Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-04
Lecture-10

So, welcome to the next lecture on this topic on this course. So, the last class we discussed about the APT instrumentation and also we little bit detailed way we understand the function of delay line detectors especially the MCP and delay line detectors which is related to the position sensitive detectors both of them. And we have estimated the position of heat of the electron cloud on the delay line detectors by measuring the time to reach the both the ends in both the directions like as X and Y. And the total time of light for the ion can be measured as the time taken for the electron cloud.

to reach all the ends like x1, y1, x2, y2 and divided by 4. So, that was the thing which we discussed about the measuring of position and time. Now, then we also introduced I think in the last class that the pulsing techniques. So, little bit more detail where we will talk about on the pulsing techniques. So, now we will describe the pulsing techniques.

pulsing techniques as I introduced before the pulsing techniques can be two ways one is HV one is thermal pulsing okay and HV pulsing so thermal pulsing by using laser. it is mostly related to the photon assisted field evaporation. HV pulsing we are pulsing the voltage okay and this will be for fast HV pulses this is around few nanoseconds used okay and the shape of this HV pulsing depends upon the time dependent evaporation probability and also the modelling of or the modelling or shape of the HP pulse. So, it has two functions, correct?

These two functions, so the shape of the HP pulse, it depends product of these two exponential functions. So, according to the evaporation rate, the adsorbed atoms, the adsorbed atoms are likely to field evaporate at a frequency, at a frequency which are related or which are near to the vibration of surface atoms. So, frequency means as I told

you mu 0 which is around 10 raise to the power minus 13 to 10 raise to the power minus 11 per second. This is the frequency.

So, as the field of operation, as the field of operation is related to the probability not all the atoms will be evaporated at the same time or same instant, okay. not all the atoms are field operated at the very same instant across the duration of pulse. It means that if you have a HV pulse, some of the atoms may get field operated at this location, some of the atoms may get field operated here, some of the atoms, depending upon the local vibration frequency of that particular atoms, correct?

So, this uncertainty, this uncertainty can lead to the resolution to the mass resolution to the lower mass resolution okay or to it will affect the accurate determination of mass to charge ratio okay so elemental identification will be difficult It will not be resolved easily because of this uncertainty. It means that the atoms at the if there is a HV pulse here, the atoms can feel evaporate

When your HV is in this position, it can evaporate here, it can evaporate here, it can evaporate here. This will induce a spread in the mass-to-charge ratio peak. Okay, so, that depends on the instant at which the ion is created; it will accelerate at different stages of the varying field. Your field is varying, correct? So, it means that for an atom to field-evaporate, it does not require the full energy of the pulse.

Some of the atoms can field-evaporate at these locations. Fine. This is called energy deficit. This is called energy deficit, and energy deficit depends upon the velocity of the ion and also its mass. Okay? So, because of this energy deficit, there is a spread in the mass peaks. Which directly affects the mass resolution during HV pulsing of the specimen. Okay? So, for HV to induce field evaporation, it requires

To induce field evaporation, the specimen should be electrically conductive. So, material with higher resistivity, like greater than 10 to 100 microamps, For these materials, the HV pulse shape is distorted. Okay, this distortion can lead to a variation in the electric field.

With time that distorts, it will have a direct distortion effect, distorting the timing resolution. So, we cannot precisely measure the m by n mass-to-charge ratio. So, it will

directly affect the mass resolution. Okay, so if the material has very high resistivity, electrical resistivity. Okay, so even though the material will have high conductivity, for brittle materials, for brittle material, the yield

Yield for the brittle material is much less than the yield for the ductile material, even though these are conductive. Okay, so HV pulsing for brittle material, even though they are conductive, the yield is much smaller than the ductile material. Okay? So, this is directly related to the electric field. Why? Because the electric field in APT generates an equivalent pressure, which is called electrostatic pressure.

Electrostatic pressure, which is up to 10 GPa, okay? And this electrostatic pressure almost approaches the theoretical strength of materials, okay? Other than electrostatic pressure, the HV pulse can also induce cyclic stress. These two factors usually increase the propensity for mechanical fracture, mechanical fracture. Okay, so mechanical fracture of the specimen. So, this electrostatic pressure can be given by sigma Q squared divided by 2 E naught, which can also be written as E naught F squared divided by 2.

