Solar Photovoltaics: Principles, Technologies and Materials

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Lecture – 31
Manufacturing of Si

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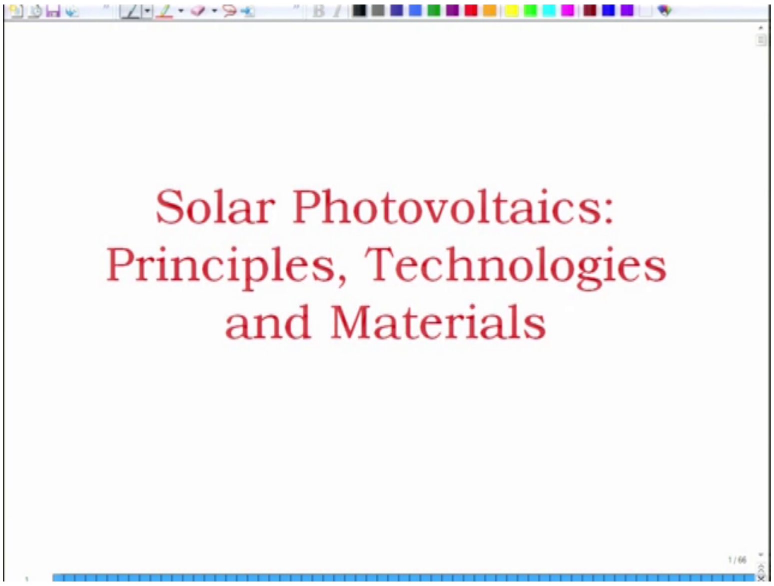

Solar Photovoltaics: Principles, Technologies and Materials

So, welcome again to a new lecture on Solar Photovoltaics: Principles, Technologies and Materials. So what we will do is that we will just have a quick recap of last lecture.

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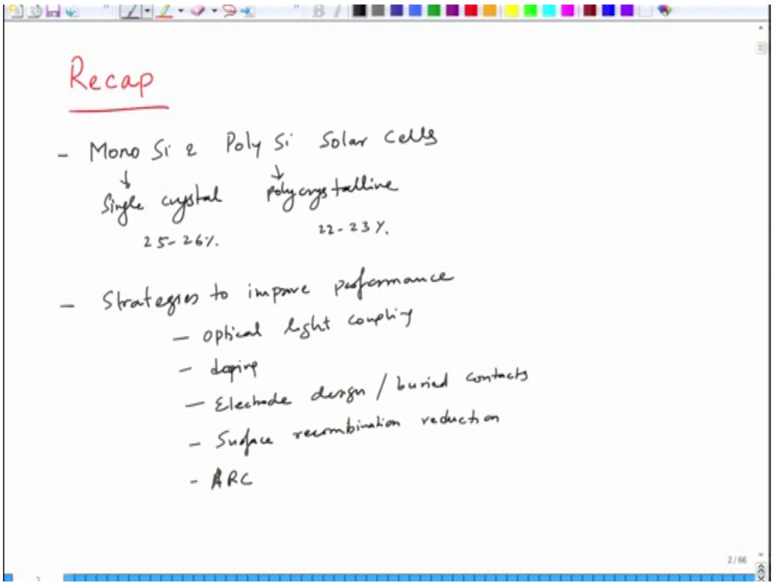

Recap

- Mono Si & Poly Si Solar cells
  - ↓ Single crystal 25-26%
  - ↓ polycrystalline 22-23%
- Strategies to improve performance
  - optical light coupling
  - doping
  - Electrode design / buried contacts
  - Surface recombination reduction
  - ARC

So, in the last few lectures we have talked about mono silicon and poly silicon solar cells. Mono silicon are basically single crystal silicon solar cells and these are poly crystalline. So, because of presence of defects the poly crystalline efficiencies are bit lower so, in this case we have efficiency above 25-26 percent efficiencies in this case we have efficiency 23 percent best efficiencies obtained.

However, they are not too bad given that there is a significant cost differential between the two. So, poly crystalline ones are cheaper than single crystals. And then we looked at the strategies to improve performance which are basically also design criterias. So, first was to improve the like optical light coupling, then we need to control the doping, electrode design, surface recombination, reduction, use of anti reflection coatings and so on and so forth and you can say here buried contacts.

