that is basically meaning that this is representing a plane. Now, we can try to look at a different plane. So just for understanding it in detail, so now assume that I have a plane, which is actually passing through the middle of the cell that is something like this. So, this is the plane and now you know that this plane is going to basically repeat two times within the unit cell. Now, if you look at the intercept of this particular plane along the x axis, you would find that this is basically cutting the a_1 into 2. So that basically means the intercept is half, but along the y and the z axis, this is again infinity, the intercept is basically infinity. So that means the inverse of this or the reciprocal of this is going to be 200. So that means this particular plane is actually known as the 200 plane in this case.

We can create this different type of planes within the unit cell in many different ways and the unit cells or the lattices are actually represented or named by this Miller index and that is actually called the Miller index and their relation to lattice planes. And we need this information very much, because we are now going to basically take the bulk lattice and cut the bulk lattice into pieces and once you cut the bulk lattice, and when you open it up, then you are going to basically get this surface. So therefore, it is quite important for us to know the miller index of a lattice plane and the surface itself is going to be basically named after this miller index. This is something that you are going to see soon in the next lecture. So, you will be given more assignments to work out on problems creating different types of cells in simple cubic faces and centred cubic and body centered cubic, so that you can do as an exercise. Now let us have a look at how to create basically an fcc lattice, a surface from an fcc bulk lattice.

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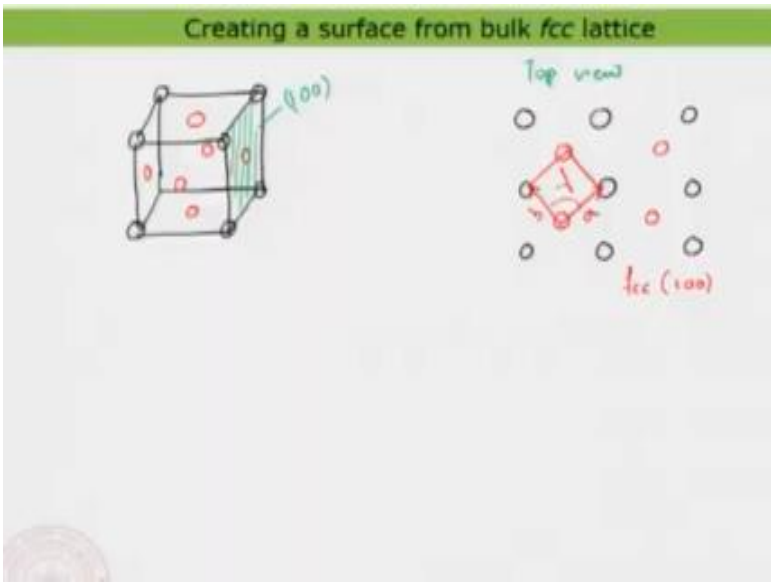

So, for that again, I am going to draw basically a bulk unit cell. So that is the same as the one we did before, so it would look like this and now I have my corner atoms which I have just represented using these open circles and you know that for the face centered cubic. So, I have basically atoms in the face, so those atoms, I am going to basically just represent using these red open circles just to have a clear understanding.

Now, you have the face centered cubic unit cells and you can see the corner atoms and the face centered atoms in this, now what I want to do basically is I want to create basically a plane, which is the 100 plane. Well, you have already seen how the 100 plane looks like this is nothing but this particular plane. Now, the point is, if I want to create basically a 100 plane, what I also need to do is, I need to take bulk crystals, and I need to do a precise cutting of the 100 plane along the given direction. This is of course done also using crystallographic measurements like x ray diffraction crystallography to assign the proper direction of a given lattice and after knowing that you can precisely cut that is actually the modern technology allows you to basically cut precisely along this given lattice. And once you do that, you would basically say, this phase of the unit cell is nothing but the surface that you have created, which is basically the 100 surface.

