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**TONIO**

**BUONASSISI:**

Why don't we go ahead and get started, folks. Just some small talk to get us started. I promise to tell you the stories about contamination and unintentional contamination.

Before we dive in, what a life, right? Steve Jobs. That was really something. Moments like that, I think the best you can possibly do is to celebrate the person. And well, in honor of his inventiveness and the way he really turned Apple around, I just wanted to focus a minute on that.

Speaking of contamination and unintentional contamination, the effect on processing, the history books are full of this folklore, if you start talking to people who grow crystals and who manufacture solar cells. The growth of the crystals that are used to actually make the wafers that ultimately wind up being solar cells is a little bit of a-- how would you say-- a little bit of an art. It is being codified rather well now. And there's some strong science behind it. But by and large, up to very recently, it was more of an art than a science.

The best crystal growers are people who are very observant it and who are able to look out and see correlations where they weren't immediately visible to others. So in one particular factory, they started noticing that they had yield losses during the winter time. And in particular they had extreme yield losses whenever there was a big snowstorm. And it was somebody, one of the shift leads, I believe, who traced it back to the salt that was marching in on people's boots as they were coming into the factory. And that sodium was contaminating the silicon melt and resulting in the poor quality of the crystals that were being grown.

Flash forward several years at Fraunhofer Institute for Solar Energy Systems in

Freiburg, Germany where the observant cell manufacture started noticing, well, gee, our efficiencies are always lower on Fridays. Why is that? And eventually, they traced the problem down to the fact that, on Fridays, the technicians would go out to lunch at a Chinese restaurant. And they would come back, and their breath and their hands would be MSG. And that was, again, the sodium was downing performance of the devices.

As so it's really interesting. This kind of sounds like something you might see in a TV show where that scientist in the lab coat waltzes into a room and says, it must be the sodium. Right? And then they test it. And oh, my gosh, it's the sodium. Now, problem solving the real world doesn't quite happen that way. It involves a very methodical approach to testing a variety of hypotheses, first brainstorming in a structured manner, identifying the most likely candidates, and going about solving the problem, performing a series of design experiments to really get to the root cause.

So it's an interesting story. It's an interesting aside. Solving contamination problems, though, is very difficult. And the best thing you can possibly do if you're growing crystals is to keep your system more clean than you think you need it to be. That's the best advice I can give.

I was just talking with some folks in Caltech the other day. They were running into contamination issues. And that advice goes a long way.

OK. Well, let's go ahead and get started in the topic today. Back from Phoenix and eyes are red from irritation of having been awake for too many hours. So that could only mean one thing. Contacts, right?

So we're going to be talking about contacts today, charge extraction, as well. And to situate us on the roadmap, we have our fundamentals right here. We're about to jump forward into the technology, which is really exciting. We're about out of the woods here, folks. And finally, into the cross-cutting themes.

And so, again, every photovoltaic device must obey this general equation right here

where the output energy over the input energy equals a conversion efficiency. And for most solar cells, this is represented by this right here. And we have now tackled every single one of those, at least in a very fundamental way. And now, finally, we are focused on the output, the charge collection, in other words, the contacting of the device. Again, the total cell efficiency is going to be the product of each of these individual cell efficiencies here.

And contacts are a very, very easy way to kill your device in a variety of ways. And we'll get to some of these points right here. As a matter of fact, this s back, this surface recombination velocity on the backside of the device, is a contact-related phenomenon. And that's exactly where the water is spilling out of this bucket right here.

Learning objectives. The idea is to start out with describing the purpose of contacts, and their most common types, then to describe the impact of good and poor contacts on I-V characteristics, in other words, to describe the device impact of contacts. So we're convinced that this is really something we should be spending a lot of time thinking about.

Then we're going to sketch the I-V characteristics of Schottky and Ohmic contacts. We'll learn what those mean. I hope you know what ohmic means. Describe what fundamental material parameters determine I-V characteristics of a contact/semiconductor junction, sketch common band alignments, and sketch common solar cell device architectures, once we're done.

And then we can look back and gaze over the fundamentals and say, Ha, ha, how far we've come. And now that you look at a solar cell device, hopefully, you'll look at it in a much more profound way than you did in the first day of class. The more you know, the more you see.

So contacts, why do we need them? We need to extract the carriers from the device. We need to prevent the back-diffusion of carriers into the device. These contacts, in general, have been studied very extensively in the semiconductor industry. Why is that? Why do we need contacts in the semiconductor industry to

make integrated circuits?

Obvious answer. We need wires. We need to extract the charges from our transistors, right? So we're injecting charge, pulling out charge. So contacts have been pretty extensively studied in the semiconductor industry. And we're going to leverage that a lot. We're not going to reinvent the wheel where we don't need to.

Contacts are semiconductor-specific. Fundamentals apply broadly, but the specifics pertain to-- or the devil's in the details, in other words. So there are very specific effects that occur, depending on the precise semiconductor metal combination. And lastly, the contacts are heavily influenced by the interface between the semiconductor and the metal. We're going to be talking about that as well.

So typical materials used for contacts include metals, transparent conducting oxides. And also, we can find heavily doped organic materials as well. Metals, we understand. OK, they're optically opaque and electrically conductive. That means they conduct electricity very nicely.

And so our series resistance along the metal wire should be low. But they're optically opaque, meaning they're resulting in a shading loss. So if we cover entire front side with metal, we're not going to have a very efficient solar cell, because our absorption of light is going to be very poor. On the other hand, transparent conducting oxides are optically transparent and electrically conductive, not quite as conductive as metals, but pretty close.

So let me think about that for a minute. A material that is optically transparent-- that means it must have a very large band gap to let the light through, does interact with it, but is electrically conductive. In other words, it has a high concentration of free carriers that can move around the material and conduct charge. How is that possible? I hope you're asking that question, because this perplexed me for a long time as well. And we'll answer that in a couple of slides.

First, the properties of TCOs. What makes a transparent conducting oxide a transparent conducting oxide? I figure I'll spend a couple slides on this, since metals

are pretty self-evident. But TCOs, this might be the first time you're encountering them. They're present in a variety of devices. If you have an iPhone, or if you've ever seen certain types of military aircraft, TCOs are involved.

So the material is very transparent. You can see the transparency over quite a broad wavelength range here, cutting off only in the several eV range here. Transparency begins to drop, because you're able to excite carriers across the band gap. So it's a very large band gap material, and yet, the conductivity is very good.

So here, we can see that the conductivity of ITO, that's indium tin oxide, that's a particular type of transparent conducting oxide, is almost as good as silver. Not quite, but it's approaching it. And so again, the conductivity, which is  $1$  over the resistivity is related to the carrier concentration and the mobility, as we've seen before. And therefore, there must be a lot of free carriers. And they must be fairly mobile, to move around the material.

So how does that work? Band gap greater than 3.1 eV, transmittance very high, as a result, but still a large number of carriers. Well, if we consider our band gap right here-- and we'll consider floating Fermi energy right now, we'll explain why that's pegged there in a minute-- we assume that the band gap is very large, so that light can go through, and it's optically transparent. But now, by doping the material with a specific type of dopant that forms mid-gap states, we're going to create a new energy level here that is partially filled. We can then excite, with relatively little energy, carriers into the excited states within that orange band, and they can transport charge throughout the material.

