

UNIT-5

INTRODUCTION TO NANOSCIENCE AND NANOTECHNOLOGY

NANO-METER AND NANOSCALE:

A **nanometer** (nm) is a unit of measure just like inches, feet and miles. By definition a nanometer is one-billionth , or 10^{-9} of a meter. A nanometer is used to measure things that are very small. Atoms and molecules, the smallest pieces of everything around us, are measured in nanometers.

Dimension which is of the order of 1nm to 100 nm is called nanoscale. Any material whose dimension is less than 100nm can be considered as a **nanomaterial**.

Scientists and engineers are now a days interested in the nanoscale, which may be taken as 100 nm to 0.2 nm approximately. Below this lies the atomic scale 0.1nm. therefore, the nano- world is a borderland between the quantum world and the macro world.

SIGNIFICANCE OF THE NANO-SCALE:

The bulk properties of materials often change dramatically with nano ingredients. Composites made from particles of nano-size ceramics or metals smaller than 100 nm can suddenly become much stronger than predicted by existing materials-science models. The causes of these drastic changes stem from the weird world of quantum physics.

The bulk properties of any material are merely the average of all the quantum forces affecting all the atoms. As you make things smaller and smaller, you eventually reach a point where the averaging no longer works. In the same time, with surface-area affects, quantum effects can begin to dominate the properties of matter as size is reduced to the nano-scale. These can affect the optical, electrical and magnetic behavior of materials, particularly as the structure or particle size approaches the smaller end of the nano-scale.

NANO-SCIENCE:

Nano-science is the synthesis, manipulation, and analysis of materials that are between 1-100 nanometers. The properties of materials in this size range (1-100 nm) are different than larger, "macro" ($>0.1 \mu\text{m}$) versions of the same material. In other words, *Nano-science is concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes, because of their small nano-scale size.*

NANOTECHNOLOGY:

Nanotechnology is the extension of existing science into the nano-scale. Nanotechnology deals with the design, manufacturing, production, synthesis and application of nanostructures (smaller than 100 nm) in useful nano-scale devices such as electronic circuits and mechanical devices at the molecular level.

The US national nanotechnology Initiative defines nanotechnology as '*the science, engineering and technology related to the understanding and control of matter at the length scale of approximately 1 to 100 nanometers.*'

NANO-MATERIALS:

Nano-materials is the structure of materials with improved properties through controlled synthesis and assembly of the material at nano-scale level. If at least one dimension of a structured component of a material is less than 100 nm, then it is called a nano-materials.

The factors that differentiate nanomaterials from bulk materials is the increase in surface area to volume ratio and quantum confinement effects. These are explained below.

(a). Surface area to volume ratio:

The nanomaterials possess large value of surface area to volume ratio as compared to the bulk material. The high surface area can be attained either by fabricating small particles or clusters where the surface to volume ratio of each particle is high. This unique property of surface to volume ratio leads to greater chemical reactivity and effect their strength. The electrical conductivity of nano-materials also enhanced appreciably due to better ordering in microstructure.

(b). Quantum confinement effects:

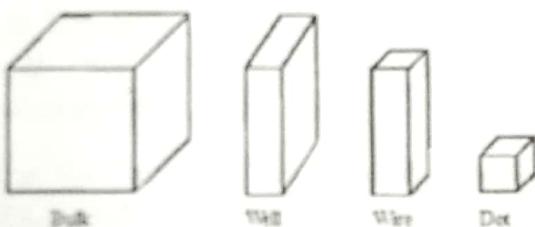
According to band theory, solid materials have energy bands and isolated atoms possess discrete energy levels. Nanomaterials are intermediate to the above two cases. For nanomaterials, if the dimensions of potential wells or potential boxes are of the order of the de-Broglie wavelength of electrons or mean free path of electrons, then the energy levels of electrons change, and the electron will remain confined to a small region of the material. This is called quantum confinement. The electrons in bulk solid material possess alternatively discrete allowed and forbidden bands of energies. As the material changes from bulk to nanoparticle size, the energies of electron changes. The quantum effects are dominant in nanoparticle materials.

QUANTUM WELL, QUANTUM WIRE AND QUANTUM DOT:

When the size or dimension of a material is continuously reduced from a large or macroscopic size, such as metre or centimetre, to a very small size, the properties remain the same at first, then

small changes begin to occur, until finally when the size drops below 100 nm, dramatic changes in properties can occur.

- If one dimension is reduced to the nanorange while the other dimensions remain large, then we obtain a structure known as **quantum well**.
- If two dimensions are so reduced and one remains large, the resulting structure is referred to as a **quantum wire**. A quantum wire is a structure such as a copper wire that is long in one dimension, but has a nanometer size as its diameter.
- The extreme case of this process of size reduction in which all three dimensions reach the low nanometer range is called a **quantum dot**. The quantum dot may have the shape of a tiny cube, a short cylinder or a sphere with low nanometre dimensions.



The word quantum is associated with the above three types of nanostructures because the changes in properties arise from the quantum mechanical nature of physics in the domain of the ultra small.

Preparation/ Synthesis of Quantum Structures:

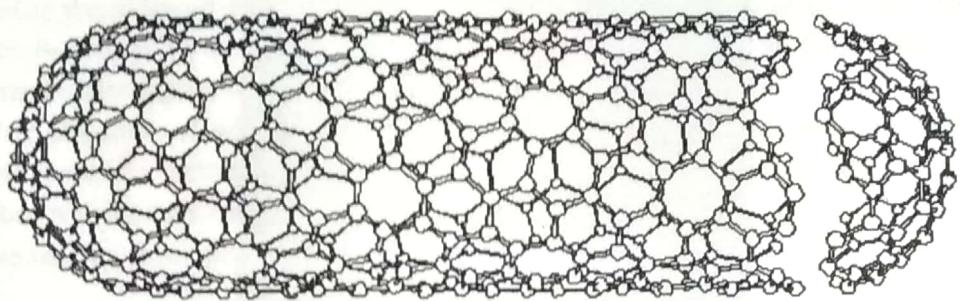
There are two different approaches of material fabrication. One is the bottom-up approach and the other is the top-down approach.

