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PROFESSOR: All right, so let's get started. So today-- our last lecture we talked about different device parameters, mainly our series resistance and shunt resistance, and how that affects our efficiencies. Today we're going to talk a lot about different material properties and how they affect certain device characteristics, and mainly just affect our output efficiency.

So we've been talking a lot about the fundamentals. I'm sure you guys are loving this right now. So we're going to complete this in probably the next three lectures and then move on to a lot of the kind of cross cutting themes in PV-- some advanced concepts, different device architectures, and that kind of thing. And so that is coming in the future, but we're still doing fundamentals today.

And so I know you're probably all aware of this equation. And again, this is kind the progress we've made, so we're almost all the way through explaining basic device physics and basic semiconductor physics so you can understand simple devices. And it's always important to remember that your device is like a leaky bucket, and you're limited by the largest hole in that bucket. So the weakest aspect of your solar cell is really what's going to limit your device performance, and especially if any of you here are trying to make devices, it's really important to think about all of these things when building it. And this is very difficult to do. I can certainly tell you that.

So I kind of like this slide. What this is saying what's the thing we care about most in our solar cells? Well, as scientists, other than dollars per watt, we want to maximize our efficiency for a certain price. And our efficiency, there's several parameters that go into it. Again, we talked about our GSC, our short circuit current, our open circuit voltage, and our fill factor. And that gives our output energy, or output power, and we divide that by the input power, which is the solar insulation.

Now we can split up that again into open circuit voltage, short circuit current, and fill factor. We talked a little bit last lecture about fill factor and how that's influenced by different resistive losses in our solar cell. Today we're going to mainly be focused on short circuit current and things like internal quantum efficiency, which are highly affected by our diffusion length. And the diffusion length is often limited by certain defects in our materials, and we're going to get into why that is. And to a certain extent, we'll talk about open circuit voltage, because your GSC really has a large effect on your open circuit voltage.

So what we're going to learn today is what is minority carrier diffusion length. It was in the homework. Hopefully you guys have some idea coming to lecture, but today we're going to talk about it a little more in depth, and why it's important, and how it's affected. What are the parameters of determinants? So mainly diffusivity and lifetime.

We're going to describe how it's actually measured in a solar cell, which is actually a really cool measurement, and we actually have the capabilities in our lab. And possibly some of you, when you're making cells, will be able to do that measurement. We're also going to look at some of the things that limit lifetime, some of the basic recombination mechanisms. Also look at how your excess carrier concentration changes as a function of lifetime and generationally. And then also talk about the last material parameter, which is mobility, which discusses of how well these excited charges can move around in your material.

So without further ado, here are minority curve, diffusion length. The definition is really simple. If you generate-- let's say, a photon comes in and hits a silicon atom and generates an electron pair over here. How far or how much volume can it explore? And that volume it can explore is described by some characteristic radius, and that radius is known as the diffusion length.

And it's really important to solar cells, because when you think about these carriers that you're generating. If they can only explore a very short area, they're not going to make it. This is a very good solar cell, so the diffusion length is really long, and all

these carriers that are just generated there will be able to make our junction. So again, just so we're familiar, this is our base. In the top, we have our emitter. So the junction would be at this line right here on that plane.

If we have a really bad solar cell-- so let's say a lot of defects present, a lot of areas for these excited carriers to recombine-- they won't make it to the junction. They'll have a very short diffusion length, and as a result, your short circuit current and your VOC will suffer dramatically. So it's really important to get good crystal quality and good material quality, but up to a certain point. There's kind of diminishing returns as you go to higher and higher qualities, so we'll talk about that in a second.

So if we assume-- what this is showing is how our short circuit current scales with our diffusion length. So we have something called the generation rate, and this is often proportional to the photon flux on your material. So the number of photons hitting your solar cell. And this generation rate is something-- the number of carriers produced per second in some given volume. So it's a volumetric term.

And if we assume that everything within one diffusion length of our junction gets collected, that'll all be counted as short circuit current. So basically your JSC has this kind of linear dependence on your diffusion length, but that's only true up to a certain point. So for example, if we have a diffusion length that is much longer than the device thickness. It's really not going to be-- you get, again, diminishing returns as you go to longer and longer diffusion lengths.

So this is a calculation I did using a 1D simulation program called PC1D, which if you want to play around with, it's free. It's a lot of fun to use, actually, and you can put in things like lifetimes-- and very basically, the lifetime, which we'll get to in a second-- how that changes the diffusion length. And you can see that there actually is a linear relation until the diffusion length is about on the order of 300 microns, which is the device thickness. So you can see this kind of trailing off and become sub linear in its response. Yeah?

AUDIENCE:

Can you clarify why when the minority carrier flux at the edge of the space charge region matters, because I'm thinking about there's the back contact and the front

contact, and there's a junction right near the front project. They're not [INAUDIBLE] connecting.

PROFESSOR: So let's think about it one step back. Why do we care about minority carriers?

AUDIENCE: Because those are the ones that are actually generating the current.

PROFESSOR: Right, so if, let's say, you generate an electron hole pair and n-type material, the hole wants to move to the p-type side. And the electric field will actually repel and keep the electron on the n-type side. So it's your minority carriers the matter in terms of the separation, and we'll talk about that again if that's still fuzzy in people's heads.

And so what matters in terms of-- you're talking about deriving the ideal diode equation?

AUDIENCE: Well, no. [INAUDIBLE]. So it seems like the important thing is that some carrier gets to the metallization?

PROFESSOR: Well, yeah, but in order to be separated, which is the first part that we care about, it matters that it's reached the junction. And so it's that concentration at the junction that determines the flux across the junction. Does that make sense?

AUDIENCE: Yeah.

