UNIT 4

SURFACE TREATMENTS

Surface properties – Hydrophobic – Super hydrophobic – Hydrophilic:

The processes of interaction of liquid droplets with solid surfaces have become of interest to many fields, Collisions of drops with surfaces significantly affect the conditions and characteristics of heat transfer.

Changes in the hydrophilic and hydrophobic properties of surfaces give the materials various functional properties—increased heat transfer, resistance to corrosion and biofouling, anti-icing, etc.

The interaction of water with surfaces is frequently used to define surface properties,

A surface is **hydrophobic** if it tends not to adsorb water or be wetted by water.

A surface is **hydrophilic** if it tends to adsorb water or be wetted by water.

The interaction processes of liquid drops with solid surfaces determine the characteristics of many technological and natural processes: inkjet printing, metal hardening, medicine applications, pesticide spraying, coating, spray cooling, etc.

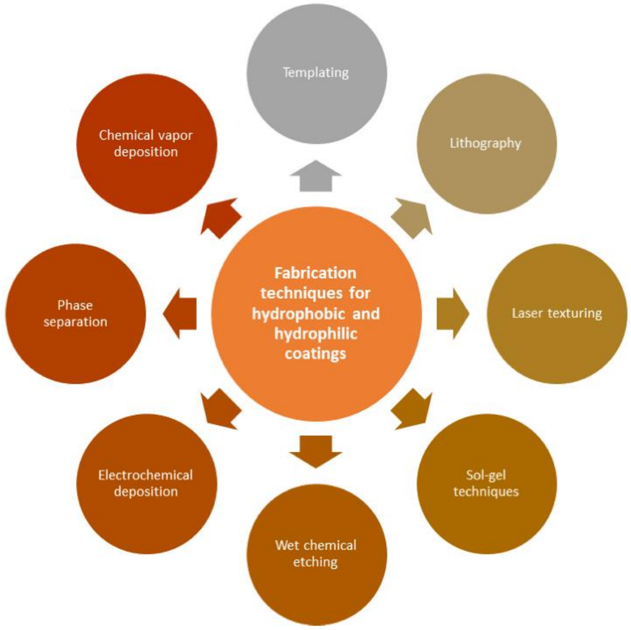
The contact time of droplets with the surface has a strong influence on the characteristics of processes in anti-icing technologies. The deposition of thin multilayer films on solid surfaces is used in the production of optics, sensors, etc.

In fluid bed reactors, the wettability of catalyst particles affects the efficiency of the catalyst and the productivity of the process. The conditions and characteristics of water drops' interaction with pipe surfaces, heaters, and coolers significantly depend on the integral characteristics of heat transfer.

In recent years, the modernization of solid surfaces through the creation of special super-thin layers has become the most important direction in the development of heat transfer technologies. Increasing the interaction area of the liquid with the surface enhances the removal or supply of thermal energy.

The characteristics of hydrophilic and hydrophobic surfaces can be controlled over a wide range. These surfaces make it possible to solve the complex technological problems of erosion, corrosion, adhesion, and freezing.

The disadvantages inherent in super hydrophobic surfaces (for example, reduced values of mechanical strength and chemical resistance of water repellents.



Hydrophobic Surfaces

Two approaches are traditionally used to obtain super hydrophobic surfaces. The first approach is to fabricate a surface with micro- and nano-textures on materials with low surface energy.

In the second approach, a layer of low surface energy material is deposited on a hard, rough surface (like fluro chemicals and silicones) .

Magnetron sputtering of thin films of zinc, titanium oxide, nickel, chromium, silver, etc., is used both to improve and degrade the surface wettability. The contact angle value on the composite surface obtained by magnetron sputtering of nickel on silicon followed by its baking with aluminum powder was 157°, which is almost two times higher than its value on the untreated Si surface.

