Non-conventional Energy Resources
Prof. Prathap Haridoss
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture – 15
Solar Cell: Growing the single crystal and making the p-n junction

Hello, in the last couple of classes we have looked at the semiconductor and we have also looked at the p-n junction. In these classes we have been looking at a series of topics associated with the idea of capturing solar energy in the form of you know directly in the form of electricity and essentially using a photovoltaic process to enable that. So, it is in that context that we looked at the semiconductor as well as the p-n junction.

When we looked at the semiconductor as an independent entity we looked at its band diagrams, we looked at the origin of those band diagrams, we tried to you know at least briefly look at how the internal structure of the material impacts the band diagram and the behavior of the electron with respect to that internal structure creates that band diagram. We also looked at those flat band diagrams we looked at the e versus k curve and how those you know interactions between e versus k curve and the periodic structure of the element creates the band diagram for you.

Then in the next class that we looked at we looked at the p-n junction where we are looking not just at an individual semiconductor, but at the idea that you can take two different semiconductors one which is p doped and one which is n doped and then bring them together at least conceptually that’s the way we would look at it. And then we try to understand what are some characteristics that happen that that are there for such a junction and possibly what could happen if you bring such a junction together what would be its you know operational characteristics so to speak.

We also looked at you know how the energy of the p side will look like with respect to the n side and that the idea of this Fermi energy being constant and then that there are some band bending features that appear. So, these are all the things that we looked at the last couple of classes it was a little bit intensive from the science side of it we will get back to that and take that forward from our next class.

In this class I wanted to do something which is a little bit more technology oriented to get a better sense of how this technology comes together because we. Now, know what the semiconductor is, we understand that there is something called a p-n junction, we understand that we wanted to be we want the junction to be good even at an atomic level. So, for example, I indicated to you that it doesn't help if we take a separately a p material and an n material and then you press them together the contact between those two surfaces is so bad even though visually we don't realize that it seems like to polish surfaces have been pressed against each other visually we do not realize it. The contact between those two surfaces is so bad that it would perform extremely poorly as the p-n junction. So, we do why we understand the signs of it we also need to acknowledge the practical aspects of it and actually create this junction in in a way that that would work as predicted based on the characteristics we are expecting.

So, in this class we will actually look at growing the single crystal and making the p-n junction and some associated aspects although the title is on the single crystal will also look at amorphous silicon and we will look at various characteristics associated with it. So, there is a little bit of a technology orientation for this class. We will get back to the science of it in our upcoming classes.

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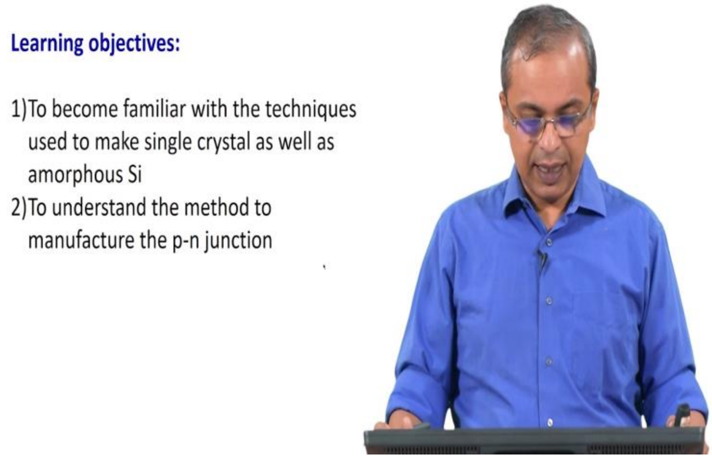

Learning objectives:

1) To become familiar with the techniques used to make single crystal as well as amorphous Si
2) To understand the method to manufacture the p-n junction

So, our learning objectives for this class are to become familiar with the techniques used to make single crystal as well as amorphous silicon. So, that is our learning objective a main objective. So, there are some specific techniques it's a good idea to get a sense of what those techniques are, so you see a chip you see it and you know you go see a solar panel you will see a chip there you can also look at you know semiconductor chip which may be there in various places in electronic devices that we use. But where does that come from and what are some challenges in putting that together. So, we will look at it so.

So, techniques used to make those single crystals as well as an amorphous version of it and having understood that we will also briefly look at starting from there how you would make a p-n junction. So, these are two things that we will look at as we go through the contents of this class.

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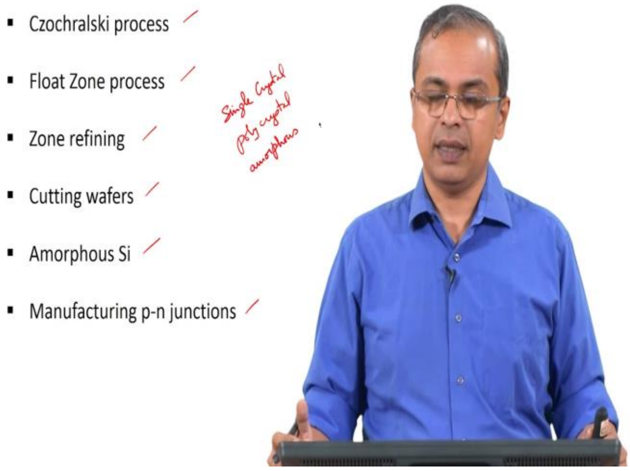

- Czochralski process
- Float Zone process
- Zone refining
- Cutting wafers
- Amorphous Si
- Manufacturing p-n junctions

Single Crystal
poly crystal
amorphous

Okay so, to do this more specifically we will look at two processes one is called the czochralski process and the other is called float zone process. So, these are two processes that are used to create that single crystal. So, they have some you know details associated with them at least briefly we will consider that. So, that you become familiar with the when you see a single crystal you know what is the effort that has gone in towards making it.

We will also look at something called zone refining it's it's an idea that is used to purify some material and purity is a very critical thing in semiconductor industry and we will see some you know parameters associated with purity, what kind of level of purity we are talking about and therefore, how challenging it is and therefore, you know you need some special techniques to do it and zone refining is one of them. So, we will talk about it. We will also look at the cut how a wafers are cut because finally, initially we when we when we go through this contents we will see that what is first created is a pretty big object solid object you know it is not anything like what you see in your computer and therefore, that or on the solar panel and therefore, that has to be cut into very fine slices before can be used anywhere. So, that is something we look at. We look at amorphous silicon how that comes about and finally, we will look at how p-n junctions are manufactured. So, this is what we would do.

So, as we go over this I think you what you will find as a common thread that goes through this set of topics that we are going to look at in this class is the fact that there is something associated with crystal structure okay. So, particularly we are talking of terms such as a single crystal, we can also talk in terms of a poly crystal and we can talk of an amorphous material, so amorphous material.

So, these are three different kinds of material that we can consider. And that’s the thread that runs through, so the same material essentially the same material. So, in this case for example, we are talking of silicon. Silicon can be made available to us in all these possibilities as a single crystal as a poly crystal and as amorphous material. So, we look we will start off first by understanding what is the difference between these and then from that we will move towards each of these techniques.