PROFESSOR: And so there's also this other loose dependence on VOC on your diffusion length. And so if you recall from a few lectures ago, this is your equation for VOC. It's dependent on your short circuit current, temperature, and your saturation current, which you can often think also think of as your reverse bias current. And your saturation current is dependent on your diffusion length. JSC, if you recall, was linearly proportional to the diffusion length, so the VOC actually scales with the natural log of the square of the diffusion length. And if you pull out that exponent, it just squares with the natural log of your diffusion length.

And again, very, very simple analogy-- we're assuming, again, that fill factor is not really affected by your diffusion length and that your efficiency is proportional to the

product of your JSC and your VOC, so your short circuit current and your open circuit voltage. And you can see as go to longer diffusion lengths, there's this area of diminishing return. And again, there's two different regimes here. One is when your diffusion length is, again, much less than your device thickness. You can see that there's a huge increase in efficiency, but as your diffusion length gets well, well above your device thickness, it becomes less and less important.

So how do you deal with this? So if you have, let's say-- suppose you want to make a really cheap solar cell, and you have a very dirty material with very short lifetime shown here. There's several ideas of what you can do. You can have a very, very thin device. Now, that's a problem if you can't absorb it very well.

So you can have some optical tricks. You can do surface texturing. There's all sorts of other ideas for basically having the carriers coming in at angles or having a good reflector on the back. So that's ways you can work with very low diffusion length materials and still get a device efficiency that's not too bad.

Now we're going to talk quickly about how our minority carrier diffusion length is measured, and again, this is something we're able to do in our lab. And one of the important things to say is defined is collection probability. So for example, if this is our junction right here-- so our space charge region-- if you generate a carrier, let's say very, very close to the junction, it's going to have a high or near unity probability of making it to the junction and being collected.

If it's generated very, very, very far away, it's going to have a lower probability. And that's what this graph is trying to show-- is that right near the junction you have near unity collection probability, and as you go way, it comes down. And the different colored lines are showing different ways of increasing that diffusion length. Surface passivation is important. We'll talk about what that is soon. And also diffusion lengths-- if you're limited by diffusion length, you can see this very, very sharp drop off.

AUDIENCE: Just a follow up. So is collection meaning collected by the front contact to be used in your external circuit?

PROFESSOR: Mm-hm. Right here it's technically defined as reaching the junction and being separated, which, in essence, will hopefully be the same thing.

AUDIENCE: So is surface passivation [INAUDIBLE] sort of like diffusion?

PROFESSOR: It can affect the diffusion length, and we'll-- or the affect of diffusion length. We'll to that in a second. It'll be a bit later. This is kind of just showing that there's a lot of different material parameters-- not just your diffusion length-- that can really affect your device performance and your collection probability.

So if you recall a few slides back, we said that our short circuit current is directly proportional to our diffusion length. And the reason is that, if you're generating carriers within the diffusion length, you generally think of that as the region of which you're actually collecting those carriers. And if you go back to the next slide, that kind of makes sense. So this is highlighted. So this is our junction here. We have our n-type material on top, our p-type below. And within a diffusion length of your minority carrier-- so on your p-type type side you care about the diffusion length of your electrons. On the n-type side, you care about the diffusion length of your holes, and that's the region where you're really collecting carriers. Of course, there's a tail off, but the first order approximation-- this is actually a very good one.

And so now putting those all together. If we know how our carriers are generated as a function of x , and we what the collection probability is as a function of x based on diffusion length, surface passivation, and other parameters, we can multiply them and then integrate to actually get what our illuminated current will be. Yeah?

AUDIENCE: [INAUDIBLE] have like three regimes because the diffusivities are different at each [INAUDIBLE].

PROFESSOR: The emitter?

AUDIENCE: [INAUDIBLE] the junction afterwards?

PROFESSOR: Mm-hm. For most models you pretty much assume that anything absorbed-- first of

all, the space charge region is very, very narrow. It's almost assumed just to be negligibly thin. And the emitter is generally very, very short, and the diffusion lengths are so poor in the emitter for reasons we'll get to soon that it's almost a dead layer. Your response, the very short wavelengths, where you're absorbing most of your light and emitter generally don't add to your short circuit current, and we'll talk about that soon. So excellent question. Yeah?

AUDIENCE: Is that first region right there--

PROFESSOR: Wait, sorry. Say that again. I couldn't--

AUDIENCE: People just approximate the first region there and not care about [INAUDIBLE] afterwards?

PROFESSOR: So for certain wavelengths of light, let's say, that are-- this curve, this is kind of representing Beer Lambert's law. If it attenuates less drastically, that characteristic absorption length, if it's a lot longer than this length here, then yes. You can assume that this emitter region is negligibly thin, and that's a little bit what the homework goes over as well in problem three. Excellent question.

And so what we care about is the spectral response of our short circuit current. So what this is is this a quantum efficiency tool. This is something we have in our lab. It's a really fun tool to play around with. How it works is you basically have-- we have a light source that's white light, and it goes through a series of filters. There's a monochromator, which basically-- it diffracts the light, so it spatially separates the light, kind of like a rainbow.

And then you can focus that onto your solar cell and measure the current output under short circuit conditions. And that will tell you-- because you know the carrier generation profile for different wavelengths of light, because you know what alpha is for silicon, you can actually pretty well calculate what your diffusion length is, and we'll talk about on the next slide. So this is kind of what your quantum efficiency will look like. This is, I think-- I actually don't know if this internal or external, but they're just related by a factor of $1/r$.

So here you're blue response-- so everything that's absorbed right in the near surface region in your emitter generally doesn't get collected, and this is due to really bad diffusion lengths in the emitter region. As you go to longer wavelengths, the absorption length is much, much deeper. You're collecting a lot of it, and then what do you think is happening here? Generally these longer wavelengths-- your alpha is so low that you're not actually absorbing much of this light, which is part of the reason that you're not collecting it, or that you're absorbing it so far away from the junction that it's not being able to diffuse there. And so that's kind of how you can look at these quantum efficiency curves, and it's this region here that's really limited by diffusion length. And again, you have a homework problem discussing how that's done.