It is known that the surface roughness influences its wetting properties (hydrophobicity and hydrophilicity). Aligned carbon nanotubes deposited by chemical vapor on the patterned Si template (pillar array) can result in both hydrophilicity and hydrophobicity.],

By varying the distance between texture elements (pillar), obtained both super hydrophobic (θ = 154.9 ± 1.5°) and hydrophilic (20.8 ± 2.3°) surfaces.

In recent years, texturing methods have become widely used in order to obtain the required functional properties of the surface. Super-hydrophobicity can be achieved by creating a periodic micro/nanostructured texture using laser irradiation and subsequent surface treatment.

Laser texturing is classified based on the delivered pulse duration of the laser beam when exposed to the surface of the material, femtosecond, picosecond, nanosecond, and millisecond laser texturing. It has been established that after laser texturing, the surfaces exhibit hydrophilic properties. The surface acquires (super) hydrophobic properties during long-term storage in the environment, low-temperature annealing, deposition of a hydro phobizator layer , etc.

Hydrophilic Surfaces

As a rule, there are two ways to make a surface hydrophilic: deposition of a more hydrophilic material film on the surface; change in the chemical composition of the surface layer. At the same time, coating is more common on inorganic surfaces. The chemical modification method is most often used in the case of polymer surfaces.

The minimum value of the contact angle (θ) during wetting was 53° when applying PVA-Nafion films on the surfaces of glass, silicon, and plastic. It was determined that the film thickness affects the anti-fog and frost-resistant properties of the resulting coatings.

Cleaned surfaces of glass and plastic with a pre-deposited poly(dimethyl ammonium chloride) layer were alternately immersed in HA and bPEI to obtain (HA/bPEI)∗n films. After that, the obtained samples were immersed in PFOS solution. When such surfaces were wetted with water, the contact angle was 49°. It has been established that the resulting films have hydrophilic and oil-repellent properties, as well as the ability to self-repair.

The dynamic inflow and outflow wetting angles on such surfaces were 30° and 0°, respectively. When thin films of silica nanoparticles and poly(acrylic acid) were deposited on glass, it was determined that the chemical composition of the surface is the main factor determining the wetting properties of the coatings.

It was found that with an increase in the volume concentration of silicon in the solution during coating on glass, the contact angle of wetting with water decreases. It was shown that with an increase in silicon from 53 vol. % to 91 vol. % θ decreases from 10° to 2°.

The super hydrophilicity of the coating is due to the presence of hydrophilic functional groups and nanoscale roughness. These surfaces with water contact angles less than 5° are made using the low-temperature chemical bath deposition technique.

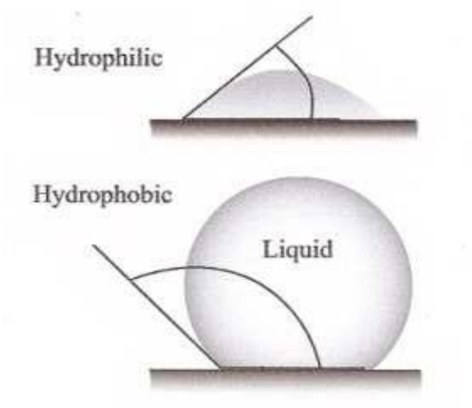
INTRODUCTION

While super hydrophobicity describes the non-wetting characteristic of a surface, super Hydrophilicity describes the converse i.e. the attraction or spreading out of water on a surface. The key aspect in obtaining super hydrophobic surfaces is the roughness of the surface. Generally, roughening a surface enhances the hydrophilicity or hydrophobicity of the surface. Since roughness is such an important factor in super hydrophobicity and super hydrophilicity.

A hydrophilic surface exhibits good wettability characteristics and so, water spreadsout and is attracted to the surface. A surface in which the equilibrium contact angle is greater than 90° is described as being hydrophobic. Hydrophobic surfaces exhibit poor wettability characteristics and so, a water droplet appears more spherical in shape on a hydrophobic surface.

