

**Advanced Material Characterization by Atom Probe Tomography and Electron
Microscopy**

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Week-01

Lecture-02

So welcome to the second class of the course. The last class we have briefly introduced the microstructure, microstructural features, then the potential energy between the atoms and also we have briefly gone through the history of towards the development of field electron emission microscope by Erwin W. Muller. And now in this class, we will proceed further towards the field ionization microscope. In the next set of experiments, what Muller did is instead of applying a negative potential at the tip, he has applied a very high positive potential at the tip.

Okay? And he has also introduced gas around the tip under a very high vacuum. Fine? So, these gas... He used, it can be either argon, correct?

So this introduction of the gas, so the atmosphere is a typically gas and he has applied a very high positive potential. Due to this positive potential, there will be a ionization of the gas has taken place. Due to which these ions which are positive, which are positive and which are positive in charge, which are positive in charge, And due to the high potential, there will be a very high electric field lines. And these positive charged gas ions will accelerate along these field lines.

Fine, and he has kept one fluorescent screen. And these positive gas ions, which are accelerated, hit the fluorescent screen. And what you are seeing here is an image which is recorded when these positive ions are hitting the fluorescent screen. And here, strikingly,

you can see that each dot corresponds to one atom. Okay? So, with this, what he has done is he actually...

imaged the atoms for the first time. He has imaged the atoms with this reverse by reversing the potential on the application of the tip. Fine. Okay, so as I told you, this is how it was developed. Professor Muller had a student who was an Indian student. His name was Kanwar Bahadur. Correct? He was a PhD student who was working during that time. And this was the first time an image was recorded in 1955.

Okay? On October 11, 1955. They used a tungsten tip which is 110-oriented. Okay? And as I told you, they injected the gas atoms.

They kept very high potential of plus or positive on the tip. So, that due to this large potential atom, due to the large potential, these gas get ionized, correct? And due to the potential, there will be an electric field, and along this electric field, these gas ions are accelerated and hit the fluorescent screen, right? And they use the gas hydrogen. So, what we call—what they call—is this, this is called an imaging gas, correct?

This is called imaging gas, which carries information about the position of the atoms on the sample lattice. Correct? So, now what was the role of Kanwar Bahadur? So, actually, these experiments were performed at room temperature in a very high vacuum. And as you know, at room temperature, the atomic vibrations are very high.

Fine, and also the needle was not sharp enough—they were not able to—it was around 100 nanometers. Okay, so one day, Kanwar, what he did was he suggested to Müller that they could cool the specimen to liquid nitrogen temperature. And also, incidentally, what happened was he had made the sharp needle 20 nanometers, which is much less than 100 nanometers. Correct? These two experiments led to the This image where you can actually see the resolved atoms—each dot corresponds to one atom. So this is how, in 1950, they published a paper in 1956 about this technique, where they called it a field ion microscope.

Because we are ionizing the imaging gas, and these gas ions are accelerated towards the fluorescent screen or towards the phosphor screen. These can be recorded as individual

atoms on the image. We will go into details about this particular image—how these are recorded and how these bright intensities are actually related to the atoms. Okay, and here on the right side, you can see an image of Bahadur during a conference related to the development of field ion microscopy. Okay, so after this experiment, how do we identify the atoms?

Now, in the previous slide, I have shown the bright spots, and these spots correspond to atoms. Now, you have to recognize these atoms, correct? So, which element is present? What is the chemistry? What is the chemical identity of these bright spots?

So, in 1967, Mueller's student, John Panitz, a PhD student, attached a time-of-flight spectrometer. Correct? He attached a time-of-flight spectrometer to the field ion microscope, and with this spectrometer, he, for the first time, identified the nature of that particular atom. Fine? What is a time-of-flight spectrometer? It means that it is related to the time of flight of the ions traveling from the tip to the fluorescent screen. Fine?

And by measuring this time of flight, you can actually identify what type of species is present in the microscope, through the microscope, correct? And this was the instrument which he developed, and he was the student, a PhD student with Mueller. And the main issue with this technique is the detection. So, in an hour, only 10 atoms were detected, correct? And also a 1-nanometer field of view.

Field of view means the region which is under field evaporation, okay? So the field of view was very small. And the time taken for individual atoms to record was around 10 atoms per hour. So this was the major issue with the first pulse. So what we call it, what they called it, is pulsed field ion evaporation and one ion at a time, fine?

