Solar Photovoltaics:
Fundamental Technology and Applications
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Lecture-12
Fabrication Process for Semiconductor Grade Silicon

Welcome everyone once again to our solar photovoltaic course, if you recall so far we have introduced the concept of p-n junction silicon solar cell. We have learnt how a silicon solar cell works or what is the fundamental concept behind the working principle of a solar cell. In this concept we have also introduced the idea of some parameters related to the solar cell, like we have learnt what is short circuit current, what is open circuit voltage, what is fill factor.

And how to calculate the efficiency based on this parameters, now these were all we can say about some fundamental aspect of the devices. But the next important question is how to make this kind of devices, now if we look closely the heart of all of this device is silicon material. So in today in week 3 module 2 lecture we will learn about how silicon is process to make silicon solar cell.

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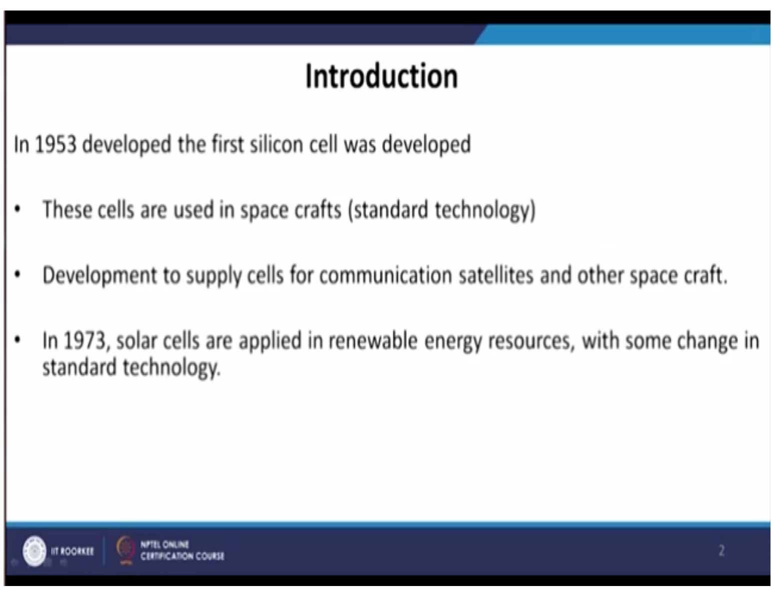

It is worthwhile to mention that the silicon solar cell was developed in 1953, these solar cells were used in spacecraft which is like very standard technology of solar photovoltaics. This solar cells technology has lead over the time and development to supply cells for communication satellites and other spacecrafts was one of the important allocation of this solar cells. In 1973, solar cells are applied in renewable energy resources with some changes in standard technology.

Like it is said that Rome was not build in a single day, similarly the revolution in the photovoltaics industry has went through several phase. Based on that we can classify the solar cell technology as first generation solar cell, second generation solar cell or third generation solar cell. We have learnt previously by first generation solar cell we mean single crystal silicon solar cell which are ultra pure silicon and the cost is very high and efficiency is also very high.

Now next is second generation solar cell, by second generation solar cell we mean amorphous silicon solar cell. Now this solar cell has crystallinity less than the crystalline silicon solar cell but their efficiency is little bit lower and cost is at the same time lower than the first generation solar cell. Now the third generation solar cells mainly they have been paved by the discovery of new materials like organic materials.

So by third generation solar cell we mean organic solar cells, dye sensitize solar cells, perovskite solar cells etc. Even today we coin this word fourth generation solar cell, so what we mean there mainly the tandem solar cell and organic, inorganic solar cell, hybrid solar cell, so singlet fission solar cells, these are different examples of the fourth generation solar cells.

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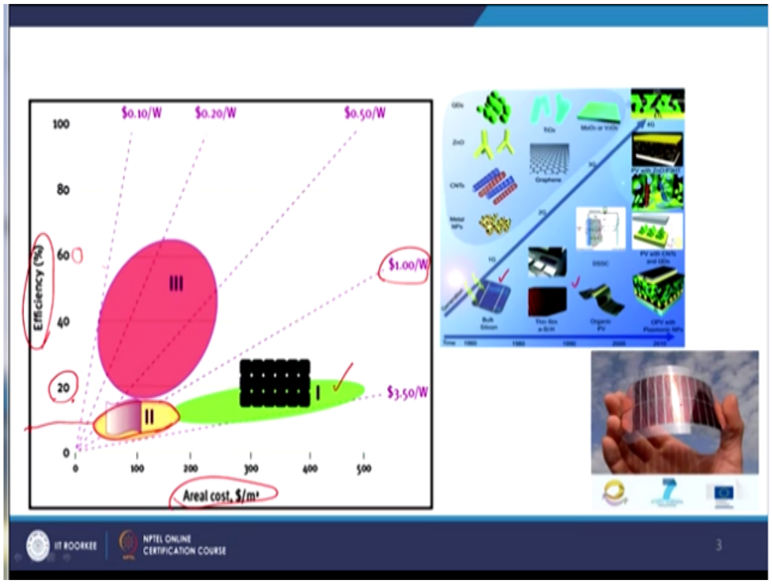

