

**1. Physical and Chemical properties of Silicon relevant to photovoltaics:****Physical properties of silicon relevant to Photovoltaics:**

- Atomic No: 14
- Atomic wt-28.08
- Hard brittle crystalline solid with blue grey metallic lustre. It is highly unreactive until in 1823 Berzelius first prepared silicon in pure form
- M.P-1414 °C ; B.P- 3265 °C ; Density 2.33 g/cm<sup>3</sup>
- Silicon is a semiconductor with a band gap of 1.12eV, It is second most element on the earth crust and more than 90% of earth crust is composed of silicate mineral
- At atmospheric pressure it is having simple cubic structure and at 15GPa pressure, it transforms to body centred cubic structure.
- Silicon unlike metal, contracts on melting and expands on solidification
- When a dopant is introduced into silicon, it ionizes at low temperatures. Thus free electrons or holes are provided
- The doped silicon has a minority carrier life time of 50 to 300us and a typical solar cell requires a minority carrier life time of at least 25us (Minority carrier life time is the time that lapses before an electron recombines with a hole)
- Silicon has high refractive index and hence has limitations for use in solar cells and this difficulty is overcome by coating it with an antireflective layer.
- Doped silicon is not hard and can easily be made into required shapes

**Chemical properties of silicon relevant to photovoltaics:**

- Silicon is stable in the tetravalent state and has a strong affinity for oxygen, forming stable oxides and silicates.
- Elemental silicon readily oxidises forming a thin protective film of silica.
- Silicon and carbon form a strong SiC bond and stable products. Silicon carbide also finds various applications in photovoltaics and electronics. Primary uses exploit the abrasive properties of SiC for wafering silicon crystals. Silicon forms hydrides, and monosilanes is a key chemical compound for the production of amorphous silicon and the purification of silicon to semiconductor grade.
- The chemical reactivity of silicon with chlorine is also very important. Trichlorosilane and tetrachlorosilane are both the intermediates and the by-products of the purification process in upgrading metallurgical grade silicon to semiconductor grade, as these compounds are volatile at low temperature and can be decomposed to elemental silicon at higher temperature.

**2. Production of solar cell grade silicon from Quartz**

Solar grade silicon synthesis process includes the following steps

**Synthesis of metallurgical grade silicon from Quartz (Carbothermic approach):**

Metallurgical grade silicon with a typical purity of 98.5% Si is produced in submerged electrical arc furnace. The furnace consists of a crucible filled with quartz and carbon. Silicon is formed as per the following reaction

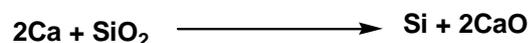
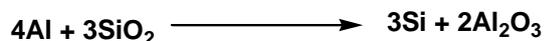
**Reaction:**



The raw material mix is heated by means of an intense electric arc sustained between the tip of the three submerged electrodes and the electrical ground of the furnace. Electrodes are also made of carbon. Liquid silicon is tapped from the bottom of the furnace, and mixed raw materials are charged from the top.

**Refining (oxidative refining):** The crude silicon in liquid state taken in large ladles is treated with silica sand ( $\text{SiO}_2$ ) and lime/limestone ( $\text{CaO}/\text{CaCO}_3$ ). Elements less noble than silicon such as Al, Ca, and Mg are oxidized.

**Reactions:**



After completion of oxidative refining in the ladle, the slag containing the impurities is removed mechanically and liquid silicon is poured into a casting mold and solidified. The solidified silicon is crushed into small lumps up to 100mm, in jaw crushers and roll crushers.

**Synthesis of semiconductor grade silicon from metallurgical grade silicon:**

Impurities in the ppb or ppt range are required for polysilicon used in semiconductor industry. This is achieved by the preparation of a volatile silicon hydride and its purification generally using fractional distillation. This is followed by the decomposition of this hydride to hyper pure elemental silicon by reductive pyrolysis or Chemical vapour deposition.

**The Siemens Process:**

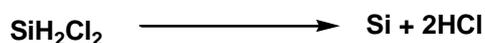
The most popular process is based on the thermal decomposition of trichlorosilane at  $1100^\circ\text{C}$  on a heated silicon rod placed inside a deposition chamber. This process is commonly referred to as the Siemens process with reference to the company that carried out its early developments. Trichlorosilane is prepared by hydrochlorination of metallurgical grade silicon in a fluidized reactor.

**Reaction:**



This reaction occurs at  $350^\circ\text{C}$  normally without a catalyst. The trichlorosilane formed is double purified silicon through fractional distillation. In the first step, the heavier impurities resulting from the direct synthesis are removed. In the second step, components lighter than trichlorosilane are eliminated. High purity  $\text{SiHCl}_3$  is then vaporized diluted with hydrogen and introduced into the deposition reactors. The gas is decomposed onto the surface of heated silicon seed rods, electrically heated to about  $1100^\circ\text{C}$ , and growing large rods of high pure silicon. The reactions involved are:

**Reactions:**

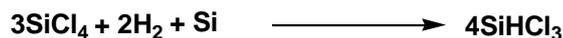


**The Union Carbide process:**

A more recent method developed by Union Carbide Chemicals in the United States of America, replaces the trichlorosilane with silane ( $\text{SiH}_4$ ). But the principle of decomposition on a heated silicon rod inside a closed deposition chamber is maintained.

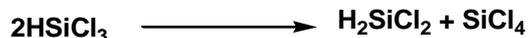
The process involves the following steps: The hydrogenation of tetrachlorosilane through a bed of metallurgical silicon is carried out in a fluidized bed reactor.

