**Advanced Material Characterization by Atom Probe Tomography and
ElectronMicroscopy
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Week-01
Lecture-03**

Welcome to the third class of this course, and I will just briefly revise what we have introduced during the last two classes. So, we went through some basic microstructure. We discussed the formation of crystals, grain structure, and then we talked about the history of the development in the field of microscopy. Then, related to some basics, we correlated the shape of the structure of the tip or the samples and how Professor Muller developed this field ion microscope. So basically, Professor Muller in 1951, as you see in the slide, sharpened a very needle-shaped specimen.

Okay. This needle-shaped specimen was cooled down to subzero temperature, mostly to liquid nitrogen temperature, by using liquid nitrogen. Then he introduced an imaging gas, which might be helium, neon, or argon. Usually, the first time he used hydrogen. This is the gas inlet, and he applied a very high positive potential such that the imaging gas ions get ionized.

When it gets ionized, due to the very high positive voltage on the tip, there will be a large amount of electric field or electric field strength, and these gas ions will accelerate along these field lines. Along these field lines, there is a channel plate or a fluorescent screen where these gas ions hit specific positions on the screen. The heating of these positions directly produces this typical FIM image, which is a field ion image where you can see these bright spots. These spots mark the locations where the imaging gas ions hit those regions.

That is why you are seeing the bright contrast. Each of these bright dots corresponds to the actual image of the atom probe tip. So, you have a tip, and these are the surface

atoms. If you magnify these surface atoms, they have a certain crystal structure. These atoms are in the form of some crystal structure or orientation. As we also explained, these imaging gas ions, which get ionized on the tip, form this FIM image, okay.

We also described the formation of these circular things, and you can see that these are the circular things, and they have certain orientations, correct. Now, if you see an atom probe tip—if you see an atom probe tip—then if you zoom out this region, you can see that these atoms have certain terraces, correct? These are called terraces, atomic terraces, and these are related to the crystallography. So, I have given you an example of a schematic where it shows the 100 direction, correct, and you will have a cubic symmetry. So, those terraces actually correspond to the crystallographic nature of the atom probe tip and due to these terraces.

Okay, the—and the local curvature effect—this is the local curvature effect. The electrons get here; it is a deficiency. Your electric field concentration is much higher at these locations than the flat surfaces, correct, due to which the ionization of the gas atoms takes place at a much higher rate at these locations. That is why you see these circular bright spots—the bright spots which are oriented circularly—and each circle corresponds to a certain crystallographic direction. These are related to a crystallographic direction.

Fine, so this is what we have covered in the last class. And in the next, what we will go through is—yes, we have seen how these gas atoms get ionized. and how these can be used to image the surface of the tip. Okay, so now in this class, what we will go through is some basics related to how these gas atoms get ionized. Okay, get ionized. So, we will go through something related to some basic physics, which is related to the ionization of these gas atoms in the presence of a metal surface. In the presence of a metal surface, fine. So, in the first class, we already described the potential energy curve between the two atoms.

Correct? So, based on that, this is the similar thing. Here, this is the potential energy curve—this is the potential energy curve with the distance, okay? And this plot is without any electric field. Okay, and the field-induced removal of an atom. So this shows that if you have a metal surface, so this is your metal surface.

So you have a metal surface, and if you have gas atoms in the vicinity of this surface, how the potential energy will change as these gas atoms approach the surface of the metal, fine. So, this is the potential energy curve for that particular case, and it is very similar to what we talked about—the Lennard-Jones potential curve where we have given the two atoms. That is the potential energy curve between the two atoms. This is a similar curve, okay?

So, based on that, this diagram shows potential energy as a function of distance to the surface of an electron. which is present inside the gas atom in the vicinity of a tip or in the absence of an electric field. Tip means it is a metal. It is a metal surface, fine? This is a metal surface, this is a vacuum, and your gas atom, which has electrons, is far apart, okay?

So, at long distances, you can see that the potential energy is almost zero. Your V equals zero. It means the electron experiences minimal interaction with both the metal and the gas atom, okay? So, the potential energy is essentially zero. As this gas atom with the electron moves near the metal surface, this is the metal surface, this is the metal surface,

and as it moves near the metal surface, it experiences the first thing: attractive forces. Attractive forces. What is, how do these attractive forces come up? It is attractive forces at intermediate distances, correct? So, you can see that your potential energy curve starts getting negative.