Now if we look at this chart the efficiency versus area of the cost in dollar/meter square, we see that as we go from the first generation to second generation to third generation what important parameters is changing here, the efficiency as well as cost. If you look the first generation solar cell which is shown by this green color circular shadow here this region, the cost of this solar cell is 3.5 dollar/watt where the efficiency is almost as high as 20%.

Now if you go to second generation solar cell which is amorphous silicon solar cell that we represent here by yellow color circular shaded region and the cost here is 1 dollar/watt. So obviously the cost is lower than the first generation solar cell. But the efficiency if we draw a line it will heat the y axis or the efficiency axis somewhat around here. So efficiency is somewhat between 12% to 15% that is lower than the first generation solar cell.

Now as we go further we come to third generation solar cell, you can see that we have drawn a very larger area which is like pinkish red in the third generation solar cells. And it covers a large value of efficiency started from it is bottom almost around like 15 to 18% to all the way up to 60% efficiency. And at the same time the cost is varied where it has an area which has cost 0.50 or 50 cent/watt to 20 cent/watt to even lower as 10 cent/watt.

So as you go to third generation solar cell efficiency and the cost both get changed, the cost/production of watt is get reduced significantly in comparison to the first generation and second generation solar cell. At the same time efficiency increase from moderately 15% to as high as 60%, now all these changes in the efficiency of the solar cell was pepped by the discovery of the materials.

As you all know that we are leaving in a age of materials and the discovery of the new materials always has lead to the new technology. In this chart on the right hand side we are showing the different generations of the solar cells and how the different materials has lead to the discovery of these new generations of solar cell. For example if you look the 1g that is the first generation solar cell, that is mainly made of the bulk silicon, so this one.

So this is mainly the crystalline silicon then we have second generation solar cell which is a thin films solar cell which mainly includes amorphous silicon solar cell or even some 6 base solar cell. Then finally we got this third generation solar cell, on the left side we are showing some material, what are these materials they are mainly engineered carbon nanomaterials like grapheme like carbon nano tubes.

Similarly we have metal oxide like zinc oxide we have quantum dot, we have titanium dioxide, we have (()) (06:48) oxide or vanadium oxide. Similarly we have metal nanoparticles or metal nano clusters, so these are all new materials which have discovered successively. As this new materials were discovered new kinds of solar cell also came into the market and those are example of a third generation solar cell.

For example dye sensitize solar cell or in brief DSSC, so D stands for dye, S for sensitize this S for solar and C for cells, this dye sensitize solar cells as the name suggest is made semiconductor and a sensitizer or dye molecule. Now there are different molecules which can act as a dye. We will learn in detail in the future classes what is the basic principle behind this dye sensitize solar cell and how to construct a dye sensitize solar cells.

Similarly we have organic photovoltaic solar cell, now as you can see that this solar cells are flexible in contrast to the silicon solar cell which is not flexible, we have organic PV which is flexible. So that means we can put it on any substrate, we can put it on our bag, we can put it on your rooftop which has an arbitrary geometry. For example any kind of surface and then finally we have the fourth generation solar cells, these are the photovoltaics with the organic inorganic hybrid like zinc oxide which is an inorganic compound.

And then P3HT it stands for poly 3 hexylthiophene, this is a conjugated polymer, this polymer is use to make organic solar cell. But when you put the inorganic oxide with the organic polymer then you get a hybrid solar cell. Similarly you have photovoltaics with carbon nanotubes and quantum dot, you have organic photovoltaics with plasmonic nanoparticle some nanoparticle shows plasmonic effect or surface Plasmon effect.

So if we use that effect to construct the solar cell we get plasmonic solar cells based on that we can construct different kind of solar cell. So as the new and new materials has been discovered, new and new different kinds of solar cell has been came into the market. At the bottom, at the bottom right corner we are showing an organic solar cell and as you can see that we have kept it between our hands.