**Reaction:**



The trichlorosilane is separated by distillation while the unreacted tetrachlorosilane is recycled back to the hydrogenation reactor. The purified trichlorosilane is passed through a fixed bed column filled with quaternary ammonium ion exchange resin acting as catalyst. Trichlorosilane gets converted into dichlorosilane

**Reaction:**



The products are separated by distillation, tetrachlorosilane is recycled to the hydrogenation reactor and dichlorosilane is passed through a second fixed bed column filled with quaternary ammonium ion exchange resin. Dichlorosilane is converted into silane.

**Reaction:**

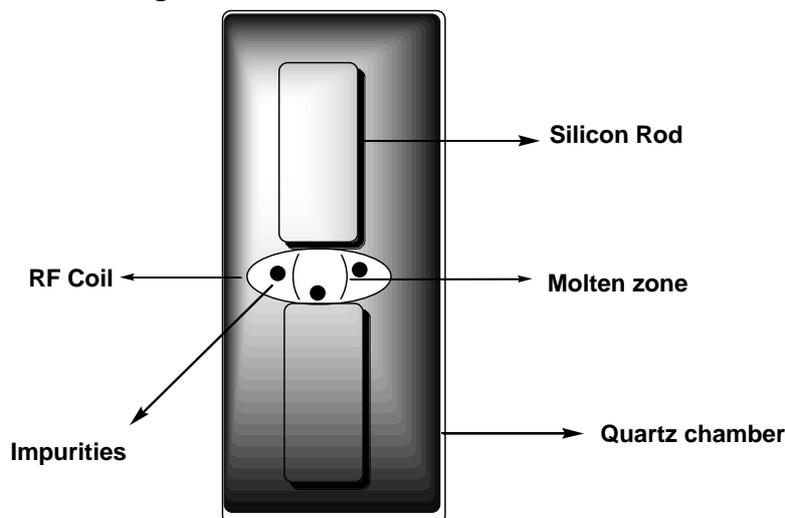


The above products are separated by distillation and trichlorosilane is recycled to the first fixed bed column. Silane is further purified by distillation and then pyrolyzed to produce polysilicon onto heated silicon seed rods mounted in a metal bell jar reactor.

**Reaction:**



**Purification by zone refining:**



#### Vertical Zone refiner

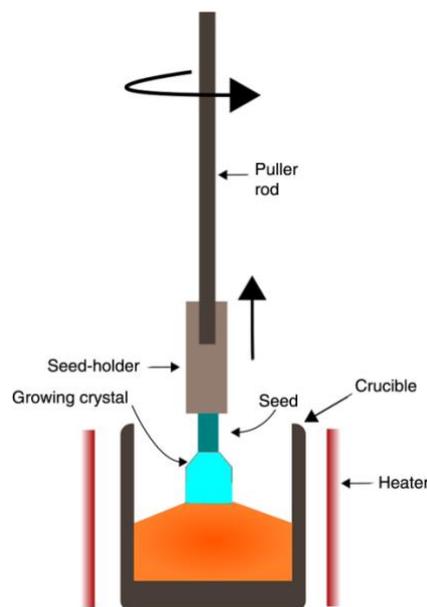
- Silicon can be purified upto 99.99% by the zone refining technique.
- The method involves a large number of successive crystallization from the melt. This method is used when the impurities are more soluble in the melt than in the solid material.
- In a bar of impure silicon held vertically to the clamp, a short zone at the top is melted by supplying heat from by using RF Coil.
- The molten zone is moved slowly down by moving the RF Coil through the length of the solid from the top to the bottom which is called one zone pass, where it is finally frozen. The process is subjected for several zone passes, and the impurities collect preferentially in the liquid zone, move with the molten zone and accumulate at the

end of the rod where they are finally allowed to freeze. Successive passes of molten zone lead to further purification, as the liquid will be less pure than the solid crystallizing from it.

- After the process is over, the bottom portion, concentrated with impurities is removed. If boron is present as an impurity, zone refining method cannot be used for its removal, because, its solubility is same in the molten and the solid silicon which is ultrapure enough to prepare PV Cells.

#### 2d. Preparation of single crystal silicon:

- Silicon obtained by the above process is polycrystalline. Polycrystalline silicon has no regularity in the crystal structure and contains many crystals of various sizes. For the fabrication of a semiconductor device, silicon should be a single crystal. One of the methods of growing single crystals is Czocharalski crystal pulling technique shown in the figure.



**Fig.Czocharalski crystal growth**

- In this method polycrystalline silicon is mixed with a calculated amount of dopant is taken in a quartz vessel placed in a graphite crucible.
- The crucible is heated using a RF power source in an inert atmosphere of argon. When the material melts, the temperature is lowered so that it is kept at the melting point of the material.
- A single crystal of silicon is attached to the tip of a puller rod and is lowered into the molten material so that it just touches the surface of the material. The rod is slowly rotated at a speed of about 100 rpm and simultaneously pulled out at a rate of 2-5 cm per hour. As the melt is pulled out, it solidifies and has the same orientation and crystals structure as the seed.

#### 3. Semiconductor Materials:

A semiconductor is a material that shows very low conductivity at room temperature but whose conductivity increases with increase in temperature (intrinsic semiconductor) or with the addition of small amount of other elements called dopants (extrinsic semiconductor).

Ex: Si, Ge etc.