Okay, so this is the electrode size of pressure. So, here σQ is the surface charge density, F is the field, and E0 is the dielectric permittivity. What is dielectric permittivity? It is nothing but the dielectric permittivity of vacuum. It is nothing but the measure of how easily a material can be polarized by the field, okay?

E0 is the dielectric permittivity. So, for aluminum, the value for P, the electrostatic P, is almost 1.6 GPa, correct? So, okay? So, this is the pressure which is induced in the material. It can lead to the fracture or early fracture of the samples.

If these are not conductive, then the fracture tendency is much higher because of the distortion caused by the HV pulse shape distortion. Okay? This variation in the electric field distorts the timing resolution and also directly affects the mass resolution. Even if it is conductive, for brittle materials, the yield is much lower than for ductile materials. Okay, so this HV pulsing induces both cyclic stress and electrostatic pressure on the tip surface, and this electrostatic pressure is given by $\sigma Q^2/2\varepsilon$. So, for insulators or semiconductors,

What we do, what we do is for less conductive applications; what we use is laser pulsing. Okay. So, my old atom probes—they were using only the HV pulsing. Okay. So, in 1970, Tsong used a light source.

In APT, okay? So, light source means this particular light source—it is nothing but the photon-assisted field evaporation, field ionization. Okay, or evaporation field ionization or evaporation. So, he has used the light source. So, along with Tsong, along with Kellogg, They used the first pulsed laser source on an APT, okay? And since 2006, you can get these laser pulsing, these laser sources. Previously, it was sub-nanoseconds; now, it is available in picoseconds and even femtoseconds. As in the last class, I told you, femtoseconds—it is nothing but 10 raised to the power of minus 15 seconds, correct?

These have been successfully implemented on the new APTs. So, a little bit, we will discuss the interaction of this laser. With the sample, correct? So, usually, on the sample, there will be interaction of electromagnetic wave Electromagnetic wave from the laser and tip, correct? And usually, the tip dimension—usually, the tip dimension is less than the wavelength of the wave, okay? So, light—so light from the laser pulse, light from the laser pulse will be absorbed by the tip.

So, light from the laser source is absorbed by the tip. So, this absorption of light on the tip will increase the temperature. Especially at the surface, at the tip surface. This increase in temperature triggers the field evaporation. Field evaporation.

So, we need to understand a little bit more about the laser-matter interaction. Okay. So, in the first few femtoseconds, in the first few Seconds, what will happen is the photon will be absorbed by the electron on the tip. So, or we can say it as the electron from the tip—the electrons from the tip will absorb the photon from the laser.

Correct? But even though the electron is absorbing the photon, it gets warmed; it gets heated up. But the lattice is still frozen. The lattice is still frozen. So you will have a combination of an electron cloud which is at a higher temperature, plus there will be a lattice frozen system, frozen.

Okay, so this is the total system for that. So, the electron cloud is warmed or heated by the photon, okay? And this particular system—electron cloud plus frozen lattice—is not in equilibrium, not in equilibrium. So, what will happen? This not being in equilibrium means the heat from the electron cloud has to dissipate toward the lattice, which is frozen. So, there will be an electron cloud that is warm.

It transfers energy—heat energy—to the lattice. This transfer of energy toward the lattice will have some characteristic time. This characteristic time is called electron-photon coupling time. Okay?

And this particular time is a few hundred femtoseconds. Okay, so this is the interaction—this is briefly about the laser-matter interaction. So, the electron cloud—electrons from the tip surface—will absorb the photon and get heated up, but if you see the total system there, the lattice is still frozen. So, it is not in an equilibrium condition. So, the heat—or there will be a transfer of energy—from the electron cloud toward the lattice, and this will have some characteristic time.

That particular time is called the electron-photon coupling time, and it is a few hundred femtoseconds. So, this characteristic time we discussed depends on the material and the shape of the tip. Therefore, the pulse duration— If the pulse duration—or the laser pulse duration—is greater than this characteristic coupling time, then the electron cloud and lattice become coupled during the laser pulse.