Some of the cool other tools-- the lab can kind of do this, but it requires a little more-- I don't know-- hand work on the operator. But if you can take different EQE or IQE curves at different points on your solar cell and you get those spectrums, you'll get a whole bunch of different spectrums. You'll scan with your light beam. You can actually get diffusion lengths as a function of position and get a spatial map of your different diffusion lengths. And it's really helpful if you're trying to fine spatial inhomogeneities in your cell.

So I believe that this is some multi-crystalline cell, and see all sorts of grain boundaries. And those are areas of very short diffusion length, and we'll talk about why that's the case, actually, on the next couple slides. Question? Yeah?

AUDIENCE: Could you just clarify the difference between diffusion length, absorption length, and band depth energy? Because I thought that the middle weight ones were more absorbed because they were bent? Their higher weight [INAUDIBLE] for bigger-- to cross bigger band depth energies. I didn't think it was because of the absorption [INAUDIBLE].

PROFESSOR: So alpha is what tells you is your absorption coefficient, and it's often in units of one over centimeters, so inverse centimeters. And so if you plot what that looks like, it's an exponential function with x . And the point to which it is attenuated by a factor of

one over ϵ , that point is $1/\alpha$. And that's often called the absorption depth or-- what am I thinking of? Absorption length of that wavelength.

And α will vary as a function of wavelength. If you recall that, if you look at λ , for silicon, it's something that continues to go down at longer wavelengths. So the short wavelengths are absorbed very strongly, and so most of the light is absorbed very, very close to the surface, where the longer wavelengths-- most of the light is actually absorbed rather far from the surface. Does that make sense?

And so there's a difference between your absorption length and your diffusion length, and that ratio is what's really important. If you're absorbing really far away from the junction, but you have a long diffusion length, there's a greater chance of it making there. And it's that ratio that's really, really important. Does that answer your question?

AUDIENCE: Yeah.

PROFESSOR: OK. So what limits this minority carrier diffusion length? We're going to get to the equation in a second for the minority carrier diffusion length, but basically when you excite an electron hole pair, you have this mobile electron, and it's in this excited state. You've given it this energy from a photon, and now it can move around, and it can only exist for a certain amount of time before it finds another whole and recombines. And that event, again, is called recombination.

And a lot of this is actually determined by the size of grains in your material. If you've seen-- I think on the cell that [INAUDIBLE] brought in earlier-- sorry I don't have a good example-- it didn't just look like one kind of flat plane. You could see different grain orientations, and the edges of those grains are called grain boundaries, and those can act as recombination centers and actually reduce your-- it's called your lifetime, which we're going to get to on this slide.

So this slide has a lot of stuff going on. What it's saying is that your diffusion length is characteristic of the diffusivity-- the square root of the product of your diffusivity in your lifetime. The way I like to think of diffusivity is that it goes up with temperature,

and it's also affected by your mobility. The mobility is saying that, if you apply, let's say, an external field, and electric field, how well can those electrons move around?

So a really high mobility means that those electrons can move really easily, and you'll accelerate them really quickly, where very low mobility means they're going to continue to hit into things, and bump around, and not move around too well. And your diffusion is this kind of thermal process. If you think of, let's say, gases in a room, and you have a hot gas, that's going to diffuse a lot faster. So it's the product of these two things. It's how well it can move around times it's thermal energy that it has to move around, the energy it has for moving. And so that's kind of what the diffusivity means to me.

The lifetime, again, is what I mentioned earlier-- is that when you create this excited electron that's now free to move, this mobile electron, it can move around and explore a certain area, that area. Volume is defined by the diffusion length. And it exists in that excited state for some amount of time, τ , and that τ is not-- not every carrier that is generated necessarily has that lifetime, but it's a characteristic lifetime that it could have. And then they're pointed out here what they are.

So that's what affects our diffusion length. So in the next bunch of slides, we're going to talk about mainly how we can affect τ . So τ is mainly affected by recombination centers-- so defects, and semiconductors, and a few other things that we're going to talk about. And then this is almost limited depending on what kind of materials you're using, the mobility, and so we'll talk about that, as well.

So what affects lifetime? We're going to go over, again, basic recombination mechanisms in semiconductors. There's a lot of them. A lot of them have some rather complex equations behind them. We're not going to delve too deeply into how to derive them. You're welcome to do that. It was actually kind of fun to do on my own and refresh myself, so it was really useful-- and also be able to calculate our excess carrier concentration, which we're going to do in the next couple slides.

So n -- let's say for n-type material, the number of mobile electrons you have is defined as n . n_0 is very frequently your doping density-- these come up one at a

time. Sorry. Wrong direction-- are generally the doping concentration. So if you're putting in phosphorus atoms into your silicon, it would be the concentration of phosphorus atoms.

Your Δn is how many extra electrons are you adding, mobile electrons, due to the photo excitation of light. And so that's what this is saying-- is that you have some-- your Δn is equal to your generation rate. So your generation rate is generally in units of carriers per volume per second-- so how many carriers you're generating in a certain volume. And because Δn is actually a density, you need to say, OK, how long do those carriers last once they're excited? And so it's the $g \tau$ product is what gives you your Δn .

Now, when working with silicon, it's really important to understand what the different ratios are of n , n_0 , Δn , the doping concentrations. So getting these relative numbers in your head is an important step in moving forward. So let's say we subject a piece of silicon to AM1.5 spectra. So your G -- sorry. This is a little off. There we go. Sorry about that. When I added some equations-- so your generation rate is on the order of 10^{16} . A carrier lifetime for silicon-- this is not a great lifetime, but an OK one-- is about 10 microseconds. And so as a result of that, you'll get about 10^{11} excess carriers per centimeter cubed.