It reduces up to a level where the potential energy is minimum, okay? So, this is related to your attractive forces, okay? So, it means that as the electron decreases, from the gas atom or as it approaches the surface—the metal surface—an attractive force due to the charge effect will come into play, okay? And this charge effect is induced by the metal. Is the metal on the electron, correct?

And it experiences attractive forces. It is very similar to the Van der Waals forces, as we described during the one-atom-to-another-atom interaction, okay? So, this leads to the decrease in the potential energy to a minimum value, a minimum value. Okay, and it leads to a minimum volume, but as you go further near to the metal surface, you can see

that the repulsive forces build up. So, this is called repulsive forces. Repulsive forces build up, and this leads to the increase in the potential energy as the gas atom moves.

Near to the metal surface. So, there is a second type of force which is called repulsive force, which builds up, okay? And these repulsive forces are at very close distances, fine? At very close distances, and this is due to the overlap of the electron cloud of the gas atom and metal. This is due to the overlap of the electron cloud, negative and negative charge, due to which there will be repulsive forces that increase the potential energy further.

And as it goes near the surface, these repulsive forces increase significantly. This is directly what we call Pauli's exclusion principle. This is related to Pauli's exclusion principle. Principle. Fine?

This is the basic thing which is the potential energy change as the gas atom approaches the metal surface. Okay? So, now the third point is the potential energy at the minimum potential energy position. Fine? And this minimum potential energy represents the equilibrium distance.

It represents the equilibrium distance. Equilibrium distance between the electron of the gas atom and the metal surface, okay. So this is the equilibrium distance between the gas atom's electron and the metal surface. So at this point, both the repulsive and the attractive forces are balanced, okay? So this is clear now. So at this position, both the repulsive and the attractive forces are balanced, okay? So now the slope of the potential energy curve—the slope of the curve means this particular slope of the potential energy curve.

Represents it represents the force acting on the electron of the gas atom. Okay, so in this, the slope changes. It shows the attractive force here. The slope is changed here, the repulsive forces. But at this minimum point, your slope is zero. Your slope equals zero, so it indicates that the net force on the electron at this position, at the lowest position, is zero. At this position, it is 0, okay? And this potential energy curve of an electron of the gas atom in the presence of the metal surface is the basis for field ionization, is the basis

for field ionization. It is the basis for the field ionization, and it helps to understand phenomena like electron scattering, adsorption.

And also the chemical reactions, also the chemical reactions, chemical reactions on the metal surfaces, okay. I hope you have understood now this potential energy curve of a gas atom with an electron near the metal surface in the absence of an electric field. Okay, this is very important. This is in the absence of an electric field. Now, in the next thing, if we apply an electric field, okay, you have the same metal, you have a gas atom with the electron cloud.

Fine? When you apply an electric field, the whole potential energy curve gets distorted. It gets distorted. How is it distorted? The potential energy curve gets distorted in this way.

Fine? And now you can see that as you approach the metal surface, The gas atom approaches the metal surface. Okay? So, you can see that there are attractive forces.

It goes to a minimum value, which is the minimum potential energy value. Okay? This particular energy is potential energy. Then again, it increases due to repulsive forces. Correct?

This particular hump is called the tunnel barrier. So, your electric field, whatever you have applied, should be enough such that the minimum potential energy of that particular gas atom should be above the Fermi level or work function of the metal surface. Okay, so the position of this minimum potential energy should be equal to or higher than the EF or the Fermi energy of that particular metal atom.

When it is equal to or higher than the potential energy of the atom, then what will happen is the tunneling process can take place. The tunneling process can take place. Okay? If the potential energy of that particular electron in the gas atom, if the electric field is enough such that that potential energy is at the level of the Fermi energy of that metal, then electron tunneling can take place.

It can go through this tunnel barrier. So, this is called the tunneling process which is taking place and due to which the field ionization, the ionization the ionization of the gas atom takes place. Fine, the electrons will travel through the tunneling process towards the

metal atom. If the potential energy, the minimum potential energy, is equal to or above the EF or the work or the Fermi energy of the electron. Fine, assume that this minimum potential energy is at this level. By application of the electric field.

