VLSI Technology

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Lecture - 21
Annealing of damages created by Ion-implantations

So, now you know that after ion implantation, there will be a lot of damage in the implanted region and until and unless these damages are annealed out, you cannot get any device made in that area. The parameters that get most affected and which are important for the performance of any device are the conductivity, the mobility and the life time. So, essentially after an implantation, we will find that the conductivity is very low signifying that the electronic activity is minimal. That is in even more simple terms that is most of the impurity which you have introduced in the semiconductor is not sitting in the proper substitutional sites. They are introduced, they have anyhow gone into the semiconductor, but they are not sitting in their proper substitutional sites and therefore not taking part in the electronic activity. So, the first effect that we will see is that the region will become almost semi insulating; the resistivity will be very high, conductivity consequently is very low. So, that is one factor.

Secondly, because of the highly disordered damaged region, the mobility of the carriers will be extremely low. So mu is the next causality and finally of course, the life time.

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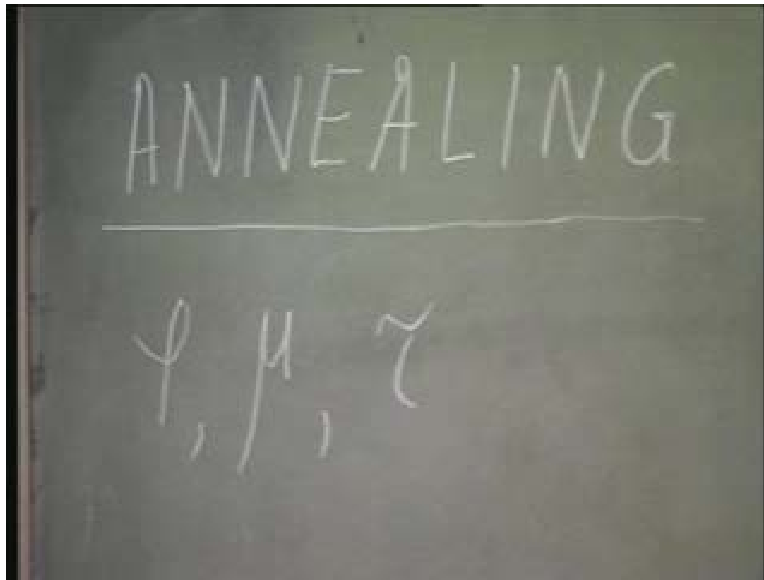

So, these three important parameters are rho, mu and tau. Our aim will be to get back the required levels of conductivity, the mobility and the life time. This is what we idly want. On the other hand, in order to get back these things, in order to anneal out the damages, the semiconductor must be subjected to high temperature treatment. We may have a number of limitations imposed on us, as to how much temperature and how long time we can employ. Now at the onset, let us see whether some compromises are permitted. First of all you see, think about the damaged region. From the definition of the ion implantation profile, its projected range, etc., you know that the mean projected range is where most of the ions are coming to a rest. That is where the peak concentration lies, agreed.

What is the region of maximum damage? You know that the damage is created mostly by nuclear stopping mechanism. That is the ion is imparting its energy to the lattice atoms. The lattice atoms in the process are getting displaced and they are probably causing secondary displacement of other lattice atoms. That is a primary mechanism of damage. So, one thing is clear that is in order to create damage, the incident ion must have a non-zero energy, agreed. That means the region of maximum damage will precede the peak concentration region. It will be lying closer to the surface than the region of peak

concentration, agreed. Now, that gives us a little bit of a break, because the damaged region is lying closer to the surface, whereas the peak concentration is lying deeper. So, we can relax the requirement of the total life time recovery, because even if in the damaged region the life time is low, it does not matter, because the depletion region is on the other side; the device activity will be taking part on the other side of the peak concentration, not towards the surface, right.

So, this in a way helps us a little bit. Because the damaged region is lying closer to the surface, we can relax some of the requirements; we may not have to go for the total recovery of life time. I am mentioning this, because it is most difficult to get back the total life time. It is much easier; in fact the simplest is to get back the full electronic activity that is the conductivity. It is simplest to get back the conductivity; mobility also comes next, once the disorder is arranged, but it is difficult to get back the life time. Because the damaged region is lying closer to the surface, the full recovery of life time may not be as essential in most cases. So, now you know that the annealing schedule that is the time and temperature, it will depend upon the dose; lower the dose, normally simpler will be the annealing and also you know that it will depend on the orientation, 1 0 0 will anneal faster than 1 1 1.

With this background, let as now try to see the annealing schedule.

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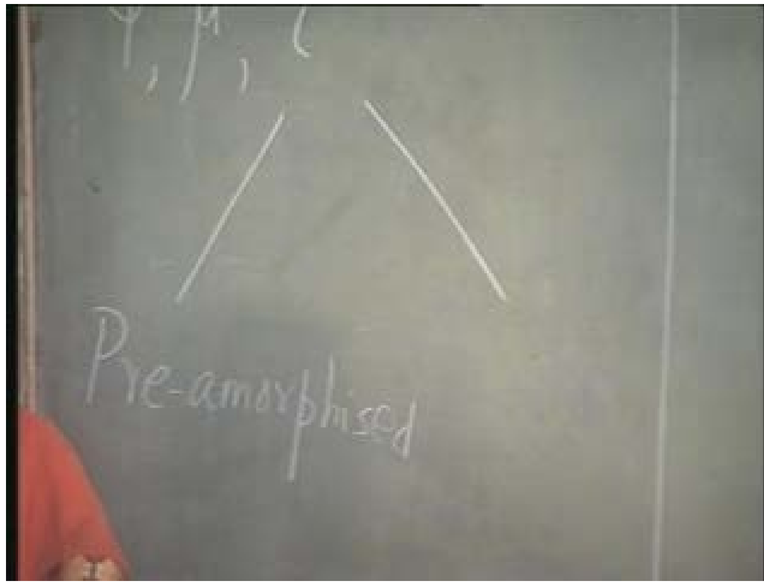

We will divide the annealing in two classes; annealing of implanted material in two classes. One is where the material has been pre-amorphized and the other where the material is not pre-amorphized. Let us take the pre-amorphized material first.