And if we compare that-- so for every excess electron we make, remember we also leave behind a hole. So we have Δn is generally equal to Δp . And that's about 10^{11} . If we look at our intrinsic carrier concentration-- so if we had no dopants, how many carriers would we have just for thermal excitation? And that's about 10^{10} . And so you can see that Δn is actually larger than your intrinsic carrier concentration for silicon under normal illumination conditions.

Now, let's take an example. Suppose we add phosphorus at the order about 10^{16} , and so that's generally about what a base doping concentration should be - in that realm. It might be a little high, but you can see that your Δp is much greater than p_0 . So p_0 would be how many holes do you have, which is a ratio of your intrinsic carrier squared over your doping density. And that's about 10^{10} to the

fourth, so it's way, way less than what was there without excitation.

So the number of holes without any light shining on it is p_0 . You generate a bunch of holes, Δp , by shining light on it, and you can see that these numbers are drastically different. And of course, your doping density is actually much, much larger than your Δn . Your majority carriers don't change very much, but your minority carriers change very, very drastically. That's really what this is trying to say here under excitation.

What is lifetime? So that bubble shouldn't be up yet. So we measure τ by creating some excess carrier population and then watch them decay. And they decay at some rate, recombination rate, and under steady state conditions-- so under constant illumination, we're not looking at transients-- your recombination rate is actually equal to your generation rate. So if you compare the two equations on the previous slide, they're true under steady state conditions. [INAUDIBLE] going to pop up.

And so your lifetimes add up like parallel resistors. So we have τ_{bulk} , which is kind of the effective lifetime of these photo excited carriers. $1/\tau_{\text{bulk}}$ is equal to $1/\tau_{\text{radiative}}$, so this is radiative recombination. And this has to do with-- basically if you read the Shockley-Queisser efficiency limit paper, this is the lifetime that they assume was limiting. And for silicon, this is absurd. This is never ever the limiting factor.

And a lot of direct band gap materials-- for those of you who don't know what that is, don't worry about it. That's often the limiting factor, and it has to do with the absorption is always equal to the emissivity in a material.

AUDIENCE: [INAUDIBLE]?

PROFESSOR: For a direct band gap material, radiative recombination can be an issue, and I'll talk about that in a second. And there's also another combination called Auger recombination. It's not "Oger" like I thought when I first came here. It's "O-jay," kind of like-- I don't know-- OJ Simpson, I guess.

[LAUGHTER]

And it's dominant only under very high injection conditions or very high doping density. So in your emitter layer where there's really, really high doping densities, you're going to have a lot of Auger recombination.

And the last one is Shockley-Read-Hall So these are three guys. They came up with this kind of a model for how recombination happens in defective materials-- so materials with levels, electronic levels, in the mid-gap. And again, these add like parallel resistors, so you're always-- so if you remember back to the leaky bucket, these your leaky buckets for diffusion length. You're always limited by your shortest diffusion length-- or, sorry, your shortest lifetime. And this is often your limiting lifetime-- is your Shockley--Read--Hall recombination.

AUDIENCE: Is it for silicon and for [INAUDIBLE]?

PROFESSOR: For silicon--

AUDIENCE: [INAUDIBLE]. The Shockley-Read-Hall is the [INAUDIBLE].

PROFESSOR: So radiative recombination. So you can probably guess from the name that radiative recombination involves a photon. The ability to absorb photons also means you have the ability to emit them, and so silicon, or many semiconductors, will emit photons when you get a recombination event across the band. And when that happens, you emit a photon under equilibrium. So equilibrium means no outside excitation. It doesn't mean steady state, so this is, let's say, in the dark.

You get your recombination rate is equal to your generation rate, because it's in thermal equilibrium with the area around it. So it's absorbing photons and emitting them at the same rate. And this is equal to B . So some material parameter times your hole in a electron concentration. And again, under equilibrium conditions, that's equal to your intrinsic carrier concentration. n_p product is equal to n_i squared.

Now, when you shine light on it, your n , which is to n_0 plus Δn -- so this is you excited carriers, your excess carriers. So your n now increases and is greater than

n sub i , and your net recombination rate is determined by this equation right here. So $B n_p$ minus $B n_i$ squared-- so the difference between your equilibrium and your now excited carrier concentrations.

AUDIENCE: I'm not sure if I missed this. Is B just a proportionality?

PROFESSOR: It's a material parameter, yeah. It depends on-- for silicon, I forget. It was on the next slide. It's 10 to the minus 15 th. I don't know for other materials, but I presume that that would change-- probably be a lot higher for other materials. And it turns out your radiative recombination lifetimes, when you plug these numbers in and you make some assumptions about what's really small compared to each other, you get these equations here. And again, this is τ is equal to Δn over R . And so you get that.

And now if you look at for silicon, you get B is about 2 times 10 to the minus 15 th. Your Δn I put-- n I determined just was 10 to the 16 th-- some doping concentration. And your radiative lifetime is incredibly, incredibly long-- about 50 milliseconds. And if you remember from before when I was calculating a generation rate for silicon, we used about 10 microseconds. So this is really, really long. And so radiative recombination is very, very slow, and it's rarely ever the limiting lifetime in silicon solar cells.

However, as you mentioned earlier, it's actually a big problem in direct band gap materials. And if you think of there's some materials we actually want a very short radiative recombination time. So for example, if you're trying to make an LED, you inject carriers using a voltage that recombination emits photons, and then you get light. And that's basically how an LED works.