According to band theory, there are three types of energy bands in solids,

- Conduction band- within which electrons must move to conduct electricity.
- Valence band- this is the band in which valence electrons are actually present.
- Forbidden band or forbidden gap- this separates the above two bands.

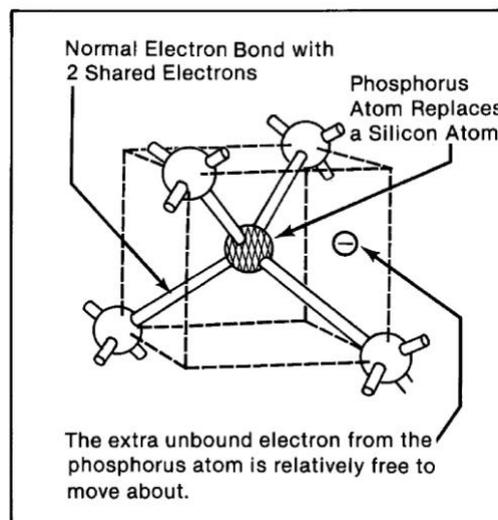
In semiconductors, the energy gap between, valence band and conduction band is very small. When a small amount of energy is supplied, the electrons hop from the valence band to the conduction band and the material starts conducting.

For example, in Silicon which has four valence electrons, each atom is bonded to four other silicon atoms by strong covalent bonds. When the temperature is raised, some of the bonds are broken and electrons jump to conduction band leaving a vacant site called *hole* in the valence band. When connected to an external source of current, silicon conducts electricity due to the movement of these electrons and holes in opposite directions.

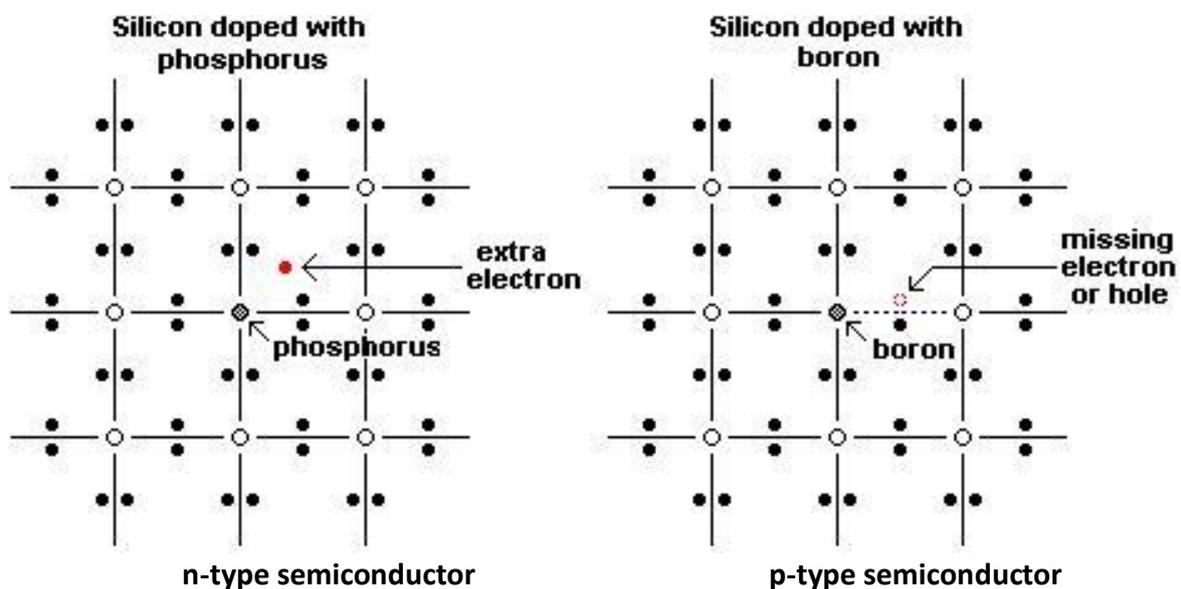
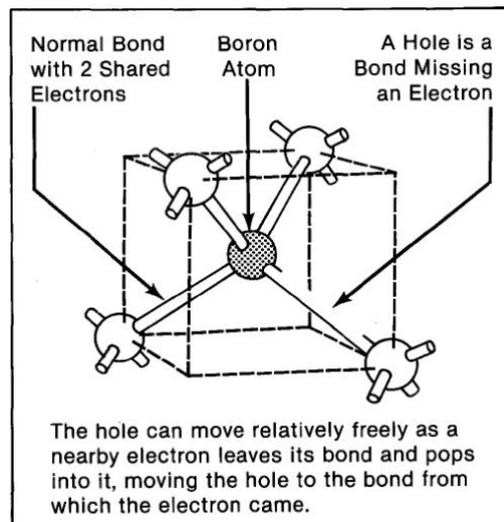
Electrons and holes can also be generated in a semiconductor by doping. Based on the type of doping, there are two types of semiconductors.

- n-type semiconductor and
- p-type semiconductor

When pure silicon is doped with an element such as phosphorous (P) which has five valence electrons, few silicon atoms are replaced by P atoms. P forms four bonds with four silicon atoms and the fifth electron is free. This conducts electricity. This type of semiconductors is called n-type semiconductor.



On the other hand when pure silicon is doped with boron (B) which has three electrons in its valence shell, it forms four bonds with four silicon atoms but out of four, three are normal covalent bonds and the fourth one has only one electron creating a vacancy. This vacancy is called a hole. To compensate this hole, electron from the neighbouring site moves to this site and this process continues. Such type of semiconductor is called p-type semiconductor.