Since water is a polar molecule, then it would be attracted to charged surfaces such as metals. Therefore, metals cause water droplets to spread out over the surface and are generally characterised as hydrophilic surfaces. Non-polar surfaces such as many polymers, which are not charged, exhibit hydrophobic properties. However, surface energies contribute to hydrophilic or hydrophobic characteristics as well. Surfaces with high surfaces energies are usually hydrophilic while surfaces with low surface energies are hydrophobic.

A super hydrophilic surface is one in which the static contact angle is less than 5° while a super hydrophobic surface is one in which the static contact angle is greater than 150°.



Super hydrophobic surfaces defines this surface as having a static contact angle of greater than 150°, resist wetting and exhibit self-cleaning properties.

Applications of Hydrophobic surfaces:

- If super hydrophobic properties are imparted to fabrics, one can make weather resistant fabrics and garments.
- If glass or display surfaces are made super hydrophobic, they will be resistant to water condensation and exhibit an anti-fogging capability.
- These materials could be useful for vehicle windshields, display panels, etc . Due to water droplets being able to easily slide off super hydrophobic surfaces, dust particles are removed along the water droplet sliding path.
- These surfaces are thus referred to as self-cleaning surfaces and as such, are used in solar cell panels or satellite dishes.
- The water repellence can also be used to move liquid in contact with the surface with no or reduced drag. This property could be used for drag reduction in microfluidics, piping, or boat hulls.

Two factors determine the wettability characteristic of a surface. These are:

1. ***Surface Chemistry*** – in general, surfaces with low surface energies are hydrophobic while surfaces with high surface energies are hydrophilic. If the liquid surface energy is significantly above that of the substrate, the substrate does not wet as well [1]. The surface energy of water is about 72 mJ/m^2 while that of Teflon is about 18.5 mJ/m^2 [21]. Thus,

Teflon will display hydrophobic properties. Other surfaces with surface energies lower than that of water and hence, would display hydrophobic properties include other polymers such as polystyrene, polyethylene, polypropylene and PVC. However, surfaces such as aluminium and glass whose surface energies are ≈500 mJ/m^2 and ≈1000 mJ/m^2 respectively, would show hydrophilic properties.

2. ***Surface Roughness*** – One of the ways to increase the hydrophobic or hydrophilic properties of the surface is to increase surface roughness; so roughness-induced hydrophobicity has become a subject of intensive investigation [29]. Both hydrophobicity and hydrophilicity are reinforced by roughness, that is, the intrinsic hydrophobicity or hydrophilicity of a surface can be increased by roughening the surface. Since currently known materials only display intrinsic hydrophobicity with contact angles less than 120°, roughness serves as a mechanism to achieve higher contact angles. In other words, super hydrophobicity can only be achieved through the roughening of a surface. Hydrophobic materials include many well-known, commercially available polymers and the largest contact angles are for those of perfluorinated hydrocarbons, which display contact angles to about 120° on a smooth surface. Superhydrophobic surfaces are brought about by micro- and nano- hierarchical structures as demonstrated by natural surfaces, including leaves of water-repellent plants such as the lotus leaf, legs of insects such as the water strider, and butterfly wings etc.

Many methods have been developed to produce rough structures on polymer surfaces, such as solidification, plasma polymerisation/etching, chemical vapour deposition, solvent-mediated phase separation, molding and template-based extrusion. Other preparation methods for superhydrophobic surfaces include electrochemical deposition, electrospinning method, chemical reaction, hydrothermal synthesis and sol-gel method. Etching is an easy way to make rough surfaces. Micrometer scale topographic structures such as grooves can be created with controlled width and depth with a high power pulsed laser beam.