So now we'll talk a little about Shockley-Read-Hall recombinations. So this is something that our lab works, I think, very, very well in. We do a lot of defects in semiconductors, specifically iron. And so iron is one of these really, really awful contaminants in solar cells. Just a little bit of iron, I think-- [INAUDIBLE], correct me if I'm wrong. I don't remember what year production this was. Maybe it was 2009 , but two grams of iron could contaminate the entire year supply of silicon

detrimentally. So that's a lot.

AUDIENCE: I think you actually calculate this in your [INAUDIBLE].

PROFESSOR: Yes, you do for a single panel, and it shocked me. So basically what we're trying to say here is that you have iron atoms and it can sit in different areas of your lattice, but you have these defects that exist, and they introduce different energy levels within the band gap. So the outer electrons of iron can either sit at these sites-- so these blue sites where they're donors, or they can create acceptor states kind of like boron does, but they're much higher up into the gap. And these act as recombination centers, and we'll talk about why that is in a second.

So these trap levels can interact with mobile carriers in a whole bunch of different ways. They can capture an electron. That electron can then sit there. If there's enough heat energy, it might actually get promoted and jump out of that, and then which case it wouldn't have actually decreased your excess carrier population. It can also capture holes, and it can also emit holes.

And there's a bunch of things that go into these equations here. It depends on a lot of the energy of this trap state. It depends on the carrier excitation. We'll talk about that in another few slides. And it also depends on these-- what are effective-- I forget the exact word, but the effective hole in electron lifetimes. And those are limited by your trap density. So these can be thought of-- suppose they're each-- let's say each iron atom is introducing one trap level. It would be the number of trap levels, the density of trap levels within your system, times some thermal energy, and then a capture cross section, which is saying, OK, that trap state exists in one location. How much area can it see in terms of what effective area is it capturing electrons?

And oftentimes under the right conditions-- so with very, very deep traps, so traps mid-gap under low injections, your Shockley-Read-Hall recombination is actually one of those two lifetimes, and it's a very simple equation. And under very, very high injection conditions, it's actually summing them up, and if you look in the previous slide, if you go to Δn goes to infinity, you can see that this becomes true. Joel?

AUDIENCE: The energy, the thermal energy type [INAUDIBLE]?

PROFESSOR: That's a good question. That would be my guess. Sorry, there's another question back there?

AUDIENCE: Yeah, so is iron worse or is gold worse?

PROFESSOR: I can't hear you.

AUDIENCE: Is iron a worse dopant, or is gold your worst dopant in terms of [INAUDIBLE]?

PROFESSOR: Oh, in terms of capture cross section?

AUDIENCE: Yeah.

PROFESSOR: I know they're both bad, really bad. [INAUDIBLE], do you know that off the top of your head?

AUDIENCE: Sure, so gold has a larger lifetime impact at lower concentrations than iron, but it's perhaps one of worst, and that's why you're not allowed to wear gold jewelry at the cleaners. They ask you to take off your wedding bands and other jewelry before entering the [INAUDIBLE] cleaners.

PROFESSOR: So no bling in the cleaner. There you go. And so for the material scientists and physicists in the room, if that does not apply to you, don't worry. This is just to explain what is going on.

Often when you want recombination to happen-- so this is a momentum, or k , versus energy-- it requires not only the emission of a photon, but also a phonon to change its momentum. When you introduce a trap level, or these localized impurities, because it's localized in real space, it's delocalized in k space, so you have this kind of flat level in k , and you have these very, very efficient pathways for recombination. If that doesn't resonate with you, don't worry about it right now.

So here we see that really the impurities can have a very, very large effect. If you think of the doping densities that we put in, we've been using about 10 to the 15th,

10 to the 16th for our doping density. This is on the order of like a million less, and it can have a huge impact on lifetime. So one of the worst, again, as we said, was iron, and these interstitial irons are especially bad. And at 10 to the-- I don't know-- looks like 10 to the 11th. Very, very low concentration. That's one in 10 to the 12th. So that's one in a trillion atoms are iron-- can detrimentally impact your solar cell. So that's really, really bad.

So keeping fabs clean-- so again, no jewelry and other things can really-- that can actually have a very large effect on your device performance. And if you plot that versus your dislocation density, you can see that if you have-- it's especially bad for very, very high lifetime silicon. Just a few dislocations can actually really, really hurt it, but the effect is mitigated if you're already starting with very low lifetime silicon.

And again, this is something our lab works on quite extensively. It's not just the number of iron atoms. So if you take a piece of silicon, and you want to know its lifetime or how iron impacts its lifetime, it's not just the total number of iron atoms in it. It's also how they're distributed. So if you have, let's say, clusters of iron atoms, that would count as one defect, or effectively less than the number of atoms in it. And so clustering these things can actually be really, really a good way of cleaning up your solar cell material, and this is an effect called gettering. And if you can getter these impurity atoms into one location, they'll have less of a detrimental impact on your material.

So this is kind of a tricky one to explain, but this is-- so Shockley-Read-Hall recombination can also show up in something called surface recombination. So if you look at your silicon lattice, each silicon atom has four valence electrons, and it bonds to four silicon atoms around it, and it has satisfied covalent bonds. So this silicon atom has all its satisfied, all its satisfied, until you get to the surface. And at the surface, you have what are called dangling bonds. And these dangling bonds can actually introduce trap states, and so you can see that actually introduces a whole ton of levels within the band gap that can provide Shockley-Read-Hall recombination pathways for your carriers.

And so surfaces are incredibly important, and the way we tend to think of it-- and this is a concept that might be difficult to grasp at first, but it scales with two things. There's two things going on. You can think of that this is the width of your cell, and you have some surface recombination velocity, which is some kind of characteristic of how well they can recombine at the surface. And at let's say infinite surface recombination velocities, it means that any carrier that comes and hits that surface will most surely recombine. So this drops to zero.

