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GANG CHEN: OK, well, let me start talking. And I ran out of my slides, I mean, since last week. I was making this a new topic. And you will see, I thought I'm pretty familiar with this, but I still struggle a lot. And there is one place I will show where I'm still confused. Maybe you can help me. And then, that's always related to this electron negative charge that always confuse me. So I struggle a lot.

So today, in the first few lectures, we discussed the thermal electric effect. And now we move on to talk about the thermionic engines. And also, I hope we will have time to discuss related topics from the discussion on thermionic engines, and also hoping to actually jump in to introduce you to really how pin junction works.

And in terms of Schottky barrier and Schottky diode, that's really just a metal semiconductor interface. Again, I think from the vacuum thermionics, we can probably appreciate the evolution. I hope you will see the evolution. And then, in the mathematical formulation-- formula, the expression for current voltage are very similar.

But let me-- I need something that we showed before. So this is the first, the Fermi-Dirac statistics. This was what we did in probably the first lecture, the occupation of electrons in a quantum state. And here you can see, it's a very-- this is the electron volts, 0.051. So the Fermi-Dirac distribution is very narrowly focused near the chemical potential. And if you are away from the chemical potential, the function-- either its state is fully filled or almost empty.

And let me just make a remark. Typically, when we talk about thermionic emission, $e^{-\mu/kT}$ is u weight. So what we-- really, at the tail end, are for the Fermi-Dirac distribution. And the $e^{-\mu/kT}$ is still u weight, kT is a 26 milli electron volts at room temperature. You can see that factor of 1 will drop out because it's insignificant. So use this when we derive the Richardson formula.

And the other point that I will use in the discussion is the electron number density. So this is, again, we did before. We did the content of number of electrons counting all the quantum states. Each quantum state have two electron spin-up, spin-down. And this is the average number of electrons, two states, spin-up, spin-down.

And from there, if we do the exponential, drop the 1, we get the electron number density is proportional. Here is, I want to point out $t^{3/2}$. So we group all this factor into n_c . And then it's the difference of the conduction band to the chemical potential exponential. So that's what we had before in terms of electron density.

And the other point is to make-- is to, again, review that we say, what's the difference between metals, semiconductors? In metal, we have the chemical potential for into the band. And semiconductor has bandgap. We dope it either n type or we dope the p type. Depends on what kind of atoms, for example, we put either boron, which is a p type, or phosphorus, which is n type. And that way we're shifting the Fermi level or the chemical potential.

So those were what we covered previously. And now let's think about, if I have a material, metal, for example, I pull the-- I want to pull out the electron. And if I pull out the electron, the ion background, in metal attract the electron. So I have to do some work to pull it out. So the minimal amount of work that I pull electrons from inside immediately to outside, vacuum, is the work function.

So from the Fermi level, this is a metal, from Fermi level, I pull electron. I pull it out to vacuum level. But this vacuum is immediately outside the metal. And then why I emphasize that, if you think about the-- I have a vacuum. I have positive charge, a negative charge. Even both positive and negative charge in vacuum, then the electrical potential at these two points, even in vacuum, are different because there is a potential from the [INAUDIBLE]. So I say, this is immediately outside the surface of how we define the work function.

AUDIENCE: For metals, right?

GANG CHEN: Yes. Semiconductor we have to use a different terminology. And that's how Einstein got the Nobel Prize. So he explained the photoconductivity effect, where the effect was you shine light on a metal, and then you get electricity, you get the electron out. So you can measure current. But what was puzzling at the time was that the number of the current not just depend on intensity, but depend on the wavelengths of the light.

And see, so there was no explanation. And Einstein then explained, you have to have the photon energy larger than the work function to leave the electron on the metal surface. So the photon energy, of course, is inversely proportional to wavelength. So long wavelength full time not effective there. So not-- you know Einstein's Nobel Prize is not because of relativity, which was too radical. And this were more or less controversial.

And then, in semiconductor, the Fermi level, there's no electron there. When we dope, it such that Fermi level fall inside the bandgap. So there are no electron between the conduction and valence band. The Fermi level is in between. So the way-- you could lift the electron, but then when you lift the electron, usually you lift from the bottom conduction band, which is ec to the vacuum level, and we give a different name. And in that case, we call it affinity.

So semiconductor, because the chemical potential level can be changed by doping. But how much energy you need to lift an electron from the bottom conduction band to vacuum level, that's fixed. So this is a number you can look into tables, the affinity of semiconductors, and typically counted from conduction band edge. So those are the basics.

And now, of course, if I think about the Fermi-Dirac statistics, there are some electrons with energy higher than w . Even though that f is very small, but it's not 0. So what I want to talk now is how much energy-- how many electrons is flowing out of the surface. And of course, you put a piece of metal there. You flow out. There are also ones that come back in randomly. And then, at the end, there may be some electron flying around the surface. I'm just looking into the flux coming out. So the flux comes out. e is the electron energy-- and say, outside.

And I probably should not-- so this is where-- OK. μ , this is one of the-- if you look at how we derive the chemical potential, you will see the derivation process is really μ is relative to the bottom of conduction band. And when I talk about work function is relative to the vacuum level. So there are some difference in the reference point. So that's the one place that can cause confusion.

So I'm looking at, really, for those electrons with an energy above the vacuum level. And those energy, you can think of this kinetic energy inside in the vacuum here, that's the-- when I write this more, $h^2 k^2 / 2m$ is the kinetic energy, So those electrons, here, that's the kinetic energy. And I want to calculate the flux of the particle. I'm not putting charge there yet. I don't like that negative e . So just a particle flux coming out.