SURFACE COATING TECHNIQUES

Mostly special surface treatments are needed for metal surfaces, especially steels' surfaces, in order to have the desired optimum properties. There are various techniques for surface treatment but the most common ones are surface coating methods. Steels require further surface coatings for enhanced corrosion resistance, wear resistance, and surface hardness. The surface coating methods differ for different applications. Therefore, the classification of coating techniques can be very complicated. However, the most common surface coating methods can be classified as below:

- Galvanizing
- Electrochemical Coatings
- Vapor Deposition
- Conversion Coatings
- Thermal Spraying

Vapor Deposition Methods for Metal Surfaces

The vapor deposition methods utilize vaporization and condensation processes for making thin-film layers. The desired metal first evaporated and condensed onto the target surface. Vapor deposition methods divide into two groups; chemical vapor deposition (CVD) and physical vapor deposition (PVD).

- **PVD**

PVD method can create ultra-thin films from 0-20 micrometers. The ionization or atomization process can be done by physical evaporation of the substance or plasma sputtering. In the physical evaporation method, the metal substance is first evaporated at high temperatures from 1000 to 2000 °C and condensated under a highly pressurized vacuum environment. In the plasma sputtering method, the coating material is emitted from the surface by accelerating different ions to the surface of the substance. Accelerated ions impact the surface of the substance and desired coating atoms are ejected from the surface and deposited onto the desired surface. This process is held under an electrostatic system where the desired substance is used as a cathode. An argon atmosphere is utilized as the medium where argon gas is ionized and ions are accelerated through the desired metal substance and eject them from the surface. The use of the plasma sputtering method enables a high adhesion between the base surface and the coating substance because of the high kinetic energy of the substance ions.

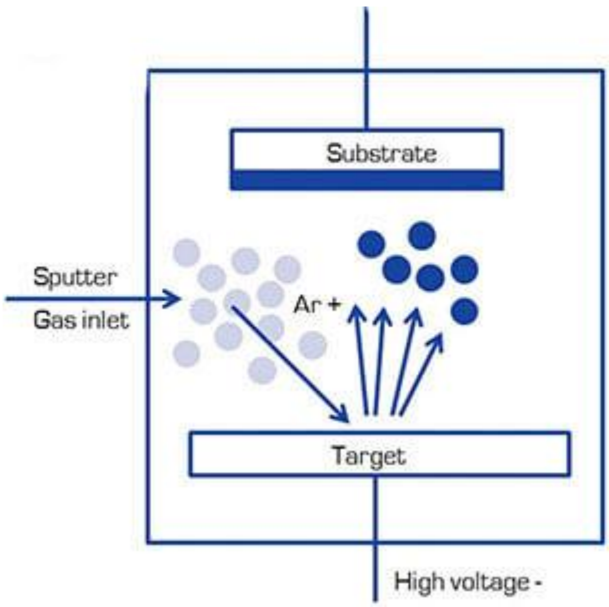
Types of Physical Vapor Deposition

1. Sputter Deposition
2. Electron-beam PVD

3. Thermal Evaporation Deposition
4. Cathodic arc Evaporation /Arc-PVD
5. Pulsed Laser Deposition

1. Sputtering Deposition

The machine coat a thin film coating on the substrate in the sputtering deposition process. In this process, the sputtered high-energy ions will fly towards the substrate ballistically and get deposited layer by layer to form the coating.



Pros

- No atmospheric pollution
- No heated parts
- Available for high-melting-point coating substance materials
- The substrate can be coated up-side-down as well as downside-side
- Target coating substances can be used again and again.

Cons

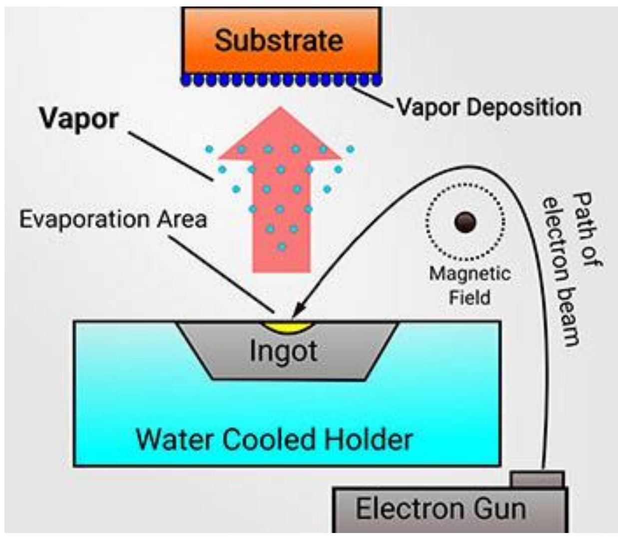
- The process is complicated
- The chamber also gets coated during the process
- May produce impurities on the surface of the substrate
- More costly