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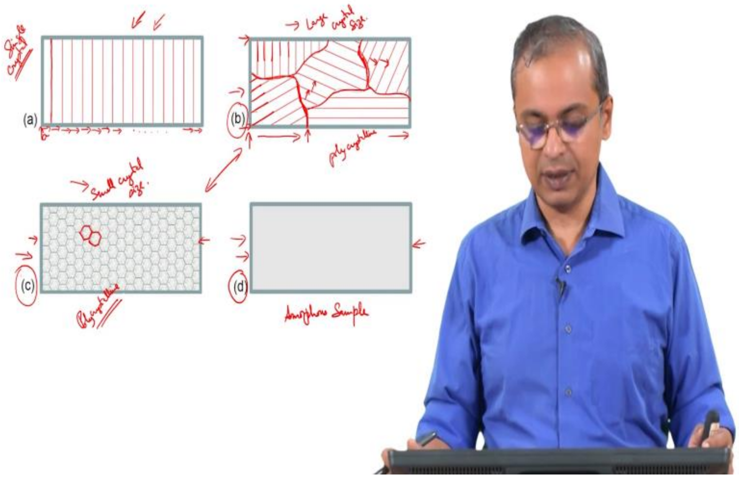

So, if you see here what you see on your left top corner is what we would refer to as a single crystal right. So, what does that mean? A single crystal basically means that if you start from one end of the material. You will see crystal in order, so you are going to see you know from start from this end and you move in some direction let’s say you move some distance a and you arrive at one plane a crystallographic plane. Then if you continue another a you will get you will again arrive at the plane one more a you will arrive at the plane and so on and this process will continue all the way till the end of the crystal. So, you can do this and you arrive at the end right. So, all the way to the end from one end, one point, one starting point in the crystal to the other end of the crystal the atomic planes will be in perfect order.

So, when I say from one end to the other I am talking of from one end to the other of an object okay an object that you can hold in your hand. So, some big object that that is sitting in your hand which you can hold and lift up with your hand from one end of the object to the other end of the object the atoms are in perfect alignment. So, they are perfectly aligned from one end to the other. So, therefore, if you see one orientation of atoms on one end you will see exactly the same orientation in the other end. So, something like that is referred to as a single crystal and that is not easy to manufacture. It takes a lot of effort to get as that kind of a sample where you can have this big block of materials sitting in your hands where this perfect atomic order from this end to the other end.

What we are more likely to see are more along the lines of b and c okay. So, both of these are polycrystalline materials material. So, this is also polycrystalline okay. So, both of these are polycrystalline. So, now, what you see here for example, are boundaries. So, this is a boundary, this is also a boundary here, you can see some specific boundaries here I am just tracing them out for you. So, it is easy to see. So, these are boundaries.

So, now, what it means is if you start off from one end of the crystal. So, first of all even the same this end of the crystal itself if you go from the bottom of the crystal to the top of the crystal you don't see the same order. So, the top of the crystal you see these planes vertically down let's assume we are looking at the same plane you see those planes vertically down and the top of the crystal, but those planes happen to be at an incline and this end of the crystal bottom end of the crystal which was not true on the in the example that we saw here right.

So so, as you start off itself when you go from the bottom of that sample to the top of the sample on your left hand side of the sample let's say the order is not maintained and further as you move into the crystal as you move away from that end as you approach this end you will find at various locations such as this the orientation will change.

So, in this example for example, it is just changing in one place. So, it changes here as you go from the left to the right following the path on the bottom of your sample, but that can vary from sample to sample you may have had 3 divisions in the middle you might have had 100 divisions in the middle, so on.

So, this idea that you have crystalline order only up to a certain location. So, for example, this location and then after that there is a breakdown of order at least at that boundary at this boundary area there is some breakdown of order. So, there is some breakdown of order there and then again order starts in this in this location. So, you see some crystalline order in that location again order breaks down in this region here and then once again you have crystalline order.

So, this idea that you have pieces of crystalline order with boundaries in between them is then referred to as a polycrystalline situation okay. So, this sample is poly crystalline in nature. It has many crystals that is why poly crystals which are now, distributed across the sample.

So, what’s the difference between these two? The main difference is the crystal size. So, this is small crystal size this is large crystal size. So, that’s the difference between these two samples both are polycrystalline. So, in both of them you as you go from one end to the other you see so many boundaries, so many boundaries here. So, for example, this is a boundary that is, so this region is a crystal a neighboring region has a crystal oriented differently and so on. I mean it’s just a pattern that I have put that, but it could be in any shape it does not have it doesn’t even have to be so uniform in size. So, this happens to be a uniform grain size crystal size sample, but this is not. So, b is not so, where a c happens to be a very uniformly sized crystal sized sample.

So, that is just an variation. So, you can have small crystal size you can have large crystal etcetera and you can notice that the 4 samples that are on screen at least for visual examination are essentially the same size. So, you can think of physically itself samples of the size that you are holding in your hand which are having all these characteristics.

The final sample that we have here is what I have marked as d which is a sample which is having complete disorder as you start from one end of the sample and you approach the other end of the sample. So, as you go from one end of the sample to the other end of the sample there is no sustained crystal in order to any degree that you can you know seriously measure. So, it is basically an amorphous sample. So it’s an amorphous sample there is no crystalline order. So, you start from an atom you head off in some direction you may find an another atom. If you head continue in the same direction at the same distance there is a chance that you will not find the next atom you have to go little bit to your right or little bit to the left to find third atom then from that again you move forward in that same direction again you may have to go a little to the right or a little to the left to get to the fourth atom and so on. So, it is just in a disordered way those atoms are sitting and so that’s an amorphous sample.

So, so this is the layout that we have of you know structure that you can have in a material and silicon for example, is available to us in all these possibilities you can get a single crystal silicon you can just know you can buy commercially you can buy or you can make in your lab, single crystal silicon, polycrystalline silicon with large crystal size, polycrystalline silicon with small crystal size and amorphous silicon all of these are possible. And as you may expect it turns out that because of the existence of these boundaries. So, essentially we are talking of something that is starting from high degree of order this is high single crystal is highly ordered sample you are increasing the level of disorder as you go to a large crystal size sample even more disorder when you come to a small crystal size sample and then finally, a very significantly disordered sample which is your amorphous sample.

So, in turns out that as you increase the level of disorder in the sample the properties of the sample change okay. So, there is some variation in property sometimes the property changes in some kind of a predictable way and then it may be that you have multiple trends, you have a trend for some range of crystal sizes, then you have another trend for another range of crystal sizes and so on and it is in this context that you infact you know you even have this field of nanomaterials. So, when you just go to this polycrystalline samples and you start reducing the crystal size more and more and more.