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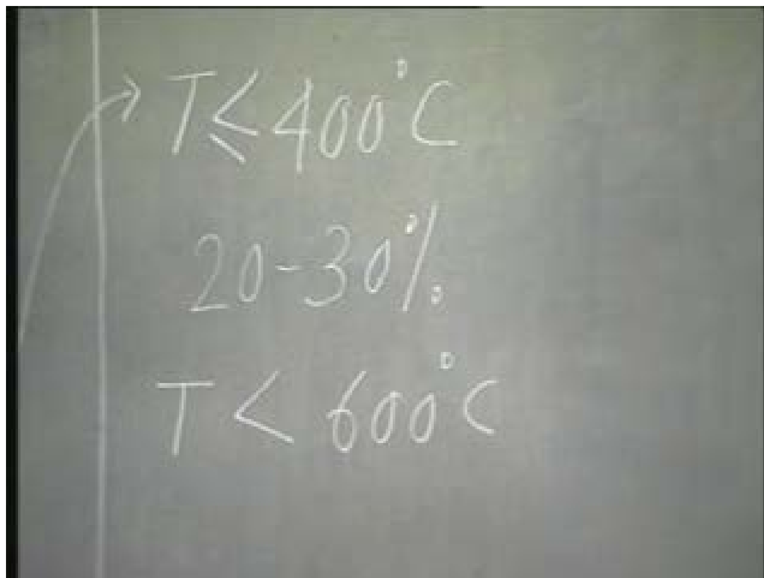

Let us say we are annealing it at a lower temperature; T is less than equal to 400 degree centigrade, pre-amorphized material annealed at T less than equal to 400 degree

centigrade. This is where the disordered clusters just begin to disappear. So, you have a partial recovery of the conductivity to the tune of 20 to 30%. So you see, the interesting the point is even at this low temperature, you do have some recovery; 20 to 30% recovery is possible at T less than equal to 400 degree centigrade. Let us increase the temperature, let us say, around 600 degree centigrade; around 550 to 600 degree centigrade. Here a very interesting thing begins to happen. Remember this material is pre-amorphized. At this temperature range 550 to 600 degree centigrade, the crystalline order emerges. This takes place by solid state epitaxy.

You have already been familiar with epitaxy, you know what epitaxy is. I have an underlying substrate of crystalline material, right and the top surface region has been pre-amorphized. So, at this temperature a solid state epitaxy process starts, where the bulk crystalline is viewed as the substrate and the top amorphized layer now begins to arrange itself according to the bulk crystalline order. So, by solid state epitaxy, the crystalline structure begins to get back; actual recrystallization takes place.

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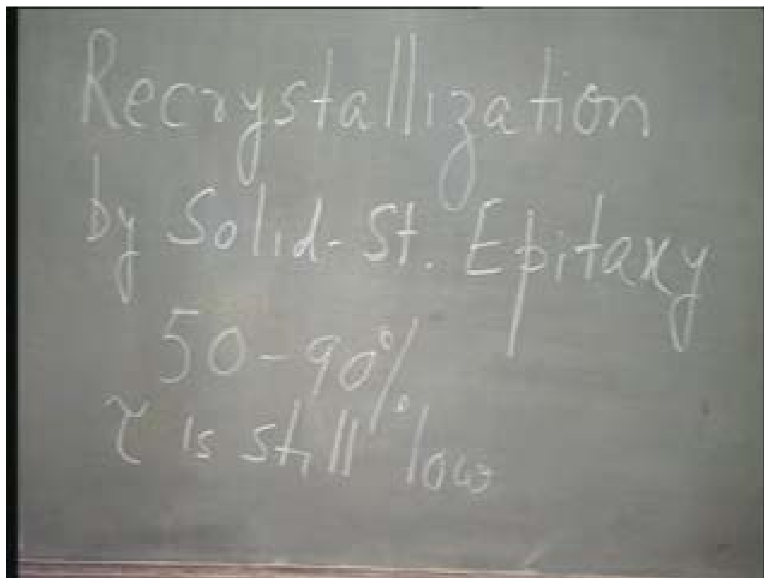

So, what you have in this temperature range is recrystallization by solid state epitaxy and carrier activation can be up to 90%, 50 to 90%. Remember, even now considerable

amount of damages will remain there. Even though recrystallization has taken place there will be quit a lot of damages and these lattice damages will serve as sink for metallic impurities. So, even though you get back up to 90% of carrier activation, conductivity, the recovery of life time is still very low. Till the temperature is less than 600 degree centigrade, the life time recovery is extremely low. In fact, that is why you know, I mentioned this point that since the damage is closer to the surface, it may not always be essential to get back the full carrier life time, simply because it is most difficult to get back.

So, even though you have an activation of 50 to 90%, tau is still very low, because even though recrystallization has taken place considerable amount of damages will remain there. You know why? That is because activation of these substitutional impurities, activation energy of the substitutional impurities is much less than the energy of self-diffusion. So, you can get back the carrier activation, you can push all the impurities in the substitutional site. But, considerable damage is still remaining. You have not supplied enough energy for these self-damages to get annealed out. So, tau is still very low.