So that means this solar cells are flexible or these solar cell is made on a flexible substrate like flexible PET coated glass substrate. So the advantage is that we can put it on any substrate but some of the disadvantage is that the processing of the solar cell. Like if the processing of the material inverse high temperature then we cannot do it on a flexible substrate because while you heat the flexible substrate that can melt because the organic materials melt at lower temperatures usually.

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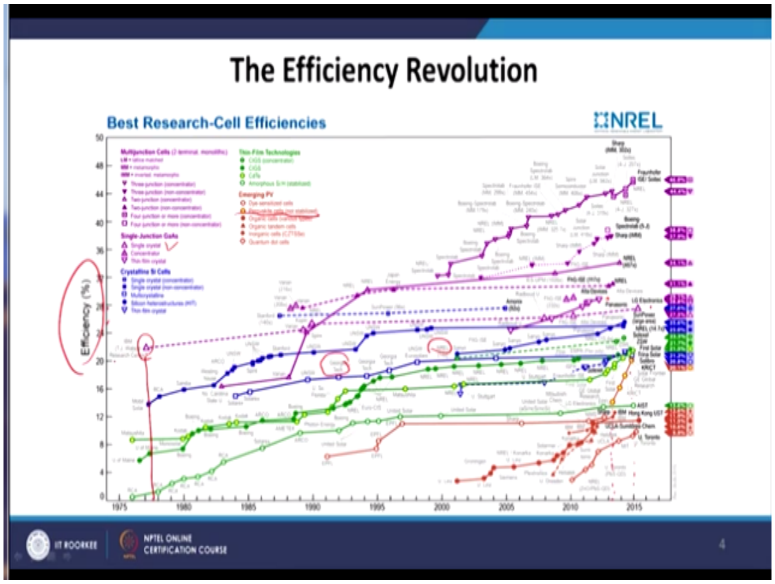

Now this master chart from national renewable energy laboratory at USA showing the efficiency revolution of different kind of solar cell over the years. This chart you will see in almost all kind of solar photovoltaics related lectures. Today we will learn how to read this chart, on the y axis of this chart is the efficiency in percentage and the x axis as you can see the years are showing or the time is showing.

So it is showing the different generations of the solar cells with the different colors and very close to the line there are different places name is shown here like Georgia take and then this n-real these are the corresponding layer where this solar cells were discovered and mainly the labs which are working on this kind of solar cell. For example if we start with multijunction solar cell or single junction gallium arsenide solar cell, this is shown by this single crystal solar cell by the open triangle.

Now we look for the open triangle here where we can find out the open triangle, if you look in this diagram you have to look where have been represented by the open triangle. So that is this curve, so this pink color curve is straighten and showing the single crystal becomes solar cell. Or even if I take this one which have been started at 1976 or 1977 and it goes all the way from here and it is still going until this point.

And you can see some of the pioneering work was done by IBM at T.J Watson research laboratory and then finally it has been worked on different laboratories going to the like IBM and also like Samsung electronics. And what is happening if you look closely to this graph the efficiency started from 20% or 22% and if you follow this graph starting from here you follow this line it goes until this point where the Panasonic is working on it.

Now you see that the efficiency corresponding to this line is 26% or 27%. Now starting from 1977 to all the way until 2014 the efficiency has changed from 26% to 28%. So this kind of growth is not very fast rate of growth. So already the efficiency already started with a very high number but the growth is almost saturated where you look for some of the young technologies for example dye sensitize solar cells or thin film solar cells or perovskite solar cells the growth is very high.

One this kind of technology which growth is very very high is perovskite solar cell. Now in this particular diagram we are showing the perovskite solar cell by this solid yellow circle and you see that this technology has been started somewhat around here 2013. And within 5 years time somewhat around 2015 or 16 starting from a descent 14% efficiency, the efficiency reach to almost 20%.

More precisely the perovskite solar cell has started with a very descent efficiency of 3.8% and only within 5 years of research the efficiency has reached as high as 22%. And even now a days the efficiency has high as 23% as also reached. So this efficiency number is almost same as silicon solar cell but this growth has happened in a very short amount of time, that is why this kind of perovskite material has reach the attention of many scientific community and there are lot of research is going on, on this perovskite solar cell.

We can take different example like 6 solar cells or cadmium telluride quantum dot base solar cells. So like here quantum dot base solar cell was as early as 1976 and starting from here it goes all the way until 2014, this curve is showing until 2016, 2014 until number 2015 until number we are showing in this curve and efficiency reach to 20%. So this master chart plot the efficiency of all different kind of solar cell over the years and the corresponding lab which is invert in the research of the solar cells.