#### 4. Doping by Diffusion Technique:

Introduction of impurity atoms into an intrinsic semiconductor crystal is called Doping.

Dopants can be introduced into silicon atoms by two methods a) Diffusion b) Ion implantation method

##### Diffusion Technique:

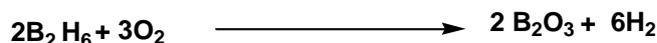
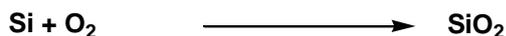
- This involves the movement of atoms, molecules or ions from a region of higher concentration to a region of lower concentration by random movement.
- Diffusion results in gradual mixing of materials. In doping of silicon by diffusion technique, the dopant atoms move through the lattice of silicon. Generally diffusion technique takes place in two steps.
- In the first step, called the deposition step, silicon is exposed to the source of dopant for a relatively short time at a temperature about 1000°C. A tube furnace of 2 to 3 meters length and 100-150 mm diameter is used for diffusion. Silicon wafers are staked in a quartz container placed in the furnace. The tube is maintained at a temperature of 1000°C

- In the second step, called the driving step, the dopant source is removed from the silicon. The dopant atoms entered in the first step, are allowed to diffuse into the body of silicon which is now kept at a higher temperature of 1200°C. After the diffusion, the material is cooled to room temperature. The entire operation is conducted in an inert atmosphere.

#### Diffusion of p-type dopant:

**Step I:** Diborane, B<sub>2</sub>H<sub>6</sub> is used as gaseous source for dopant. Diborane is introduced into the furnace in the presence of nitrogen gas which provides an inert atmosphere. A small amount of oxygen is also passed. The following reactions take place.

**Reactions:**



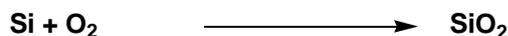
The process is referred to as chemical vapour deposition and a glassy layer called borosilica glass is formed on the surface of silicon. The glassy layer is a mixture of silica glass and boron glass. It is a viscous liquid at diffusion temperature and boron atoms with ease. Also the concentration of boron in the glassy layer is such that the surface of silicon will be saturated with boron as long as glassy layer is present.

**Step II:** In the next step the source of boron is removed so that no additional boron atoms are introduced. The temperature of silicon is raised and the boron atoms, that are already present, move further inside the silicon wafer and gets redistributed.

#### Diffusion of n-type dopant:

Phosphine, PH<sub>3</sub> is used as source of dopant.

**Reactions:**



In this case, the glassy layer is composed of phosphorous and silica glass and is called phosphorosilica glass. The phosphorous concentration in the glassy layer is maintained at the solid solubility limit and the phosphorous atom can move with ease. The process is same as that of boron. The second step which involves driven in of p atoms is carried out in the same manner as in boron

#### Ion implantation method:

In this technique, the semiconductor is impacted with an ion beam of impurity ions. This results in the implantation of some dopant atoms into the semiconductor crystal. The extent of implantations is controlled by the energy of the ion beam.

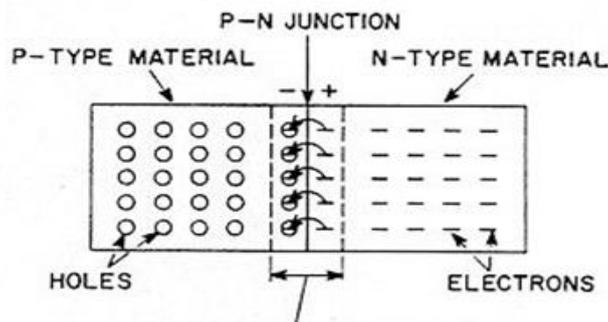
### 5. Solar cells

**Definition:** "A solar cell is a semiconductor device which when exposed to electromagnetic radiations like sun light, generates electricity". It is also called as Photovoltaic cell.

#### p-n junction or semiconductor diode

Certain electronic devices require a semi conduction system with a combination of p- and n-type semiconductors. Solar cell is one such device. Such combinations of semiconductors are **p-n junctions or semiconductor diodes**. When p-n junctions are formed, there is high concentration of holes on the p-side and high concentration of electrons on the n-side. Since there is concentration gradient across the junction, the holes will diffuse towards the n-side and electrons towards the p-side. This results in electron-hole recombination at the vicinity

of the junction. This region as a result has no charge carriers and is called as *depleted zone* or *depleted region*. The thickness of this is of the order of wavelength of light. Before diffusion, the p-side and n-side of the semiconductor diode were neutral. During diffusion, n-side loses electrons and becomes progressively positively charged and resists the diffusion of electrons away from it. Similarly the p-side loses holes and progressively becomes negatively charged and resists the diffusion of holes away from it. Thus equilibrium is reached when the diffusion of holes and electrons across the junction stops. At this equilibrium, the n-region will acquire a positive charge and p-region acquires a negative charge. However, the depletion zone acts as a barrier for further diffusion. Only when an energy exceeding this barrier potential is applied, the material starts conducting.