The way the property changes actually becomes very interesting. So, whereas, it may have had a certain trend up to a point as you keep decreasing the crystal size when you go to very fine crystal size suddenly the trend becomes inverted or it becomes something totally different. And therefore, the same material is now, suddenly available with you with some properties that you never anticipated that that material will have. And that’s that that’s the whole field of nanotechnology regardless of you know which nano material you are talking about the idea that when you go into that nano scale with extremely small crystal sizes the material behaves dramatically different from the exact same material in a large crystal size sample okay.

So, that is anyway something that we can keep in mind. So, anyway, you we can get silicon in all these possibilities. And as we look through other techniques in this class this is essentially what we are going to do. We are mostly trying to look at techniques that get us the single crystal and then the end we will also look at techniques that get us this amorphous sample so, but in general if you look at say solar cells you can get single crystalline solar cells you can get polycrystalline solar cells and you can get amorphous solar cells. Cost wise the that’s the order I mean the single crystal is most expensive, the polycrystalline is a less expensive, amorphous is a relatively the cheapest of those cells.

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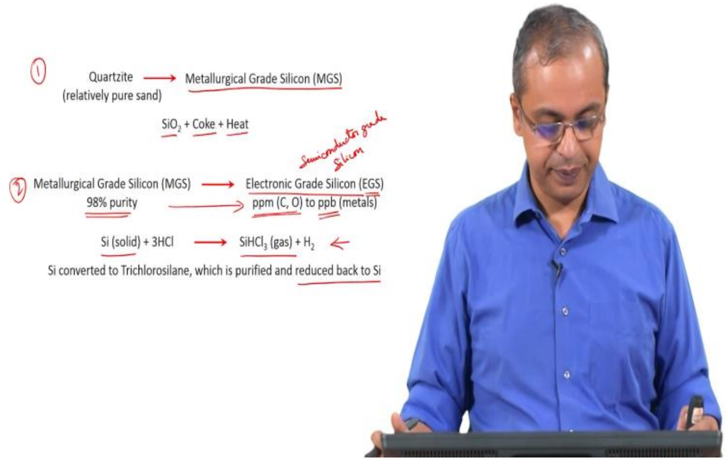

① Quartzite → Metallurgical Grade Silicon (MGS)
(relatively pure sand)

SiO_2 + Coke + Heat

Semiconductor grade Silicon

② Metallurgical Grade Silicon (MGS) → Electronic Grade Silicon (EGS)
98% purity → ppm (C, O) to ppb (metals)

$Si\ (solid) + 3HCl \longrightarrow SiHCl_3\ (gas) + H_2 \leftarrow$

Si converted to Trichlorosilane, which is purified and reduced back to Si

Okay so, if you go back go all the way to the beginning and start you know where you going to get the silicon, silicon is well abundantly available it is sand it is there as part of sand. So, silica is there in our sand. So, what normally happens in the silicon industry is that we first start with sand and we find some good quality sand which is relatively pure which does not have too many impurities in it and so on and we take that sand and we create something called metallurgical grade silicon. So, metallurgical grade silicon is what we try to generate and this is basically starting from sand which is SiO_2 and then you essentially reduce it and you will get silicon.

So, and for that primarily you take SiO_2 you add coke and you add heat and then you continue that reaction process. It it has some steps associated with it I am not going into the chemistry in a great deal, but this is the basic idea you start from silica and then you get silicon SiO_2 becomes Si, when you go from quartzite which is relatively pure version of sand to silicon which is the metallurgical grade silicon. So, this is sort of bulk processing of silicon and this is relatively inexpensive you can get you know significant quantities of metal metallurgical grade silicon.

This silicon is 98 percent pure okay. So, 98 percent pure many times when we think of purity you know nineteen percent seems like a good number I mean you say it is pretty pure its pretty good pretty clean material, but if you actually look at what is required with respect to the electronic industry 98 percent is like which means 2 percent impurities, 2 percent impurities is an extremely poor quality sample. It’s an extremely poor quality sample to the point that you really cannot do anything meaningful with it will not give you the properties that you want, it will give you really bad properties you cannot really done many significant tests with it you cannot really do something you cannot really create the kind of you know devices that you would like with a material that is only 98 percent pure.

So, from metallurgical grade silicon we need to create something that is referred to as electronic grade silicon EGS it is also referred to as semiconductor grade silicon okay. So, its metallurgy electronic grade silicon or semiconductor grade silicon you can see here the difference what was you know 2 percent impurity, now suddenly drops to ppm parts per million of carbon and oxygen in it and parts per billion of any other metallic material present in it. So, this is a remarkable you know shift from going from you know several orders of magnitude you are changing in purity when you go from something that’s 98 percent pure to something that is you know having parts per million of impurities parts per billion of impurities and so on.

So, to do that in fact, what they do is actually a process where you take silicon solid. So, you have to start with silicon solid and you have to arrive back at silicon solid right. So, you are going to start with silicon solid you going to do some processing. So, it may in the middle it may become something else and then in the end you again get back the silicon solid except that. Now, it is a purer silicon solid. So, that’s essentially the idea in this step here. So, if you consider this is a step 1, this is essentially step 2.

So, step 2 is you take silicon solid you react it with HCL and you will essentially get this trichlorosilane gas trichlorosilane. So, that is the, it is in gas phase and then once it is in the gas phase we can purify the gas. So, there is it may be it may have other constituents in the gas we do some separation some kind of you know fractional distillation etcetera etcetera and then you you can separate out the trichlorosilane such that you now have trichlorosilane in a purer form you don’t have anything else along with it. So, that way we separate out this silicon fraction and then you again reduce it back to silicon you reduce it back to silicon.

So, in many ways this reaction is the same you simply go in the forward direction initially to create this trichlorosilane and then go in the reverse direction to get back your silicon. So, you set the condition such that it will go on the forward direction get this trichlorosilane and then go on the reverse direction get back your silicon except that in the middle there is a purification step the trichlorosilane is separated out from any other constituent that is there and so you have a purer version of this trichlorosilane that is then reduced and you get back your silicon. So, when you do this process you get this electronic grade silicon okay. So, so that's how you arrived at this electronic grade silicon.

Most likely that sample is going to be polycrystalline nature. So, most likely you are having polycrystalline electronic grade silicon which is a so pretty significantly pure silicon sample typically polycrystalline in nature which is going to be available to you which on which you have to do further processing to generate whatever sample you are interested in working with okay. So, this is the base background situation from where we start and then we try to create the samples that we are interested.