So, these are certain strategies which are used to improve the quality of both poly crystalline and mono crystalline silicon solar cells. The way it is done in two solar cells may be slightly different, but they are by large similar.

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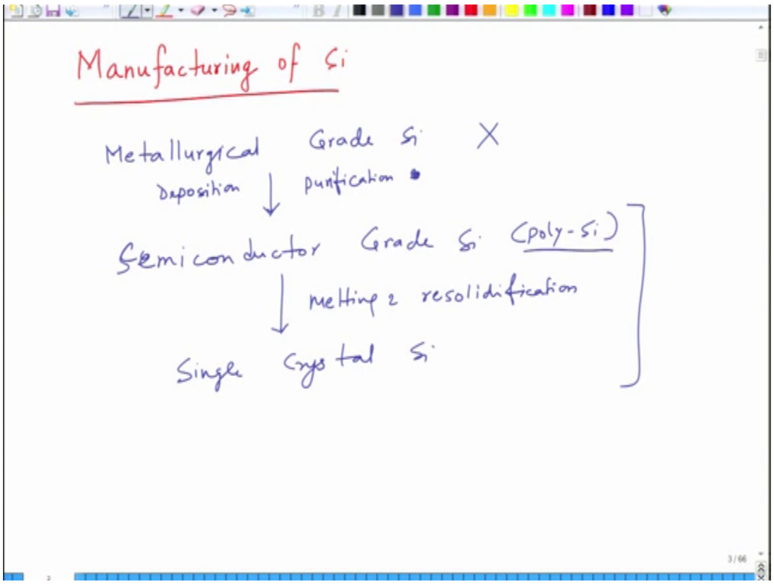

Now we will look at a bit of about bit about the silicon manufacturing. How do you do silicon and silicon device manufacturing?

So, to begin with we talk about silicon manufacturing. Silicon is generally manufactured in three steps. So, the first step is we have metallurgical grades silicon which is very impure. This metallurgical grade silicon is then converted into semiconductor grade silicon which is essentially you can say poly silicon and then we have third one called as single crystal silicon. So, we; obviously, cannot use this for semiconductors, but we can use these two for semiconductor processing.

Semiconductor grade silicon that is poly crystalline silicon is used for poly crystalline silicon solar cells and the silicon single crystal silicon is used for mono crystalline silicon solar cell. So, there is a additional step that is used to convert the poly crystalline into single silicon solar cell which basically involves melting followed by re solidification to make single crystals.

So, essentially it is about melting and re solidification and this is about purification and deposition; deposition and purification. So, you have two steps deposition purification. So, metallurgical grade is complete no no, but semiconductor grade and single crystal silicon both are used in practice. So, metallurgical grade silicon; how do you produce metallurgical grade silicon first of all.

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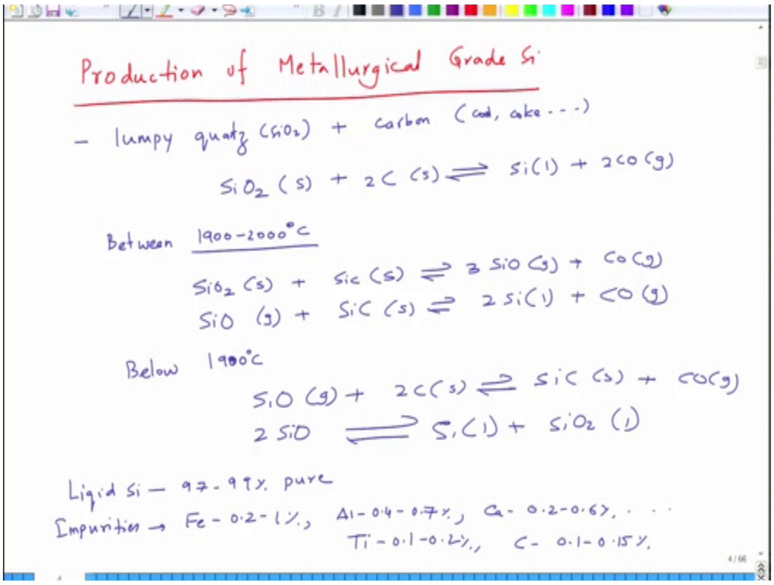