So later, this was developed in 1967. In 1972, there was a development related to spherical microchannel plate amplifiers, correct? So, it means that one ion striking this amplifier will generate a large amount of secondary ions or secondary electrons which corresponds to what can increase the detection efficiency, detectability. So, with this in 1972, they were able to generate 3D data with 2D maps, okay?

But the issue with this type of technique is you can only record single atom type at a time. It means that if you have atom probe tip, if you have atom probe tip which consists of aluminum and copper, so at the top part, you can actually at a time, you can only record either copper or detect or only aluminium. Once copper is detected, then later you can detect aluminium. So, it was only the disadvantage was single atom type at a time.

Later in 1988, there was drastic change where position sensitive detectors were developed. Position sensitive detector and it was Termed as POS atom probe. POS atom probe, okay? Position-sensitive atom probe, which was developed in the 1980s by Goodfrey and Smith, was published in a scientific instrument journal. They used position-sensitive detectors, solving the problem of single-atom detection at a time, okay? Additionally, the field of view was improved to up to 15 nanometers.

It means that in a particular tip from this region, you can record or detect both aluminum and copper at the same time. So, this was the development in 1988. Later, in 1993, a professor from Japan, Professor Nishikawa, kept a funnel-shaped electrode. Just ahead of the tip—these sharp needles can be considered as samples or specimens in the needles—what he did was place a small electrode near the tip. Assume there is an atom probe tip, and he placed a hollow, funnel-shaped electrode in position,

Okay, and he has applied a very high potential. What is the effect of this electrode? Actually, in this case, the electric field generated around the tip can be more concentrated. Correct? So, the fraction of ions that pass through—those which are generated—means your efficiency or the detectability of these ions is much increased. This means the number of atoms detected in a very short time was possible by introducing this electrode just ahead of the atom probe tip.

Okay, then in 2001, based on this design—a similar design—okay, so what Thomas Kelly and his colleagues developed the local electrode atom probe. Okay? So this idea came from the work by Nishikawa, where they used a local electrode just near the atom probe tip, and this due to which the electric field lines just ahead of the atom probe tip got concentrated. and the field of view improved significantly, up to 150 nanometers, okay?

And this is one typical modern atom probe, which we call a LEAP, L-E-A-P, Local Electrode Atom Probe. And this is—it was named as 3000 XHR, 3000 XHR, correct? Very high data collection, up to 10^7 atoms per hour. Also, there is a reduction in energy spread, which means the mass resolution improved very effectively with this. So here, you can see the schematic of this setup, where this is the microtip specimen, similar to the specimens shown by Nishikawa, and this is called the local electrode.

This is called a local electrode, correct? And the voltage was applied between this local electrode and the needle specimen. A very high voltage. Positive voltage and negative voltage here. Due to which the electric field lines are all concentrated.

That is why you will see that the data collection of a large number of atoms was possible by this setup. Okay, and in this setup, I will come to the construction of this local electron atom probe later. Here, this is the imaging detector. This is called the imaging detector. And I will tell you more about how this imaging detector works. The development related to the image injector increased, which led to the collection of a high number of atoms per unit time. So, parallelly, when I told you about the FEEM, okay,

Field Emission Electron Microscope, FEM. Correct? It uses electrons for imaging purposes. Okay? When Mueller was working on this, parallelly in the same institute, there was a professor called Max Noll.

And he had a student whose name was Ernst Ruska. Actually, he was working on a new instrument based on this FEM. Correct. And it was called the electron microscope, for which he got the Nobel Prize in Physics in 1986. So this was the first electron microscope, which was designed by Ernst Ruska, who was a student of Professor Max Knoll.

So it was designed in 1931, and in the same university, Mueller was working on this FEM microscope, okay? So Mueller—the only difference is Mueller used the FEM technique for microscopy. But here, Ernst Ruska used electrons to create images. By interacting them with the samples, okay? So this was the difference between the two, where they were working together at the same time during the 1930s. So here, there are two cases: the first and the second case. This is related to FEEM, and this is related to FIM.

Field ionization microscopy, fine. And you can see the comparison of the images between these two. Here, there are bright diffused spots, which correspond to the electrons hitting the screen. But here, due to the ionization of gas atoms, you can actually resolve individual atoms. The bright spots correspond to individual atoms. So, with this basic understanding, we will further proceed toward the microscope. So, as we see, this is related to the resolving power.

Fine, resolving power. I will come to the definition of resolution later. So, this is from the macro to the nanoscale, fine? So, we can see that at the centimeter and millimeter scale, we can actually see the features with the naked eye, while it might be the hair, okay? And we use an optical microscope. Electron microscopes, okay? Based on the resolution—based on the resolving power—what we want, okay? So, an optical microscope uses light.

