Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy
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Week-03
Lecture-07

So, welcome to the next class. As in the last class, we have just gone through the field introduction to field evaporation, which consists of both field ionization and the desorption of atoms from the tip surface. So, I will just briefly go through and revise it again for at least 2 to 3 minutes. So, on the screen, you can see the atomic structure. There is one atom protruding, and this is with no field.

So, if you see the potential curve for this particular protruding atom, you can see that the potential energy curve corresponds to this blue line. Okay, and this has a certain binding energy. Fine. Now, if you think about an ion, where some number of electrons have been drained out, then the ion potential energy curve will shift upwards. So, that is related to the number of electrons which have been drained out, which is related to the ionization energy, and as these electrons have been drained into the structure. So, there will be a negative of the work function depending upon the number of electrons. So, you will have a total theta 0.

Q0, which is an energy barrier. Okay, so this is with no electric field. If you apply an electric field, Okay, so what will happen? The first thing that will happen is field ionization. Okay, so your electrons get drained out towards the tip, towards the lattice, towards the tip. Then the protruding atom will get ionized depending upon the number of electrons which are drained out, and usually, what will happen in the presence of a field is they will accelerate.

And due to which, on application of the field, what will happen is their potential energy curve will be distorted. Okay, so previously the potential energy curve was like this. Now, on application of the field, it gets distorted, okay, and it will develop an energy barrier, which is nothing but a hump or Schottky hump or Schottky barrier. Okay, so the two

important things: one is that by applying the electric field, what we are doing is reducing the energy barrier. So, this energy barrier is a direct function of the electric field applied, okay, and also— When there is a Schottky hump, when there is an energy barrier due to thermal activation, the ions can overcome that energy barrier and accelerate towards the fluorescent screen, okay?

So, this is the assumption that only thermal activation is considered. At low temperatures also, tunneling can occur for the acceleration of the ions along the field lines, okay? Now, so now we will go through some of the basic equations which can—okay. So now we will just go through the basic equations which can describe the energy barrier. So, first we will talk about the energy barrier, or it can be related to the height of the barrier, which can also be called the Schottky hump, okay?

So, this is termed as QF. So, this is nothing but a superposition of the charge image potential—I am talking about the ion charge image potential—and the potential of the electric field. So, this is nothing but the superposition of the charge image potential and the potential of the electric field. Theta F is given by Theta 0 minus the square root of n cubed E cubed divided by 4 pi Epsilon F. Here, F is the field. And E naught or epsilon naught is the dielectric permittivity of the vacuum, okay? Other terms are the number of electrons, and E is the charge, okay? And Q0, as I told you—

In the last class, you will have, for an atom—this is for an ion—Q0 is the total energy barrier, okay? So, when you apply an electric field, this field line, there will be an energy hump, and this particular hump is called theta F or the Schottky hump. And this theta F is given by this particular equation, which is a function of electric field, okay? So, it being a function of electric field means you can increase the electric field such that you can get theta F equals 0. The energy barrier is 0.

When the energy barrier is 0, then what we call that particular field is the evaporation field. Evaporation field of that particular element, or the sample, or the needle evaporation field Okay, remember, when theta F, the energy barrier, is a function of the electric field, which is present just ahead of the tip surface, when this electric field is sufficient enough that your theta F becomes 0, then the field is called the evaporation

field of that particular element, okay? So, another term that is important is evaporation rate, evaporation rate.

And to understand this evaporation rate, first we need to understand the probability, which is P_EVAP, the probability of field evaporation. Probability of field evaporation, and as I told you, this particular field evaporation model by Müller is usually assumed to be a thermally assisted process. Thermally assisted process, so due to this thermal nature, what we can do is we can actually write the equation based on the Maxwell-Boltzmann equation, and it can be written as P_evaporation is proportional to the exponential of minus theta F, which is an energy barrier, divided by K_B T. This is why we call it a thermally activated process.

