

**Advanced Material Characterization by Atom Probe Tomography and  
Electron Microscopy  
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Week-05  
Lecture-11**

So, welcome to this class. Just briefly, in the last class, we discussed the different types of pulsing methods: HV pulsing, laser pulsing, and we also described in HV pulsing what the importance of energy deficit is. What is—what do you mean by energy deficit? And in laser pulsing, what is the role of cooling time, which governs the shape of the particular mass spectrum curve? Fine. And also, we have gone through the estimation of peak temperature during pulsing, okay. Then, once we finish this difference between the HV and the laser pulsing,

we also talked about how this ionization process takes place. So, especially in the laser mode, it is a photo-assisted ionization process. Correct? So, photo-assisted ionization process.

So, basically, there are three phenomena where we can understand how this ionization of an adsorbed atom takes place. So, the first one is, as I showed, this particular adsorbed atom—the electron from the adsorbed atom can directly tunnel to the conduction band. Fine. This is the simplest one where this ionization can take place, okay. The second part is the electron from the adatom—from the adatom—is excited by the resonant absorption of the photon, which is  $h\nu$ , okay, and this, due to which this particular electron can go to this position and it can tunnel to the conduction band.

This is the second path which an electron can follow. And the third path which it can follow is it involves the absorption of photon into the material. So, this photon absorption into the material will create, excite the electron from the position which creates a hole. And the electron from the adsorbed atom will pass through this particular hole, go to the particular hole.

So, or pass through or the tunnel towards the hole in the valence band. So, the first, second and third, these are the three paths through which the electron from the adsorbed atom can tunnel through the material. So, this first and the second, first and the third method is enhanced by the large number of electrons in the material, okay? And at low temperatures, if it is a very at low temperature, the number of electrons in the conduction band in semiconductor insulators are negligible.

So, in this the third path is more dominant. at low temperature for the semiconductors and the insulators okay but regardless of this path these three paths to for the photo resistor ionization the photon induced induces field evaporation involves creation of an ion on the surface and it consequent acceleration acceleration by the surrounding field okay so this is the broad idea for the laser pulsing so from the laser pulsing which is different from HP pulsing the APT the atom probe tomography application of that atom probe tomography got broaden up to semiconductors functional materials

And also the insulators, okay. So, this is broadly what we described during the last class. Now, I will—now we can talk about the HV pulsing, okay. So, as you know, in the HV pulsing, In HV pulsing, you will have an increase in the voltage at that particular point, okay? So, there is a certain frequency at which these pulses can be generated.

So, there will be an increase in the voltage and then a return to the baseline. Now, you can see that on the tip surface, the atoms which are present on the tip surface, those are all in vibration—the frequency, the vibration, correct? So, some of the atoms can get polarized, maybe at these locations, during the HV pulsing. It is not necessary that the atoms will polarize exactly at the peak of the HV pulsing, fine? So, the atoms can get polarized at the voltage

of the pulse in these locations, not necessarily at the peak of the pulse, fine. So now, this has a direct consequence, okay. So, what? There will be a—so, because of this particular difference in polarization of these atoms at different locations of an HV pulse, due to which there will be a broadening of the peak. Okay, so, broadening of the mass.

So, in your mass spectrum, you will see a broadening of the peak of that particular mass to charge ratio. So, for this purpose, to improve the resolution, what we call it as a, we

use an energy compensation device. technique or device what is this energy compensation device it actually corrects the energy deficit of during HV pulsing okay so ions so whatever the ions which are entering at an electric field with a low energy will be deflected first so ions with a which is entering the electric field with low energy, low energy ions will be deflected first and will have a shorter flight path.

Shorter flight path means shorter distance. It will travel the shorter distance, correct? These than the ions which have high energy. which have high energy. So, it means ions which have high energy will have a longer flight time.

So, high energy and low energy mean that the ions which are field-evaporated during this particular region of the pulse and ions which are accelerating or atoms which are polarizing at the location of this particular pulse. So, it is possible that the ions of the same mass-to-charge ratio have different energies. Due to this pulsing, HV pulsing, and due to which there will be an energy deficit. So, it means that the ions which have the same mass-to-charge ratio but different energies can arrive.

at the detector at the detector with similar time of flight. This can be possible, okay? And this particular will only raise, we will only lead to the broadening of the mass spectrum peak, okay? And this of different energy. So, the ions which have the same mass-to-charge ratio of different energies can arrive at the same at the detector with the similar time of flight. This is possible by using the energy compensation devices which are called a reflectron, okay? By using the reflectron, so what is the function of reflectron? It is So, we use Reflectron.

