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3.091SC Introduction to Solid State Chemistry, Fall 2010  
Transcript – Session 14

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PROFESSOR: OK, so this takes us into the paper by Heitler and London, where, by using the concept of linear combination of atomic orbitals into molecular orbitals for a large number of atoms, instead of splitting one plus one atoms, making a bond into two energy levels of bonding and AN antibonding, we take a large number of atoms, bring them together, and we get a large number of bonding orbitals and a large number of antibonding orbitals. And they have to lie within a zone of about 5 to 10 electron volts, which means if you put Avogadro's number of these things together, you're going to end up with an energy difference between successive energy levels on the order of about 10 to the minus 20 electron volts, or 10 to the minus 40 joules. And for all intents and purposes, that is a continuum, and hence, the term band.

And now we start populating this with electrons, and each one of these is a separate state. And electrons go in two by two, just like Noah's Ark, all the way up-- either halfway up or all the way up. But now the energy difference is very, very tiny.

And a second instance, we looked at insulators where-- for example, in diamond-- where the bonds are really strong. So that means if the atomic orbital is roughly at the middle here, the depression to make the bonding orbital is very, very great, and very negative. And therefore, the elevation to the antibonding orbital is great and relatively positive.

And when we start putting Avogadro's number of these things together, we still end up with the 10 to the minus 40 joules. But when we get to the top of the bonding orbitals, we have still got 3 or 5 or 5 electron volts to get to the bottom of the antibonding orbitals, hence the formation of the band gap with an energy of-- as I mentioned.

So up here, we have the conduction band where electrons are free to move about. And this is derived from the antibonding orbitals. And down here, we have the valence band, which consists of the bonding orbitals derived from sigma and pi.

And then the semiconductor is sort of like an insulator-- as they say in California, it's like an insulator-- but the band gap isn't quite so severe. It's down on the order of 1 to 3 electron volts, and that gives it unique properties. Why? What's magical about 1 to 3 electron volts?

Number one, visible light. Visible light is 2 to 3 electron volts. So visible light shines right through an insulator, because visible light has an energy of about 2 to 3 electron volts. If that's the energy of 2 to 3 electron volts, and this is 6, it zooms

right through. But if it's 2 electron volts and this is 1 electron volt, we're going to get thermal excitation.

I know Professor Ballinger talked about thermal excitation the last day and what happens, and it's very reminiscent of excitation in the case of the Bohr model. Photoexcitation across the band gap. Incident photon with energy greater than the energy of the band gap. And it's the same drill as you've seen before. That's why those early lessons on-- photon comes in or electron comes in, strikes the Bohr atom, electron rises up, momentarily sits there, falls back down, photon emitted. It's the same set of ideas.

Only instead of moving from  $n$  equals 1 to  $n$  equals 2 in the Bohr atom, you're moving from the valence band to the conduction band, sitting in the conduction band momentarily, you fall back down, and you get a photoemission. So that was covered last day. And I know towards the end of the lesson, he started talking about thermal excitation.

So let's look at that in a little more detail. Thermal excitation. So thermal excitation of what? Thermal excitation of electrons across the band gap. So this is matter energy interaction, only in this case, it's thermally inspired.

So let's draw our cartoon again. Up here, we have the conduction band, and below we have the valence band. So in the conduction band we have free electrons. In the valence band is where all the bonds live. And we've got an energy gap here of some value. Could be semiconductor, could be insulator. In this case, we're going to use visible light.

And we've gone through the analysis with incident photon and the emission. In this case, I want to look at thermal excitation. So with thermal excitation, I start with an electron down here in a bond. This electron lives in a bond. And with thermal excitation, the electron jumps out of the bond and up into the conduction band.

So I'm going to designate the electron in the conduction band with an  $e$  minus and a circle around it. And it leaves behind a broken bond. As you know, every bond has two electrons in it. Well, one of the electrons left the bond, leaving a hole. Little  $h$  with a plus sign. This is a broken bond, and a broken bond is highly unstable and very mobile.

If I put a potential across here. If I put this material-- and I'm doing a mixed metaphor-- this is an energy level diagram. But now I'm going to put a couple of plates across an energy level diagram. But you're smart. You can understand this.

So this is not energy. Now I'm going to make the right electrode negative and I'm going to make the left electrode positive. What would happen?