So then you're limited by, OK, how well can they actually diffuse to your surface? So it's again some kind of ratio of your self thickness squared over the diffusivity, your carrier diffusivity, and that that gives you an idea of what your limiting factors are. So under very low surface recombination velocities, you're limited by this term here, the first one, and then the very high ones, you're limited by this term. And do there's two effects going on there.

And it's summarized as well here. At very, very low surface recombination velocities, your τ_{surface} almost goes to infinity-- very high. And you can passivate these bonds using hydrogen. So for example, if you use hydrofluoric acid, what it does is it etches away the silicon oxide layer that sits there, and you have these hydrogen atoms that now sit and satisfy these bonds. And if they're perfectly satisfied, you'll have a mobile carrier. It'll actually elastically scatter off, not lose any energy, and not recombine through these trap states.

AUDIENCE: I have a question. I thought [INAUDIBLE] is a very good passivation barrier for silicon?

PROFESSOR: What is?

AUDIENCE: I thought silicon dioxide is a really good passivation barrier for silicon.

PROFESSOR: I've seen some diagrams of what silicon oxide looks like on silicon. It passivates many of the bonds. You're absolutely right. HF is actually probably the best. The problem is that it etches glass and other things that are in your source material, and it's incredibly dangerous. It can kill you rather dramatically. So it's only used in

laboratory settings. If you're trying to actually take lifetime measurements and negate the effect of surface recombination, silicon oxide can be a good one. If you actually look at the structure, there's a few dangling bonds in there, but it can passivate most of them-- just not all of them.

Another good passivation technique is actually the silicon nitride ARC coating. That passivates the surface very well. So yeah, good question. There's other ways to mitigate surface recombination, as well, and we'll talk about that, I think, in either next lecture or the one after that.

So yeah, this slide is just telling us that, if we vary our thickness of our silicon, we can actually measure our surface recombination velocity, and we can fit it so we can figure out our tau surface, which is a really important material parameter. Generally, I think good surface recombination velocities are anywhere from like 10 to maybe in the 100ths for centimeters per second, and really bad ones are much, much higher.

And the last type of recombination mechanism we're going to talk about today is Auger recombination, and this looks like-- when I first saw this, I'm like, why on earth would this ever happen? And the fact is it does until you get to very, very high carrier concentration.

So you can see that it involves three particles. Let's say an n-type silicon. It needs two electrons in the hole. What happens is that you get the simultaneous relaxation and excitation. So you get this relaxation of this excited electron into a hole, and then you get this excitation of this other electron into a higher energy state, and then it thermalizes down and releases a phonon, releases heat. Yeah, Jessica?

AUDIENCE: [INAUDIBLE] terms of p-type here?

PROFESSOR: So this is going to be our n-type material. And again, because this type of recombination event requires two particles, it requires two electrons, so it's n^2 in one hole. So the recombination rate goes up with pn^2 at high enough concentrations. And so your tau goes out with the $1/n^2$. And this is particularly bad, again, only at very-- because it goes up with the square of

the carrier concentration, it's really bad at very high carrier concentrations. So if we look at this plot, we can see that our minority carrier lifetime drops well below a microsecond around 10^{18} , so you generally want to stay out of that range of doping concentrations in your base, because you'll have very, very bad lifetimes.

AUDIENCE: [INAUDIBLE] are both sides-- is that the top blue part and the bottom blue part n-type?

PROFESSOR: I didn't label this. You're right. This is the valence band. That's the conduction band. And so this is kind of driving home, again, that leaky bucket idea-- that is, you're really limited by your worst lifetime. And so if you remember, we're thinking about parallel circuits here. Your bulk, or your effective lifetime of each carrier, is determined by these three here-- your radiative. Sorry, that should be tau band, which is the same as your radiative recombination-- Auger and Shockley-Read-Hall.

And so at different excess carrier densities-- so we're varying Δn by shining various intensities of light. And we can kind of activate different limiting lifetimes. So at very low, you're limited by Shockley-Read-Hall. And Shockley-Read-Hall can actually go down with higher illumination conditions. And your Auger, remember it gets really, really bad around 10^{18} -- becomes your limiting. So your tau bulk is never doing better than your worst lifetime.

AUDIENCE: So on that graph is tau and emitter also the same thing as--

PROFESSOR: Tau Auger?

AUDIENCE: [INAUDIBLE] tau [INAUDIBLE].

PROFESSOR: This came out of Daniel McDonald's thesis. Tau emitter-- it's complicated because it has other influences in it. Auger, I always think of recombination in the emitter as Auger, but you also have other carriers coming in due to injection currents. And so your excess carrier population is also a function of that, and so the equation for it gets a little more complicated, but it would make sense that, as you increase illumination, you're increasing your current into the emitter. And you would get more carriers, and it would decrease. And it looks almost exactly like Auger in his regime

over here. I'm not sure of the other things that go into it, but if you look up his thesis, I think it gives a pretty good description.

So you're probably bored of hearing me say this, but again, we're always limited by our weakest. So in defect mitigated recombination materials-- so where your shortest lifetime is due to some kind of Shockley-Read-Hall recombination. Your lifetime for Shockley-Read-Hall is always going to be much, much shorter than your radiative lifetimes, which is a characteristic we can exploit for measuring the lifetimes of our materials.

So because very, very few carriers will actually radiatively recombine and emit a photon, that, if more of them are radiatively recombining, then we know that it's a very high lifetime material. If there's a lot of defects and we have very, very short lifetimes, very few of them will radiatively recombine. And so this emission of photons with energy at the band gap can give us an idea of the lifetime within our material, and that's how we measure.