Bottom-up approach: The bottom-up approach is used to build something from basic materials, for example, assembling materials from the atoms/molecules up, and therefore very important for nano-fabrication. Examples of bottom-up technique are self-assembly of nano-materials, sol-gel technology, electro-deposition, physical and chemical vapor deposition etc.

Top-down approach: In top-down method, the bulk solids are dis-assembled (broken or dissociated) into finer pieces until the particles are in the order of nanometer. Examples of this type of technique are the manufacturing of integrated circuits using a sequence of steps as crystal growth, lithography, etching, ion implantation, etc.

An approach where both these techniques are employed is known as a **hybrid approach**. Lithography is an example in which the growth of thin film is a bottom-up method whereas etching is a top-down method.

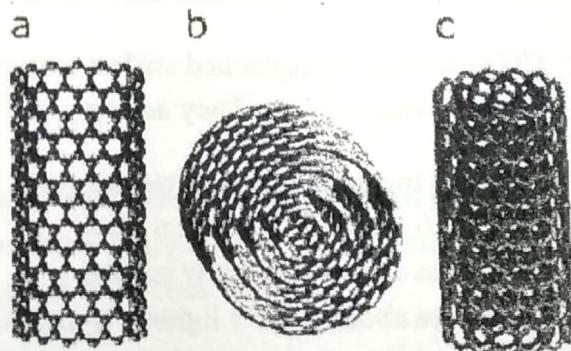
arranged in a hexagonal pattern. These are also known as tubular fullerenes. This cylinder can be closed or open at the end.



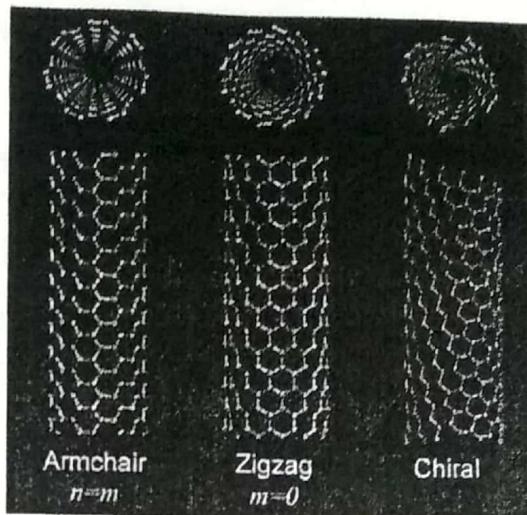
The diameter of a CNT is typically in the nanometer range ($\approx 1 \text{ nm}$ to 20 nm) and length can be several hundred times the width. Their hexagonal structure give them great tensile strength and elastic properties. The tubes are tough and when bent or squeezed, they spring back to their original shape. They are 600 times stronger than steel and 6 times lighter than it. They have many other unusual properties which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology.

STRUCTURE AND TYPES OF CNT:

There are many types of carbon nanotubes, including **single wall carbon nanotubes** (SWCNTs), **double wall carbon nanotubes** (DWCNTs), and **multi wall carbon nanotubes** (MWCNTs). SWCNTs consist of a single sheet of graphene forming a cylinder (Fig.a). DWCNTs consist of two such cylinders in a concentric arrangement (Fig.c), whereas MWCNTs consist of an array of concentric cylinders (Fig.b) that are positioned 0.35 nm distant from each other.



Depending on the way of rolling of grapheme sheets, single walled nanotubes of different types, viz. **armchair**, **zig-zag** and **chiral** could be produced. All these tubes are characterized by the (n,m) notation. The figure illustrates the three types of nanotube: the armchair tube with indices (n,m) where θ is 0° , the zigzag tube with indices $(n, 0)$ where θ is 30° . These two types of tubes have high symmetry and a plane of symmetry perpendicular to the tube axis. Any other tube with indices (n,m) is a chiral tube, which can be either left-handed or right-handed.



PROPERTIES OF CNT:

The properties of the nanotube arise by adapting the properties of graphite to the conditions imposed by rolling up the graphene sheets. This may be classified into electrical conduction properties, mechanical properties, thermal properties and chemical properties.

Mechanical properties:

- The carbon –carbon chemical bond in a graphene layer is probably the strongest chemical bond in an extended system known in nature.
- CNTs are the strongest and stiffest materials on earth, in terms of tensile strength and elastic modulus respectively. They are very stiff and hard to bend.
- Young's modulus of CNTs ranges from 1.3 to 1.8 tera-pascal. This data shows that a CNT is almost 10 times stronger than steel.
- The tubes are mechanically robust.
- CNTs are about 6 times lighter, 10 times stiffer and 20 times stronger than steel.
- Many of the envisaged applications of nanotubes such as composite reinforcement or lubrication are related in one way or other to their mechanical properties.

Electrical properties:

- The tube behaves as a metal and as a semiconductor depending on its structure. As a metal, its electrical conductivity is 1000 times more than that of copper while others behave more like silicon.
- The differences in conductivity can easily be derived from the graphene sheet properties.
- The electrical conductivity of nanotubes is a function of diameter, conductivity in multi-walled nanotubes is quite complex.

Chemical properties:

- A SWNT consists of two separate regions with different physical and chemical properties. The first is the sidewall of the tube and the second is the end cap of the tube. The end cap structure is similar to or derived from a smaller fullerene, such as C₆₀. C-atom placed in hexagons and pentagons form the end cap structure.
- The other structure of which a SWNT is composed is a cylinder. It is generated when a graphene sheet of a certain size that is wrapped in a certain direction. As the result is cylinder symmetric we can only roll in a discrete set of directions in order to form a closed cylinder.
- For these reasons, a smaller nanotube diameter results in increased reactivity.