On the other hand, if we come in with a high energy photon or a moderate energy photo, let's say, in the visible, it doesn't have quite enough energy to excite from that orange band into the conduction band, nor from the valence band into the orange band, the intermediate band there. And that's the general principle of how transparent conducting oxides function.

You can have indium doped tin oxide, for instance, ITO, as a classic example. And this is the basic premise. Any questions so far, because this is kind of important,

before we launch into-- yeah.

**AUDIENCE:** So how big are those, that E1, E2?

**TONIO**  
**BUONASSISI:** Yeah. So this E3 right here is around 0.4 eV, for a typical TCO. And E1 and E2, the sum of both of them could be on the order of three to four eV. Maybe higher. Well actually, no. Sorry. Just one of these transitions right here could be on the order of three eV. So the entire band gap could be quite large.

If you think of metal oxides-- most metal oxides have very large band gaps. And most TCOs fall into that category. They could be tin oxide or zinc oxide, but heavily doped with an element, like indium, or fluorine, or aluminum, to provide that intermediate band.

**AUDIENCE:** What are the doping concentrations required [INAUDIBLE]?

**TONIO**  
**BUONASSISI:** Yes. So this is a deep dive, and I'm happy to entertain that question. For those who it kind of goes over your head, don't worry about it. We'll return, so plant a flag post in your mind where we're at.

Remember the hydrogenic donor model for a dopant atom. You introduce it into the lattice. And that loosely bound electron is there, kind of like a hydrogenic donor. It has a certain radius. And if you begin doping at a very high concentration, those electrons will begin interfering with each other. They'll begin interacting. And so instead of forming one isolated defect level, they'll start splitting and forming a band.

And the density at which you have to dope depends on that donor radius. So you're typically talking about concentrations in the 10 to the 20 per cubic centimeter, or one atomic percent or higher. So that's the dopant density that's required to force this transition.

It's pretty cool. I mean, there are people who do their PhDs on transparent conducting oxides. Maybe some of you are. You could probably come up and give a lecture about it.

So it's a fascinating subject. And because ITO, or indium tin oxide, is just so

amazing in terms of its conductivity-- it's almost up there buttrussing again silver-- it's very difficult to replace with something else. Zinc oxide and its variants get pretty close, like aluminum doped zinc oxide, sometimes called AZO in the PV community.

They get pretty close, but they're not quite as good in terms of optical transparency and conductivity as ITO. Now ITO is a problem. It contains indium. And the world supply of indium is limited. It's not the most abundant element on the Earth's crust. If you look at a periodic table, it's pretty far down there.

And as you know, the elemental abundance, it has a relative decay from-- a power law decay-- from light elements to heavy elements with some fluctuations in between. But in general, the star dust that we have here is less abundant in the heavier elements. And indium is one of those elements. And so people are searching for alternatives to ITO. And it's an active area of research right now.

OK. So for now, let's go back to the flag post that we planted just a few minutes ago. For everyone who didn't quite follow the detailed explanation, the important thing to keep in mind is that TCOs are conductive and transparent. And they are so, because of the unique band structure.

So we can create contacts to semiconductors and extract charge using either a metal or a TCO. And right now, we're going to dive into the impact of good and bad contacts on device characteristics. So during our last-- I believe it was two lectures ago, we talked about the equivalent circuit diagram of a solar cell, this being the simplest case, now corrected with our minus 1 term right here. And we can see our I-V curve in linear, linear scale and log, linear scale there, log current linear voltage. And because this is an exponential, you would expect a straight line, and you do see that indeed.

Now the I-V curve, in the upper part, you can really see has a very nice fill factor as a very sharp kink. Pops straight up. And so the fill factor of that I-V curve, when illuminated, will be very high. And hence, the solar cell efficiency will be high.

Not so when you introduce a series resistance. So when you have that series

resistance component, now, at higher bias voltages, you begin to be series resistance limited, which causes the fill factor to decrease. And you can see that by going back and forth between these two slides. High fill factor, no series resistance. Lower fill factor, higher series resistance. Especially, if you focus right here at this point right there, you can really see the decrease of fill factor as a result of adding a series resistance component.

So contacts, when improperly performed, can add a series resistance component, a rather significant one, and drop the performance of your device. Likewise, shunt resistance. We saw a simple effect right here of shunt resistance. If the shunt resistance goes down further and the saturation current goes up even higher, it begins to affect the fill factor as well. And so shunting can also be impacted by contacts.

Particularly when you fire your contacts, in other words when you heat your sample up, or you heat your stack up to create good contact between the metal and the semiconductor underneath, or the TCO and the semiconductor underneath, a couple of things can happen. If you don't get the chemistry just right at the interface-- maybe didn't clean your sample properly, maybe you didn't heat it up high enough, so that the atoms really started to interdiffuse and interact-- you can under-fire your contact. And that results in poor contact with your semiconductor and large series resistance. So large series resistance will, essentially, impede charge flow and result in a fill factor loss.

On the other hand, if you over-fire your contact-- let's say you heat it up, but fire it a little too long-- then the contact material can drive too far into your semiconductor, and you wind up shunting your device. What does a shunt mean? A shunt means that the metal goes straight through the PN junction and contacts the base material on the other side.

So remember, the PN junction region of the solar cell is only about a micron away from the surface. It's really close. So if you have a fast diffusing metal species and you heat it up too much, you get the metal going straight through, in this case, the

n+ layer into the P, you'll shunt your device.

So this is the fine balance that you have to walk when you're putting contact metallization on the device. You can't over-fire it, because we wind up with shunts. You can't under-fire it either, because you might wind up with a very large contact resistance. So it's a very tricky thing to get right.

We just finished installing a contact metallization printer in our lab. And Joe, how many human hours total have been spent trying to optimize the firing process?

**JOE:** Probably about 30 or 40 now?

**TONIO BUONASSISI:** 30 or 40 human hours? So it's still a work in progress, but it takes a while to really nail that. Yes, Ashley?

**ASHLEY:** So would you want your TCO to melt at a lower temperature than your semiconductor? Is that another consideration?

**TONIO BUONASSISI:** So let's back up a step. For the metal case, it's pretty straightforward. This is a homogeneous element. Let's call it a unary material, meaning one element comprising that metal, typically. And it's very simple for us to see, OK, if we keep it up and it reacts with our material, it drives in.

For a TCO, it's a little less straightforward, because you typically have a multinary compound, meaning several elements comprising your TCO. The formation of this intermediate band right here that forms, really, the conductivity of the TCO, is predicated upon the principle that you have these dopant atoms homogeneously spaced throughout your material. If you heat it up too high and they begin to cluster, in other words, precipitate out of phase, you can wind up destroying your TCO, or increasing the resistivity, maybe even decreasing the optical transparency. And so it really is material-specific when we start talking about TCOs. I'd rather not generalize about them. About metals is more straightforward.

**ASHLEY:** OK. I guess then, for metals, you would have to choose a metal that melts before your semiconductor melt-- or [INAUDIBLE].

**TONIO** Typically, you wouldn't have your mental melting, per se. What you're looking for is  
**BUONASSISI:** a chemical reaction here at this interface. You're looking for the metal, most often, to form a binary compound between your metal and the semiconducting material underneath. Let's say you have nickel and silicon. You'd be looking for it to form a nickel silicide at that interface.