So we now learnt how to read this curve, now the next important questions in this context is that how to make these solar cells. Now as we have learned there are 3 different generations of the solar cell, first generation solar cell, second generation solar cell and third generation solar cell. Now first generation solar cells are mainly single crystal silicon solar cell, it is important to mention that this single crystal silicon solar is very very costly to produce.

Because their processing very very complex, we will learn today about the standard technology behind fabrication of the single crystal silicon solar cell. But before making a single crystal silicon solar cell we have to make a single crystal silicon. And single crystal silicon is made from the sand, starting from the sand how we can make a single crystal silicon that we will learn here today, there are several methods or several steps involved here.

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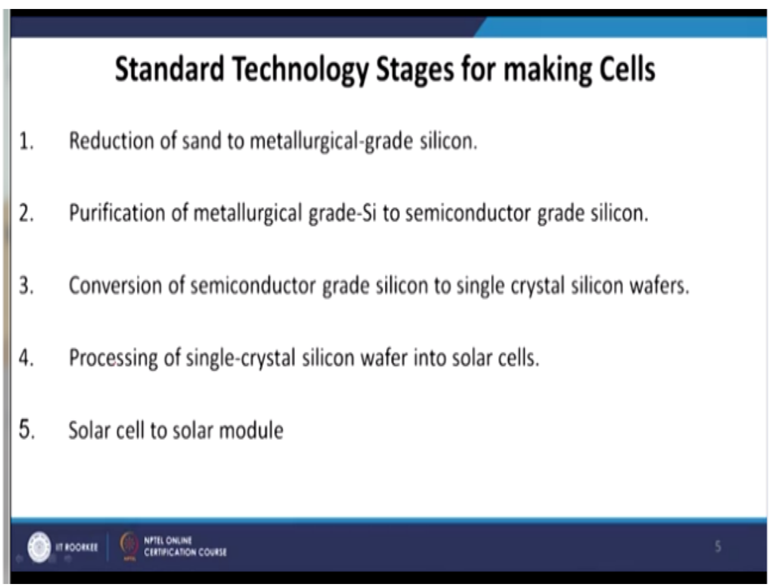

The first step is reduction of the sand to metallurgical grade silicon, the second stage is purification of metallurgical grade silicon to semiconductor grade silicon. Now this semiconductor grade silicon is highly pure 99% 99999999% so there are 0.6 decimal after the point value that much purity is needed to make a chip based silicon re semiconductor grade silicon.

Now the silicon which we usually get by the purification or by heating the sand that is not as pure as this semiconductor grade silicon, that has a purity of 99% eve after doing different process and that kind of silicon is called metallurgical silicon. And metallurgical grade silicon has to be further purified to get a semiconductor grade silicon. Now the third process is that conversion of the semiconductor grade silicon to single crystal silicon wafers.

So next once we get a semiconductor grade silicon then we have take that semiconductor grade silicon to make a single crystal silicon wafer. Now when we have silicon wafer then the fourth stage is that processing of single crystal silicon wafer into silicon solar cells. So this silicon wafers are then assemble to make a silicon solar cell. And finally when we have too many solar cell we arrange them in series or in parallel to make a solar module which we use in our practical life.

Now we will learn each of this step one by one, so the first step is reduction of the sand to metallurgical grade silicon.

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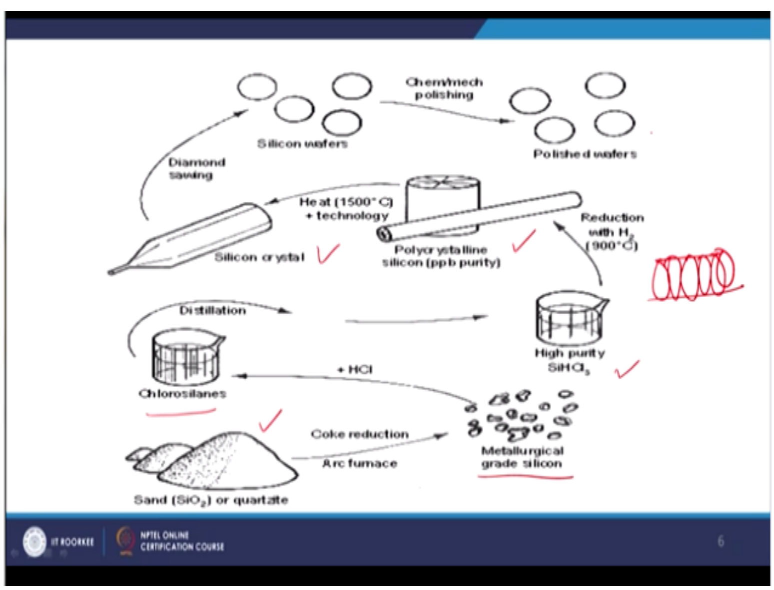

In this blog diagram we are trying to show the whole process involved starting from the sand or silicon dioxide to make a single crystal silicon. As you can say here that sand are which is quartzite or silicon dioxide is the main source of silicon. This sand usually is reduced in a high temperature arc furnace in the presence of carbon and then we make it metallurgical grade silicon.