So here, because it's coming out with k_x , the wave vector, which is the momentum, it is the positive x direction. I don't do both from negative infinite to positive infinite. So now I do this summation. Because I'm looking at flux, so v_x is the velocity in the x direction coming out. And then f is [INAUDIBLE] state. So I'm still doing my counting. The number of electrons, each electron has a velocity, and that gives me the flux there.

So if you start from here, you do your normal way of converting this weight, because this is a flux, we should already be divided. That's a typo here. So if you do your normal conversion of the summation into integration, that's what we do here. And then, in reality, because the electron is-- or in terms of weight vector, it's not very large. So you actually can extend this integration really rather than 0 to π or a 0 to infinite.

So what's the v_x ? v_x here is a p divided by momentum. So I'm doing that because, at the end, you can do either energy integration or momentum integration. And in this case, you can say k , I integrate over k is easier. Because if I put this, drop the 1, and e minus μ is work function plus the kinetic energy.

And you can see, if I do this integration, I can actually, because of the summation here, I can split each term and do integration k_x , dk_y , dk_z . So that's an easier integration than I convert it into energy. I show this because, like I said, the density of states is just a mathematical tool. If you use-- it's sometimes convenient to use it in energy, sometimes convenient to use just as momentum itself.

So if I do this, go rather than 0 to π over a , 0 to infinite, because this exponential function drops out quickly, this is what I get. And the exponential here, w , is the work function. it's the energy. $k_B T$ is also energy. This is a very small number because w is a few electron volts. $k_B T$ is 0.026 at room temperature. So that's a big negative exponent.

But the front side, this term you can see is temperature-dependent. And we could write it in terms of t squared times a constant. So now I put it-- before I said it's particle flux. Now I put the charge, because each particle carries a negative e . So this is my current flux. So the current flux, now I have a t squared. And whatever in the front, I group it into a , so a t squared dot exponential. And this is the Richardson formula. And Richardson got, say, did a lot of experiment, and he was awarded a Nobel Prize for this work in the thermionic emission.

But there are also, if you go to check the literature, in fact, the Dushman had a paper before him. So sometimes people call Richardson-Dushman formula rather than just Richardson formula. But the point is, we have a t square, we have exponential function for the flux of electrons coming out of the surface.

And this is a constant a is called the Richardson constant. But, say, in more general form, because the quantum reflection, so this is, in fact, not just an a , there is a factor in the front. That's the electron get reflected even though its energy is larger than the work function. But the waves has always a possibility to get reflected. So that's a $1 - r$ shows the transmission. And the rest is the-- what's the-- this one sometimes we use w , sometimes you use ϕ . It's all work function. So any question here? Yes.

AUDIENCE: How did he measure that?

GANG CHEN: How did he measure that? You put the voltage or, in fact, Edison did a lot of work too. This is this-- the beginning, so you see people develop vacuum tubes. So you can, in this case, you change the temperature, you measure the current that come out of the electrode.

And what Richardson did different is before, if you go to read the literature, and people do the charge, this kind of thermionic emission, not in vacuum, just in air, in a, say, gas environment. And sometimes the surface is negative, sometimes is positive. So it made the explanation very difficult. What Richardson did was do it in vacuum. And that made the explanation much more cleaner.

AUDIENCE: This is just for metal or everything?

GANG CHEN: This is just for metal. And the w is for the work function. Now, next, this is where my confusion starts kicking in. And I mean, let's talk about two metals. They have different work functions. And you connect them together. And once you connect them, let's say, the charge will flow from one to the other. This is a mass diffusion. If the chemical potential are different, they always at the end will pull together equal chemical potential. You don't have any driving force. You just connect and put a wire in between them.

So of course, two pieces of metal lie in contact, far away, each has a local vacuum level, no torque. But if I connect a piece of wire between the two, then the chemical potential is flat. So that means initially there is a current flow from one side to the other. And I was trying to think-- you can tell me now-- I was trying to think, now, what's the direction of this current flow? What do you think? What's the direction of the current flow? Sometimes we're forced to think, ask questions, try to explain to you. Even though I can't make it clear, but maybe I can make it clear when we all talk and think.

So now I have one piece of metal at larger chemical potential-- larger work function, a piece of metal smaller work function. And I connected them together. If I don't connect them together, I think, when I put them very close to each other, I know the direction of current. When connected, I don't know. If I don't connect-- let me tell you. If I don't connect them, but I put them very close to each other, I think the electron will go from the high work function side to the lower work function side through the vacuum again.

Do you agree? Or you have different argument? But when I connect them together, my question was, will the electron flow from the other way? Because that means, the question is, which one is positive, which one is negative at the end? I don't have-- I still don't have a good answer.

AUDIENCE: When electron travels from the left to the right, then doesn't it increase the Fermi level of the right side? Then if you--

GANG CHEN: If the electrons go from left to right, it increased the Fermi level-- well, so this is another thing there. What's really increased is furthermore, it depends on how you measure it. I said that the way we calculate from Fermi level before is relative conduction band. Fermi level chemical potential is a measure of number of electrons.

Maybe you're right. Maybe this is the way we should think about it. And maybe I should say, far away for the vacuum is the same. And then, so this is the-- because here I have a larger work function. Here I have smaller work function. Far away. So when I connected it together, so electron should go this way, the wire. But that's different from what I was saying. If I put the vacuum, the electron probably will go this way.

AUDIENCE: Why?

GANG CHEN: Huh?

AUDIENCE: [INAUDIBLE]

GANG CHEN: Why? Because I was thinking somehow those electrons-- OK, this are they-- here is the energy, and this is the kinetic energy. Of course, you have to-- this kinetic energy must overcome the work function. So what's left over here is still 0. Just those kinetic energy just above the chemical-- the work vacuum is still 0, because the rest is used to overcome this work function.