Remember, I am talking about the pulse duration. If the laser pulse duration is greater than the coupling time, then your electron-lattice system becomes coupled during that laser pulse. This leads to the direct absorption of energy from the laser pulse by the lattice, resulting in a rapid rise in temperature—a rapid rise in the temperature of the tip, correct? And the peak temperature that can be attained depends on the tip material.

We will come to the peak temperature, we will describe the peak temperature later. So, but the peak temperature on the tip is depends upon the tip material, tip geometry and other various parameters, parameters such as pulse duration, wavelength, position of spot and spot focus on the sample correct. So, these are the parameters which can increase or

decrease in increase the peak temperature. So, the temperature of peak temperature depends upon these factors okay.

So, in thermal pulsing or laser pulsing, the concept—the main concept—is the transient temperature increase due to the absorption of light. It means that the transient temperature increases by the absorption of light from the laser source, okay? And this increase in transient temperature will increase the thermal agitation—the thermal agitation of the surface atoms. Okay, this particular thermal agitation again provokes the field evaporation, okay? So, when the temperature of the tip surface when the temperature of the tip surface increases in subsequent pulses of temperature—so, for example, if there is a laser pulse, okay?—so when

the first laser pulse is applied, the tip temperature increases, and during the decline of the pulse, it increases again. In between these two times, the temperature of the tip also reduces. Okay, so it means that as the tip surface is heated, this particular heat—as the surface gets heated—will propagate toward the inside of the specimen. So, your surface will be treated as a quenched state.

Okay, so there is a successive increase and decrease in the laser pulse or the specific temperature of the pulse. This is called thermal pulsing. This is called thermal pulsing. Okay. So, the field evaporation takes place at a temperature.

So, with this we can see that the field evaporation takes place at a temperature which is higher than the base temperature. Okay. And this that particular temperature is called a effective evaporation temperature. Okay. effective evaporation temperature okay so so what is the difference from the HP pulsing what are the diff

what are what is the difference what is the difference of thermal pulsing towards the HP pulsing so based on the lambda based on the lambda the light is absorbed by all materials, correct? Whether it is a conductive material, whether it is an insulator, whether it is a semiconductor, the light can be absorbed by all the materials, okay? So, the first point is the application of thermal pulse. Application of thermal pulse can overcome the limitation posed by the HV pulsing which is which requires a conductive specimen.

So, it overcomes the limitation because of HP pulse that is it requires conductive specimen that can be overcome by the application of thermal pulse. Second thing is the ions important thing is the ions are accelerated by only the field electrostatic field near to the tip surface which is generated by the DC voltage which is at a constant field correct so therefore in this particular thermal pulse or laser pulsing we do not see energy deficit we do not see the energy deficit in the time of flight distribution correct as in HP pulse we see the energy deficit

That is evaporation of atom, that is polarization of the atom of the tip surface at different location of the HV pulse, okay? Not necessary at the high voltage, correct? So, this energy deficit is not seen in the thermal pulsing. And the third point, which is different, is here the temperature decreases, okay? Between the pulses applied to the specimen, this temperature decrease is due to the heat dissipation along the tip shank, okay? So, you have

an atom probe tip with a center, so the heat dissipation can take place either in this direction or in this direction. So, the time to cool down the tip to the base temperature, to cool down the tip to the base temperature, that controls the uncertainty over the evaporation process. Of ions. So, the time to cool down the tip to the base temperature controls the uncertainty over the evaporation of the ions.

This particular thing will limit the mass resolution. So, this difference in HV pulsing and thermal pulsing, how the mass spectrum looks, we will cover in the next few classes. But you should understand that the difference between HV and thermal pulsing: HV has energy deficits, but in laser pulsing, this is due to the time taken to cool down the specimen to the base temperature. This limits the mass resolution.

Okay, so, as you know, in the TIP, The light is absorbed, so if you apply a laser, the light is absorbed on the tip surface, so it will absorb to a certain distance, correct? The energy can be absorbed on the tip surface up to a certain distance. This particular distance is called skin depth. So, it is the depth through which the light is absorbed into the material.

Okay, so, we can say that this is the distance of penetration of a photon or the light wave inside a material. Inside a material, okay, and this is called skin depth, delta s, correct?