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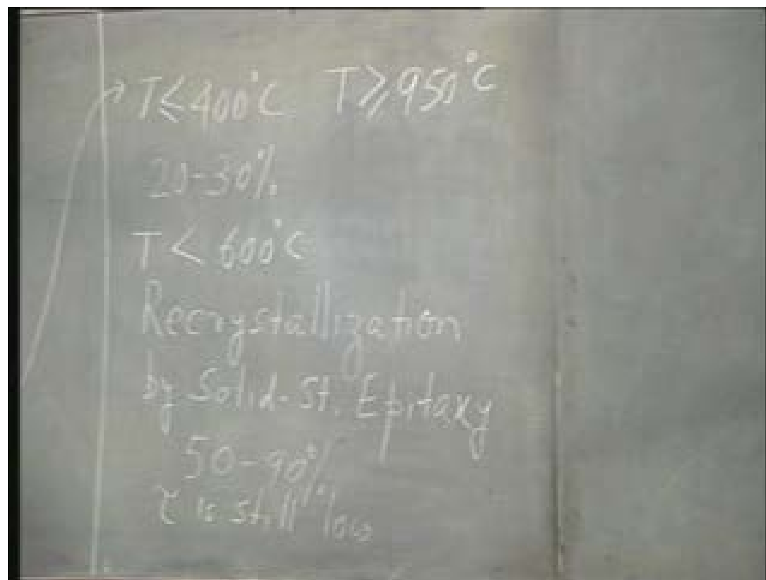

If you really want to get back this carrier life time, if that is very essential to you, then you have go to higher temperature, t greater than or equal to 950 degree centigrade, at which you can get life time recovery. In order to get full life time recovery, we have to go to above 1000 degree centigrade. So you see, the annealing can take place in three phases so to speak; at lower temperature less than equal to 400 degree centigrade, there is partial recovery; 20 to 30% of carrier activation is possible when this disordered cluster just begin to disappear. At about 600 degree centigrade, you have almost 90% of carrier activation that is because of the solid state epitaxy, recrystallization by solid epitaxy; you get back about 90% of carrier recovery. But, the life time recovery is still not there, life time is still very low. If you really want to get the full life time back, you have to go to high temperature, about 1000 degree centigrade that will give you full life time recovery.

So, now depending on what your requirement is and what your obligations are, you can choose your annealing schedule, right. If you can live with low life time, I mean on the other hand, you would like to maintain the annealing temperature and time low, then this phase would be sufficient. On the other hand, if you are really very particular about life time recovery, you have no other options but to go to high temperature. So, this is about the pre-amorphized material, in which case by 600 degree centigrade you have considerable carrier activation.

Let us now discuss the case where the pre-amorphization was not done; either the dose was light or prior to the implantation, we did not carry out a self-implantation. Whatever be the case there was no pre-amorphization. In this case of course, if I have a low dose implant, low dose, light ion implantation, you have full recovery of all the parameters; conductivity, mobility, as well as life time by 800 to 950 degree centigrade.

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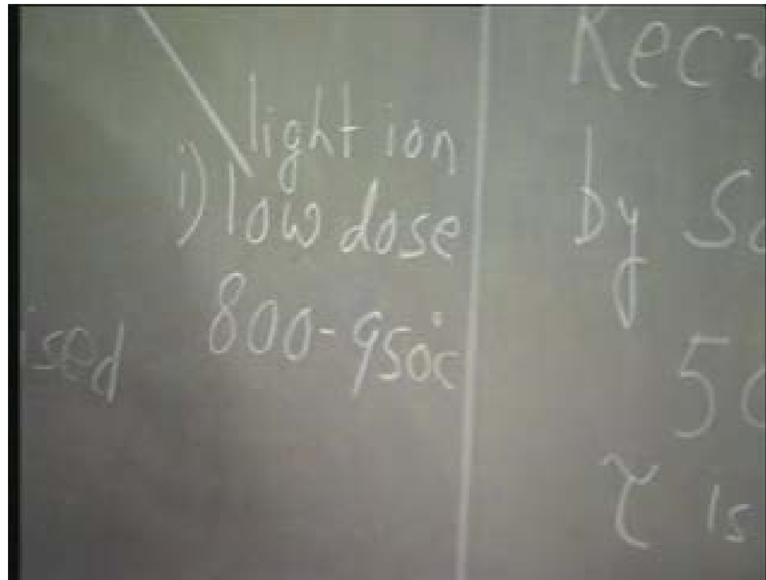

So, if I now look at this other branch - low dose, light ion, what do these things signify? It is low dose combined with light ions. That means the damages are much less. It is light ion, so damages are less; also it is low dose, therefore damages are less. So, this combination, light ion and low dose will have less damage, which can be annealed out in the temperature range of 800 to 950 degree centigrade; all the parameters you will get back, rho, mu as well as tau.

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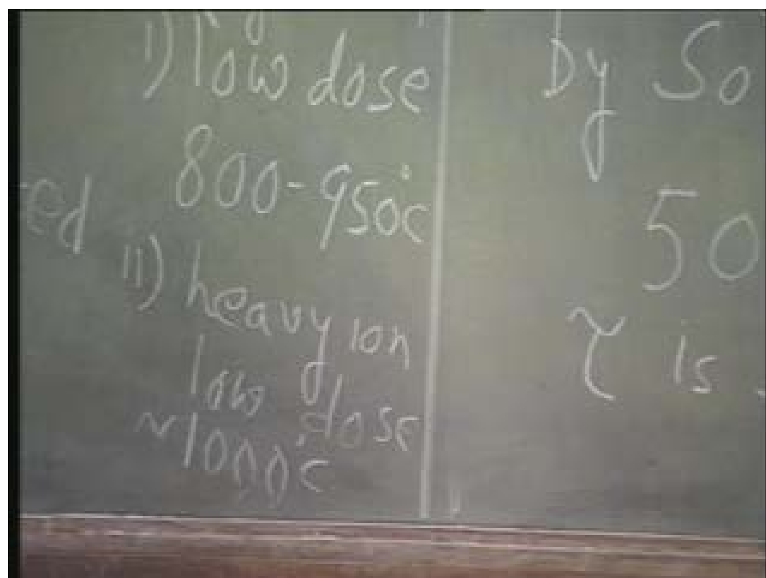

However, if you have heavy ions, situation is slightly difficult. Well, heavy ions still with low dose, you will get back about 1000 degree centigrade, will give you recovery of all the parameters. But, if you have heavy ion in high dose and still it is not pre-amorphized that is the dose is not high enough to make it pre-amorphized, then you have a problem. It will be very difficult to get full activation. Now the interesting point I want to draw your attention to is you see, when the material is pre-amorphized, on the face of it, it looks as if the material is pre-amorphized, it is more damaged, isn't it. Either I have put very heavy dose like, very heavy dose and heavy ion like phosphorus put in very high doses, which will cause pre-amorphization or prior to the implantation itself, I have done some self-implantation which has caused the layer to be pre-amorphized. But there you see, it is much easier to get back the carrier activation; by 600 degree centigrade, I can get back the carrier activation. Compare it with this case. I have light ions in low doses, where the damages are much less, but here I need to go to at least 800 degree centigrade, 800 degree centigrade to 950 degree centigrade in order to get back the full activation.