But anyway, so if I think this way, if I connect with the wire, then the electrons should flow this way. And that's what they were saying. In that way, maybe your reason-- so electron now, the chemical potential is raised, but you don't change the work function. So the vacuum level is raised here local. And then you have a, say, so this is the-- if I draw, that might be the local-- this is the vacuum, local vacuum level, this is local vacuum level.

And then, my question then, so if the electron is flowing this way, how should I think which one is the positive? Yes.

AUDIENCE: Does it depend on the difference between the Fermi level and the work functions, how they interact with each other? Because in this diagram, when you connect them, the Fermi levels become the same.

GANG CHEN: Well, after you connect, the Fermi level has to be same.

AUDIENCE: Right. So the work functions, depending on their differences, they can-- that you can have no flow or flow in either direction--

GANG CHEN: Yes. But see, I'm drawing a schematic where I have one side is a larger work function. So now with this work function is really relative to Fermi level to vacuum level, right? So my question is, which side is flowing?

AUDIENCE: So-- looking at the Richardson formula, the smaller the w , the bigger the current.

GANG CHEN: OK, so you're right. So the smaller-- OK, that's a good way to think about it, I think.

AUDIENCE: That's kind of--

GANG CHEN: So the larger is the w . OK, good. So maybe this will be consistent. The larger is-- smaller w , more flux going this way and higher, less flux. So at the end, you will have more electrons on this side. So this will be positive, this will be negative. And that's consistent with my connecting wire. OK, now I agree. Thank you.

AUDIENCE: The local vacuum level is shifted by the electrical potential.

GANG CHEN: Well, that's the-- so, OK. Once you get more electrons here, now you think about, this is the-- electric field, the direction is this way. That's your electric field direction. And you will resist the further going to the other side. And then you draw your potential.

Now, if you say, electrostatic field equals the energy, which is the potential divided by charge, which is negative, so when I fill this way, that means this flag here is higher, this flag is lower, that means the energy is higher, and this is lower. That's consistent. It's just this e , you have to think about the voltage opposite to e , to the local energies because of the negative charge.

That's the part I really don't like. Every time I draw this diagram, I have to say, ah, electron is a negative. How I'm going to draw? Whether I'm drawing a potential here, here, here, OK, they're really-- OK. Here we have an energy or e . When that's talked about the electron energy or local energy.

I say, when I talk about voltage, I talk about electrostatic potential. And electrostatic potential is really divided by charge, u divided by q . This q electron is [INAUDIBLE] to reverse the sign. So when I draw this way, as the potential, I'm drawing this work function. That's an energy unit. So when I draw the electrostatic, I have to reverse this way. See? This has a higher electrostatic than this side because the [INAUDIBLE].

That's where the confusion every time I have. But I do want to mention this. So now, clarify the question. So you get a w , so that's the w minus w prime. So really, this negative e is-- because I did w on this side, if I put the positive electrode, negative electrode, and I should mention negative voltage, that means this positive this negative.

AUDIENCE: What does the dotted line mean?

GANG CHEN: Huh?

AUDIENCE: In the figure, we have a line in the middle.

GANG CHEN: Oh, that's not my figure. I should have cited this. I got some-- this one was from [INAUDIBLE].

So what he's saying is that you are checking the electrostatic energy. Because this is a chemical potential, and there is also electrostatics. So here, the voltage is a positive here, but for electron, the electrostatic can move up.

AUDIENCE: But in the upper figure, isn't it true that the right side should go up so that the work function level should be the same? I mean--

GANG CHEN: Work function doesn't change. Work function is that you pull electrons from metal--

AUDIENCE: Yeah, so--

GANG CHEN: --immediately out to the local vacuum.

AUDIENCE: So when electrons are out from the metal, then the energy of the two electrons should be the same.

GANG CHEN: No, that's the point. That's what I say at the beginning. You have a local vacuum. Once you see-- once the electron goes from this side to the other side, right? So here is positive. We got a negative. So the local vacuum locally on the surface here, a metal surface, there is a higher electrostatic potential than here. So the local vacuum level varies.

AUDIENCE: But in your figure, in the middle--

GANG CHEN: Yeah?

AUDIENCE: --the highest level that is the work function level is the same. It's different from--

GANG CHEN: No, what I put there is thinking at the beginning, far away. No talk to each other. If you put together, they start talking, you have local electrostatic influence, you will create an imbalance in the field, electrostatic field.

AUDIENCE: OK, I see. So the upper figure does it mean that the two--

GANG CHEN: There is no talk. This is just a random, because you really can't align it. But this is where contact potential is-- this is actually defined as the contact potential. And I say this because, if it turns out that very often we want to measure the work function. And this is when I realized-- I suddenly realized this is an easy way to-- relatively easy way to measure work function.

And one way to measure work function is just to measure the contact potential. You take a standard piece of material where you know the work function. And then you come close to the other piece, and you start to have current flow. Because when you close it, and your potential is the same, but when you change distance, your current-- because they used to think of capacitor, you still have current flow. And that's the so-called Kelvin probe.

Kelvin probe, Kelvin method actually measure the contact potential. And using that, if you have a standard piece, you can measure the other contact potential. And I think Kelvin probe is standard [INAUDIBLE] rate if you buy atomic force microscope. You can add a few thousand and it will have a Kelvin probe software with it.

So let's move on. Now I'm talking-- I'm thinking about, really, the diode. That's what I drew on the board. And again, I draw a higher and anode and a lower function cathode. So in this case, just as we discussed, you have a local vacuum level higher and then eventually the chemical potential is flat. And at the equilibrium, at the transient, they will have current. But eventually, you establish equilibrium. So this is the-- normally, this is the cathode current going from left to right. And this is the anode current from right to left.

And you can say, I do not just do w_c , I do a w_c plus $e\phi$. This is because I'm thinking about the static state. I'm not thinking about the transient initial establishing equilibrium. So you can see, once you got a potential, the electron from here cannot really go here anymore. So only the electron with the energy u on this side, with the energy higher than this point can go to the other side.