Well, the electrons in the conduction band are going to be attracted to the positive electrode or repelled by the negative electrode, but the complementary situation occurs in the valence band. This broken bond is like a hot potato, and it has an effective charge. This is a zero in a land of minus one. A broken bond is a zero in a land of minus one.

So therefore, if I make the right side negative, this hole is going to be drawn. So I have two forms of electronic conduction. I have electrons moving to the left in the conduction band and I have holes moving to the right in the valence band.

So for every thermal excitation I get two carriers. Every excitation of electron from valence band to conduction band generates two carriers. Carriers of what? Water? Carriers of electrical charge. Two carriers of electrical charge.

And what are they? The electron in the conduction band and the hole-- little  $h$  with a plus sign-- in the valence band. So that's how thermal excitation works. And you can see that the numbers have to be equal. So we write, therefore, that the populations are equal. The number of electrons in the conduction band equals the number of holes in the valence band.

Now electrical engineers have a similar expression, but they don't care about numbers and electrons and holes, they care about the functionality. And the electron is a carrier of negative charge and the hole is a carrier of positive charge. So the electrical engineering books will write, thermal excitation gives rise to pair generation. Pair of what? Pair of charge carriers. And the population of negative charge carriers equals the population of positive charge carriers, which in chemistry is the number of electrons equals the number of holes, or the number of broken bonds.

So that's the way it works, but there's a conundrum here. Thermal excitation is based upon the thermal energy, and we know that the average thermal energy in an environment is roughly given-- I mean there are fancier calculations-- but to a first order, I can approximate it as the product of the Boltzmann constant and absolute temperature.

So at room temperature-- room temperature, I like to say, about 300 Kelvin. 300 Kelvin is 27 Celsius. That's kind of a warm room, but 300 is a nice number. All right? So if you take 300 Kelvin, you get on the order of about  $1/40$  of an electron volt.  $1/40$  of an electron volt, which is a lot less than one electron volt, which is roughly the band gap of a semiconductor.

So how is it that we get any thermal excitation of data indicate that there is some thermal excitation even at room temperature? So the question is, if the average thermal energy is a fortieth of electron volt according to this-- and this is correct-- and the band gap is one eV, then it should be no thermal excitation. But we know what happens. So, one eV, which I'm going to say is  $E_g$ . All right?

So how do we get any thermal excitation under these conditions? So there's an answer to this. And for this we go to merry old England and James Clerk Maxwell, that you know or will come to know in 8.02 as the annunciator of Maxwell's equations of electricity and magnetism.

He also thought about physical chemistry, and in particular he thought about the physical chemistry of gases. And what did he teach us about gases? He said, if you look here in this room, you see nitrogen and oxygen and all the other constituents of air. But to a first approximation, we have four parts nitrogen, one part oxygen. The room is roughly 300 Kelvin.

What Maxwell taught us is that velocities of the gas species zooming around in this room are not all equal. Some of the gas species are moving around as though they're at 500 Kelvin. And some of them are moving around very slowly as though they're at 100 Kelvin. On average, it's 300 Kelvin, because we can feel it as 300 Kelvin. But some of them are zooming around. Some are really lazy and they're just moving along really slowly.

And furthermore, he was quantitative about it. He said, I'm going to tell you what the distribution of energies is. So let's get that on the board for starters.

That in any ensemble of gas species, could be gas atoms or it could be gas molecules or gas compounds, in any ensemble of gas species, that all molecules-- because you can always say the atom is a degenerate form-- all molecules do not have the same velocity. And furthermore, he gave us the distribution. He calculated the distribution of velocities. So that was about 1859.

Forgive me here. Velocities. OK.

And then Boltzmann came along in 1872. And Boltzmann generalized this idea. He made the link between gas velocity and temperature.

So, he took the idea and he said, if the gas molecules move at different velocities, that means they have different energies. And why do we call this the Boltzmann constant? Because Boltzmann made the link between particle energy and temperature.

So he said there's a variation of instant temperature. All right? So Boltzmann generalized Maxwell's idea to energy and then ultimately temperature. And so I'm going to show you, instead of the Maxwell distribution, I'm going to give you the Maxwell-Boltzmann distribution.

But before I do, I want to make sure you understand the math and appreciate what I'm going to plot for you. So we just had a test, right? In fact, we can go back to the slide. All right.