This metallurgical grade silicon is further reacted to hydrochloric acid to make this liquid chlorosilanes. This chlorosilanes is further distilled to make a purity $SiHCl_3$ and this $SiHCl_3$ is reduced in the presence of the hydrogen at high temperature at 900 degree Celsius to make polycrystalline silicon. So this polycrystalline silicon is has to be needed further purified to get a single crystal silicon.

And this has achieved by heating it at high temperature 1500 degree centigrade and then also using some more further purification to get a single crystal silicon. Now if you get a single crystal silicon in a cylindrical shape then we can cut it by a diamond sawing and get a silicon wafer like this. So if you have a cylindrical shape like this and we know that this is made of is lot of this wafer kind of things, you take an example of a cucumber.

So if you take a cucumber, so a cucumber is a single crystal silicon, now if I cut it with a knife I will get a single piece of cucumber. So that single piece of cucumber is a single piece of silicon wafer, now this single piece of silicon wafer that needs to be polished. Because their surface is very very rough, so after doing the proper polishing we get a polished wafer and this polished wafer is an intrinsic silicon.

To make it useful for fabrication of a solar cell we need to dope it, so as you have learned earlier that we can dope this silicon either by using a p-doped material or by an n-doping material. So we can put either an acceptor impurity like boron to get a p-doped material or we can put a donor impurity like aluminum to get a n-dope material. Once we get different doping of this silicon then we assemble them together to get a silicon solar cell.

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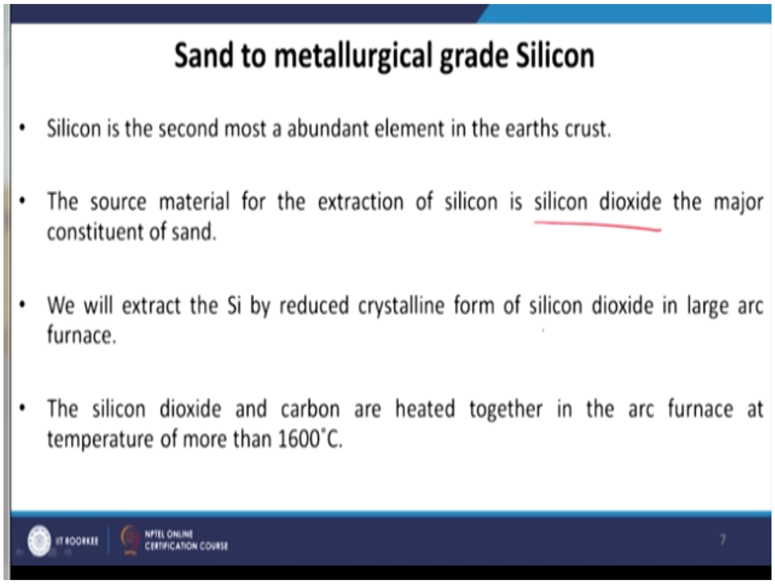

The first stage is that sand to metallurgical grade silicon, silicon is the second most abundant element in the earth crust. And that is why although the first technology of the photovoltaics started with gallium arsenide rather it is switch to silicon because silicon is very very abundant. The source material for the extraction of the silicon is silicon dioxide that is the major constituent of the sand, so sand has silicon dioxide.

So nowadays there are lot of different other materials like some biological materials also which people are suing to extract the silicon. But commonly for an industrial process the silicon is obtained from the sand which contain silicon dioxide. Now we will extract silicon by reducing the crystalline form of the silicon dioxide in a large arc furnace, arc furnace is a furnace which is made in such a way that we can heat any substrate very very high temperature.

Now the silicon dioxide and the carbon which are heated together in the arc furnace and silicon dioxide is reduced in the presence of carbon and we use at very high as high as 1600 degree Celsius.