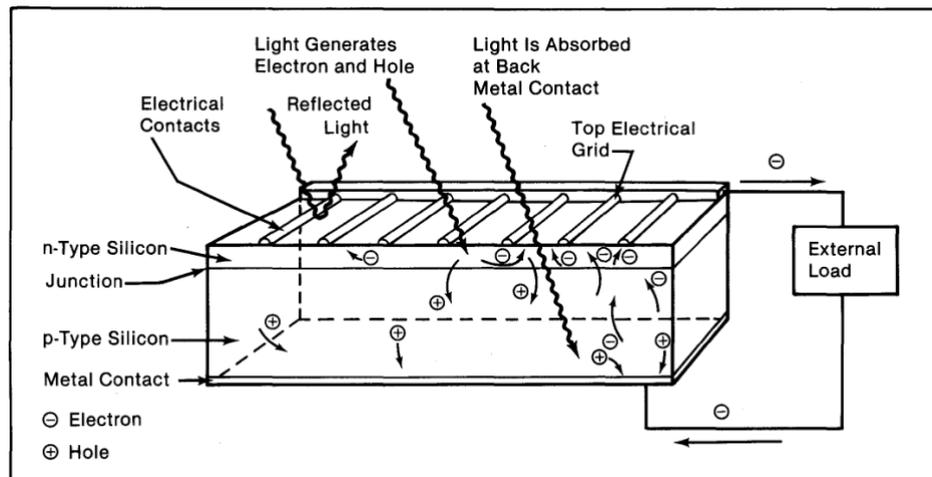


**Depletion zone with a barrier potential**

#### 5b. Construction and working of solar cell or Photovoltaic cell

**Construction:** A typical silicon photovoltaic cell is made up of a thin wafer consisting of an ultra thin layer of phosphorous doped (n-type) silicon on top of boron doped (p-type) silicon. Hence a p-n junction (A semiconductor diode) is formed between the two. A metallic grid forms one of the electrical contacts of the diode and allows light to fall on the semiconductor between the grid lines. This grid like metal contact is made up of fine “fingers” and larger “bus bars” is screen printed onto the front surface using a silver paste. An antireflective layer of silicon nitride or titanium dioxide between the grid lines increases the amount of light transmitted to the semiconductor. The rear metal contact is also formed by screen printing a metal paste of aluminium. The two ends i.e. front metal contact and rear metal contact are electrically connected externally by a metallic conductor to complete the circuit.

**Working:** The sun light consists of particles called photons. The energy of these photons is given by Planks quantum equation, i.e.  $E = hv = hc/\lambda$ , Where h- Planks constant, c- velocity of light and  $\lambda$ - wavelength of light radiation. When light falls on a semiconductor diode or p-n junction diode, the semiconductor absorbs the light energy and produces electrons and holes. A portion of the energy absorbed is also delivered to electrons and holes. The semiconductor diodeseparates the electrons and holes and collects then in a particular direction. The electrons drifted to and collected at the n-type and the holes are drifted to and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use.



### Importance of Solar cells

- With fossil fuels are fast depleting, PV cells are considered to be the future sustainable energy system.
- Solar energy is unlimited, inexhaustible and renewable.
- PV cells can serve for both off-grid and on-grid applications.
- PV cells provide power for space crafts and satellites, an extraterrestrial dimension of photovoltaics.
- Development on the field of photovoltaics will boost the semiconductor and storage battery industries.

### Advantages:

- Solar energy source is vast and essentially infinite.
- No recharging is required.
- Environmentally benign-no combustion, no emission or radioactive residues for disposal.
- Low operating cost
- No movable parts and no wear and tear
- Ambient temperature operation
- Highly reliabilities in modules (> 20 years)
- No corrosion
- Quick installation
- High public acceptance and excellent safety record

### Disadvantages:

- Sunlight is a diffuse source i.e it is relatively low density energy
- High installation cost
- Poor reliability of auxiliary elements including storage
- Energy can be produced only during the day time
- Lack of widespread commercially available system integration and installation.

### Application of solar energy:

- For generating electricity in rural (villages) or remote (Mountains) areas where individual families live far away from electric grids.
- **Domestic applications:** Lighting, spinning of fans, grinding of grains, transistor radios, small TV sets & tape recorders.

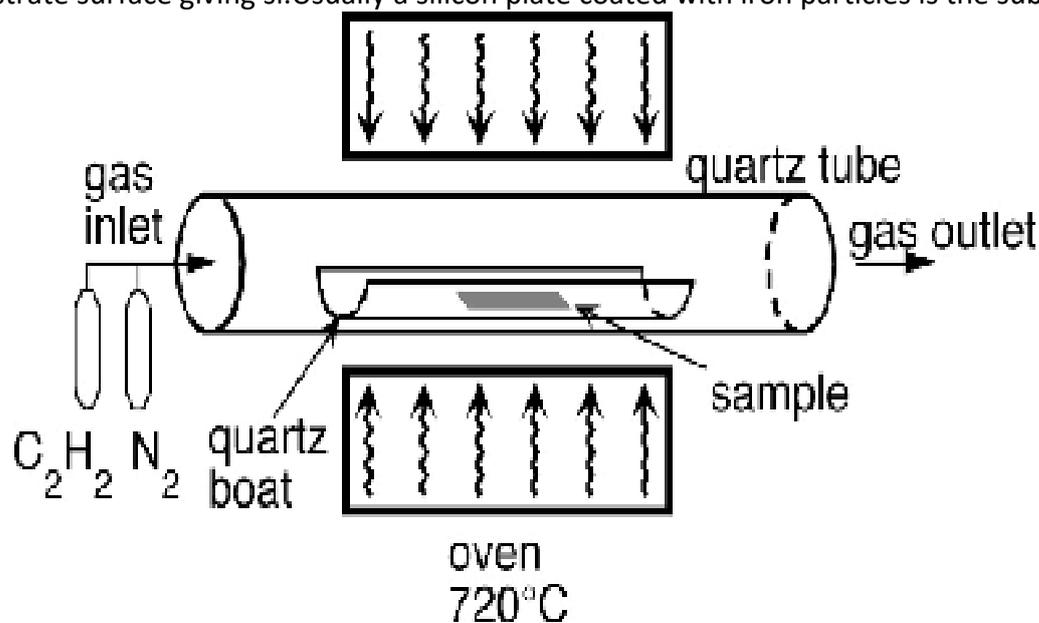
- **Community applications:** In schools for educational TV, internet and satellite linking
- **In health centre:** For surgery, for refrigerators and sterilisers
- In Telephone broadcasting stations and street lights or traffic signals
- **In Agriculture:** For irrigation, animal husbandry for watering and milking
- **In Production activities:** Milling, sawing, sewing

