

# SCHOOL OF MECHANICAL ENGINEERING DEPARTMENT OF MECHATRONICS ENGINEERING

**UNIT – I - NANOELECTRONICS - SEC1615** 

### **NANOELECTRONICS - SEC1615**

### **UNIT 1 FUNDAMENTALS OF NANOELECTRONICS**

Moorels Law, Wave functions, wave packets, Schrodingers wave equation, potential barriers and tunneling, Fermi Dirac statistics, Density of states, Limitations of conventional FET in nano scales, Quantum Well, Quantum wire, Quantum dot, current flow in two terminal Quantum dots, ballistic transport, Single Electron Transistor

#### 1. Introduction to Nano Electronics

The term nano electronics refers to the use of nanotechnology in electronic components. These components are often only a few nanometers in size. However, the tinier electronic components become, the harder they are to manufacture. Nano electronics covers a diverse set of devices and materials, with the common characteristic that they are so small that physical effects alter the materials properties on a nano scale – inter-atomic interactions and quantum mechanical properties play a significant role in the workings of these devices. At the nanoscale, new phenomena take precedence over those that hold sway in the macro-world. Quantum effects such as tunneling and atomistic disorder dominate the characteristics of these nanoscale devices. The first transistors built in 1947 were over 1 centimeter in size; the smallest working transistor today is 7 nanometers long – over 1.4 million times smaller (1 cm equals 10 million nanometers). The results of these efforts are billion-transistor processors where, once industry embraces 7 nm manufacturing techniques, 20 billion transistor-based circuits are integrated into a single chip.

### • Nano electronic Devices

### • Spintronics

Besides transistors, nano electronic devices play a role in data storage (memory). Here, spintronics – the study and exploitation in solid-state devices of electron spin and its associated magnetic moment, along with electric charge – is already an established technology. Read more: "Graphene spintronics - from science to technology".



Fig 1.1 Electron spin in a Graphene lattice

Spintronics also plays a role in new technologies that exploit quantum behavior for computing (read more: "Quantum computing moves forward with spintronics progress" and "The birth of topological spintronics").

# • Optoelectronics

Electronic devices that source, detect and control light – i.e. optoelectronic devices – come in many shapes and forms. Highly energy-efficient (less heat generation and power consumption) optical communications are increasingly important because they have the potential to solve one of the biggest problems of our information age: energy consumption. In the field of nanotechnology, materials like nanofibers (see for instance: "Light-emitting nanofibers shine the way for optoelectronic textiles") and carbon nanotubes have been used and especially graphene has shown exciting potential for optoelectronic devices.

# • Displays

Display technologies can be grouped into three broad technology areas; Organic LEDs, electronic paper and other devices intended to show still images, and Field Emission Displays. For more, read our special section on Nanotechnology in Displays.

# • Wearable, flexible electronics

The age of wearable electronics is upon us as witnessed by the fast growing array of smart watches, fitness bands and other advanced, next-generation health monitoring devices such as electronic stick-on tattoos. If current research is an indicator, wearable electronics will go far beyond just very small electronic devices or wearable, flexible computers. Not only will these devices be embedded in textile substrates but an electronics device or system could ultimately become the fabric itself. Electronic textiles (e-textiles) will allow the design and production of a new generation of garments with distributed sensors and electronic functions. Such e-textiles will

have the revolutionary ability to sense, act, store, emit, and move – think biomedical monitoring functions or new man-machine interfaces – while ideally leveraging an existing low-cost textile manufacturing infrastructure (see for instance "wearing single-walled carbon nanotube electronics on your skin", a "temporary tattoo to monitor glucose levels" or "graphene nanosensor tattoo on teeth monitors bacteria in your mouth").



Fig 1.2 Graphene wireless sensor bio transferred onto the surface of a tooth

### • Nanoelectronics in Energy

Solar cells and supercapacitors are examples of areas where nanoelectronics is playing a major role in energy generation and storage. To learn more read our detailed sections on Nanotechnology in Energy and Graphene Nanotechnology in Energy.

### • Molecular Electronics

Distinct from nanoelectronics, where devices are scaled down to nanoscale levels, molecular electronics deals with electronic processes that occur in molecular structures such as those found in nature, from photosynthesis to signal transduction. Molecular electronics aims at the fundamental understanding of charge transport through molecules and is motivated by the vision of molecular circuits to enable miniscule, powerful and energy efficient computers (see for instance: "Adding an optoelectronic component to molecular electronics").

### • Nanoelectronics Applications

With the development of microscopes in recent decades, scientists got the ability to see nanosized materials which are as small as atoms and this had opened up a world of possibilities in a variety of industries and scientific endeavors. Designers Face hurdles for the future of Nanoelectronics. Nano-materials are miniaturization of materials. Building of machines at the molecular scale that involves the manipulation of materials on an atomic scale were about twotenths of a nanometer is called Nanotechnology. Nanotechnology is also defined as the study of structures which are in size between 1 to 100 nanometers. Its size is eight hundred 100 nanometer particles placed side by side will be equal to the width of a human hair.



Fig 1.3 Applications of Nanoelectronics

# • Nanometer

As shown in the above, the chart starts with objects that can be seen by the unaided eye such as an ant and progresses to objects about a nanometer or less in size such as the ATP molecule used in humans to store energy from food.

# • Nanoelectronics : Nanotechnology in Electronics

Nanoelectronics is defined as nanotechnology which allows the integration of purely electronic devices, electronic chips and circuits. The digital systems are combined with analog/RF circuits. This type of technology fusion can be described as the 'More than Moore' domain of development. The nanoscale dimensions of nanoelectronic components for systems of giga-scale complexity measured on a chip or in a package. This scaling feature and the road to giga-scale systems can be described as the 'More Moore' domain of development.

Nanotechnology improve the capabilities of electronic components as given below-

- By reducing the size of transistors used in integrated circuits.
- Researchers are developing a type of memory chip with a projected density of one terabyte of memory per square inch and this increases the density of memory chips.
- By improving display screens on electronics devices and this reduces power consumption and also the weight and thickness of the screens.

• By traditional scaling limits in standard CMOS technology. This development of nanoelectronic components are called as 'Beyond CMOS' domain of development.



Fig 1.4 Nano Technology in electronics

# • Nanotechnology in Electronics

In giga systems, when systems are designed using nanoscale components the number of components in a system may reach gigascale orders. This increases number of challenges like complexity in scaling, gigascale complexity. There is also a scaling of electrical properties such as power dissipation, supply voltage, speed, and leakage currents. Design at the architectural level is required in order to overcome problems of scaling properties. In Technology fusion, Nanotechnology makes it possible to develop new components which may be used together with electronic components in system design. Nano-sized particles of titanium dioxide and zinc oxide are used in many sunscreens to block UV radiation more effectively.



Fig 1.5 CMOS technology

# • Nanotechnology Beyond CMOS Devices

The phenomenal growth in the CMOS technology over the past four decades and it has high performance and storage systems. Planar CMOS technology is the main component for embedded electronic system design from several decades. It has been scaled according to Moores law resulting in ever decreasing device sizes and in a number of technology nodes, the present one being the 45nm node and in general, the scaling cannot go below approximately 10nm for MOS transistors and this limit is expected to be reached about 2015.

### • Transfer Characteristics Using CMOS Technology

High-performance logic circuits and Semiconductor memory had been the technology drivers to architect the miniaturization of the MOS transistor. The scaling of MOS transistor in nanoelectronics explores new materials like high-k gate dielectrics such as HfO2, Er2O3, Gd2O3; new channel materials such as germanium and grapheme and finally new device structures like double-gate FET, FinFET, Schottky source/drain FET. Clockwise from top left: a wave packet plotted on the complex plane, a model for charge injection and transport through a ballistic nanowire, a billiard ball model of a reversible computer, and the simplified energy band structure of graphene.

### • Nanotechnology Applications

Nanotechnology has many applications and has a variety of uses such as the ones listed below-

- Reactivity of Materials Nanoparticles have a greater surface area per weight than larger
  particles and properties of some standard materials were changed when formed as nanosized particles then they become more reactive to some other molecules.
- Nanotechnology Applications in Chemical Sensors allows the detection of a very low concentration of chemical vapors.
- Nanotechnology Applications in Space
- Nanotechnology and Water Quality Nanoparticles can be used to convert the contaminating water through a chemical reaction to make it harmless
- Nanotechnology Applications in Sporting Goods
- Nanotechnology Applications in Batteries



Fig 1.6 Nanotechnology Applications

# • Nanotechnology Applications

- Drug delivery Most harmful side effects of treatments such as chemotherapy are a result of drug delivery methods which donot pinpoint their intended target cells accurately.
- Nanoparticles of iron can be effective in the cleanup of chemicals in groundwater because they react more efficiently to those chemicals than larger iron particles.
- Strength of Materials Nano-sized particles of carbon like nanotubes and bucky balls are composed of only carbon and they are very strong. A T-shirt weight bullet proof vests made out of carbon nanotubes is the best example that shows how much strong will be the nanosized particles of carbon. This is because their strength comes from special characteristics of the bonds between carbon atoms.
- Nanotechnology Applications in Medicine
- Nanotechnology Applications in Electronics
- Nanotechnology Applications in Food nanomaterials that will make a difference not only in the taste of food, but also in food safety, and the health benefits
- Nanotechnology Applications00 in Solar Cells

- Molecular Manufacturing Star Trek replicator is a device that could produce anything
  from a space age guitar to a cup of Earl Grey tea. Researchers are working on developing
  a method called molecular manufacturing that may someday make the Star Trek
  replicator into reality. a molecular fabricator is a device which uses tiny manipulators to
  align the atoms and molecules in order to build an object.
- Nanotechnology in Fuels production of fuels from low grade normal raw materials more efficient.
- Nanotechnology and Air Quality can improve the performance of catalysts used to transform vapors escaping from cars or industrial process plants into harmless gases
- Nanotechnology in Fabrics In fabrics, the clothing manufacturers were making water using nano-sized whiskers in the fabric that cause water to beat up on the surface. Fibers allow improvement of fabric properties without a significant increase in weight, thickness, or stiffness.
- Coatings and Surfaces Coatings with thickness controlled at the nano- or atomic scale have been used in molecular beam epitaxy or metal oxide chemical vapor deposit ion for optoelectonic devices and the applications include the self-cleaning window that is coated in highly activated titanium dioxide. olymers and inorganics.
- Harder Cutting Tools Cutting tools made of nanocrystalline materials, such as tungsten carbide, tantalum carbide and titanium carbide.

# • Applications of Nanoelectronics under Development:

Below were the nanoelectronics applications and projects into which Researchers were looking -

• Cadmium selenide nanocrystals deposited on plastic sheets are to form flexible electronic circuits. The aim of Researchers is for low power requirements, simple fabrication process and combination of flexibility.

# • Applications of Nanoelectronics under Development

• Integrating silicon nanophotonics components into CMOS integrated circuits. This optical technique is intended to provide higher speed data transmission between integrated circuits than is possible with electrical signals.

- Researchers at UC Berkeley have demonstrated a low power method to use nano magnets as switches, like transistors, in electrical circuits. Their method might lead to electrical circuits with much lower power consumption than transistor based circuits.
- Silver nanoparticle ink was used to form the conductive lines needed in circuit boards. A
  method to print prototype circuit boards using standard inkjet printers was developed by
  Researchers at Georgia Tech, the University of Tokyo and Microsoft.
- Developing a lead free solder reliable enough for space missions and other high stress environments using copper nano particles.
- Functioning of integrated circuits using carbon nanotubes have been developed by Researchers at Stanford University. They had also developed methods to remove metallic nanotubes, an algorithm to deal with misaligned nanotubes.

# • Nano Integrated Circuits

- Laser that uses a nano patterned silicon surface that helps produce the light with much tighter frequency control developed by Researchers at Caltech.
- Nanowires that would enable flat panel displays to be flexible made from electrodes.
- Transistors built in single atom thick graphene film to enable very high speed transistors.
- Building transistors from carbon nanotubes to enable minimum transistor dimensions of a few nanometers and developing techniques to manufacture integrated circuits built with nanotube transistors.
- Researchers have developed an interesting method of forming PN junctions, a key component of transistors, in graphene.
- Combining gold nanoparticles with organic molecules to create a transistor known as a NOMFET (Nanoparticle Organic Memory Field-Effect Transistor).
- Making integrated circuits with features that can be measured in nanometers (nm)
- Using carbon nanotubes to direct electrons to illuminate pixels, resulting in a lightweight, millimeter thick "nanoemmissive" display panel.
- Using nanosized magnetic rings to make Magnetoresistive Random Access Memory (MRAM).

- Researchers have developed lower power, higher density method using nanoscale magnets called magnetoelectric random access memory (MeRAM) and also developed molecular-sized transistors which increase transistor density in integrated circuits.
- Using self-aligning nanostructures to manufacture nanoscale integrated circuits.
- Using nanowires to build transistors without p-n junctions, buckyballs to build dense, low
  power memory devices, magnetic quantum dots, silver nanowires embedded in a polymer
  to make conductive layers without damaging the conductor, nanowires made of an alloy
  of iron and nickel to create dense memory devices.
- Memory chip that uses carbon nanotubes developed by IMEC and Nantero. This memory is known as NRAM for Nanotube-Based Nonvolatile Random Access Memory.

# • Future of nanoelectronics – Electronics without current

- The waste heat produced by integrated circuits and consumption of power are the problems that face both laptop users and high-performance data centers.
- The researchers are exploring new way for designing and making logic circuits by integrating photosensitive organic molecules into tiny particles of semiconductor material called quantum dots.
- Researchers at the Optoelectronics Research Centre (ORC) of TUT are developing a technology platform for the logic circuit made up of quantum dots.
- Researchers at Tampere University of Technology have launched a cross-disciplinary project entitled "PhotonicQCA" that combines expertise in organic chemistry, semiconductor growth and nanofabrication.
- Current is simply the flow of electrons in a particular direction. This new type of logic circuit consumes no current because the movement occurs when a single electron travels from one quantum dot to another.

# • Future of Nanoelectronics

- Researchers at the Department of Chemistry and Bioengineering are looking into ways of bridging the gap between nanoscale and macroscale. Researchers at the Department of Electronics bring their expertise in novel architectures to the project.
- The form of carbon called a "nanotube" is one of the earliest forms of nanotechnology.
- Nanostructures could serve as new kinds of drugs for treating common conditions such as cancer.
- Nano-engineered solar panels produce more energy.
- Nanotech batteries last longer, lighter and more powerful.
- Dangerous side effects of current treatments like chemotherapy.
- Novel Parkinson's, and cardiovascular disease, or as artificial tissues for replacing diseased kidneys and livers.

Thus, the nanoscale is the scale of atoms and molecules, the fundamental building blocks of the material world and future applications will increase including treating cancer, generating renewable energy and providing clean water anytime, anyplace. The greatest challenge to benefiting from nanotechnology is having the foresight to develop and use it wisely.

### 1.1.Moore's Law

Moore's Law refers to Moore's perception that the number of transistors on a microchip doubles every two years, though the cost of computers is halved. Moore's Law states that we can expect the speed and capability of our computers to increase every couple of years, and we will pay less for them. Another tenet of Moore's Law asserts that this growth is exponential.

- Moore's Law states that the number of transistors on a microchip doubles about every two years, though the cost of computers is halved.
- In 1965, Gordon E. Moore, the co-founder of Intel, made this observation that became Moore's Law.
- Another tenet of Moore's Law says that the growth of microprocessors is exponential.
- In 1965, Gordon E. Moore—co-founder of Intel (NASDAQ: INTC)—postulated that the number of transistors that can be packed into a given unit of space will double about every two years. Today, however, the doubling of installed transistors on silicon chips occurs at a pace faster than every two years.

Gordon Moore did not call his observation "Moore's Law," nor did he set out to create a "law." Moore made that statement based on noticing emerging trends in chip manufacturing at Intel. Eventually, Moore's insight became a prediction, which in turn became the golden rule known as Moore's Law.



### Fig 1.7 Moore's Law

### How has Moore's Law impacted computing?

Moore's Law has had a direct impact on the progress of computing power. What this means specifically, is that transistors in integrated circuits have become faster. Transistors conduct electricity, which contain carbon and silicon molecules that can make the electricity run faster across the circuit. The faster the integrated circuit conducts electricity, the faster the computer operates.

#### Is Moore's Law coming to an end?

According to expert opinion, Moore's Law is estimated to end sometime in the 2020s. What this means is that computers are projected to reach their limits because transistors will be unable to operate within smaller circuits at increasingly higher temperatures. This is due to the fact that cooling the transistors will require more energy than the energy that passes through the transistor itself.

### **1.2 Wave function**

A wave function in quantum physics is a mathematical description of the quantum state of an isolated quantum system. The wave function is a complex-valued probability amplitude, and the probabilities for the possible results of measurements made on the system can be derived from it. The most common symbols for a wave function are the Greek letters  $\psi$  and  $\Psi$ 

The wave function is a function of the degrees of freedom corresponding to some maximal set of commuting observables. Once such a representation is chosen, the wave function can be derived from the quantum state.

### • Formula of Wave Function:

For the wave function formula, one must look to the Schrodinger equation. Below is the Schrodinger equation: Time dependent Schrodinger equation:  $ih99t\Psi$  (r,t) = Undefined control sequence \ triangle down

Time independent Schrodinger equation: Undefined control sequence  $\forall riangle down = E\Psi(r)$ Where,

m: mass of the particle
i: imaginary unit
h=h/2π: Planck constant that is reduced
E: constant that is equal to the energy level of the system

### • Derivation of the Formula of Wave Function:

An observation was made by the experts that one can write the wave function of a particle of fixed energy E as a linear combination of wave functions of the form

$$\Psi(\mathbf{x},t) = \operatorname{Aei}(\mathbf{k}\mathbf{x} - \mathbf{w}t) \qquad (1)$$

This is representative of a wave that travels in the positive x direction, and a corresponding wave that travels in the opposite direction. Therefore, the result is a standing wave which is in accordance with the boundary conditions. This corresponds, in an intuitive manner, to the classical notion of a particle bouncing. Furthermore, this particle bounces back and forth between the potential well walls. Most noteworthy, it is possible to adopt the wave function as being the suitable wave function

for a particle that is free. The momentum of this free particle is p = hk and its energy is  $E = h\omega$ . So, one can see that

 $\vartheta 2\Psi \vartheta x 2 = -k2\Psi$ (2)By making use of  $E = p^2/2m = h^2k^2/2m$ , one can write $-h2\vartheta 2\Psi 2m\vartheta x 2 = p2\Psi 2m$ (3)Furthermore, similarly $\vartheta \Psi \vartheta t = -i\omega\Psi$ (4)One can also write this, using  $E = h\omega$ : $ih \vartheta \Psi \vartheta t = h\omega \psi = E\Psi$ (5)Now generalizing that this is possible to the situation is

Now generalizing that this is possible to the situation in which there is a potential energy as well as a kinetic energy present, then  $E = p^2/2m + V(x)$  so that

 $E\Psi = P2\Psi 2m + V(x)\Psi \tag{6}$ 

where  $\Psi$  is now the wave function of a particle whose movement takes place in the presence of a potential V (x). However, considering the results Eq. (3) and Eq. (5) still apply in this case, then what we are left with is

 $-h2\vartheta 2\psi 2m\vartheta x2+V(x)\Psi=ih\vartheta\psi\vartheta t \tag{7}$ 

Most noteworthy, this is the Schrödinger wave equation.