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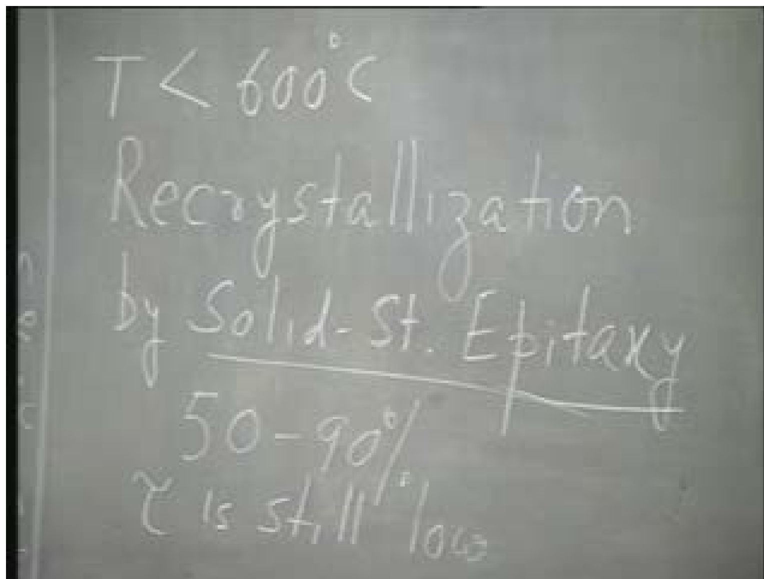

So, if the life time recovery is not very important to me, I would much rather go for a pre-amorphized material where, by 600 degree centigrade I get back 90% carrier activation, if that is my only criteria. So, what I am trying to point out is pre-amorphization is not a bad

thing. In fact in some cases it can be used to your advantage. In order to get life time recovery, anyway you have to go to 950 degree centigrade or above. But, if life time recovery is not that important to you, if you are bothered only about the carrier activation primarily, then you know, it is much better to go for a pre-amorphized material, get it pre-amorphized by a self-implantation, so the carrier activation is obtainable at a much lesser temperature and that is possible because of this solid state epitaxy which can take place at this 600 degree centigrade temperature. So, essentially this is the principle of annealing.

Now, let us consider a few practical cases. That is we will take the case of phosphorus in silicon, boron in silicon, arsenic in silicon and see how exactly the annealing, on annealing, upon annealing how exactly the carrier activation recovery takes place, because that is the prime concern. You know, I mean, you can live with probably a low life time, but you cannot live without the full carrier activation or at least 90% of carrier activation.

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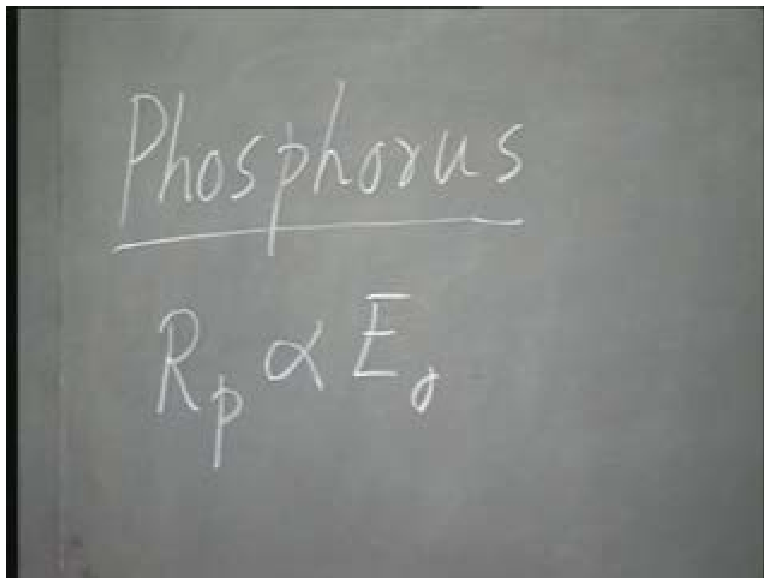

So, first of all let us talk about phosphorus implanted in silicon. Phosphorus is a relatively heavy ion, so it loses its energy primarily by the nuclear stopping mechanism and you

know therefore, the projected range should be proportional to the incident energy. Remember, for nuclear stopping, R p is proportional to the incident energy, for electronic stopping it is proportional to the square root of the incident energy.