So what do we have here? I could plot on this axis, the abscissa, the grade--  $g$ -- and on the ordinate, I'll plot the number of people who have any given grade--  $n$  of  $g$ . Now the class av was 66, all right? This is going to go from 0 to 100.

Now what we see here is-- and by the way, I'm going to normalize it. Instead of dealing with 463 or whatever, I'm going to divide by the total class. So the number is going to go from 0 to 1. So this a normalized distribution.

What I'm teaching you applies all through science. As I told you, this is the most important class. Not because I'm teaching, but because the subject matter is general, just as Boltzmann did.

So let's look at the normalized distribution. Now the class av was 66. Now we didn't have everybody getting 66. That was not the distribution. That's one solution to the problem, isn't it? Instead, what we got was we got that.

Now one possibility would be this one, the bell-shaped curve. Goes like this. That's bell-shaped. This is Gaussian. This is a Gaussian distribution, and its functionality is  $y$  equals  $e$  to the minus  $x$  minus  $x$  average, quantity squared.

Now, to have a normal distribution, you have to have a class of normal people, so that didn't happen on this test. That's a joke. God, you're so serious. Have you no fun in your lives? Have you ever laughed?

AUDIENCE: [LAUGHTER]

PROFESSOR: Overachievers, you. OK.

So we're not going to have a Gaussian distribution. We're going to have that one there. It's kind of a skewed Gaussian with a long tail. All right, so that's the one thing.

But what Boltzmann gave us, instead of the number of atoms of a given grade, he plotted it as a function of energy. So instead, the Maxwell-Boltzmann distribution has energy as the ordinate instead of the grade, and up here, the number of atoms-- or more importantly-- the atom fraction. The fraction of atoms in the distribution that have that energy.

And it doesn't look like a normal distribution. It looks sort of off-normal. Skewed, like this. It rises to a peak and it has a long tail that moves off to the right.

So this is the Maxwell-Boltzmann distribution. It's not  $y$  equals  $x$  minus  $x$  bar squared. So this is Maxwell-Boltzmann distribution of energies.

And furthermore, what we see here is that the area under this line has to equal 1. If you integrate the fraction from 0 to infinity, because this asymptotically goes out to infinity, the integral under this line is 1. OK. Area equals 1, which is the integral of  $n dE$ .

Now, because of the asymmetry here, clearly this is the average energy. The average energy isn't the maximum energy.

Whereas in the Gaussian-- let's keep the Gaussian over here, just for grins and chuckles-- so the Gaussian looks like this. It's symmetric. And this is the  $n$  of  $g$  max and also a  $g$  average, whereas here, the average is a little bit to the right. A little bit higher. OK.

So now, if this is the distribution, and this at room temperature is 1/40 of an electron volt, and way, way up here is the band gap energy, there's a tiny but non-zero fraction of this distribution that has energy in excess of the band gap energy. And so this tiny fraction of the total distribution has the thermal energy to allow this excitation and pair generation to occur.

And furthermore, this is a function of temperature. This is a function of temperature. So  $E$  average is related to temperature. So, I'll say  $E$  average 1 at  $T_1$ .

And then what I'm going to do is I'm going to heat this to a higher temperature, so I'll use red chalk to indicate it's hotter. And what happens to the distribution under an increase in temperature? Well, the average had better move to the right, and

that's what happens. But it doesn't just move to the right, it skews a little bit and broadens. So in point of fact, at a higher temperature, it looks like this.

OK. So this is now  $E$  average 2 at  $T_2$  where  $T_2$  is greater than  $T_1$ .  $T_2$  is greater than  $T_1$ . OK, so that's the Maxwell-Boltzmann distribution.

But here's where the interesting stuff occurs. So I'm going to blow up this high energy end of the distribution. So again, this is going to be  $n$  of  $E$  normalized, and this is  $E$ .

And what we're going to find here is that at  $T_1$ -- this is the curve at  $T_1$ , and the area under the line is shown here-- and then-- not to scale-- we're going to put a break in this. And I'll show you how much of a break is needed. And then, at  $T_2$  I'm going to have this come down. This is  $T_2$ . And the area under the line  $T_2$  captures the  $T_1$  plus all of this.

And so what we see, is that for a modest increase in temperature, this maximum shifts modestly, but the area under the line in excess of this critical energy increases radically. And that's the powerful leveraging factor of increase in temperature. And I've done some calculations just to show you what this does.