So at the end you get the-- at the equilibrium, the difference of the two is 0. There is no net current flux. You put the two pieces of metal together, you connect them. Rather than just the initial current, at the end, it should be no current flow. Otherwise you get a perpetual motor. So that's the vacuum at equilibrium.

Now I'm going to put a temperature difference across it. One side is hotter cathode, I made it hotter, and one is colder. And of course, I still have the current. And if I write the Richardson expression-- OK. Now, in this case, if you think about it, when you heat it up, there should be more electrons gaining kinetic energy, higher kinetic energy, higher temperature. So the electron will go from cathode to anode. So electron, there are some current go here.

And so, eventually, relative to speaking, the chemical potential will no longer be the same. And really, this chemical potential is the electrochemical potential. Because what I added here, the voltage that's generated added to the chemical potential. So this level is the electrochemical potential. And that's what I can measure. When I put the two electrodes, I'll measure a voltage difference. And that voltage difference is these two points, voltage difference.

So because of that, my current, cathode current, now-- and this is what I originally had. And this is the additional. And again, this is where I don't like it because I put a-- I should put a negative sign. Because if you think about, the electron here now, the electron that needs to go over this, so from electrochemical potential μ_c to the maximum point is-- the distance is shorter. And I put a positive sign here. So ideally, I should get the negative solution v_0 . That's my open circuit voltage.

And I don't think I get that. I still don't know why. My sign doesn't seem to be right. So I give you the challenge. You go back to sort it out and come back and teach me. And this is the cathode. This is the anode. And of course, at steady state, if I don't put any connectors there, I have a voltage difference between these-- real voltage that I can measure.

So again, this doesn't relate to the negative charge, but at the equilibrium, I should not say at equilibrium, at steady state, not equilibrium. When you have temperature difference, you have chemical potential difference, you don't have equilibrium. Accurate way to say is at steady state. At steady state, there is no net current flow because I didn't connect it to any load. I have open circuit. So current is 0.

So if I go through this steps, put this two expressions, this one minus this one is 0. So I'm going to do that. This are the two terms. And I take the ratio, I take a log, get rid of my exponential. Second step, I was hoping I'd get a negative sign, but I don't get it. So tell me where I should get it. I didn't see, I get a negative sign. I still don't know why.

But anyway, the magnitude is correct. The sign somehow, I don't know. But let me also look at this and point out that if you think about before, when we talk about Seebeck effect, is a voltage divided by ΔT . So if I do a voltage divided by ΔT , not ΔT , just an order of magnitude, this term I put it here.

And here is k_B divided by e . $2k_B$ divided by e , that's of the same order of Seebeck coefficient. So this term actually come from-- is a very similar to the thermoelectric. And this term is the thermionic term here because it depends on the barrier height of the anode-- anode barrier height.

So that's the open circuit voltage. And of course, open circuit is useless. You don't generate any power. You have maximal voltage, but you don't generate power. This is the same for photovoltaic cell, So you need to put a load here. Once your current start flow, you don't get that high open circuit voltage anymore. You get your actual voltage. That's the actual voltage.

And you can change this voltage by changing your load resistance. That's a load matching. That's for all solid state device, solar cells, thermoelectrics, thermionic, you have to optimize your load or optimize the device itself to match the internal and external. That's load matching.

So if I write-- I rewrite the expression because the contact potential is the same as ϕ_a . And you can say my current depends on the voltage. And of course, power is just current times the voltage. So that's my unit volume power, unit surface, I think, because j is the surface. And so, that's the power.

Now, for thermionic generator, I have to do the efficiency. So I have to look at how much heat transfer happen. I have now electrical power output. I have to look at how much heat transfer. So what are the mode of heat transfer here if you look at this? First, this side is hot. This side is cold. There is a radiation. Any other heat transfer?

AUDIENCE: Electron carries heat.

GANG CHEN: That's right. Just, we don't forget electrons also carry heat. So first, let's look at-- that's a fundamental site. Radiation is not necessarily due to electrons. It could be due to lattice. But electron, when you have charge flow, always carry the heat. So I have to count that part of heat. So this is the first step. What's the kinetic energy? That's the-- just the $\frac{1}{2} mv^2$. So this is $\frac{1}{2} m v^2$ divided by $2m$. That's the kinetic energy above the barrier.

So I do my integration in the same way I did before as I do particle flux. I didn't start from beginning here. I just write the expression. And I do my integration. And it turns out the heat flux, kinetic part of the heat flux is proportional to current flux then $2k_B t$, That's the Seebeck coefficient-- times t .

So Peltier coefficient, remember, in the thermoelectrics, Peltier coefficient equal Seebeck times t . So you can see, this is very much the Seebeck part. This is the Peltier coefficient, Seebeck times t , times part. So this is the [INAUDIBLE] carried by electrons from cathode to anode.

But then heat is more than this. Because, remember, when we define the heat is the energy minus chemical potential, $e - \mu$, relative to chemical potential. So relative to chemical potential, I have this part is kinetic energy. Then I have really from here to here. This is a cathode site.

The energy, the one that really go over the barrier, the rest of it from here to here. So that's my $w = e - \mu$ here. So this is from here to here. That's my potential part, and this is the $\frac{1}{2} mv^2$ kinetic. So that's all the heat it carries.

What is this in terms of resemblance? If you're a mechanical engineer, think of this. Give me an analogy. Huh? This is evaporation of water. The water molecule coming out of the surface carry a lot more energy because you have to say the energy is-- say every other-- so if you think about the water, and there are some molecules flying around.