**ASHLEY:** OK.

**TONIO** And that's where you go to your phase diagrams and figure out what temperature  
**BUONASSISI:** those, say, intermetallics should form. And then you're targeting that particular temperature during your ramp.

**ASHLEY:** OK.

**TONIO** And of course, it's not only phase diagrams which are under equilibrium conditions,  
**BUONASSISI:** kinetics are involved as well. So it becomes a rather tricky process. Yeah, question in the back.

**AUDIENCE:** This picture is drawn where it says doping is concentrated underneath [INAUDIBLE].

**TONIO** Yep.

**BUONASSISI:**

**AUDIENCE:** How do we manage to concentrate the dopant in just that certain section [INAUDIBLE]?

**TONIO** Very good question. So we'll explain toward the end of lecture why dopant is  
**BUONASSISI:** concentrated underneath there. For those who are a little bit more advanced, it relates to a tunneling junction effect or a field emission effect. But we'll explain what that is for everyone else.

The way you typically get an enhanced dopant concentration right underneath the metal, first, let's appreciate the length scales involved here. The width of that contact metal is probably on the order of somewhere between, let's say, 80 and 120 microns, maybe a little more. And so, at those length scales, we don't need photo

lithography to really nail a particular location. We're not talking about tens of nanometers. It's really something more macroscopic.

So we can do it in a few ways. On the high end, we could use an ion implantation tool to pattern our material with a mask. On the low end, we might diffuse in the emitter very deeply, to create a highly doped region everywhere, and then create a mask using not exactly a photo lithography process. It could be a much simpler contacting process, and then etch away some of the emitter in other regions to make it more lightly doped or, even in silicon's case, create a poor silicon layer and etch that off, to distinguish between the heavily doped and the lightly doped regions.

There are a few different ways to skin that cat. And that's one of the beauties of solar cell processing is that it really pertains to the specific material system involved. But the length scales are such that you're really not typically limited by photolithography. You can probably get around that and use other techniques for masking it off.

Mm-hm. Great. I see folks are awake today, despite the P-set due.

Sketch the I-V characteristics of Schottky and Ohmic contacts. OK, so what we're going to do here is talk about how Schottky and Ohmic contacts come into being. And first off, define them. So let's define them.

An Ohmic contact is one in which I sweep my voltage, and I obtain a linear current response. So this is pretty straightforward. It's Ohm's law, follows Ohm's law, so  $V$  equals  $IR$ . This is a linear relationship then between voltage and current, the slope of which is dictated by the resistance.

A Schottky contact, on the other hand, follows this beautiful exponential curve that we've come to know and love from our ideal diode equation. As a matter of fact, it follows that same expression rather nicely. There's an exponential relation between voltage and current.

So whenever we have an exponential relation between voltage and current, now that we know how a PN junction works, and we recall that it's really that diffusion

current that's driving the forward current right here under forward bias conditions. We've learned that, when the barrier's too large, the electrons just can't make it over. But as a barrier begins dropping, an exponentially increasing number of electrons can jump over that barrier and move from the region of high concentration to the region of low concentration, or from the n-type material to the p-type material.

So when we see an exponential current voltage response, we should immediately think about some barrier involved in our system. And as we begin biasing this device-- in this case, a semiconductor metal junction-- as we begin biasing the semiconductor versus the metal, we begin seeing an exponential current response. We should imagine that there must be some barrier in between the metal and the semiconductor. And we'll explain how that barrier comes into being.

So again, just to recap, making sure we hit all the points. Ohmic, a linear I-V curve. And Ohmic contacts are typically used when charge separation is not the goal for your metallization.

Let's say you've already achieved your charge separation through the PN junction, and now, you just want to contact your semiconductor to extract the charge, you'd use an Ohmic contact. But you would use a Schottky contact when you want to enforce some charge separation. Typically, not quite as good as, say, a PN junction for separating charge, not quite as high voltage. But it's a useful tool, for example, in research.

So we're going to describe what fundamental material parameters determine the I-V characteristics of both the Ohmic and Schottky junctions, more generally, a contact semiconductor junction. And this dives into Schottky band theory. This is a very idealized version of the real world. It's an idealized version, because it gets us started and points us in the right direction. Then we'll add layers of complexity, until we build up to really understand what's going on inside of these devices.

So let's start here. This is a very nice, elegant view of contact theory.

We have our semiconductor over here. Let's walk through this. So this is our energy

band diagram. We have  $E$  on the vertical axis that represents the energy of the electron, versus  $X$ , some real space parameter. We have our semiconductor material here. We have our valence band, our conduction band, and our Fermi energy. This looks to be an n-type semiconducting material. And we have our vacuum level.

The vacuum level is essentially the energy at which we remove an electron from the semiconductor. If the semiconductor were placed, let's say, in a vacuum, and we were to excite an electron out of the material through some, let's say, a photoemission effect, we would have to overcome the energy between the Fermi energy and the vacuum level. This  $\chi$  right here is essentially the electron affinity of the semiconductor. That's the delta in energy, or  $q$  times  $\chi$  is the delta in energy between the vacuum level and the conduction band.

So we have all of the variables mapped out for the semiconductor. Most of them should be familiar for us already. We've added the vacuum level for completeness.

The metal, we also have a Fermi energy, we also a chemical potential of the metal. And we have a work function of the metal, right here. So this work function is defined as the energy necessary to remove an electron from the metal. Say again, by if you shined a light on the material, it has a high enough energy, you can begin exciting electrons off of the metal with a photoemission effect.

And so we have our vacuum levels in this particular diagram lined up. And our chemical potentials are a little bit different between the metal and the semiconductor. So what do you think will happen when we put the two together? If we put the two together, the chemical potential throughout the entire system has to be the same, right? Because now, they're in good contact with one another.

But what about that vacuum level? What's going to happen? Will there be discontinuity, first of all, in the vacuum level? Can there be a discontinuity in the vacuum level? If I move one little delta  $x$  from the semiconductor into the metal, do I expect there to be a discontinuity in the vacuum level? No, probably not. So there has to be some smooth change in the vacuum energy, relative to the Fermi energy.

And if the vacuum level changes, that means that the conduction band and valence band energies are also going to change, relative to the Fermi energy, because the valence band and conduction band energies track with the vacuum level-- the vacuum level being defined as the amount of energy necessary to remove the electron from the system.

So what you get when you put these two materials together is something like this right here. This dashed blue line representing the Fermi energy, or the chemical potential throughout the entire system, is the same. In this particular case, we didn't bias our device. We're not applying a battery or some bias voltage between one side and the other. So we have the same chemical potential throughout.

If we have the same chemical potential throughout, notice that we had to push this up, or push the Fermi energy up, to reach-- and of course, the work function in the metal's not changing, and so the vacuum energy also goes up. But since there can't be a discontinuity in the vacuum energy, you see a little bit of a rise of the vacuum energy in the semiconductor. And of course, the valence band and conduction bands follow. And that results in this little rise right here, right next to the interface between the semiconductor and the metal. Any questions so far?

**AUDIENCE:** Is there a discontinuity in the first derivative of the vacuum level? Is there a kink in it?

**TONIO BUONASSISI:** Ha. A very interesting question. So typically, we draw it as having a discontinuity in the first derivative. We would draw a very sharp interface right there. But in a practical sense, I'll reserve judgment on that, until I think a little bit more deeply about it. It's difficult for me to believe that there would be, if you zoom in very, very closely, very finely.