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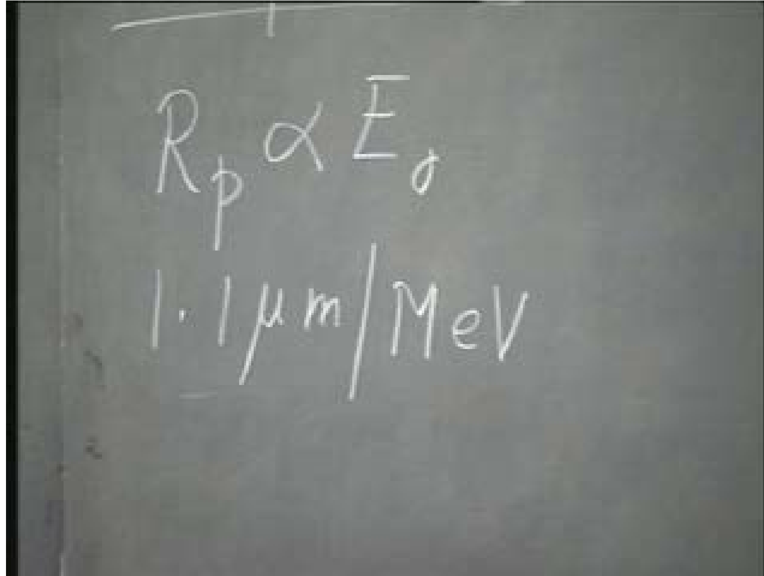

So, because phosphorus is a heavy ion and it loses energy primarily by nuclear stopping mechanism, R p is proportional to E 0 and it is given as 1.1 micrometer per mega electron volt, per thousand kilo electron volt. That means if you have 100 kilo electron volt energy, R p will be 0.11 micrometer. So, obviously it needs a lot of energy to put phosphorus deep into the silicon. During implantation some channeling will occur; some channeling will occur and it will manifest itself as tail in the profile; there will be a deviation from the Gaussian profile, but that will be in low doses only. We have seen, in higher doses since the material gets close to amorphized state, its effect of channeling also gets reduced. So, only in low dose, phosphorus exhibits the channeling behaviour.

Now, let us talk about the annealing of phosphorus.

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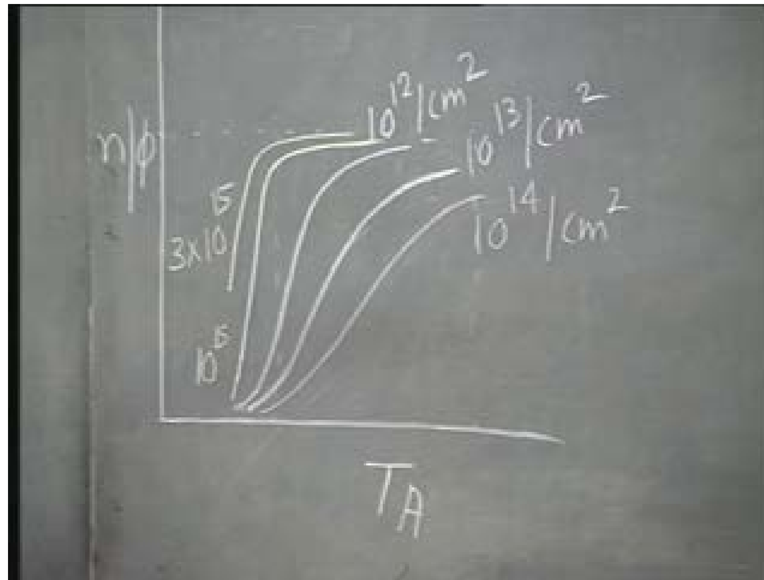

Let me plot the relative active carrier concentration that is n by phi versus the annealing temperature. When I write n by phi, phi is the total dose that you know, you have decided on the total dose and what you are measuring, after the implantation and annealing what you are measuring is the active carrier concentration that is n, so n related to phi, at most it can go to 1. So, the phosphorus annealing actually exhibits a pretty interesting behaviour, you know and you can explain it based on our discussion so far. That is to say, in the range of 10 to the power 12 per centimeter square to 10 to the power 14 per centimeter square, this behavior is like this. Let me first show you how exactly it behaves with changing the dose, then we will discuss why it behaves like this.

Now, if I use phosphorus with higher dose, let us say, we want to you use phosphorus in the dose of 10 power 15 or 3 into 10 power 15, then what happens? Then it follows a path like this. So, look at these curves properly. What is happening? I started from a very low dose, 10 power 12 per centimeter square and I see that as the temperature increases, this is the temperature, as the temperature increases the carrier activation increases till eventually at a point it sort of acquires full activation or let us say, 90% of activation. This line corresponds to full activation, we will say.

Now if I go to a higher dose, from 10 power 12 if I go to 10 power 13, expected that there will be more damages, it will be a bit more difficult to anneal out these damages and although it follows the same sort of trend, the full activation is taking place at a higher temperature; understandable. If I go to a still higher dose, the same trend continuous, the full activation is taking place at even higher temperature. So, this is around 800, 800 degree centigrade, 800 to 900 degree centigrade you could say. But, we see a reversal of trend if we go to still higher dose. You see, when I have gone to 10 power 15, I find that a sharp recovery is taking place, much sharper than these cases, a sharp recovery is taking place at a much smaller temperature. This is about 600 degree centigrade. Same thing is seen for even higher dose of 3 into 10 power 15; in fact if anything it showed a much faster recovery.

Can we explain it on the basis of our previous discussion? Yes, we can. You see, when the dose is comparatively less, light dose, then the material is not pre-amorphized. Even though phosphorus is a heavy ion, since the dose is so small, the material is not getting amorphized. So, in that case you see, the annealing schedule depends entirely on the dose, the lighter dose gets annealed faster, the heavier dose gets annealed later. So, by 1000 degree centigrade, everything will get annealed out. This is what you see. This is at around 800 to 900 degree centigrade, so by 1000, it gets completely annealed out. On the other hand, when I use a really heavy dose of phosphorus, in excess of 10 power 15 per centimeter square, then the material gets pre-amorphized and when it gets pre-amorphized, you know that up to 90% of carrier recovery is possible by 600 degree centigrade itself, due to recrystallisation by solid state epitaxy and this is what is taking place here. By 600 degree centigrade, I have come to the mu of this curve that is at around 90% of carrier activation. So, this is the annealing behavior of phosphorus.