Production of Metallurgical Grade Si

- lumpy quatz (SiO_2) + carbon (coal, coke - - -)

$$SiO_2\,(s) + 2C\,(s) \rightleftharpoons Si(l) + 2CO\,(g)$$

Between 1900-2000°C

$$SiO_2\,(s) + SiC\,(s) \rightleftharpoons 3\,SiO\,(g) + CO\,(g)$$
$$SiO\,(g) + SiC\,(s) \rightleftharpoons 2\,Si(l) + CO\,(g)$$

Below 1900°C

$$SiO\,(g) + 2C(s) \rightleftharpoons SiC\,(s) + CO(g)$$
$$2\,SiO \rightleftharpoons Si(l) + SiO_2\,(l)$$

Ligid Si — 97-99% pure

Impurities → Fe - 0.2-1%, Al - 0.4-0.7%, Ca - 0.2-0.6%, . . .
Ti - 0.1-0.2%, C - 0.1-0.15%

So, metallurgical grade silicon is basically made from to begin with you start with lumpy quartz. Quartz we know is nothing, but SiO 2 and essentially you made it react with carbon. Carbon is in the form of coal or you can say coke etcetera various forms of carbon is present essentially you make SiO 2 react with in the solid form react with carbon in the solid form and this gives rise to silicon that is liquid and which is in the gas form.

This is a very energy intensive process because free energy formation of silicon oxide is extremely negative. So, thermodynamically this reaction is very energy intensive; so it goes at very high temperatures. So, first you have to go to between about 1900 to 2000 degree centigrade; your silicon oxide in the solid form reacts with silicon carbide in solid form to give you 3 SiO in the gas form plus carbon monoxide in gas form.

And then this SiO 2 in gas form reacts with again silicon carbide in solid form gives you 2 Si liquid plus CO g this is a multi step process. And below 1900 degree centigrade the reactions that occur are this Si O g plus 2 C in the solid form this makes Si C solid plus CO g and then 2 Si O gives rise to Si liquid plus SiO 2 liquid. So, the liquid that you get after this processing is first you go to 1900 2000 then below 1900 gradually and then you obtain from this liquid silicon which is 99, 97 to 99 percent pure with impurities like iron is about you know 0.2 to 1 percent.

Aluminium is about 0.4 to 0.7 percent then we have calcium which is 0.2 to 0.6 percent and so on and so forth. But if there is a bit of titanium 0.1 to 0.2 percent and then we have carbon 0.1 to 0.15 percent. There may be some other impurities also this is what is the composition. This is complete nono for semiconductor processing; this is very impure

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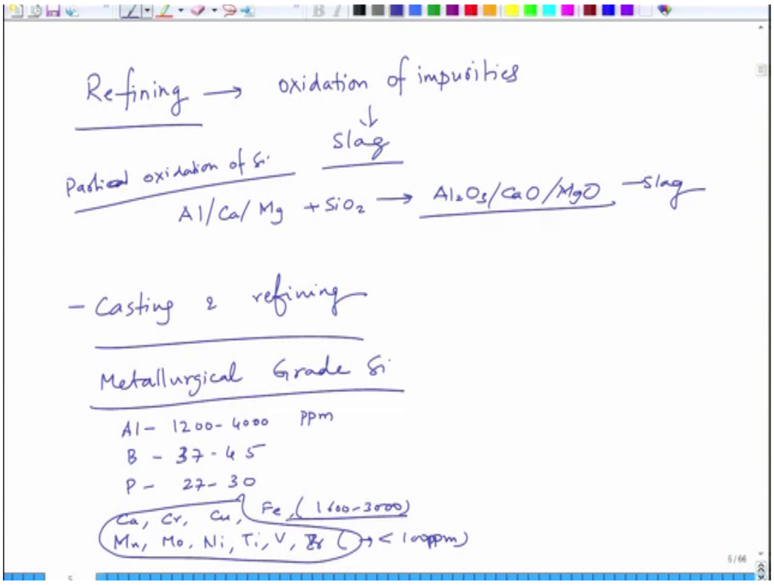

Refining → oxidation of impurities

↓

Slag

Partial oxidation of Si

$Al/Ca/Mg + SiO_2 \rightarrow Al_2O_3/CaO/MgO$ – slag

– Casting & refining

Metallurgical Grade Si

Al – 1200 - 4000 ppm

B – 37 - 45

P – 27 - 30

Fe (1600-3000)

Ca, Cr, Cu, Mn, Mo, Ni, Ti, V, Zr (→ < 100ppm)

So, what is the next is next you do refining. Refining is always the energy intensive process and this is used refining is done by agents which react with the impurities. So, basically its oxidative process essentially it is oxidation of impurities. So, this is a very tricky process because you have to choose conditions which do not lead to oxidation of silicon, but the impurities and remember silicon is very silicon has high affinity to react with oxygen.