There is no way that the electron can tunnel through this barrier, okay? So, the minimum requirement for the electron to tunnel towards the metal surface is that the minimum potential energy should be at the level of the Fermi energy of the electron metal surface, fine? Now, the distance, so the distance, the critical distance which is required for the tunneling process to take place is called the X critical. X critical is the minimum distance which is necessary for the tunneling process to take place, correct? And if the electron or if the gas atom with the electron goes below the XC, meaning it comes near to the XC, you can see that the repulsive forces come into the picture.

And due to this repulsion action, your tunneling process cannot take place. So, the electron, the gas atom with the electron should be either at xc or greater than xc. Then only this tunneling process can take place. And this is the second condition. The first condition is that the electric field should be strong enough such that the minimal potential energy is equal to the Fermi energy of the metal atom.

The second condition is that the gas atom distance should be equal to Xc or greater than Xc. If it is less than Xc, the repulsive forces come into play, and the tunneling process cannot take place, or the electron cannot pass through the metal via tunneling. So, these two concepts are now understood. So, how do we measure Xc? Xc can be given by I0.

I0 is the energy of the first ionization of the gas atom, which is represented by this term I0. Phi E is the work function of the metal surface, and F is the applied electric field, fine. So, your Xc, the minimum distance required for the tunneling process to take place, can be given by this particular equation, okay. So, I hope this is clear now. This entire theory was developed by Professor Gomer at Harvard University, Cambridge, in 1961. This is the basic principle related to field emission or the field ionization of gas atoms in the vicinity of a metal atom.

So, if you revise it, you can see that the energy of the electron from the gas atom must be equal to or higher than the lowest available conduction level in the metal. This level is

close to the Fermi level, which is called EF, as I explained in the previous slide, okay? If this condition is not fulfilled, there are no vacant energy levels in the metal available for the tunneling of the electron. Fine. So, the minimum potential energy should be either near the EF or higher than the EF. So, your electric field should be high enough such that the electron can tunnel through the barrier, fine.

As a result, this process can only take place when the gas atom is beyond a critical distance, called Xc, from the surface. Okay. So, ionization is impossible if x is less than Xc because the repulsive forces come into action, but ionization is maximum at x equal to Xc, where the potential energy is minimum, and the main condition is that it must be near the Fermi energy level. Fine? So, this is the basic principle related to the electric field-induced ionization of the gas, which is nothing but the removal of an electron

from the gas atom towards the metal, so that the imaging gas gains a positive charge. Okay? So, if you have an atom probe tip, you apply a very high positive potential bias. You have a metal surface. This metal surface has a certain structure.

The atoms are arranged in a crystallographic structure. You are introducing the imaging gas, which might be neon or argon. Fine? And these gas atoms These gas atoms, due to this very high positive potential, will go near to the surface. At a distance of xc, at a distance of xc—so if you have a tip, you have this particular gas atom at a distance of xc—the electron from the gas atom, in the presence of an electric field, In a sufficient electric field, the electron can travel towards the metal surface. As these electrons travels to the metal surface, these atoms gets ionized developing a positive potential.

And if you put up a screen or the phosphor screen, then what will happen due to this positive potential at the tip? These electric field lines will accelerate these gas atoms which goes towards and hits to the fluorescent screen. So, these gas atoms actually are the image formers of the tip surface. These actually, wherever the position which they are hitting on the fluorescent screen, it is exactly the position of the atoms or the crystallographic terraces. Correct?

More importantly crystallographic terraces develops on the fluorescent screen by these imaging gas atoms. Okay? So I hope the physics behind this field ionization is clear now.

Fine? So here this is just a schematic taken from this particular book Atom Probe Microscopy where this is the atom probe tip.

This is atom probe tip and as you can see that these circular things are nothing but the crystallographic terraces of that particular sample or the tip on the surface. These are called the imaging gas atoms okay and this particular tip is kept at the very subzero temperature at liquid nitrogen temperature so that you can minimize the atomic vibrations. Then you will apply a very high positive potential. Due to which these ions at the surface will go and stick to those terraces. Because terraces as I told you these terraces have a very high electric field concentration.