If we consider the case of arsenic in silicon, arsenic also behaves in a manner very similar to that of phosphorus. Here also R p is proportional to the incident energy. The only difference is in the value of R p. In case of phosphorus, we have taken it to be 1.1 micro meter per mega electron volt. In case of arsenic, it is about half of that. It is 0.58 micrometer per mega electron volt; otherwise the behavior is very much the same.

Let us now move on to the other important material, other important dopant material in silicon, almost the only p-type dopant that is available to us and that is boron.

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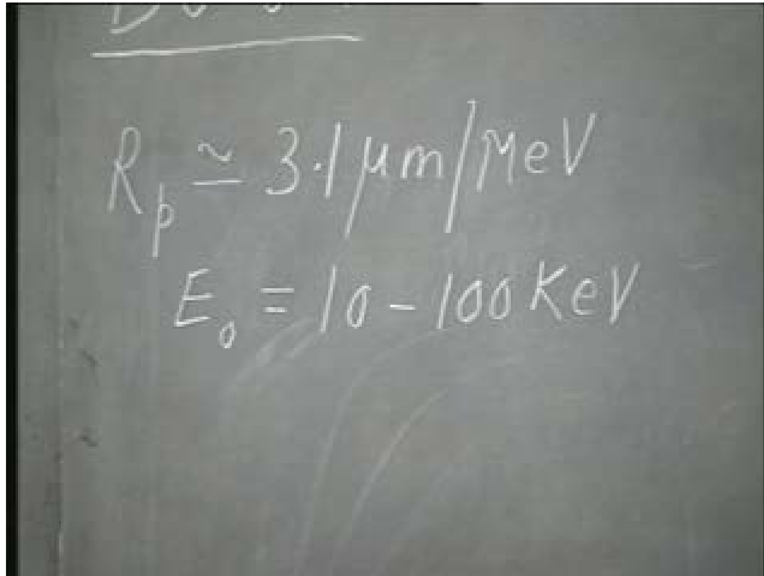

Now, boron is a light ion. Boron is much lighter compared to phosphorus. So, for boron R p is given as …… Since boron is a much lighter ion usually the implantation energy is much smaller. So, for boron, for the incident energy range in 10 to 100 kilo electron volt, the projected range is given as 3.1 micro meter per mega electron volt. So, imagine, it is three times that of phosphorus. But, the more important point is if the incident energy is greater than 100 kilo electron volt, then nuclear stopping will no longer dominate. It will be dominated by electronic stopping and in that case R p will be no longer proportional to the energy, but it will be proportional to the square root of energy.

In another word, we could say that R p will become sub linear with energy. It will not follow a linear pattern with energy, it will deviate from that, it will become sub linear and boron distribution is not really a Gaussian distribution, instead it is a slightly skewed function and that is given by Pearson …. distribution. In fact you are using the process simulation package called supreme. In supreme, the boron implantation profile is given as the Pearson ….. distribution while that for phosphorus is given as a Gaussian. Phosphorus

represents a Gaussian profile more closely, but boron will represent a Pearson …. that is a skewed function, not really a symmetric function like a Gaussian.

Now, let us also investigate the annealing behavior of boron.

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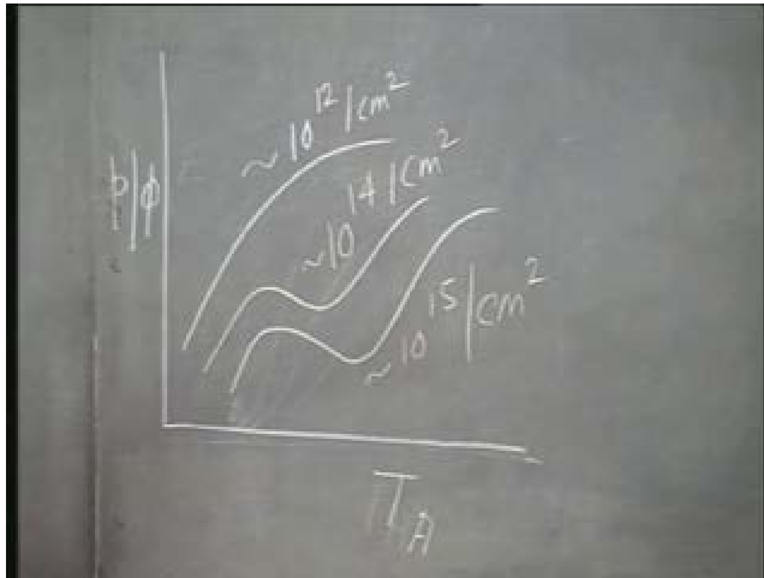

This also has certain anomalies. Again as before, let me plot the relative carrier activation p by phi that is active hole concentration as a function of the dose, normalized to the total dose versus the annealing temperature. What would you expect? You would expect since in this case it is light ion, no question of any pre-amorphization. In all the cases I am assuming that there is no self-implantation, I have deliberately not created a pre-amorphized layer. So, whatever is happening is happening only because of boron implantation or in the previous case for phosphorus implantation. So, in this case, since boron is light ion, I do not expect any pre-amorphization to take place. So, what should I expect? I should expect that as the annealing temperature increases, the full carrier activation is also increasing. In other words, what I would expect is a profile like this, agreed. Everybody has agreed, right.