Now, what I am going to do is I am going to basically take this and then open it up and then view from the top. So now the 10 surface is going to be viewed from the top, so it is a top view, basically. So now let us see, the corner items need to be put in black, so you can see that it actually forms a nice square and then the center item is basically going to be the circular atoms. So now, you can propagate this crystal by just adding more unit cell. So, you basically can just

add more unit cells in this and then you can see how the entire surface looks like. So, the entire surface would look like this with the corner atoms in black and the center atoms in red. Now, you see, this is basically the surface going to look like all, if you see fcc of gold or copper or whatever you take, now all the atoms are going to be the same. So, this color is basically only representing the different location from where you cut. Now, you can see that the unit cell of this particular surface is basically going to be represented by this square and that is actually showing that this surface is a perfect four-fold symmetric surface. Now in this you can represent this using a and b, this would be basically the two different lattice directions of the surface and there will also be something called an angle between the lattice vectors and this is actually normally represented by gamma and then that is basically the surface. So now, what we have created is basically an fcc 100 surface, so this is how you are going to create so you can basically create many different types of surfaces from this, basically like 110 surfaces, you can create a 111 surface or 121, so you can actually just create any different type of surfaces using this, all what you need to do is, you need to cut the crystal along the given crystallographic direction.

So, I will show you one more example, basically from the bcc cells. This is to just get an exercise and then you can do more problems, to understand how you create more different types of cells.

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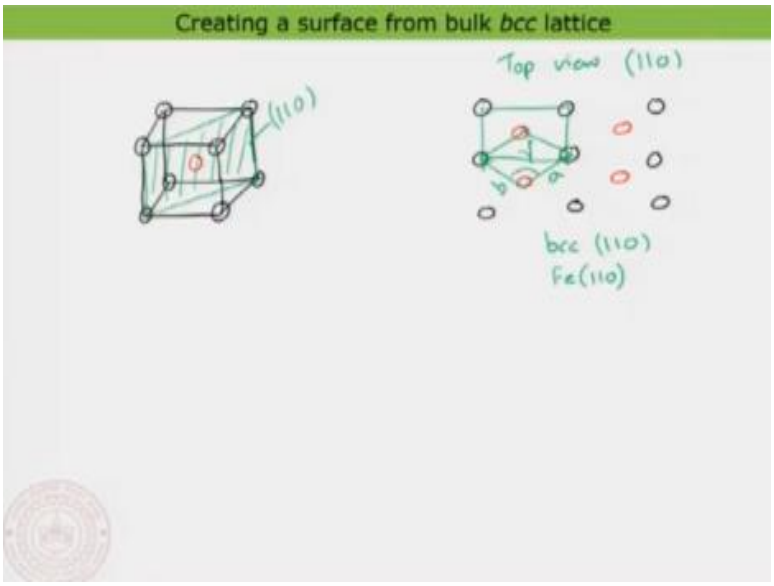

So now, let us have a bcc cell, so the difference in the bcc cell is that you have an atom at the center of the unit cell. The cells are connected like that, so I am going to basically represent the corner atoms with the black dots, a black open circle, and I am going to represent the center atom