Which has a very high wavelength, okay? So, based on the wavelength, you can actually resolve the technique—resolve the features which are required, fine? And if you use electrons as a source, then you can resolve. Actually, these electrons are accelerated toward the sample at a very high voltage. And this particular voltage is directly related. Higher is the voltage, smaller is the lambda.

Lambda means smaller is the wavelength. And smaller is the wavelength, and then the resolving power will also be very high, fine? So, this is how a complete spectrum—from macro to nanoscale—and how this evolved with time. Okay. So, I am showing you an SCM image.

Okay. This is an electron image. Correct. And as you can see in this image, there is a certain relation to the gray contrast. There is a gray contrast.

There is a dark contrast and still there are darker contrasts. Fine. And you can easily see the dark contrast across these boundaries. Correct. These are called grain boundaries.

Fine. These are called grain boundaries. And you can see, somewhere, the twin boundaries also. Fine. So, this is the contrast.

This is an electron image, a secondary electron image, recorded in an SCM where you can see the contrast related to the grain structure. Now, as I told you before, this particular structure, The grain structure is developed by this particular route. Fine? So, it will form a nucleus.

Correct? After the formation of nuclei, the nucleus will grow at different positions. Positions 1, 2, 3, 4, and this develops into a grain structure which we are seeing. As also described in the previous class, this one particular grain has one particular crystal structure. Correct?

One particular grain has one particular crystal structure, and this crystal structure is nothing but a repetition of the unit cell. Now, if I prepare a sharp needle with this particular region only, if I am preparing a sharp needle which has a radius of curvature of around 100 nanometers, less than 100 nanometers. Correct? So, this is a particular needle. We will come to the sample preparation later, but now consider this is a sharp needle which has a radius of curvature less than 100 nanometers or mostly around 50 nanometers.

I am talking about the radius, correct? This is a very sharp needle made from this particular grain, fine? If you go further, if you go further on that particular tip, You can see that this tip consists of these blue spheres, correct? And these blue spheres are nothing but atoms arranged in a periodic fashion, correct?

So now, I will connect all these things together to understand this, correct? And these blue-colored spheres are nothing but atoms arranged in a periodic fashion in a periodic fashion, correct? If you zoom in on this particular tip, if you zoom in on this particular tip, you can see that these atoms have a certain orientation in this direction. It might be a 1, 1, 1, triple 1 orientation, and you can see that this is your first plane.

This is your second plane. This is your third plane. So, I am talking about two dimensions, correct? I am talking about something like this, interplane. So, between these two planes, you can see there is a step.

There is a step. Okay? So, if you zoom out, you will see one plane. There is a step. Another plane.

There is a step. So, you will have a ledge. So, this is called a ledge or a terrace. Okay? A ledge, or we can call it a terrace.

Fine? This is the zoomed-out region of that particular tip. Fine? If you look at the atomic level, at still magnification, you can see what I have shown here on the terrace. These are called terraces.

Correct? These are called terraces. What is the importance of these terraces? I will come in the next few minutes. So, if you see this particular tip in this direction, in the Z direction—meaning the top view—

The top view of this is the top view. Fine? And if you see that, you can see that these atoms are arranged in a certain crystallographic direction. Okay?

And this particular orientation is 001. Okay? So, you can see the cubic symmetry. Fine? So, if you zoom in more, you can see that these atoms are actually in the cubic direction.

You can see here. This is the atom. And this region between these two is the terrace. Correct?

So, this is another plane, again a terrace. This is another plane; this is again a terrace. So, here you can see the complete crystallographic nature of the atomic distribution or the position of the atoms at the tip surface, at the top tip surface. Okay? And if you see the cross-section of this particular image, you can see that I can assume this is a big, this is the tip. Fine?

And this is the top part of the tip, and you can see that I have shown you these terraces. So, this is one particular plane; there is a terrace, there is a terrace. There are planes, the edges where the edges of these terraces are prone to very high electric fields when you apply a field. Then the electric field around these edges, around these edges, will be much higher than the electric field concentration at these flat faces. Okay? This is related to your radius of curvature. As I told you, F is equal to voltage divided by R .

Correct? The voltage applied and the field above, field is directly, is directly inversely proportional to the R. So, due to this terrace effect or due to this sharp point, the field around this region, at this region will be very high as compared to the flat surface. This will have a direct consequence of the field ion image which we have gathered it okay so now you remember that we are actually seeing this atomic structure on the tip surface and these are called terraces

which are very important consequence for the field ion images okay how how it is related so what muller has done is This is in 1951. This is published in 1951, the instrument. So that instrument, it is called field ionization microscopy. So what he has done is, this is the liquid nitrogen to cool the tip.