And the delta s for a wave which has a pulsation of omega in a material with electrical conductivity sigma e and permeability mu e can be given as: the skin depth can be given as the square root of 2 divided by sigma e mu e omega. So, here sigma e is the electrical conductivity of the material, mu is the permeability, fine, and omega is the pulsation of the wave. Further, this particular delta S, if this delta is smaller than the mean free path of the electron at a given temperature, this equation can be modified by

delta S is the cube root of 2 lambda e divided by sigma e mu e omega. Here, the lambda e is the mean free path, okay. So, there is another model which is called the Drude-like model, the Drude-like model. which estimates that delta S can be estimated by using this mean free path value; you can actually measure, you can estimate the mean free path value as m e c squared mu e 2 pi e squared n e w. Here, c is the speed of light, okay, and e is the charge, mu e is the velocity.

And n_e is the density and m_e is the mass of the electron, okay. So, this is the equation which is proposed by the Drude-like model, okay, based on the condition where the skin depth δ_S is less than the mean free path of the electron at a given temperature. So, for example, δ_S is equal to δ and is approximately equal to 0.2 nanometers, For a λ of 1 micrometer, if you calculate for iron—for iron, okay—but if you calculate this particular δ_S. If δ_S is less than the mean free path λ, we can call it δ_S_analogous. δ_S_analogous is calculated as 36 nanometers. This shows that the

It means that the penetration of the wave is much greater than expected, okay. This is the case when your δ_S is much less than the mean free path λ_e of the electron. Okay, so now we will come to the temperature distribution for the whole tip axis. Okay, so Robbins et al. (I will give the reference in the PPT) proposed that the whole tip apex is homogeneously illuminated, Okay, and the temperature distribution means that the temperature along the length of the tip exhibits cylindrical symmetry. So, if you have an atom probe needle,

So, what he has proposed is that the illumination on the tip surface has cylindrical symmetry. He has proposed that along the tip axis, okay, it has cylindrical symmetry. Therefore, the surface The surface can be regarded as heated over a width of δ_S,

okay? And it can be regarded as heated over the heat diffusion from the layer towards the core of the tip over a time t, okay? So, this heat will diffuse from the layer Towards the core over a time t. So, the distance over which the heat diffuses is estimated by $2\sqrt{(\lambda_t t)}$. Here, λ_t is the thermal diffusivity of that particular material.

And this alpha T can be given as K rho CP, where K is the thermal conductivity, CP is the specific heat of the material, and rho is the density. So the heat diffusivity D can be given as the distance diffusivity. From the layer towards the core of the tip over a time t can be given as root over 2 lambda t t. So for a pulse of a few picoseconds, the distance of diffusivity is around 5 to 10 nanometers for a laser on the tip material. So these are some defined variables, such as the skin depth and the distance over which the heat diffusivity takes place.

These are some terms and variables which are a function of the tip shape. Now, coming to another variable, which is the peak temperature. So when you are applying a laser to your tip. Absorbs the photon from the laser, the tip temperature increases. But what is the peak temperature that the tip surface can reach?

So, usually experimentally it is measured or estimated that this can go up to 800 Kelvin at that particular fraction of a pulse. So, 800 Kelvin for tungsten, which is shown by a 5-nanosecond laser pulse. It is estimated, so this can be estimated for different materials depending on the laser pulse. The temperature can also vary, okay? Based on this, there are several works which were carried out to estimate the peak temperature in the 1980s, okay? So So, in the 1980s, there are several seminal works which were actually carried out to estimate the peak temperature attained during laser pulsing.

So, the two key findings from these are: the first is the heat is highly concentrated at the apex. of the specimen, of the tip. So, this is the first observation which has been proposed by several works, and the second is a strong dependence. Strong dependence of temperature on the position of the spot, the laser spot along the shank. and the shank angle.

So, these are the two major observations which were proposed, which govern the peak temperature of that particular needle specimen. So, this can be estimated. So, how can it be estimated? Remember in the previous class, we talked about the calibration, the field, the relative field calibration. versus temperature remember there is a there was a graph which is a f divided by f evap and there is a temperature and you can you can do the calibration

okay so we have derived one equation about this correct so with the by using equation actually we can for different kinds of material we can actually get the calibration curve now if this estimation is done by using this particular plot. So, it is nothing but this estimation is nothing can be done as the field necessary to generate field evaporation at a given evaporation rate. So, remember we kept the evaporation rate constant. evaporation rate constant in that equation, okay?