with a red dot, so this is basically the bcc. And now in this, what I am interested in creating is actually a surface called 110 surface. So, the 110 surface if you want to create it is slightly different from what you have done before. So, you basically need to move along the x axis once and along the y axis once and then on the z axis infinite. That means, the lattice that you are going to create is basically going to pass through these corner atoms and this is basically going to be the plane which is represented as 110 plane. Now, let us take this plane out and have a look at it, an interesting thing to note is that in this circular, the body center atom is basically within the plane. So, this is quite important, so now when I basically take this out and then view from the top, now let us have a top view of the 110 surface and then when you do that, what you would find is that I have four corner atoms. Now you see the difference here is that the corner atoms are looking like rectangular and not anymore a square in the case of 100 surface. Now I can actually add another unit cell as well. So, I can basically create many of them and then in the middle of each of this rectangle, I will have basically the red label which is representing the atom which was actually in the middle of the cell. Now, you can see the unit cell of this is slightly different, so the unit cell of this one is going to be represented using this or I can basically represent the using another unit cell and so, there are two possible ways that I can represent this 110 surface either using this unit cell or using the other one. Now, I can also label it using two different lattice vectors which are a b and the angle between them, which will be called as the Gamma. So, this is basically my bcc 110 surface. So, whenever you create a surface, the first label of the surface will be bcc that is actually representing the type of the cell and 110 which is representing the type of the plane and now if you know the material itself, let us say like iron for example, you would be calling it as iron 110 that already represent that it is iron crystal and the new half now, the iron 110 surface open to you for working. Now, these kinds of crystals are extremely stable only in something called a ultra high vacuum chamber or an ultra high vacuum technology is therefore very important. In the next class, we will also be looking at the development of ultra-high vacuum technology and also, we will be basically just learning the technology that is extremely important in stabilizing these kinds of surfaces as clear as possible. Otherwise, what is going to happen is that these kind of surfaces are extremely reactive and they would basically get contaminated quickly and then you will not be able to use them further.

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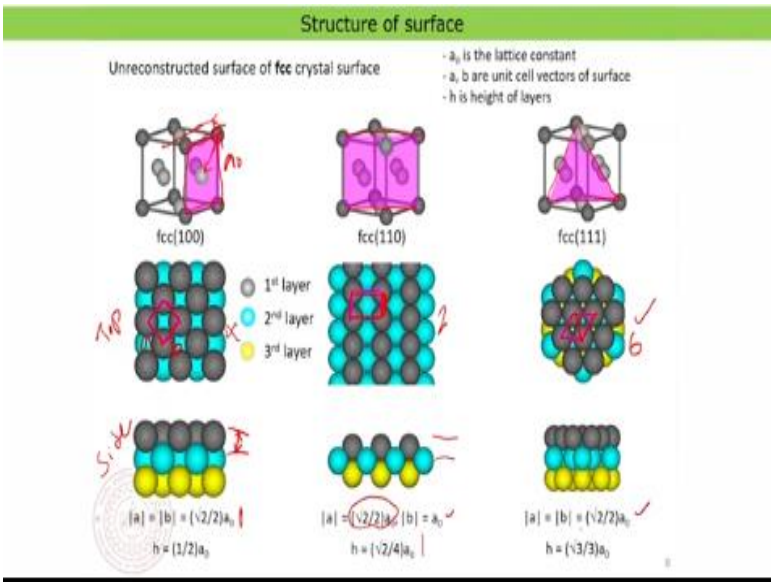

So, in the previous slide, you have seen how to create different surfaces from bulk lattice. Now, let me summarize the different aspects of the surfaces that we have created from the bulk. So, now here, we have the fcc 100 surface as you see here, this is basically the phase plane of the bulk unit cell. Now, if I would basically view the surface from a top view, then this is basically the top view and then you basically notice that the atoms on the surface IS arranged in the corners of a square. That means a symmetry of the surface you can call it a square type symmetry and the distance between the adjacent atoms will be basically noted as a and b these are the unit lattice parameters of the surface and if you would be using a_0 as the bulk lattice parameter then you can ideally calculate using the bulk lattice parameters, what are the values of a and b and the a b values are actually equal because it is a square and that is equal to root 2 by 2 a_0. Now, that distance is nothing but this distance here, so you can ideally use the same construction of the bulk lattice and then calculate basically the unit cell of the surface. Now, if you look at the side view, so this is basically the side view of the lattice and in the side view of lattice we can also calculate the height of the adjacent lattice and that is nothing but half a_0, which is basically this distance, the distance between the adjacent lattice planes.