So, as a result it is not very easy. So, oxidation of impurities to form slag; slag is nothing, but the impurities molten pool of a impurities. So, essentially and but you cannot completely prevent the oxidation of silicon. There is always some oxidation of silicon that happens. So, as a result what happens is that you have you a you also add some SiO 2 in this process; so, aluminium, calcium, magnesium etcetera. They react with SiO 2 to form Al 2 O 3, CaO and MgO and these make what we call as slag.

And then of course, you do so, essentially you are saying you have partial oxidation of silicon here. And then what happens is that you do casting in further refining all right. There is a very tedious energy intensive process you have to go multiple stages of refining and that is why silicon sand is cheap, but silicon is not.

So, a typical metallurgical grade silicon wind consists of your aluminium; so metallurgical grade silicon. So, this is where we have this rather purified metallurgical grade silicon. We have aluminium of the order of 1200 to 4000 ppm, boron of the order of 37 to 45. So, all in ppm phosphorus about 27 to 30 and then we have calcium, we have chromium, we have copper iron. Iron is relatively large 600 to 3000 ppm and then we have manganese, we have moly, we have nickel, we have titanium, we have vanadium, we have zirconium and all these are less than about 100 ppm ok; all of them except iron.

So, these are less than 100 ppm typically some of these may be 200 ppm so, so, but generally about in less than 100 ppm. So, this is the metallurgical grade silicon. This is very very impure not fit for suited semiconductor processing. So, what you do is that then you process this metallurgical grade silicon to purify this using other processes.

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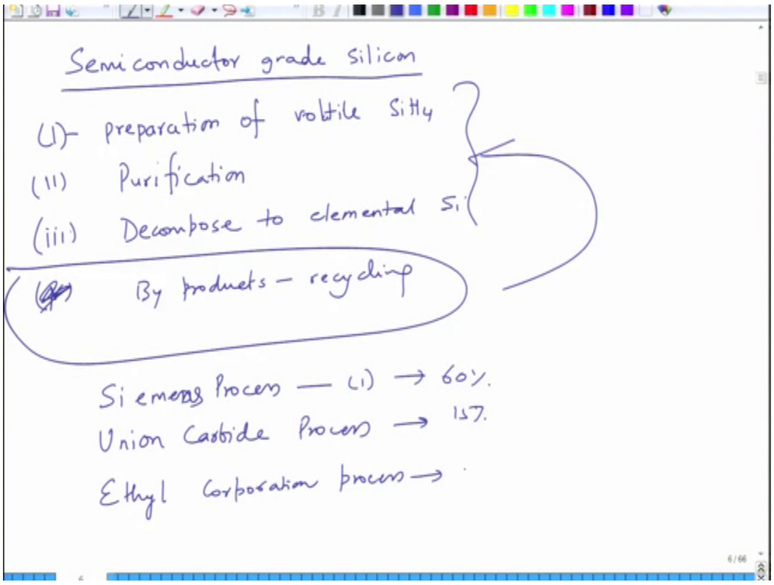

Semiconductor grade silicon

(i) preparation of volatile SiH_4
(ii) Purification
(iii) Decompose to elemental Si

By products – recycling

Siemens Process — (i) → 60%
Union Carbide Process → 15%
Ethyl Corporation process →

So, the semiconductor grade silicon is made by; so from this silicon that we obtain we make first volatile silicon hydride SiH 4, then we purify it, then we decompose this to elemental silicon and then we go to byproducts. In the process we have well it is not a part of the process at such, but this is what happens you have byproducts which are recycled into these stages.

So, so essentially you first fit material grade silicon and convert the metallurgical grade silicon into these silicon compounds like silicon hydride because remember no matter how much liquid processing you do, you cannot make very pure silicon. So, you have to take it to vapour stage where only silicon is able to come out rest all does not come out. So, after you have done primary refining using the metallurgy processes, you have to go to the processes which are more of deposition processes than liquid based processes. So, that in this case there are three processes that we generally use, but generally and the Siemens process is the one.