So, this is given by the Maxwell-Boltzmann equation. Now, in that Boltzmann equation, Qf is the energy barrier. And we have seen that the energy barrier is a function of the field which is present, correct? Kb is the Boltzmann contrast and T is the temperature, absolute temperature. Now, when there will be a thermal agitation, thermal agitation, then there will be a vibration of atoms.

at the tip surface, okay? So, this vibration will have a certain frequency which is given by V0, okay? This is the frequency of atomic vibration perpendicular to the surface. So, due to the thermal agitation, there will be a vibration of atoms and they have a certain frequency which is given by mu 0. So, combining mu 0 and the probability of evaporation, you can get the number of atoms which are field evaporated per second, okay, that can be given by

RMS equation okay that is equals to this is the number of atoms per second for the field of operation is the frequency exponential of minus theta f divided by kBT okay. So, this is the evaporation rate which is the number of atoms which is evaporated per Okay. And this particular equation holds very good with the experimentally determined values. Okay.

So, as I told you, even though we have—even though it is neglected that the tunneling process does not occur—the experimental values can be, are easily matched. With these values, okay? So, this is the evaporation rate. Then, this evaporation rate—the

frequency—so with experiments, Kellogg has by experiments on Arrhenius plots. Actually, Kellogg has estimated or measured the frequency to be in the range of 10 raised to the power 11 to 10 raised to the power 13 Hertz, okay?

And depending upon the electric field, the theta F or the QF is almost near to 1 electron volt. These are the experimentally measured values by Professor Kellogg, okay? So, in the later Song, what he has shown is the evaporation rate as a function of field, okay? As you know, this particular evaporation rate directly depends upon your theta F and theta, or what the QF and QF is the energy barrier.

And this energy barrier is a function of field, fine. So, Song has— Plotted the evaporation rate versus field—relative field, okay? So, if you see the plot—if you see the plot which is made by Song—you can see this is the field. And this is the evaporation rate. You can see that by changing a field by a minimum of 5%, the evaporation rate changes by 2 to 5 orders of magnitude higher. Okay, so, and he has plotted for different elements—for different elements—and you can see that.

that by changing a 5% field or increase in 5% field, there is a significant increase in the evaporation rate. It is almost around 2 to 5 orders of magnitude. Okay? So, now coming back to the evaporation field okay so as I told you that this evaporation field we have a mu 0 exponential minus QF divided by KBT okay it might possible that the electric field the electric field

Is we made the electric field sufficient so that this electric field is enough for the theta f to become 0, okay? So, the 0, this is called the 0-barrier evaporation field, where the field—this is the field at which the energy barrier energy barrier becomes 0, okay. And this particular field where the energy barrier is 0 is called the evaporation field. We can put it as EVF, EVAP. So, this is a very important term, and this is a value that can be calculated for different elements.

So, now we know that in the previous expression, we have QF equals Q0 minus the square root of n cubed E cubed divided by 4 pi E0F. Okay, and Q0, which is the initial barrier, can be given as the binding energy plus the summation of I n to the n minus n work function. Okay, so now, as I told you, theta f equals 0, correct? If you make theta f

equal to 0, then your theta 0 becomes the square root of n cubed E cubed divided by 4 pi E0, and during that time, the field is called the field evaporation. With this, you can get FEVAP equals theta 0 squared times 4 pi E0 divided by n cubed E cubed.

So, this is the expression for the evaporation field where the energy barrier is 0. So, this is the field required to make the energy barrier 0, fine. So, based on this expression, you can again put theta 0—this particular expression—in this equation. You can write it as EVAP equals 4 pi E0 divided by n cubed E cubed times binding energy plus summation of ionization energies minus n work function. So, this is called field evaporation.

And you can see that this field evaporation—the evaporation field—changes with the charge states. So, it varies. So, evaporation field varies as the charge states for one element. For example, if you have a tungsten. If you have to charge state of plus 1, 2 plus, 3 plus and 4 plus, then your field, evaporation field can, will also vary as 102 nanometer, 57, 52 and 62 nanometers, okay?

So, the evaporation field changes as the charge state also changes for that particular element, okay? So, Brandon... has made a criteria for field EVAP okay is that he has defined as the F evaporation field which is having a lowest value which is having a lowest value and the corresponding charge state corresponding charge state will be the dominant of the ions during the field evaporation okay.

So I hope you understand what Brandon has told is that the evaporation field, which has the lowest value for that particular charge state during field evaporation. That particular charge state will be dominant among the other ions, okay? So, most of the metals Most of the metals have a charge state; they have an evaporation field between 10 to 60 volts per nanometer. Okay?