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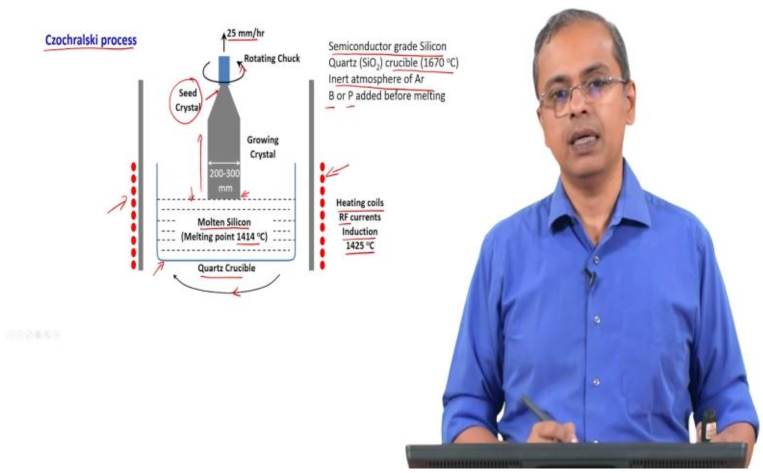

Czochralski process

Semiconductor grade Silicon
Quartz (SiO_2) crucible (1670 °C)
Inert atmosphere of Ar
B or P added before melting

So, from here we will now, move to the czochralski process. So, in the czochralski process what we do is we are trying to now the next two processes we are looking at we are trying to create a single crystal of this sample we have electronic grade silicon available to us from there you would like to create a single crystal of silicon.

So, there are a few things that are done there. Essentially what is the basic idea is you have to melt this material and then when it recrystallizes you have to set the conditions right that it cannot it recrystallizes as a single crystal that’s the basic idea. So, you take something that may be polycrystalline in which case the atoms are you know the order is being broken repeatedly at several locations which are those grain boundaries and then you melt it so that you now, have atoms in a molten state. And then when it recrystallizes you don’t allow them to break order you will try to encourage them to stay ordered. So, that is the basic working principle here.

So, what we do here is we have a crucible a quartz crucible in which we have molten silicon. So, you have molten silicon. So, this melting point is about 1414 degree C. So, molten silicon is there this is electronic grade silicon or semiconductor grade silicon this is what is being used here. And the crucible itself is actually of a higher melting point 1670 degree C or higher based on you know the exact phase that is there, but that is the melting point that is present there and you have to heat it. So, you have to first heat it. So, you have heating coils here. These heating coils are essentially using this induction process sort of you know like the induction stove that we that seems to be prevalent these days it’s an induction process.

So, you have an alternating current in the with radio frequency RF frequency current that is flowing and that causes the induction and because of the induction that’s heating and because of heating the silicon the silicon melts. So, that’s how the melting occurs and we are trying to maintain about 1425 degrees C which is just above just a few degrees above the melting point of silicon.

So, we melt it, but we don’t go to very high superheat we just stay just a little bit above the melting point. The reason being from this melt we want to crystallize something. So, what is crystallizing has to you know naturally be a little cooler only then it will crystallize. So, we have to maintain the liquid at a slightly higher temperature the solid at a slightly lower temperature compared to the melting point and then in that process you can keep the solids separately.

So, this is the basic idea. So, on both sides you have these heating elements and we have some inert atmosphere because we are already taken some effort to you know prevent impurities from coming into the system. So, we want to make sure that we don’t reintroduce impurity. So, you keep an inert atmosphere so that impurities do not come in. However if you want to do doping, so this is a good time to do it, you can add either boron if you want to create a p-type semiconductor or phosphorous if you want to create an n-type semiconductor one of those two can already be added into this melt. So, that the single crystal that forms will automatically already have this boron or phosphorus present in it, so the doping can be taken care of in that sense.

So, we have molten silicon and then what we do is we first introduce something called a seed crystal okay. So, in the next slide I will show you that in a step by step basis in this I am showing in the overall picture. So, we introduce something called a seed crystal which is right now, up here. So, originally that seed crystal would have just come in contact with this molten liquid.

So, once it comes in contact with the molten liquid and there is cooling occurring very close to this then what happens is the liquid begins to solidify, the atoms in the liquid begin to attempt to solidify they will try to solidify on this seed crystal. So, the seed crystal is a small single crystal which you can easily cut out of a polycrystalline sample if you wish, where you know the orientation. So, you know the orientation you keep that orientation some crystal surfaces there the front of that crystal and that comes in contact with that molten liquid. When you do that the atoms which are below actually in the liquid state find it energetically more favorable to line up with the atoms that are in the solid instead of randomly lining up.

So, they line up they given a chance they would line up with those solids because that is the lowest energy state for them. If they did not line up with atoms in the solid that’s a little higher energy state, if you give them a chance they would line up, and you are at the melting point. So, you are in a position to give them a chance and to actually increase their chance you actually rotate that you know very slowly you rotate the seed crystal you also rotate the crucible by rotating it you are giving the atoms some level of movement without too much movement some level of movement. So, that they can skip reorienting reorienting and then getting into the lowest energy state possible they have enough thermal energy you give them some ability to reorient they reorient and you get this lowest energy state lining up with the atoms in the seed crystal.

And then you gradually pull that seed crystal out very very slowly you pull the seed crystal out. So, you are pulling it out at 25 millimeters an hour okay just two and a half centimeters every hour every hour you pull it out the two and half centimeter slowly gradually it is getting pulled out averaging 25 mm per hour okay. So, when you do that this single crystal begins to grow.

So, as you keep pulling it out more and more liquid keep solidifying and in all the solidifying liquid is forming a single crystal in line with the seed crystal and then it continues to grow and then eventually do you have a large single crystal and you have essentially consumed all of the molten silicon that is present. We of course, just have a sum holder here which is being referred to as a chuck and the chuck holds that seed crystal and then and it can be rotated. So, that is the basic idea that we use in this czochralski process and you get this single crystal that grows.

Generally given the nature of the, you know the dynamics of this whole process the induction heating that is happening you know the kind of conditions under which we are operating. Generally the kind of diameter they are able to succeed to get is about 200 to 300 millimeters diameter these days they are finding ways to make even larger single crystals larger diameter single crystals, but this is the kind of diameter you are looking at. I will also tell you that in in both these processes the czochralski process as well as the next process that I am going to talk about the because there is you know liquid which is trying to solidify onto a solid there is always some surface tension related behavior. That's the reason why you get the circular shape circular cross section, otherwise you could even get a square cross section or you know some other cross section.

But because it's a liquid which is in a position to you know shape itself based on its surface tension you get that circular cross section because that gives it's the least parameter and if it where you know 3 dimensional it will take the spherical shape, but here you are you know your position of interaction is a 2 dimensional surface the bottom of the seed crystal and the top of the liquid. So, you are only have a 2 dimensional surface there they are in contact with a 2 dimensional location.

So, there instead of a sphere it takes a circular shape and so, these single crystals that grow are typically circular in cross section. And, so what you eventually get what you are seeing here is actually a cylinder it's a cylinder cylindrically shaped a single crystal. In fact, that's the reason if you look at solar panels where they have used slices of the single crystals you see circular cross section there you don't see some random shapes you see circular cross section. So, anyway, so that is the idea of the czochralski process.

So, it is czochralski is a person credited with it apparently he discovered it by accident and he found that you know when he was working with some melt he could pull out a single crystal by you know pulling contacting it and then pulling something out which was cooling very well. So, that is the basic idea. So, this is one way in which you can generate the single crystal.