It's a technique called photoluminescence, and what you do is you shine light on it, generally with a laser. We put a diffuser in front of the lasers so the laser beam spreads its photons over a large area. We excite all these carriers. So this laser has very, very short wavelengths, and I think in our-- well, very short. It's 900 nanometers. Silicon's band gap corresponds to about 1,108 nanometers. And so 900 is easily absorbed, not just right near the emitter, but also somewhat well deep below the junction as well.

And then as you begin to see recombination, when radiative recombination happens, we emit a photon. And that can happen in certain areas better than others, and a lot of it depends on, like I said, defect density and other lifetime eliminating defects. And it's a good way to spatially locate where problems are in your solar cell. Any other questions? Ben?

AUDIENCE: How good is spatial resolution on [INAUDIBLE]?

PROFESSOR: It depends on your camera. So we use, I think, a germanium camera to detect

those photons, because Silicon won't have a very good response. And it depends on the CCD array within your camera. It can be really good. I do a similar technique to measure shunts, and we have microscope objectively. We just have to zoom in really, really far, and then we just scan over an area.

And last little thing is that, if you recall-- hold on. Let me-- this slide. Traps cannot only trap an electron, but you can also emit an electron, assuming it has enough thermal energy, and you can see that on this plot. And so this is an Arrhenius plot. So again, high temperatures are in this direction. Low temperatures are over here. And you can see that your lifetime actually increases at higher temperatures because electrons that see that trap fall into it, then can easily come back out of it because they have enough thermal energy to escape. And that's really what this is depicting.

So one of the things I think for researchers in the room who are studying these types of materials, varying temperature is often a really, really good way of looking at electronic structure materials. And it can be very, very powerful, and this is one example of a tool to look at these types of traps. Oh, good. We have plenty of time. We actually might end early.

So now we're going to talk about mobility. We've given a lot of-- sorry?

AUDIENCE: I was just wondering, is it possible to somehow introduce defects that are at the energy levels [INAUDIBLE]?

PROFESSOR: That's a good question. So phosphorus actually has, if you draw it on an e versus x diagram-- so if we have our conduction band here, our valence band here, we said iron puts states in the middle of the gap. Phosphorus and boron actually put states very, very, very close to the valence band and conduction band. If you go to low enough temperature-- so let's say a below 100 Kelvin-- you can actually freeze out those donor electrons onto the phosphorus atoms. And below certain concentrations of phosphorus atoms, for example-- so below like 10 to the 18th-- at 0 Kelvin, you cannot conduct electricity. It actually becomes a total insulator. That's an excellent question.

But at room temperature, when kT is on the order-- so kT is your thermal energy, and at room temperature, if you put that for electrons, it's 0.026 electron volts or 26 millielectron volts. This is a good number to have in mind, by the way. When that number is on the order of this binding energy for phosphorus, they're almost always fully ionized and free, but that's a very good question. Anyone else?

So if we remember our definition mobility is related to or diffusivity, and again, our mobility is saying how well these excited charges can move around. And it's related to how much thermal energy these charges have, so that's why we have this kT factor. And what's plotted on the right is the Shockley-Queisser efficiency limit, which are the stars. And then how if you-- let's say you reduce your mobility by, let's say, a factor of 10 or 100. What's the impact on the overall efficiency? And you can see that, if you detrimentally impact your mobility, you can really have a large effect on your diffusion length, and it can really hurt your device performance. So it's a really important material parameter to think about.

So there's lots of ways that these mobile electrons can do what's called scattering. So if I'm a mobile electron, I'm moving down through the silicon lattice. And let's say I see a defect, and this defect, because it has these extra electrons, it creates this kind of area of charge. It can see that it can scatter off of it and lose its energy, and so that's called a scattering event. Not really lose its energy. Sorry. It'll change direction. It kind of impacts the movement of that carrier.

And there's all sorts of other defects scattering mechanisms. You can also scatter with an oscillating atom or a phonon. There's another type of scattering mechanism, and it's heavily dependent on what you put into your material, and we'll talk about that in a second. And for a lot of materials that are, let's say, porous or amorphous in some way, or even a lot of, let's say, organic semiconductors, having a good percolation network is really important to transport these charges. And often it's a very limiting factor in, let's say, like organic photovoltaics.

And so this is a relatively simple scattering mechanism. What time-- oh, we have plenty time. What's going on here is that we can see that, as we add carriers-- so

this is n is 10 to 14th. Very, very low concentration of dopants-- as we increase the number carriers, are scattering off of those ionized impurities. So every time you add a phosphorus atom, lets say, you introduce a static positive charge and a mobile negative charge when that electron leaves. And so you now have all of these scattering centers of positive charge. And so as you increase the number of dopants-- this for silicon-- you decrease the mobility of your material, and it's also greatly a function of temperature. I think that's mostly due to either phonon scattering-- is that right? Is there any other mechanism I'm missing, [INAUDIBLE], if you're still there?

AUDIENCE: Sorry, I was on mute. Yes, I think you're good so far. We'll keep it simple, and use the simplest case first. I think that makes [INAUDIBLE].

PROFESSOR: But importantly is that higher temperatures, you generally get a much lower, lower mobility. And again, hitting home for-- this is not true necessarily for silicon, but for a lot of these heterojunction devices-- so for example, organics have very, very low diffusion lengths, and a lot of it's limited by mobility. And so what you do is you make these Interdigitated-- what I would call p and n. I forget the organic analogy, but p and n layers that interdigitated so that they only have to diffuse not the width of the device, but the length of those fingers. So you effectively need a much shorter diffusion length. And so this is talking about some of those other different ideas, and--

AUDIENCE: I'm sorry, that was a heterojunction? [INAUDIBLE].

PROFESSOR: A heterojunction is two different materials.