2. Electron-beam PVD

In this process, a high-speed electron beam converts the coating substance into a gas phase. Then these gas vapors are deposited on the substrate surface.

The procedure takes place in the line-of-sight, which means if you want to coat the upside of a substrate, then you need to turn it upside down so that the upside can face the vapors, and the same process goes for other sides.

Thus, the substrate is placed in the rotating shaft. The shaft can also move to adjust the distance between the coating substance and the substrate.



Pros:

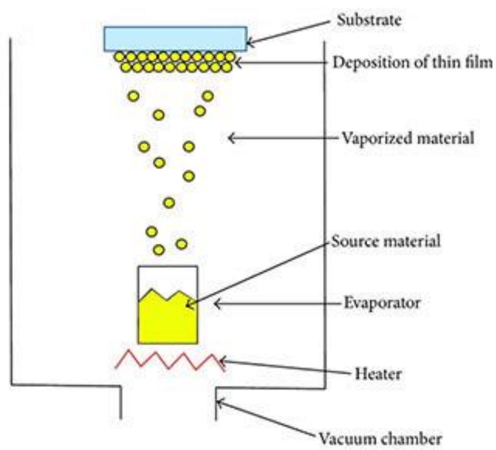
- No atmospheric pollution.
- Higher material utilization

Cons:

- Can produce unnecessary coating in the chamber
- Needs very low vacuum conditions
- Certain materials are not suitable

3.Thermal Evaporation Deposition

In this process, a filament is used to heat and evaporate the coating substance in the vacuum chamber. The gas vapors are then deposited on the substrate surface.



Pros

- Simple process
- High deposition rate than others
- No atmospheric pollution overall
- More affordable than other processes

Cons

- Can only be used for low melting point materials
- Need a water-cooling system for substrate
- Only the line-of-sight deposition is available

Uses

Due to its simplicity, the Thermal Evaporation PVD comes with the following applications:

- Toys
- Solar cells
- Cosmetics
- Shoe heels
- Computers
- Cell phones
- Optical applications

4. Cathodic arc Evaporation /Arc-PVD

This process is also very famous. In this process, the electric arc evaporates the target coating substance. Then the vapors get deposited on the substrate surface.

Pros:

- Environmental-friendly
- Uniform thickness on the substrate surface
- Very dense and hard coatings are possible
- Low cost
- The degree of ionization of evaporated species can approach from 30% – 100%, which is not easily possible in other processes.

Cons:

Need water-cooling system

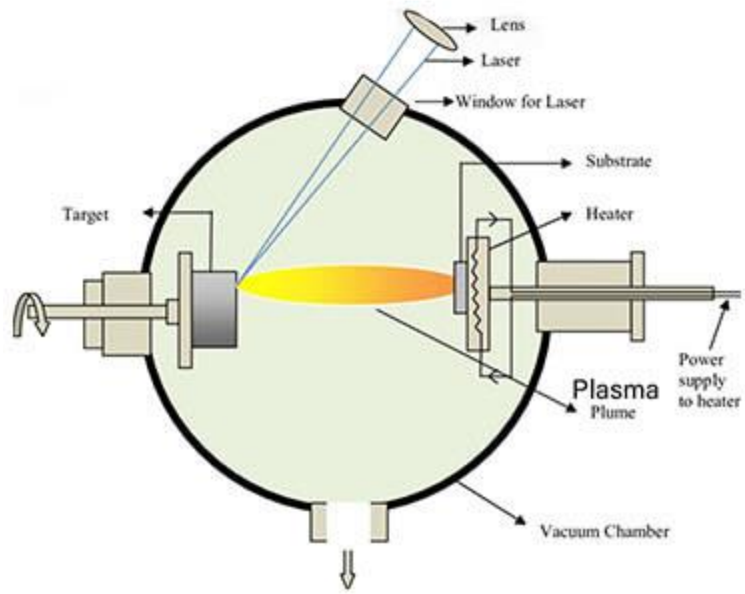
Uses

The cathode arc evaporation method has the following applications;

- Hard wares dense coatings
- Protective coating on lamps
- Wear-resistant watches coatings
- Very hard coating on cutting tools
- A wear-resistant coating on the jewelry
- Diamond-like carbon coatings are possible with this method

5. Pulsed Laser Deposition

This is a very new process, and it is still in its developing phase. In this process, the coating substance is first evaporated by a laser beam, and afterward, emitted vapors get deposited on the substrate surface to form the coating.



Pros:

- Real-time thickness control
- No limitation in using a coating substance
- Can be used both with inert and reactive gases.
- Suitable for low melting point substrates such as plastics

Cons:

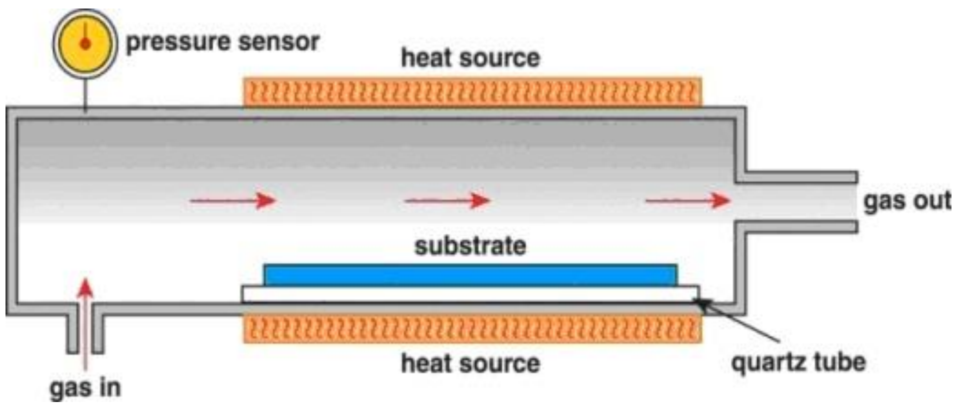
- Equipment used is expensive
- No effective commercial machine yet

Uses

- Jewelry
- Solar Cells
- Semiconductors
- Medical applications
- Cutting tools, drills, e.t.c.
- Used to coat bioactive glass on implant metals
- And it can use for almost any application