The bending, let's think about it from another way, from what we already know. This is essentially the second integral of the charge distribution across that interface. And if the charge distribution is sharp enough, sure, I suppose you could get some difference. But I think-- I'll have to research judgement, but my gut is telling me that

there would not be at a very fine microscopic level. In general, though, we draw it looking much like this. OK?

Any other questions about this, about how we constructed it, using the Anderson method? No? OK. Why don't we continue?

What we've done right here is fill in those diagrams, the same ones that you were looking at, with many more variables. The purpose of this is to get to the point where we can describe the built-in voltage. Remember, we mentioned that, if we have some exponential current voltage response, there should be some barrier embedded inside of our system. And this right here is that barrier. So these series of variables are teaching us how to derive it, how to discover how large that barrier is. And this other component right here, which is the width of the space charge region, which is the width of this, so-called, curved region, if you will, is also going to be of importance.

So first off, let's think about it this way. If we are looking at this system from the electron's perspective, we have an n-type semiconductor right here coming up against the metal. If our work function of the metal is larger than the work function-- or the so-called work function of the semiconductor, which is really the electron affinity plus the delta in energy between the conduction band of the Fermi energy.

But if the work function of the metal is larger than that, we can see that the electrons should very easily plop down into the metal. And there shouldn't be-- let's see, in that particular case, work function of the metal should result in an Ohmic contact for the minority carriers, in that case. But in terms of the barrier height, this barrier height right here would be determined by that equation there.

The contact potential, the built-in bias voltage would be here, and the barrier height there. And the width of the space charge region, once again, is dependent on the dopant density inside of the semiconductor. Here, we've defined it as  $N_d$ , because we're assuming that this is an n-type semiconductor with donor atoms. But of course, if this were a p-type semiconductor, we'd just replace this with  $N_a$  to determine the width.

And if the dopant density is small, this means that the width of the space charge region is going to be large. And that makes sense, because there has to be an equal amount of charge on either side of the junction. And if there is less charge per unit volume here, you need a larger volume to compensate the charge on the other side. So this is, again, a similar expression to the one that we saw when we were studying the PN junctions.

Now, the important thing to recognize here is that, if we have the bands bending this way, for electrons in our system, there may be a barrier to hop out. For holes in the system, though, this could be a favorable exit strategy, if the bands are bent that way. If the bends are bent the other way, electrons can rather easily roll down. But holes will have a barrier to go out of the material.

So the same type of metal that might make an Ohmic contact for an n-type material might make a Schottky contact for a p-type material. Yeah, that's about it. So we have to be very careful in terms of our matching or pairing between the specific type of metal and the specific semiconductor involved.

Let me put that into perspective here with something we've already seen. Again, the Ohmic contact is one in which we have a linear IV characteristic. And the electron barrier height has to be less than or equal to 0, to have the electrons very easily pop down into the contact. Whereas, for a Schottky contact, there should be some barrier height. It should be finite. And we should have a difficulty of moving the electron from the semiconductor into the metal, in that particular case.

So the natural question is, what metals should we use? Or what is the range of metals that are available? If the barrier height is a function of the work function of the metal, what is the range of work functions that are available to us?

On this green arrow right here, which is  $\phi_m$  times the work function of the metal, we have a range of different metals, from aluminum to platinum, and titanium, zinc, tungsten, molybdenum, copper, nickel, gold, in between. And of course, there are other metals, too, in the periodic table that you can add to this chart. But this gives

you a sense of where the Fermi energy of the metal would lie, relative to the vacuum level, and how that would match up against your arbitrary semiconductor.

This one here happens to be a silicon carbide material. But if you happen to be working on a different semiconductor and place it right here, you can see where your Fermi energy would lie, relative to the work function of the metal, if you line up the vacuum levels. And this gives you an idea already of how the bands will bend, once you adjust the position of the metal to match up the Fermi energy inside of your semiconductor material. Yeah.

**AUDIENCE:** So on the left is an intrinsic semiconductor? Is it?

**TONIO**  
**BUONASSISI:** Yeah, it's pretty close to intrinsic. It's a little n-type, it looks like. But it's pretty close to intrinsic. This, in this case, just a variant of silicon carbide. There are many polymorphs of silicon carbide, meaning same composition, same silicon carbon ratio, but different crystal structures, depending on how it was grown. Yep?

**AUDIENCE:** Do you know where silver would fall?

**TONIO**  
**BUONASSISI:** Silver?

**AUDIENCE:** It's not listed [INAUDIBLE].

**TONIO**  
**BUONASSISI:** No, it's listed.

**AUDIENCE:** [INAUDIBLE] a lot for [INAUDIBLE].

**TONIO**  
**BUONASSISI:** Yeah. I'm going to have to guess that it's going to fall around here, just from a similarity of other elemental species in that list. Do you happen to remember the work function of silver, Joe? Been working with it a lot lately.

**JOE:** Yeah. I don't know.

**TONIO** OK. Quick, interesting aside about silver, since it was brought up. It is used very

**BUONASSISI:** often in contact metallization in solar cells. As a matter of fact, a bit too much now. So much so that it's driving up the price of silver on the market.

We talked about this, I think, in a few classes ago, right? 10%, approximately, of all silver worldwide is currently being used in contact metallization in solar cells. That's a pretty high number.

OK, so we have a variety of metals to choose from, almost like a menu. And then the semiconductor here, and we can see, OK, if we make contact-- and let's say we pick nickel, in this case-- if the Fermi energies line up, that means we shift the metal down. That means that our vacuum level is going to fall down here in the semiconductor. And for electrons, at least, will be very easily contacting this silicon carbide material. So from a simple energy band diagram point of view, we can begin to see which contacts will create Ohmic contacts, and which contacts will create Schottky contacts. That's in the ideal world.

In reality-- well, let me make sure that we grasp this before we move on. Any questions concerning this so far? Yeah?

**AUDIENCE:** How would we be able to tell if it's Ohmic or Schottky in this sense?

**TONIO** Sure. Sure.

**BUONASSISI:**

**AUDIENCE:** [INAUDIBLE].

**TONIO** Absolutely. So from this diagram right here, let's walk through it. So if I, say, have a semicondting-- let's first line up the vacuum levels, like we've done right here. That's a good first step on, what we call, the Anderson method of identifying with the band diagram or band structure will look like.

**BUONASSISI:**

We start with the vacuum levels lined up. I'm going to write to this vacuum. And I'm going to dray my semiconductor on one side. So let's say I have conduction band and bands bent like so. And I have my Fermi energy like so,  $E_f$ . So this is my semiconductor. And then I have an imaginary barrier, and I have my metal on the

other side.

So now, let's say we have a metal that has a work function somewhere up here. So this is the work function of the metal. We'll call it the Fermi energy inside of the metal. What happens when I put these two materials together?

Well, step one is to remove that imaginary barrier in between them. And now, you begin to look at this and say, well, if they're in contact, in good electrical contact, and there's no resistance throughout the material, the chemical potential should be identical all throughout the material, from left to right. And so now, I merge into phase two, which is to say, I've removed this barrier here in the middle, and now my Fermi energy is going to be equilibrated throughout. So my  $E_f$  is going to be the same throughout.