If I take all the molecule away, and then there's another molecule we created behind. And the creation of this molecule from the liquid phase to the vapor phase, this is the lock and key. Essentially, those terms, this and the heat of the electrons when you come out of the surface. And this is the kinetic part.

But at the end, also I see this. I still have a little bit of trouble thinking this as a evaporation process, because I'm trying to think of an analogy of, OK, here is a potential, the bottom. You come out here, so that's the minimum. So each molecule carry out this. I say, that's an evaporation process.

But what about suddenly a bottle-- OK. What about this process? If I have a high energy electron, and the potential here suddenly fall off a cliff? And then that's excess energy, potential energy. Do I consider that as a evaporation process also? Then I'm a little bit confused whether to think of mechanical. I don't know what's the-- whether I can give an analogy of this two different processes in terms of evaporation.

And this one is more, to me, somehow, to me, is I have a container of liquid, I open a hole. This is a high temperature. When the liquid come out here to the other side, the vacuum, it suddenly evaporate, change from a liquid phase to vapor phase. I'm making this to this and this to this. You can tell me whether you agree. But at the end, I'll give you one example where I struggle on this question-- why I struggle on this question. So that's the electron heat.

And of course, there's also another side from a-- I can reverse this. This is from anode to cathode. This is from cathode to anode. And the difference give me-- this is the electronic part of the heat. That's the first two. And then we have radiation part. And then you have a lead, that lead conduct heat. So that's a conduction heat loss. So if you have a real device, you have to consider all those heat losses.

And of course, the efficiency is defined as the power out divided heat in, always what we do when we do efficiency. And if I do most ideal situation, I neglect radiation. Why you can neglect? I say, well, I have my perfect photonic crystal, no radiation. It's impossible. But let's say, I make this small. So if I neglect all other heat, just for the electronic part, I cannot neglect it-- intrinsic. And that's the curve you will get. And this time, I remember to cite the reference.

And you can see, in terms of the efficiency you can get, it's very much a $e v_a$. That's w_a , $e v_a$. v is the voltage. So it's w work function of the anode side divided by kT_a . So that's one parameter. And you optimize this parameter. And this is the ratio of the hot to the cold-- the cold to hot side temperature. So that's the ratio. So you can see the heat efficiency, pretty impressive, very high efficiency. Of course, this is when you neglect the radiation. You can't get rid of the radiation part. You also have additional heat loss.

But compared to thermal electric, because you're using vacuum, so you don't have full-on heat conduction. That's why this can give you a high efficiency theoretically. And the first experiment was done by [INAUDIBLE]. Some of you are from that lab. He was a-- he did the-- this was in the '50s. So he came from-- he told his story. He came from Greek and trying to get a topic, and he were able, at the time-- it was since, didn't have really research government funding. But somehow he was able to get some funding to do the thesis. And he did a thesis. He went out and open company.

He had a very nice book, *Thermionic Energy Conversion*, two volumes. I was reading some of it. I couldn't read all of this, but very detailed. He actually talk about the detailed electron-- I'm very impressed. So he talk about from basic quantum mechanics to work function. But that's Hatsopoulos and Gyftopoulos. Gyftopoulos is still professor emeritus in nuclear engineering. So they wrote a book together.

And you can see, they did an experiment, 2,300 F per high temperature, hot side. And cold side, 1,000 F. That's the challenge with thermionics, it's a very high-temperature device. And the efficiency was, at the time, 1958, it was pretty good, 13%, 13%, 14%, pretty good efficiency.

And so, they were very ambitious here. He also put his voltage negative. And you should read this paper. I'll send it as a reading. So his story is, he started-- he was a faculty member in our department. And he went out to start the company-- assistant professor at MIT started a company that's called a Thermo Electron. You go 128, 95, you will see the signs, Thermo Electron. Now it's called Thermo Fisher. And I believe they were trying to commercialize this.

The story is, he said, he told me he went to Washington on Washington trade, and then he realized NASA-- the business really depends on whether NASA flies or not. And so he changed direction. Good for him, I think. Otherwise, I can't really say something. And the company, Thermo Electron, really does a lot of instrumentation. So it's no longer doing really thermionic energy conversion. And the recent merger is now with Fisher. Fisher is another big, I'd say, company name. So now it's Thermo Electron-- Fisher Thermo Electron. That's a good story.

And the real device was not as simple as I draw, of course, the high temperature. But also there is really a fundamental problem. This is the fundamental problem is charging. If you have an electron in the vacuum, So any electron, any charge, surrounding charge, there is a field, a charge there will free the field. So when you've got a lot of electrons, they will create electrostatic potential. And this potential distribution, you can see now, I draw rather than a linear one, and really depends on the gap, depends on the charge number.

But the point is, now your barrier is higher than just work function. You got an additional barrier to overcome due to space charge effect. So this is a big problem. Space charge is a big problem. And in addition to this, there are also many other problems. Of course, the most mature work functions are very large. That means you have to operate at higher temperature, few electron volts.

So if you check most material, metals is about four electron volts. There are some materials like [INAUDIBLE], two electron volts. So if you use a cesium, cesium is actually-- you can first, you can generate cesium to neutralize the positive charge system vapor, to neutralize the negative electrons. So they reduce the space charge. But cesium is very corrosive, so there's problems at high temperature.

And you can use either vacuum, or there are other modes where you just put a gas in between. When you put the gas, there's a plasma formation. So there's this vacuum mode or plasma mode of operation thermionic devices. But historically, think about this, the transistor, the diode, the solid state were invented in the '50s. And before that, computers were built on vacuum diodes. The vacuum diode is essentially this, except they operate in a near room temperature. And this is just a one site to operate the high temperature outside the room. Problem is, we go to 1,000 degrees.