#### 6. Manufacturing of photovoltaic cells by Chemical Vapour Deposition Techniques:

Chemical vapour deposition is the formation of non-volatile solid film on a substrate by the reaction of vapour phase chemicals (reactants) that contain required constituents

The reactant gases are introduced into a reaction chamber and are decomposed and reacted at heated surface to form a thin film.

In typical CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. In the production of Si, silicon source in the gas phase is passed into the reactor along with a carrier gas. In the reactor, at the prevailing high temperatures the silica source undergoes pyrolysis giving small silicon particles. These particles get deposited on the substrate surface giving Si. Usually a silicon plate coated with iron particles is the substrate.



Manufacturing of photovoltaic cell

#### Purifying the silicon

- **Step-1**  
The silicon dioxide of either quartzite gravel or crushed quartz is placed into an electric arc furnace. A carbon arc is then applied to release the oxygen. The products are carbon dioxide and molten silicon. This simple process yields silicon with one percent impurity, useful in many industries but not the solar cell industry.
- **Step-2 (zone refining)**  
The 99 percent pure silicon is purified even further using the floating zone technique. A rod of impure silicon is passed through a heated zone several times in

the same direction. This procedure "drags" the impurities toward one end with each pass. At a specific point, the silicon is deemed pure, and the impure end is removed.

#### Making single crystal silicon

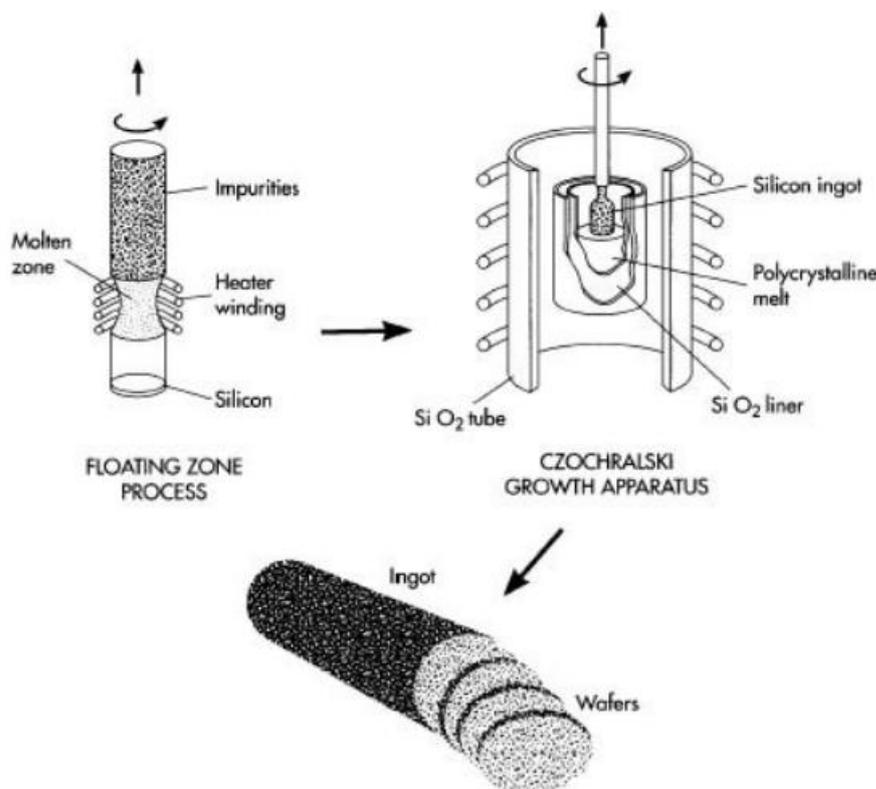
- Step-3(czochralski crystal pulling technique)

Solar cells are made from silicon boules, polycrystalline structures that have the atomic structure of a single crystal. The most commonly used process for creating the boule is called the *Czochralski method*. In this process, a seed crystal of silicon is dipped into melted polycrystalline silicon. As the seed crystal is withdrawn and rotated, a cylindrical ingot or "boule" of silicon is formed. The ingot withdrawn is unusually pure, because impurities tend to remain in the liquid.

#### Making silicon wafers

- Step-4

From the boule, silicon wafers are sliced one at a time using a circular saw whose inner diameter cuts into the rod, or many at once with a multiwire saw. (A diamond saw produces cuts that are as wide as the wafer— .5 millimeter thick.) Only about one-half of the silicon is lost from the boule to the finished circular wafer—more if the wafer is then cut to be rectangular or hexagonal. Rectangular or hexagonal wafers are sometimes used in solar cells because they can be fitted together perfectly, thereby utilizing all available space on the front surface of the solar cell.