# **1.3 Wave Packets:**

A wave packet refers to the case where two (or more) waves exist simultaneously. A wave packet is often referred to as a wave group. This situation is permitted by the principle of superposition. This principle states that if any two waves are a solution to the wave equation then the sum of the waves is also a solution. This principle holds only for linear systems. Here we consider linear, one-dimensional sinusoidal disturbances.



Fig 1.8 Linear, one-dimensional sinusoidal disturbances

- The red curve displays a simple wave form. The blue curve is another wave with a different wavelength. The wavelength is defined as the horizontal distance between two crests or between two troughs. (A crest corresponds to a wave maximum; a trough to a wave minimum.) The wavelength of the red wave is longer than that of the blue wave.
- The amplitude of the two waves is the same. Here the amplitude corresponds to the half the vertical distance between the crest and the trough. The amplitude of each wave equals the distance between the vertical tic marks in the diagram.
- The green curve shows the sum of the two waves. It is the wave packet.
- The top purple curve is called the average wave. It has the same amplitude as either the red or blue curve but its wavelength is the average of that of the red and blue wave. Count the number of crests in each of the waves and confirm this statement.
- The average wave is also called the carrier wave.
- The middle yellow curve is the wave envelope. It has an amplitude twice that of either the individual wave but its wavelength is half the difference of the red and the blue wave. The wavelength associated with the wave envelope is much larger than that of the carrier wave. The wave envelope is also called the wave modulation or wave amplitude.
- The product of the carrier wave and the wave envelope appears as the bottom green curve. It is the same as the wave packet.

### **1.4 Schrodinger Wave Equation:**

Schrodinger wave equation is a mathematical expression describing the energy and position of the electron in space and time, taking into account the matter wave nature of the electron inside an atom.

 The Schrödinger wave equation in its time-dependent form for a particle of energy E moving in a potential V in one dimension is

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V\Psi(x,t)$$

 The solution (wave function) is not restricted to being real. Only the physically measurable quantities must be real. These include the probability, momentum and energy.

Schrodinger Wave Equation Derivation (Time-Dependent)

Considering a complex plane wave:

$$\Psi(x,t) = A e^{i(kx - \omega t)}$$

Now the Hamiltonian of a system is

$$H = T + V$$

Where 'V' is the potential energy and 'T' is the kinetic energy. As we already know that 'H' is the total energy, we can rewrite the equation as:

$$E = rac{p^2}{2m} + V(x).$$

Now taking the derivatives,

$$egin{aligned} rac{\partial\Psi}{\partial t}&=-i\omega Ae^{i(kx-\omega t)}=-i\omega\Psi(x,t)\ rac{\partial^{2}\Psi}{\partial x^{2}}&=-k^{2}Ae^{i(kx-\omega t)}=-k^{2}\Psi(x,t) \end{aligned}$$

We know that,

$$p=rac{2\pi\hbar}{\lambda}$$
 and  $k=rac{2\pi}{\lambda}$ 

where ' $\lambda$ ' is the wavelength and 'k' is the wave number.

We have

$$k = rac{p}{\hbar}$$
 .

Therefore,

$$rac{\partial^2 \Psi}{\partial x^2} = - rac{p^2}{\hbar^2} \, \Psi(x,t).$$

Now multiplying  $\Psi(x, t)$  to the Hamiltonian we get,

$$E\Psi(x,t)=rac{p^2}{2m}\,\Psi(x,t)+V(x)\Psi(x,t).$$

The above expression can be written as:

$$E\Psi(x,t)=rac{-\hbar^2}{2m}\,rac{\partial^2\Psi}{\partial x^2}+V(x)\Psi(x,t).$$

We already know that the energy wave of a matter wave is written as

$$E = \hbar \omega$$
,

So we can say that

$$E\Psi(x,t) = {\hbar\omega\over -i\omega} \, \Psi(x,t).$$

Now combining the right parts, we can get the Schrodinger Wave Equation.

$$i\hbar \, rac{\partial \Psi}{\partial t} = rac{-\hbar^2}{2m} \, rac{\partial^2 \Psi}{\partial x^2} + V(x) \Psi(x,t).$$

The wave function  $\Psi$  in Schrodinger wave equation, has no physical significance except than it represents the amplitude of the electron wave. However, the square of the wave function ,that is,  $\Psi$  gives the probability of an electron of a given energy E, from place to place in a given region around the nucleus.

#### **1.5 Potential barriers:**

In quantum mechanics, the rectangular (or, at times, square) potential barrier is a standard onedimensional problem that demonstrates the phenomena of wave-mechanical tunneling (also called "quantum tunneling") and wave-mechanical reflection. The problem consists of solving the one-dimensional time-independent Schrodinger equation for a particle encountering a rectangular potential energy barrier. It is usually assumed, as here that a free particle impinges on the barrier from the left. Although classically a particle behaving as a point mass would be reflected if its energy is less than , a particle actually behaving as a matter wave has a non-zero probability of penetrating the barrier and continuing its travel as a wave on the other side. In classical wave-physics, this effect is known as evanescent wave coupling. Time-Dependent Schrodinger Wave Equation

$$\begin{split} & i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x)\Psi(x,t) \\ & \swarrow \\ & \uparrow \\ & \downarrow \\ & \uparrow \\ & \downarrow \\ & \uparrow \\ & \downarrow \\ & \downarrow \\ & \uparrow \\ & \downarrow \\$$

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x)$$

The likelihood that the particle will pass through the barrier is given by the transmission coefficient, whereas the likelihood that it is reflected is given by the reflection coefficient. Schrödinger's wave-equation allows these coefficients to be calculated.

### **1.6. Tunneling:**

**Quantum tunneling** refers to the nonzero probability that a particle in the quantum mechanics can be measured to be in a state that is forbidden in classical mechanics. Quantum tunneling occurs because there exists a nontrivial solution to the Schrodinger equation in a classically forbidden region, which corresponds to the exponential decay of the magnitude of the wave function. To illustrate the concept of tunneling, consider trying to confine an electron in a box. One could try to pin down the location of the particle by shrinking the walls of the box, which will result in the electron wave function acquiring greater momentum uncertainty by the Heisenberg uncertainty principle. As the box gets smaller and smaller, the probability of measuring the location of the electron to be outside the box. The easiest solvable example of quantum tunneling is in one dimension. However, tunneling is responsible for a wide range of physical phenomena in three dimensions such as radioactive decay, the behavior of semiconductors and superconductors, and scanning tunneling microscopy.

### • Applications of tunneling:

### In Electronics

current leakage in very large scale integration (VLSI) electronics and results in the substantial power drain and heating effects that plague such devices. It is considered the lower limit on how

microelectronic device elements can be made Tunneling is a fundamental technique used to program the floating gates of flash memory.

### • Cold emission

Cold emission of electrons is relevant to semiconductors and superconductors physics. It is similar to the thermionic emission,, where electrons randomly jump from the surface of a metal to follow a voltage bias because they statistically end up with more energy than the barrier, through random collisions with other particles. When the electric field is very large, the barrier becomes thin enough for electrons to tunnel out of the atomic state, leading to a current that varies approximately exponentially with the electric field. These materials are important for flash memory, vacuum tubes, as well as some electron microscopes.

### • Tunnel junction

A simple barrier can be created by separating two conductors with a very thin insulator. These are tunnel junctions, the study of which requires understanding quantum tunneling. Josephson take advantage of quantum tunneling and the superconductivity of some semiconductors to create the Josephson effect. This has applications in precision measurements of voltages and magnetic fields as well as the multifunction solar cell.

### Nuclear fusion

Quantum tunneling is an essential phenomenon for nuclear fusion. The temperature in stars' cores is generally insufficient to allow atomic nuclei to overcome the Coulomb barrier and achieve thermonuclear fusion. Quantum tunneling increases the probability of penetrating this barrier. Though this probability is still low, the extremely large number of nuclei in the core of a star is sufficient to sustain a steady fusion reaction.

### Radioactive decay

Radioactive decay is the process of emission of particles and energy from the unstable nucleus of an atom to form a stable product. This is done via the tunneling of a particle out of the nucleus (an electron tunneling into the nucleus is electron capture. This was the first application of quantum tunneling. Radioactive decay is a relevant issue for astrobiology. as this consequence of quantum tunneling creates a constant energy source over a large time interval for environments outside the circumstellar habitable zone insolation would not be possible (subsurface oceans) or effective.

### • Quantum biology

Quantum tunneling is among the central non-trivial quantum effects in quantum biology. Here it is important both as electron tunneling and proton tunneling. Electron tunneling is a key factor in many biochemical remix reactions (photosynthesis, cellular respirations) as well as enzymatic catalysis. Proton tunneling is a key factor in spontaneous DNA mutation.

#### **1.7 FermiDirac statistics**

There were many theses proposed and accepted explaining the characteristics and behaviour of electrons. But some behaviour of electron such as the independence of emission current on temperature etc... still remained a mystery. Then a breakthrough statistic, Fermi Dirac Statistics, published by Enrico Fermi and Paul Dirac in 1926 helped to solve these puzzles. From then Fermi Dirac Distribution is being applied to explain the collapse of a star to a white dwarf, to explain free electron emission from metals etc....

#### • Fermi Dirac Distribution

The maximum energy of a free electron can have in a material at absolute temperature i.e., at 0k is known as Fermi energy level. The value of Fermi energy varies for different materials. Based on the energy possessed by electrons in a semiconductor, electrons are arranged in three energy bands – Conduction band, Fermi energy level, Valence band. In energy band diagram of semiconductor, Fermi level lies in the middle of conduction and valence band for an intrinsic semiconductor. For extrinsic semiconductor, Fermi level lies near valence band in P-type semiconductor and for N-type semiconductor, it lies near to the conduction band. Fermi energy level is denoted by  $E_F$ , the conduction band is denoted as  $E_C$  and valence band is denoted as  $E_V$ .



Fig 1.9 Fermi energy level, conduction band and valence band

• Fermi Dirac Distribution Function

The probability that the available energy state 'E' will be occupied by an electron at absolute temperature T under conditions of thermal equilibrium is given by the Fermi-Dirac function. From quantum physics, the Fermi-Dirac Distribution Expression is

$$f(E) = \frac{1}{\frac{1}{1+e^{(E-E_F)}/k_BT}}$$

Where k is the Boltzmann constant in 0K, T is the temperature in 0K and  $E_F$  is the Fermi energy level in eV.k= 1.38X10-23 J/K. The Fermi level represents the energy state with a 50% probability of being filled if no forbidden band exists, i.e., if  $E = E_F$  then f(E)=1/2 for any value of temperature. Fermi-Dirac distribution only gives the probability of occupancy of the state at a given energy level but doesn't provide any information about the number of states available at that energy level

• Fermi Dirac Distribution and Energy Band Diagram



Fig 1.10 Fermi Dirac Distribution and Energy Band Diagram

The above plot shows the behavior of Fermi level at various temperature ranges T= 0K, T= 300K, T= 2500K. At T=0K, the curve has step-like characteristics. At T = 0K, the total number of energy levels occupied by electrons can be known by using the Fermi-Dirac Function.

### 1.8. Density of states

The density of states function describes the number of the states that are available in a system and is essential for determining the carrier concentrations and energy distributions of carriers within a semiconductor. In Semiconductors, the free motion of carriers is limited to two, one and zero spatial dimensions. When applying semiconductor statistics to system to systems of these dimensions, the density of states in quantum wells (2D), quantum wires (1D) and quantum dots (0D) must be known.

• For zero-dimensional quantum dots semiconductors, the excited electron-hole pairs are confined within a small volume, the density of states concentrate carriers in a certain energy range. The quantum confinement of carriers converts the density of states to a set of discrete quantum levels.

$$E_n = \left[\frac{\pi^2 \hbar^2}{2mL^2}\right] \left(n_x^2 + n_y^2 + n_z^2\right)$$

• For One-dimensional quantum wires,

$$E_n = \left[\frac{\pi^2 \hbar^2}{2mL^2}\right] \left(n_x^2 + n_y^2\right)$$

• For two dimensions the density N(E) of states changes from a continuous dependence  $N(E) \sim E1/2$  to a step like dependence. The optical absorption edge for a quantum well is at a higher photon energy than for the bulk semiconductor, the spectrum is stepped rather than smooth the steps, at each step, sharp peaks appear corresponding to electronhole (exciton) pair states.

$$E_n = \left[\frac{\pi^2 \hbar^2}{2mL^2}\right] \left(n_x^2\right)$$

#### **1.9 Limitations of conventional FET in nanoscales**

• Response time of a biosensor for nanoscales as a function of the subthreshold swing for different concentration of biomolecules.

- Decrease in subthreshold swing leads to significant decrease in response time
- TFETs allows detection at lower biomolecule concentration only
- FETs have a poor frequency response due to its high input capacitance

• FETs have a very poor linearity, and generally they are less linear than Bipolar Junction Transistor

• FETs can be damaged due to the static electricity

### 1.10 Quantum Well

A quantum well is a potential well with only discrete energy values. The classic model used to demonstrate a quantum well is to confine particles, which were initially free to move in three dimensions, to two dimensions, by forcing them to occupy a planar region. The effects of quantum confinement take place when the quantum well thickness becomes comparable to the de Broglie wavelength of the carriers (generally electrons and holes), leading to energy levels called "energy subbands", i.e., the carriers can only have discrete energy values.

A wide variety of electronic quantum well devices have been developed based on the theory of quantum well systems. These devices have found applications in lasers, photodetectors, modulators, and switches for example. Compared to conventional devices, quantum well devices are much faster and operate much more economically and are a point of incredible importance to the technological and telecommunication industries. These quantum well devices are currently replacing many, if not all, conventional electrical components in many electronic devices.



Fig 1.14 quantum well

### 1.11 Quantum wire

Quantum wires are extremely narrow structures where electron transport is possible only in a very few transverse modes (with energies less than the Fermi energy). Quantum wires can be used as electron waveguides. Semiconductor quantum wires have been used to make switchable

high-speed lasers. Quantum wires can be fabricated by an appropriate arrangement of metallic gates on top of a 2D electron gas. The electron gas beneath a negative gate voltage is depleted, slicing the quantum well into two, a. Nanotubes can also be used as quantum wires. Interesting physics emerges when quantum wires are used in transport experiments. Quantum wires are easily attached to electrical contacts that are formed within the underlying 2D electron gas, and this allows transport measurements. The length and width of a quantum wire can be controlled during an experiment. By varying the width, the number of transverse propagating modes that contribute to the conductance of the wire is changed. The Landauer formula, described below, predicts that the conductance of a perfectly clean wire equals 2e2/h times the number of transverse modes below the Fermi energy (assuming noninteracting electrons). As the width of the wire is varied, the conductance as function of gate volatge is expected to display a step structure with plateaus quantized in units of 2e2/h. This has been experimentally observed. However, in some recent experiments, there are plateaux at 0.7e^2/h. The origin of this phenomenon is still under study, but it is well accepted that the reason is related to the interaction between the electrons



Fig 1.15 quantum wire

#### 1.12 Quantum dot

Ouantum dots (ODs) are semiconductor particles few nano a metres in size. having optical and electronic properties that differ from larger particles due to quantum mechanics. They are a central topic in nanotechnology. When the quantum dots are illuminated by UV light, an electron in the quantum dot can be excited to a state of higher energy. In the case of a semiconducting quantum dot, this process corresponds to the transition of an electron from the valence band to the conductance band. The excited electron can drop back into the valence band releasing its energy by the emission of light. This light emission (photoluminescence) is illustrated in the figure on the right. The colour of that light depends on the energy difference between the conductance band and the valence band. In the language of materials science, nanoscale semiconductor materials tightly confine either electrons or electron holes. Quantum dots are sometimes referred to as artificial atoms, emphasizing their singularity, having bound,

discrete electronic states, like naturally occurring atoms or molecules. It was shown that the electronic wave functions in quantum dots resemble the ones in real atoms. By coupling two or more such quantum dots an artificial molecule can be made, exhibiting hybridization even at room temperature. Quantum dots have properties intermediate between bulk semiconductors and discrete atoms or molecules. Their optoelectronic properties change as a function of both size and shape. Larger QDs of 5–6 nm diameter emit longer wavelengths, with colours such as orange or red. Smaller QDs (2–3 nm) emit shorter wavelengths, yielding colours like blue and green. However, the specific colours vary depending on the exact composition of the QD.



Fig 1.16 Quantum dot

### 1.13 Current flow in two terminal Quantum dots

In this section we present a simplified model for conduction through a molecule. It is based on the "toy model" of Datta, et al. which despite its relative simplicity describes many of the essential features of single molecule current-voltage characteristics. At equilibrium,  $\mu 1=EF=\mu 2$ . Since there are two contacts, this is an example of a two terminal device. In keeping with convention, we will label the electron injecting contact, the source, and the electron accepting contact, the drain. We will model the molecule by a quantum dot. This is accurate if the center of the molecule is much more conductive than its connections to the contacts.



Fig 1.17 A two terminal device with a molecular/quantum dot conductor.

At equilibrium no current flows and the Fermi levels are aligned.

Now, when we apply a potential between the source and drain contacts we shift Fermi level of one contact with respect to the other, i.e.

$$\mu D - \mu S = -qVDS$$

There are two effects on the molecule:

- 1. The electrostatic effect: the potential at the molecule is changed by the electric field established between the contacts. The energy levels within the molecule move rigidly up or down relative to the contacts.
- 2. The charging effect: Out of equilibrium, a current will flow and the amount of charge on the molecule changes. It may increase if current flows through the LUMO, or decrease if current flows through the HOMO.

Unfortunately, these effects are linked: moving the molecular energy levels with respect to the contact energy levels changes the amount of charge supplied to the molecule by the contacts. But the charging energy associated with charge transfer in turn changes the potential of the molecule. We will first consider static and charging effects independently.