So, as I told you, the above model, whatever we have seen in the equations, these are for pure metal. These are for pure metal. Meaning that each atom, the neighboring atom, is also the same. So, the bonding states will be the same; the bonding energies will be the same. But for a multi-component alloy, for multi-component alloys, this is not true.

So, that is why it is not clearly defined. Clearly defined, okay? So, this is due to the difference in potential energy, the potential energy of the adsorbed atoms. Of the adsorbed atoms that depends upon the chemistry or the atoms, the neighboring atoms surrounding that particular atom, okay? Or the local neighboring atoms. And one more important point is that these evaporation fields also depend upon the crystallography. Crystallography means that, as I told you, poles—these crystallographic poles—directly correspond to the atomic terraces.

Okay, so based on the crystallographic pole, either 100 or 110, the atomic terraces—the distribution of atomic terraces—also changes. This will have a direct impact on the field around those atomic terraces. So, your evaporation field also changes based on the crystallography of that particular tip. It may vary up to 10% to 25% from one pole to another pole. Okay, so up to now, we have seen the energy barrier.

We have also seen how the evaporation rate changes, and we have also gone through the evaporation field where the barrier θF becomes 0, okay. So, these are the three important terms. Which we have understood. Now, another important thing is calibration, which is called field-temperature calibration. We assume that the field evaporation—field evaporation—is a thermally assisted process, a thermally assisted process.

Okay, and so from the equation, if you see, field evaporation equivalence, which is equal to μ_0 exponential of minus θQF divided by KBT. You can see that there is an energy barrier term, and there is also a temperature, okay? Based on these two values, you can have infinite combinations to make a constant field of evaporation rate. Correct? So, you can choose different QF and different temperature values such that your evaporation rate is constant.

How to change the QF value? It depends upon your applied field, the electric field. Fine? So, you allow infinite combinations to make it at the same evaporation rate. So, if for approximation...

Assume that for approximation, assume that the electric field value F is very close to field evaporation. Field evaporation is where θF is equal to 0. For approximation, if we assume that the field value, the electric field, the actual electric field value is very close to the

evaporation field. Then the height of the energy barrier, which is QF, will vary linearly with the field, okay? So, with the expression, what we can do is QF is equal to Q0 minus n^3e^3 divided by $4\pi\varepsilon_0 F$, okay?

So, this expression we understood previously, okay. So, now what we can do is rewrite this expression as Q0 minus $Q0\sqrt{(n^3e^3}$ divided by $4\pi\varepsilon_0$) $FQ0^2$, okay? You can see that I have multiplied the denominator and the numerator by Q0 to get this particular expression.

Now, based on the expression of FEVAP which is equals to 4 pi E0 by n cube E cube Q square if you put this expression here what we get is QF is equals 1 minus F divided by FEVAP okay because you can write this particular expression as F1 by FEVAP correct so this particular expression you can write as a 1 upon FEVAP okay so you can see that the field the barrier the energy barrier as a function of the electric field and also the evaporation field.

So, what does it mean? So, here the above expression can be combined with the field with the evaporation rate. which is given by mu 0 exponential of minus theta F divided by kBT. Okay? So, therefore, the dependence of electric field, the dependence of electric field required to field evaporate a specimen at a given evaporation rate

as a function of time can be given by F divided by F E by P is given by 1 plus KBT theta naught ln mu naught okay. So this expression can be given so if you how it came this expression you can see that if you take this expression in log scale so what you can do is you can write this as a ln field of operation divided by mu naught which is equals to minus theta F divided by KBT, fine. Now, put this expression in here.

So, you will have a QF, you will have a KBT divided by Q naught ln. Evaporation divided by mu naught, which is equal to F divided by F EVAP minus 1, okay? So, this expression can be rearranged into this form. Okay, so this is how you are getting the field as a function of the evaporation rate, okay? And this particular expression has also been experimentally The values are matching with the values which are calculated, okay. So,

this is nothing but this particular, it is a relative field required to evaporate a metal at constant field evaporation.

as a function of temperature, okay? So, if you want to keep this evaporation rate constant, correct? And you have two variables. One is the relative field, and also the temperature. These two terms you can experimentally vary such that you will get a field evaporation rate as constant.