The functionality of the Maxwell-Boltzmann distribution is  $e$  to the minus some critical energy divided by the product of Boltzmann constant temperature. So we can put in a value here-- eg-- what have you. All right.

So I chose for silicon-- for silicon, I know the band gap energy is 1.1 eV-- and I have it at room temperature-- when I go through the calculation-- the fraction underneath that line is  $10$  to the minus  $19$ . One part in  $10$  to the minus  $19$ . This is the area. Area under the curve is greater than the band gap energy of 1.1 eV.

So then I said, let's go up to the melting point. I'm not going to melt the silicon, I'm just going to bring it up to its melting point but not melt it. So it's like ice cubes at 0 Celsius. It's still solid. OK? The melting point of silicon, you can look in your Periodic Table, it's over 1400 degrees C.

And this is  $10$  to the minus  $4$ .  $10$  to the minus  $4$ . Area under curve: da da da da. So that means that the red area--  $A_2$ , the red. Actually, let's use red chalk so that everybody is in tune.  $A_2$  to  $A_1$  is equal to  $10$  to the  $15$ , whereas  $T_2$  over  $T_1$ -- well, red chalk. It's my chance to use red chalk and I'm not going to squander it.

$T_2$  divided by  $T_1$ -- it's about 1700 Kelvin divided by 300 Kelvin-- is about 6. So for a change in temperature by a factor of 6, I get a change in population of  $10$  to the  $15$ . So you can see how modest increases in temperature have a huge impact on thermal excitation.

So now you say, if we wanted to make a device, we can't heat our computers up to 1600 degrees, 1500 degrees C in order to get an adequate number of charge carriers. There has to be another way to get charge carriers. I'm going to show you a third way that's called chemical promotion.

So now I want to talk about charge carrier generation. Charge carrier generation by change of chemistry, and it's going to be specifically by the introduction of impurities. Charge carrier generation by introduction of impurities.

You might say, gee, aren't impurities bad for a system? Well, I want to tell you, there are two kinds of impurities in this world. There are bad impurities which we call contaminants, and that's what you're commonly taught to think about. That's bad.

But there are good impurities, and these are called dopants. Dopants are impurities that we are happy to have in our system. And so by the introduction of impurities of value, we can lead to engineered materials. So I'm giving you the introduction to high technology, where we're going to control the engineering properties of a material through control of chemistry.

So that's chemical composition tailored-- for specific-- for targeted values of properties. And that's the essence of material science. We control the chemistry. We control the properties by controlling the chemistry.

So what I want to do is give a vivid example of this, and it's not going to be an isolated example. It's going to be the example that pertains to all of the microelectronic devices in our world. So that's silicon. So let's look at how doping works in silicon. It also applies to germanium, but we don't use much germanium in devices. It's dominantly silicon.

So what we're going to do is dope. The gambit here is to dope-- that's introduce an impurity-- with aliovalent impurity. What do I mean by aliovalent? You know the word alias? It's another name. Alio in Latin means other. So we're going to dope silicon with something that has a different valence from that of silicon. Can't before.

So let's look at the simplest example. And I'm going to put phosphorus into silicon. I'm going to dope phosphorus into silicon, and phosphorus is Group 5, or more properly, IUPAC calls it Group 15. So we're going to put Group 15 element into silicon, which is Group 14 element. So we call phosphorus a supervalent dopant, meaning it has a valence higher than that of the silicon. So it's a supervalent dopant. Supervalent dopant.

So now let's look at how that supervalent dopant works. I'm going to show you some silicon here, and I'm going to give you the silicon. This is  $sp^3$  hybridized. it's sitting here as a single crystal.

Here are three silicons. So it's a single crystal. All these silicons on the bottom row line up. All the silicons in the center line up. And there are silicons at the top and they all line up. So that if I look at it on the edge, it's a perfectly, atomically smooth system.

And I have one of these. I know Professor Ballinger made reference to it last day. This is last-generation technology. It's only eight-inch diameter.

But this is an eight-inch diameter silicon wafer. So this started as a giant salami, eight inches in diameter-- probably two meters long. Single crystal. Every atom here is adjacent to the next atom according to the rules of atomic arrangement.

And when this thing is cut and polished, it's flat to one atom. It is atomically flat. And it makes a fantastic shaving mirror.

Actually Dave, can you cut to this? Yeah, here we go. Here's the penny. And this is silicon here. It's going to drive this thing nuts because it can't focus on this thing, because it's so-- there we are.