### • Electrostatics

The Capacitive Divider Model of Potential

Our two terminal device can be modeled by a quantum dot linked to the source and drain contacts by two capacitors, CS and CD, respectively. The values of these capacitors depend on the geometry of the device. If the molecule is equi-spaced between the contacts we might expect that CS CD. On the other hand, if the molecule is closely attached to the source but far from the drain, we might expect CS>CD. (Recall that the capacitance of a simple parallel plate capacitor is inversely proportional to the spacing between the plates.)





We are concerned with the voltage in the center of the molecule. This is determined by the voltage division factor,  $\eta$ . It can be obtained by from a voltage divider constructed from capacitors. These two potential profiles are shown in Figure . The voltage is calculated from the capacitive divider. Thus, an applied voltage, V, shifts the chemical potentials of both the source and drain contacts:

$$E_F = -\frac{1/C_S}{1/C_D + 1/C_S} q V_{DS} + \mu_S$$

It is convenient to use the Fermi energy of the molecule at equilibrium as a reference, i.e. if we set EF=0:

$$\mu_{S} = + \frac{C_{D}}{C_{S} + C_{D}} q V_{DS}$$
$$\mu_{D} = - \frac{C_{S}}{C_{S} + C_{D}} q V_{DS}$$

We can define a voltage division factor,  $\eta$ . It gives the fraction of the applied bias that is dropped between the molecule and the source contact, i.e.

$$\eta = \frac{C_D}{C_S + C_D}$$

As shown in Figure , the voltage division factor determines in part whether conduction occurs through the HOMO or the LUMO. If  $\eta$ =0, then the molecular energy levels are fixed with respect to the source contact. As the potential of the drain is increased, conduction eventually

occurs through the HOMO. But if the potential of the drain is decreased, conduction can occur through the LUMO. The current-voltage characteristic of this device will exhibit a gap around zero bias that corresponds to the HOMO-LUMO gap. If  $\eta$ =0.5, however, then irrespective of whether the bias is positive or negative, current always flows through the molecular energy level closest to the Fermi energy. In this situation, which is believed to correspond to most single molecule measurements,11 the gap around zero bias is *not* the HOMO-LUMO gap, but, in this example, four times the Fermi energy – HOMO separation. The voltage division factor is a crude model of the potential profile, which more generally could be obtained from Poisson''s equation.  $\eta\eta$  is also likely to vary with bias. At high biases, there may be significant charge redistribution within the molecule, leading to a change in  $\eta$ .



Fig 1.19 HOMO-LUMO separation

The voltage division factor is crucial in determining the conduction level in a single molecule device. In this example, when  $\eta$ =0, conduction always occurs through the HOMO when the applied bias is positive, and through the LUMO when the applied bias is negative. The conductance gap is determined by the HOMO-LUMO separation. When  $\eta$ =0.5, conduction always occurs through the molecular orbital closet to the Fermi Energy. In this example that is the HOMO, irrespective of the polarity of the applied bias. Charging. Previously, we defined the charging energy as the change in the molecule"s potential per additional electron. To calculate the net effect of charging we need the number of electrons transferred. At equilibrium, the number of electrons on the molecule is determined by its Fermi energy.

$$N_0 = \int_{-\infty}^\infty g(E) f(E,E_F) dE$$

Under bias, the electron distribution on the molecule is no longer in equilibrium. We will define the number of electrons under bias as N. Thus, the change in potential at the molecule due to charging is

$$U_C=rac{q^2}{C_{ES}}(N-N_0)$$

### **1.14 Ballistic Transport**

Ballistic conduction (ballistic transport) is the unimpeded flow (or transport) of charge carriers (usually electrons), or energy-carrying particles, over relatively long distances in a material. In general, the resistivity of a material exists because an electron, while moving inside a medium, is scattered by impurities, defects, thermal fluctuations of ions in a crystalline solid, or, generally, by any freely-moving atom/molecule composing a gas or liquid. Without scattering, electrons simply obey Newton's second law of motion at non-relativistic speeds.



Fig1. 11 Ballistic conduction (ballistic transport)

The mean free path of a particle can be described as the average length that the particle can travel freely, i.e., before a collision, which could change its momentum. The mean free path can be increased by reducing the number of impurities in a crystal or by lowering its temperature. Ballistic transport is observed when the mean free path of the particle is (much) longer than the dimension of the medium through which the particle travels. The particle alters its motion only upon collision with the walls. In the case of a wire suspended in air/vacuum the surface of the wire plays the role of the box reflecting the electrons and preventing them from exiting toward the empty space/open air. This is because there is energy to be paid to extract the electron from the medium.

Ballistic Transport is a phenomenon in physics where electrons travel at high speeds within a medium without scattering off of obstacles such as atoms or other electrons. It is a free flow of energy carrying particles (mostly electrons) over relatively long distances in a medium or material. This ballistic transportation is very suitable in Nanodevices because the smaller the conductor, the greater will be the probability that the charge transportation will be ballistic. The reason is that the probability of an electron collision is enhanced by defects and temperature since the electron scattering is usually caused by interactions between electrons and the nuclei and the vibration of the nuclei increases with the increase in temperature. For ballistic transport, the electron has no interaction with the conductor. Thus, the electron is not necessarily in equilibrium with the conductor, i.e., the electron is not restricted to the lowest unoccupied energy states within the conductor. There are two categories of scattering. They are:

### • Elastic Scattering:

The scattering event may change the moment of the electrons but its energy level remains constant. In elastic Scattering: The Energy of the electron is not conserved. Equilibrium may be established by inelastic scattering.





In the above given representation, the difference between the Ballistic Transport and Diffusive Transport is given. For a transport of electrons to be ballistic, the length L of the carrier nanomaterial should be less than the Mean Free Path  $\lambda$ .

 $L << \lambda$ 

This  $\lambda$  can be increased by reducing the number of impurities in the crystal or reducing the temperature of the crystal or even reducing the defects present in the crystal. The mean free path can be obtained by

$$1/\lambda = 1/\lambda_1 + 1/\lambda_2 + 1/\lambda_3 + 1/\lambda_4 + 1/\lambda_5 + 1/\lambda_6 + 1/\lambda_7$$

Where  $\lambda_1$  = Electron-Electron scattering length.

 $\lambda_2$  = Acoustic Phonon scattering length.

 $\lambda_3$  = Optical Phonon Emission scattering length.

 $\lambda_4$  = Optical Phonon Absorption scattering length.

 $\lambda_5$  = Electron Impurity scattering length.

 $\lambda_6$  = Electron Defect scattering length.

 $\lambda_7$  = Electron scattering length with Boundaries.

Ballistic Transport can be applied in:

- Carbon Nanotube Transistors (CNT).
- Ultra-Short Channel Semiconducting Field Effect Transistors.

### **1.15 Single Electron Transistor**

A single –electron transistor (SET) is a sensitive electronic device base on the coulomb blockade effect. In this device the electrons flow through a tunnel junction between source/drain to a quantum dot (conductive island). Moreover, the electrical potential of the island can be turned by a third electrode, known as the gate, which capacitively coupled to the island. The conductive island is sandwiched between two tunnel junctions, which are modeled by a capacitor (Cd and Cs) and a resistor (Rd and Rs) in parallel.



Fig 1. 13 single electron transistor (SET)

A Single Electron Transistor (SET) is a three-dimensional device which can transfer electrons from source to drain one-by-one. The main purpose of SET is to control the tunneling of electron into or from the Quantum Dot. Quantum dots are semiconductor particles of a few nanometers in size having optical and electronic properties that differ from larger particles due to quantum mechanics. The structure of SET consists of the following components.

- Quantum Dot
- Two Tunnel Junctions
- A Gate Electrode
- A Gate Capacitor

The quantum dot is placed between the source and the drain and is separated by a small thin insulating layer. A Gate Electrode is present which electrostatically influences the electrons to flow between the source and drain. In between the quantum dot and the gate, there is a gate capacitance.

Working:

- To control Tunneling, voltage bias is given to the gate electrode.
- A separate voltage bias is applied between source and drain electrode for the current direction.
- When gate bias voltage must be larger to overcome coulomb blockade energy, the current will flow.
- The energy needed to move charge Q inside quantum dot is given by

$$E = VQ$$

$$V = E/e = W_c/e$$
Where Q = e and E = W<sub>c</sub>

$$V = e^2/2C/e = e/2C$$

With this voltage applied to the quantum dot, an electron can tunnel through the quantum dot. When the gate voltage  $V_g$  is zero, there is no current flow. In order to tunnel a single electron, the gate voltage  $V_g = V_{coulomb}$ . To tunnel double electrons at a time, the gate voltage  $V_g = V_{coulomb} + e/2C$ . To tunnel more electrons, we need to add e/2C for each electron.



# SCHOOL OF MECHANICAL ENGINEERING DEPARTMENT OF MECHATRONICS ENGINEERING

**UNIT – II - NANOELECTRONICS - SEC1615** 

#### **NANOELECTRONICS - SEC1615**

### **UNIT 2 PHYSICAL DEPOSITION (THIN FILM) TECHNIQUES.**

Basics of physical methods, Glow discharge DC Sputtering, Triode sputtering, Getter sputtering, Radio frequency sputtering, Magnetron sputtering, Ion beam sputtering, AC sputtering, Vacuum evaporation, Resistive heat Evaporation, Flash Evaporation, Electron Beam Evaporation, LASER evaporation

### 2. Physical Deposition (Thin Film) Techniques:

Thin film deposition is the process of creating and depositing thin film coatings onto a substrate material. These coatings can be made of many different materials, from metals to oxides to compounds. Thin film coatings also have many different characteristics which are leveraged to alter or improve some element of the substrate performance. For example, some are transparent; some are very durable and scratch-resistant; and some increase or decrease the conductivity of electricity or transmission of signals. Thin film deposition is an important manufacturing step in the production of many opto-electronic, solid state and medical devices and products, including consumer electronics, semiconductor lasers, fiber lasers, LED displays, optical filters, compound semiconductors, precision optics, microscopy & microanalysis sample slides, and medical implants. There are a few different technologies and methods that can be used to apply thin film coatings, and an array of tools and equipment that can be used to streamline or enhance the thin film deposition process. There is no one-size-fits-all, perfect thin film deposition system or method. Your technique and configuration of choice depends on the performance and production requirements that are unique to your application.



Fig.2.1 Different Thin film deposition technologies

Thin film deposition of porphyrinoids is a critical step for the development of reliable chemical sensors. The binding properties, in liquid phase, of these compounds should be in fact preserved as much as possible in the solid state, to allow an efficient recognition of target analytes. However, the solid-state arrangements of these macro cycles could offer additional binding mechanisms that exceed those possible to the single molecules allowing to even enhance the superb binding versatility of porphyrinoids. In this manuscript, we have reviewed mostly our approach for the thin film deposition of porphyrinoids, going from the simple, non controlled techniques to the preparation of composite inorganic/organic materials. All these opportunities drive the aggregation of porphyrinoids by supra molecular interactions and the possibility to merge their properties with those of inorganic materials open the way to an almost unlimited possibility to prepare optimized sensing layers.

Thin film deposition involves processing above the substrate surface (typically a silicon wafer with a thickness of  $300-700 \mu m$ ). Material is added to the substrate in the form of thin film layers, which can be either structural layers or act as spacers later to be removed. MEMS deposition techniques fall into two categories, depending on whether the process is primarily chemical or physical (Madou Marc, 1997). In chemical deposition, films are deposited via a chemical reaction between the hot substrate and inert gases in the chamber at low or atmospheric pressure. Depending on the phase of the precursor, chemical deposition is further classified into plating, spin coating, chemical vapour deposition (CVD) (e.g. low pressure CVD, plasma-enhanced CVD, and very low pressure CVD), and atomic layer deposition. In physical deposition, the raw materials (solid, liquid or vapour) are released and physically moved to the
substrate surface, e.g. thermal evaporation, sputtering and ion plating. The choice of deposition process is dependent upon several factors, e.g. substrate structure, operating temperature, rate of deposition and source. These film layers are deposited and subsequently patterned using photolithographic techniques, then etched away to release the final structure.

## 2.1 Basics of physical methods:

- Inert-gas condensation:
- **Physical Methods:** (IGC) is a bottom-up approach to synthesize nanostructured materials, which involves two basic steps. The first step is the evaporation of the material and the second step involves a rapid controlled condensation to produce the required particle size.



Fig. 2.2 Inert-gas condensation

## • Electrical arc discharge:

It is based on laser vaporization; here an electric arc is used to vaporize the material directly, rather than indirectly through a laser pulse source. About 10% of the clusters formed are ions, and this avoids the need for a separate cluster ionization stage. Generally, cluster sizes of up to around 50 atoms are deposited on the target. Nano sheld uses the arc discharge heating to produce ultrafine powders of Fe, Si, SiC, and Al2O3. Gas pressure and arc current are the critical parameters that need to be controlled during evaporation to obtain the desired particle size.

• Physical Methods:

Nanoparticles are also synthesized by **RF plasma method** in Nanoshel. This plasma is generated by RF heating coils. The starting metal is contained in a pestle and this pestle is contained in an evacuated chamber. The metal is heated above its evaporation point by using high voltage RF coils wrapped around the evacuated chamber. Helium gas is allowed to enter the system and this gas forms high temperature plasma in the region of the coils. The metal vapor nucleates on the helium gas atoms and diffuses up to a cold collector rod, where nanoparticles are collected. Finally these nanoparticles are passivated by the introduction of appropriate gas (Oxygen).



Fig. 2.3 RF plasma method

#### • Pulsed Laser Method:

This method is capable of high rate of production of 3gm/min. Nanoshel mainly uses this method in the synthesis of silver nanoparticles. Silver nitrate solution and reducing agent are allowed to flow into a blender like device. This device consists of a solid disc and this disc rotates with solution. Hot spots are created on the surface of the disc by subjecting it to pulses from a laser beam. Silver nitrate reacts with reducing agent at these hot spots and as a result, nano silver particles are formed. These particles can be separated by centrifuge. The size of the particles is controlled by the energy of the laser and angular velocity of the disc.



Fig. 2.4 Pulsed Laser Method

# • Sputtering

**Sputtering or Ion Sputtering** involves vaporizing materials from a solid surface by bombarding a target with high-velocity ions of an inert gas, which causes ejection of atoms and clusters. Since high pressure hinders transportation of the sputtered material, sputter sources such as an ion gun or a hollow cathode plasma sputter source are normally used under vacuum. Positive, negative, as well as neutral charged clusters are produced. The clusters produced are hot and cool down by evaporation in flight.



Fig. 2.5 Ion Sputtering

# Laser ablation

**Laser ablation** (LA) is a process in which a laser beam is focused on a sample surface to remove material from the irradiated zone. Laser ablation has been considered and used for many technical applications, including: the production of nano materials, deposition of thin metallic and dielectric films, fabrication of superconducting materials, routine welding and bonding of metal parts, and micromachining of MEMS structures. Recently in Nanoshel laser ablation has been used for the production of various materials.

**The laser pyrolysis technique** is usually classified as a vapor-phase synthesis process which is also used in Nanoshel for the production of nanoparticles. In this class of synthesis routes, nanoparticles formation starts abruptly when a sufficient degree of super saturation of condensable products is reached in the vapor phase. Once nucleation occurs, fast particle growth takes place by coalescence/coagulation rather than further nucleation.

**The ball milling method:** A ball mill contains a stainless steel container and many small iron, hardened steel, silicon carbide, or tungsten carbide balls are made to rotate inside a mill (drum). The powder of a material is taken inside the steel container. This powder will be made into nanosize using the ball milling technique. Nanoshel uses this method for reducing the size of Nanoparticles.

**Molecular Beam Epitaxy** (**MBE**) can be considered as a special case of evaporation for single crystal film growth, with highly controlled evaporation of a variety of sources in Ultrahigh-vacuum of typically ?10 <sup>-10</sup> torr. Nanoshel uses MBE for synthesis of various thin films.

**Chemical vapor Deposition** (**CVD**) is chemical process used to give high quality, high performance, and solid materials. Here one or more volatile precursors are transported via the vapor phase to the reaction chamber, where they decompose on a heated substrate. Nanoshel have both vertical as well as horizontal CVD used to produce various materials.

#### 2.2 Glow discharge DC Sputtering:

The non-magnetically confined, coldcathode DC (and low-frequency AC) glow discharge (also called a gas discharge) is probably the most simple plasma generation technique used in vacuum coating. The plasma thus generated is used as a source of high-energy ions for sputtering and ion plating ("atomic peening"). The primary glow discharge properties of concern in these

applications are the particle species, charged particle density in the plasma region, cathode fall voltage and the gas pressure. A low gas pressure allows ions and electrons to be accelerated to a high energy in an electric field. This requirement confines the pressure range of interest to the low end of the gas-pressure range for which a self sustained discharge can be maintained (e.g.,  $\approx$  10–50 mTorr for argon). At low voltages, the electrodes will collect naturally occurring ions and electrons and the current will be very small (ohmic region). electron-atom impact will increase the current. In this region (Townsend Discharge region) the If the gas particle density is high enough, at some voltage there will be a "breakdown" and the electric field distribution will change—the discharge will become a "normal glow discharge.It is in this region that sputtering is normally performed.The anode can be a separate electrode (electrically floating), or may be the grounded portion of a metal vacuum chamber.



Fig. 2.6 Plasma generation technique used in vacuum coating

A typical cathode current density for non-magnetic DC diode sputtering is 1 ma/cm2 at an applied voltage of several thousand volts. At some higher voltage, there will be another electrical breakdown and an arc will form between the cathode and the anode. This type of arc is influenced by cathode properties such as oxide inclusions, gas release and sharp points. Arcing will cause a substantial increase in current and decrease in voltage. Arcs are normally detrimental in sputter deposition and ion plating since they can be destructive to the power supplies and the deposited coatings. In the abnormal glow discharge region, ions are accelerated to the cathode through the cathode darkspace region from the edge of the plasma regionThese chargeexchange collisions thus create a spectrum of energetic ions and atoms that strike the cathode. For example, if the applied voltage is 1500 volts, the average ion energy may be 400 eV. The cross-section (probability) for chargeexchange collisions is much greater than that for physical (momentumexchange) collisions. The secondary electrons that are emitted under ion

bombardment of the cathode are accelerated away from the cathode, causing electron-atom ionizing collisions. The process is then repeated. High-energy secondar



Fig. 2.7 DC diode sputtering

## 2.3 Triode sputtering:

Triode sputtering has separated the conventional diode sputtering plasma formation and sputtering functions to permit greater control of film thickness than that achieved with diode sputtering. The deposition rate is constant as a function of time and yield curves for various materials can be used to determine the required sputtering rate.