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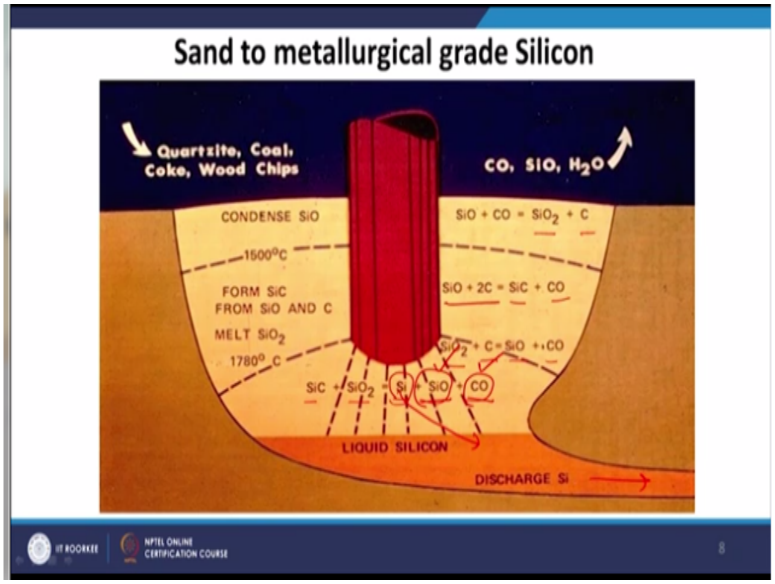

So what will happen let us take a look at that, so this is a very giant reactor this arc furnace is a very giant reactor. So we put the quartzite which is like silicon dioxide, coal, coke and wood chips they are source of the carbon together in this arc furnace, you can see this is a very arc furnace is here and what will happen there are different temperature regions are there. We can heat at 1500 degree centigrade, so from silicon carbide w can get silicon carbide + silicon dioxide.

They can react each other to make silicon, SiO and carbon monoxide. Now this silicon oxide or SiO they are reduced by the carbon to get a silicon carbide and carbon monoxide. Similarly this SiO2 silicon dioxide they are reduced by the carbon to get SiO and carbon monoxide. And you see that this silicon monoxide they further get reduced by the carbon to silicon carbide. So this reaction goes on and then the silicon oxide can also react with carbon monoxide.

Because in this process when carbon bonds you get not only the carbon monoxide but you also get carbon dioxide right. So if you take carbon monoxide then silicon oxide will react with carbon monoxide to get a silicon dioxide and carbon. Now what happened this silicon dioxide is get reduced by the carbon and we get a liquid silicon and that liquid silicon get discharge through here.

So the silicon dioxide and silicon carbide they react to make a silica, silicon monoxide and carbon monoxide. Now this silica or the silicon this forms a liquid silicon and that comes from the bottom of this chamber and it the discharge is collected from here. Now the other gaseous form of the byproduct like silicon monoxide, carbon monoxide and also we get some water vapor in this process they go from the top.

So this gaseous product is collected from the top ad from the bottom we get the liquid silicon. Now we have a liquid silicon you can call it as a metallurgical grade silicon, metallurgical grade silicon in brief we give MG silicon.

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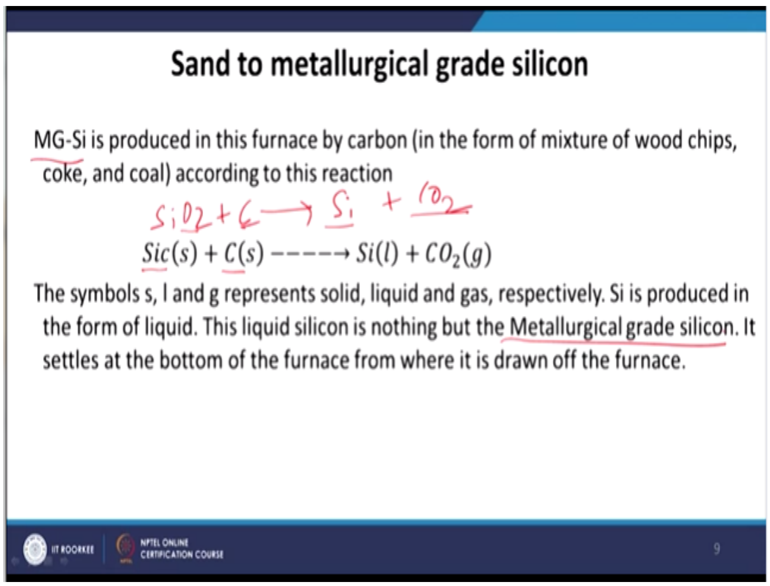

So MG silicon, so MG stand for metallurgical grade silicon, now metallurgical grade silicon is produce in the furnace by carbon in the form of mixture of wood chips, coke and coal. So what reaction they follow, so silicon carbide or if I write it also as silicon oxide + carbon = silicon + carbon dioxide or if I get silicon carbide if it reacts with carbon, so you will get silicon + carbon dioxide.