If somebody has forgotten the equation, you can go through the previous class notes. where you can see that there is an equation which relates the relative field temperature and the field evaporation. So, for a constant field evaporation rate, for a constant field evaporation rate, we can generate the field and the temperature calibration curve, correct? So, now in experiment, What we can do is during the experiment, during the laser experiment, we can measure the total applied voltage,

okay, is measured and this value is used by using this calibration curve to estimate the actual specimen temperature. Okay, So, with this technique what we can get is that peak temperature can go from 50 Kelvin to 500 Kelvin depending upon the illumination condition. Okay, This is the one method which they used to estimate the peak temperature of the tip surface during the laser pulsing. Another method which is also a reliable method is used as the as the temperature at which there will be activation of, activation of thermally induced, temperature at which the activation of thermally induced random walks of atoms.

Okay, So, this is the temperature at which for any specific material, for example, the tungsten, so the temperature at which there will be random walks of atoms on the tip surface, that the particular temperature indicates the peak temperature which is attained.

Okay? So, Kellogg has with few nanoseconds and with a wavelength of 337 nanometers, random walk begins at temperature and that increases the random walk begins at a temperature when it is increased to 800 Kelvin with a DC field okay this is the estimation by for by Kellogg okay and this particular at this temperature it is it is this is around 66 percent of

Threshold field needed to induce evaporation, okay? For a tungsten tip, so he has calculated for the tungsten chip, okay. So these are the two methods where they can estimate the peak temperature during the laser pulsing. Fine. So, as I told you before, The difference between the HV pulsing and the laser pulsing is that in laser pulsing, the main governing factor is the time to cool down the tip temperature to the base temperature, which will directly affect the mass resolution. But in HV pulsing, the energy deficit is the factor that affects the mass resolution.

Fine. So, this is the... So now, the next part is the determination of cooling time. Now, we have talked about the peak temperature, and also we can estimate the cooling time. Okay. This cooling time of the tip surface depends on the ability of the tip to transfer the heat acquired. Ability of the tip surface to transfer the heat acquired at the surface towards the core or along the tip axis. Okay?

So, along the core, towards the core or along the tip axis. So, the rate of heat transfer, the rate of heat transfer, the rate of heat transfer is directly proportional to the temperature differential. What is temperature differential? It is the difference in temperature between the two locations.

Okay, so, the larger the temperature differential, the higher the rate of heat transfer will be. It means that if there are two materials, if there is a tip, if you are putting a laser which is more focused, a more focused spot on the tip surface, the heat zone is reduced in size. Okay, so it will be locally heated, so your heat zone will be much smaller if you use a more focused spot, due to which the temperature difference between the apex and the shank tip, and the shank temperature and the shank of the tip will be higher.

It means that the higher the temperature difference will be. This will cool faster. Okay. So cooling will be faster for this particular case. So, a more focused spot.

on the tip can be used to create a large temperature difference between the apex and the shank of the tip, so that the cooling will be much faster. The other factor is the shank angle, okay? This parameter also governs the increase, so usually if you have two tips, for example, if you have two tips, one is sharp, with a very small shank angle, and one has a very large shank angle. Correct? So, in this case, the heat is diluted very little.

But in this case, the heat dilution occurs in a large way. It is very high. Very high heat dilution. Okay, so whichever atom probe tips which have a shank angle larger than the heat dissipation will be much higher because the heat dilution is much higher. Okay, so it means that the cooling will be much faster. Cooling

time is the main parameter to govern the mass resolution in the cooling time, so this cooling time is a very important factor. To govern the mass resolution in the case of thermal pulsing or laser pulsing, fine. So, if you want to use a laser pulsing method, usually what we do is keep the needle specimens thicker, which have a higher shank angle, not the thin samples. Their heat dissipation will not be as much as you see for the thicker sample. So, the cooling time is more important for the laser in determining the mass resolution.

As I told you before, in laser, there is no energy deficit. No energy deficit. So, the mass resolution is governed by the uncertainty of the departure of the ion from the tip surface. So, longer cooling time. If there is a longer cooling time, then what will happen is it will take a longer period.