Well, this really happens when the dose is comparatively less say, of the order of 10 power 12 per centimeter square or something into 10 power 12, say 5 into 10 power 12 for example, this really happens. If however you go to higher doses, then you begin to find a very funny situation. This is happening say, for around 10 power 14 per centimeter square. If I go to still higher dose ……

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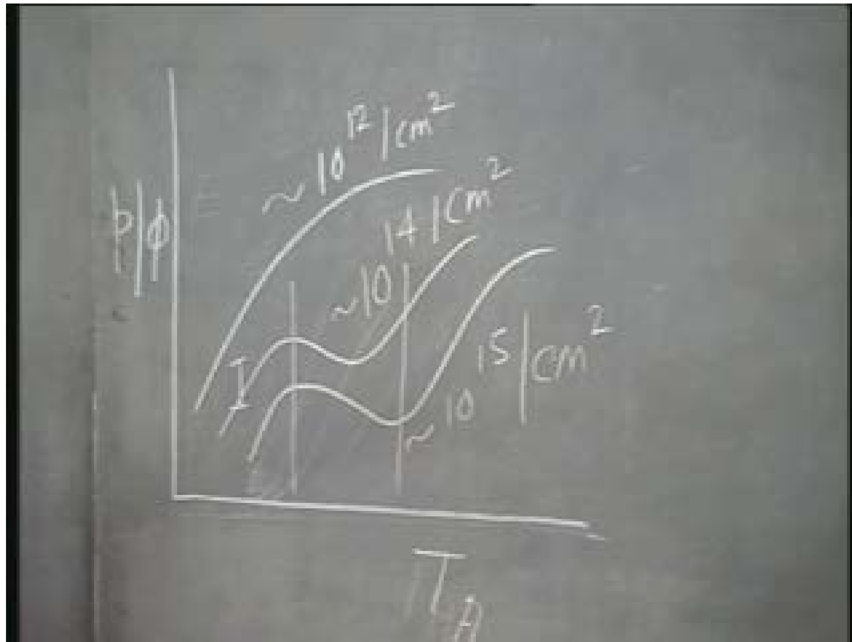

I can divide this anomalous curve in three regions. What is happening in region I? Region I is very straight forward; it is merely following what was happening in case of the low dose case. That is as the annealing temperature increased, the carrier activation also increased; no problem. This is what you expect, right. As the temperature increases, the point defects are getting removed, carrier activation is increasing; expected behaviour. What is happening in region II, is more difficult to explain. What is happening there? Even though I keep on increasing the annealing temperature, the activation as a matter of fact, is decreasing. Again, when I move on to region III, I find that the carrier activation begins to increase with annealing temperature, which is again perfectly understandable.

What really is happening in region II? Why should the carrier activation decrease with an increase in the annealing temperature? This is an anomalous behaviour in boron implantation. You know what really happens? You see, because of the implantation damages you have borons sitting not in the substitutional sites, they are probably sitting in the interstitial sites and you also have a number of host atoms that is silicon sitting in the interstitial sites, right. So, when you are annealing out, you are annealing both these defects that is you are trying to push boron in the substitutional sites as well as you are trying to push the silicon atoms back in the substitutional sites. So, it is like a race between silicon and boron. Both of them are racing to occupy the substitutional sites and in this region II, in this race boron is losing, silicon is winning.

So, silicon is kicking the boron out from its substitutional sites and itself going and sitting in those places. Therefore, your active carrier concentration is actually going down even though you have increased the annealing temperature. What is happening is silicon atom is going and sitting in its lattice site. It is not allowing the boron to occupy the substitutional sites. So, essentially it is a race between silicon and boron and silicon seems to be winning in this place. However as I go to region III that is as I increase the annealing temperature, then you are creating a lot of vacancies, you are supplying a lot of thermal energy; you see, when you are increasing the temperature, you are supplying a lot of thermal energy and therefore you are promoting the vacancy formation. So, now there is enough place for boron as well as for silicon. So, now boron can get back into its substitutional sites and therefore, the active carrier concentration also increases. So this is the annealing behavior of boron.

Now remember, when you are carrying out this annealing, you are also promoting some diffusion. At this high temperature, the profile can change to a certain extent. It will not, it may not remain exactly as the implantation profile. So, how is the profile going to change? Let us think about the two profiles. During implantation, the profile you had is a Gaussian profile, had a Gaussian ion implanted profile and now, when you are carrying out the annealing, you are not supplying any extra dopant material, right. So, it is actually a constant total impurity case; drive-in, analogues to drive-in, right. I am not supplying

any extra impurity; whatever impurity was put inside the semiconductor is still remaining there. So, what was the profile for the constant total impurity case? That is also a Gaussian profile.

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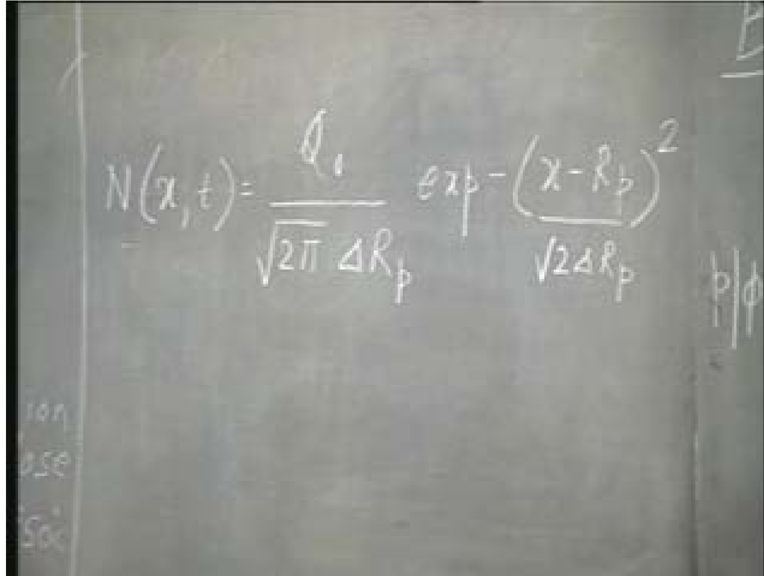

So, I have essentially two Gaussian profiles and at the end of annealing therefore, I can have a superposition of these two Gaussian profiles, which will work out to be something like, remember for ion implantation it was like this. Q 0 that is the total dose divided by root 2 pi delta R p exponential minus x minus R p by root 2 delta R p whole square. That was the profile just after ion implantation.