Thermal properties:

- All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as ballistic conduction, but are good insulators laterally to the tube axis.
- The thermal conductivity of CNTs is 10 times that of silver.

Optical properties:

- The optical activity of chiral nanotubes disappears if the nanotubes become larger.
- Use of optical activity might result in optical devices in which CNTs play an important role.

SYNTHESIS OF CNT:

There are a number of methods of making nanotubes.

Laser ablation method:

In this method, the samples can be prepared by laser vaporization of graphite rods with equal amounts of cobalt and nickel powder at 1200° C in flowing argon. After this, heat treatment is carried out at 1000° C in vacuum to remove C₆₀ and other fullerenes.

Arc discharge method:

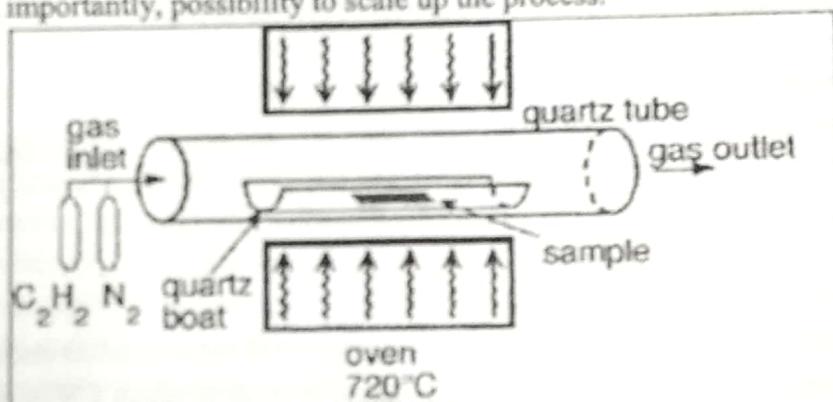
In this method, two high purity graphite electrodes as anode and cathode are held a short distance apart under a helium atmosphere. This technique involves evaporation of graphite anode rod and condensation of the deposit on the cathode rod under inert atmosphere. The nanotubes that are synthesized by this means are typically very ropey and multiwalled.

Chemical vapor deposition:

CVD technique can be achieved by taking a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. The CVD process uses hydrocarbons as the carbon sources including methane, carbon monoxide and acetylene. The hydrocarbons flow through the quartz tube being in an oven at a

high temperature ($\sim 720^{\circ}\text{C}$). Schematic diagram of the chemical vapor deposition apparatus is shown in Fig. 1. At high temperature, the hydrocarbons are broken to be the hydrogen carbon bond, producing pure carbon molecules. Then, the carbon will diffuse toward the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained. This method can produce both MWNTs and SWNTs depending on the temperature, in which production of SWNTs will occur at a higher temperature than MWNTs.

The advantages of the CVD process were low power input, lower temperature range, relatively high purity and, most importantly, possibility to scale up the process.



APPLICATIONS OF CNTs:

The unusual properties of carbon nanotubes make possible many applications ranging from battery electrodes, to electronic devices, to reinforcing fibres, which make stronger composites.

1. Hydrogen storage: Storing hydrogen in nanotubes is another possible applications, one that it is related to the development of fuel cells as sources of electrical energy for future automobiles. Because of their cylindrical and hollow geometry, and extremely small diameters, carbon nanotubes can store hydrogen in the inner cores through a capillary effect. It is estimated that to be useful in this application, the tubes need to hold 6.5% hydrogen by weight. At present only about 4% hydrogen by weight has been successfully put inside the tubes.

2. In chip designing as a transistor and interconnect:

The carbon nanotubes with diameter of 2 nm have extremely low resistance, and thus can carry large currents without heating, so they can be used as a interconnects. Due to their high thermal conductivity, they can serve as a heat sinks, allowing heat to be rapidly transferred away from the chip. Nanotube-based transistors, also known as carbon nanotube field-effect transistors (CNTFETs), have been made that operate at room temperature and that are capable of digital switching using a single

electron. It has been estimated that the switching time of these devices will be very fast, allowing clock speed of a terahertz, which is 10^4 times faster than present processors. The small size of switch and interconnects made by carbon nanotube allow more switches to be packed on a chip.

3. Field emission and Shielding:

The high aspect ratio of CNT makes it ideal field emission material. The emission current depends on the strength of the local electric field at the emission surface and its work function. The applied electric field must be very high in order to extract an electron. This condition is fulfilled for carbon nanotubes, because their elongated shape ensures very large field amplification. Examples of potential applications for nanotubes as field emitting devices are flat panel displays, gas discharge tubes in telecom networks, vacuum tube lamps, electron guns from electron microscopes, atomic force microscope (AFM) tips and microwave amplifiers.

4. Nanoprobes and sensors:

Nanotubes may ultimately become indispensable in their use as nanoprobes. Since MWNT tips are conducting, they can be used in scanning tunneling microscope (STM) and atomic force microscope (AFM) instruments. Biological molecules, such as DNA can also be imaged with higher resolution using nanotube tips, compared to conventional STM tips. Also, being flexible, the probes are not susceptible to frequent crashes, unlike in the case of normal STM tips.

Nanotubes can also be used as molecular probes, with potential applications in chemistry and biology. For example, as probes for drug delivery, molecular recognition, chemically sensitive imaging, and local chemical patterning, based on nanotube tips that can be chemically modified in a variety of ways.

The nanotube actuators are proved to be superior to conducting polymer-based devices, since in the former no ion intercalation (which limits actuator life) is required. This interesting behavior of nanotube sheets in response to an applied voltage suggests several applications, including nanotube-based micro-cantilevers for medical catheter applications and as novel substitutes, especially at higher temperatures, for ferroelectrics.