So this was a part of a giant salami, and now it's been cut. And obviously you can't cut it one-atom thick. It's some submillimeter thickness, because you need to have some mechanical strength to it. But the surface is absolutely flat to one atom. All right.

And that's what we're going to dope into. We're going to dope into this thing, and I'll show you how we're going to dope it later.

Actually, why don't we cut to that. Here's something that's already been doped and made into devices. So there's the plain old silicon, which you're having a hard time seeing anything except a little bit of reflection. And now here's the thing that's been processed, so let's zoom.

Zoom. OK. So now you can see all the features.

So these features involved gas phase reaction to introduce dopant atoms into the silicon lattice. And then we're going to chop these little things up and put them in your cell phones and in your laptops and whatever other devices are out there. OK. So this is what we're talking about, and if we live long enough, we'll see one of these.

This is a Pentium chip. OK. So where's the chip? The chip is underneath this piece of gold.

Where did I put my pointer? Ah, it's over here. All right.

So the actual silicon device is underneath this. And all of these are this spider's web of leads. It's trying to access all the tiny devices. It doesn't do you any good to have a device density that's greater than your access density. So the technology that goes into this is phenomenal.

Plus, these things all generate heat. When you put all these tens of thousands of devices into something the size of your fingernail, you've got a toaster oven working here, and you have to get that heat out. And this is several generations old. What you have in your machines today is even denser than this.

And supercomputers? Forget it. You have to have those things so aggressively cooled or else they'll heat up and it'll be just like a light bulb, just bursting. So that's what's going on inside.

So let's see how that happens. Let's cut back to-- well, you can leave that up. It's a pretty image and will probably soothe the nerves of the students.

So now I'm going to put phosphorus in here. I'll put phosphorus in here, but where does phosphorus go? Phosphorus goes onto a silicon site. So it actually comes in and sits here. Phosphorus comes and sits at a silicon site.

Now what do we know about the number of bonds that phosphorus likes to form? It has five valence electrons. So it forms one, two, three, four bonds, and it has a fifth



electron. And that fifth electron is sitting there somewhere. It's sitting there somewhere in the lattice. All right.

It's sitting somewhere in the lattice because it has no place to go. Now in energy space, I know where it goes. So here's the conduction band of silicon, and this is the valence band. And this is all of the silicon host crystal, because the dopant is in a tiny, tiny amount. We're talking parts per million. So for all intents and purposes, it's still a silicon crystal. It has tiny amounts of phosphorus in it.

So this is the band gap of silicon, where this is about 1.1 electron volts. And where does this fifth electron go? This fifth electron sits up in here in the conduction band, doesn't it? And every time I introduce a phosphorus, I have a fifth electron that goes in the conduction band.

But I don't have to generate a hole. I don't need to break bonds in order to put electrons in the conduction band. Because the fifth electron is like the fifth wheel. You know? It goes in the conduction band. So there's no generation of holes here. All right.

And furthermore, I can control the conductivity. At the end of last lecture, Professor Ballinger showed you that the conductivity of a substance is related to the number of charge carriers. So if I want to double the number of phosphoruses, I will double the number of electrons in the conduction band, independent of temperature. All right.

So for every phosphorus dopant atom, we get one electron in the conduction band. We get one electron in the conduction band and no holes. No holes in the valence band. It's direct. It's direct. All right.

Now, electrical engineers would look at this and they'd say, I don't care if it's phosphorus. They don't care about the chemistry, they care about the functionality. What kind of carriers am I throwing into this crystal? For an electrical engineer, there are only two kinds of carriers. Positive carriers and negative carriers. For every phosphorus, what's the outcome? A negative carrier.

So this is now doped silicon. It generated negative carriers, so this is called n-type. This is now n-type silicon. And its properties are governed by the population of these-- because I'm going to show you in a second that the number of these far exceeds the number that are thermally generated-- so the properties here are called extrinsic. So now we have a crystal that is exhibiting it's extrinsic behavior, thanks to the doping with the supervalent impurity.

One more thing. One more thing. Something very, very cool here.

You see this electron? It's sitting here somewhere in the-- now this is Cartesian map. I'm looking through a scanning electron microscope. I see all the silicons. I get the phosphorus. And there's an electron in here somewhere.