Fig. 2.8 Triode sputtering setup

The application of rf gives the possibility for sputtering of non-conductive materials such as glass or silicon monoxide, etc. The low power input permits attainment of a given deposition rate with minimum heating of target and substrate. This permits metal and alloy films to be sputtered onto plastics with excellent adherence to some plastics without an undercoat. The higher energy of sputtered atoms (about 40 times that of evaporated atoms) results in excellent adherence. Beryllium copper films sputtered directly onto a glass substrate, without a base film of chromium, show good adherence and can be soldered successfully.

# 2.4 Getter sputtering:

The deposition of high purity thin films at ordinary vacuum levels by using a getter to remove contamination remaining in the vacuum. A getter is a deposit of reactive material that is placed inside a vacuum system, for the purpose of completing and maintaining the vacuum. When gas molecules strike the getter material, they combine with it chemically or by absorption. Thus the getter removes small amounts of gas from the evacuated space. The getter is usually a coating applied to a surface within the evacuated chamber.



Fig. 2.9 Getter sputtering

A vacuum is initially created by connecting a closed and tight container to a vacuum pump. After achieving a sufficient vacuum, the container can be sealed, or the vacuum pump can be left running. Getters are especially important in sealed systems, such as vacuum tubes, including cathode ray tubes (CRTs) and vacuum insulated panels, which must maintain a vacuum for a long time. This is because the inner surfaces of the container release adsorbed gases for a long time after the vacuum is established. The getter continually removes residues of a reactive gas, such as oxygen, as long as it is desorbed from a surface, or continuously penetrating in the system (tiny leaks or diffusion through a permeable material). Even in systems which are continually evacuated by a vacuum pump, getters are also used to remove residual gas, often to achieve a higher vacuum than the pump could achieve alone. Although it is often present in minute amounts and has no moving parts, a getter behaves in itself as a vacuum pump. It is an ultimate chemical sink for reactive gases

#### 2.5 Radio frequency sputtering:

RF or Radio Frequency Sputtering is the technique involved in alternating the electrical potential of the current in the vacuum environment at radio frequencies to avoid a charge building up on certain types of sputtering target materials, which over time can result in arcing into the plasma that spews droplets creating quality control issues on the thin films – and can even lead to the complete cessation of the sputtering of atoms terminating the process. Traditional DC Sputtering is a cost effective way of applying metal target coatings that are electrical conductors like gold. However, DC Sputtering is limited when it comes to dielectric target materials - coatings which are non-conducting insulating materials that can take on a polarized charge. Examples of common dielectric coating materials used in the semiconductor industry include Aluminum Oxide, Silicon Oxide and Tantalum Oxide. As with DC Sputtering, RF Sputtering runs an energetic wave through an inert gas in a vacuum chamber which becomes ionized. The target material or cathode which is to become the thin film coating is bombarded by these high energy ions sputtering off atoms as a fine spray covering the substrate to be coated. RF Sputtering offers several advantages depending upon your specific application. RF plasmas tend to defuse throughout the entire chamber rather than concentrating around the cathode or target material as with DC Sputtering.RF Sputtering also reduces the creation of "Race track erosion" on the surface of the target material. With Magnetron Sputtering, a circular pattern

becomes etched into the surface of the target material as a result of the circular magnetic field of the magnetron focusing the charged plasma particles close to the surface of the sputter target. The diameter of the circular pattern is the result of the magnetic field.



Fig. 2.10 RF sputtering

RF Magnetron sputtering uses magnets behind the negative cathode to trap electrons over the negatively charged target material so they are not free to bombard the substrate, allowing for faster deposition rates. Over time, positive ions are produced which accumulate on the surface of the target face giving it a positive charge. At a certain point this charge can build up and lead to a complete secession of sputtering atoms being discharged for coating.

### • Advantages:

RF Sputtering offers several advantages depending upon your specific application. RF plasmas tend to defuse throughout the entire chamber rather than concentrating around the cathode or target material as with DC Sputtering.RF Sputtering can sustain a plasma throughout the chamber at a lower pressure (1-15 mTorr). The result is fewer ionized gas collisions equaling more efficient line-of-site deposition of the coating material.

#### **2.6 Magnetron sputtering:**

Magnetron sputtering is a deposition technique that involves the generation and confinement of a gaseous plasma in a space containing the target. The high-energy ions erode that target surface within the plasma that results in the liberation of atoms. Liberated atoms then go through the vacuum and deposit on the target substrate to form a thin film. A high voltage application is necessary to generate gaseous plasma. Electrons present in the gas accelerate away from the cathode and collide with nearby atoms. An electrostatic repulsion is caused by the collision the ejects the electrons from the sputtering gas atoms to turn them into ions. Now, the positively charged ions make a dash towards the cathode and collide with the target surface with great energy. Those collisions have the potential to cause surface atoms to knock-off into the vacuum environment with enough kinetic energy to reach the substrate to form thin films. To achieve the maximum number of high energy collisions and increased deposition rates, it is imperative to choose a sputtering gas with the highest possible molecular weight such as xenon or argon. In order to achieve reactive Sputtering, gases like nitrogen or oxygen can also be used to the sputtering chamber. Magnetron sputtering does not rely on melting and evaporation of the target material, and that is the reason that it has numerous advantages as compared to the physical vapor deposition processes.



Fig. 2.11 Magnetron sputtering

A magnetron sputtering source takes advantage of the above phenomena by using very strong magnets to confine the electrons in the plasma at or near the surface of the target. Confining the electrons not only leads to a higher density plasma and increased deposition rates, but also prevents damage which would be caused by direct impact of these electrons with the substrate or growing film. Magnetron sputter deposition does not require melting and evaporation of the

source material, leading to many advantages over other PVD technologies: first, nearly all materials can be deposited by magnetron sputtering regardless of their melting temperature; second, sources can be scaled and positioned anywhere in the chamber based on the requirements of the substrate and the coating; finally, films of alloys and compounds can be deposited while maintaining similar composition to that of the source material. Magnetron sputtering is a high-rate vacuum coating technique for depositing metals, alloys, and compounds onto a wide range of materials with thicknesses up to millimetre. It exhibits several important advantages over other vacuum coating techniques, a property that led to the development of a large number of commercial applications from microelectronic fabrication to simple decorative coatings. There are various advantages of magnetron sputtering such as

- ➢ High deposition rates
- > Ease of sputtering any metal, alloy, or compound
- ➢ High purity films
- Extremely high adhesion of films
- Excellent coverage of steps and small features
- Ability to coat heat-sensitive substrates
- ➢ Ease of automation
- Excellent uniformity on large-area substrates, for example: architectural glass.

# 2.7 Ion Beam Sputtering:

Ion beam deposition (IBD) is a thin film deposition method that produces the highest quality films with excellent precision. Also referred to as ion beam sputtering (IBS), it's a process that's used when tight control over film thickness and stoichiometry is needed



Fig. 2.12 Ion beam deposition (IBD)

Ion Beam Sputtering (IBS), also called Ion Beam Deposition (IBD), is a thin film deposition process that uses an ion source to deposit or sputter a target material (metal or dielectric) onto a substrate to create either a metallic or dielectric film. Because the ion beam is monoenergetic (ions possess the equal energy) and highly collimated, it enables extremely precise thickness control and deposition of very dense, high quality films as compared to other PVD (physical vapor deposition) technologies. Typical configuration of an IBD system is a gridded ion source, a target, and the substrate. The ion beam is focused on a target material, and the sputtered target material deposits onto a nearby substrate. It is common practice to utilize a second gridded ion source directed at the substrate to provide for ion assisted deposition (IAD). IAD is particularly useful when depositing metal oxide or nitride films to improve the film's physical density, moisture stability, optical, and mechanical properties. In addition, it may be desirable to heat the substrates during deposition to improve overall performance.

A key advantage of IBD is independent control of several parameters, including target sputtering rate and IAD parameters – ion energy, ion current density, and angle of incidence for control of film stoichiometry and microstructure. This level of control is the main difference between ion beam and other sputtering processes, making IBD a great choice for the most challenging applications such as precision optics or semiconductor production.

#### • Ion Beam Etching:

Ion beam etch (IBE) is an IBS process that can be used to pre-clean a substrate, or to create a specific pattern on the substrate's surface using masking. Similar to other pre-clean methods, IBE completely removes particles from the substrate before deposition; it can also be used to remove a layer from the substrate surface itself to ensure excellent coating uniformity and adhesion.IBE is an excellent option for materials and applications that require precise specs for material removal. It offers tight process control and repeatability for etching patterns onto a substrate, particularly for etching stacks of multiple materials or layers. As a pre cleaning method, IBE features high-energy ions for a high-impact plasma treatment. By leveraging Denton Vacuum's portfolio of Infinity ion beam products, you can achieve excellent uniformity and repeatability in a system that is fully equipped for high-volume production.

#### • Advantages of Ion Beam Sputtering:

Like other physical vapor deposition techniques, ion beam sputtering provides advantages such as deposition rate, uniformity, composition, thickness control, adhesion, and material properties. However, ion beam sputtering offers additional sputter deposition features which include a wide range of materials with indifference to target thickness or properties, precision deposition stops, clean and low pressure processing (<0.5mTorr), and reactive deposition not susceptible to high energy arcs due to cathode target poisoning. In the ion beam deposition process, there is no plasma between the substrate and the target as one would find with magnetron sputtering. This means the ion beam deposition technique can be used to deposit on sensitive materials and reduces the likelihood that the final product will contain gas molecules. Generally, an ion beam sputtering platform incorporates a multi-target carousel with a high energy, high current primary ion source to generate a well confined ion beam for target sputtering. The reactive deposition configuration will typically include a secondary low energy, high ion current ion/plasma source to provide ion assist process benefits. The substrate stage will tilt and rotate in either single or planetary rotation. The deposition process is well defined and controlled by natural and engineered means. This ability to control makes ion beam sputtering well suited for applications such as precision optics.

## 2.8 AC Sputtering:

AC sputtering uses alternating (periodically reversed) voltage between the electrodes (target and substrate). The frequency of the alternating voltage is 10-100 kHz. AC sputtering method allows deposition of electrically non-conductive materials (e.g. oxide films). Obtaining non-conductive coatings by DC sputtering is impossible because of the effect of disappearing anode. AC spattering technique is used in Dual Magnetron configuration in which the AC voltage is applied between two targets. Their surfaces are periodically coated and cleaned according to the alternating potential, which prevents the effect of disappearing anode. Mid-frequency AC Sputtering has become a mainstay of thin film sputtering technologies, particularly for the deposition of dielectric or non-conducting film coatings on surfaces such as solar panels, optical glass such as telescope mirrors or rolls of plastic. It is largely replacing RF Sputtering for coating dielectrics because it operates in the kHz rather than MHz range requiring less sophisticated and

expensive power sources and is a process that is adaptable to large scale applications. MF or Mid-frequency AC power supplies cover a wide range of voltage outputs between 300 V to 1200 V - generally in the 25 to 300 kW range - at frequencies between 20 to 70 kHz with 40 kHz used most commonly.



Fig. 2.13 AC sputtering

It is a process frequently used with Reactive Sputtering where a reactive gas such as oxygen or nitrogen is introduced into the plasma to form oxides or nitrides on the substrate. Two cathodes are used with an AC current switched back and forth between them which cleans the target surface with each reversal to reduce the charge build up on dielectrics that leads to arcing which can spew droplets into the plasma and prevent uniform thin film growth. Combined with sophisticated arc detection and suppression circuitry, MF or Mid-frequency AC Sputtering offers the advantages of improving process stability and increasing deposition rates as well as overcoming the problem known as the "Disappearing anode" effect. When trying to reactively sputter a dielectric coating with DC sputtering, the anode can become coated with an insulating coating and disappear. This is known as the disappearing anode effect. In the case of AC sputtering, the cathodes act as an anode every half cycle and provide a "clean" anode surface. Mid-frequency AC Sputtering often employs dual magnetrons to confine the electrons above the target and reduce arcing for process control. These include what are known as either "Balanced" or "Unbalanced" magnetrons that can be arranged side by side, tilted towards each other, or face to face. Conventional magnetrons are most commonly of the balanced type, where the null point or area where the opposing magnetic fields cancel each other out is usually high in the plasma above the target. When the null point is high above target, there is the least chance of electrons escaping the magnetic field .Compared with balanced magnetrons, unbalanced magnetrons

possess stronger magnets with the null point closer to the target surface, so electrons can escape more easily from the electron trap into the plasma. These electrons undergo ionizing collisions with the inert gasses like Argon farther away from the target surfaces in the plasma and closer to the substrate being coated.AC Sputtering with unbalanced magnetrons has the great advantage of allowing a bias or charge to be applied to the substrate being coated which effectively forms a secondary plasma in the vicinity of the substrate. As gas ions from this secondary plasma accelerate towards the substrate it produces a much denser plasma around the substrate compared to balanced magnetrons. This results in a much higher ion bombardment of the substrate with unbalanced magnetrons which can be used to control and enhance the properties of the thin film being deposited.

#### 2.9 Vacuum Evaporation:

The objective is to controllably transfer atoms from a heated source (which can be a liquid or a solid) to a substrate located a distance away to grow a film. The source is heated directly or indirectly until the point is reached where it efficiently sublimes or evaporates. When analyzing this method, we need to start from evaporation rates and vapor pressure. Thermal evaporation is a well-known method for coating a thin layer in which the source material evaporates in a vacuum due to high temperature heating, which facilitates the vapor particles moving and directly reaching a substrate where these vapors again change to a solid state. In this method, a charge holding boat or resistive coil is used in the form of a powder or solid bar. In order to get the high melting points necessary for metals, the resistive boat/coil is exposed to a large direct current (DC), where the high vacuum (below  $10^{-4}$  Pa) supports the evaporation of the metal and further carrying it to the substrate. This technique is specially applicable for material with low melting points.

#### 2.10 Resistive Heat Evaporation:

In this process, the solid source material is evaporated in vacuum, and the vapor particles are carried by the vacuum to the substrate. The deposited layer, which is usually a thin film, is formed as the source material evaporates. The process is pictured below

#### **Resistance heating evaporation**



Fig. 2.14 Resistive Heat Evaporation

## 2.11 Flash Evaporation:

Flash evaporation (FE) is one of the prominent techniques for the deposition of thin films of multi-component alloys whose constituents have different vapour pressures. This technique requires only one boat maintained at sufficiently high temperature to evaporate the least volatile component of the alloy. The main advantage of FE is that it does not require maintaining the critical vapour pressures of the components and temperatures of the boats unlike multi-source thermal evaporation.

#### **2.12 Electron Beam Evaporation:**

The electron beam is accelerated to a high kinetic energy and focused towards the starting material. The kinetic energy of the electrons is converted into thermal energy that will increase the surface temperature of the materials, leading to evaporation and deposition onto the substrate.



Fig. 2.14 Electron beam Evaporation

## 2.13 Laser Evaporation:

Laser ablation is a process that involves the fabrication of various kinds of nano particles, such as carbon nano tubes, semiconductor quantum dots, and core shell nanoparticles. The process generates these new particles by vaporizing a gas containing laser-vaporized species. Laser ablation is a method for fabricating various kinds of nanoparticles including semiconductor quantum dots, carbon nanotubes, nanowires, and core shell nanoparticles. In this method, nanoparticles are generated by nucleation and growth of laser-vaporized species in a background gas.



Fig. 2.15 Laser Evaporation process

The applications of laser radiation are shown to range from fabricating, melting, and evaporating nano particles to changing their shape, structure, size, and size distribution, through studying their dynamics and forming them into periodic arrays and various structures and assemblies.



# SCHOOL OF MECHANICAL ENGINEERING DEPARTMENT OF MECHATRONICS ENGINEERING

**UNIT – III - NANOELECTRONICS - SEC1615** 

#### **NANOELECTRONICS - SEC1615**

#### **UNIT 3 CHEMICAL DEPOSITION (THIN FILM) TECHNIQUES.**

Fundamentals of chemical methods, Chemical Vapour Deposition, LASER chemical Vapour Deposition, Photo Chemical Vapour Deposition, Plasma enhanced Vapour Deposition, Metal Organo Chemical Vapour Deposition, Chemical Bath Deposition, Electro less Deposition, Anodisation, Liquid Phase Epitaxy, Sol-Gel method, Spin Coating, Spray-Pyrolysis Technique, Polymer Assisted Deposition

### 3. Chemical Deposition (Thin Film) Techniques

Thin-film vapor deposition may not sound terribly exciting it is one of the most important ways of making integrated circuits, and is also on its way to becoming one of the building blocks of nanotechnology. Basically, it involves applying a thin coating to another surface, usually by coaxing the coating material from a vaporous or dissolved state using electricity, high heat, chemical reactions, evaporation, or other techniques. One of the most common (and oldest) types of thin-film deposition is electroplating. Here, the target object (such as a piece of jewellery) is immersed in a chemical bath that contains dissolved metal atoms (such as gold). An electric current applied between the target and the bath causes the atoms to deposit onto the target. Electroplating has been very widely used since the early 19th century to make plated silverware, chrome automobile bumpers, and thousands of other objects.

Most deposition techniques follow these three major sequences:

- 1. Synthesis of the deposition species,
- 2. Conveyance from source to substrate,
- 3. Deposition and adhesion of the source onto the substrate and subsequent film growth.

#### **3.1 Fundamental methods of Chemical Vapour Deposition**

#### • Thermal (or vacuum) evaporation

Thermal (or vacuum) evaporation is an old deposition process used for the formation and growth of the thin film on the surface of solid materials. The process is still beneficial in a contemporary

environment and extensively applicable in the laboratory and industries for deposition of the thin film. The basic sequential steps for thermal or vacuum evaporation are given below:

• The vapour is created from subjecting the target material to very high temperature by subliming or boiling

• The ejected vapour from the target material is transported to the substrate through a vacuum.

• Condensation of the vapour takes place to form a solid thin film on the surface of the substrate, and further repeatability of the deposition cycles result in thin film growth and nucleation.

## • Sputtering

Sputtering is a vital and prominent procedure among the PVD processes. It's a non-thermal vaporization process whereby individual atom escapes from the target surface due to atomic collision cascades by suitable high energy ion bombardment. Unlike evaporation, the source is no longer created by thermal but by ion impact on the target. Also, the target to substrate distance is shorter and, in many cases, it has outperformed other PVD processes with more functionality and performance like improved adhesion and thicker film. During the sputtering process, atoms are removed from the surface of the target material by transfer of sustainable momentum from an atomic-sized energetic bombarding particle usually gaseous ion accelerated from a plasma.

