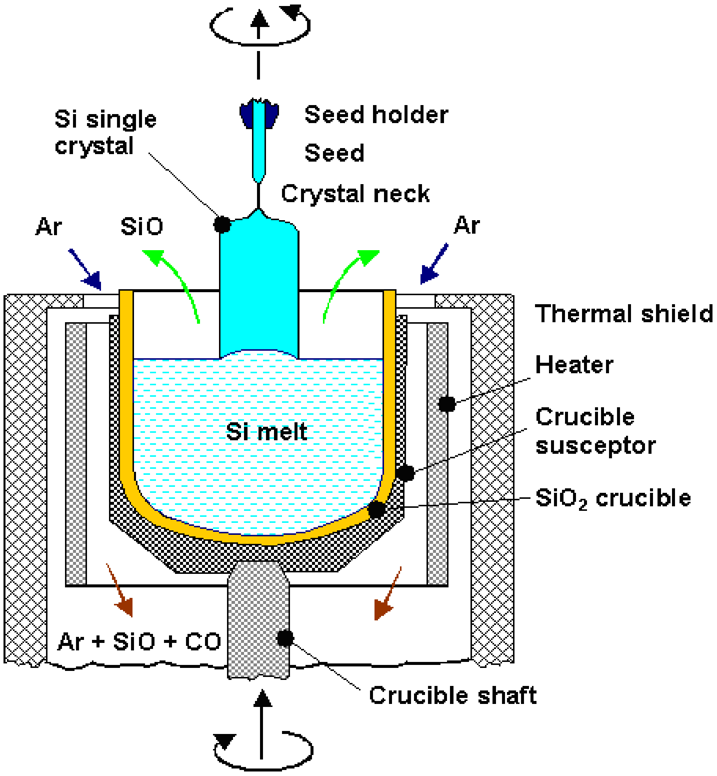
Chapter 3: Synthesis, Characterization and Applications of semiconductors

3.1 Synthesis of semiconductors

a) Synthesis of single crystalline semiconductors:

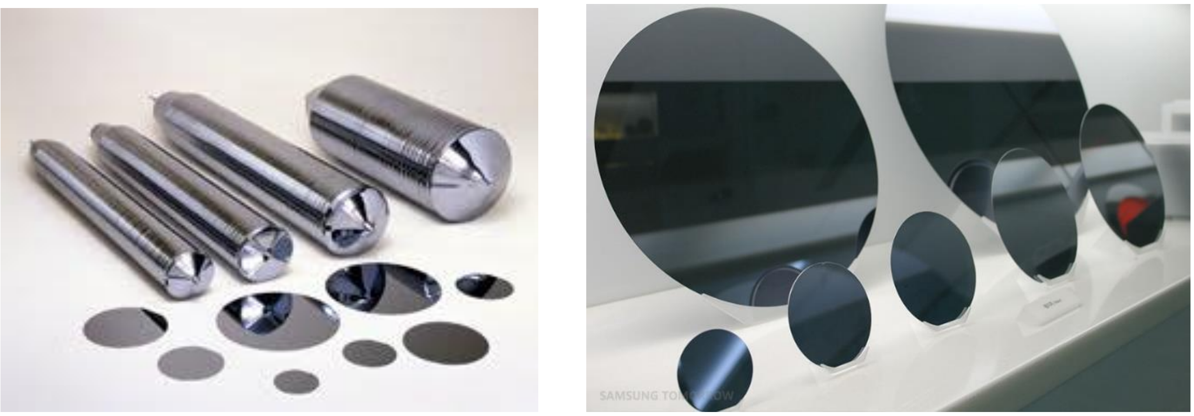
Monocrystalline silicon (also called **single-crystal silicon**) is the base material for silicon-integrated circuits used in all modern electronic equipment. Mono-Si also serves as a photovoltaic, light-absorbing material in the manufacture of solar cells. Mono-Si can be prepared as an intrinsic semiconductor that consists only of exceedingly pure silicon, or it can be doped by the addition of other elements such as boron or phosphorus to make p-type or n-type silicon. Due to its semiconducting properties, single-crystal silicon is perhaps the most important technological material of the last few decades. because its availability at an affordable cost has been essential for the development of the electronic devices on which the present-day electronics and IT revolution is based.

Monocrystalline silicon is generally created by one of several methods that involve melting high-purity and the use of a seed to initiate the formation of a continuous single crystal. The most common production method is the **Czochralski** process. The **Czochralski** process is a method of crystal growth used to obtain single crystals of semiconductors (e.g. silicon, germanium. High-purity, semiconductor is melted in a crucible at 1425 °C, usually made of quartz. Dopant impurity atoms such as boron or phosphorus can be added to the molten silicon in precise amounts to dope the silicon, thus changing it into p-type or n-type silicon, with different electronic properties. The figure below shows a diagram representing the manufacturing process of single crystalline Silicon.



Czochralski process of the synthesis of single crystalline silicon

Monocrystalline cylindrical ingot up to 2 meters in length and weighing several hundred kilograms sliced into thin wafers during a process called wafering. After post-wafering processing, the wafers are ready for use in fabrication.