So, here the more energetic ions will have a longer flight path. The reflectron is used to make the more energetic ions have a longer flight path, okay? So, reflectron is nothing but an electrostatic mirror, an electrostatic mirror. So, if you see the atom probe deconstruction now you will have an atom probe tip, you have an electrode, okay? And there will be a reflectron here, and the ions which are traveling in this electrostatic field get reflected here, and there will be a detector here, okay? So, the ions which have more energy will travel

more into the reflectron and travel back to the detector, okay? So, this particular reflectron acts as an electrostatic mirror made up of a succession of planes of progressively increasing electric field. So from this location to this location there will be an increase in the electric field progressively increasing electric field so ions which are having a high energy will travel further into the reflectron before being reflected so by this you are increasing the time of flight. So, this is just a, you can see that this is the needle specimen. This is your local electrode and this is called a reflectron.

As I told you, this is a succession of all the planes which progressively increase the electric field. So, the ion which is having a higher energy, low energy. Higher energy it will actually travel into this reflectron at more distance before being deflected and will reach the detector at the same time of flight which is having a low energy and it will be deflected much earlier and reach the detector. So in this way if you have a pulse, HV pulse

If there is an ion which is actually polarized and accelerated at this region and there is an ion which is accelerated at this region, but they have a same mass to charge ratio, same mass to charge ratio, the difference in the time of flight can be similar or can be same by using the reflectron, okay? So, these ions... and these ions will come to the detector at the same time of flight at the same time okay so the high energy ions will go further than the low energy ions before deflection okay so this is the reflectron here in the right side I am showing you a mass to charge ratio

Okay, and these are the number of ions and you can see that without reflectron, the broadening in the peak is much higher. In this case, the broadening in the peaks are much higher. You can see the chromium, vanadium, manganese, iron, the broadening in the peak is much higher. But after using the reflectron, you can see that the broadening in the peaks got reduced significantly. So it improves the mass resolution.

It improves the mass resolution. So, the main function of reflectron is to improve the mass resolution, especially during the, for the HV pulsing, which compensates for the energy deficit. Okay? So, during the pulsing, as I told you, At same mass to charge ratio

can have a different energies but to detect the mass to charge ratio what we should do is it should reach the detector at the same time of flight.

That can be possible by using the reflectron which is a succession of planes which are progressively increasing the electric field. and the higher energetic ions will travel more inside to the reflectron in that electrostatic field before being deflected as for the low energy ions and they reach the detector at the similar time of flight. So that the broadening of the peaks gets lowered so that it will improve the mass resolution. Basically, it reduces the size of the tail of the mass spectrum, of the mass peaks.

Size of the tail. So, this particular region is the tail of that particular mass peak. That size of the mass peak, size of the tail of the mass peak reduces. So, this is how we can improve the mass resolution. So I hope now the instrumentation part of atom probe tomography, the basic instrumentation is covered.

Fine. Now what we do is briefly go through the important experimental protocols needed during field ionization and field evaporation. So, we will just go through the experimental protocols for FIM and APT. First, we will talk about FIM, the basic protocols which have to be followed. So, we introduced field ionization in a couple of classes before.

So, what is the exact procedure? So, the first thing is there should be a very sharp needle. Okay, that creates an intense electric field. The chamber should be ultra-high vacuum, and the specimen stage should be cooled down to cryogenic temperature. It is about 20 to 80 Kelvin. We will come to the importance of temperature later.

Okay. The second important step is, after the stabilization of temperature and pressure, a low-pressure imaging gas is introduced. This gas can be at a pressure in the range of 10 to the power of minus 5 to 10 to the power of minus 6 Torr. Okay, so this low pressure is usually limited by the maximum acceptable pressure for the MCP plates, multi-channel plates. The imaging gas can be

Helium, neon, or their mixture—this depends upon the material under investigation, okay? And the third important point is the specimen. A DC voltage is applied, which progressively increases until the electric field at the specimen is very intense, okay? It is

enough to ionize the imaging gas. Ionization of the imaging gas. Okay, so the DC voltage is applied to the specimen. The fourth thing is the voltage is increased to reach the optimum imaging condition.

Okay, so the voltage—the fourth condition—is the voltage should be increased to an optimum condition. What is the optimum condition now here? The optimum condition corresponds to what we described before—the best image voltage, or we can call it BIV. Okay. And it means that we can also call it BIF.