#### • Ion plating

Mattox was the first to report Ion plating technique in 1960. It uses continuous or intermittent bombardment in an inert gas discharge system for the deposition of a film by atomic sized energetic particles to amend and regulate the properties of the depositing film. The plasma is created in a hollow cathode discharge source. The substrate material is subjected to bombardment by a high energy flux ions adequate to cause substantial sputtering on the surface of the substrate before and during thin film growth.

#### • Arc vapour deposition

Arc vapour deposition is a deposition process that uses electric arc at high current and low voltage to vaporize a cathodic electrode (cathodic arc) or anodic electrode (anodic arc) and

deposit the vaporized material on a substrate. The substrate is usually biased so as to fast-track the film ions to the surface and also, the vaporized material are highly ionized. Flux is generated by creating an arc that travels across the surface of the target. The arc strikes lead to ejection of atoms from the target materials and condense on the substrate as a thin film coating. A substantial proportion of the metal atoms become ionized and makes it distinguished from vacuum or thermal evaporation. This substantial proportion of ionized atom makes it reliable for the formation of a thick coating and can be used for hard decorative surface-coating operations

## • Laser Chemical Vapour Deposition

In recent times lasers are being increasingly employed in various types of material processing. Diverse types of lasers are available over a wide energy spectrum in continuous wave (CW) or pulsed mode for such uses. The unique properties of the laser beam, e.g. coherence, spectral chromaticity, low divergence and tunability, contribute in giving a concentrated beam of large energy density (irradiance) in a chosen spectral region. In addition, the laser beam can be manoeuvred to the required place of use and can be focused according to requirements. These properties have led to the laser being used for analysis, synthesis, evaporation, etching, doping, etc. in material processing (Boyd 1983) as well as in many industrial processes like drilling, cutting, welding, etc. (Ready 1978). The use of lasers in the biological and medical fields is also well known. The laser has proved to be an important tool in material processing both in the area of fundamental development and in industrial applications. Both attributes of a laser beam, viz. heat and light, have been utilized effectively in the laser processing of materials. Figure I is a block diagram showing the extensive network of laser processing techniques currently being employed or investigated for possible application in semiconductor manufacturing. The present review concerns a limited aspect of laser processing, viz. laser-induced chemical vapour deposition (LCVD). LCVD is becoming an interesting new area of research in material science. It has high potential as a technique for thin film deposition and is still in the research and development stage. In the next section, we will briefly describe general chemical vapour deposition (CVD) techniques and their variants and how they are related to LCVD. After that, we will review LCVD, the mechanism and applications, and the results obtained till now. The paper will conclude with general remarks on the future possibilities of LCVD processes as a viable technology.

#### • Chemical Deposition (Thin film) Techniques

Although "thin-film vapor deposition" may not sound terribly exciting it is one of the most important ways of making integrated circuits, and is also on its way to becoming one of the building blocks of nanotechnology. Basically, it involves applying a thin coating to another surface, usually by coaxing the coating material from a vaporous or dissolved state using electricity, high heat, chemical reactions, evaporation, or other techniques. One of the most common (and oldest) types of thin-film deposition is electroplating. Here, the target object (such as a piece of jewelry) is immersed in a chemical bath that contains dissolved metal atoms (such as gold). An electric current applied between the target and the bath causes the atoms to deposit onto the target. Electroplating has been very widely used since the early 19th century to make plated silverware, chrome mautomobile bumpers, and thousands of other objects. Another type of thin-film vapor deposition or electroplating is "sputtering." Sputtering uses an electrode, usually heated to a temperature high enough to cause it to fling off hot atoms, which find their way to the "target" surface and form layers. Known since at least the early 1850s, Thomas Edison was apparently one of the first to use this process for a commercial product when he used it to apply a thin layer of metal to the outside of his wax phonograph recordings in 1904, in order to make metal molds of the recordings for mass-duplication. An important variation of sputtering is called "anodizing," which is used to give aluminum automobile wheels and trim items a uniform, shiny surface. It's also widely used on cookware to make it resistant to food sticking. Beginning in the 1960s, researchers at Bell Telephone Laboratories used a new type of thin-film vapor deposition (which they called molecular beam epitaxy) to "grow" thin layers of a certain type of semiconductor material onto another type of semiconductor base, in order to create a sort of sandwich that could then be further processed to make transistors. In a special chamber, the coating material is heated to high heat, and then as atoms "boil" off, they are guided to the coated surface, where they form an extremely thin, crystalline layer.



Fig.3.1 Chemical Deposition (Thin film) Techniques

#### 3.2 Chemical vapour deposition

Chemical vapour deposition (CVD) is a powerful technology for producing high-quality solid thin films and coatings. Although widely used in modern industries, it is continuously being developed as it is adapted to new materials. Today, CVD synthesis is being pushed to new heights with the precise manufacturing of both inorganic thin films of 2D materials and highpurity polymeric thin films that can be conformally deposited on various substrates. In this Primer, an overview of the CVD technique, including instrument construction, process control, material characterization and reproducibility issues, is provided. By taking graphene, 2D transition metal dichalcogenides (TMDs) and polymeric thin films as typical examples, the best practices for experimentation involving substrate pretreatment, high-temperature growth and post-growth processes are presented. Recent advances and scaling-up challenges are also highlighted. By analysing current limitations and optimizations, we also provide insight into possible future directions for the method, including reactor design for high-throughput and lowtemperature growth of thin films. Irrespective of the variations in CVD types, the fundamental process is similar and consists of the following common elementary step First, the reactant gases are transported into the reactor. These reactant gases then either undergo gas-phase reactions to form intermediate reactants and gaseous by-products via homogeneous reactions or diffuse directly through the boundary layer to the substrate. In both cases, the reactant gases and the intermediate reactants adsorb onto the heated substrate surface and diffuse on the surface. The subsequent heterogeneous reactions at the gas-solid interface lead to continuous thin film formation via nucleation, growth and coalescence as well as formation of reaction by-products. Finally, any gaseous products and unreacted species desorb from the surface and are carried away from the reaction zone. The gas-phase reactions occur when the temperature is sufficiently high or additional energy is introduced, for example, in the form of plasma. In addition, the heterogeneous reaction is essential if the deposition reaction relies on the surface catalysis of the underlying substrate, such as in the case of the catalytic growth of graphene on a metal surface.



Fig. 3.2 Chemical vapour deposition (CVD)

First, reactant gases (blue circles) are transported into the reactor (step a). Then, there are two possible routes for the reactant gases: directly diffusing through the boundary layer (step b) and adsorbing onto the substrate (step c); or forming intermediate reactants (green circles) and by-products (red circles) via the gas-phase reaction (step d) and being deposited onto the substrate by diffusion (step b) and adsorption (step c). Surface diffusion and heterogeneous reactions (step e) take place on the surface of substrate before the formation of thin films or coatings. Finally, by-products and unreacted species are desorbed from the surface and forced out of the reactor as exhausts (step f). CVD, chemical vapour deposition.

To obtain high-quality thin films by CVD, suitable equipment is needed, and custom-built systems provide the flexibility of operation often desired by CVD researchers. In this section, we discuss a series of designs that satisfy the requirements of materials synthesis, including the heating methods, gas-flow control, the loading of substrate and so on. In addition, the growth parameters, including substrate, temperature, atmosphere, pressure and so on, are essential for controlling the quality of as-grown materials as well as the reaction rate (growth rate). Here, we will introduce CVD growth of graphene following the procedure of substrate pretreatment, heating, annealing, high-temperature growth and cooling.

#### • CVD equipment

A CVD system must meet the following basic requirements: delivery of the gas-phase reactants in a controllable manner; provision of a sealed reaction chamber; evacuation of the gases and control of the reaction pressure; supply of the energy source for the chemical reactions; treatment of the exhaust gases to obtain safe and harmless levels; and automatic process control to improve the stability of the deposition process. Figure below shows a typical CVD system consisting of a gas delivery system, a reaction chamber, a vacuum system, an energy system, an exhaust gas treatment system and an automatic control system.



Fig.3.3 horizontal chemical vapour deposition (CVD) system

Schematic diagram of a typical horizontal chemical vapour deposition (CVD) system, which includes a gas delivery system, the quartz reaction chamber, a vacuum system, the energy system and an auto-control system. A liquid precursor bubbler, which can also be used to provide solid precursors by dissolution in a suitable solvent. A vertical reactor for scalable growth of graphene wafers, where the 25 wafers can be loaded on the quartz substrate holder. The multiple gas inlet nozzles are designed to improve the uniformity of gas flow, which is simulated based on the finite element method. The Bourdon gauge and capacitance manometer which are commonly used to measure the pressure of the vacuum system.

## 3.3 Laser chemical vapour deposition

transfer in the gases Both LCVD and LIFT have been used to fabricate 3D microstructures; however, LCVD is limited by the small amount of material that can be delivered to the location of interest by the use of gaseous metal-organic precursors; thus, its writing speed cannot exceed 0.1 mm/s and must take place inside a vacuum to avoid contamination and <u>dilution</u> of the source precursor, which limits the ability of LCVD to generate patterns over an existing structure. The decomposition pathways of the precursor gas in LCVD can be either photoactivated (photolytic LCVD) or thermal (pyrolytic LCVD). In either case it is possible to achieve submicrometer 3D structures of a wide range of materials (mainly metals, semiconductors, and some oxides) on a variety of substrates. LCVD has found commercial application in the additive repair of transistor arrays for flat panel displays; however, given its limited writing speed, its use for other micro-AM applications has been limited at best.



Fig. 3.4 Laser chemical vapour deposition LCVD

During LCVD, the spot on the substrate under laser irradiation is at a very high temperature (1200 K or higher). Temperature gradients in the source gases will cause natural convection in the chamber. The concentration of the gas mixture near the hot spot on the substrate is affected by the chemical reaction taking place on the substrate. Concentration differences in the chamber become another force driving natural convection in the chamber. The physical model of LCVD under consideration. A substrate made of Incoloy 800 with a thickness of *h* is located in the bottom of a chamber. Before the vapor deposition starts, the chamber is evacuated and then filled with a mixture of H<sub>2</sub>, N<sub>2</sub>, and TiCl<sub>4</sub>. A laser beam moves along the surface of the substrate with a constant velocity,  $u_b$ . The initial temperature of the substrate,  $T_i$ , is below the chemical reaction temperature. Vapor deposition starts when the surface temperature reaches the chemical reaction temperature. The chemical reaction that occurs on the top substrate surface absorbs part of the laser energy and consumes the TiCl<sub>4</sub>. A concentration difference is thereby established and

becomes the driving force for mass transfer. The physical model of the LCVD process includes: natural convection, heat transfer in the substrate and gases, and chemical reaction, as well as mass.



Fig.3.5 Physical model of the LCVD process

The laser beam travels with a constant velocity  $u_b$  along the surface of the substrate, constituting a typical moving heat source problem. If the substrate is sufficiently large in comparison to the diameter of the laser beam, which has an order of magnitude of  $10^{-3}$  m, a quasi-steady state occurs. The system appears to be in steady-state from the stand point of an observer located in and traveling with the laser beam. By simulating LCVD with a moving laser beam in the moving coordinate system, the computational time will be substantially shortened, thereby enabling numerical simulation for a significant number of cases.

#### 3.4 Photo Chemical Vapour Deposition:

A photochemical vapor deposition method which comprises introducing a starting gas into a reaction chamber, irradiating the starting gas with a light energy, and forming a deposition film on a substrate by utilizing a photochemical reaction, characterized in that the plural starting gases are introduced into the reaction chamber and the film is formed on said substrate by causing chemical reactions by irradiating molecules of these starting gases with individual light energy having a wavelength region corresponding to an absorption spectrum of each of said starting gases.



Fig. 3.6 Photochemical vapor deposition method

## 3.5 Plasma enhanced chemical vapour deposition:

Plasma-enhanced chemical vapor deposition (PECVD) is a chemical vapor deposition process used to deposit thin films from a gas state (vapor) to a solid state on a substrate. Chemical reactions are involved in the process, which occur after creation of a plasma of the reacting gases. The plasma is generally created by radio frequency (RF) (alternating current (AC)) frequency or direct current (DC) discharge between two electrodes, the space between which is filled with the reacting gases.



Fig. 3.7 Plasma-enhanced chemical vapor deposition (PECVD)

A simple DC discharge can be readily created at a few torror between two conductive electrodes, and may be suitable for deposition of conductive materials. However, insulating films will quickly extinguish this discharge as they are deposited. It is more common to excite a capacitive discharge by applying an AC or RF signal between an electrode and the conductive walls of a reactor chamber, or between two cylindrical conductive electrodes facing one another. The latter configuration is known as a parallel plate reactor. Frequencies of a few tens of Hz to a few thousand Hz will produce time-varying plasmas that are repeatedly initiated and extinguished; frequencies of tens of kilohertz to tens of megahertz result in reasonably time-independent discharges.

#### 3.6 Metal organic chemical vapour deposition:



Fig. 3.8 Metal organic chemical vapour deposition

MOCVD is a widely used technique for various electronic, optoelectronic, piezoelectric, ferroelectric, and multiferroic materials. In this process, precursors consisting of complex metal organic ligands of metal ions are used as a deposition source. A great benefit with MOCVD is that the precursors are maintained outside the deposition chamber, compared to the physical vapour deposition techniques, and hence can be refilled continuously during long deposition runs. Additionally, numerous mixtures of various precursors can be made with varying levels of dopants very quickly and effectively. Furthermore, high deposition rates of more than 0.5  $\mu$ m/min have been achieved in superconductor film growth Such high rates are unusual for MOCVD of other materials where rates of only about 1  $\mu$ m/hour are used. Since the MOCVD precursors can be deposited over a large area, coupled with high deposition rates, high throughput can be achieved, which is very important for large-scale manufacturing.

#### 3.7 Chemical Bath Deposition:

Chemical bath deposition (CBD), or chemical solution deposition (CSD), is a method to deposit thin films and nano materials. It can be employed for large-area batch processing or continuous deposition. This technique is extensively used to deposit buffer layers in thin film photovoltaic cells.



Fig. 3.9 Chemical bath deposition (CBD)

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, the molarity of concentration, and time. Chemical bath deposition does not cause physical damage in the substrate.

## **3.8 Electroless Deposition**

Electroless deposition or plating of metals such as silver, aluminium, copper, nickel, and iron is a uniform coating of metallic layer on the surface of fibres through chemical reduction of metal ions in an aqueous solution and the subsequent deposition of metal without the use of electrical energy. The electroplated fibres benefit from electrical conductivity and electromagnetic interference also called as EMIshielding effectiveness depending on the applied metal. It is a process of coating a superior metal over the base or the inferior metal by catalytic reduction using a reducing agent in the electrolyte containing the soluble salt of the coating metal without the use of electricity. In most cases, prior or simultaneous surface modification of fibres through physical or chemical methods is required for good adherence of the electroplated layer on the surface.

# • Objectives

• To improve the corrosion resistance of the metal. Eg chromium and nickel coated components.

• Improves the aesthetic appearance of the metal and reduces the cost. Eg Gold covering ornaments.

- Increases the thermal conductivity of the material. Eg Copper bottomed vessels.
- To increase the tensile strength of the metals. Eg Aluminium coatings.

Electroless deposition of Ag is an important industrial process for printed circuit boards (PCBs) to prevent degradation of the copper surface and is usually done by plating silver on copper from an AgNO<sub>3</sub>/HNO<sub>3</sub> solution. Compared to the corrosive nature of the aqueous solution which also affects the copper in PCBs, an ionic liquid or DES does provide a safer alternative. Secondly, in aqueous solutions for the electroless deposition to prolong beyond few nanometres, a palladium catalyst is used. However, in the case of ionic liquids, it was shown that the galvanic displacement reaction of silver continued beyond a few nanometres without the use of any additional catalyst. In ChCl:EG eutectic ionic liquid, the galvanic displacement reaction took place according to the equation.

$$Ag^{+}IL + Cu(s) = Cu^{+}IL + Ag(s)$$

Electroless deposition or plating of metals such as silver, aluminum, copper, nickel, and iron is a uniform coating of metallic layer on the surface of fibers through chemical reduction of metal ions in an aqueous solution and the subsequent deposition of metal without the use of electrical energy. The electroplated fibers benefit from electrical conductivity and electromagnetic interference (EMI) shielding effectiveness depending on the applied metal. In most cases, prior or simultaneous surface modification of fibers through physical or chemical methods is required for good adherence of the electroplated layer on the surface. For instance, Lu et al. (2010) formed a silica-like layer on polyester fabric using acetone solution of (3-aminopropyl) trimethoxysilane following anhydrous solution containing 3by toluene mercaptopropyltriethoxysilane to produce silver-plated polyester fabric with good conductivity and strong adherence using ultrasonic-assisted electroless plating. Moreover, Wang et al. (2012) carried out the electroless plating of silver on polydopamine-functionalized polyester fabric. In addition to these methods requiring preactivation of surface for durable electroless plating, Montazer and Allahyarzadeh (2013) proposed a novel route to introduce compact nano

layer of silver <u>nano particles</u> on polyester surface. In this method, silver was directly plated onto the polyester fabric using simple, low-cost conventional exhaustion process without the need for sensitization and activation processes. The polyester fabric was hydrolyzed with sodium hydroxide to introduce carboxylate and hydroxyl functional groups onto the polyester fabric surface and also to produce terephthalic acid, ethylene glycol, and other forms of water-soluble low-molecular-weight polyester structures as reducing agents, as a result of polyester alkali hydrolysis. Silver ions were then absorbed onto the polyester fabric surface through binding to the carboxylate and hydroxyl functional groups and then reduced to silver metal. This step was followed by the formation of a condensed nano layer of silver nano particles on the polyester fabric surface by post treatment with ammonia. Field emission scanning electron microscope (FESEM) image of the silver-plated polyester fibers using the proposed method is shown in Fig. indicating a uniform and condensed silver nano layer coated on the polyester.



Fig. 3.10 FESEM image of the silver-plated polyester fibers

#### **3.9 Anodisation**

Anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is called anodizing because the part to be treated forms the anode electrode of an electrolytic cell. Anodizing increases resistance to corrosion and wear, and provides better adhesion for paint primers and glues than bare metal does. Anodic films can also be used for several cosmetic effects, either with thick porous coatings that can absorb dyes or with thin transparent coatings that add reflected light wave interference effects. Anodizing is also used to prevent galling of threaded components and to make dielectric films for electrolytic capacitors. Anodic films are most commonly applied to protect aluminium alloys, although processes also exist

for titanium, zinc, magnesium, niobium, zirconium, hafnium, and tantalum. Iron or carbon steel metal exfoliates when oxidized under neutral or alkaline micro-electrolytic conditions; i.e., the iron oxide (actually ferric hydroxide or hydrated iron oxide, also known as rust) forms by anoxic anodic pits and large cathodic surface, these pits concentrate anions such as sulfate and chloride accelerating the underlying metal to corrosion. Carbon flakes or nodules in iron or steel with high carbon content (high-carbon steel, cast iron) may cause an electrolytic potential and interfere with coating or plating. Ferrous metals are commonly anodized electrolytically in nitric acid or by treatment with red fuming nitric acid to form hard black Iron(II,III) oxide. This oxide remains conformal even when plated on wiring and the wiring is bent.