Now similarly, we can also have a look at the fcc 110 lattice and that plane is basically created by cutting through the diagonal of the bulk lattice. Now, if you would be viewing basically that plane the fcc 110 plane, then you would basically recognize that the atoms are arranged at the corners of a rectangular lattice. And that is the difference here, the fcc 110 the unit cell is nothing

but a rectangular lattice and again, you can calculate a and b the lattice parameters were one of the lattice parameter is exactly the same. So, this one is exactly the same as a bulk lattice parameters, which is a_0 and the other one is nothing but the diagonal of the bulk crystal lattice in which is basically a root 2 by 2 a_0. And again, you can also calculate the height of the unit cell, again using the bulk lattice parameters and which is actually root 2 by 4 a_0. So let us also have a look at the fcc 111 surface and the fcc 111 surface is created through this plane and now you see basically the plane is looking like a triangle within the unit cell. So that means the atoms must be arranged at the corner of a triangle. And if you now create basically a surface by cutting this plane through the bulk crystal lattice and then you would be basically generating this as a top view of the surface where you can see that the atoms are arranged basically in the corners of a triangle. Now you have basically several such triangles put together is nothing but the surface and now you can see that the lattice unit lattice of this one is nothing but an oblique or you can call it as a hexagonal arrangement of the atoms. Now, you see by comparing you see that the fcc 100 is actually a fourfold symmetric surface, a fourfold symmetric surface and fcc 110 is actually a twofold symmetric surface and an fcc 111 is actually a sixfold symmetric surface. So that is basically the difference by creating the surfaces through different planes. And of course, I have already shown you the planes that are constructed along the 100 and 110 and 111. But you may also create different types of planes and then see basically how the atoms are arranged. So again the a, b values of the unit cell are also given here.

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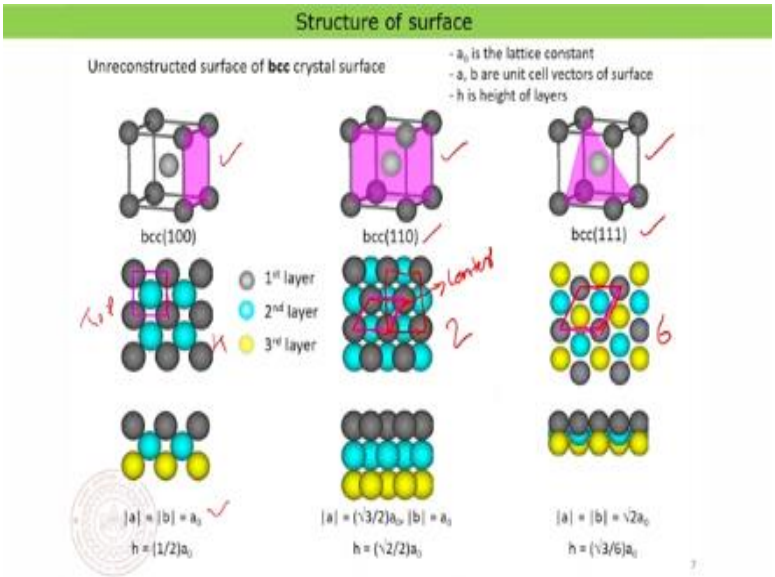

Now, let us also have a look at the planes that you create basically using an bcc type of a crystal unit cells, so they again the planes are basically the same as you have seen in the case of the fcc, but when you create the plane from the bcc bulk crystal and view it from the top that means, when you create a surface out of this. There is a slight difference in the way the atoms are basically arranged or the atoms are basically packed. Well in the case of bcc 100, so the top view basically showing you that the arrangement of the atoms are again the same which is basically a square, so that means it is a four-fold symmetric surface. So, there is almost no difference, but you obviously see that the spacing between the atoms so or that the value of basically a and b are much larger in this case compared to the fcc 100 that means, although the symmetry of the surface is the same, the position or the distance between the atoms are actually different. So that means, a clear difference is basically there although the symmetry is the same, but now when you look at the bcc 110 surface here either you can represent the surface using this kind of an oblique or you can basically represent the surface using a rectangle like this, but here the rectangle has a difference the rectangle has actually an atom at the center. This is not the case when you have created basically the fcc 110 surface where it was clearly a rectangle with nothing at the center, but here you have something at the center. Similarly, bcc 111 surface you see it is again the same, but the atoms are basically arranged in the same way you have basically kind of a hexagonal arrangement of the atoms which is leading to the fact that this surface is also following a six-fold symmetry and this one basically is a two-fold symmetric surface. So, in principle symmetry wise all the surfaces are looking same, but you obviously see the spacing between the atoms are changed and particularly when it comes to the bcc 110 there is also a slight difference in the way the atoms are arranged because you have basically a centred atom in this case of the bcc 110 and for the bcc 111 you see that although the atoms are basically arranged in a six-fold symmetric manner, the spacing between the atoms are basically much larger compared to the fcc 111 surface.