Okay, so based on this, you can see the plot. You can see the plot by Francis, which he has published in APL, where this is the relative field. This is nothing but F divided by F evaporation field, and this is your temperature, fine. So, as the equation says, F divided by FEVAP can be written as 1 plus KBT by theta 0 ln EVAP divided by mu naught. Okay, to keep this constant, you can actually vary the relative field and the temperature, and you can see that this expression—this is what he has recorded for pure tungsten and you can see that it exactly fits in a linear way, fine. So, based on the species or the elements

The slope can vary depending upon the element of which is measured to the fourth of field evaporation rate. Okay. So, I hope that all the equations are understood. So, the most important part is all the equations above assume that this is a thermally activated process, okay?

So, based on Muller's model, which is a very simplified model to understand the potential energy of the atom and the ion without the field and in the presence of the field, okay? Post-ionization, so there is another term called post-ionization. This is, as I think in the third class, we talked about field ionization of gas atoms. Field ionization of gas atoms which are near the tip surface. So, this is a similar phenomenon called post-ionization.

It means that If you have a needle specimen, if there are atoms which are field-evaporated as ions, field-evaporated as ions. So, these ions, which correspond to the sample or the specimen, can actually reionize. It means these directly act as gas atoms. Fine.

So, this is called post-ionization. So any atom which gets polarized and ionized accelerates near the tip surface if they are present at a certain critical distance. At this

critical distance, it is possible that these ions get reionized into +2 or +3 states, okay. So, the drawback of the above model is that it cannot predict the experimentally observed charge states of the evaporated ions above Müller. Okay, so scientists Haddock and Kingham proposed that when an ion leaves the surface as a single-charged ion, it can reionize in the

vicinity of the tip, similar to the field ionization of any gas atom. So, I hope you remember this particular diagram. We understood the potential of a gas ion near the tip surface. So, this is your tip surface. This is vacuum, and on application of a field, the potential energy gets distorted like this.

This is called the work function. This is your minimum potential energy. So, post-ionization in this case occurs at a critical distance, and this critical distance is what we call Xc for a gas atom, given by $X_c = (I_{n+1} - \varphi) / F$, where I_{n+1} is the (n+1)th ionization energy, φ is the work function, and F is the electric field. Okay, where I_{n+1} is the (n+1)th ionization energy, φ is the work function, and F is the electric field.

So, the probability of field ionization is directly dependent upon the field. Okay, so also for a given electric field, the probability for a given electric field, the probability of an electron tunneling through the energy barrier, through the energy barrier, okay. So, the electric field or the applied electric field can also govern the probability of the tunneling event across the energy barrier, and this totally depends upon the time the ion spends in the ionization zone, in the ionization zone, fine. So, if this depends upon it, then it can be directly related to the probability of n, the probability of n plus 1 ion depends upon the

velocity of the ion, which is also a function of mass. Okay, so, for each atomic species, based on the mass, their velocity will change, and based on that, it also depends upon the time which is spent near the ionization zone. So, the more time it spends near the ionization zone, the more the probability will increase for the tunneling effect and also the reionization of these ions for the n plus 1 electron, okay. So, the variation, what we infer from this, is the variation can occur between the charge states charge states that totally depend upon the element or different isotopes, okay. Different isotopes can be treated as different isotopes.

Okay, so, based on this, we have explained some fundamental equations equations which can be used to calculate the actual evaporation rate, your evaporation rate, estimate the field, the relative field which is required. to keep the evaporation rate constant as a function of the temperature, the combination of temperature. We also discussed the energy barrier, which is a function of the applied field, and the energy barrier when it becomes zero, that particular field we call the evaporation field, okay. So, based on this, and also, we have discussed the post-ionization.

Post-ionization, it is nothing but the atoms which are ionized—atoms which are ionized from the tip surface—they get re-ionized. This depends upon the time they spend in that ionization zone. Okay, and they will have some critical distance where this ionization can take place, so that is why the different charge states—different charge states— can be obtained for that singular species, okay. So, with this, I will end this class, and in the next class, we will also go on to understand how these field-evaporated ions are reconstructed, okay. So, we will also talk about the reconstruction to mimic the exact

exact nature of the atomic structure which was present in the tip. Thank you.