And so, far away from the junction region here in the middle, I'm going to draw my conduction band here and my vacuum level here. And now, far away from the junction on the other side in the metal, if my Fermi energy is here and my vacuum energy is going to be somewhere down around here. So semiconductor and metal.

Now, what happens closer to the interface right here-- this is the Fermi energy. This is the conduction band. This is the valence band. This is the vacuum level in the semiconductor, the vacuum level in the middle.

And like we just described, the vacuum level has to be continuous. There has to be a continuity throughout. And so what we see here at the interface, since the density of charge is very high in the metal, but lower in the semiconductor, there's going to be band bending at the interface. And there's going to be a lot more bending on the bands in the semiconductor than there will be in the metal, as a result of the difference in charge densities.

And so what you'll see is something that looks like this. The vacuum level will drop as it reaches that semiconductor metal interface, in order to match either side. And the conduction band and valence bands will track the vacuum level on either side of that junction. So this is the junction right here, in between.

And now I look at this situation right here, and I say, OK, if I have an electron approaching this junction right here, there is no barrier to going from the semiconductor into the metal. As a matter of fact, there's almost an energy gain to be had from going from the semiconductor into the metal.

But now, from the hole's perspective, if I'm a hole right here in the valence band and approaching this junction, there's actually a repulsion away from that interface, if I'm a hole. And so this particular junction here allows electrons to pass, but repels holes. This is looking an awful lot like a diode.

So it's this construction right here that allows you to tell-- asterisk, tell, asterisk, according to the Schottky band diagram-- whether or not this should behave in an Ohmic fashion or a Schottky fashion for the particular karyotype that you're probing. And I say asterisks, because, in real life, contacts are never that simple.

This is an example right here of the calculated-- make sure I get all my variables right. Yeah. So work function in the middle. The calculated barrier height for different metal species here on a certain type, a certain polymorphous silicon carbide. And these are the major barrier heights for different metals, titanium, nickel and gold, at different faces of the silicon carbide.

So if you have a binary semiconductor, meaning a semiconductor comprised of two elements, if you terminate at a surface and you cut the plane just right, you could wind up exposing a plane of silicon atoms or of carbon atoms, if you have silicon carbide, let's say, depending on where you cut. So if you cut right here, you might expose a plane of silicon atoms. You cut one atomic layer above, you might expose a row of carbon atoms. Cut a row above that, it's silicon again. And so depending on what face you expose and depending on the orientation of that face, your barrier height, relative to the metal, could be different.

So, hm. You glance at that, and you begin thinking to yourself, OK, this is macroscopic right here. This tells you, kind of from a continuum point of view, what the interface should behave like, what the context should be. But what I'm seeing right here from the data is that the atomic configuration at the interface really

matters. So there must be something going on in an atomic level, as well, that's determining the barrier at that interface.

In fact, there is. The dipole at the interface between the metal and that last layer of semiconductor, in other words, the distribution of charge between those two sets of atoms that are meeting at an interface determines, in part, the barrier height. We'll get to that in a few slides, as well.

So this is meant to shine light on a much broader picture, which is to say that there can be substantial deviations from Schottky theory at the interface. And some of the effects are due to orientation-dependent surface states. It could be due to the specific elemental nature of the terminated surface, as we just discussed, whether you're terminating at the silicon plane or the carbon plane.

Orientation-dependence means, gee, if I have an anisotropic crystal, meaning a crystal that looks a little bit different, if I rotate it around in different orientations, if I make cuts in different directions exposing different planes, they're going to be a different density of atoms in that plane. There's going to be a different charge distribution in that plane. And hence, I would expect there to be some different interaction between the semiconductor and the metal at that interface.

And finally, interface dipoles, this relates back up to the first one in part. This just goes to say that, if I have an ionic material or an element there at that interface that is grabbing charge, I could result in a small region of negative charge and positive charge forming a dipole right there at the interface. And if I have a buildup of charge, I have a field. If I have a field, I have a potential. And if I have a potential, I'm going to be disrupting this precise interface right here.

And we can, as well, vary the density of interface states-- I got you, Ashley, I'll be there in a second-- so we can, as well, vary the density of defect states here at this interface that can trap charge. And again, with the accumulation of charge, comes a field. With a field comes a deviation of the potential.

So what we've done for ourselves is, effectively, using the Schottky model, we've set

up for ourselves the energy band diagram of a metal semiconductor contact in its simplest case. And what we're going to do over the next few slides is explore some of the more complexity behind what goes into a semiconductor metal contact. Ashley?

**ASHLEY:** So going back that with the green line, so these metals, given some [INAUDIBLE] up there on the left, would all result in Schottky contacts? Is that right? Because all of their work functions are above the Fermi level?

**TONIO** Yeah.

**BUONASSISI:**

**ASHLEY:** Assuming [INAUDIBLE].

**TONIO** So yeah, it depends on what is the minority carrier in this particular junction that's driving it. Because this is intrinsic, it's a little difficult to say, actually. But if it was clear there was n- or p-type, and the minority carrier density at that interface was determining the current flow across it, then we'd be able to say with certainty whether it was one type or another.

**ASHLEY:** OK.

**TONIO** But, yeah.

**BUONASSISI:**

**ASHLEY:** So if it were--

**TONIO** So in this case right over here-- let's make it specific.

**BUONASSISI:**

**ASHLEY:** Yes.

**TONIO** In this case right over here, let's make this an n-type material. So my  $E_f$  is now higher. Ew. OK. That actually had the opposite effect. Let's exacerbate this a bit. I'm actually going to invert that and make this a p-type material. The reason is I want a big delta in my Fermi energies right here, if my vacuum level is constant, so to

exacerbate that band bending at the interface.

And so now, I'm going to get a pretty drastic band bending. It'll be even more extreme than what I drew here. But let's say it's fine. So what we would have to do is we would have to move this down further, right? Actually, no. Sorry. This wouldn't change, because this is still the same.

What we've done here is essentially shifted everything up further. So to be more precise, we'd have to move this up, move this up. And we'd have to move this up, as well. Again, p-type material. Excellent.

And now, again, just going through the logic of the process here, we have to make the vacuum levels match. And there's going to be an equal amount of charge on either side of that junction. Now, when there's a charge, there's a field. When there's a field, there's a potential. And the potential will be manifested in the bending of those bands approaching the interface.

The bands will bend a lot more in the semiconductor than they will in the metal, because the free charge density here in the semiconductor is a lot less than it is in the metal. And going back to this equation right here, the width of the region of bent bands is going to depend inversely on the dopant density or the amount of charge in that region.

So this is to say that we'll have a much more extreme bending here in the semiconductor than we will in the metal. Virtually imperceptible there in the metal. And we drop this down, as well. And we drop this down, as well.

So some really interesting things have happened right here to the position of the Fermi energy in the band gap, right? Over here, we have a p-type material. And over here, at the surface layer, it almost looks like this material is going n-type.

**ASHLEY:** Right.

**TONIO**  
**BUONASSISI:** Let me pause right here, because this is just utterly fascinating, and tell you the story about indium nitride. It's a common material that many people-- I see a few

knowing nods here in the audience.