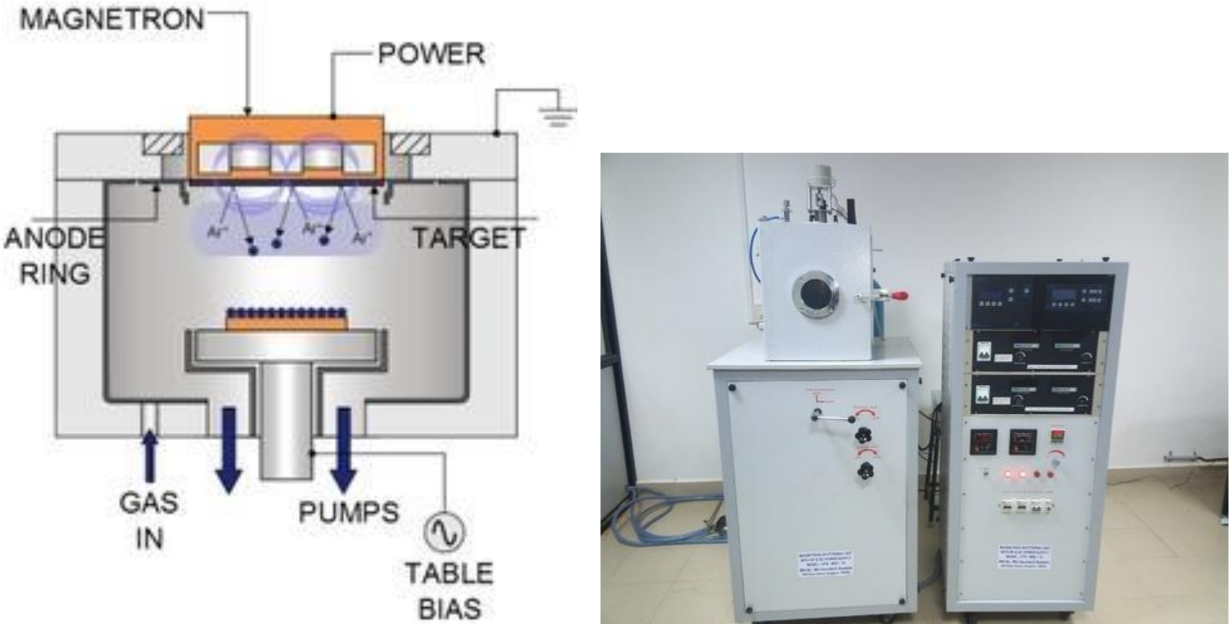


Single crystalline silicon wafers

b) Physical preparation approaches of semiconductor

- Physical vapor deposition (PVD):

Physical vapor deposition (PVD) describes a variety of vacuum deposition methods which can be used to produce thin films and coatings. PVD is characterized by a process in which the material goes from a condensed phase to a vapor phase and then back to a thin film condensed phase. The most common PVD processes are sputtering and evaporation. PVD is used in the manufacture of items which require thin films for mechanical, optical, chemical or electronic functions. Examples include semiconductor devices such as thin film solar panels. The use of PVD is increasing rapidly in the industry to replace less environment-friendly chemical and galvanic methods.



PVD synthesis process with the used machines

Advantages

- PVD coatings are sometimes harder and more corrosion resistant. Most coatings have high temperature and good impact strength, excellent abrasion resistance and are so durable that protective topcoats are almost never necessary.
- More environmentally friendly than traditional coating processes such as electroplating.