We can call it the best image field. Field condition—that is called the optimum condition, okay? So, it means that the best image field corresponds to the maximum number of atoms to be imaged with maximum contrast. Okay, so usually the best image field critically depends upon the imaging gas used. So, for example, helium, which has an ionization energy of 24.6 electron volts, has a BIF value of 44 volts per nanometer.

Similarly, for neon, the ionization potential is around 21.6 electron volts. The BIF value is around 35 volts per nanometer. It means that at these voltage conditions, you will get an optimum condition for a good contrast image on the fluorescent screen. Okay, so remember in one of the previous classes, we actually talked about this BIF and BIV value. Okay, and this is in terms of ionization zone size, which is a  $\Delta 0$  that is related to your spot size, the minimum spot size that is related to your resolution.

Resolution in the FIM image, correct? So this is the ionization zone size now. There are two conditions in this: one is, remember that if the electric field is very low, it means that the critical distance  $X_c$  is very large. If the critical distance  $X_c$  is large, then the field distribution in the zone may not reflect the structure of the surface with atomic resolution, okay? If  $X_c$  is large, if these are the imaging gas ions because of this large  $X_c$ , then the atomic structure on the tip surface cannot be mimicked or cannot be replicated. Okay, so the field distribution in the zone may not reflect the actual structure of the tip surface.

If the field is too high, if your electric field is too high, then what will happen? There will be an overlap of the ionization zone. Zone ahead of the tip surface or ahead of the atomic structure of the tip surface of each atom, okay? So, this overlap of ionization will blur the image. These are the two conditions which are important related to the BIF, okay?

So, this is the fourth condition where the optimum voltage or where the optimum best image voltage or best image field is. The fifth point is pulsing. Okay, pulsing can also be used to induce field evaporation. Okay, pulsing can also be used to induce field evaporation in FIM.

So, how to choose the imaging gas? So, this is a very crucial step during FIM: the choice of imaging gas. Usually, the imaging gases we use are hydrogen, helium, neon, argon, and xenon. Okay, so they have different BIF values. Okay? So, for hydrogen, it is around 22 BIF volts per nanometer; for helium, it is 45; for neon, it is 38; for argon, it is around 2; and for xenon, it is around 15.

Okay, so depending on the imaging gas, we choose which type of gas to use for FIM microscopy. Usually, the rule we follow is that the choice of gas depends on the material being imaged, okay? So, the optimum ionization field of gas, the optimum Optimum condition is that the ionization field of the gas should be lower than the evaporation field of the specimen, okay? So, the ionization field of the gas—the optimum condition we usually follow—should be lower than the

field of the specimen. If this is not the case, then what will happen is the specimen will field evaporate continuously, continuously and there will be no proper image will be formed. There will be no proper image. The image will not form properly. So, this is the optimum condition what we follow is the ionization field of the gas should be lower than the evaporation field of the specimen.

So, for example helium is selected for most of the refractive metals which is having a high electric evaporation field. Okay. And usually other materials, most of the system which use neon, chosen for most of the systems. Okay. Sometimes hydrogen can be used for silicon material.

And also what we can do is we can use the combination of these imaging gases. Combination of imaging gases. if the specimen if the specimen has different phases okay which different phases means it will have a different evaporation fields fine so you can use the combination of imaging gases as per that okay so this is the basic condition to

choose the imaging gas fine so So, for example, if your phase exhibits a dark contrast with high ionization field,

Okay, if your face exhibits a darker contrast with a high IF gas, with high then it can be imaged as a bright face or bright contrast face by using a lower IF gas. Okay, so, it will create a better visualization, better visualization. of the structure of the tip fine so this is one of the things which is very important first The second is if you have if the second case is if your material is having a very high electric very high evaporation field material means the tip surface specimen If your specimen has a very high evaporation field and your gas has a relatively lower IF value.

What will happen is that it will create it is very difficult to observe the surface during field evaporation. It is very difficult to observe the surface during field evaporation. This is why because as the field increases. The ionization takes place at much farther regions. The ionization of the imaging gas takes place at a much farther region.

This is due to which it cannot exactly replicate the atomic structure of the tip surface. Okay, so imaging is not precise of that particular atomic structure of the tip surface. Okay, if you have a very high evaporation field with respect to a low ionization field imaging gas. This is another problem which we usually face. Fine So, a clear image, for a clear image,

What we can do, for example, for tungsten, for the field evaporation of tungsten, is that a clear image can be formed by using high voltage and laser pulsing. Okay? So, it means that for a So, a clear image can be possible when we use either high voltage or laser pulsing, which induces the field evaporation of the adsorbed atoms of tungsten. So, if you have a very high electric field for any material, for example, tungsten, Correct?