What are the recent trends? The research in this is relatively small, I would say. A Russian actually put this in space station. I tried to dig out a picture, I couldn't find one. But they call it the Topaz. And so Russia had a few space station, space missions that use thermionic engines rather than thermoelectric engines. You can search whether you can find more information if you're interested.

And so, some of the idea people explore, one is the negative electron affinity. So if you let-- maybe electron just jump off itself. Negative electron affinity, vacuum level is lower than what's inside. And so that's one, people still look at this.

And the other is a small gap. And this small gap, there were actually some programs, so the gap goes to angstroms. It's crazy in the sense-- of course, in that case, what happens is the electron can tunnel quantum mechanically from high side to low side. So you don't have this space charge limitation anymore. The electron don't have to be having an energy higher than the top of the electrostatic.

So you can really just zip through, when this one is of the order of angstroms, that's a scanning tunneling microscope principle. Electron can go from one side to the other tunnel. But say, like I said, that's pretty-- technologically, it's too challenging, because think about the maintain hundreds of degrees at angstrom level.

And then, the most recent is solid state thermionic where you run into still the heat conduction problem. Once you got a solid, everything solid state, then you have heat conduction. So that's the same as thermal electric operation.

But I just want to give you one sketch on what does the electron affinity means? Because normally you can see, the work function is between chemical potential and vacuum level. That's a work function. And of course, the space charge created a higher. And the negative electron affinity still doesn't mean the electron will all-- for other metal, you don't get the metal anymore.

Here is the bottom of conduction band. But this is a, say, in negative electron affinity, which is typically semiconductors, very wide gap semiconductors, the electron actually sits in here, more the Fermi level is here. So it does not come out. So you still need to overcome the space charge to [INAUDIBLE] come out. So that's the liquid [INAUDIBLE] affinity material. So people have interest in this, not only for thermoelectrics and thermionics.

So that's a discussion on thermionics, which is in formula, what's important. Yes.

AUDIENCE: You said that [INAUDIBLE] is very [INAUDIBLE].

GANG CHEN: Right.

AUDIENCE: What happens if you just put some [INAUDIBLE]?

GANG CHEN: Dielectric material is-- the problem now you got a heat conduction.

AUDIENCE: Oh.

GANG CHEN: So run into this classical thermoelectrical problem. And what are we-- now somebody ask, say, semiconductors? And let's think about now we have a metal and a semiconductor. You always have that in any microelectronic device. Because, at the end, you want to make a contact. You put the metal on the semiconductor. So that's a typical classical situation.

And now let's see what happens. And now, of course, here is the Fermi level. Here is the semiconductor Fermi level. I'm talking about the along degenerate. So Fermi level is in the gap. This is really where electron sits in. And when I put these two together, I still got the same problem.

If I collect them electrically or put them in contact with the shutter, the chemical potential difference will drive the charge flow. So eventually, the chemical potential on the two sides will be the same. That is always the driving force for diffusion, mass transfer, charges of mass. Mass transfer is chemical position. Heat transfer is temperature. Mechanical is pressure. So the thermodynamic quantities.

And then, when I put them together, so the Fermi level will align to each other, chemical potential align to each other eventually. That's a driving force for charge flow. And here the work function here is the affinity. And then at the point of all the contact, you can think that they have to have the local same vacuum level, same vacuum level. At that point, if I put these two pieces together locally, I pull electrons out to vacuum, that's the same point as the metal side.

So there is a mismatch between the work function and the affinity. And this mismatch is Δ here, which you can check. For different material you can always define-- not always. Sometimes people have measured it. But in theory, you can find this. So there's Δ . That's the-- this Δ is the Schottky barrier height. That's the barrier height. There is a potential difference of the electrons in the semiconductor and metal side.

Now, of course, if you think about this, electrons here, so this electron will fall into the lower-- the metal side. Electron go from high energy to lower energy. Anything go higher energy to lower energy. So once they fall, there is less-- there are positive charge, less electron here. So chemical potential is measured between e_c and here, and less electron means larger distance.

So you can see here, I'm going far away from the interface. That's my bulk region. Interfacial region, the semiconductor side, there is a band bending. e_c is no longer flat. And that's because intuitively electron fall on this side, less electron, so bigger separation there. Yes.

AUDIENCE: Are the Fermi levels--

GANG CHEN: Same.

AUDIENCE: Same level?

GANG CHEN: Yes. I didn't draw it level.

AUDIENCE: So the vacuums are different?

GANG CHEN: Vacuum now--

AUDIENCE: It's different.

GANG CHEN: Vacuum--

AUDIENCE: It's three levels.

GANG CHEN: Yes. Yes, thank you for telling me that. Vacuum level is different.

AUDIENCE: So is the drop the same on the other side because the e_c will go down [INAUDIBLE]?

GANG CHEN: So locally, the vacuum level also changing. So this is where, again, you have to really think, this is defined really, really low quality. This rule is actually sometimes violated, particularly when you put two different semiconductors. You first think about the lack of vacuum level, then look at the affinity, and that's the [INAUDIBLE]. It doesn't always work.

AUDIENCE: Because I'm trying to tell-- so if Δ , before you bring into contact, you have e_c between-- e_c and the Fermi level.

GANG CHEN: Right.

AUDIENCE: The level, right?

GANG CHEN: Right.

AUDIENCE: So that's the original level. When you bring it together, e_f and the vacuum drops down for the semiconductor, then e_c drops down as well. Is that correct? So that's why that's why [INAUDIBLE]

GANG CHEN: Does the vacuum level change? Let me draw the vacuum level. What I saw with the vacuum level here, this is a vacuum. Let me draw it. This is the metal side. And this seems to be the semiconductor side. And this is the ec. And here is the-- so here is the work function. Here is my electron going into vacuum. So this is my affinity. The difference can be the [INAUDIBLE].