The same thing in a step wise sequence I am just showing you here. The same czochralski process just to you know make it better make a better image in your mind about what is happening.

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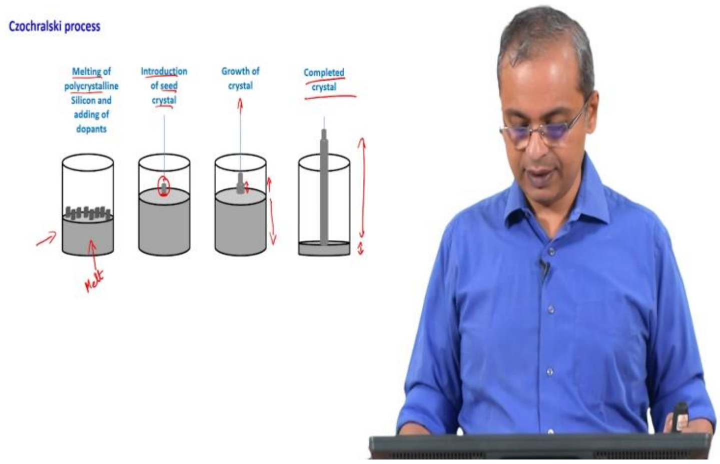

Czochralski process

Melting of polycrystalline Silicon and adding of dopants

Introduction of seed crystal

Growth of crystal

Completed crystal

So, you would you can say you are starting off with this situation here your melting polycrystalline silicon and adding dopants if you want add dopants. So, at that point you simply have a melt you have a melt that is here and you can build up the melt to how much over degree that you want and it is a high purity melt okay it is semiconductor grade silicon that you have chosen. So, it is a high purity melt.

So, in the next step of the schematic we introduce the seed crystal. So, that is the seed crystal that is sitting here it is a small single crystal as I said and it comes in contact with this liquid at that one location there. And then you start slowly you start pulling this out you start pulling this out. So, you can see here this is the growing a single crystal that has started appearing okay.

So, as you slowly pull this out over a period of time. What is happening is this two things are happening your single crystal is growing and of course, the liquid is getting consumed. So, the liquid level is continuing to drop the single crystal is continuing to grow. So, those two things are happening. So, in the end you will have a relatively tall single crystal up to here and then a very small amount of remaining liquid, so this is the basic process and so that we would call as a completed single crystal process. So, this is what we have and further processing is done with this single crystal okay. So, that is the czochralski process as an overview and you can look up more details of it, it's a pretty extensively used process for a single crystal manufacture.

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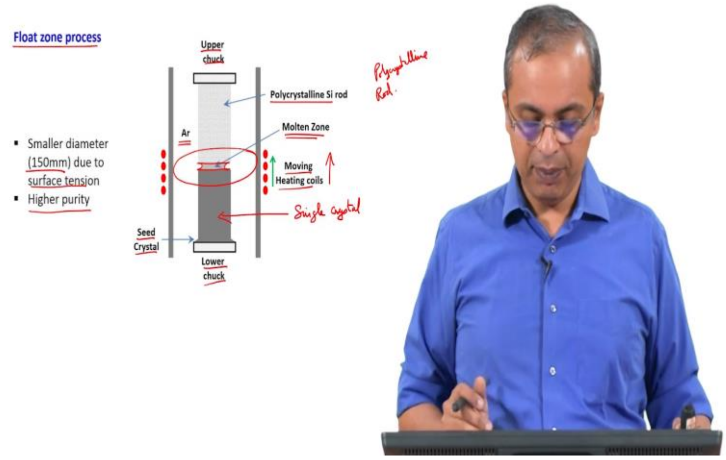

Float zone process

- Smaller diameter (150mm) due to surface tension
- Higher purity

The other process we have is called a float zone process okay. So, another process here called the float zone process. So, it has some advantages and disadvantages over the czochralski process.

So, the first thing is in the float zone process we don't melt the entire silicon. So, we don't start off with a melt we don't start off with a molten you know container a container full of molten silicon that is not our starting point instead our starting point is actually a rod, we pick up a polycrystalline rod.

So, for example, the top part of this sample that you see here is that polycrystalline rod originally the entire sample would have been polycrystalline from top to bottom. So, I have something here called the upper chuck and then there is a lower chuck these are the two things that are holding that sample together originally from the upper chuck to the lower chuck entire thing would have been a polycrystalline silicon rod. So, that is what we would have had. At the bottom we have a small seed crystal at the bottom we have a small seed crystal.

Now, the interesting thing that we do is we have heating coils same same process we are using we are using some RF based heating coils, but these heating coils are moving. So, they are moving. So, we have heating heating coils that are moving upwards and therefore, their sphere of influence is a very small region. So, that's the region that is the sphere of influence that is where the sample is actually hot. So, the sample may be cold on top may be cold at the bottom, but there is a region in the middle which is hot.

So, you have a small molten zone that is what you see here in this region that is your molten zone. So, the silicon melts there alone locally okay. So, there alone it melts and it has some shape mainly because of surface tension effects it has some shape it's trying to minimize its surface energy. So, you get that kind of a shape and it melts.

So, on top you have polycrystalline sample, in the middle you have this melt in the bottom you have a solid. So, given that you have a seed crystal and you have given that melt some opportunity to align itself with respect to that seed crystal and that's the direction in which it is cooling it begins to form a single crystal at the at the bottom. So, this becomes a single crystal okay. So, that becomes a single crystal. So, bottom becomes a single crystal because seed is there and plus you are moving away from that direction. So, you are continuing to melt towards the polycrystalline side you continuing to solidify towards a single crystalline in side and because you do this steadily it the sample becomes single crystal from bottom to top okay.

So, the big advantage here is that you are not having to melt the entire sample okay and here also you use argon because you want you don't want to introduce further impurities into the process. So, you do keep inert atmosphere, but the main disadvantage perhaps is that because you have this you know this small region that is that has to hold a stable you know physical state in in without you know collapsing and it is you know limited by surface tension forces and so on. So, there is some limitation to the size or the diameter of this rod that you can use.

So, generally it is found at about 150 millimeters is the sort of the largest diameter a sample that you can create using this process called the float zone process where you know you are just have this small region of melt that is moving up and that is primarily due to surface tension. But the nice thing is you get very high purity you get much higher purity relative to the czochralski process.

In the czochralski process you do get some impurities from that cross the quartz crucible, the quartz crucible is adding because it has SiO_2 it is actually adding some amount of tiny amounts of tiny amounts of oxygen into the process it also gets affected a bit by the thermal process that is occurring there. And so therefore, some the level of purity that you get here is a little bit less than the level of purity that you get with the float zone process and therefore, from the purity perspective this is better, but size wise you get a little larger size if you work with a czochralski process.

So, these are two major processes that are used to create your single crystal silicon and you know the focus is to both these single crystalline and also to have high purity. So, in this context we will also look at the idea of zone refining which is primarily focused at the purity aspect of it. You already got a single crystal what can you do to purify it okay.