Okay, and during this, the ion gets emitted. So, a longer cooling time means a longer period for ions to get field-evaporated. So, you will develop a large tail, which we call a thermal tail. So, in the mass spectrum, this is your mass-to-charge ratio. We will come to this mass spectrum later, and this is your counts.

So, if you are giving a larger cooling time or if your tip is very sharp, then what will happen? You will develop a very large thermal tail, so this particular increase decreases the mass resolution. Okay, so this is called a thermal tail in laser pulse fine, which limits the mass resolution. Okay, so the next topic is which I want to just introduce: photo-assisted ionization. Photo-assisted ionization.

So, if you see, okay, so here I can give an example. So, here there are two tips with a very low shank angle. and this has a very high shank angle. You can see that the heat dissipation—you can see the temperature profile—the heat dissipation is much higher for this particular case, but the heat dissipation here is much lower. Okay, so this particular tip, if you analyze, then you will get a large thermal tail, but here the mass spectrum will be sharper.

So, this will directly affect the resolution, the mass resolution of that. So, now here, briefly, I will introduce the photo-assisted ionization. What is this photo-assisted ionization? It can be understood by three different parts, okay? So here, we have indicated one, two, and three—one, two, and three. So, the first one is if an electron from the surface atom can directly tunnel into the vacant bulk electron state, so assuming this is a material, okay? And the material has some conduction band, This is a valence band.

So, if any electron in the valence band gets sufficient energy, it might be possible that this electron can go to the conduction band. So, at the tip surface, if you have an atom with an electron, So an electron from the surface atom, it might be possible that this field ionization can happen between the three methods. The first one is it is a simple electron from the surface atom. From the surface atom, it can directly tunnel into the vacant bulk electron state in this direction.

This is the one case. The second case is the electron from the adsorbed atoms. The electron from the adsorbed atoms is excited by the resonant absorption of one or more photons. Okay, so if the laser falls on the surface atoms, it might be possible that the electron can get excited to the resonant absorption of one or more photons. Consequently, they can tunnel into the vacant site inside the conduction band. This is the second method. The third is it involves the absorption of photons by the electron in the material. Okay, that will create holes in the valence band by the release of electrons

to the conduction band. Then the electron from the adsorbed atom can go to this particular hole or can tunnel through this particular hole and into the valence band, okay? So, these are the three phenomena which can describe the photo-assisted ionization, okay? So, and the first and third phenomena are enhanced by the large number of

electrons in the material. A large number of electrons in the material at low temperatures. At low temperatures, the number of electrons in the conduction band in semiconductors or insulators is negligible. Okay, for this the third process is more dominant.

In semiconductors and insulators, the number of electrons in the conduction band is negligible. So, the third process, which is the absorption of energy by the material, creates a hole by transferring the electron to the conduction band, and the electron from the adsorbed atom can tunnel through and occupy that hole position. Okay, so this is more dominant at low temperatures for semiconductors and insulators. Okay, so regardless of this path, these three parts through which the electron can tunnel towards the metal surface, the photon-induced field of operation involves the creation of an ion on the surface. The

adsorbed atoms consequently get accelerated by the surrounding electric field. Okay, so with this, the laser pulse, which uses these three phenomena, actually broadens the application of APT towards semiconductors, functional materials, and also in some cases, insulators. Where the HV pulsing method is very limited in use, the yield is very low for the HV pulsing methods. So, these are the three phenomena by which the photo-assisted ionization of the adsorbed atoms can take place.

Okay, so with this, I will end this class now. So, briefly, I will just summarize: we have gone through the pulsing conditions and, in a little more detail, the difference between HV pulsing and laser pulsing. In HV pulsing, we have discussed that energy deficits are the major concern, which limits the mass resolution. However, in laser pulsing, the cooling time is important to determine the mass resolution. Okay? So, in the next class, I will briefly go through a method where we can actually reduce this energy deficit.

By putting a reflectron inside the atom probe, okay? With this, you can improve the mass resolution significantly. Needless to say, laser pulsing definitely gives higher mass resolution because of the thermal pulse and the lack of energy deficits. But it also broadens the use of APT towards semiconductors, insulators, and some functional materials. Then, I will end this class now, and we will meet in the next class. Thank you.