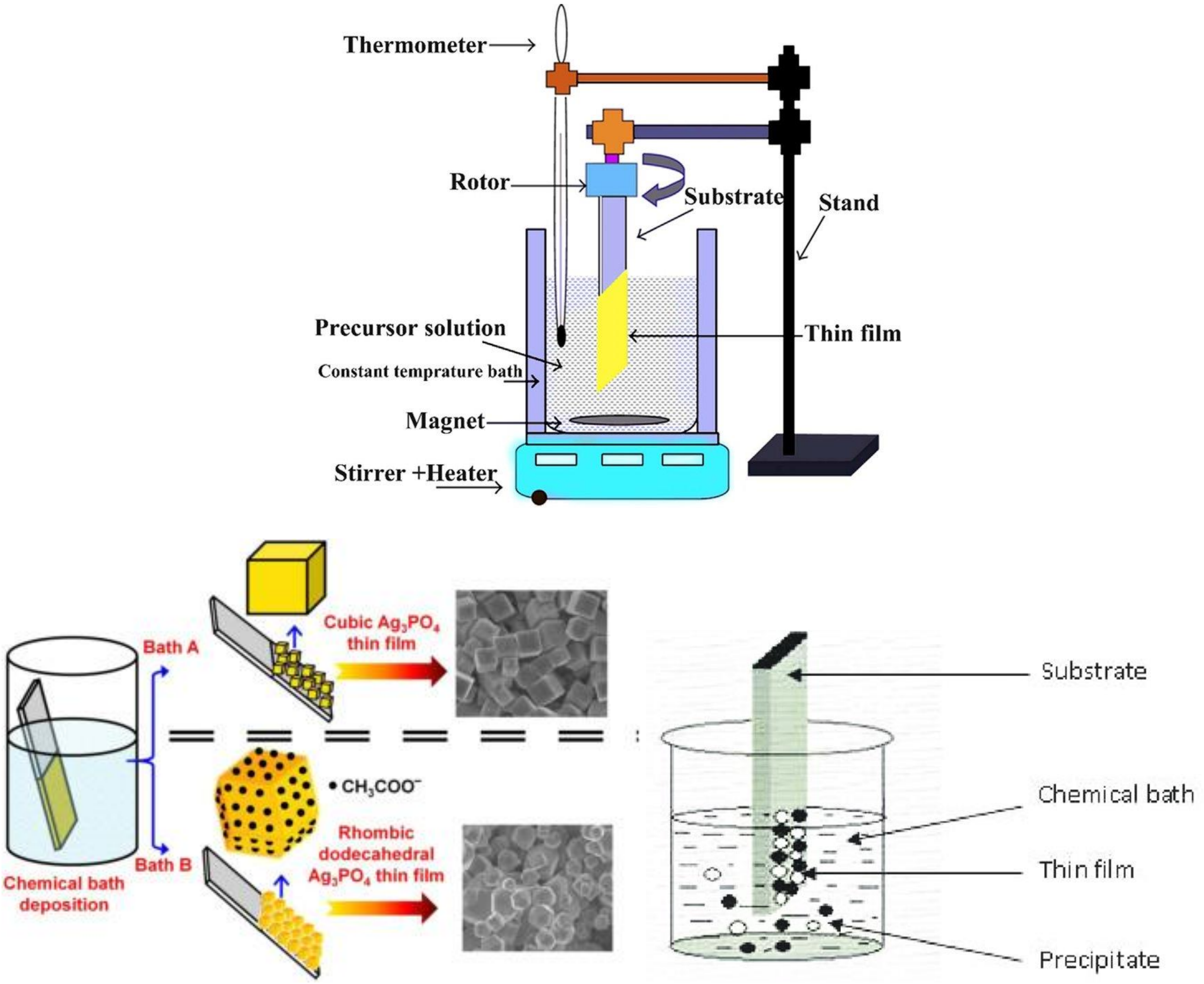
Disadvantages

- Some PVD technologies typically operate at very high temperatures and vacuums, requiring special attention by operating personnel.
- Requires a cooling water system to dissipate large heat loads.

c) Chemical synthesis approaches

- Chemical bath deposition (CBD)

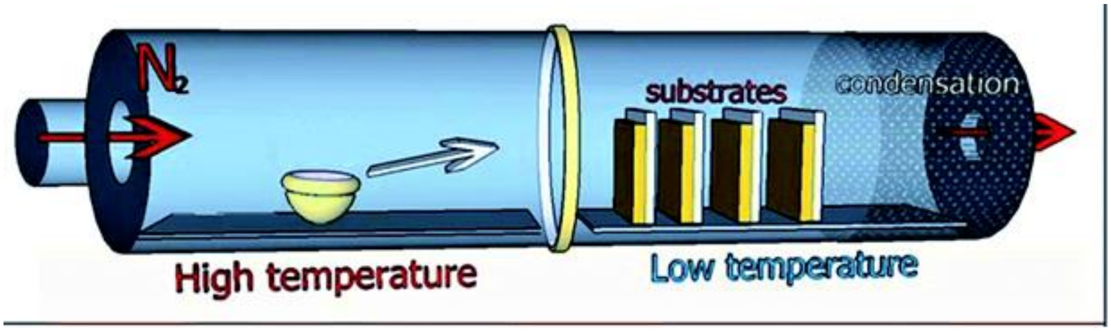
Chemical bath deposition (CBD), or chemical solution deposition (CSD), is a method to deposit thin films and nanomaterials. It can be employed for large-area batch processing or continuous deposition. The major advantage of CBD is that it requires in its simplest form only solution containers and substrate mounting devices. One of the drawbacks of this method is the wastage of solution after every deposition. Chemical bath deposition yields stable, adherent, uniform and hard films with good reproducibility by a relatively simple process. The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition and temperature of the solution and chemical nature of the substrate. The chemical bath deposition involves two steps, nucleation and particle growth, and is based on the formation of a solid phase from a solution. In the chemical bath deposition procedure, the substrate is immersed in a solution containing the precursors. This method depends upon parameters like bath temperature, pH of the solution, molarity of concentration and time.



CBD technique and preparation process

- Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is a vacuum deposition method used to produce high quality, high-performance, solid materials. The process is often used in the semiconductor industry to produce thin films. 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. Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline materials. Advantages of the method include a potential for both conformal and large-area growth, and the possibility of achieving, reproducibly, very high levels of purity in the as-grown materials. A schematic representation of the process is shown in the below Fig. The N_2 gas assisted in the precipitation (deposition) of the semiconductor on the required substrate.



Schematic representation for CVD process

The CVD process involves depositing a solid material from a gaseous phase; this is achieved by means of a chemical reaction between volatile precursors and the surface of the materials to be coated. As the precursor gases pass over the surface of the heated substrate, the resulting chemical reaction forms a solid phase which is deposited onto the substrate. The substrate temperature is critical and can influence the occurrence of different reactions.

3.2 Characterization techniques of semiconductor:

Semiconductor materials and devices continue to occupy a preeminent technological position due to their importance when building integrated electronic systems used in a wide range of applications from computers, cell-phones, digital cameras, to electronic instrumentation for medical diagnostics and environmental monitoring. However, when assessing material quality and device reliability, it is important to have fast, nondestructive, accurate and easy-to-use electrical characterization techniques available, so that important parameters such as carrier concentration (doping density), type and mobility of carriers, optical generation and recombination rate, carrier lifetimes and defect concentration. In this part, important methods used to experimentally characterize a semiconductor material will be summarized.

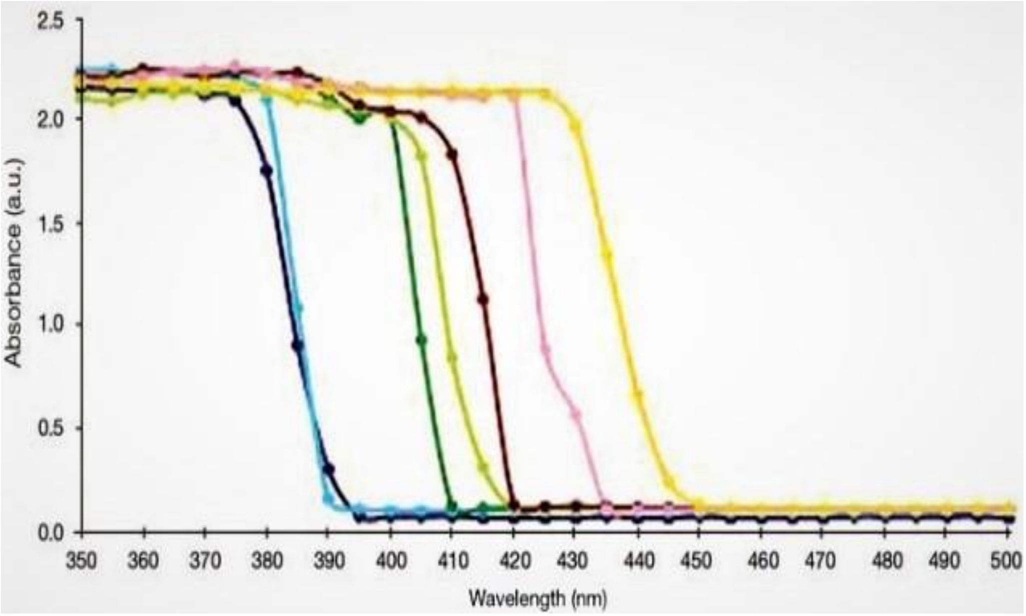
Characterization of a semiconductor falls into three categories:

1) Optical characterization
2) Electrical characterization
3) Structural characterization

1. **Optical characterization:**

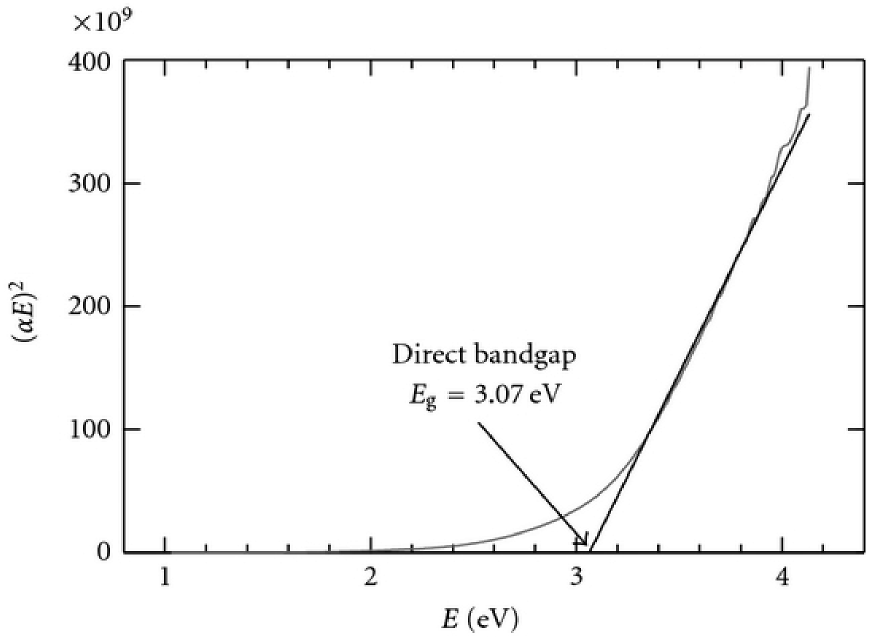
Optical Characterization may include the most two powerful techniques, **a:** Ultraviolet–visible spectroscopy (***UV–Vis***) and **b:** Photoluminescence spectroscopy (***PL***).

a) **Ultraviolet–visible spectroscopy** (***UV–Vis***): refers to absorption spectroscopy in part of the ultraviolet and the full, adjacent visible spectral regions. This means it uses light in the visible and adjacent ranges. The absorbed light range is directly related to the band gap of the examined semiconductor as it can be seen in the figure below. Absorption spectrum produced by the absorption of light by different semiconductors. Each absorption edge represents a specific bandgap.



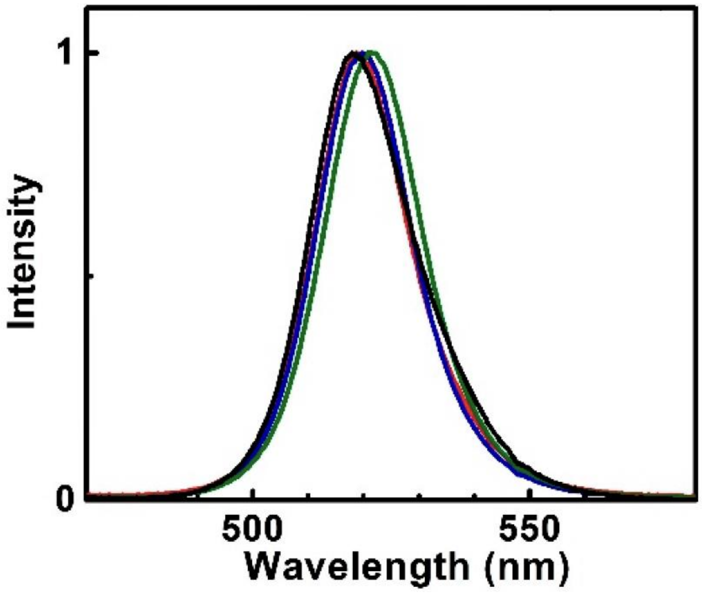
Absorption edges of light by the semiconductors. Each edge represents a specific bandgap

The **UV-Vis** spectrum can be used to calculate the band gaps of semiconductor material (direct and indirect bandgap), by plotting the graph between $(ahv)^{(1/n)}$ versus photon energy (hv). Where $\boldsymbol{a}$ is the optical absorption coefficient, which can be calculated from absorbance ($\boldsymbol{A}$), and thickness of the sample ($\boldsymbol{t}$) using: ($\boldsymbol{a=2.303A/t}$); and ($\boldsymbol{hv}$) can be calculated form wavelength using: ($\boldsymbol{hv = 1240/wavelength}$); The power factor ($\boldsymbol{n}$) takes the values of 0.5 for direct and 2 for indirect bandgap. The figures below illustrated plotted graphs to determine the energy gap of a semiconductor. The point of intersection between the tangent and the *x-axis* gives the value of the energy gap.