So, Siemens process is the first process that is used to make silicon and then we have union carbide process. Siemens process accounts for about 60 percent silicon in the world and union carbide process accounts for about 15 percent silicon production. And then third is what we call as ethyl corporation process which is about again 15 percent or so. So, let us see will not go into all of these, we will just look at the Siemens process ok.

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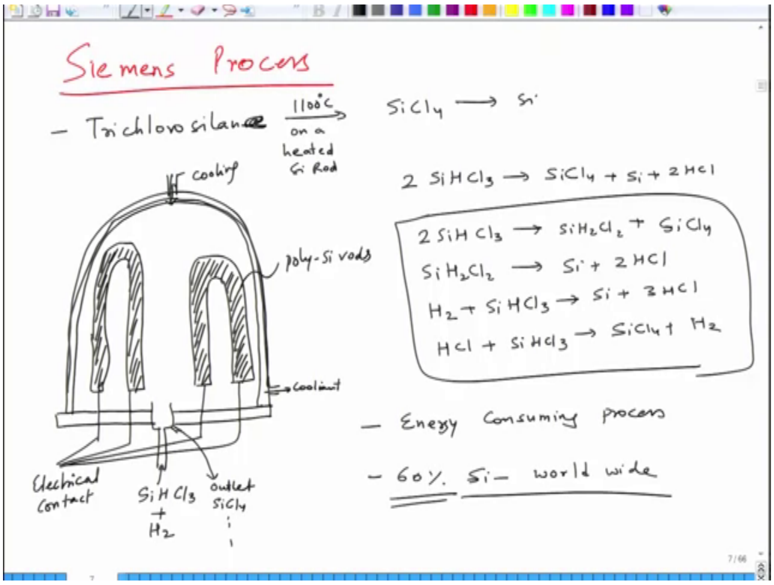

Siemens Process

- Trichlorosilane $\xrightarrow[\text{on a heated Si Rod}]{1100^\circ C}$ $SiCl_4 \longrightarrow Si$

$2\,SiHCl_3 \rightarrow SiCl_4 + Si + 2\,HCl$

$$\boxed{\begin{aligned} &2\,SiHCl_3 \rightarrow SiH_2Cl_2 + SiCl_4 \\ &SiH_2Cl_2 \rightarrow Si + 2\,HCl \\ &H_2 + SiHCl_3 \rightarrow Si + 3\,HCl \\ &HCl + SiHCl_3 \rightarrow SiCl_4 + H_2 \end{aligned}}$$

- Energy Consuming process
- 60% Si – world wide

So, Siemens process; so what happens in Siemens processes, you have basically we are doing we first make trichloro silane ok; Trichlorosilane. This is thermally decomposed at 1100 degree centigrade on a heated silicon rod inside a decomposition chamber and then it gives rise to what we call as silicon SiCl 4 and this SiCl 4 is then converted into silicon. So, the way we go about it is we have this chamber which is a dome shaped chamber alright within these we have.

So, we have these silicon rods like these are silicon rods prefabricated silicon rods. So, these are you can say poly silicon rods this. And then of course, you have some cooling medium here vent sorry cooling and then what we have here is we have this; these are electrical contacts electrical contacts to heat these rods to high temperatures.

So, temperatures are about 1100 degree centigrade and then through this thing we pour in what we call as we put in Si H Cl 3 which is the silicon trichlorosilane and hydrogen and then somewhere here we also have a outlet for other gases like SiCl 4 etcetera; they come out.

So, and then that the coolant goes out from this side because we also have to keep the chamber clean cool otherwise so, it said this is a double body chamber like this. So, this is a double walled chamber. So, keep the coolant; so this has coolant flowing. So, coolant flows and keeps this cooled ok; so this is coolant. Now in this the reactions that happen are two of SiHCl 3 makes SiCl 4 plus silicon plus 2 HCl. So, it is not a very friendly reaction you can see that the things that are forming is not very benign and this happens in multiple stages.

So, you have 2 SiHCl 3 goes to SiH 2 Cl 2 plus SiCl 4 then SiH 2 Cl 2 forms Si plus 2 HCl and then this hydrogen also reacts with HSi Cl 3. You can see, I have replaced it here. So, this becomes Si plus 3 HCl and HCl plus Si H Cl 2 they make SiCl 4 plus H 2; so, you can say this is Si HCl 3 sorry.