5. Medical:

Medical implants made of porous plastic, coated with carbon nanotubes. Therapeutic drugs, which are attached to the nanotubes can be released into the bloodstream, for example, when a change in the blood chemistry signals a problem. NASA is developing these implants, called a "biocapsule", to protect astronauts from the effects of radiation however the implants may also be useful for releasing insulin for diabetes patients or for delivering chemotherapy drugs directly to tumors.

UNIT-5, PART-II

Material processing by chemical vapor Deposition:-

Chemical vapor deposition is a chemical process used to produce a solid material from a gaseous phase.

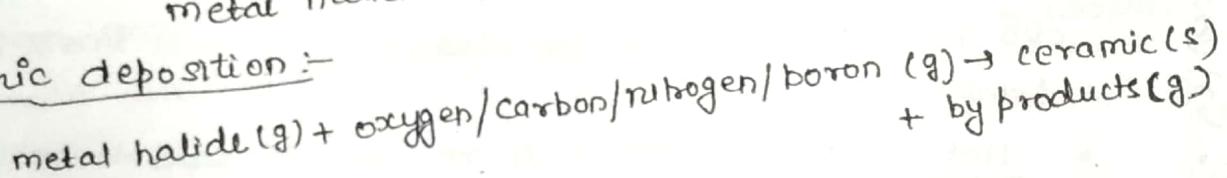
Microfabrication processes widely use CVD to deposit materials in various forms. These materials include: silicon, carbon fiber, carbon nanofiber, SiO_2 , tungsten etc.

Working concept :- In CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

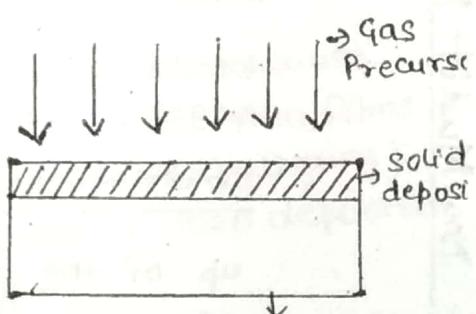
metal deposition :-



ceramic deposition :-



Process :- In a CVD method, a gaseous carbon source, such as acetylene, methane and carbon mono-oxide, is used. An energy source, such as a heating coil, provides energy to the gaseous carbon molecules, cracking them into reactive atomic carbon. The carbon then diffuses towards the substrate, on which carbon nanotubes are formed. Usually, the substrate, is coated with a catalyst, such as Ni , Fe or Co , and in the synthesis procedure. It is heated to 650 - 900°C . Using this method, excellent alignment and positional control at the nanometer scale can be achieved. SWNTs can be synthesized by using an appropriate metal catalyst. This method has a yield of about 30%.



(*) (Precursor \rightarrow a substance, from which another substance is formed)

5. Templates

Because of the small channels, strong capillary forces exist in nanotubes. These forces are strong enough to hold gases and fluids in nanotubes. In this way, it may be possible to fill the cavities of the nanotubes to create nanowires.

4.6 Material Processing by Chemical Vapor Deposition

Introduction

This process is used in semiconductor industry to produce thin film.

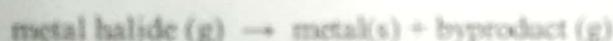
Chemical vapour deposition or CVD is a generic name for a group of processes that involve depositing a solid material from a gaseous phase. Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include: silicon, carbon fiber, carbon nanofibers, filaments, carbon nanotubes, SiO_2 , silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride and titanium nitride. CVD process is also used to produce synthetic diamonds.

Working Concept

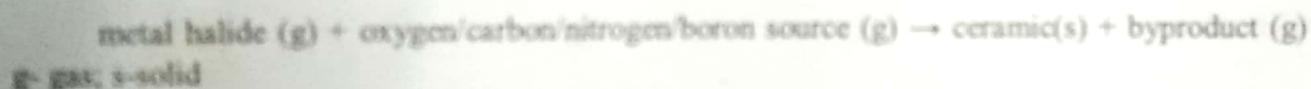
CVD is a chemical process for depositing thin film of various materials.

Chemical vapor deposition (CVD) results from the chemical reaction of gaseous precursor(s) at a heated substrate to yield a fully dense deposit. Thermodynamics and kinetics drive both precursor generation and decomposition. Control of thermodynamics and kinetics through temperature, pressure, and concentrations yields the desired deposit. A simplified concept diagram is shown as Fig.4.9.

Metal deposition



Ceramic deposition



A basic CVD process consists of the following steps: 1) a predefined mix of reactant gases and diluent inert gases are introduced at a specified flow rate into the reaction chamber; 2) the gas species move to the substrate; 3) the reactants get adsorbed on the surface of the substrate; 4) the reactants undergo chemical reactions with the substrate to form the film; and 5) the gaseous by-products of the reactions are desorbed and evacuated from the reaction chamber.

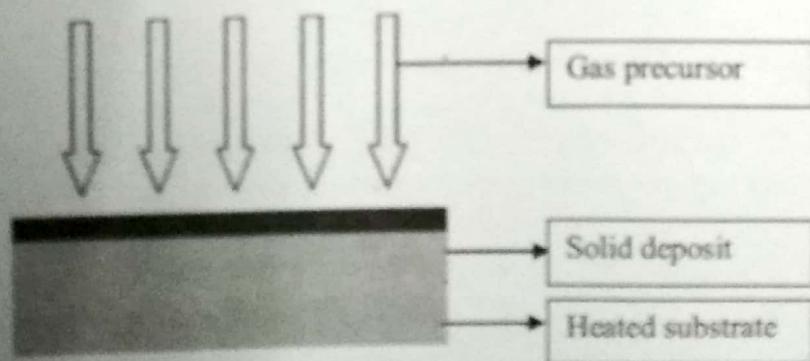


Fig.4.9 CVD reaction

During the process of chemical vapor deposition, the reactant gases not only react with the substrate material at the wafer surface (or very close to it), but also in gas phase in the reactor's

atmosphere. Reactions that take place at the substrate surface are known as heterogeneous reactions, and are selectively occurring on the heated surface of the wafer where they create good-quality films.