And this is your tip. If you zoom out, it will look as a very sharp needle. Now, he has introduced a gas. This is the gas inlet. He has introduced the gas, hydrogen.

You can use also argon. So, this gas, when you apply a very high voltage between the tip, positive voltage and this is the channel plate. Where the for the detection okay if you apply a very high voltage between the channel plate and the atom probe tip what will happen there will be a high field ionization of the gas at gas which is injected which is called imaging gas. ionization of the imaging gas and due to the field developed by the potential applied the electric field lines will be in this direction

okay and these gas ions will accelerate towards these field lines and it will hit to the channel plate. This in the right side, this is the schematic and I am showing you one image here which is called a field ion image. Fine? Now, in the previous slide, if you remember in the previous slide, what we see here is this particular top view, okay? And after application of the field potential,

The gas atoms, the imaging gas atoms, what will happen is the imaging gas atoms will get ionized much faster in these regions because you are injecting a gas, correct? So, these gas atoms gets ionized faster and so they will accelerate at a very much faster than the or they accelerate at very less time. ok than the atoms which are gas atoms which are present under flat surface fine due to which you will develop these these spherical things and each sphere actually corresponds to a certain crystallographic orientation so the

arrangement so if you zoom out this particular region or if this zoom out you will get atoms which are arranged in a circular fashion, correct?

And these circular fashion atoms, it is nothing but the gaseous atoms which are field evaporated from the terraces. And the symmetry of these terraces and the position of these terraces or the symmetry of these terraces shows the crystallography, crystallography or the orientation of that particular region or the tip. So, now you understand that how the terraces which we have schematically shown is related to the bright spots which are recorded in the field ion image. So, and you can see that these all bright spots

Corresponds to single atoms which are the image of the surface atoms of the particular tip. So, what we call is a FIM provides the atomic resolution imaging of the surface of the specimen and imaging gas. We can use helium, neon, argon. It is introduced around the highly positive charge sharp needle. Then,

The electric field around the apex, as I told you, around the apex of the specimen is of the order of 10^{10} volt per meter. It means that 10^{10} , it means that 10 volt per nanometer. Such a high electric field is generated when you apply a voltage of that sharp needle. Then the image that is formed is by the impact of the gas ions which is called imaging gas on the phosphor screen maps and it shows the distribution of electric field at the surface. It is nothing but you are imaging actually the distribution of electric field around the tip as I told you.

These are the terraces, fine? And the distribution of electric field is different at the flat surface and at the terraces. And actually in your film image, you are seeing that distribution directly, okay? And it is intrinsically related to the local topography of the tip. This is how you can resolve actually the atoms by the field ionization, field ion microscopy.

So, here one more important point is the specimen is maintained at extremely low temperature and to optimize the spatial resolution because at room temperature the atoms vibrations are very high. So, they are kept at very low temperature, and the voltage applied is high enough to provide a direct image of the individual surface atoms. So, the

voltage is applied in such a way that the imaging gas, which is used, should get ionized—fine, should get ionized. We will come to the ionization in the coming slides—fine.

So, for a non-flat surface, as I explained, for a non-flat surface, the protruding atoms are subject to a greater charge. So, this particular region we call it protruded atoms, and the electric field distribution along this and the electric field distribution here is totally different. Here, it is more intense and more concentrated than the flat surface. So, the electric field at the surface is directly proportional to the charge density. It is higher around these local protrusions.

So, in the case of atomically smooth curved surfaces, these protrusions correspond to the edges of the atomic terraces. So, what we call atomic terraces. Then, by imaging the distribution of field intensity. So, there is an electric field around the tip. By imaging the distribution of field intensity at the surface, the field ion microscope provides an atomically resolved image of the surface itself.

So, this particular image on the right side is actually the image of the electric field distribution across the tip, which is directly related to your local protrusions. These are nothing but the atomic terraces, which also provide crystallographic information. Correct? So, this is how Mueller developed this technique in 1951. So, with this, I will end the class, the second class here.

Now, I have given you a brief overview from the field emission electron microscope to field ion microscopy. Now, in the next class, what we will do is We will discuss the basic physics related to field ionization. Fine? So, we will cover the basic physics related to field ionization, which is very important to understand the electric field distribution across the atom tip or the needle specimen.