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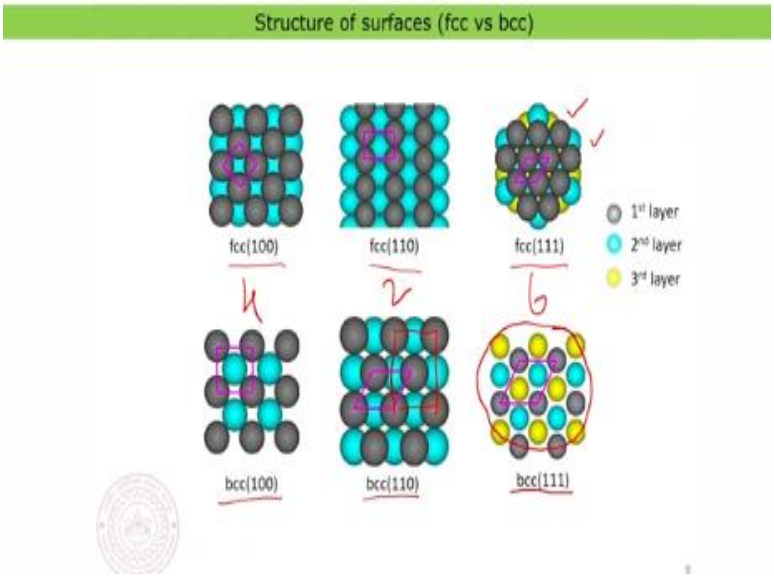

Now, if you would also make a summary of all these, what we have already seen so basically the fcc 110, fcc 100, fcc 111 and also the bcc 100, bcc 110 and bcc 111. In general, I will also mark here basically the rectangular unit cells so that the correlation is basically there, so always you can see this is a fourfold symmetric surface, this is a twofold symmetric surface, this is a sixfold symmetric surface. So, in general, their appearance or the way the atoms are arranged on the surface is clearly the same but the main difference is going to be that, the spacing between the atoms are much larger in the case of bcc surfaces compared to that of the fcc surfaces and particularly not that the bcc 111 surface you can see that. The surface is much more corrugated in a way compared to that of the fcc 111 surface. Because you can see effectively if you look at the packing density, so that something we will see in the next slide. So, the packing density is very, very high in the case of fcc 111 surface, but that of the bcc 11 surface is very very less, so which also means that the roughness of the bcc 111 surface is actually much higher compared to the fcc 111 surface or in general out of all the surfaces that we are looking at the bcc 111 surface is basically a much more rough surface than the others.

So, what is the implication of this roughness or the packing density of the atoms on the surface has a direct consequence on the reactivity of a surface. That means, for example in fcc 111 surface will be the least reactive surfaces out of this and bcc 111 surface would be the most reactive surface. The reason is very simple that you have a much higher surface roughness for this bcc 111 surface than the other, what you see on the slide. But nowadays, you can also

commercially buy these kinds of surfaces, there are companies that would be providing you surfaces with the defined crystallographic directions as you require and then you can basically use the surfaces in further study. So, we will also be basically using these kinds of surfaces later in our lectures in basically creating different type of understanding or basically making interfaces and so on. These are also now commercially available, you can actually just buy ideally gold 111 surface, copper 111 surface, silver 111 surface or iron 111 surface or 100 surface. Any type of surfaces are also commercially available and but to maintain the cleanness of the surface, you need actually this ultra-high vacuum technology, that we will also be looking in the next class. So, one more thing to familiarize at this point is something known as the packing density the packing density is also something like a measure of the surface roughness or about the number of atoms that are present in a unit area for example.