So, these are multiple reactions that occur in this process to give you eventually the silicon. This is a very energy consuming process. It is a slow process it is a energy consuming process and this is what is used for making silicon in the industry. Over 60 percent silicon is made worldwide using this. So, this results in the formation of silicon which is quite pure semiconductor grade silicon and basically the silicon which comes here it gets deposited on these rods.

And these rods become thicker and thicker and thicker and thicker and then you of course, take them out, cut them, make wafers that is what you do ok. And so, there is a whole scheme of this process, I will not go into details of that process. So, this is what is the basics of making silicon ok.

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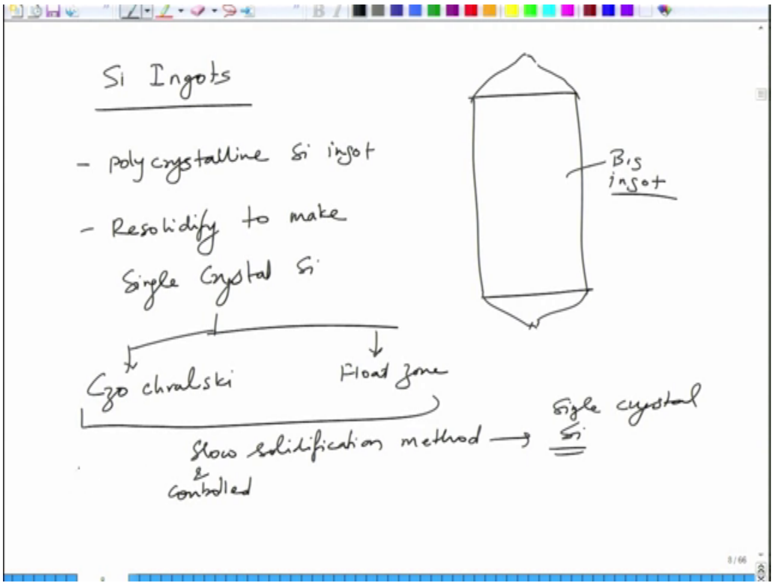

Si Ingots

- polycrystalline Si ingot
- Resolidify to make Single Crystal Si

Czochralski

Float Zone

Slow & controlled solidification method → Single crystal Si

And then we make silicon in got from so. Now, if you want to make silicon single crystal, you make silicon ingots. So, silicon ingots are made by melting silicon ok. So, whatever poly silicon you make that is pure, then you melt it. After melting you make ingot it is casted and once it is casted, it is a begin cut off. So, after casting it becomes like a big ingot and generally it is like it has a little nozzle shaped nose on the two sides. So, this is a big ingot and these ingots are then if you want to make single crystal silicon, they re casted and re solidified.

So, you can make a poly crystalline ingot or you can you need to re solidify it to make single crystal silicon; first process is called as Czo chralski Czo chr alski and then second method is called as float zone. So, principles of solidification and impurity segregation are used to make high highly pure and highly single crystalline highly defect free silicon.

So, essentially what happens here is in these two methods. So, in using these two methods basically these are slow solidifying slow solidification; slow and controlled solidification methods which give rise to formation of single crystal silicon. So, you can read them through the books Czo chralski and float zone method. They are basically solidification and methods to make single crystal silicon.

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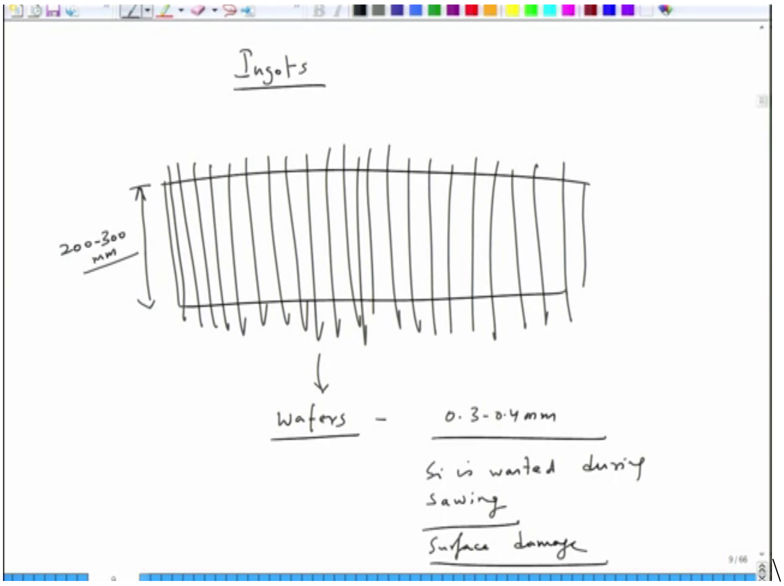