So I didn't have that jump in the vacuum. Locally I put the same. So this is the-- this kind of interface here, is often between metal and semiconductor. And this is a Schottky barrier. And now if I think about the flying flow electron, I put a-- I talk about contact. You apply a voltage, how the electron flows? And of course, you can always say, again, from left to right, right to left, same kind of thinking there.

And now here is a p type. So before I draw an electron, and here is a pulse. Pulse is a-- this from here to here is barrier. This is a positive charge-- [INAUDIBLE] holes. And here there are less holes because the electron fall into here neutralize-- make less hole really. Because electron fall into-- wait. Where I'm confusing?

Think about-- so positive, so really, so electron should fall into this side, from here to here, because the electron is at a higher energy than here. So electron fall into this side. There's less hole here because the electron fell in the empty state. And the holes are just what's left over, the empty states of electrons.

So what's hole? There's really no hole. In the [INAUDIBLE] span, this is the ev, the electron field over here, and left behind the few empty space. Those are the empty area. Now the metal, electron from the metal, electron from the metal fall into this side, fill in some of those empty states. So this is no longer available for full. So this is less holes space. So there are less holes here. This is less hole. So the Fermi level return, the chemical potential, and the span becomes larger. So this is the Schottky barrier for the p type.

AUDIENCE: Professor.

GANG CHEN: Yes.

AUDIENCE: So in the p type, [INAUDIBLE], so you are bigger actually [INAUDIBLE] p type [INAUDIBLE] level will go up. But it seems like in the vacuum--

GANG CHEN: Vacuum level, I didn't draw a vacuum level here.

AUDIENCE: The green region.

GANG CHEN: Where is it? Where do you mean?

AUDIENCE: I mean, the [INAUDIBLE], the ec and the [INAUDIBLE] is the [INAUDIBLE].

GANG CHEN: No, no, no. The p type has to be-- you have to look at the-- I think this is your w on the other side.

AUDIENCE: Yeah.

GANG CHEN: And you have to think about this will be here. And so, from here, vacuum level--

AUDIENCE: Yeah.

GANG CHEN: --vacuum level here. And now electrons start to fill in, because the electrons go from high energy states to lower energy states.

AUDIENCE: Yes, you mentioned that [INAUDIBLE]. That's why.

GANG CHEN: So the Fermi level will be-- because this is p type. So the p type will be going here. This is the Fermi level. So this is the-- this will be the--

AUDIENCE: Do the ec all the way around? [INAUDIBLE]

GANG CHEN: No, ec doesn't go in. This one, ec the background has to be the same. So between here and here, this it hasn't been done.

AUDIENCE: Oh, [INAUDIBLE].

GANG CHEN: Yeah. But there are not much electrons in the p type. So you say, why the electron doesn't flow.

AUDIENCE: And the vacuum he has right now too.

GANG CHEN: Huh?

AUDIENCE: The vacuum he has right now too are the semiconductor side.

GANG CHEN: Vacuum also has to bend down, yeah. So this is your vacuum level.

AUDIENCE: So [INAUDIBLE].

GANG CHEN: Huh?

AUDIENCE: That's exactly what I was telling, [INAUDIBLE].

GANG CHEN: Oh, vacuum, I see. Yeah, vacuum is [INAUDIBLE]. I thought you were asking the ec. Very tricky. Now let's check. I'm giving you the formula. I'm not deriving. But the point is, it's a Richardson formula. Negative what we wrote for vacuum. And when I-- but there is some difference also.

So the first factor here is the same Richardson factor. And then I have this exponential $e^{-eV/kT}$. And then you can see, that depends on whether my voltage is positive or negative. So when I see positive, is I raise the Fermi level on this side, on the semiconductor side. So the voltage is applied, so this will be, in this case, this will be positive electrode, negative electrode, raise the electron on this side.

And of course, the electron raised, so there is more chance for this electron going from left to right-- from right to left. So that's where my $e^{-eV/kT}$ comes from exponentially. So I have-- this is a forward bias. Now, when I reverse bias it, let's say when the electrons go this way, it really tried to go this way. That's what I draw. This is a positive metal, positive semiconductor, and it's [INAUDIBLE], right? And when we reverse pass it this direction, the Fahrenheit is fixed, didn't change.

So this current is always the first-- this saturation current here. Now there is less going this way. But that's not much less because you see here, that difference is small. So now, this is the same as a diode. Biased differently, you have, say, different current characteristics. So that's similar to a diode, typical diode. And this is a Schottky diode, positive bias, negative bias, saturation current here, not 0. And this is if we invest too much, it break down. So you can just punch over this barrier and under not reverse bias.

And you can see, a metal semiconductor interface, and if you make a contact like this, it's not good. Typically, you don't want to make a Schottky contact. And how you solve that problem? And the way people solve this problem is they dope it very heavily. So let's say, when you dope heavy, this becomes-- say, so basically, when you dope very heavy, few electrons come over, this is very narrow. This is very sharp.

So when we draw, this becomes very sharp when you dope heavy. And when it becomes very sharp, so the electron tunnel through rather than have to go over the barrier. So that's one way to overcome the Schottky resistance here. Otherwise you'll see, so this is how people make [INAUDIBLE] contact is you dope the region very heavily. And of course, you want to use the right metal to start with so that the work function, the delta here is not large.

So that's why, if you want to make a metal-- a contact, you want to know your work function, you want to know your electron affinity, [INAUDIBLE]. And of course, there are many other reasons where you do make a good contact and other than this. You may have a physical long contact, a vacuum gap here that could also-- vacuum gap is essentially a very high barrier. You have to power through that. You can power through that. Or if it's too wide, there's no chance you can go through. Schottky diode.