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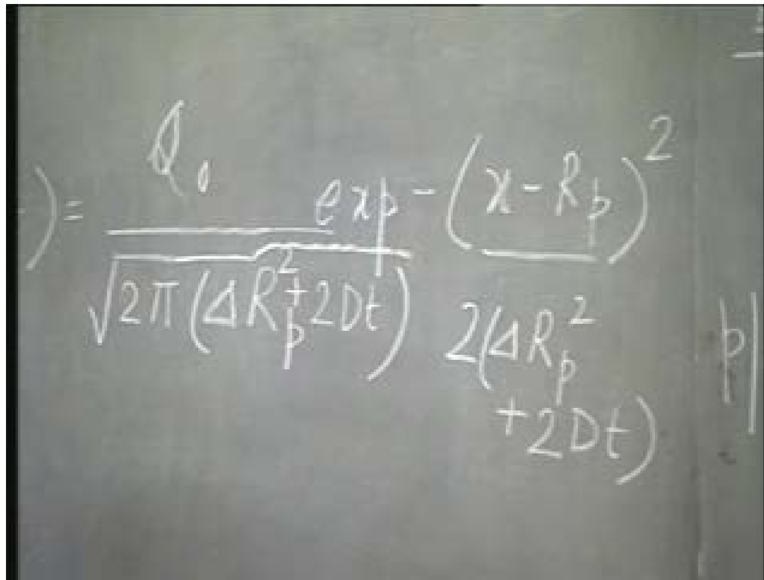

Now, because of annealing it gets modified by ….. and this I can write simply by …… That is I am merely replacing delta R p as square root of delta R p square plus twice D t.

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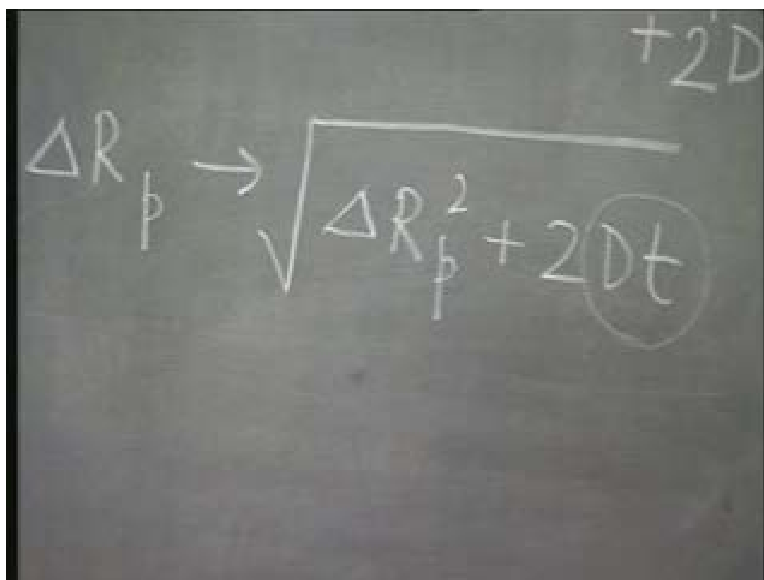

I am replacing delta R p. So, unless and until this term becomes really very large, there is no change, not major change in the shape, in the nature of the doping concentration profile. Only when D t is much greater than delta R p square, so that this term begins to

dominate, you would not have much appreciable change. But because there is a possibility that the ion implantation profile can get modified to a certain extent when you carry out the annealing, nowadays, after implantation annealing is done by a rapid processes. See, the annealing process we have discussed so far, it is actually conventional furnace annealing. That is you subject the samples to high temperature for a given amount of time say, 20 minutes or 30 minutes, at different temperature. So, you can have, you have the annealing going on for a finite amount of time.

Nowadays, the process that is favoured is you subject it to a very high temperature, but for a very short duration, one minute or even then less than that. This is called rapid annealing. This rapid annealing can be a rapid thermal annealing or RTA; it can be a laser annealing. That is you subject the wafer to a laser beam, a pulsed laser beam, where the laser beam is switched on for may be a few milliseconds, it recrystallizes the surface of the sample. So, the advantage is that there is absolutely no change in the doping profile.

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You see, this t, you are keeping this t extremely small. So, even when the temperature is large, the product D t still remains very small. Therefore, the dopants do not have sufficient time to move inside. There is absolutely no change in the doping profile and the

recovery is comparable or even better than the conventional furnace annealing. So, you have increased the throughput also, because these rapid processes, they need much less time; rapid thermal annealing or pulsed laser annealing will be accomplished in a much shorter duration. So, the two basic ideas are one is rapid thermal annealing, in which case the samples are actually taken inside a chamber, chamber is evacuated, then you can put in, pump in some inert ambient or hydrogen and usually the heating is provided by a battery of lamps.

An array of lamps are there, kept inside. The inside surface is a reflecting surface that is it is mirror coated, so as to improve the efficiency and you switch on the light for a few seconds, may be 30 seconds or so. So, very quickly the temperature stabilizes. It reaches a high temperature and then it stabilizes. So, you subject your wafers to that high temperature for a short period of time and then switch off the lights and cool it; air cooling or liquid nitrogen cooling or water cooling, a variety of such cooling systems are possible, so that the temperature is brought down also very quickly. Both the things are very important, remember. You have to raise the temperature very fast and you also have to bring down the temperature very fast. These are the two prime concerns in a rapid thermal system and on the other hand, in case of laser annealing, you have a pulsed laser beam which can melt the amorphous layer and then recrystallizes without any extended defects. So you see, again the recovery will be total and it will be very fast, because you are actually doing a recrystallization; you are very quickly removing all the damages.

So, these are the two major branches of rapid annealing, which is very popular nowadays. After implantation, the rapid thermal annealing or pulsed laser annealing, they are very popular. They are also, in a way they are very convenient because they are absolutely contamination free, you know. Most of these things are done in a vacuum chamber. You keep the wafer in an evacuated chamber, so there is less chance of contamination. It is inherently cleaner process; cleaner, less contamination and very short time and the recovery is even better than that of the furnace annealing cases, without any chance of modification in the doping profile.