Reactions that take place in the gas phase are known as homogeneous reactions. Homogeneous reactions form gas phase aggregates of the depositing material, which adhere to the surface poorly and at the same time form low-density films with lots of defects. In short, heterogeneous reactions are much more desirable than homogeneous reactions during chemical vapor deposition.]

— Dr. Mudet P. Srivastava

15.

Types of chemical vapor deposition:-

A number of forms of CVD are in wide use. These processes differ in the means by which chemical reactions are initiated and process conditions.

CVD reactors can be classified on the basis of operating pressure.

- Atmospheric pressure CVD (APCVD) :- reactors operate at atmospheric pressure.
- Low-pressure CVD (LPCVD) :- reactors operate at medium vacuum ($30-250\text{ Pa}$) and higher temp. than APCVD,
- Plasma enhanced CVD (PECVD) :- Also operate at very low pressure (10^{-6} Pa).

CVD reactors can also be classified on the basis of reactor temperature :

- Hot wall reactor :- A reactor is said to be hot-wall if it uses a heating system that heats up not only the wafer, but the walls of the reactor itself.
- Cold-wall reactor :- cold wall reactors use heating systems that minimize the heating up of the reactor walls while the wafer is being heated up.

CVD Coatings and their properties :-

The range of CVD coatings are diverse and consequently this generates a wide range of properties as indicated in the Table 4.4.

Table 4.4 CVD Coatings and their properties.

CVD Coatings containing	On to various substrates	Properties
Chromium	Solid solution alloys (i) with Iron, Nickel and Cobalt (ii) on Iron as carbides and nitrides	(i) Corrosion / oxidation resistance (ii) Wear / corrosion resistance
Aluminium	As Aluminides with Iron, Cobalt and Nickel	High temperature oxidation resistance
Boron	As Borides with Iron, Cobalt and Nickel	Wear / erosion resistance
Silicon	As Silicides with Iron, Tungsten and Molybdenum	High temperature oxidation resistance
Titanium	As Carbides, nitrides and carbonitride on ferrous and non-ferrous alloys	Wear resistance
Manganese	Solid solution alloys on carbon steels	Wear resistance

Advantages of CVD

- Can be used for a wide range of metals and ceramics
- Can be used for coatings or freestanding structures
- Fabricates net or near-net complex shapes
- Is self-cleaning—extremely high purity deposits (>99.995% purity)
- Conforms homogeneously to contours of substrate surface
- Has near-theoretical as-deposited density
- Has controllable thickness and morphology
- Forms alloys
- Infiltrates fiber preforms and foam structures
- Coats internal passages with high length-to-diameter ratios
- Can simultaneously coat multiple components
- Coats powders

Applications

CVD processes are used on a surprisingly wide range of industrial components, from aircraft and land gas turbine blades, timing chain pins for the automotive industry, radiant grills for gas cookers and items of chemical plant, to resist various attacks by carbon, oxygen and sulphur. Some important applications are listed below.

- Surface modification to prevent or promote adhesion
- Photoresist adhesion for semiconductor wafers

- Silane/substrate adhesion for microarrays (DNA, gene, protein, antibody, tissue)
- MEMS coating to reduce stiction
- BioMEMS and biosensor coating to reduce "drift" in device performance
- Promote biocompatibility between natural and synthetic materials
- Copper capping
- Anti-corrosive coating

4.7 Physical Vapour Deposition (PVD)

Introduction

Physical vapour deposition (PVD) is fundamentally a vaporisation coating technique, involving transfer of material on an atomic level. It is an alternative process to electroplating. The process is similar to chemical vapour deposition (CVD) except that the raw materials/precursors, i.e. the material that is going to be deposited starts out in solid form, whereas in CVD, the precursors are introduced to the reaction chamber in the gaseous state.

Working Concept

PVD processes are carried out under vacuum conditions. The process involved four steps:

- Evaporation
- Transportation
- Reaction
- Deposition

Evaporation

During this stage, a target, consisting of the material to be deposited is bombarded by a high energy source such as a beam of electrons or ions. This dislodges atoms from the surface of the target, 'vaporising' them.

Transport

This process simply consists of the movement of 'vaporised' atoms from the target to the substrate to be coated and will generally be a straight line affair.

Reaction

In some cases coatings will consist of metal oxides, nitrides, carbides and other such materials. In these cases, the target will consist of the metal. The atoms of metal will then react with the appropriate gas during the transport stage. For the above examples, the reactive gases may be oxygen, nitrogen and methane.

In instances where the coating consists of the target material alone, this step would not be part of the process.

Deposition

This is the process of coating build up on the substrate surface.

Depending on the actual process, some reactions between target materials and the reactive gases may also take place at the substrate surface simultaneously with the deposition process.

Figure 4.10 shows a schematic diagram of the principles behind one common PVD method.