AUDIENCE: OK, what was the thing you were just describing with the--

PROFESSOR: That's an interdigitated pn structure. Yeah, so what we're going to be talking about is the product of n and μ . And if you recall that your conductivity-- so hold on. Let's go back. What we have here is that we have a highly doped semiconductor. So this is about 10 to the 16th, and then we have our intrinsic silicon. So this has no dopants in it whatsoever.

And now, you remember from last lecture when we applied a voltage across the terminals, a current started to flow, and when we heated it up, what had happened? Who remembers?

AUDIENCE: Current increased.

PROFESSOR: Current increased, and that's due to more thermally excited carriers. And so your intrinsic carrier concentration goes up. And so what was-- for room temperature, what's the intrinsic carrier concentration? It's about 10^{10} to the 10^{10} th-- in that range. And so in increase-- so a small increase in temperature can greatly increase the intrinsic carrier concentration-- maybe something like 10^{10} to the 10^{12} th.

Now in a doped semiconductor, is that going to affect it as much? How about you guys think about that for a little bit. Mute and talk to your neighbor. And so I'm going to heat both of these up, one with a high dopant concentration, and one with a low. And which one you think will have the highest relative change in conductivity and in which direction? So I'll give you three minutes.

So we're now going to subject. You've seen this demo before. We're now going to subject our intrinsic carrier to my hair dryer. And right now we're getting-- let's see. It's about 10 microamps. And if we heat this guy up-- did I mix these two up? Ah, there we go. So you can see we get a rather large increase in current. That was up to 100 microamps, so a factor of 10. So quite a large increase.

So let's see a show of hands. So right now we're getting-- maybe we need to put this on milliamps. So we're getting about 58 milliamps of current through the semiconductor. Who thinks that the current is going to increase when we add more thermal carriers? This is where the doped one. We just saw the intrinsic. Do you think it'll go up, the conductivity? So this is the doped semiconductor.

Now who think it's going to stay the same? Who thinks it's going to go down? All right, so this is split. Wow. So right now we're getting about 57 milliamps, and let's heat this guy up and see what happens. And so you can see, it's actually going down. It's now 52, 50, 49.

So what's important is that we're measuring conductivity. It's not only how many carriers we have, but also how well they can move around. And it's, again, that product of number of carriers times the mobility. And again, each of those carriers carries an electric charge. So you put the electric charge of an electron in front of it. This is what I was supposed to have up in the background while that was happening.

AUDIENCE: The intrinsic still had to go change, right? [INAUDIBLE].

PROFESSOR: Yeah, so again, remember there was huge changes. One was measuring milliamps. One was measuring microamps. So if we look at room temperature, we have about 10^{10} intrinsic carriers. So this is for intrinsic silicon with no dopants whatsoever. As we increase the heat, I don't think we're going to 500 degrees, but let's say we get the 400. We're only going up by a factor of 100, which is substantial, but if we had 10^{16} carriers originally from our dopants, these added number of intrinsic carriers aren't going to have really much of an effect at all in terms of the conductivity. So what's really affecting the doped case is that our mobility actually goes down with temperature due to the scattering events with temperature.

And for intrinsic silicon, you get a little bit better mobility, so it's a little bit higher, but they both have the same general trend of lower mobility, but only by, let's say, this is about a factor of 10, where it was about a factor of 100 for the intrinsic carrier. So again, our carriers in the intrinsic case go up by a factor of 100. Our mobility goes up by a factor of 10, so the conductivity then has to increase by a factor of 10. And for our doped semiconductor, really the heat is just hurting our conductivity because of the decrease in mobility, and the thermal carriers don't really add-- they're washed out by the sea of dopant atoms that are really adding all the carriers. Yeah?

AUDIENCE: So if you were to obviously heat up [INAUDIBLE] more-- [INAUDIBLE] the doped more, it would probably eventually get to the intrinsic case where there are constant increases, but would you ever want your solar cell that hot?

PROFESSOR: Would you ever you your solar cell that hot? That's a good question.

AUDIENCE: Yeah, I don't know how [INAUDIBLE] would it melt [INAUDIBLE].

PROFESSOR: So let's go-- there's an equation for that, and we'll talk about that later, too. So if you look at our VOC, if we have a large saturation current, that means that we're going to have a very low VOC. We have this reverse current that's going in the opposite direction of our illumination current that's opposing that illumination current. And so if it's large, then it'll hurt our VOC. And you can see that it scales with d , which scales with kt , and so we get this increase in temperature is increasing this J_0 .

And so for most types of cells, heat is very, very bad, especially for crystalline silicon. For amorphous silicon, it's different. Well, I'm not going to get into that today, but for crystalline silicon, heat is generally very bad for the performance. And when you do testing-- so for example, when NREL does testing, they'll rate all your cells at AM1.5G, some calibrated solar simulator that's illuminating your sample. And they're kept at constant temperature, so the temperature is always reported, and it's generally kept at the 25 C. So the temperature is a very important characteristic.

But to answer your question, if, again, we looked at an Arrhenius plot-- so this is $1/kt$. So this is high temperatures over here, low temperatures over here. And this is carrier concentration. At very, very high temperatures, when your thermal carrier-- so if you extend this out to higher temperatures, you can see that this will actually surpassed the number of dopant atoms, and you'll actually increase. So this is high temperature over here.

Your carrier concentration will actually increase at much, much higher temperatures, and this is what's the extrinsic region. So your donor concentration is pretty much only determined by your dopant density, so this is N_D . And then at low enough temperatures-- so this is very low temperatures-- you actually start freezing out you're donor electrons into these donor states. So that actually sums it up. If you guys have other questions, feel free to ask them, but we actually can end a little bit early. I do have your homework, so if you want those, come up here. And I think [INAUDIBLE] posted the projects online so you can finish homework number three. That's it.