So indium nitride was a semiconducting material that people really didn't have a good handle on for a variety of reasons. And there was a renewed interest in it, because people finally started to understand why the band gap was the way it was. And many groups started studying it. And they also reporting this n-type indium nitride behavior, very highly n-type material, highly doped n-type material.

It turned out that there was this band bending here at the surface. And they were measuring a high electron concentration at the surface, because of the bending of bands. It was in reality the intrinsic material deep in the bulk was p-type. But they just couldn't see it because their probes were touching the semiconductor at the surface.

It took a certain scientist by the name of Becca Jones in Berkeley, Lawrence Berkeley Lab, I believe, at the time. She immersed the sample into a liquid solution of an acid-- I believe it was hydrofluoric acid-- and managed to relieve the pinning of the bands at the surface. And so they returned to normal. And she was able to probe using a semiconductor liquid junction, the true conductivity type of the bulk of the material.

Becca Jones then went on to produce what is now the-- oh, she was on the team that produced one of the highest efficiency cells on the efficiency versus time plots. So she's doing well for herself there in the PV world. Yeah.

**AUDIENCE:** [INAUDIBLE]?

**TONIO BUONASSISI:** Sorry. Sorry. So let me get back to that. What would happen if you were an electron right here and you were approaching this junction? This is E. This is the energy of electrons. So the electron will seek to minimize, it will seek to encounter a lower energy state. So if you're approaching this junction as an electron, what would happen?

**AUDIENCE:** [INAUDIBLE].

**TONIO** Zoom. Yep. So it's go down. And there wouldn't be any barrier for it to do so.  
**BUONASSISI:**

**AUDIENCE:** Right.

**TONIO** It would just go, [MAKES WHOOSH SOUND] straight down. Now, let's inverse the  
**BUONASSISI:** situation and imagine, what if you're a hole right here? What now? If you think of electrons as bowling balls that want to roll down hills, holes would be the opposite, which would be like balloons that want to rise, right?

**AUDIENCE:** Right.

**TONIO** And so this is actually a barrier for a hole.  
**BUONASSISI:**

**AUDIENCE:** Right.

**TONIO** You need a certain amount of energy to get the hole across. And so the hole  
**BUONASSISI:** naturally will be repelled by this junction. The hole will want to go this way. The electron will want to go that way.

**AUDIENCE:** OK. So this is Schottky for electrons, but Ohmic-- sorry, Schottky for holes and Ohmic for [INAUDIBLE].

**TONIO** Let's imagine we have a device that is driven by the minority carrier flux here at this  
**BUONASSISI:** interface, right?

**AUDIENCE:** Right.

**TONIO** And so what is the minority carrier in this particular case?  
**BUONASSISI:**

**AUDIENCE:** So the left is p-type, and so the minority carrier would be electrons?

**TONIO** Yep. Exactly. So what would you expect this contact to behave like?  
**BUONASSISI:**

**AUDIENCE:** So it'd be Schottky for-- no, Ohmic for electrons.

**TONIO**  
**BUONASSISI:** So this one right here, the electrons would be able to flow over quite easily. So in the illuminated case where the current would be driven by the minority carrier flux, you would expect to see a behavior without a barrier.

**AUDIENCE:** OK. So Ohmic for--

**TONIO**  
**BUONASSISI:** Yep.

**AUDIENCE:** OK.

**TONIO**  
**BUONASSISI:** Now, it can become a little bit more complicated, but let's leave that right there.

**AUDIENCE:** Right. OK.

**AUDIENCE:** If you have a Schottky barrier like that, it's just extracting electrons or holes, then is the relevant quantity on the left a quasi-Fermi energy for electrons or holes? Or is it it's always the overall Fermi energy?

**TONIO**  
**BUONASSISI:** Yeah. So you raise an interesting point, which is the question of quasi-Fermi energy. So if you illuminate your device or you forward-bias it, what happens? Now, you start injecting carriers. And as we discussed during class the time, the total carrier density is going to be equal to, let's call it, the intrinsic carrier concentration plus the dopant density, if this  $n$  would be the density of donors, plus my  $\Delta n$ , which is the injected carrier concentration.

So in this particular case-- let's parse this through-- this is going to be small, so we can ignore that. Well, actually, no. For the electrons in this case, this will actually be quite big. This is going to be smaller, rather negligible. And let's think this through carefully here.

So under equilibrium conditions, under equilibrium conditions-- let's describe this as an  $n_0$ , briefly. So under equilibrium conditions, my  $n_0$  is going to be rather small

because, if I have a high dopant density of p-type material, that means that my electron and my  $n_0$  is going to be equal to  $n_i$  squared divided by  $p_0$ .

And if  $p_0$  is in the order of, say,  $10^{16}$ ,  $n_i$  would be nearer to  $10^{10}$ . We'd have something in the order of  $10^4$  for  $n_0$ . That would be a rather small number.

Now, if I inject light on it, I could have, say,  $10^{14}$  electrons being created. So this drowns out everything else. So now, my electron concentration is going to be driven by the free carrier concentration, the photo-excited carrier concentration.

Now, on the p, on the other hand, this is going to be equal to  $p_0$  plus  $\Delta p$ . So let me drag this over here. The  $\Delta p$  is still on the same order as the  $\Delta n$ , let's say,  $10^{13}$ , somewhere in that range. But my  $p_0$  is equal to the dopant density, acceptor density, which could be on the order of  $10^{16}$ . So this will be somewhere in the range of, say,  $10^{16}$ , driven by the acceptor concentration.

And so now, I have a situation in which I have  $10^{13}$  electrons and maybe  $10^{16}$  holes. And if I multiply the two together, I'm not getting the intrinsic carrier concentration squared, because I'm not under dark conditions. I'm not under equilibrium conditions. I'm in a steady state condition. I'm shining light. I'm exciting carriers. They're recombining, but at steady state. I'm shining light, generating the carrier again. And we reach this quasi-equilibrium.

And so what we have, at the end of the day, is a separation of the Fermi energy between electrons and holes. The Fermi energy for holes is going to be relatively constant. But the electrons for the minority carrier, you'll have a rise of that quasi-Fermi energy, because now you're filling in more of your electrons up here.

And so the Fermi energy, as defined as the energy state that has a 50% occupancy probability, is now at a different energy for electrons or for holes. Awesome. It's really one of those things that takes a while to really wrap your mind around.

And so now, we might have a situation which my electron quasi-Fermi energy is somewhere up here. Let's make it a little bit-- I don't want to get into what's called a

two-dimension electron gas. I'll draw it somewhere down here. So now, I have this distance here is defined by the minority current diffusion length, typically, from the junction.

**AUDIENCE:** And as the electrons drop from that quasi-Fermi energy to the Fermi energy of the metal, what happens?

**TONIO BUONASSISI:** So the important thing to think about is current flow can be reduced to electrons within the conduction band, discrete particles that are seeking to minimize their free energy. The voltage or the potential across is dictated by the ensemble. And that's where the Fermi energies come into play.

So in that particular case, it might even cause the Fermi energy over here to rise a bit. And then you have a potential across. If you had a wire connecting this to an external load, you'd actually be able to power it. The electrons would be photo-excited in here, would be driven over into the metal, because of the built-in field. And then they'd be able to power an external circuit and come back into the back. So you're beginning to see something that looks a lot like a PN junction.