We can actually use very high voltage and laser pulsing so that you will get a good-quality image. Okay? This is due to the field evaporation of those adsorbed atoms. If you have a low evaporation field material and it is imaged with a high ionization field gas this is if you want to image a low evaporation field material with a high ionization field gas

then this has to be done this is possible only when the base temperature is kept very low. So, for example, for imaging aluminium via helium which is having a very high IF value and aluminium has a very low IF value, then the temperature should be kept at 20 Kelvin, okay? So, reducing the temperature, reducing the temperature avoids the departure of atoms from the surface. Departure of the atoms on the surface. Raising the electric field to reach the IF of the gas.

Okay? So in this, the temperature plays a very important role. In this condition, the temperature plays a very important role. So, to summarize, what we can summarize is if your electric, if your evaporation field of specimen is larger than ionization field of gas, this is the optimum condition. You will have a better visualization.

If you have a very high, very high evaporation field of specimen, then it is very difficult to observe surface during field evaporation, okay? Then it is very difficult to observe the surface during field evaporation. So, for that purpose what we use is high voltage plus laser pulsing can be used. So, this can be for better imaging purpose. If you have a low evaporation field material or specimen.

Then, with a high ionization field gas, this can be imaged only when the base temperature is kept very low. So, it is around 20 Kelvin for aluminum if we image with helium gas, okay. So, all in all, these are the three important conditions where you can use it for imaging. For imaging clear and resolved, atomically resolved images, okay. Now, as I told you, the temperature plays a very important role here, okay? So, a stable image plus optimal resolution can be adjusted by the base temperature, okay, which is at the cryogenic temperature between 20 Kelvin to 60 Kelvin.

Why is it so? High temperatures usually increase the velocity of the imaging gas, okay? Gas atoms, so it will degrade the resolution. The second is any species present on the tip surface, which are adsorbed on the surface, for example, water, H<sub>2</sub>, chemicals from sample prep, chemicals from sample prep. They can contaminate the imaging gas, and due to which they will migrate onto the surface, which can blur the image.

Remember, these are the species which are present, such as water, hydrogen, or chemical species from the sample prep. These can directly affect the image quality, which are

absorbed. So, they actually contaminate the imaging gas. However, very low temperature also has a problem. It might induce the possibility that the gas atoms can be physically absorbed on the surface, okay.

at a very low temperature it might possible that the imaging gas atoms can be physically absorbed on the surface so this is a problem then okay so so the specimen is kept cooler than the gas to liquid transition so if if the specimen is kept at a very low temperature or cooled then the gas to liquid transition temperature of the imaging gas then it will form a layer of liquid okay and that can create the blurring of images okay so the temperature should be optimum it should not be very high and it should not be a very low temperature especially less than the gas to liquid transition temperature So for helium we can keep as a should be less than 20 Kelvin.

Other gases we usually use require higher temperatures, around 30 Kelvin or more, for example, for neon. Okay. So now we have just talked about the specimens which have a single element. So, what if there are alloys? Alloys, then the temperature can induce significant changes.

So, for the alloys, if you change the temperature, it can induce significant changes in the image quality, such as changes in contrast or image. Okay, by changing the temperature in the alloy case. For example, you can see in this image that this particular image is taken at 20 Kelvin, and this particular image is taken at 80 Kelvin. So here you can see that in this image, in this location, we do not see any precipitate.

Okay, at 20 Kelvin. However, in this particular FIM image, you can see that there is a contrast which is related to a titanium-rich precipitate in an alloy. Okay, so this effect is due to the local change in curvature caused by the presence of the precipitate. Due to the presence of pressure, this change in local curvature induces an effective change, meaning that the effective evaporation field (EF) changes with the temperature. and therefore it differs for different fields or phases.

Okay, so temperature is very crucial, especially in the alloy case where, depending upon the nature of the precipitate or the phase present, the temperature actually plays an important role. This is due to the local change in the curvature that effectively changes

the evaporation field, and that changes for different fields and phases. Okay, so, If you see, for—we also talked about the best image field to get sharp images, okay. So, once the temperature—to get an optimum image—once the temperature is set, once the temperature is set, then gas is introduced

into the chamber. Then, voltage is applied—high voltage is applied—and increases, and correspondingly there will be an increase in the electric field intensity. Okay, so then after that, if any oxides or surface contamination are present from the sample preparation, they get field-evaporated first. Field-evaporated first. Okay?