Anodizing changes the microscopic texture of the surface and the crystal structure of the metal near the surface. Thick coatings are normally porous, so a sealing process is often needed to achieve corrosion resistance. Anodized aluminium surfaces, for example, are harder than aluminium but have low to moderate wear resistance that can be improved with increasing thickness or by applying suitable sealing substances. Anodic films are generally much stronger and more adherent than most types of paint and metal plating, but also more brittle. This makes them less likely to crack and peel from ageing and wear, but more susceptible to cracking from thermal stress. These carabiners have an anodized aluminium surface that has been dyed; they are made in many colours.

Anodizing is an electrochemical process that converts the metal surface into a decorative, durable, corrosion-resistant, anodic oxide finish. Anodizing is accomplished by immersing the aluminium into an acid electrolyte bath and passing an electric current through the medium. The anodic oxide structure originates from the aluminum substrate and is composed entirely of aluminum oxide. This aluminum oxide is not applied to the surface like paint or plating, but is fully integrated with the underlying aluminum substrate, so it cannot chip or peel. It has a highly ordered, porous structure that allows for secondary processes such as colouring and sealing. Anodizing is accomplished by immersing the aluminum into an acid electrolyte bath and passing an electric current through the medium. A cathode is mounted to the inside of the anodizing tank; the aluminum acts as an anode, so that oxygen ions are released from the electrolyte to combine

with the aluminum atoms at the surface of the part being anodized. Anodizing is, therefore, a matter of highly controlled oxidation the enhancement of a naturally occurring phenomenon.



Fig. 3.11 Surface of the part being anodized

## Advantages:

• Protects satellites from the harsh environment of space.

• Provides attractive, minimum-maintenance, highly durable exteriors, roofs, curtain walls, ceilings, floors, escalators, lobbies and staircases in skyscrapers and commercial buildings throughout the world.

• Considered environmentally safe, producing few, if any, harmful effects on land, air, or water.

• Revolutionized the construction of computer hardware, exhibit displays for trade shows, scientific instruments, and a constantly expanding array of home appliances, consumer products, and building materials.

## 3.10 Liquid Phase Epitaxy (LPE)

Epitaxy refers to a type of crystal growth or material deposition in which new crystalline layers are formed with one or more well-defined orientations with respect to the crystalline seed layer.Liquid-phase epitaxy (LPE) is a method to grow semiconductor crystal layers from the melt on solid substrates. This happens at temperatures well below the melting point of the deposited semiconductor. The semiconductor is dissolved in the melt of another material. At conditions that are close to the equilibrium between dissolution and deposition, the deposition of the semiconductor crystal on the substrate is relatively fast and uniform. The most used substrate is indium phosphide (InP). Other substrates like glass or ceramic can be applied for special applications. To facilitate nucleation, and to avoid tension in the grown layer the thermal expansion coefficient of substrate and grown layer should be similar. Centrifugal liquid-phase epitaxy is used commercially to make thin layers of silicon, germanium, and galliumarsenide. Centrifugally formed film growth is a process used to form thin layers of materials by using a centrifuge. The process has been used to create silicon for thin-film solar cellsand far-infrared photodetectors. Temperature and centrifuge spin rate are used to control layer growth. Centrifugal LPE has the capability to create dopant concentration gradients while the solution is held at constant temperature.



Fig. 3.11 Liquid phase epitaxy (LPE) process

In liquid phase epitaxy (LPE), the growth cell is normally a rectangular cavity where the solution is placed. Therefore, modeling the LPE growth process is actually a three dimensional problem. However, most models in the literature developed for LPE are two dimensional. This is mainly for two reasons: for simplicity, and due to the physical nature of the growth system. Crystals grown by LPE show 3-D and edge effects in the regions very close to the crucible wall. Except the very edges, the LPE process in general produces uniform and flat crystalline layers. Thus, two-dimensional models provide reasonably accurate predictions for most purposes.

#### 3.11 Sol-Gel Method

Sol-gel process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides, especially the oxides of silicon (Si) and titanium (Ti). The process involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers.

A "sol" or a colloidal solution is formed that then gradually evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any

number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation. Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing. Afterwards, a thermal treatment, or firing process, is often necessary in order to favour further polycondensation and enhance mechanical properties and structural stability via final sintering, densification, and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.



Fig. 3.12 Sol-gel process

## • Applications:

• **Protective coatings** - Protective and decorative coatings, and electro-optic components can be applied to glass, metal and other types of substrates with these methods.

• **Nano-scale Powders** - These powders of single and multiple component compositions can be produced on a nanoscale particle size for dental and biomedical applications.

• **Medicine** - A sol-gel processed alumina can be used as a carrier for the sustained delivery of drugs and as an established wound healer.

• **Opto-Mechanical Particles** - Macroscopic optical elements and active optical components as well as large area hot mirrors, cold mirrors, lenses, and beam splitters all with optimal geometry can be made quickly and at low cost via the sol–gel route.
# 3.12 Spin Coating

Spin-coating technique is used to prepare uniform thin films in the thickness range of micrometer to nanometer. The substrate is mounted on a chuck that rotates the sample, and the centrifugal force drives the liquid radically outward. Viscous force and surface tension are the main causes for the flat deposition on surface. Finally, the thin film is formed by the evaporation. Spin coating consists of several stages, such as fluid dispense, spin up, stable fluid outflow, spin off, and evaporation, respectively.



Fig. 3.13 Spin Coating Technique

In the first stage the material is deposited on the turntable and then spin up and spin off occur in sequence while the evaporation stage occurs throughout the process. The applied solution on the turntable is distributed via centrifugal force. High spinning speed results in thinning of the layer. This stage is followed by drying of the applied layer. Uniform evaporation of the solvent is possible because of rapid rotation. High volatile components are removed from the substrate because of the evaporation or simply drying and the low volatile components of the solution remain on the surface of the substrate. Thickness of the deposited layer is controlled by the viscosity of the coating solution and the speed of rotation. Spin coating is a procedure used to deposit uniform thin films onto flat substrates. Usually a small amount of coating material is applied on the center of the substrate, which is either spinning at low speed or not spinning at all. The substrate is then rotated at speed up to 10,000 rpm to spread the coating material by centrifugal force. A machine used for spin coating is called a spin coater, or simply spinner. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and

simultaneously evaporates. The higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the viscosity and concentration of the solution, and the solvent. Pioneering theoretical analysis of spin coating was undertaken by Emslie et al., and has been extended by many subsequent authors (including Wilson et al., who studied the rate of spreading in spin coating; and Danglad-Flores et al., who found a universal description to predict the deposited film thickness). Spin coating is widely used in microfabrication of functional oxide layers on glass or single crystal substrates using sol-gel precursors, where it can be used to create uniform thin films with nanoscale thicknesses. It is used intensively in photolithography, to deposit layers of photoresist about 1 micrometre thick. Photoresist is typically spun at 20 to 80 revolutions per second for 30 to 60 seconds. It is also widely used for the fabrication of planar photonic structures made of polymers. One advantage to spin coating thin films is the uniformity of the film thickness. Owing to self-leveling, thicknesses do not vary more than 1%. However, spin coating thicker films of polymers and photoresists can result in relatively large edge beads whose planarization has physical limits.

## Advantages:

- Less loss of materials than with vapor-phase deposition.
- It is a relatively inexpensive technique a spinning plate is far cheaper than a vacuum deposition system.
- The spin-coating means we can quickly and easily deposit thin layers.

## **Disadvantages:**

- Difficulty of creating multilayer structures.
- Difficulty of accurately controlling the deposition (homogeneity, rugosity, etc.)
- Cannot create extremely thin films.

## 3.13 Spray Pyrolysis Technique

Spray pyrolysis method is based on forming an *aerosol* from various precursor solutions, which could be a solution of metallic salts or a colloidal solution. The generated solution droplets are then very rapidly heated in a furnace at given temperature, thus passing through several stages:

1. Evaporation of the solvent from the surface of the droplets.

- 2. Drying the droplets containing the precipitated solute.
- 3. The annealing of the precipitate at high temperatures (thermolysis).
- 4. Formation of microporous particles of defined phase composition.
- 5. Formation of solid particles.
- 6. Sintering of solid particles.

Spray pyrolysis is a technique that requires a precursor solution, for example, TiCl<sub>3</sub> or Ti<sub>4</sub>, and a heated substrate and atomizer. In this process, the solution is atomized in small drops and these droplets are transferred to the heated substrate due to gas that generates thin films. The atomic cloud aerosol generates larger droplets due to the ultrasonic spraying method that determines the smaller droplets. This influences the surface morphology of the material. Spray pyrolysis is very efficient, cost effective, and utilizes simple equipment. The thin films produced have large surface area of substrate coverage and potential and homogeneity of mass synthesis. However, spray pyrolysis seems not useful due to poor quality of thin film, thermal decomposition, and vapor convection. The vapors are generated due to temperature difference, which restricts the source from binding with the substrate.



Fig.3.14 Spray pyrolysis process

Because the particles obtained after thermolysis are very reactive, inner ("in situ") sintering is needed. In the spray pyrolysis procedure, preparation of uniform and fine droplets of reactants and their controlled thermal decomposition are demanding operations. Compared with other synthetic techniques, a spray pyrolysis approach possesses several distinctive advantages. Primarily, because of its simple equipment and experimental arrangement, spray pyrolysis technique is a cost-effective method, and, likewise, it does not require the use of high-quality reagents and the compositions. Furthermore, the morphology and size of particles can be efficiently controlled by varying the preparative conditions, nature of additives, flow rate, and concentration of reactants in the precursor solution. Also, there are continuous processes by which it is possible to establish control over morphology and get fine powders with spherical particles and the desired diameter dictated by the size of the drops.

#### **Disadvantages:**

- It is not easy to scale-up because the yield is very low.
- Oxidation of sulfides when processed in air atmosphere is possible.
- There are difficulties with determining the growth temperature.

#### **3.14 Polymer Assisted Deposition**

Polymer assisted deposition (PAD) is a chemical solution route to high quality thin films of metal oxides. This technique employs metal ions coordinated to polymers as the film precursor. The use of polymer bound metals has several advantages. The polymer controls the viscosity and binds metal ions, resulting in a homogeneous distribution of metal precursors in the solution and the formation of uniform metal oxide films. The nature of the metal oxide deposition is dominated by bottom-up growth, leading to ready formation of crack-free epitaxial metal oxides and the ability to coat nanofeatured substrates in a conformal fashion. However, problems with surface/interface roughness, control of stoichiometry in multicationic or precisely-doped materials, and a lack of accurate control of the thickness in the thin limit range (<20 nm) has reduced the competitiveness of these processes over high vacuum physical methods. This is particularly true in the case of multicationic oxide thin-films, which have experienced frantic research activity in recent years associated with phenomena of interactions across atomically sharp interfaces; the vast majority of oxide thin films used in these studies were deposited under high vacuum. Here, we review the Polymer Assisted Deposition (PAD) of epitaxial thin-films, with particular emphasis on the case of oxides. As we will show in this review, PAD is very versatile for producing different structural phases (perovskites, spinels, garnets, etc.), demonstrating its competitiveness in producing oxide thin-films with the quality required for fundamental studies and applications, as well as its complementarity to physical methods for stabilizing metastable materials and composite heterostructures. We also provide a detailed step by step description of the most relevant chemical aspects of the method, in order to make it reproducible and attractive to laboratories with little experience in complex chemistry tasks.



Fig. 3.15 Polymer-assisted deposition of metal-oxide films

Metal oxides are emerging as important materials for their versatile properties such as highsuperconductivity, ferroelectricity, ferromagnetism, temperature piezoelectricity and semiconductivity. Metal-oxide films are conventionally grown by physical and chemical vapour deposition1:2. However, the high cost of necessary equipment and restriction of coatings on a relatively small area have limited their potential applications. Chemical-solution depositions such as sol-gel are more cost-effective3, but many metal oxides cannot be deposited and the control of stoichiometry is not always possible owing to differences in chemical reactivity among the metals. Here we report a novel process to grow metal-oxide films in large areas at low cost using polymer-assisted deposition (PAD), where the polymer controls the viscosity and binds metal ions, resulting in a homogeneous distribution of metal precursors in the solution and the formation of uniform metal-organic films. The latter feature makes it possible to grow simple and complex crack-free epitaxial metal-oxides.



# SCHOOL OF MECHANICAL ENGINEERING DEPARTMENT OF MECHATRONICS ENGINEERING

**UNIT – IV - NANOELECTRONICS - SEC1615** 

#### **NANOELECTRONICS - SEC1615**

## **UNIT 4 THIN FILM CHARACTERIZATION TECHNIQUES.**

Cyclic Voltammetry and Linear Sweep Techniques, Thickness measurement Techniques, X-Ray Diffraction Technique, Raman Spectral Study, Scanning Electron Microscopy, Energy Dispersive Analysis by X-rays measurements, Atomic Force Microscopy

## 4. Introduction

In the past years the advancement in science has taken place mainly with the discovery of new materials. Characterization is an important step in the development of exotic materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural and surface characterization, which have strong bearing on the properties of materials. In this section different analytical technique used to characterize our thin films are described with relevant principles of their operation and working.

### 4.1 Cyclic voltammetry (CV) and Linear sweep techniques (LSV)

Cyclic voltammetry is often the first experiment performed in an electro analytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect media upon the redox process. In cyclic voltammetry a reversible dc potential sweep (using a triangular potential waveform) was applied between working electrode (film) and counter electrode and resulting current response versus a reference electrode (SCE) is measured.



Fig. 4.1 Variation of Applied Potential for Cyclic Voltametry

In cyclic voltammetry, on reaching t = t1 the sweep direction is inverted and sweep until Emin, then inverted and sweep to Emax etc. The important parameters involved are

- The initial Potential Ei
- The initial sweep direction
- The sweep rate v
- The maximum potential, Emax
- The minimum potential, Emin
- The final Potential, Ef

The kinetics of electrode reactions does not measure the rate of electron transfer itself, as this is an adiabatic process, following Frank-Condon principle, and occurs in approx. 10-16s. What it measures is the time needed for the species, once they have reached the interfacial region, to arrange themselves and their ionic atmospheres into position for electron transfer to be able to occur. According to kinetics of the reactions there are three types of reactions,

- Reversible
- Irreversible
- Quasi reversible





# • Reversible

The curve can be understood in the following way. On reaching a potential where the electrode reaction begins, the current rises as in a steady state voltammogram. However, the creation of a concentration gradient and consumption of electroactive species means that, continuing to sweep the potential, from a certain value just before the maximum value of the current, peak current,

the supply of electroactive species begins to fall. Owing to depletion, the current then begins to decay, following a profile proportional to t -1/2 which is shown in Fig.2.B.3, similar to application of potential step.



Fig.4.3 Typical cyclic voltammetry (CV) for reversible system

Another practical factor affecting the voltammogram is the solution resistance between working and reference electrode. This resistance leads to a shift in the potential of the working electrode by  $IpR\Omega$  where  $R\Omega$  is the resistance (uncompensated) of the solution.

• Irreversible system

In the case of an irreversible reaction of the type O + ne- R. liner sweep and cyclic voltammetry lead to the same voltammetry profile, since no inverse peak appears on inverting the scan direction.

• Quasi reversible systems

The extent of irreversibility increases with increase in sweep rate, while at the same time there is a decrease in the peak current relative to the reversible case and an increasing separation between anodic and cathodic peaks. On increasing sweep rate, there is less time to reach equilibrium at the electrode surface; reactions which appear as reversible at low sweep rates, can be quasi reversible at high sweep rates



Fig.4.4 Effect of increasing irreversibility on the shape of cyclic voltametery

Cyclic Voltametery (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions taking place at the electrode - electrolyte interface. It offers a rapid location of redox potentials of the electroactive species in agitated or quiescent electrolyte and convenient evaluation of the effect of media upon the redox process[30-34]. In CV the potential is continuously changed as a linear function of time in potential window + volts VS SCE and resulting current response is recorded. The resulting current versus potential plot is termed as a cyclic voltammogram. A smooth curve indicates that no well defined phase change occur during the reaction. It is assumed that only the oxidized ionic species are present initially, the mass transfer under concentration gradient is diffusion controlled and Fick's law of diffusion holds good for both oxidized and reduced ionic species. The redox potentials are predicted by Nernst equation given by,

E = Eo + (0.059 / n) log (Co / Cr) ----- 2.1

Where, n = No. of electrons transferred Co and Cr = concentration of oxidized and reduced ionic species During a negative potential scan (coloration) in the first half cycle, as the applied potential approaches the characteristic reduction potential (Epc) predicted by Nernst equation, the cathodic current attains a peak value (Ipc). At least 90/n mV beyond the peak, the direction of applied potential is reversed. This helps in locating the presence of another reducible species in the bath. During the reverse positive scan (bleaching) the reduced ionic species get oxidized and with similar trend the anodic current a peak value (Ipa) at an oxidation potential (Epa). If the redox reaction is reversible i.e. maintain the surface concentrations of oxidized and reduced species as per the Nernst equation, the voltammogram is symmetrical otherwise it is asymmetrical.

#### Diffusion Coefficient;

It is the measure of ease with which an ionic speices can intercalate /deintercalate in the host. It is given by Randles and Sevick equation  $D \ 1/2 = Ip / 2.69 \times 105 .n \ 2 / 3.C.A.V \ 1/2 ----- 2.2$ Ip = Cathodic or anodic peak currentC = Concentration of ionic speciesn = Ionic charge • Pulse techniques

A step in applied potential or current represents an instantaneous alteration to the electrochemical system. Potential and current step give complimentary information because, where as in first case the potential causes a brief capacitive current peak, in second case a part of the applied current, the value of which probably vary with time, is always used to charge the double layer as the potential changes.