Now both these things like silicon carbide they are solid, silicon dioxide this is the solid which is the source of that sand. Now what we are reacting with we are reacting with carbon where this carbon is coming we are adding this carbon in the arc furnace. And this reaction is happening at a high temperature and here the carbon is also solid and what we are getting from this reaction we are getting silicon which is l, l stands for liquid and carbon dioxide which is g, gas stands for gas.

So once we react the silicon carbide or silicon dioxide with carbon, so they get reduced by the carbon and we get the liquid form of the silicon and some gaseous form of carbon dioxide. So the symbol here the s, l and g this stands for solid, liquid and gas respectively. Silicon is produced in the form of liquid, this liquid silicon is nothing but the metallurgical grade silicon, it settles at the bottom of the furnace from where it is drawn out of the furnace.

So in the first step of the reaction, first we start with the sand which contain silicon dioxide, now silicon dioxide is reduced in the presence of the carbon at very high temperature as high as 6000 degree centigrade. And what we get it called liquid silicon which we call as metallurgical grade silicon and some gaseous product. Now this metallurgical grade silicon this is not very pure, we need to further purify it to make a device or any chip.

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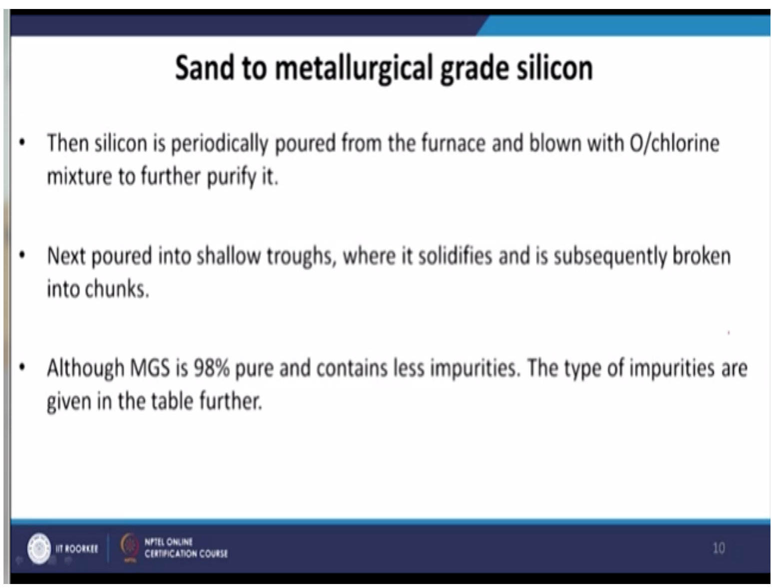

Then silicon is periodically poured from the furnace and blown with oxygen and chlorine mixture to further purify it. So whatever the liquid silicon we collect from the furnace that we blow with oxygen and chlorine. So what will happen, so this liquid silicon can react with oxygen or chlorine and whatever the impurity the oxygen and chlorine can get rid out of that. Next it is poured in a shallow troughs where it solidifies and subsequently broken into chunks.

So then we put in a shallow troughs, so because of the volume confinement, so it got solidified and then it is broken into some smaller smaller chunks. Although metallurgical grade silicon is 98% pure and contains les impurity, this types of impurity is not good for making device. So if we really wanted to make some solar cell device we have to further purify this to make a very pure grade silicon 99.99% grade silicon, how we can achieve that, we will learn in the next stage.

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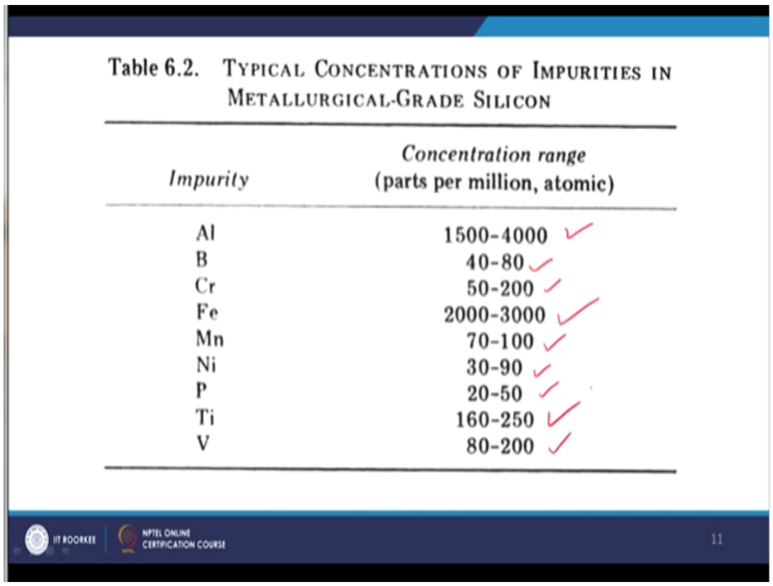