After the initial purification, the silicon is further refined in a floating zone process. In this process, a silicon rod is passed through a heated zone several times, which serves to 'drag' the impurities toward one end of the rod. The impure end can then be removed.

Next, a silicon seed crystal is put into a Czochralski growth apparatus, where it is

dipped into melted polycrystalline silicon. The seed crystal rotates as it is withdrawn, forming a cylindrical ingot of very pure silicon. Wafers are then sliced out of the ingot.

- Step-5  
The wafers are then polished to remove saw marks. (It has recently been found that rougher cells absorb light more effectively, therefore some manufacturers have chosen not to polish the wafer.)

#### *Doping*

- Step-6 (diffusion technique or ion beam implantation)  
The traditional way of doping (adding impurities to) silicon wafers with boron and phosphorous is to introduce a small amount of boron during the Czochralski process in step #3 above. The wafers are then sealed back to back and placed in a furnace to be heated to slightly below the melting point of silicon (2,570 degrees Fahrenheit or 1,410 degrees Celsius) in the presence of phosphorous gas. The phosphorous atoms "burrow" into the silicon, which is more porous because it is close to becoming a liquid. The temperature and time given to the process is carefully controlled to ensure a uniform junction of proper depth.  
A more recent way of doping silicon with phosphorous is to use a small particle accelerator to shoot phosphorous ions into the ingot. By controlling the speed of the ions, it is possible to control their penetrating depth. This new process, however, has generally not been accepted by commercial manufacturers.

#### *Placing electrical contacts*

- Step7  
Electrical contacts connect each solar cell to another and to the receiver of produced current. The contacts must be very thin (at least in the front) so as not to block sunlight to the cell. Metals such as palladium/silver, nickel, or copper are vacuum-evaporated through a photoresist, silkscreened, or merely deposited on the exposed portion of cells that have been partially covered with wax. All three methods involve a system in which the part of the cell on which a contact is not desired is protected, while the rest of the cell is exposed to the metal.
- Step8  
After the contacts are in place, thin strips ("fingers") are placed between cells. The most commonly used strips are tin-coated copper.