And this has 15, right? This has 15 protons. This has 14 protons. So in a land of 14 plus, 15 plus is relatively positive, isn't it? The phosphorus is locally positive in comparison with the rest of the silicon lattice.

And it's pinned, because it's covalently bonded. And there's an electron sitting here with no place to go. Do you know of a model that describes the behavior of a one-electron system around a pinned positive nucleus?

AUDIENCE: The Bohr model.

PROFESSOR: Bohr model? Just for grins and chuckles, what if we were to use the Bohr model to describe the behavior of that electron? You can say it's crazy. That doesn't make any sense, because that's not a one-electron system. But what if we modeled it as though it were?

I'm going to-- just for grins and chuckles-- get a sense of what that ground state value is. And recall that in hydrogen, the ground state--  $E_1$ , ground state of the electron-- is equal to minus  $k$ . Which is minus  $m_e$  to the fourth over  $8 \epsilon_0$  naught squared times Planck constant squared. Which is minus 13.6 electron volts

So what is the energy of that electron there if we use the Bohr model? Well, we have to modify it a little bit, because the electron isn't moving in a vacuum. Depending on how far this electron is from the center, it could be moving around, and there are all kinds of silicon atoms and bonds and whatnot. So there are all kinds of stuff between the electron and the center here.

So I have to use a modified form. I don't use the permittivity of vacuum. I map the permittivity of vacuum into the dielectric constant. This is the dielectric constant of silicon. Remember there's so little phosphorus there that it doesn't alter the properties.

And then for reasons I can't go in to here, I have to change the mass of the electron into the effective mass-- we saw this when Bohr did the calculation about the lines of helium plus-- effective mass of electron in the conduction band. So if you put both of those in-- and I've got numbers for this-- this value is 11.7 and the second one is about 1/5 of the rest mass of the electron. So if you put all of that in, you end up with the energy of this ground state electron equal to minus  $k$  times 0.2 divided by 11.7 squared, which equals minus 0.02 electron volts. 0.02 electron volts.

So this is 2/100 of an electron volt below something. What's it below? It's below the conduction band. It's right here. This is the ground state of the electron from phosphorus. It's the ground state of the electron from phosphorus.  $E_1$  of electron from phosphorus.

And phosphorus, the electrical engineers call a donor. A donor of what? It's a donor of electrons. So this thing here is called the donor level.

And that's the ground state. So the electron should be sitting. Isn't the ground state here lower than the bottom of the conduction band? Sure it is. So the electron really should be down in here. There's the electron.

Now you're saying, how are you going to get conductivity? Well, we just figured out that the energy level of the ground state of the donor-- so I'm going to call this the energy of the donor level, ground state-- is 0.02. How does that compare with thermal energy at room temperature? It's comparable. So at room temperature with 1/40 of an electron volt, there's enough energy to promote this electron up into the

conduction band by thermal excitation from the donor level. Thermal excitation from the donor level.

And in fact, if we want to do something really, really-- I want to use an adverb here-- really, really cool. If that's the ground state-- I'm going to blow this up.

So this is the bottom of the conduction band. And now this is the ground state. This is the donor level. This is the donor level, which I was calling E1.

Is it just the donor level here and the conduction band, or can you see that there's an E2 and an E3 and an E4? And I have a whole set of quantum states from the donor level right up to the conduction band. And if I have enough energy-- if E thermal is on the order of E donor-- I get promotion of these up in here.

Now what would we say if this were the Bohr model? You'd have an electron loose in a ground state up in here where it's free to move. What's that process called? Ionization.

And you know what the electrical engineers call these electrons? They call them ionized electrons. But they're referring to the ionization of the electron out of the donor level into the conduction band, not out of the silicon crystal. So these are ionized electrons out of donor level.

So we've come full circle. By the way, this is a calculation. You know what the measured value is? It was measured as minus 0.045 electron volts.

You might look at that and say, whoa, that's about two times this. Hey, wait a minute. We started at 13.6. We went from 13.6 to this, and the real value is this, and so we are in good shape.

Now, what happens if I put another phosphorus in here? Another phosphorus, it's also going to sit at this-- I'm going to do it over here. If I put another phosphorus, it also has the same donor level. And another phosphorus, it has the same donor level.

How can I justify this? Am I not violating the Pauli exclusion principle? How come all the phosphorus donor states are at the same level? Or put another way, under what circumstances is this diagram accurate? If the number of phosphorus atoms that I introduce is tiny-- parts per million-- the separation, the physical separation of this phosphorus from its nearest phosphorus neighbor is so great, that for all intents and purposes, they are at infinite separation. And therefore, all of the phosphorus donor atoms establish a donor level at the same value.