Since we're talking about diode, I'll continue. This is a metal semiconductor. A regular diode is not a metal semiconductor. It is a semiconductor-semiconductor diode. So let's look at semiconductor-semiconductor. So we make a semiconductor n type, semiconductor p type. And I put the two pieces together, contact, same thing happened. The chemical potential must align each other. So what that align looking like, what it really means is, here, n type got a lot of electrons. So electrons go this side. P type I got a lot of hole. Hole go the other side.

And so, when electrons go from this side to this side, what's left behind? Positive atoms there. So what do you have here is positive atom. This atom do not move. Those atoms are just charged there. They don't move. On this side, holes left, so they left behind-- really, just get a holes left is, you get an excess electron to-- for this case, p type or boron.

Say you get an excess electron, not called the neutral now in this region. So those, when I draw this, is the ions, positive ions, negative ions on the two sides of the interface. That's a space charge region, not a mobile ion, mobile electrons.

And if I draw the bandgap-- band alignment. So if I-- oops, I forgot-- e_c should be μ . No, this one, there should be a line here. That's a e_f . I disappear. This is a e_f . And this e_f and this e_f will have to align each other. So it's easy to think about the connection. If I have far away from the interface, I have n type. And far away from the interface, I have p type. And now p type Fermi level is close to e_b , and type of Fermi level is close to e_c . And then connect in between. And at the end it's equilibrium. That's equilibrium.

And in between this region, a space charge region, no charge there. No free carrier, no electron, no holes, just a positively ion, negative ions. And that means I got that now I have positive ion, negative ion. I have a potential pointing from positive negative. So that potential is building potential point negative to positive. And this potential will resist further diffusion. So at the end, you've got the equilibrium. So this is the view of the input picture that resists diffusion of charge from one side to other. Change junction.

Now let's look at what's the current voltage characteristics. Very similar to Richardson's formula. So I'm going through this. That's what you learned before. So this is a-- I threw at you. Electron number density, hole number density, and the electron in any semiconductor, if you [INAUDIBLE] the electron, you can also derive similar hole.

And then you take the product, you found out the product is constant. This p and n , so if you dope the electron, dope for n type, there are less hole because p times n is constant. p times n here is a relative band structure, effective mass conduction, effective mass balance, bandgap, and kvt , right? So p times n is constant. That's the-- now, how I calculate building potential?

From on this side, I can say, because I know this is a constant, so I just need to calculate this. I need to calculate this. And the difference is this. That's the building potential. So from-- or look at this side. I have e_c minus n . That's e_{cn} minus μ , that's this distance. So I can start from the-- let's suppose each of the donor, each phosphor, for example, I put in give me a electron. And I reverse it, I get this. And I can do the same on this side. Given the number of the acceptor, that's the number of phosphor I-- boron I put here. Each boron create a one hole.

So I find the distance between here and here. This is from-- oh, well, I already converted it into e_c . That's from here to here. And now this, from here to here, that's here, that's here. The difference of these two give me the building potential. So this is the building potential. And it's the acceptor/donor, acceptor on this side, donor on this side. How much I dope it, because the more I dope it, the higher is the building potential.

How wide is the space charge region? Now that you can solve this equation. I'm not solving. I'm just agreeing [INAUDIBLE]. But I want you to look at this. If it's just an electrostatic, that's the-- this is the width of the space charge region. And it depends on the dielectric constant. Larger dielectric constant, wider is the, say, space charge region. So if I look at this one side, either acceptor, donor, that's roughly how wide it is.

And that's why I said I want to dope heavily to make a-- to reduce the Schottky effect for contact. If you can see that if I dope heavier, the width of the space charge region is narrower. And this is where you will talk to people with intelligence. They say, oh, what's the bi-length? That's essentially a measure of the weight, the intrinsic weight. And then the bi-length is essentially what we have here, replaced by the building potential by kvt , this spread, thermal spread.

So heavier doping, shorter is the space charge region. Some people do nanowire surface effect, depends on you can see whether surface effect [INAUDIBLE] or not, depends on your doping. So bi-length.

Finally, this is a-- I want to show you this because it's the same as Richardson formula. That's a pn junction, i times v , current voltage relation, except j_s -- except j_s . And that has a lovely price there. The j_s is no longer a t square. That exponential barrier, no longer the Richardson form. And the one we have here is the diffusivity of hole, diffusivity of electron, recombination time of hole on each side with the electron on each side. So this is a complete different mechanism. And so, this are the definition.

Here I'm going there quickly, but I want you to chew on it and come back I will do-- I will explain more. And basically, this is a different-- here you can see, the formula is the same. Saturation current j_s is different. But it's a complete different mechanism in terms of transport. Because in a pn junction, the electron will go from this side to this other side. There are no electron anymore. p side, there are not much electron there.

So how the transfer happened? And it turns out, there's really the hole recombined with the electron. So the holes here recombine with the electron. And then hole has to supply-- keep supplying. So there is a-- so in a pin junction is a recombination that's important, that drives the current flow. While in a Schottky diode, it's just electron go this side, electron go this side. There's no supply issue there. So one is a majority carrier device. The other is a minority carrier device-- very different. Formula is the same-- almost the same.

So just the last slide. And again, I want to show us a-- I'll come back to do a little review. But to go think about this. So this is the electron current, hole current. And they add up to the total current must be continuous. That's a pin junction. And what most people do not know, even electrical engineer, I'm pretty sure, is that inside of the just space charge region, there's no heat. In fact, it's cooling.

You look at the Peltier effect, you go to analyze the thermoelectric effect in the semiconductor device, you'll find out that in the space charge region, the cooling effect. And this is really the recombination outside the space charge region that created the cooling-- heating. Of course, heating is a big issue in microelectronics. But in a diode, the center, the interface is actually cooling type.

OK, I'll stop here. And I'm thinking about the same topic. Again, a lot of materials.