Ingots

Wafers - 0.3-0.4 mm

Si is wasted during sawing

Surface damage

So, once you make these single crystal ingots they are like this. So, they are of the diameter about 200 to 300 millimeter. These are ingots and they are quite tall, they could be you know I think about a meter long or so out of these you need to make wafers. So, what you do is that you do wire showing of these to make wafers ok; so these are cut into small pieces to make wafers.

So, this gives rise to wafers. Each wafer is of the order of 0.3 to 0.4 mm thick when you make these wafers because of sawing, you create silicon dust. So, silicon is wasted a lot of silicon is wasted during sawing and sawing also leads to damage to the surface right; sawing also leads to damage to the surface so, wasted as well as surface damage. So, to make a device quality silicon, you again need to n do a lot of processing.

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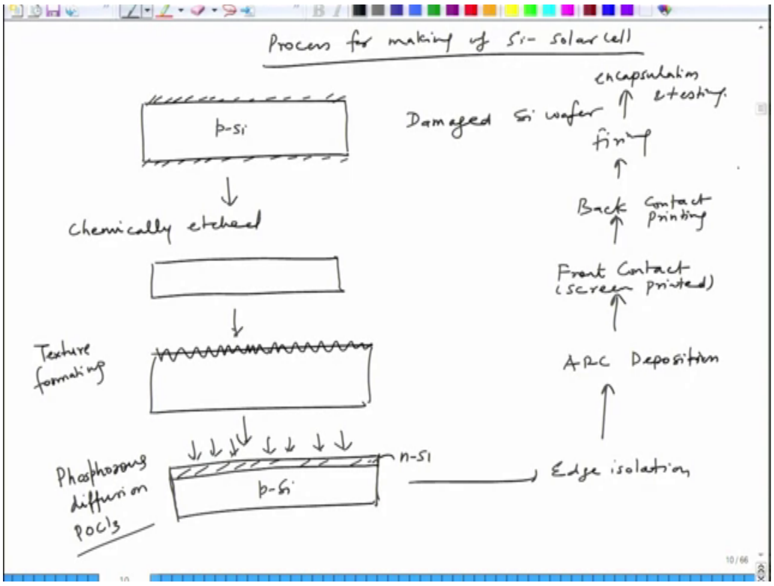

So, this is for example, so initially the silicon is more or less p type to begin with the dopants that happen to be there. So, essentially you have a silicon. This is let us say p silicon to begin with it has lot of surface damage. So, this is damaged silicon wafer, this is then chemically treated chemically etched on the surface; so that you get a nice clean surface. So, the surface is cleaned by etching to remove the rough material of the surface and then after that you do texture etching; texture formation.

This is to improve the light coupling. So, you create this kind of so, this is called as controlled etching use of right etchants; so that you have right plane and the wafer which is etched. So, you create this kind of surface etching and then you do the diffusion of a phosphorus diffusion to make n type silicon on top. So, this is p type to be in with the phosphorous comes from top. So, gases containing phosphorus come. For example, you can have gasses like you know PoCl 3 ok. So, PoCl 3 will come from top phosphorus will diffuse.

So, this region will make n silicon, this will remain as p silicon and then you after you have done that you chop off the edges a little bit. So, you can do what we call as edge isolation because there will be some damage on the edges as well. So, you chop off the edges to make little smaller. After you have done edge isolation we do the process called as ARC deposition.

So, then you do ARC deposition on top of it. So, anti reflection coating is deposited and then we make front contact which can be screen printed and then you make what we call as back contact. So, this is sort of that you can say a procedure for making a silicon solar cell and then you do firing.

So, back contact printing you can say here; firing to just make sure that a contacts stabilizes and it is solidifies and after that you do testing encapsulation and testing encapsulation and testing. So, this is the complete flow chart of the way silicon is made ah.