So, in some ways it is also related to the float zone process because the general idea is the same you will have you will have you will have this kind of a single crystal. Now, from bottom to top, but you can do this moving meltings in this case you know as you move this heating coil the melt the molten region is moving from the bottom to the top right. So, the whole sample is not molten only once a small region is molten and that molten region is moving from one end of the sample to the other end of the sample.

So, that’s an idea you keep in mind. We go ahead and look at this situation here.

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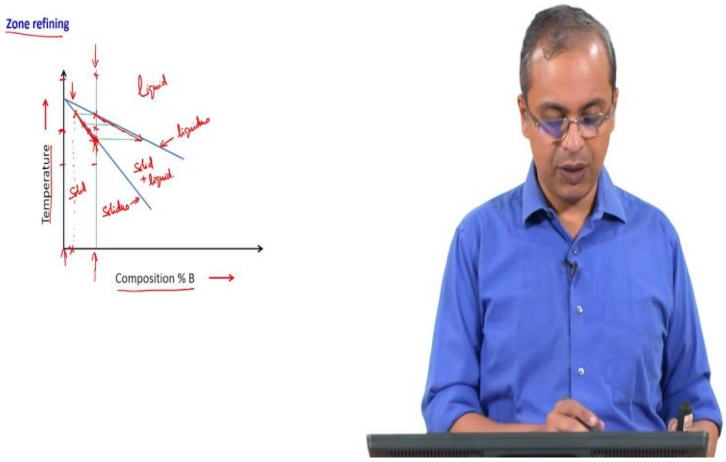

What do you see on your screen is a phase diagram a section of a phase diagram, of some hypothetical material we will assume let’s say it is a section of a phase diagram let’s say for silicon. But of the point B on your y axis you have temperature. So, that is what you have here on the x axis you have composition in percentage B. So, percentage B is any impurity in this case it is some impurity that is there in silicon which you don’t want in silicon. So, you want to remove it. So in fact, you want this percentage you want to be as close to this end of your final sample to have a composition as close to this end of the x axis as possible right.

Supposing you start with a sample that has this composition okay, you start with the sample that has this composition and you start cooling it. So, we call this the liquidus this is the liquid state this is a solid state and this is solid plus liquid okay and this is called the solidus this line is called the solidus okay. So, what this means is if you take this composition and you start cooling down if you stop here if you are at this temperature let’s say you are at this temperature and that temperature they sample will be entirely in liquid state okay. The same composition if it were at this temperature corresponding to this region on your y axis then the sample will have partly solid partly liquid and we can use the lever rule to find out the you know how much of it is liquid how much of it is solid.

If you are at this temperature if you are at this temperature this sample will be entirely in the solid state. So, this is how the phase diagram works. Now, what is of interest is the transition that happens when you are between here and here, where you start off being completely liquid and you arrive to a state where you are completely solid okay. So, when you do that the interesting thing about this phase diagram is it tells you what is the composition of the solid that is separating out at any given instant okay at any given circumstances.

Even though you start off with a liquid that has this uniform composition, it is uniform composition, what happens is as a virtue of this phase diagram the first solid that comes out does not have this uniform composition. In fact, it has this composition down here okay. So, that’s the composition that the first solid that comes out of this liquid will have.

Progressively as you keep decreasing the temperature the next I mean if you go down somewhat and further in temperature you will have solid that is coming out with this composition etcetera. So, the composition of the solid that comes out will slide down this line, the composition of the liquid will slide down this line. So, in the end you will you will have a solid which is a single crystal in this case. But the point is if you have done this the solid this single crystal let’s say you started at the bottom and you finished off this process at the top of that single crystal the bottom will have this composition, the top will have this composition.

So, therefore, the the you will have a situation where basically the composition has been changing continuously through this sample right. So, therefore, the end of the sample which solidified first is actually a much purer sample than the end of the sample that solidified last. So, therefore, you can do this process and you can remove the last part of the sample which was impure and you will have now, a sample which may be slightly smaller in size, but has higher purity than the sample you started with. You can continue this process repeatedly and each time you do this you will keeps getting one end of the sample that keeps getting purer and purer and purer. So, this is a process they use to make this overall sample as pure as possible and that is how you get this high purity you know sample.

So in fact, if you do this in an equilibrium state then you will actually move across then the composition of the entire solid will move on up along this line. So, that the final solid has this composition, but normally we do it in n non-equilibrium sense. So, you will actually have a range of compositions in the solid. So, you will such that the overall average composition is this okay. So, the average composition you cannot move away because that is a composition of the solid, but it will not necessarily move down this solidus because you will be doing it in a non equilibrium sense right.

So in fact, you will have a range of compositions and you will have you know not exactly finishing off with this exact composition that you see on the that you will not follow this line directly you would be a little bit away from the line because you are doing it in a normally equilibrium sense. So, that is the practical aspect of it, but this is the concept behind it and you can keep getting a solid that is purer and purer and purer. So, that is zone refining that is used for refining single crystals.

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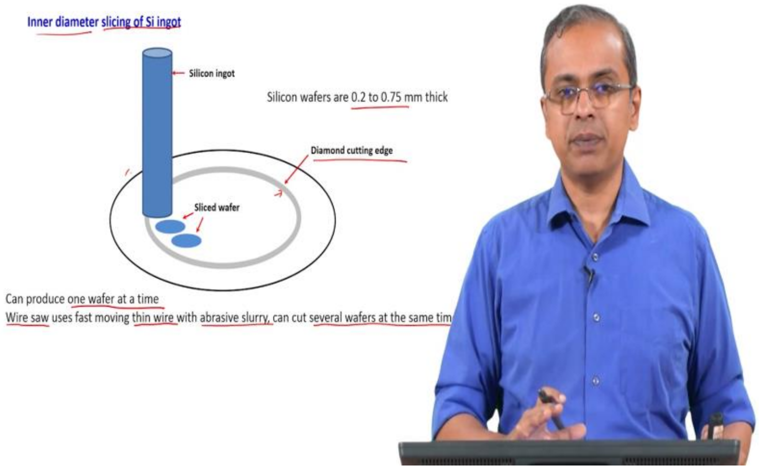

Inner diameter slicing of Si ingot

Silicon wafers are 0.2 to 0.75 mm thick

Can produce one wafer at a time

Wire saw uses fast moving thin wire with abrasive slurry, can cut several wafers at the same tim

So now, now that you have a solid you know single crystal available to you in the form of tubular structure what is the next step that is done. The next step that is done is basically slicing, slicing of silicon ingot to get wafers. So, that is what we keep here you know silicon wafer silicon wafer is a term that we keep here this is what is happening at that point. So, they have taken this cylinder that we got through the single crystal process either czochralski process or float zone process, and then we purified it all that we did they are now satisfied that the quality of that you know single crystal is what we want it to be the composition is right the orientation is right all that we figure out. Once you have figured all that out we do this slicing.