Table 6.2. TYPICAL CONCENTRATIONS OF IMPURITIES IN METALLURGICAL-GRADE SILICON

Impurity	*Concentration range* (parts per million, atomic)
Al	1500-4000
B	40-80
Cr	50-200
Fe	2000-3000
Mn	70-100
Ni	30-90
P	20-50
Ti	160-250
V	80-200

Now let us have a look that what is the typical concentration of impurities in a metallurgical grade silicon. Now it is worthwhile to mention that although the metallurgical grade silicon is not very useful for the so called semiconductor industry especially the chip base industry or solar cell device industry. But this metallurgical grade silicon has a lot of different other use, especially in metallurgical engineering this silicon is used a lot.

Now it contains impurities like aluminum, boron, chromium, iron, manganese, nickel, phosphorous, titanium etc. Now aluminum has a very high amount in this thing, the concentration range is showing in parts per million ppm. So the aluminum concentration in metallurgical silicon is quite high 1500 to 4000 ppm whereas the iron contains is also very high 2000 to 3000 ppm.

Now the next important concentration for the impurity is titanium which is 160 to 250 and also thee are bromine, there are chromium, there are manganese, nickel, phosphorous and vanadium. So this impurity are good if you wanted to make some kind of product which is based on the impurity like some kind of steel or some kind of metallurgical grade material using this silicon. But because of the presence of this aluminum, born and iron this will be not be good to make electronic circuit. So we need to get rid of this aluminum, boron and chromium to make a pure grade silicon.

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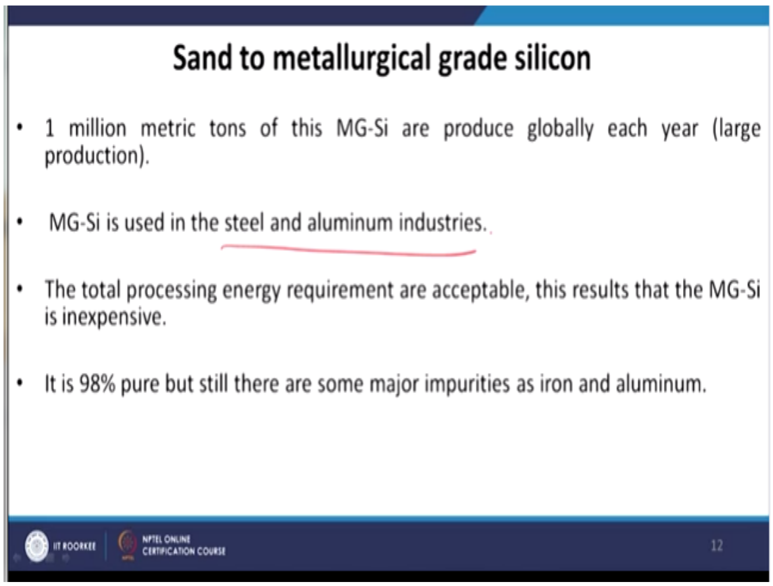

1 million metric tons of the metallurgical grade silicon are produced globally each year. So the production is very very large 1 million metric tons and this number is increasing every year. Metallurgical grade silicon as you just mention it is used in steel and aluminum industry, so in the steel industry basically the different forms or different kind of steel with different brittleness or different mechanical rigidity of the steel is needed.

For that we use different form of the metallurgical grade silicon, the total processing energy requirement or acceptable, this results that the metallurgical grade silicon is inexpensive. And similarly since we have to make this steel in a large amount the processing of the metallurgical grade silicon should be inexpensive. And this process is requires the less amount of cost comparison to the making a final very pure single crystal silicon.

Now it is 98% pure but still there are some major impurities like iron and aluminum. So as you just mention we cannot make an electronics devices out of it and we have to further purify it to make a pure silicon semiconductor. So today we will learn until this in the next class we will see that how this silicon is used to make purified silicon and to fabricate a solar cell, thank you.