The point of intersection shows the value of the energy gap (*Eg*= 3.2 eV)

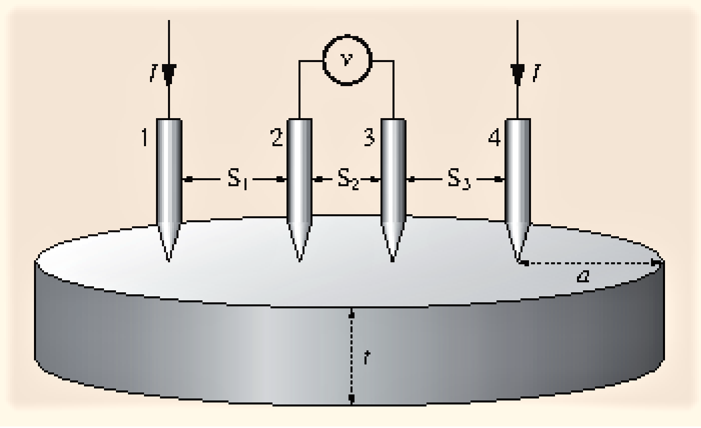
b) Photoluminescence spectroscopy (PL): is a powerful optical method used for characterizing materials. PL can be used to find impurities and defects in silicon semiconductors, and to determine semiconductor band-gaps. A material absorbs light, creating an electron-hole pair; an electron from the valence band jumps to the conduction band leaving a hole. The photon emitted upon electron-hole recombination corresponds to the energy-difference between the valence and conduction bands and is hence indicated the energy gap. The peak of the graph represents an approximated value of a semiconductor energy gap as shown in the figure below.



PL measurement; the graph has a peak at about 525 nm represents an approximated value of the semiconductor energy gap

2. Electrical characterization:

Electrical characterization can be used to determine resistivity, carrier concentration (*n* or *p*) and mobility of charge carriers. Carrier density (*n* or *p*) or the carrier mobility (μ_n or μ_p) are considered to be fundamental. Such measurements can be performed using the *four-point-probe* technique and by the ***Hall*** effect. For the *four-point-probe* technique, two probes are used for current injection and the other two probes are used to measure the voltage drop. The more usual probe geometry configuration is when the four probes are placed in a line, as shown in the figure.



Linear four-point probe configuration. The sample thickness is *t* and *a* is the distance from the edge or boundary of the sample

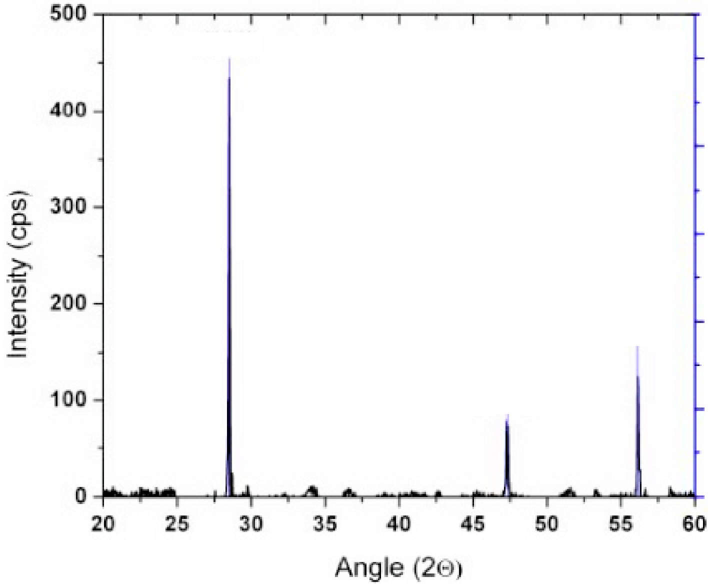
By measuring the voltage drop between probes and the current *I* through probes 1 and 4, the resistivity can be determined.

In the ***Hall*** effect experiment, the measurement of the ***Hall*** coefficient leads to the direct determination of the carrier concentration and mobility. Moreover, the indicated sign can be used to determine the type of conductivity of the semiconductor sample *n* or *p* type. Currently, ***Hall*** effect measurements are one of the most commonly used characterization tools in the semiconductor industry and research laboratories.

Hall effect measurement

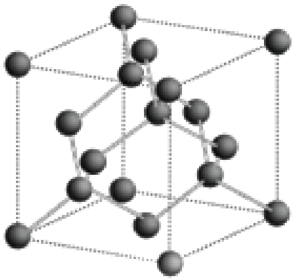
3. Structural characterization

The structural characterization of a semiconductor can be determined by using the X-ray diffraction (**XRD**) technique. It is a powerful non-destructive test used to determine the crystal properties (**crystallinity**) of the examined material (semiconductors). In brief, the spatial distribution and intensity of scattered x-rays provide information on the arrangement of atoms in a periodic sample. Different materials have different and unique diffracted patterns that provide detailed information about the examined material. The figure below shows a diffraction pattern of a Si crystal. The pattern has diffracted intensities at specific angles theta (Θ) as indicated by the plotted data along ***x*** and ***y*** axes.