So, normally what they use is they use a diamond cutter, diamond cutting wheel and they use the inner edge of it that is why it is called the inner diameter slicing and then you slice the silicon wafers one by one you get a slice. And typically those silicon wafers are about 0.2 to 0.75 mm thick there is some limitations because if you get thinner than this you may actually you know you may you will have some problem in stably making it. So, you tend to get in this dimension 0.2 to 0.75 mm thick.

But this kind of a cutting process will get you one wafer at a time they also have some other processes which is based on some wire saw. So, wire saw that you see here can be used where you basically have a thin wire with an abrasive slurry and then you can have several of these thin wires or the same wire you know wound in different directions etcetera so that you can cut the sample simultaneously at several locations so that at a at an instant you get a huge number of wafers okay. So, simultaneously the wire is cutting the same cylinder at several locations and therefore, you end up getting several slices. So, that’s another way in which you can get several wafers at the same time.

So, this is an important step. Once this is done there is still some cleaning that is required of the surface of that sample and also to make it as flat as you would like it to be. So, there is still some processing steps involved, but this is the after you have made the single crystal the next major step is to make this wafer and this is the general idea that you just cut it slice by slice by slice and you get this way these wafers. So, that’s the next major step.

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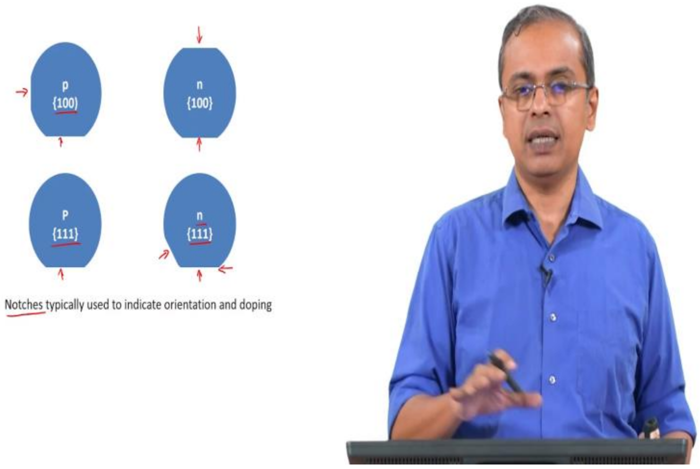

Notches typically used to indicate orientation and doping

So, having done this what is also done in the semiconductor industry. So, that it becomes easy because once you have all these wafers it can get very confusing you will doped them and p doping you have done n doping. And usually based on the crystal faces that are available you can either have 100 planes on the, as being the planes that are the you know parallel to the top surface. So, the entire cylinder consists of 100 planes going from one end to the other or you can have 111 planes going from one end to the other.

So, these are the two you know crystallographic planes oriented with respect to the face of the cylinder of the cylindrical sample that are most commonly present in this silicon single crystal. So, that doesn't have to be true for other systems in this system,these are the two that are of interest that typically these samples are made in this form.

So, just to make it easier for people who just look at a sample and say okay this is n-type or p-type and this is a 111 or 100 plane on the surface they usually use notches. So, this is a notch that you see here. So, you can see what was the circular cross section you know a small bit of it has been cut off. So, you can have this you know initial notch that is present here if you have only that notch it means it's a p-type sample which has 111 orientation on the surface. If you have this notch as well as another notch you know perpendicular to it, it is still a p-type sample, but it has a 100 orientation associated with it.

Instead of this second notch being at you know 90 degrees to the first notch if you had it on top then that is an n-type sample also with 100 orientation and finally, you can have n with a 111 orientation where you have this initial notch as well as this notch on the side at the edge at an angle to it.

So, we they do these notches to help you quickly identify at a glance you know what are you dealing with n-type or p-type 100 or 111 and that is useful for further you know processing or further any further activity you want to do with the wafer this is a very important piece of information and you cannot keep on going back to the x-ray diffractometer to find out what sample you have what orientation is it what is the composition is it p-type or n-type we are using some analysis technique. You know initially what it is, so you just mark it in such a way that you can see it permanently.

These days they have come up with some for larger you know wafers they have come up with a slightly different kind of a notch process or at least there is some modification on it, but this is still a there in many of the samples that you are going to see. So, this is another important step. So, you made the single crystal you did the slicing, you introduced these notches. So, this is this is what we have done.

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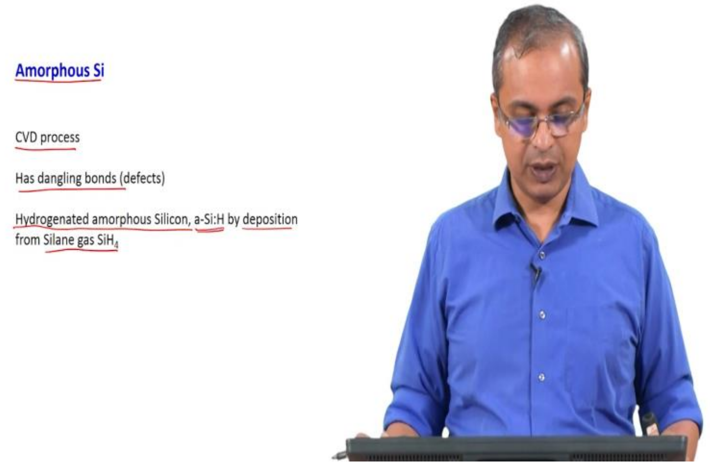

Amorphous Si

CVD process

Has dangling bonds (defects)

Hydrogenated amorphous Silicon, a-Si:H by deposition from Silane gas SiH_4

And then that can be used. So, we will talk briefly about how it can be used in the next slide, but before that we will also talk about amorphous silicon because that is another this so far we have spoken about a single crystalline silicon.

So, amorphous silicon is basically made by chemical vapor deposition process CVD process essentially; that means, that you create a vapor which carries this you know silicon atoms. So, typically from silane gas is used that has silicon atoms in it and then you will have some substrate on which it can deposit.

The nice thing about amorphous silicon is that it can be deposited on any surface. So, you can put a semiconductor on any surface any curved surface you don’t have to worry about the shape of the surface. So, potentially for example, let us say you are trying to make a solar cell powered car, instead of buying flat you know rigid flat solar cells and then placing it on top of a car you can almost deposit this amorphous silicon all over your car, and so your car can be in any shape you will have a amorphous silicon all over it and then you can use that for any process that you want. So, that’s the basic idea that in any shape you can do it I mean that is the idea it may not be that easy to just put it on the car, but that’s the concept that you can put it in any shape that your wish. And it also happens to be one of the cheapest ways for in which you can handle the silicon.

So, the issue with it is that it has dangling bonds. By nature an amorphous material is one where you know you don’t have order and therefore, the bonds have not been satisfied. So, there all of these dangling bonds which are defects from the from a crystallographic perspective from a bonding perspective those are considered as defects. The issue with the defects is that it impacts the movement of electrons or holes and therefore, you know if you are trying to use it as a semiconductor where movement of those electrons and holes is so, important this is a material that will actually get in the way of the movement of those electrons and holes and therefore, that is not particularly great to have.