#### • Potential Step: Chronoamperometry (CA)

The study of variation of the current response with time under potentiostatic condition is chronoamperometry. The current resulting from a potential step from a value of the potential where there is no electrode reaction to one corresponding to the mass transport limited current was calculated for simple system O + ne-R, where only O or only R is initially present. This is the faradic current, If since it is due only to faradic electrode process (only electron transfer). In the present study we have used double potential step chronoamperometry to measure the speed of electrochromic response and to apprehend intercalation and de-intercalation. An overview of CA experiment is shown in figure. The potential is altered between two values. We consider an initial step from a potential where there is no electrode reaction to a value to the limiting reduction current (only O initially present in solution); at  $t = \tau$  the potential reverts to its initial value and there is oxidation of R that was produced. As mass transport under these conditions is solely by diffusion, the i-t curve reflects the change in the concentration gradient in the vicinity of the surface. This involves a gradual expansion of the diffusion layer associated with the depletion of the reactant and hence decreased slope of the concentration profile as time progresses. Accordingly, the current decays with the time (Fig.2.B.6) as given by Cottrell equation

$$I_f(t) = \frac{nFAD^{1/2}c_{\infty}}{(\pi)^{1/2}}$$
 (2.3)

It indicates the decrease of the current with t  $\frac{1}{2}$ 

Such a  $i(t\frac{1}{2})$  constancy is often termed a "Cottrell behavior". The time required for the transition from colored to bleached state or vice-versa under the application of voltage pulse is termed as response or switching time. Though the magnitude of response time depends upon end use demand, a minimum switching time is necessary in advanced opto-Electronic EC devices.

### 4.2 Thickness measurement Techniques

### • Auger Electron Spectroscopy (AES)

This destructive technique is widely used in material science to evaluate the composition of a surface. It's also handy for assessing the precise depth of a coating. The example below shows the composition and depth of a Dursan coating sample. Note how the silicon/steel diffusion zone is clearly delineated. The AES technique measures the material that comes off the surface as an electron beam is focused onto the surface. The electron beam bores into the surface and material characteristics are measured by a detector as the sputtered material is emitted.



Fig.4.5 Auger Electron Spectroscopy

AES equipment can be expensive and require specialized knowledge to operate. It also can be time consuming and is destructive to the surface so AES is not a realistic quick measurement tool for field or production surface evaluation.

## • Sectioning and optical techniques

A tried and true method for evaluating a thickness. Cutting a part in half and optically measuring the coating thickness can be an effective tool for micron level coating thickness measurement. It can however be difficult to measure the exact coating to base surface transition and is of course a destructive test. Again not a realistic quick measurement tool for the field. Accuracy is limited, especially when measuring sub-micron thick coatings.

#### • F20 Thin-film Analyzer

SilcoTek's F20 thin-film analyzer is a bench top tool that can be configured to measure thin film thicknesses (30Å to 350 mm), optical constants such as refractive index, extinction coefficient and transmittance. It is primarily used by SilcoTek as a quick, accurate and non-destructive way to measure surface thicknesses and to assure consistent coating quality. The analyzer relies on the refraction of light as it passes through a thin surface, reflects off the base surface, and then passes through the coating again. The instrument measures the change due to refraction and correlates that change to thickness standards. The base material, the surface roughness, and coating refractive index can play a big part in the effectiveness and reliability of this measurement technique.

#### • X-ray Fluorescence Analyzers (XRF and ED-XRFA) and X-Ray Spectrometry

Used primarily by plating shop for measuring the thickness of metallic plating, <u>XRF</u> can be a relatively low cost method to measure coating thickness. The surface is bombarded with x-ray, the coating and base material result in x-ray fluorescence radiation. The coating surface will attenuate the base material radiation, allowing the instrument to correlate thickness between the coating emission and base material emission. The method is non destructive and can be effective for sub micron measurement. XRF is effective in measuring most elements and alloy materials but not organic materials. The technique is commonly used in metal finishing operations.

## • Magnetic Induction and Pull-off Style Gauges

Magnetic based pull-off or electromagnetic induction measurement tools rely on the differential of a magnetic base metal and a non conductive coating (like paint). The thicker the paint the less force needed to pull away the gauge. These can be an effective field test for rough evaluation of a coating thickness but not effective for extremely thin coatings or conductive coatings. Electromagnetic measurement tools can have an accuracy of +1%.

#### • Ultrasonic measurement

These hand held tools measure coating thickness on metallic base materials, ie. paint on a wood surface for example. There a quick non destructive way of measuring coating thickness, but not for a coating on a metal surface.

# • Gravimetric comparison

Basically measuring the weight of a coated and uncoated part. This method is a good way to measure bulk coatings but not effective for precision thin film measurement or for evaluating exact thickness at a particular location.

# • ASTM Methods Highlighting Coating Measurement

Table 5.1 ASTM Coating Measurement Methods
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ASTM Method	Description
ASTM E376-17	Standard Practice for Measuring Coating Thickness by Magnetic-Field or Eddy Current (Electromagnetic Testing Methods)
ASTM D4138-07a(2017)	Standard Practices for Measurement of Dry Film Thickness of Protective Coating Systems by Destructive, Cross-Sectioning Means
ASTM D7091-13	Standard Practice for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to Ferrous Metals and Nonmagnetic, Nonconductive Coatings Applied to Non-Ferrous Metals
ASTM D6132-13(2017)	Standard Test Method for Nondestructive Measurement of Dry Film Thickness of Applied Organic Coatings Using an Ultrasonic Coating Thickness Gage
ASTM B748-90(2016)	Standard Test Method for Measurement of Thickness of Metallic Coatings by Measurement of Cross Section with a Scanning Electron Microscope
	Standard Test Method for Determining Plastic Film Thickness

<u>ASTM D8136-17</u>	and Thickness Variability Using a Non-Contact Capacitance Thickness Gauge
<u>ASTM D7378-16</u>	Standard Practice for Measurement of Thickness of Applied Coating Powders to Predict Cured Thickness
ASTM B568-98(2014)	StandardTestMethodfor Measurement ofCoating Thickness by X-Ray Spectrometry
ASTM B567-98(2014)	StandardTestMethodfor Measurement ofCoating Thickness by the Beta Backscatter Method
ASTM E252-06(2013)	Standard Test Method for Thickness of Foil, Thin Sheet, and Film by Mass Measurement
ASTM D5235-18	Standard Test Method for Microscopic Measurement of Dry Film Thickness of Coatings on Wood Products
ASTM D1212-91(2013)	Standard Test Methods for Measurement of Wet Film Thickness of Organic Coatings
ASTM D5796-10(2015)	Standard Test Method for Measurement of Dry Film Thickness of Thin-Film Coil-Coated Systems by Destructive Means Using a Boring Device
ASTM D1005-95(2013)	Standard Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers
ASTM B487-85(2013)	Standard Test Method for Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of Cross Section

#### 4.3 X-ray diffraction (XRD) Technique

X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material A primary use of XRD analysis is the identification of materials based on their diffraction pattern. As well as phase identification, XRD also yields information on how the actual structure deviates from the ideal one, owing to internal stresses and defects. Crystals are regular arrays of atoms, whilst X-rays can be considered as waves of electromagnetic radiation. Crystal atoms scatter incident X-rays, primarily through interaction with the atoms' electrons. This phenomenon is known as elastic scattering; the electron is known as the scatterer. A regular array of scatterers produces a regular array of spherical waves. In the majority of directions, these waves cancel each other out through destructive interference, however, they add constructively in a few specific directions, as determined by Bragg's law:

# $2dsin\theta = n\lambda$

Where *d* is the spacing between diffracting planes,  $\theta$ {\displaystyle \theta } is the incident angle, *n* is an integer, and  $\lambda$  is the beam wavelength. The specific directions appear as spots on the diffraction pattern called reflections. Consequently, X-ray diffraction patterns result from electromagnetic waves impinging on a regular array of scatterers.

X-rays are used to produce the diffraction pattern because their wavelength,  $\lambda$ , is often the same order of magnitude as the spacing, *d*, between the crystal planes (1-100 angstroms).

#### • Measurement of Thickness of Thin Films by the X-Ray Diffraction Method

X-ray diffraction method can be used to measure the thickness of thin films (coatings). The principle and the experimental details of the x-ray diffraction methods are described. The intensities of the diffracted beams are derived assuming a random orientation of the crystallites in the diffracting medium. Consequently, the expressions are not valid when the sample has preferred orientation. To check the performance of the method, thicknesses of nickel deposits on mild steel plates were .determined by the x-ray diffraction method and the results compared with those obtained by the weighing method and metallographic examination. The weighing method

which gives an accuracy of  $\pm 0.1$  micron is taken as the standard. The x-ray diffraction methods and the metallographic examinations give values within  $\pm 1$  micron of the value obtained by the weighing method.

# • XRD Benefits and Applications

XRD is a non-destructive technique used to:

- Identify crystalline phases and orientation
- Determine structural properties:
  - Lattice parameters
  - Strain
  - Grain size
  - Epitaxy
  - Phase composition
  - Preferred orientation
- Measure thickness of thin films and multi-layers
- Determine atomic arrangement

# 4.4 Raman Spectral Study

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase and polymorphy, crystallinity and molecular interactions. It is based upon the interaction of light with the chemical bonds within a material. Raman is a light scattering technique, whereby a molecule scatters incident light from a high intensity laser light source. Most of the scattered light is at the same wavelength (or color) as the laser source and does not provide useful information – this is called Rayleigh Scatter. However a small amount of light (typically 0.0000001%) is scattered at different wavelengths (or colors), which depend on the chemical structure of the analyte – this is called Raman Scatter. A Raman spectrum features a number of peaks, showing the intensity and wavelength position of the Raman scattered light. Each peak corresponds to a specific molecular bond vibration, including individual bonds such as C-C, C=C, N-O, C-H etc., and groups of bonds such as benzene ring breathing mode, polymer chain vibrations, lattice modes, etc.



Fig.4.6 Raman principle

Raman spectroscopy probes the chemical structure of a material and provides information about:

- Chemical structure and identity
- Phase and polymorphism
- Intrinsic stress/strain
- Contamination and impurity

Typically a Raman spectrum is a distinct chemical fingerprint for a particular molecule or material, and can be used to very quickly identify the material, or distinguish it from others. Raman spectral libraries are often used for identification of a material based on its Raman spectrum – libraries containing thousands of spectra are rapidly searched to find a match with the spectrum of the analyte. In combination with mapping (or imaging) Raman systems, it is possible to generate images based on the sample's Raman spectrum. These images show distribution of individual chemical components, polymorphs and phases, and variation in crystallinity. Raman spectroscopy is both qualitative and quantitative. The general spectrum profile (peak position and relative peak intensity) provides a unique chemical fingerprint which can be used to identify a material, and distinguish it from others. Often the actual spectrum is quite complex, so comprehensive Raman spectral libraries can be searched to find a match, and thus provide a chemical identification. The intensity of a spectrum is directly proportional to concentration. Typically, a calibration procedure will be used to determine the relationship between peak intensity and concentration, and then routine measurements can be made to analyze for concentration. With mixtures, relative peak intensities provide information about the relative concentration of the components, while absolute peak intensities can be used for absolute concentration information. Raman is used for microscopic analysis



Fig.4.7 Raman microscope system

Raman spectroscopy can be used for microscopic analysis, with a spatial resolution in the order of 0.5-1  $\mu$ m. Such analysis is possible using a Raman microscope.

A Raman microscope couples a Raman spectrometer to a standard optical microscope, allowing high magnification visualization of a sample and Raman analysis with a microscopic laser spot. Raman micro-analysis is easy: simply place the sample under the microscope, focus, and make a measurement. A true confocal Raman microscope can be used for the analysis of micron size particles or volumes. It can even be used for the analysis of different layers in a multilayered sample (e.g., polymer coatings), and of contaminants and features beneath the surface of a transparent sample (e.g., impurities within glass, and fluid/gas inclusions in minerals).

Motorized mapping stages allow Raman spectral images to be generated, which contain many thousands of Raman spectra acquired from different positions on the sample. False color images can be created based on the Raman spectrum – these show the distribution of individual chemical components, and variation in other effects such as phase, polymorphism, stress/strain, and crystallinity.

# • History of Raman microscopy

HORIBA Scientific now incorporates the major innovators of Raman instrumentation from the 1960s to the 1990s - Spex Industries, Coderg/Lirinord/Dilor, and Jobin Yvon. From these beginnings through to the present day, HORIBA Scientific and its associated companies have been at the forefront of the development of Raman spectroscopy. The Raman microscope was developed in Lille, France under the direction of Professor Michel Delhaye and Edouard DaSilva, and was commercially produced as the MOLE<sup>TM</sup> (Molecular Optics Laser Examiner) by Lirinord (now HORIBA Scientific). It developed as the molecular analog of Castaing's electron microscope. As such it provides bonding information on condensed phase materials; in

addition to detection of molecular bonding, identification of the crystalline phase and other more subtle effects also proved of significant interest. The microscope was initially integrated with the scanning double grating monochromator (c. 1972). When high sensitivity, low noise multichannel detectors became available (mid 1980s), triple stage spectrographs were introduced with the microscope as an integrated component. In 1990 the holographic notch filters were demonstrated to provide superior laser rejection so that a Raman microscope could be built on a single stage spectrograph and provide enhanced sensitivity. Compared with the original scanning double monochromators, collection times for comparable spectra (resolution and signal to noise for a given laser power) is now at least two to three orders of magnitude higher than what it was 35 years ago. These core innovations have been pioneered in the HORIBA Scientific labs in northern France by the scientists and engineers who were trained in Professor Delhaye's laboratory, taking advantage of hardware as it came available. This included holographic gratings, notch filters, air-cooled lasers, multichannel detectors (first intensified diode arrays and then CCDs), high power computers, and associated developments in electronics and software.

More recent developments in the Raman technique include SRS (Stimulated Raman Scattering), SERS (surface enhanced Raman scattering), TERS (tip enhanced Raman scattering), integration with electron microscopes and atomic force microscopes, hybrid single bench systems (e.g., Raman-PL, Epifluorescence, Photocurrent), Transmission Raman (for true bulk material analysis). Because of the leadership that HORIBA Scientific and its associated companies have played in the industry, well- equipped applications laboratories with highly qualified scientists have been employed continuously for more than 30 years in developing the applications of these innovative instruments.

## • Type of samples analyzed with Raman

Raman can be used to analyze many different samples. In general it is suitable for analysis of:

- Solids, powders, liquids, gels, slurries and gases
- Inorganic, organic and biological materials
- Pure chemicals, mixtures and solutions
- Metallic oxides and corrosion

In general it is not suitable for analysis of:

• Metals and their alloys

Typical examples of where Raman is used today include:

- Art and archaeology characterization of pigments, ceramics and gemstones
- Carbon materials structure and purity of nano-tubes, defect/disorder characterization
- Chemistry structure, purity, and reaction monitoring
- Geology mineral identification and distribution, fluid inclusions and phase transitions
- Life sciences single cells and tissue, drug interactions, disease diagnosis
- Pharmaceutics content uniformity and component distribution
- Semiconductors purity, alloy composition, intrinsic stress/strain microscope.

# • Analysis of solids, liquids and gases

Raman spectra can be acquired from nearly all samples which contain true molecular bonding. This means that solids, powders, slurries, liquids, gels and gases can be analyzed using Raman spectroscopy. Although gases can be analyzed using Raman spectroscopy, the concentration of molecules in a gas is typically very low, so the measurement is often more challenging. Usually specialized equipment such as higher powered lasers and long path length sample cells are necessary. In some cases where gas pressures are high (such as gas inclusions in minerals) standard Raman instrumentation can easily be used.

# • Analysis from a mixture of materials

The Raman spectrum from a material will contain Raman information about all of the molecules which are within the analysis volume of the system. Thus, if there is a mixture of molecules, the Raman spectrum will contain peaks representing all of the different molecules. If the components are known, the relative peak intensities can be used to generate quantitative information about the mixture's composition. In case of complex matrixes, chemometrics methods might also be employed to build quantitative methods.

# 4.5. Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of microscope which uses a focused beam of electrons to scan a surface of a sample to create a high resolution image. SEM produces images

that can show information on a material's surface composition and topography. SEM produces magnified detailed images of an object by scanning a focused beam of electrons. This works differently to transmission electron microscopes (TEMs) as the electron beam goes straight through the object. Electrons are created and fired using an electron gun which accelerates down the microscope passing through a series of lenses and apertures creating a focused beam which then interacts with the surface of a sample. The sample is positioned on a stage in the chamber of the microscope before a vacuum is created in the chamber via a series of pumps. The level of the vacuum depends on the microscope's design, while some microscopes are designed to operate in low vacuum environments, meaning that the chamber does not need to be evacuated. Scan coils control the position of the electron beam above the objective lens. These coils allow for the beam to scan across the surface of the sample, enabling information about a defined area to be collated. The interaction between the sample and the electron create a number of signals in the form of secondary electrons, backscattered electrons, and characteristic X-rays that are then detected by detectors. The detector creates images which are displayed on a computer screen.



Fig.4.8 Example of a Scanning Electron Microscope Image

The distance that the human eye can distinguish two parts in visible light is 0.2mm apart, however this can be increased through the use of a lens. This distance is called the resolving power of the lens, which can magnify the distance many times over. However, a light microscope has a resolving power of about 1000x, as it is limited by the wavelength of the light as well as the quality and number of lenses used. However, electron microscopes provide a shorter wavelength, which creates a better resolution. The spatial resolution is dependent on the size of the electron spot. Unlike conventional image forming cameras (film or CCD array), SEM uses an electron beam to rapidly scan over a specimen sample to yield an image. The resolution of SEM is normally around 10 nanometres (nm). The maximum resolution for a scanning electron microscope image depends on factors such as the interaction volume of the beam and the electron spot size. SEMs can achieve a high resolution of below 1 nanometre (nm), although

they cannot provide atomic resolutions. Most modern SEMS provide a resolution of 1-20 nm, while smaller desktop versions offer a resolution of 20 nm or more.

# Advantages of a Scanning Electron Microscope:

- Produces detailed three-dimensional and topographical images
- Easy to operate with training
- User-friendly software
- Can perform quick scans (BSE, EDS and SEI analyses can be performed within a few minutes)
- Samples require a small amount of preparation

# **Disadvantages of SEM:**

- Expensive to buy and run
- Large (takes up lots of space)
- Needs to be in an environment where there is no electric, magnetic or vibration interference
- Needs a trained operative to prepare the samples and operate the microscope
- Small risk of radiation exposure
- Restricted to samples small enough to fit into the vacuum chamber
- Requires cool water and a steady voltage

# 4.6 Energy Dispersive Analysis by X-rays measurements

Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an x-ray technique used to identify the elemental composition of materials. Applications include materials and product research, troubleshooting, deformulation, and more. EDX systems are attachments to Electron Microscopy instruments (Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM)) instruments where the imaging capability of the microscope identifies the specimen of interest. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analysed. Elemental mapping of a sample and image analysis are also possible.