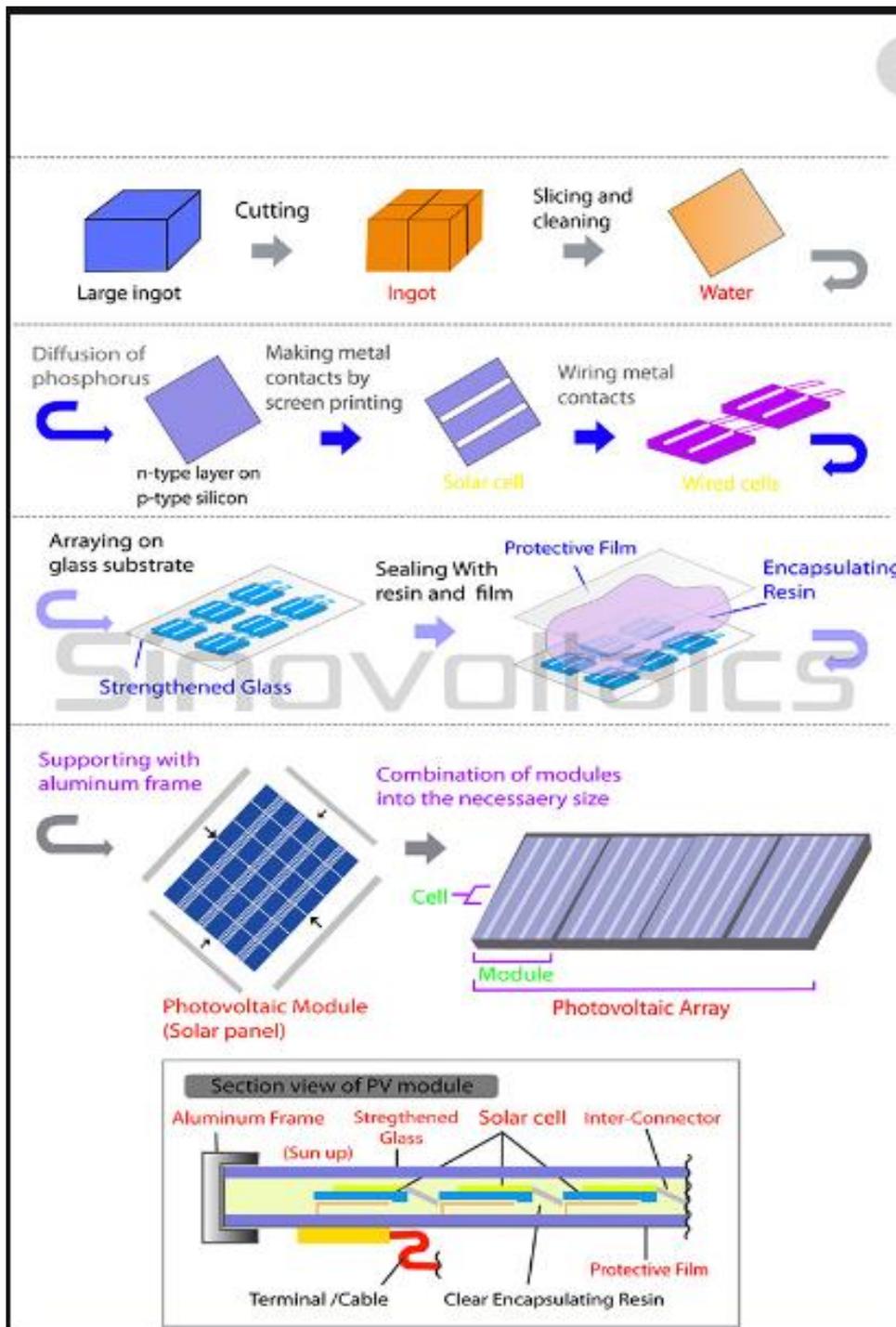
#### *The anti-reflective coating*

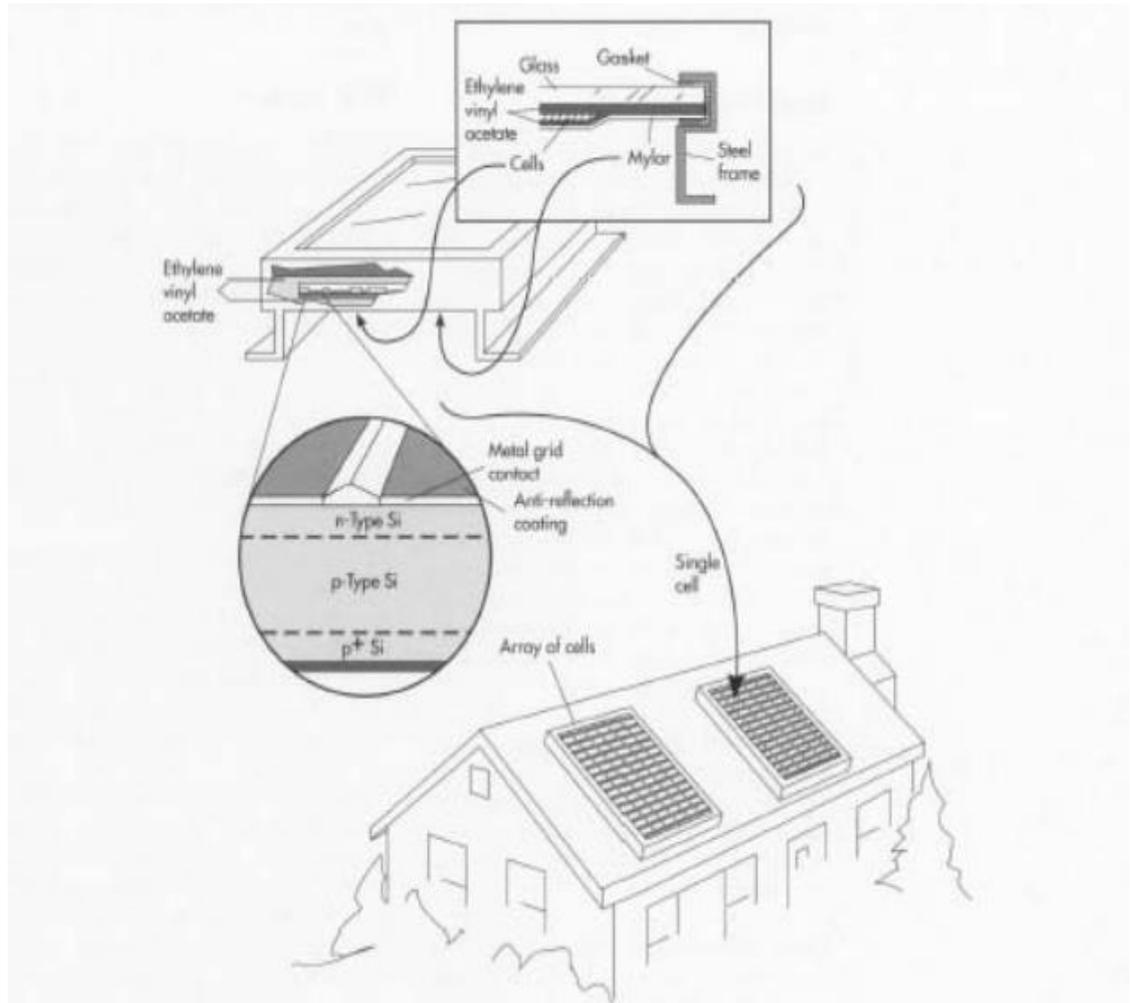
- Ste 9  
Because pure silicon is shiny, it can reflect up to 35 percent of the sunlight. To reduce the amount of sunlight lost, an anti-reflective coating is put on the silicon wafer. The most commonly used coatings are titanium dioxide and silicon oxide, though others are used. The material used for coating is either heated until its molecules boil off and travel to the silicon and condense, or the material undergoes sputtering. In this process, a high voltage knocks molecules off the material and deposits them onto the silicon at the opposite electrode. Yet another method is to allow the silicon itself to react with oxygen- or nitrogen-containing gases to form silicon dioxide or silicon nitride. Commercial solar cell manufacturers use silicon nitride.

Encapsulating the cell

- Step10

The finished solar cells are then encapsulated; that is, sealed into silicon rubber or ethylene vinyl acetate. The encapsulated solar cells are then placed into an aluminum frame that has a mylar or tedlarbacksheet and a glass or plastic cover.





This illustration shows the makeup of a typical solar cell. The cells are encapsulated in ethylene vinyl acetate and placed in a metal frame that has a mylar backsheet and glass cover.