Then they have figured out that you know if you do hydrogenated amorphous silica which is given by this notation a-Si-H if you do that by a deposition from zile silane gas then that hydrogen seems to do a good job of you know controlling these dangling bonds and then that is a much better material to use as amorphous silicon and then you can utilize it for with much better capabilities okay.

So, that’s the basic idea, you take this vapor and then you it condenses when it condenses it forms this amorphous material and that material can be used and that’s how we get amorphous silicon. So, commercially when you look at least with respect to solar cell applications. Those are the 3 types of variations of the silicon that’s available single crystalline silicon, a polycrystalline silicon and amorphous silicon.

And we have sort of seen you know all of them the original cleaning process that gets you that electronic grade or semiconductor grade silicon, we will typically get you I mean most likely we will get to all these polycrystalline samples. Then you do the processing get yourself a single crystal or you start with that material and you know given that it already has the purity you will do this other processing which gets you amorphous silicon. So, this is a these are the two things that are done.

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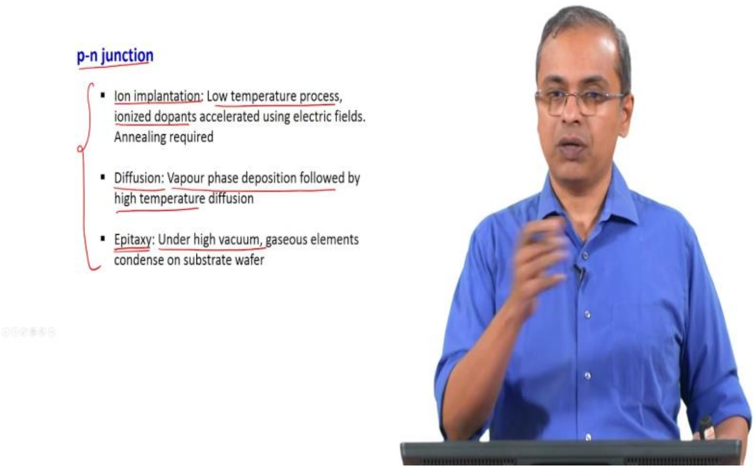

p-n junction

- Ion implantation: Low temperature process, ionized dopants accelerated using electric fields. Annealing required
- Diffusion: Vapour phase deposition followed by high temperature diffusion
- Epitaxy: Under high vacuum, gaseous elements condense on substrate wafer

So, we will close with this you know final discussion on the p-n junction, having got your silicon sample how do you get the p-n junction. So, normally what we do is we start off with a sample that is already doped in a certain way it could either be the p-type or the n-type doping and on that we introduce the other dopant. So, that is the typical way in which we do it we introduce the other dopant into this sample.

So, in this case for example, we can introduce it using ion implantation this is a generally a low temperature process. So, that is what is typically used the idea here is that ionized dopants are accelerated using electric fields and implanted into that sample. The this is considered a very effective way of doing this the only issue with this is that it destroys it does some crystallographic damage to the sample and so then after you have done this process you have to do some annealing to you know sort of even out those the damage that you have done at a crystallographic level smoothen it out and get it back to a you know fully functional a single crystalline material, but it is a very popular way in which this can be done.

The other way we could do it is to actually do diffusion where you do a vapor phase deposition of some dopant that you want on top of the single crystal that you have and then you have to do some annealing. So, this is a now a high temperature processing, you have to now go to a you know significantly high temperature maybe even say let’s say about let’s say about 1000 Kelvin for example. So, some high temperature you would have to go to and at that temperature the dopants will diffuse. So, because for diffusion you need high temperature and that temperature only the dopants will diffuse. So, it needs thermal treatment which typically needs significant amount of energy, but that’s another way in which you can do this process. Here you are not really doing any damage to the sample, but inherently you have to do this diffusion because it will start from the top surface and move inwards.

Finally we can also do this thing called epitaxy. This is something that is done under very high vacuum and what we do there is you take gaseous elements and they come in condense on top of the sample and when they do so because they are coming in almost atom by atom, atom by atom they are arriving at the sample they get an opportunity to line up perfectly in a crystallographic in a oriented manner on top of the sample that you have as your base material. So, that’s an other way in which you can get a junction.

So, in all these cases you are you can get a junction where you have a p material as your base material and on top of it you have grown an n material of some sort, either you have implanted an n material or you have diffused in the dopants or an n material or you have grown in n material on top of it. And so that’s those are essentially the three ways in which we can create a p-n junction starting off with any of the materials that we just discussed.

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Conclusions:

1) It is quite challenging to produce single crystal Si
2) Multiple process steps involved
3) Purity and dimensions can have significant impact on costs
4) Amorphous Si is an option

So, in summary our conclusions are these it is quite challenging to produce a single crystal of a silicon, but there are techniques that are there czochralski process is one the float zone processes the other. And these are commercially being used in you know the silicon industry semiconductor industry, but there is a lot of you know detail that is there primarily because you want a well oriented single crystal and you want very high purity. Those are the two major challenges that are there. There are multiple steps involved and as I said you know purity and dimensions both have a very significant impact on the cost. If you didn’t have dimension as a requirement, if you didn’t have purity as an requirement it is quite cheap.

The minute you start talking of ppm and ppb and you want a single crystal that is you know say 300s and millimeters and diameter or more you want 400 millimeters diameter and you start pushing that boundary then the cost start going up. And of course, as I said the other option that is available to us is amorphous silicon which then you know is a much lower cost material and it can put in any shape and therefore, is a very convenient material to work with, except that performance wise amorphous silicon is essentially the lowest performing of the lot that we have discussed okay.

So, those are the main conclusions for our class and what we will look as we go forward is that having gotten some know scientific knowledge on what the semiconductor is, how the band gaps are and what happens with respect to the band gaps, what the p-n junction is. And now, having understood you know physically, how these things come together we will look in our classes ahead on, how the solar cell comes together and how the solar cell functions and what are some characteristics that we need to keep track of for the solar cell.

Thank you.

KEYWORDS:

Single Crystal; Amorphous Silicon; Czochralski process; Float zone process; Zone Refining; Wafer Cutting; p-n Junction manufacturing; Poly Crystal; Single crystal silicon; Polycrystalline silicon with large crystal size; Polycrystalline silicon with small crystal size; Silicon; Metallurgical grade Silicon; Quartzite; Semiconductor grade Silicon; Electronic Grade Silicon; Trichlorosilane gas; Polycrystalline electronic grade silicon; Seed Crystal; Phase Diagram; Liquidius; Solidus; Wire Saw; Diamond Cutter; Noteches; Chemical Vapor Deposition; Hydrogenated amorphous Silica; Ion Implantation; Epitaxy

LECTURE:

The various methods of producing Single Silicon Crystals, Amorphous Crystals are explained. The purification of thus produced Silicon Single Crystal and its slicing process is also discussed in detail to create p-n junctions, in the context of Solar energy application.