And in this particular case, the dark current for electrons would be dictated by their flow back into the semiconductor. So yes, in this particular case here-- let me correct myself-- in this particular case here, for the electron, you would have a barrier for the diffusion current, which would be driven from the metal into the base right here.

And so the diffusion current of the electrons would be facing this barrier here. And this would be Schottky-like in nature. If you illuminate it, your illumination current would-- so let me back up one step right here.

So in the dark, a completely dark sample right here, that I-V characteristic is driven by the diffusion current of electrons to the metal and to the semiconductor. And that is, in this case, with the barrier. And as you begin forward-biasing it, you would have more and more carriers coming across. And that would drive the diffusion current forward.

The illumination current would be driving the opposite way. And so, if you illuminated this entire system, your blue curve would shift down. Let's say, if you're photo-exciting carriers within the base right here, they can very easily reach the metal. But if you're putting contacts and probing the total current flowing through your system, in the dark, you would be measuring the diffusion current from the metal into the semiconductor.

There's some positive electrons over here. And so the electrons will be driven from the metal into the semiconductor. And they would be facing this barrier. And hence, you would see a Schottky-like behavior.

**AUDIENCE:** OK. So in the dark, it would be Schottky-like for electrons. And in the [INAUDIBLE]--

**TONIO** So you think of it in terms of total current. Yes, you're absolutely right.

**BUONASSISI:**

**AUDIENCE:** Right.

**TONIO** And the holes would be equal and opposite. Then, when you illuminate it, current  
**BUONASSISI:** would start flowing the other direction. So in the dark, the current is flowing, say, in the positive direction. And let's define the positive direction as electrons flowing from here to here, which means that positive flow is going from left to right. So that makes sense.

And when we illuminate it, now, instead of the electrons flowing from the right into the left, we have the illumination current driving electrons from the left and to the right. So the direction of current is reversed, when we illuminate this. And that's the same thing as saying, I'm going to shift this down under illumination and wind up with something that behaves very similar to a PN junction.

**AUDIENCE:** Wait. I thought we said that, under illumination conditions, this situation is Ohmic for electrons. Or is that not true?

**TONIO** Sorry. The electrons have no barrier to travel over here for the illumination current.

**BUONASSISI:**

**AUDIENCE:** Right. Oh, so this--

**TONIO** So the illumination current's going to be constant throughout.  
**BUONASSISI:**

**AUDIENCE:** So it's-- [INAUDIBLE].

**TONIO** But for the diffusion current-- the net current behavior, the net I-V characteristic of  
**BUONASSISI:** this will be Schottky-like.

**AUDIENCE:** OK.

**TONIO** But the diffusion current is the one that's driving the current in that case. And the  
**BUONASSISI:** illumination current is being driven by the minority carrier flow right here at the edge of the metal semiconductor contact.

**AUDIENCE:** OK.

**TONIO** Joe, why don't we flag this? I sense this is going to be an item for discussion during  
**BUONASSISI:** the recitation session.

**JOE:** Sorry. [INAUDIBLE]?

**TONIO** Just the metal semiconductor interface, I think, we're going to have to go through it  
**BUONASSISI:** from scratch again. This is very, very similar to a PN junction.

**AUDIENCE:** Yep.

**TONIO** So I think where folks are getting tripped up is thinking about-- and even I  
**BUONASSISI:** sometimes get tripped up-- is thinking about what happens to the illuminated current and what happens to the drift current and the diffusion current.

**AUDIENCE:** Right.

**TONIO** So it's all very similar. It's all stuff we've seen before. We just have to think through it  
**BUONASSISI:** step by step and make sure we don't get tripped up along the way.

**AUDIENCE:** Yep.

**TONIO BUONASSISI:** OK. So let's talk about some of the non-idealities because this is where the fun stuff lies. When we have a metal on a semiconductor, a lot goes into it. For example, if we have interface states or surface states, we can form band bending there at that interface. Let me demonstrate how.

This is an article that everyone should have read already. It was part of the assigned reading today. And if my past experience is a guide, there is a fixed percentage of you who haven't seen it yet, so I'm going to pass around the article that you should have read. So this is something-- feel free to skim through it, gain an appreciation for, really, the spectacular nature of that article. And then pass it around your colleagues. Make sure everybody gets to see them.

On the left-hand side, we have an example of a semiconductor, let's say, surface. The surface is represented by this really large band gap material right there, that box, that rectilinear box, very thin and skinny. It's thin because the surface layer is very thin. It's maybe a few nanometers, typically, in a semiconductor. And it's very large and band gapped because we formed a semiconductor and oxide, let's say, a silicon oxide, a silica layer at that surface.

So if we have pure silicon and we expose it to air, the silicon will react with air and form a very thin SiO<sub>2</sub> layer or silicon oxide layer. And that's what this represents. This is a very large band gap material, and it's very thin.

And so if there are no interface states, if we have an ideal material, we have our semiconductor over here and our surface layer there. And at that interface, boom. You just have a discontinuity in the conduction bands. And of course, the vacuum levels are matching up.

But in the case where you have surface states at that interface, what happens? Well now, those surface states can be filled by electrons in the neighboring region. And as a result, you'll have a natural band bending at that interface.

So as you begin filling in those states, another way to think about it is that you're

pulling the Fermi energy toward mid-gap, because now, as the electrons are depleted from that near-surface region, as they fall into those surface states, the Fermi energy is going to shift towards mid-gap. And if you indeed look at the semiconductor, right here at the surface, you'll see the Fermi energy is almost at the mid-gap.

And so this is a very curious phenomenon that occurs in many semiconductors. There's a natural band bend toward the surface, depending on the surface chemistry. If you have a semi-conducting oxide forming at the surface, or if you happen to be exposing it to a sulfur based gas right after you grow it, and you form some sulfide at the surface, the surface chemistry is very important for dictating the band bending at the surface.

Why is that important? That's important because, when you go ahead and deposit a metal on top of it, now, you not only have to contend with what the semiconductor is doing, but what that semiconductor surface layer is doing. Now, the situation is really becoming complex.

So this is meant to represent right here what happens when you have a metal-- in this case, a semi-conducting oxide semiconductor interface, also known as a MOS, metal oxide semiconductor-- what happens? Well, in an ideal case, you would have the bands bending a certain way. And then, with the metal oxide layer in between, you can have a definite shift.

So what this is meant to represent right here is a metal with a work function that is larger than the electron affinity, and a work function that is smaller than the electron affinity. And so, given what we've seen before, given the Schottky method of producing the band diagrams here, we would expect that, in this case, we would see bands bending, say, down. And in that case-- let's see.

No. In this case, we'd see bands bending down in the semiconductor. And in this case, the bands would bend up in the semiconductor as we reach that interface. But because the Fermi energy is pinned by these surface states here, we have very little motion of those bands. And so we wind up in a case where we pin the Fermi

energy at the surface and, pretty much, no matter what metal we deposit on top of our sample, we can wind up with a certain type of behavior of the semiconductor, a certain current voltage response.

And this can drive someone absolutely insane when you're in the laboratory trying to get a repeatable contact and everything is changing all the time. And you walk through the math, and you know that you should be getting, let's say, an Ohmic contact. You walk through the math, and you derive the energy band diagram of the interface. And you go to the lab, and over, and over, and over again, you obtain a Schottky contact. And it just drives you insane.