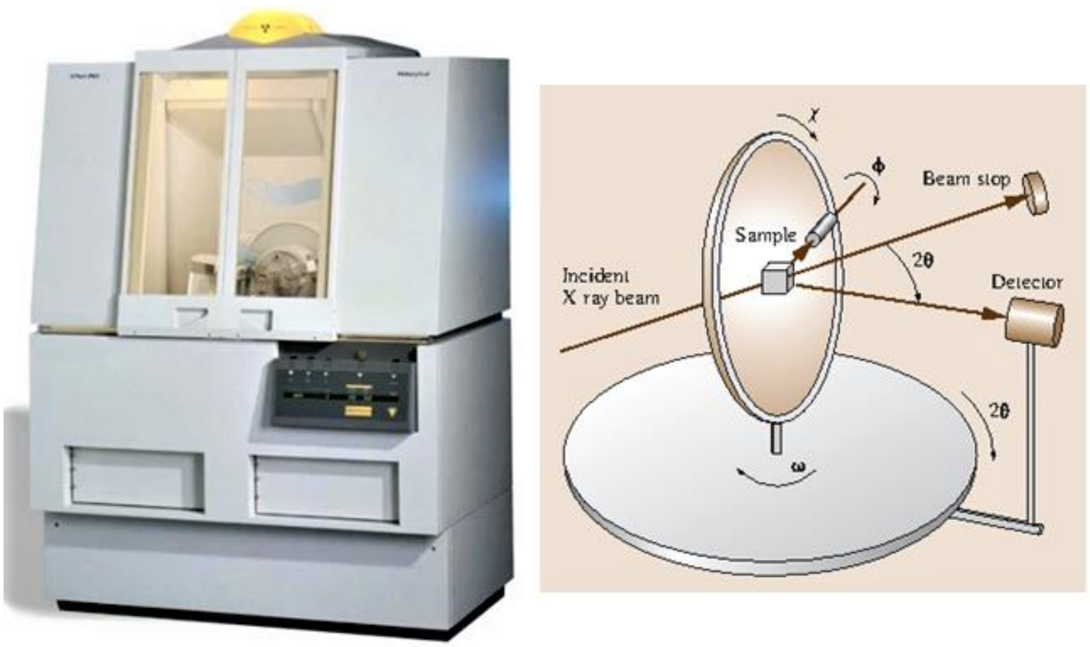
XRD pattern of standard Si. The pattern shows diffracted X-rays at specific angles (*Θ*) corresponding to the Si material

Silicon crystallizes in a giant covalent structure at standard conditions, specifically in a diamond cubic lattice.



A cubic structure of Si

The figures below can be useful to demonstrate the XRD machine and the measurement diagram to determine a material crystallinity.



XRD machine with measurement diagram

3.3 Applications of semiconductors

1. Device fabrication technology

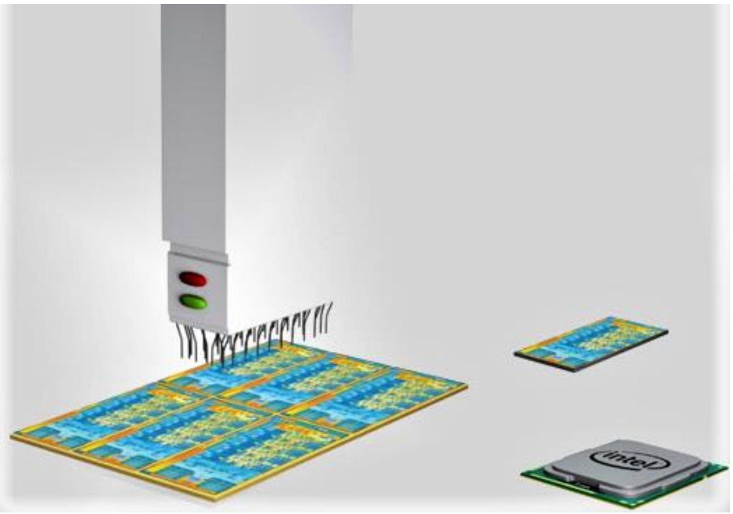
Semiconductor devices are responsible for the arrival of the “computer age”. At the heart of the information and communication technologies, ICs of all descriptions also find applications in consumer electronics, automobiles, medical equipment, and industrial electronics. As a result, semiconductor devices are making contributions to every segment of the global economy and every branch of human endeavors. One of the most important devices that needs to be highlighted in the fabrication technology is the fabrication (manufacturing) of the central processing unit (CPU) which plays major roles in daily life requirements such as cellphones, computers, cars, washing machines and etc. In this regard, the fabrication of CPU devices will be discussed in the following section.

Fabrication of the CPU:

CPUs are made mostly of an element called silicon. Silicon is common in earth’s crust and is a semiconductor. The first stage in making a CPU is to make the wafers (Silicon wafers). The silicon wafers are then polished in order to provide the best possible surface for the following fabrication steps.

A polished Silicon wafer

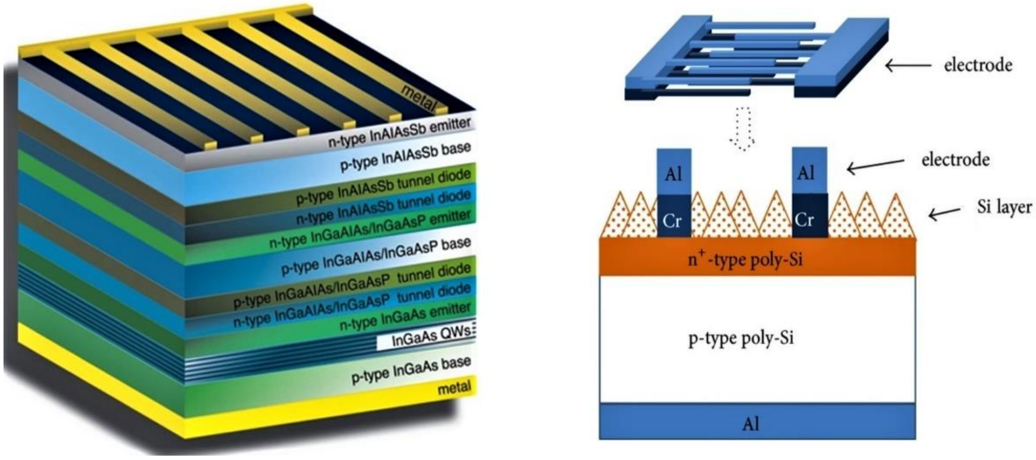
After being polished for the process, a layer of photoresist is spread thinly across the wafer and shaped in the pattern of the microprocessor’s circuits. Next, manufacturers use a process called electroplating to deposit copper ions on the surface of the chip, forming a layer of copper on top of the CPU.