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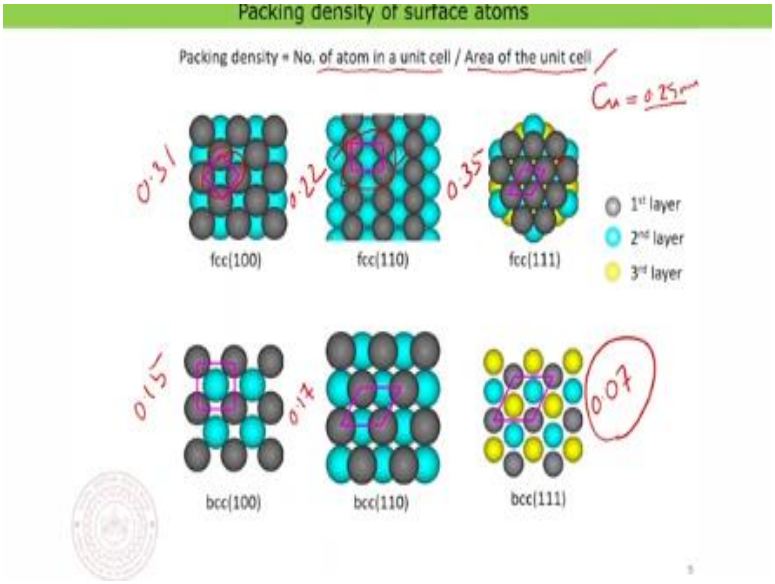

So, the packing density of a surface is defined as the number of atoms in a unit cell divided by the area of the unit cell. Of course, we know the geometry of all these different unit cells, which is nothing but a square rectangle or an oblique; therefore, if I would know the edge length, that means the a and b of the unit cell, then ideally, I can calculate the area of the unit cells. Now what you also notice is that what I am basically representing here is that all these unit cells are nothing but the primitive unit cells. Because you have ideally one atom in each of this unit cells, so once you calculate, therefore area of the unit cell, so now it is the packing density can be calculated by basically just one divided by the area of the unit cell. Now, let me show you an

analogy, let us assume that for copper the bulk lattice parameter that means a_0 is 0.25 nanometer. That of course, is an fcc lattice and if I would basically using the bULK lattice parameter 0.25 nanometer of copper. Then, I can basically just calculate the fcc 100 packing density and that is coming out to be 0.31 and for fcc 111 that comes out to be 0.22 and for fcc 111 that comes out to be 0.35. Now, you see clearly that the fcc 111 surface is the highest packing density surface. Now, if I would also idealize a situation that the bcc for a comparison is also created for copper with the same bulk unit lattice distance which is not correct; Of course, it is only for a comparison we are doing that and if I do that, using the same bulk lattice for the bcc type of surface and then you would be able to calculate the packing density of the bcc 100 surface and then it will come out to be 0.15 for the bcc 100 and for bcc 111 it will be 0.17 and for the bcc 111 it will be 0.07. So, you clearly see that the bcc 111 surface is the lowest packing density surface out of all this. And this is exactly, what I was also telling you in the previous slide that the packing density of the bcc 111 within this comparison is actually the lowest which is also meaning that the surface roughness of the bcc 111 will be the highest which is actually meaning that the bcc 111 surface will be the highest reactive surface and the fcc 111 surface will be the lowest reactive surface. We will also see this aspect a little bit in detail in the upcoming lectures and with this, I would like to conclude the lecture number 3. Thank you very much.