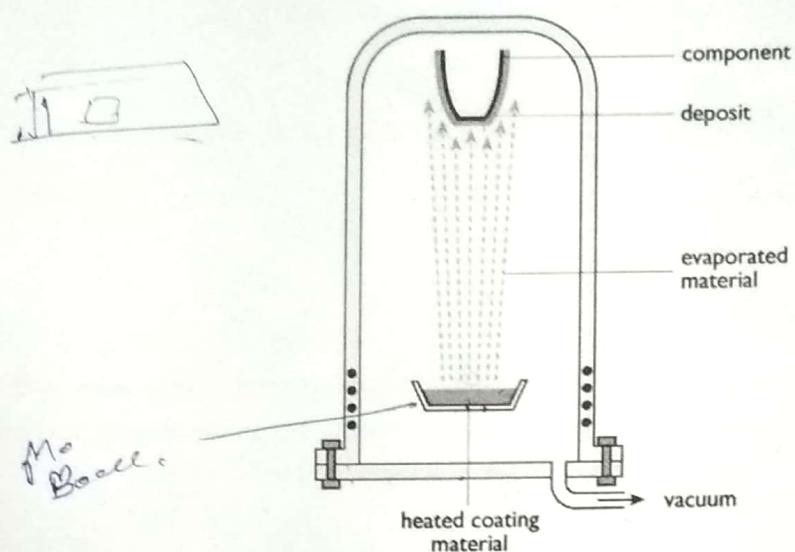


Fig.4.10 The vacuum evaporation PVD process

The component that is to be coated is placed in a vacuum chamber. The coating material is evaporated by intense heat from, for example, a tungsten filament. An alternative method is to evaporate the coating material by a complex ion bombardment technique. The coating is then formed by atoms of the coating material being deposited onto the surface of the component being treated.

Table 4.5 Summary of Merits and Demerits of evaporation methods

Method	Merits	Demerits
E-Beam Evaporation	1. high temp materials 2. good for liftoff 3. highest purity	1. some CMOS processes sensitive to radiation 2. alloys difficult 3. poor step coverage
Filament Evaporation	1. simple to implement 2. good for liftoff	1. limited source material (no high temp) 2. alloys difficult 3. poor step coverage
Sputter Deposition	1. better step coverage 2. alloys 3. high temp materials 4. less radiation damage	1. possible grainy films 2. porous films 3. plasma damage/contamination

Variants of PVD include, in order of increasing novelty:

1. **Evaporative Deposition:** In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in "high" vacuum.
2. **Electron Beam Physical Vapor Deposition:** In which the material to be deposited is heated to a high vapor pressure by electron bombardment in "high" vacuum.
3. **Sputter Deposition:** In which a glow plasma discharge (usually localized around the "target" by a magnet) bombards the material sputtering some away as a vapor.

4. **Cathodic Arc Deposition:** In which a high power arc directed at the target material blasts away some into a vapor.
5. **Pulsed Laser Deposition:** In which a high power laser ablates material from the target into a vapor.

Importance of PVD Coatings

PVD coatings are deposited for numerous reasons. Some of the main ones are:

- Improved hardness and wear resistance
- Reduced friction
- Improved oxidation resistance

The use of such coatings is aimed at improving efficiency through improved performance and longer component life. They may also allow coated components to operate in environments that the uncoated component would not otherwise have been able to perform.

Advantages

1. Materials can be deposited with improved properties compared to the substrate material
2. Almost any type of inorganic material can be used as well as some kinds of organic materials
3. The process is more environmentally friendly than processes such as electroplating

Disadvantages

1. It is a line of sight technique meaning that it is extremely difficult to coat undercuts and similar surface features
2. High capital cost
3. Some processes operate at high vacuums and temperatures requiring skilled operators
4. Processes requiring large amounts of heat require appropriate cooling systems

The rate of coating deposition is usually quite slow

Applications

As mentioned previously, PVD coatings are generally used to improve hardness, wear resistance and oxidation resistance. Thus, such coatings use in a wide range of applications such as:

1. Aerospace
2. Automotive
3. Surgical/Medical
4. Dies and moulds for all manner of material processing
5. Cutting tools
6. Fire arms

4.8 Electron Microscopy Techniques

Introduction

Electron Microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. The main advantage of **Electron Microscopy** is the unusual short wavelength of the electron beams, substituted for light energy. The wavelengths of about 0.005 nm increases the resolving power of the instrument to fractions of a nanometer. This examination can yield the following information:

- Topography
The surface features of an object or "how it looks", its texture; direct relation between these features and materials properties (hardness, reflectivity...etc.)
- Morphology
The shape and size of the particles making up the object; direct relation between these structures and materials properties (ductility, strength, reactivity...etc.)
- Composition
The elements and compounds that the object is composed of and the relative amounts of them; direct relationship between composition and materials properties (melting point, reactivity, hardness...etc.)
- Crystallographic Information. How the atoms are arranged in the object; direct relation between these arrangements and materials properties (conductivity, electrical properties, strength...etc.)

Types

There are two main electron microscopy techniques:

- Transmission electron microscopy, which essentially looks *through* a thin slice of a specimen.
- Scanning electron microscopy, which looks *at* the surface of a solid object.

4.8.1 Transmission Electron Microscope (TEM)

Working Concept

[TEM works much like a slide projector. A projector shines a beam of light through (transmits) the slide, as the light passes through it is affected by the structures and objects on the slide.] These effects result in only certain parts of the light beam being transmitted through certain parts of the slide. This transmitted beam is then projected onto the viewing screen, forming an enlarged image of the slide. [TEMs work the same way except that they shine a beam of electrons (like the light) through the specimen (like the slide). Whatever part is transmitted is projected onto a phosphor screen for the user to see.] A more technical explanation of typical TEMs workings is as follows:

1. The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.
2. This stream is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens (usually controlled by the "spot size knob") largely determines the "spot size"; the general size range of the final spot that strikes the sample. The second

lens(usually controlled by the "intensity or brightness knob" actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam.