Synthesis of processor chips

Device fabrication technique may follow the following basic steps:

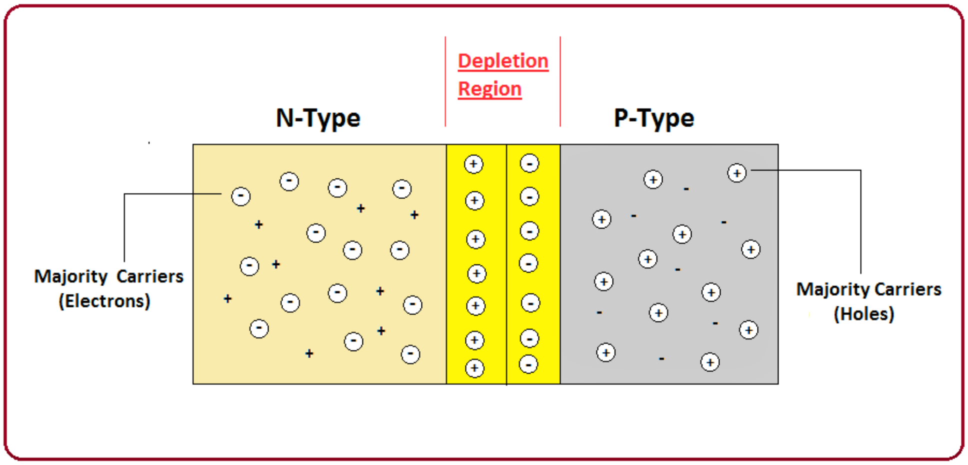
1. Synthesis of the required semiconductor (p or n type) following one of the required synthesis techniques (physical or chemical based technique).
2. Cleaning the semiconductor surface.
3. Go for the required characterization technique to determine the quality of the semiconductor.
4. Do the metallization by the deposition of a required metal contact (Al, Cu, Ag,) on the cleaned semiconductor surface to make metal contacts.



Schematic illustrations represent semiconductor-based device structure

2. The p-n junction:

A p–n junction is a boundary or interface between two types of semiconductors, p-type and n-type, inside a single crystal of semiconductor. The "p" (positive) side contains an excess of holes, while the "n" (negative) side contains an excess of electrons in the outer shells of the electrically neutral atoms. The *p*-*n* junctions are formed by joining *n*-type and *p*-type semiconductors. The *n*-type region has a high electron concentration and the *p*-type a high hole concentration, electrons diffuse from the *n*-type side to the *p*-type side. Similarly, holes flow by diffusion from the *p*-type side to the *n*-type side. This diffusion process would continue until the concentration of electrons and holes on the two sides were the same. However, in a *p*-*n* junction, when the electrons and holes move to the other side of the junction, they leave behind ions (charges). On the *n*-type side, positive ion cores are existed. On the *p*-type side, negative ion cores are existed resulting in an electric field (*E*) forms between the positive ions in the *n*-type material and negative ions in the *p*-type material (the junction). This region is called the "***depletion region***" because the region is depleted of free carriers. The figure below represents a schematic p-n junction semiconductor.

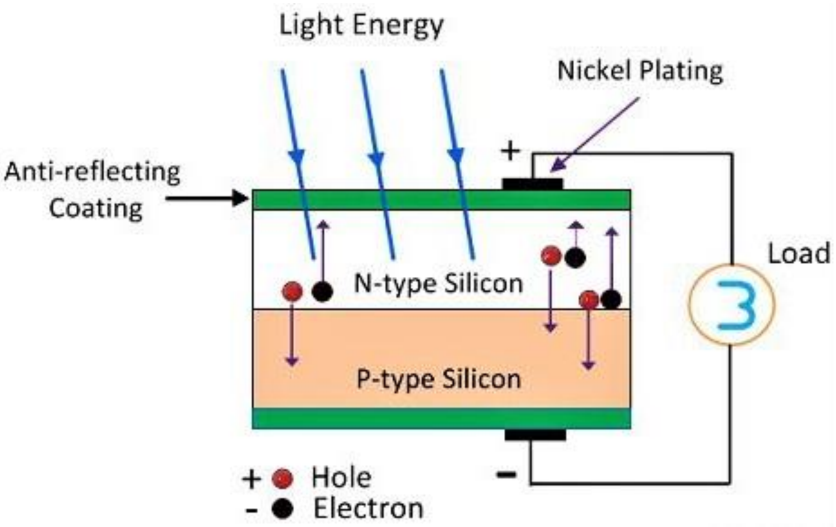


p-n junction-based semiconductor device

A "built-in" potential V_{bi} is formed at the junction due to the electric field (E) allows current to flow in one direction. p–n junctions are basic in semiconductor electronic devices such as diodes, transistors, solar cells and LEDs.

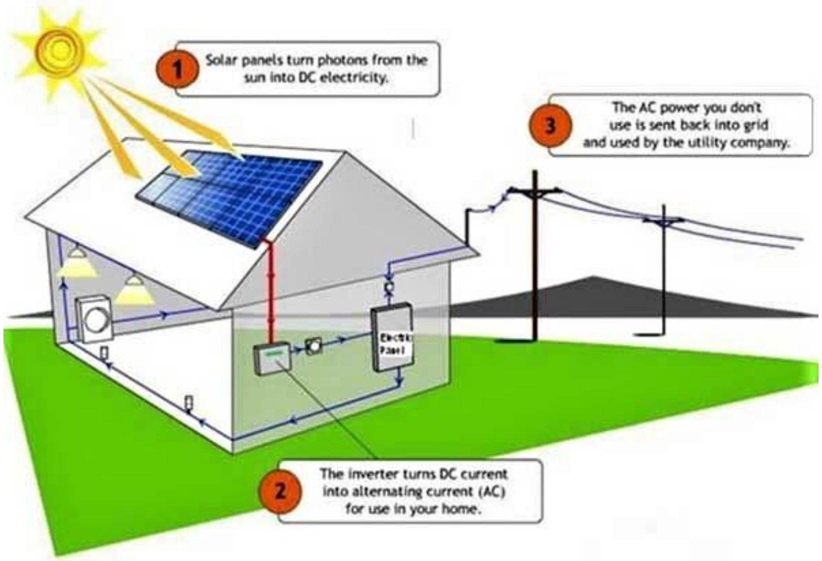
Solar cell:

A **solar cell**, or **photovoltaic cell**, is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect. Solar cell has specific advantages as a clean energy source; renewable energy. The most commonly known solar cell is configured as a large-area p–n junction made from silicon. Usually, silicon is used in two layers. One layer p-type and the other layer is n-type. Semiconductors in thicknesses of about one-hundredth of a centimeter or less (few microns) can absorb all incident visible light. Other possible solar cell types are organic solar cells and dye sensitized solar cells. The illuminated side of a solar cell generally has a transparent conducting film for allowing light to enter into active material and to collect the generated charge carriers. Typically, films with high transmittance and high electrical conductance.



Solar cell diagram with working principle

Photons in sunlight hit the solar panel and are absorbed by semiconducting materials. Electrons are excited from their orbital, once an electron is excited free electrons are generated and the current will flow through the material. p–n junction, Single crystalline silicon-based devices are now approaching the theoretical limiting power efficiency of 33.16%.


1 Solar panels turn photons from the sun into DC electricity.

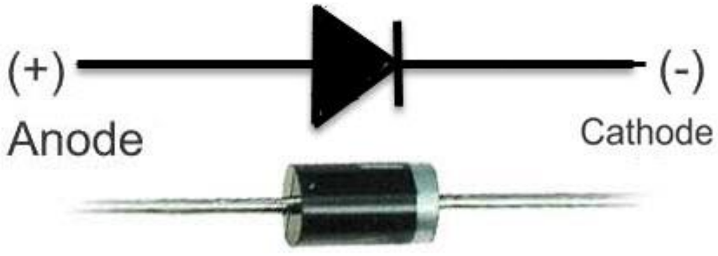
3 The AC power you don't use is sent back into grid and used by the utility company.

2 The inverter turns DC current into alternating current (AC) for use in your home.

Solar cells as a source of clean and renewable energy

Diodes

Diode is an electrical component that allows the flow of current in only one direction. In circuit diagrams, a diode is represented by a triangle with a line across one vertex.

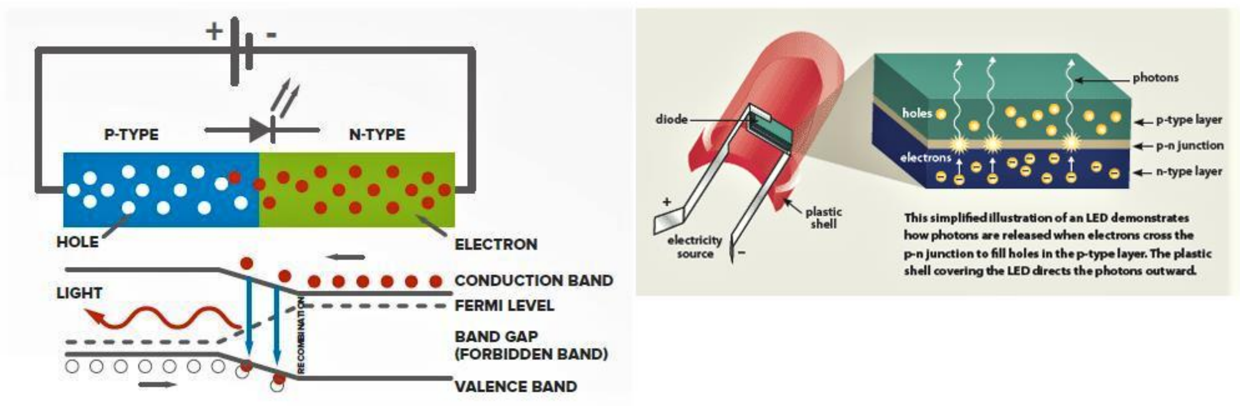


Diode structure

The most common type of diode uses a *p-n* junction. In this type of diode, one material (*n*) in which electrons are charge carriers bounds a second material (*p*) in which holes act as charge carriers. At their interface, a depletion region is formed across which electrons diffuse to fill holes in the *p*-side. This stops the further flow of electrons. The Light-emitting diodes (LEDs) are *p-n* junctions that emit light when a current flow through them.

LEDs

LED stands for light-emitting diode. LEDs are widely used as a standard source of light in electrical equipment. It has a wide array of applications ranging from your mobile phone to large advertising billboards. They find applications in devices for showing what the time is and for displaying different types of data. **Physics of LEDs:** The holes lie in the valence band, while the free electrons are in the conduction band. When there is a forward bias in the p-n junction, the electron which is a part of the n-type semiconductor material would overrun the p-n junction and join with the holes in the p-type semiconductor material. Therefore, regarding the holes, the free electrons would be at the higher energy bands. When this movement of free electron and hole takes place, there is a change in the energy level as the voltage drops from the conduction band to the valance band. There is a release of energy in the form of photons emit light energy due to the motion of the electron. The entire process is known as electroluminescence, and the diodes are known as a light-emitting diode. The color and wavelength of the light emitted can be determined by doping it with several impurities.



This simplified illustration of an LED demonstrates how photons are released when electrons cross the p-n junction to fill holes in the p-type layer. The plastic shell covering the LED directs the photons outward.

LED working principle

Uses of LED

- Used for TV back-lighting
- Uses in displays
- Used in automotive
- Signboard lighting

Applications of LED