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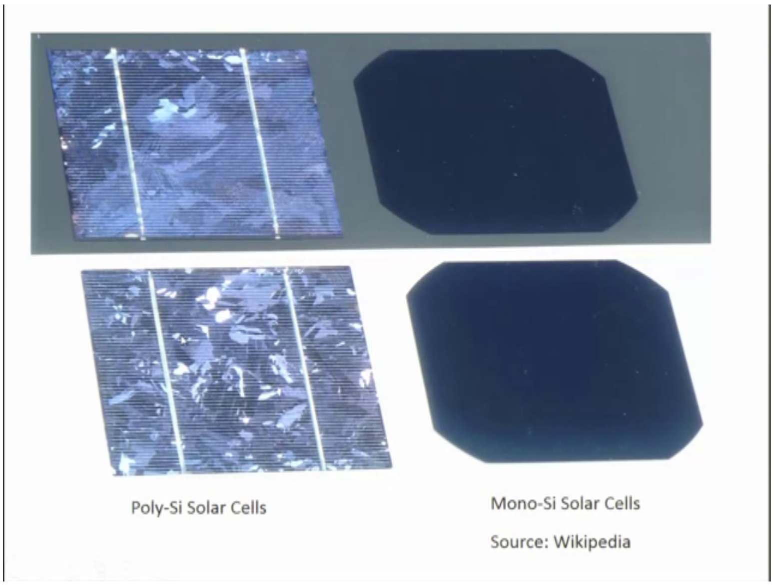

So, if you have seen in one of the earlier lectures that what does it look like after once you make the contacts. On the backside, of course, you will have completely printed surface with aluminium all over the place the front side looks like this. So, these are screen printed contacts, but it will have a contacts on top.

So, you have a; you have a thicker contact on top to connect all of these layers together, but these are the fine contacts running across the length or breadth of silicon; so this is what is silicon manufacturing all about.

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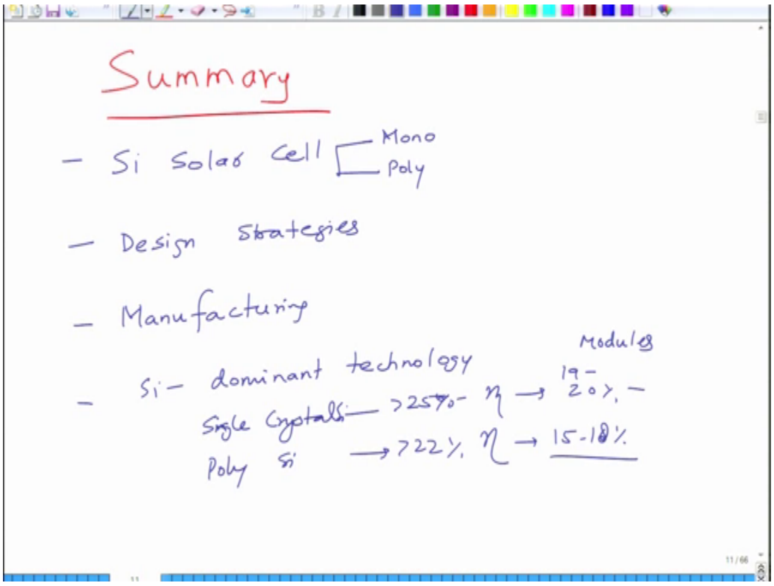

Summary

- Si Solar Cell – Mono / Poly
- Design Strategies
- Manufacturing
- Si – dominant technology
  Modules
  Single Crystals – >25% – η → 19-20% –
  Poly Si → >22% η → 15-18%

And so, just to summarize for silicon, we have looked at silicon solar cells in quite detail for both mono and poly. We also looked at design strategies to improve the silicon quality to improve the performance, we also looked at the manufacturing in some detail not very detailed, but just a flow chart of how silicon solar cell is made. Currently silicon solar cell stands silicon is the dominant technology in the market. With single crystal silicon having about more than 25 percent efficiency and poly silicon having efficiency of more than 22 percent.

The modules are of about 19-20 percent and in this case the modules would be about 15-16 percent; this is 4 modules let me check the numbers. So, a modules would be a lower than what you gets about 20 percent, you will get 4 single crystal about 15-16 maybe 17 percent. Further you can say 15 to 18 percent for the poly silicon and these two other dominant technologies right now in the world.

So, what we will do in the next lecture is we will talk about a little bit about gallium arsenide just to look at a basic structure of gallium arsenide solar cell and then we move on to second generation technologies which is thin film solar cells.

Thank you.