CVD

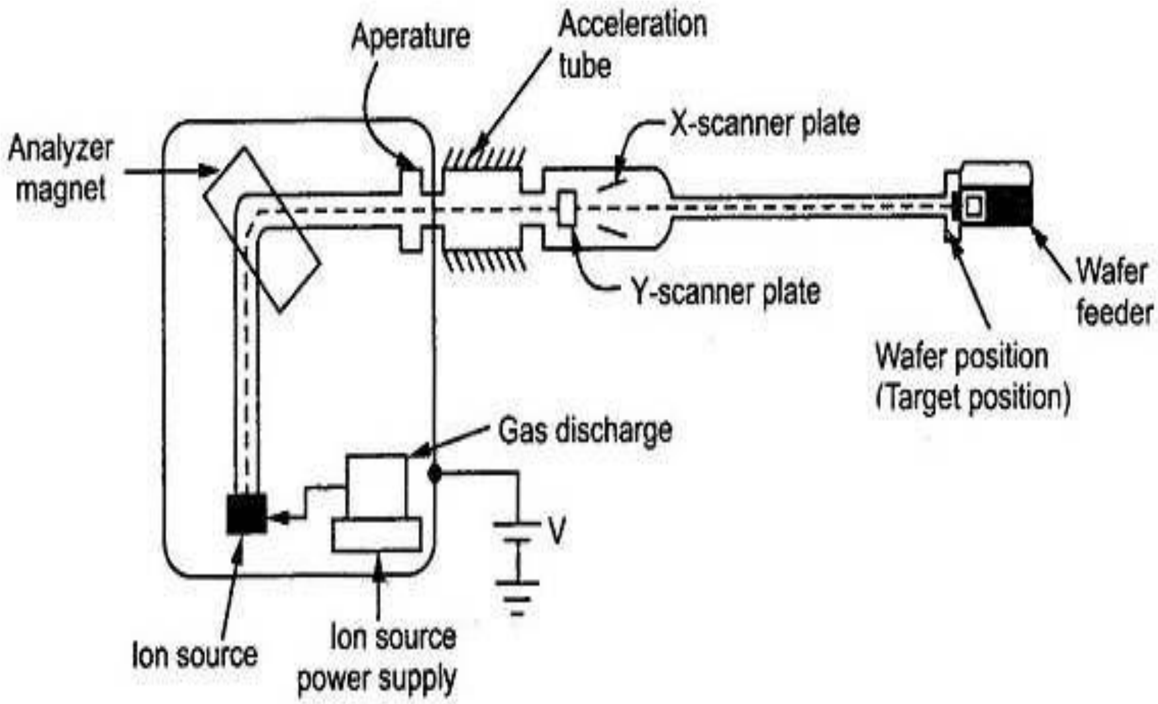
The CVD technique also uses the gaseous phase of the desired metal substance, condensed onto the target base metal surface. In the CVD technique, the substrate is heated at high temperatures over 850 °C. This high-temperature process restricts material selection because only materials with high melting temperatures can be used in this process. First, the precursor substances are introduced into the hot reaction chamber where the target surface is located. The precursors vaporize and are absorbed onto the target surface. Adsorbed substances chemically react with each other and leave behind the desired coating metal on the surface of the target. The desired metal coats an impervious thin layer on the surface of the base metal. This surface coating method is commonly used in the coating of hard materials such as nitrides, carbides, or borides.



ION Implantation

Ion Implantation is an alternative to deposition diffusion and is used to produce a shallow surface region of dopant atoms deposited into a silicon wafer. This technology has made significant roads into diffusion technology in several areas. In this process a beam of impurity ions is accelerated to kinetic energies in the range of several tens of kV and is directed to the surface of the silicon. As the impurity atoms enter the crystal, they give up their energy to the lattice in collisions and finally come to rest at some average penetration depth, called the projected range expressed in micro meters. Depending on the impurity and its implantation energy, the range in a given semiconductor may vary from a few hundred angstroms to about 1micro meter. Typical distribution of impurity along the projected range is approximately Gaussian. By performing several implantations at different energies, it is possible to synthesize a desired impurity distribution, for example a uniformly doped region.

A gas containing the desired impurity is ionized within the ion source. The ions are generated



and repelled from their source in a diverging beam that is focussed before if passes through a mass separator that directs only the ions of the desired species through a narrow aperture. A second lens focuses this resolved beam which then passes through an accelerator that brings the ions to their required energy before they strike the target and become implanted in the exposed areas of the silicon wafers. The accelerating voltages may be from 20 kV to as much as 250 kV. In some ion implanters, the mass separation occurs after the ions are accelerated to high energy. Because the ion beam is small, means are provided for scanning it uniformly across the wafers. For this purpose the focussed ion beam is scanned electrostatically over the surface of the wafer in the target chamber.

Repetitive scanning in a raster pattern provides exceptionally uniform doping of the wafer surface. The target chamber commonly includes automatic wafer handling facilities to speed up the process of implanting many wafers per hour.