In a multi-technique approach EDX becomes very powerful, particularly in contamination analysis and industrial forensic science investigations. The technique can be qualitative, semiquantitative, quantitative and also provide spatial distribution of elements through mapping. The EDX technique is non-destructive and specimens of interest can be examined in situ with little or no sample preparation. In situations where combined Microscopy and EDX data acquired are insufficient to identify a specimen, complementary techniques are available, typically Infra-red (FTIR) Microscopy, RAMAN Microscopy, Nuclear Magnetic Resonance Spectroscopy (NMR) and Surface Analysis (X-ray photoelectron spectroscopy (XPS) or Time-of-Flight Secondary Ion Mass Spectrometry (SIMS)).

# **EDX analysis applications:**

- Product deformulation and competitor analysis
- Adhesion, bonding, delamination investigations
- Optical appearance, haze and colour problems
- Disputed claim investigations and expert witness
- Failure investigations, identification of cause
- Catalyst quality, poisoning and elemental distribution
- Product imperfections and defect analysis
- Contamination detection, isolations and identification
- Quality control, raw material and end product
- Filler, pigment, fibre, additive distribution, orientation
- Assessment of plant particulate emissions
- Construction and maintenance monitoring (asbestos)

# **Benefits from EDX analysis:**

- Improved quality control and process optimisation
- Rapid identification of contaminant and source
- Full control of environmental factors, emissions etc
- Greater on-site confidence, higher production yield
- Identifying the source of the problem in process chain

#### **Atomic Force Microscopy (AFM)**

Atomic Force Microscopy (AFM) **is a** high-resolution non-optical imaging technique first demonstrated by Binnig, Quate and Gerber in 1985. Since then it has developed into a powerful measurement tool for surface analysis. AFM allows accurate and non-destructive measurements of the topographical, electrical, magnetic, chemical, optical, mechanical, etc. properties of a sample surface with very high resolution in air, liquids or ultrahigh vacuum. This unique combination of capabilities makes AFM indispensable in most advanced science and technology labs around the world.

# • AFM Operation Principle

The basic operation principle of a standard AFM system with optical feedback involves scanning an AFM probe with a sharp AFM tip over a sample surface in a raster pattern. The AFM tip is usually made of silicon or silicon nitride and is integrated near the free end of a flexible AFM cantilever. A piezoelectric ceramic scanner controls the lateral and the vertical position of the AFM probe relative to the surface. As the AFM tip moves over features of different height the deflection of the AFM cantilever changes. This deflection is tracked by a **laser beam** reflected from the back side of the AFM cantilever and directed into a **position sensitive photodetector**. A **feedback loop** controls the vertical extension of the scanner in order to maintain near-constant AFM cantilever deflection and hence a constant interaction force. The coordinates that the AFM tip tracks during the scan are combined to generate a **threedimensional topographic image** of the surface.



Fig.4.9 AFM schematic.

## • Modes of AFM Operation

There are two basic modes of imaging surface topography with an Atomic Force Microscope: Static or Contact Mode and Dynamic Mode. Dynamic Mode is further sub-divided into Tapping or Intermittent Contact and Non-Contact Mode depending on the interaction forces between the AFM tip and the surface.

1. In **Contact Mode**, the AFM probe tip is scanned across the sample surface while maintaining constant contact with it. The feedback system aims to maintain constant AFM cantilever deflection and consequently a constant interaction force. The forces between the AFM tip and the surface are repulsive (Fig. 3). Soft AFM cantilevers with force constants  $\leq 1$ N/m are usually used in order to minimize AFM tip wear and surface damage and in order to increase sensitivity.



Fig.4.10 Contact Mode AFM operation schematic and Operation regions for Contact, Tapping and Non-Contact Mode.

Among the main drawbacks of Contact Mode operation are the susceptibility of AFM tips on soft AFM cantilevers to both lateral forces and sticking to the surface contamination layer that is present on most surfaces in ambient air. These result in image distortions. In addition, lateral forces can be damaging to the AFM probe tip and to soft samples.

2. In **Tapping Mode**, the AFM probe cantilever is oscillated by a piezoelectric actuator at or near its fundamental resonance frequency, usually several tens to several hundred kilohertz. The AFM probe is lowered towards the sample surface so that the AFM probe tip slightly touches the surface at the lower end of the AFM cantilever oscillation (Fig. 4) and its oscillation amplitude is damped. The feedback loop maintains a constant AFM cantilever oscillation amplitude and hence a constant interaction force. The forces that dominate the interaction between the AFM tip and the surface are repulsive.



Fig.4.11 Tapping Mode operation schematic.

Stiff AFM cantilevers with force constants in the range of 10-100N/m and high resonance frequencies >190kHz are used for standard Tapping Mode operation. These AFM cantilevers do not suffer from sticking to the surface when measuring in ambient air. For measuring soft samples, e.g. living cells, softer AFM cantilevers with force constants <10N/m and sometimes as low as sub-0.1N/m are used.

3. In **Non-Contact Mode** the AFM cantilever is oscillated at or near its resonance frequency with a smaller amplitude (1nm or less) than in Tapping Mode and the AFM probe tip is kept at a distance of several nanometers to several tens of nanometers away from the surface in the region of attractive interaction forces. In some cases, the feedback loop maintains a constant AFM cantilever oscillation frequency and hence a constant interaction force (FM-AFM). This method gives more precise force control and super high-resolution images in liquid.



Fig.4.12 Non-Contact Mode operation schematic.

The advantage of Non-Contact Mode is that it offers the lowest possible interaction between the tip and the sample surface. Small interaction forces help preserve AFM tip sharpness and achieve high resolution. The disadvantage is that it is challenging to keep at the AFM tip in the attractive regime. For small tip-surface distances, high performance feedback controls are needed. AFM cantilevers with high force constants and high resonance frequencies are most suitable for Non-Contact Mode.

## • Additional AFM Imaging Techniques

Beside topography, Atomic Force Microscopy allows investigating a variety of other surface properties. These additional imaging techniques are based on one of the three basic modes of operation. They help extract additional information about the sample surface simultaneously with its topography. Some of these modes such as e.g. EFM and MFM often use the secondary technique Two-Pass Mode, Lift Mode or Hover Mode. In Lift Mode the AFM acquires topography data and electric or magnetic data on the same scan line independently. The first pass is a regular topographic scan. During the second pass, second line scan or retrace scan, the AFM tip traces the surface topography at a preset vertical distance, usually 5-50nm, gathering information about the long-range electrostatic, magnetic, etc. forces via changes in the resonance frequency or phase of the AFM cantilever oscillation.

More recently developed **Single-Pass Methods** allow gathering topographic and other data simultaneously in a single pass with the help of lock-in amplifiers with improved sensitivity and higher resolution.

Below is a list of some commonly used additional imaging techniques.

**1. Phase Imaging:** Recording the phase difference between the drive signal and the AFM cantilever oscillation in dynamic mode gives additional information about material properties such as elasticity, adhesion, etc.

**2. AFM in Liquids:** Measurements of biological and other samples in aqueous solutions are possible in both Contact and Tapping Mode. For applications in liquids, silicon nitride probes are commonly used. Measuring with soft AFM cantilevers in liquids helps avoid sample surface damage by the AFM tip.



# SCHOOL OF MECHANICAL ENGINEERING DEPARTMENT OF MECHATRONICS ENGINEERING

**UNIT – V - NANOELECTRONICS - SEC1615** 

#### **NANOELECTRONICS - SEC1615**

#### **UNIT 5 - NANOELECTRONIC DEVICES**

Digital and Switching abstraction, Quantum Cellular Automata (QCA), Realization of logic gates using QCA, Types and synthesis of molecular bundles, principle and types of spin wave devices, Array minimum/ maximum computation with spin wave devices

#### 5. Introduction

Current high-technology production processes are based on traditional top down strategies, where nanotechnology has already been introduced silently. The critical length scale of integrated circuits is already at the nanoscale (50 nm and below) regarding the gate length of transistors in CPUs or DRAM devices. Nano electronic devices consists of nano sized transistors, capacitors, circuit lines etched on a Silicon chip. Carbon Nanotube, Optoelectronic devices and Micro mechanical systems use Nano electronics techniques.

#### **5.1 Digital and Switching abstraction:**

In terms of digital circuit design, we design them using Boolean logic which considers only two states for an Input/output – 1s and 0s. However in the underlying circuit there are no discrete values such as 1 or 0. Rather, there is continuous current in the circuit that transitions between two preset voltage levels. The transition is continuous and not immediate either. Generally, 5V (or 3.5V) is considered as digital 1 and 0V is considered as digtal 0. Deviation from these values is expected in the transient state, so anything that is above 2.5V is considered as digital 1 and below that is considered as digital 0. By abstracting all the continous and transient state effects from the end results (1 and 0), we are able to freely work with a more broader view for circuit design. This process is known as **Digital Switching**. The voltage levels in the circuit are being switched between these values by using digital devices such as transistors or MOSFETs or SCRs. We abstract ourselves from the internal workings of switching too, for easier design process. This is **switching abstraction**.

#### 5.2 Quantum-dot Cellular Automata (QCA)

Quantum-dot Cellular Automata (QCA) is an emerging which has been technologically advanced to support simulation of multidimensional quantum circuits and devices. Compared to classical computer, in QCA the digital information are represented as configurations of pair of electrons coupled together to form quantum dot arrays. Boolean logic functions are implemented using these quantum dot arrays in QCA designer. With the advancements in QCA and due to the enhancements in the field of the quantum mechanical effects, digital circuits designed using QCA have significant size reduction and hence the area, and achieves high speed of operation at very low power levels. Hence the neighboring cells interacts with each other the state changes happened in QCA due to electrostatic or magnetic fields. Consequently, in QCA, electron localization are used to represent the binary values in quantum dots, instead of using ranges of voltages and currents to indicate binary values as used in traditional computers. Large number of QCA integrated circuits are designed and implemented in densities up 1014 cells/cm<sup>2</sup> and there is a rapid increase in circuit switching frequency which is almost close to a terahertz. In spite of having some prominent features such as stability, high speed, reduced area and less energy consumption, QCA circuits lack design automation tools and modular architecture which facilitates the design and simulation of large electronic circuits and circuit fabrication as hindered the full development of Nano electronic technology.

An Automaton (or automata in plural) is an automatic machine, that decides the state of it's internal components based on time and states of other internal components with some predefined rules/functions. Combinatory circuits, Turing machine are all a form of automaton. A Cellular Automaton is an automatic machine that follows a set of rules to assign one of the finite number of states to the cells on a 2D grid of finite dimensions. The rules are mostly mathematical functions. The state of a cell at time t depends upon the state of it's neighbouring cellsat time t - I. This can be used to model natural phenomenons in Biology, Physics, Chemistry, etc., since it is quite intuitive that each state in a natural phenomenon is time and environment reliant. A Quantum cellular automation is a type of cellular automation that combines the quantum effects in its rules of automation.

#### 5.3 Realisation of Logic gates using QCA:

Any QCA circuitry is built with two basic gates – The invertor and the Majority Gate (gives AND and OR functionalities). Combining both these gates one can make the Universal Gates – **NAND** and **NOR**, from which we can realise any kind of logic/combinational/sequential circuit we want.

## • QCA Cell:

A QCA circuitry doesn't consist of transistor, but it has QCA cells, that hold or propagate one of the binary values. It is a 2x2 grid of 4 Quantum wells in which 2 electrons are present. Due to the repulsion between the two electrons they tend to stay as seperated as possible from each other, which is obviously along the diagonal cells. Therefore for a given QCA cell we have two separate states for the electrons to exist along the diagonals. These two states are abstracted as digital 1 and 0. But more formally the polarity (value representing which diagonal they are in) is given as -1 and +1.



## • QCA Invertor:

An Invertor Inverts the input polarity. It is equivalent to digital NOT Gate. In the below diagram the left most cell is input and right most is the output. The cell just before output is critical for the realisation of NOT operation. The polarity of this cell is adjusted according to repulsion coming from the cells that are diagonally connected to it. The diagonal cells are given to ensure that for any input polarity, atleast on of the cell is aligning its polarity near the corner of the output cell, forcing the output cell to shift it's polarity to a less repelled one.



Fig.5.2 QCA Invertor

# • QCA Majority Gate:

A QCA Majority Gate Contains 5 Quantum Cells arranged in a '*PLUS SHAPE*'. It works as the name suggests – the output polarity is the polarity of the majority cells in the gate. It has 2 Inputs, 1 output, 1 Permanent polarity cell (this decides whether the gate will act as AND or OR gate) and a Central Cell, which is free to switch to any polarity based on whichever is the least repelled polarity. The working is that, the permanent polarity is fixed and doesn't change in operation. If it is -1 AND operation is carried out. If is 1 OR operation is carried out. The inputs are set to respective polarities. The central cell, fixes its polarity in the least repelled direction. There will always be a comparitively less repelling diagonal on the central cell, because for each set of input, the electrons near one diagonal corner is always 1 higher than the other (excluding the output cell). The output cell on the right side adjusts itself in the same polarity as the central cell (only this cell is set to have an effect on the output cell).



Fig.5.3 QCA Majority Gate

# • QCA Logic Gates:

It is generally known from classic digital logic that using *Universal Gates – NAND*, *NOR* one can build any other logic gates. We get *NAND* (*AND* + *NOT*) and *NOR* (*OR* + *NOT*) by combining a *Majority Gate with an Invertor at the output*. From here we can construct any logic required.

# 5.4 Types and synthesis of molecular bundles:

- The vascular bundles are arranged in three layers, developing unequally at different levels. Main vascular bundles form a single conspicuous abaxial arc, alternating with air canals, and embedded in chlorenchyma.
- The abaxial conducting systems consist of an arc of vascular bundles of different sizes that are circular in outline.

- The adaxial conducting system consists of vascular bundles that are similar in appearance to the main vascular bundles, but are sclerenchymatous sheath above the xylem and below the phloem, extruded protoxylem, small
- mass of metaxylems and phloem tissue. Vascular bundles of accessory arcs have
- reduced vascular tissues and contracted protoxylem. Abaxial bundles are enveloped within
- almost a complete fibrous sheath.
- The epidermal and stomatal structures of turmeric. They have reported that the upper epidermis
- consists of polygonal cells which are predominantly elongated at right angles to the long axis of
- leaf. Irregular polygonal cells are present on the lower epidermis, except at the vein region,
- where they are vertically elongated and thick-walled. The epidermal cells in the scale and sheath
- leaves (the first 2–5 leaves above ground without the leaf blade) are elongated parallel to the axis of the leaf.
- They observed that the leaves are amphistomatic, with a distinct substomatal cavity and stomata may be diperigenous, tetraperigenous, or anisocytic.

# 5.5 Spin Wave

A **spin wave** is a propagating disturbance in the ordering of a magnetic material. These lowlying collective excitations occur in magnetic lattices with continuous symmetry. From the equivalent quasiparticle point of view, spin waves are known as magnons, which are bosonic modes of the spin lattice that correspond roughly to the phonon excitations of the nuclear lattice. As temperature is increased, the thermal excitation of spin waves reduces a ferromagnet's spontaneous magnetization. The energies of spin waves are typically only µeV in keeping with typical Curie points at room temperature and below.

- Spin Wave:
- A spin wave is a propagating disturbance in the ordering of a magnetic material.

- These low-lying collective excitations occur in magnetic lattices with continuous symmetry.
- As temperature is increased, the thermal excitation of spin waves reduces a ferromagnet's spontaneous magnetization.

# • Principle of spin wave devices:

- Spin-wave devices use wave amplitude, phase, and frequency as the carrier of information transmission and processing.
- The process of spin-wave propagation is only based on electron spin interactions; thus, no physical particle transportation is involved.

# • Spin wave causes:

- If we now deflect one or a few of these magnetic moments from their equilibrium position the surrounding moments will "feel" this, as every magnetic moment produces a small magnetic field,
- so, they will also be deflected a bit, then the next surrounding moments feels this and gets also deflected

# • <u>Types of spin wave</u>:

Spin waves are observed through four experimental methods:

- Inelastic neutron scattering,
- inelastic light scattering,
- inelastic electron scattering,
- spin-wave resonance.

# 5.6 Array minimum/maximum computation with spin wave devices

- The fundamental circuit element in this framework is the transistor, which can serve both as a switch and an amplifier.
- Today's large-scale integrated circuits are based on complementary metal–oxide– semiconductor (CMOS) field-effect transistors because of their high density, low power consumption, and low fabrication cost.

- Using CMOS transistors, logic gates can be built that represent a full set of Boolean algebraic operations.
- Such basic Boolean operations are fundamental for the design of mainstream logic circuits and, together with charge-based memory devices, of computing systems.
- A group of disruptive spintronic logic device concepts have been based on spin waves as information carriers.
- Spin waves are oscillatory collective excitations of the magnetic moments in ferromagnetic or antiferromagnetic media and are introduced in more detail in Sec.
- As their quanta are termed *magnons*, the field is also often referred to as *magnonics*. The frequency of spin waves in ferromagnets is typically in the GHz range, their intrinsic energy is low, and their propagation velocity can reach values up to several km/s (□µm/ns).
- At low amplitude, spin waves are noninteracting, enabling multiplexing and parallelism in logic devices and interconnections.
- By contrast, spin waves can exhibit nonlinear behavior at high amplitudes (Sec., which can be exploited in spintronic devices and circuits. As shown in Sec.,
- spin waves are especially suitable for the implementation of compact majority gates due to their wave-like nature.
- Their short wavelengths down to the nm range at microwave (GHz) frequencies allow for the miniaturization of the devices while keeping operating frequencies accessible.
- The state of the art of benchmarking such hybrid spin-wave–CMOS systems is reviewed, and the current challenges to realize such systems are discussed.
- The benchmark indicates that hybrid spin-wave–CMOS systems promise ultralow-power operation and may ultimately outperform conventional CMOS circuits in terms of the power-delay-area product.
- Current challenges to achieve this goal include low-power signal restoration in spin-wave circuits as well as efficient spin-wave transducers.
- It is clear that the step from individual basic spintronic device concepts to operational circuits and systems is large and an additional complementary effort is still required to successfully compete with CMOS in practice.
- Such an effort is inherently multidisciplinary and needs to involve both spin-wave and device physics as well as circuit and systems engineering.
- This paper provides a tutorial introduction to spin-wave computing technology and its potentials from a circuit and computation viewpoint.
- The focus is on the achievements but also on the gaps in the current understanding that still inhibit the realization of practical competitive spin-wave circuits.