The trick is to always use repeatable surface preparation. Always prepare your surfaces using the same chemistry, the same way, every single time. And if you do that, most likely, in many cases, you can get rid of this native surface oxide on your semiconducting sample.

But if you take your sample out of the growth chamber and move it around in air and then put it into the metallization chamber where you evaporate your contacts, you're exposing your sample to the air. You'll form some surface layer on it, and your contacts will be different.

There was a colleague of mine, who's now a professor at a university. And during his PhD, I think he spent about a year on a problem like this, trying to make good contacts. And unfortunately, contacts, it's such a basic thing that it's one of the first skills to go when the field moves on.

So for example, people really knew how to make good contacts at MIT 30 years ago, when the IC industry was the hot topic of the day. Then, as that phased out, the knowledge of how to make good contact onto silicon disappeared. There was maybe one or two professors who really had that knowledge embedded in their minds.

And so, when a new PhD student came along at Harvard University trying to make Ohmic contact into silicon, there wasn't anybody he could go to and talk to. He didn't

know where to start or who to talk to, because this is kind of base knowledge. It's really fundamental, instrumental knowledge that is going to be infinitely useful. But it quickly gets lost when a field moves on, when the next material system becomes hot, or the next topical area is the key research area of the day.

If you know how to make good contacts onto a semiconductor, I guarantee you, you will find someplace in industry or someplace in academia where you'll be well-sought out, and that skill will be put to good use.

Let's talk about this space-charge region width very briefly, because we're running out of time. We've talked about this barrier as being this insurmountable barrier, let's say, for an electron to travel over, in this case, to get to the metal. But what happens if we increase the dopant density within the semiconductor?

If we increase the dopant density in the semiconductor, then the amount of charge per unit volume at that interface or per unit thickness at the interface increases. So to compensate some buildup of charge in the metal, we would need a thinner region of the semiconductor, because it's more heavily doped, because there are more dopants per cubic centimeter. And hence, there are more free carriers per cubic centimeter as well.

And as a result, the width of this space-charge region will decrease. And if the width of the space-charge region decreases, what happens? This barrier height still stays the same. The barrier height doesn't change, but the width changes. And what do we know from quantum mechanics, if our barrier is very, very thin or very narrow? What happens? Electrons will?

**AUDIENCE:** Tunnel.

**TONIO BUONASSISI:** Tunnel. And that's exactly what happens right here. So if we have a very narrow space-charge region, we'll have a tunneling junction, field emission effect, it's also known as. And irrespective of the barrier height, you will get electrons moving straight across.

Now, if we have a wide barrier-- represented there at the top-- there is an energy

barrier for the electrons to overcome before they reach the metal on the other side. And so there, we have a thermionic emission, which means that you need to have an excited electron, thermally excited-- that's where the name therm comes from-- so thermally excited electron, before it manages to hop across. And because there's an exponentially decaying number of electrons with higher and higher energies, we'll get a very small number of electrons that can actually make it.

So the thermionic emission case will, in effect, manifest itself as a higher series resistance than the field emission case. You can have the same metal contacting a semiconductor. But if the dopant density is changing, you will make a better Ohmic contact.

And of course, when you're actually trying to measure the contact resistance here or measure the barrier height, you really have to know this interface really, really well. You can measure experimentally. But to determine from theory, you get a good start by using the Schottky models we described right here. But to really nail it, you need to perform density functional theory and determine the charge distribution across that interface. It's really the best way to go about it.

So in terms of experiment, thankfully, there are big tables that we can look up. If we have a particular semiconducting material that's well-studied, we can look up the contact materials that would make the best contacts, and what techniques we can use to deposit them, what temperature we should anneal at to form that alloy. These are very practical look up tables that exist in reference books, trusted websites-- not any website, but the trusted ones-- review articles.

But let's say you're working on a semiconducting material that's not on this list. Let's say you're working on cuprous oxide, for instance, and you have to start from scratch. The best way to go about it would simply be to measure the contact resistance using the techniques that we described two lectures ago where we described the TLM method or the-- sorry, not much sleep-- the Transfer Line Method. So the important thing here is to know that you do have a few tools at your disposal to measure barrier heights experimentally. And at the end of the day, you

can obtain precise numbers.

Just going quickly into heterojunctions. This is similar to the Schottky junctions we've been talking about so far, Schottky, Ohmic contacts between metals and semiconductors. This, very, very briefly, is what happens when a semiconductor meets a semiconductor.

Not always can you form a homo-type junction, meaning not always can you have n- and p-type dopants in a semiconductor like silicon. Sometimes, it just won't dope both n- and p-type. And so you have to make contact with another semiconducting material. And for that, we call it a heterojunction.

And there are three general types of heterojunctions. One in which you have a wide band gap material on the left, a narrow band gap material on the right. The two are in contact with each other. And the vacuum levels line up into such a way as to wind up with this band alignment.

Now, let's say I excite an electron hole pair in this wide band gap material. The hole will be able to move across. The electron will be able to move across. So both the electron and hole have moved across the junction, and we have not separated charge.

So type one, very bad from the photovoltaic point of view. Type two, this is more similar to the PN junction, what we've seen so far. And in this particular case, if you excite an electron-hole pair, the electron will move across because of the field, but the hole will be repelled. And so the type two junction is actually preferred, from a photovoltaic point of view.

Type three junction will still separate charge. The electron will move from the left-hand side to the right-hand side. And the hole will be repelled.

But now that the electron has moved to the right-hand side, it actually has a lower energy than on the right-hand side. So there is no driving force. There's no voltage built up for the electron to go across, outside of an external circuit and power and external load. And so, from a photovoltaic point of view, the type three, unless under

very high illumination conditions, is generally considered not desirable, as well. So the type two junction is the preferred junction type for photovoltaic devices.

And yeah, that's pretty much it. So you can go through the exercise shown right here on your own and determine, for this particular system right here, what will happen at that junction. How will those bands align?

You have the cheat sheet shown right after. But an open question for you is, using what you know from today where we first lined up the vacuum levels, drew out the band diagrams independently for material one and material two, just like we've done there, now we eliminate that barrier in between them. We put them together, and we match the Fermi energies. In other words, this Fermi energy,  $E_f 1$  has to equal  $E_f 2$ . So there has to be this shift going on like that. What happens then? How will the bands align?

Follow the vacuum level. That's my best advice I can give you. Let the conduction band and valence bands follow the bending of the vacuum level. And then, from there, you should be able to determine the final structure that'll look something like that. But that's a take-home assignment, just to see if the concepts really jelled today.

So what did we learn how to do? Or at least, what do we have a greater appreciation for? We have a greater appreciation for all of these different components, how to make different types of contacts on a material, what they're good for, and ultimately, how this band alignment that we've learned in our PN junction expropriations can be applied as well to metal contacts, and ultimately, how this can also be applied to semiconductor, semiconductor contacts where we might have two different types of semiconductors coming together and forming a junction. How do we predict what the energy band diagram is going to look like, once we have our final junction right here? And what do we expect that to mean, in terms of charge transport across that layer?

So those are the building blocks, the basic building blocks that you will need to be able to predict how two materials will behave when they encounter each other and

so that you can make solar cell devices. And I think, with that, we can pretty much wrap up our fundamentals portion of the class. Woo-hoo! We get to talk about technologies next.