So, this is due to the presence of oxide. This is due to the local creation of roughness. Creation of local roughness or high local curvature due to the presence of these contaminants. Okay, so basically in the step of FIM, this particular method, this particular stage—usually what we call it—is you are cleaning the specimen, cleaning the tip surface. Okay? So, then after the cleaning of the tip surface, the voltage is increased up to a value of BIV.

Which also corresponds to BIF. Based on your sample and the gas used, you can select the combination of imaging gas for a metal or an alloy, as well as the temperature. has a very important role for the image which is having a very high resolution image which can resolve the which gives the atomic resolution okay. So, BIF is the as I told you is the highest field that enables the ionization of the imaging imaging gas just above the most protruding atoms on the surface, okay?

So, it is the highest field that enables the ionization of the most protruding atoms on the surface. where the electric where the field where the electric field where the electric field is maximum locally while not inducing any field evaporation of the surface atoms okay so in during FIM you should be very careful that the voltage should be in such a way that it should not feel evaporate the surface atoms it should be enough so that it should reach an highest field which requires which have a the enough electric field which where the gas must get ionized okay and it will image the most protruding atoms which are present in the surface there are other parameters which are very important

other than these, one is the quality of vacuum, second is the purity of argon or purity of gases. So, purity means if it contains the contaminants, they have a different IF. okay and the third thing is counter electrode okay counter electrode it means that the distance between the tip surface and the electrode will have a direct impact on the voltage on the voltage which is necessary to reach the required electric field okay so this is the role of counter electrode this will have a direct impact on the image quality

so these are the other three factors which are which we have to be taken care during for getting a good image quality so here by changing the electric field By changing the electric field distribution around the specimen apex, this changes the concentration of electric field at the specimen apex. So, to form the image, the polarized gas atoms, to form the image, so if you have, so for example, if you have an atom probe needle, if you have two atom probe needle, same sample and here there is no counter electrode. And here there is a counter electrode, correct?

And there is a phosphorous stream. Now difference between will be there. To form an image, the polarized gas atoms—if you have gas atoms on the top—these polarized gas atoms move forward towards the specimen apex. Okay, and this happens through successive hops on the surface. So, this atom will move like this on the surface. Okay, these are the successive hops, and it moves towards the apex of the tip. Okay, so if you have a counter electrode—

If you have a counter electrode, then during these successive hops, what will happen is the particular gaseous atom actually loses energy, meaning it loses velocity. Okay, so the farther the atom is from the tip surface— The greater will be the loss in thermal energy. So, the farther the atom is, as it comes to the apex, the velocity will become slower and slower. So, there will be a reduction in lateral velocity.

Remember this lateral velocity term as we described in relation to the resolution. This is one of the three factors which is responsible for the FIM resolution or the spot size, correct? Lateral velocity. So, the higher the spread in the lateral velocity, the lower the resolution, fine? So, you can see that here as if there is no electrode, no counter electrode, the atoms which are moving towards the apex,

okay, and as they go on the surface, they lose thermal energy and the velocity becomes much lower and lower. So, the spread between the lateral velocities will increase, but in the case of a counter electrode, as you know, the electric field is concentrated, so the number of hops that the atoms have to make towards the apex reduces drastically. So, what will happen is that the lateral velocity decreases, the spread in the lateral velocity decreases, and is minimized, which will have a direct impact on the resolution of the image. Okay, so that's why this lateral velocity describes the spatial resolution in the image, the FIM image.

Okay. So, there is a difference between the presence of an electrode. Due to the intense electric field, the spread in the lateral velocity will be minimized, but if there is no electrode, you can see that the spread in the lateral velocity will be much higher. So, your resolution will be affected by this, okay. So, this lateral velocity increases the spot size.

Fine, so with this, we will end today's class where we have just gone through the experimental protocols which are necessary for field ion microscopy. Okay, and we also described the parameters which are required to get an optimum. You can achieve optimum conditions where you can get the highest spatial resolution for imaging in the FIM. So, in the next class, we will follow the experimental protocols required for atom probe tomography, where we will first describe mass spectroscopy. Then we will see how detection is carried out, okay?

And how we measure the time of flight, okay? So, based on this, what are the important conditions or parameters to be optimized to get highly resolved atom probe tomographic reconstructions, okay? So, with this, I will end the class, and we will meet in the next session. Thank you.