And if you dope to very, very high levels, you see this break down. If you go to very, very high concentrations of phosphorus dopant, you will discover what happens if these two energy levels get close enough together in real space. They have to split. And so you'll see all of that happening down here at the miniature level.

The last thing I wanted to do was to push the Bohr model just a little bit harder. And so I've given you an energy, and the energy seems to make sense. Even though you might say, this is the crazy. It's not a one-electron system, but it gave us a reasonable number. Let's just for interest's sake determine: what's this radius? I wonder how far this electron is away from the donor phosphorus?

So I plug into the  $r_1$ . That's the radius of the ground state electron. And that's the Bohr radius, right? 0.529 angstroms in elemental hydrogen, but now this has to be modified by adding the dielectric constant and the effective mass. And the number is 30 angstroms, or 3 nanometers, if you must. All right?

And compare that to silicon-silicon bond distance. The silicon-silicon bond distance is 2.35 angstroms. So clearly this electron is very far removed from the central phosphorus. It's not as I depicted. It has to be way over here, going way, way around. This is really, really something. So now you understand how you can get extrinsic properties and the behavior of the system governed by the introduction of impurities.

What I'm going to do next day, is to show you that at typical doping levels, when you dope, dope at about 10 to the minus 6-- 1 part per million-- 10 to the minus 6 phosphorus per silicon. It turns out that the number of electrons from this operation is much greater than the number of electrons from thermal excitation, which is tiny. And therefore, we argue that the properties are governed by the dopant atom, and so we have extrinsic behavior that we see.

OK, well that's a day's work. David, may we go to the slides, please?

OK, so you saw all that last day, and this, this, this. All right, there's the insulator, and that. So I'm just doing the lecture again and fast. You can read. You can parse visual images.

See? There's the n-type semiconductor. We're going to look at p-type next day, quickly.

There's a silicon crystal. There's the salamis-- there's the little wafers that are cut. And there's the spectrum, the x-ray spectrum indicating you have a single crystal.

There's the first transistor-- this was a single crystal of germanium lying here on its side-- the point transistor in the fall of 1947. Three gentleman at the Bell Labs that demonstrated the rectification. And they won the Nobel Prize for this in 1956.

Now, you can also make semiconductors that have compounds. So these are compound semiconductors-- Professor Ballinger showed you last day-- tin, germanium, silicon, carbon.

And look at all of these. This is a Group 3 element with a Group 5 element. 5 plus 3 is 8. Group 3 and 5. This is Group 2 and 6. 2 plus 6 is 8. It's always about octet stability. But they make strong covalent bonds that give band gaps all over the map.

So suppose I wanted to have something like a stoplight. Suppose I wanted a stoplight, and I wanted to make a red light. Well, I need-- I can go backwards from 660 nanometers, and I can go  $e \text{ equals } hc \text{ over } \lambda$  and calculate-- I need a material with 1.97 electron volts band gap, and I look on here and there's nothing that's exactly 1.97.

Well, I can mix these things. I can mix them. I can mix something that has 1.52 with 2.3 and get 1.97. That's called band gap engineering.

And there's more than one mix here, so why would I choose one mix over another? It's cheaper, or it's easier to process, or it's stable in the atmosphere. You don't want a semiconductor that can't stand rain and snow.

And so I'm showing you here a variety of compound semiconductors, and this is the basis of things like-- the LED, the CD reader, the DVD reader is based on light that's generated from these. What was the big deal about Blu-ray? Why is Blu-ray so cool? Because the original reader was red.

And what's the wavelength of red light? Red light is around 600 nanometers. And what's the wavelength of blue light? It's down around 300 nanometers.

So all other things being equal, my stylus is half the size, which means for a given area, I can get double the density of information without changing the size of the disc. But it wasn't trivial to find a blue laser. And the person who found the right mix of compounds that could give blue in an efficient manner became a very wealthy individual.

So this is our stoplight now. These are the materials that go into the stoplights. No more do you have that giant lens with a 150-watt incandescent bulb. Now you have the array of these LEDs that are designed to be in this band gap.

So I think at this point, we've probably run out of time. So we'll resume the discussion tomorrow. Same time, same place.

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