And these gas atoms will the intensity the very high number of gas atoms will sit at these terraces. Okay? And these terraces get field ionized by the process which I described just before and it develops the field lines. So, you will have a field lines and these positive gas ions will go and hit to the fluorescent screen by and create image an image of the of the of the tip surface of the tip surface as these gas atoms are atomic at the ionization.

So, the ionization field is in the atomic scale. So, this field is at the atomic scale. So, usually you can see the atomically resolved image of that particular tip surface. So, this is the one field FIM of tungsten which is a BCC and you can see these concentric rings. These are nothing but the terraces.

These are nothing but the terraces along a certain crystallographic direction. Now, you can see that these terraces or these rings are having a certain orientation. They have a certain symmetry. And this symmetry is nothing but a stereographic projection. Stereographic projection of the BCC lattice along the 110 direction.

So, you are getting an inside-the-film image; you are actually getting the crystallography or the crystallographic orientation of that BCC crystal along 110, and by the symmetry, you can index these terraces or these rings as different poles or different crystallographic directions. So, we can index these film images as per the crystallographic directions based on the imaging gas which is hitting the fluorescent screen. So, this is just another schematic in a little bit more detailed way. So, this is just a high-mag image of that particular tip which shows the terraces.

So, this is nothing but the same principle I have explained. Okay, so these are some examples which I have taken from this particular book—very nice examples. So, as I told you, the pure tungsten along the 110 direction has a symmetry of 110; fine, you have a symmetry of 110, and these are the concentric rings. So, in the second image, it is of a copper-iron-nickel alloy; this is a particular film image. And in this copper-iron-nickel alloy, it is mostly an FCC matrix where you have a certain precipitate.

Okay. And you can see that particular precipitate; the field ionization has not taken place. So, that means there is no—the gas atom, the density of those spots is very low. Okay. So, in this way, you can see the precipitate in the FIM image—the distribution of the FIM image.

Okay. So, and here you can see that the nanocrystals of pure aluminum. okay and in an amorphous AL9SM2 alloy. So, this is an alloy and in this amorphous matrix, you can see that there is no crystallography associated with this matrix because these spots are randomly arranged but you can see that there are certain terraces which are like this, this first location, second location, third location, fourth location

where you can see that these terraces corresponds to aluminium. pure aluminum nanocrystals which are embedded in the amorphous matrix which are embedded in the amorphous matrix. Some more examples it is related to the nitrided iron chromium alloy where there are iron chromium nickel nitride platelets. Okay, as these platelets has a different composition, the bonding between iron chromium and nitride are different from the alloy iron chromium alloy. So, your field evaporation of the gases atoms around the tip surface, if these platelets are present on the atom probe tip, then those field evaporation also will be different from the matrix.

So, these lines correspond to those platelets which are present in the matrix of the iron-chromium alloy. Fine? And here, there is a very nice example of pure iron, and you can see that these—if you remember the previous FIM images—all the concentric circles are exactly at these concentric circles. Fine? But here, you can see that this particular concentric circle is not finished.

It is like this. Fine? So, this particular stoppage of this concentric stellar corresponds to the dislocation. It is imaging of a dislocation in pure iron. So, you can see how these FIM images are used to identify the dislocations in the sample of the tip surface.

Okay, so with this, I will end this class now, where we have briefly gone through the physics—we have gone through the physics behind field ionization—and I hope that you have understood the basics related to the ionization of the gas atoms near the metal surface in the presence of the electric field and how it is different without the electric field. And the major takeaway is that the electric field should be sufficient enough such that the minimum potential energy of the electron inside the gas atom should be equal to or more than the Fermi energy level of the metal surface. This will lead to the tunneling of electrons across the tunnel barrier.

Otherwise, if the potential energy is not near the Fermi energy, then the tunneling process cannot take place. Okay, and the second part is the X critical, the critical distance between the electron of the gas atom and the metal surface. So, if you go near the metal surface, the repulsive action takes place, so this tunneling process cannot take place. So, it should be at a certain X critical or more than that, such that the electron tunneling can take place in the presence of the electric field. And with this, I will end this class. In the next class, we will discuss the electric field, the difference in the electric field around the tip surface

and, ideally, the sphere where we explain the point projection model. So, whatever the field FIM we are getting, it has to be reconstructed. So, based on the point projection model, we will cover that topic. Thank you.