3. The beam is restricted by the condenser aperture (usually user selectable), knocking out high angle electrons (those far from the optic axis, the dotted line down the center)
4. The beam strikes the specimen and parts of it are transmitted.
5. This transmitted portion is focused by the objective lens into an image
6. The image is passed down the column through the projector lenses, being enlarged all the way.
7. The image strikes the phosphor image screen and light is generated, allowing the user to see the image

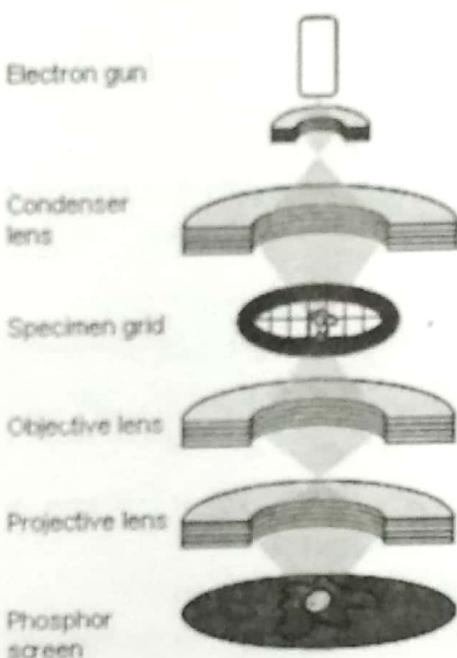


Fig.4.11 Working concept of TEM

Specimen Interactions and utilization

1. Unscattered Electrons

Source: Incident electrons which are transmitted through the thin specimen without any interaction occurring inside the specimen.

Utilization : The transmission of unscattered electrons is inversely proportional to the specimen thickness. Areas of the specimen that are thicker will have fewer transmitted unscattered electrons and so will appear darker, conversely the thinner areas will have more transmitted and thus will appear lighter.

2. Elasticity Scattered electrons

Source : Incident electrons that are scattered (deflected from their original path) by atoms in the specimen in an elastic fashion (no loss of energy). These scattered electrons are then transmitted through the remaining portions of the specimen.

Utilization: All electrons follow Bragg's Law and thus are scattered according to Wavelength=2*Space between the atoms in the specimen*sin(angle of scattering). All incident electrons have the same energy (thus wavelength) and enter the specimen normal to its surface. All incidents that are scattered by the same atomic spacing will be scattered by the same angle. These "similar angle" scattered electrons can be collated using magnetic lenses to form a pattern of spots; each spot corresponding to a specific atomic spacing (a plane). This pattern can then yield information about the orientation, atomic arrangements and phases present in the area being examined.

3. Inelastically Scattered Electrons

Source : Incident electrons that interact with specimen atoms in a inelastic fashion, loosing energy during the interaction. These electrons are then transmitted trough the rest of the specimen

Utilization : Inelastically scattered electrons can be utilized two ways

- Electron Energy Loss Spectroscopy: The inelastic loss of energy by the incident electrons is characteristic of the elements that were interacted with. These energies are unique to each bonding state of each element and thus can be used to extract both compositional and bonding (i.e. oxidation state) information on the specimen region being examined.
- Kakuchi Bands: Bands of alternating light and dark lines that are formed by inelastic scattering interactions that are related to atomic spacings in the specimen. These bands can be either measured (their width is inversely proportional to atomic spacing) or "followed" like a roadmap to the "real" elasticity scattered electron pattern.

4.8.2 Scanning Electron Microscope (SEM)

Working Concept

SEM allows surfaces of objects to be seen in their natural state without staining. The specimen is put into the vacuum chamber and covered with a thin coating of gold to increase electrical conductivity and thus forms a less blurred image. The electron beam then sweeps across the object building an image line by line as in a TV Camera. As electrons strike the object, they knock loose showers of electrons that are captured by a detector to form the image.

A simplified working concept of SEM is illustrated below.

1. The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.
2. The stream is condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to both form the beam and limit the amount of current in the beam. It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam
3. The beam is then constricted by the condenser aperture, eliminating some high-angle electrons
4. The second condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob"
5. A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed (usually in the microsecond range)

6. The final lens, the Objective, focuses the scanning beam onto the part of the specimen desired.
7. When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments
8. Before the beam moves to its next dwell point these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number (the more reactions the brighter the pixel).
9. This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.

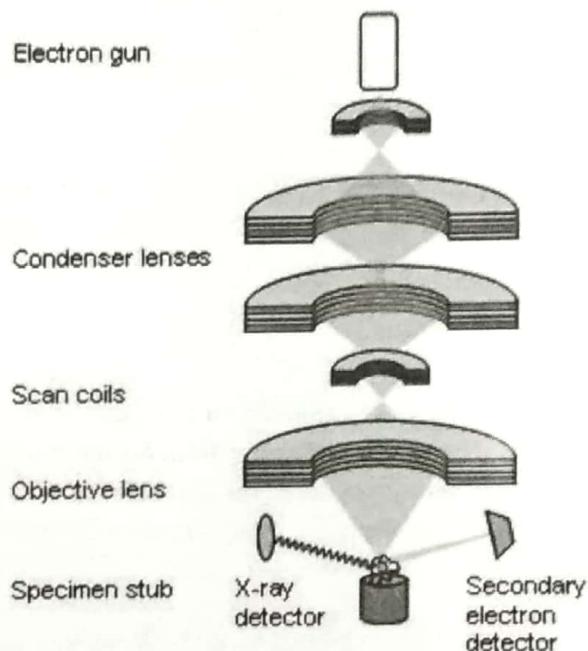


Fig.4.12 Working concept of SEM

Specimen Interactions and utilization:

1. Backscattered Electrons

Formation : Caused by an incident electron colliding with an atom in the specimen which is nearly normal to the incident's path. The incident electron is then scattered "backward" 180 degrees.

Utilization : The production of backscattered electrons varies directly with the specimen's atomic number. This differing production rates causes higher atomic number elements to appear brighter than lower atomic number elements. This interaction is utilized to differentiate parts of the specimen that have different average atomic number.

2. Secondary Electrons

Source : Caused by an incident electron passing "near" an atom in the specimen, near enough to impart some of its energy to a lower energy electron (usually in the K-shell). This causes a slight energy loss and path change in the incident electron and the ionization of the electron in the specimen atom. This ionized electron then leaves the atom with a very small kinetic energy (5eV) and is then termed a "secondary electron". Each incident electron can produce several secondary electrons.

Utilization : Production of secondary electrons is very topography related. Due to their low energy, 5eV, only secondaries that are very near the surface (<10nm,) can exit the sample and be examined. Any changes in topography in the sample that are larger than this sampling depth will change the yield of secondaries due to collection efficiencies. Collection of these electrons is aided by using a "collector" in conjunction with the secondary electron detector. The collector is a grid or mesh with a +100V potential applied to it which is placed in front of the detector, attracting the negatively charged secondary electrons to it which then pass through the grid-holes and into the detector to be counted.

3. Auger Electrons

Source : Caused by the de-energization of the specimen atom after a secondary electron is produced. Since a lower (usually K-shell) electron was emitted from the atom during the secondary electron process an inner (lower energy) shell now has a vacancy. A higher energy electron from the same atom can "fall" to a lower energy, filling the vacancy. This creates an energy surplus in the atom which can be corrected by emitting an outer (lower energy) electron; an Auger Electron.

Utilization : Auger Electrons have a characteristic energy, unique to each element from which it was emitted from. These electrons are collected and sorted according to energy to give compositional information about the specimen

4. X-rays

Source : Caused by the de-energization of the specimen atom after a secondary electron is produced. Since a lower (usually K-shell) electron was emitted from the atom during the secondary electron process an inner (lower energy) shell now has a vacancy. A higher energy electron can "fall" into the lower energy shell, filling the vacancy. As the electron "falls" it emits energy, usually X-rays to balance the total energy of the atom so it .

Utilization : X-rays or Light emitted from the atom will have a characteristic energy which is unique to the element from which it originated.

Comparison between SEM and TEM

- SEM is based on scattered electrons while TEM is based on transmitted electrons.
- SEM focuses on the sample's surface and its composition whereas TEM provides the details about internal composition. Therefore TEM can show many characteristics of the sample, such as morphology, crystallization, stress or even magnetic domains. On the other hand, SEM shows only the morphology of samples.
- The sample in TEM has to be cut thinner whereas there is no such need with SEM sample.
- TEM has much higher resolution than SEM.
- SEM allows for large amount of sample to be analysed at a time whereas with TEM only small amount of sample can be analysed at a time.
- SEM is used for surfaces, powders, polished & etched microstructures, IC chips, chemical segregation whereas TEM is used for imaging of dislocations, tiny precipitates, grain boundaries and other defect structures in solids
- SEM provides a 3-dimensional image while TEM provides a 2-dimensional picture

4.9 Scanning Probe Microscopy

Scanning probe microscopy (SPM) is a new branch of microscopy that forms images of surfaces using a physical probe that scans the specimen. An image of the surface is obtained by mechanically moving the probe in a raster scan of the specimen, line by line, and recording the probe-surface interaction as a function of position. SPM was founded with the invention of the scanning tunneling microscope in 1981.

Some important types of scanning probe microscopy

- AFM, atomic force microscopy
- EFM, electrostatic force microscope
- FMM, force modulation microscopy
- MFM, magnetic force microscopy
- STM, scanning tunneling microscopy
- SVM, scanning voltage microscopy
- SHPM, scanning Hall probe microscopy

4.9.1 Atomic Force Microscope (AFM)

Introduction

The atomic force microscope (AFM) or scanning force microscope (SFM) was invented in 1986 by Binnig, Quate and Gerber. Similar to other scanning probe microscopes, the AFM raster scans a sharp probe over the surface of a sample and measures the changes in force between the probe tip and the sample.

Working Concept :-

The physical parameter probed is a force resulting from different interactions. The origin of these interactions can be ionic repulsion, van der Waals, capillary, electrostatic and magnetic forces, or elastic and plastic deformations. Thus, an AFM image is generated by recording the force changes as the probe (or sample) is scanned in the x and y directions.

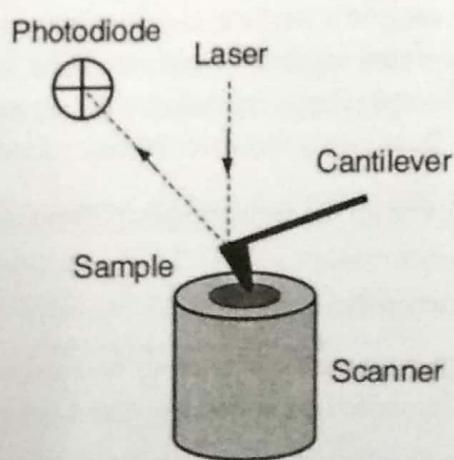


Fig.4.13 Working concept of AFM

The sample is mounted on a piezoelectric scanner, which ensures three-dimensional positioning with high resolution. The force is monitored by attaching the probe to a pliable cantilever, which acts as a spring, and measuring the bending or "deflection" of the cantilever. The larger the cantilever deflection, the higher the force that will be experienced by the probe. Most instruments

today use an optical method to measure the cantilever deflection with high resolution; a laser beam is focused on the free end of the cantilever, and the position of the reflected beam is detected by a position-sensitive detector (photodiode). AFM cantilevers and probes are typically made of silicon or silicon nitride by micro fabrication techniques.

Basic set-up of an AFM

In principle the AFM resembles a record player and a stylus profilometer. The ability of an AFM to achieve near atomic scale resolution depends on the three essential components: (1) a cantilever with a sharp tip, (2) a scanner that controls the x - y - z position, and (3) the feedback control and loop.

1. Cantilever with a sharp tip. The stiffness of the cantilever needs to be less than the effective spring constant holding atoms together, which is on the order of 1 - 10 nN/nm. The tip should have a radius of curvature less than 20-50 nm (smaller is better) a cone angle between 10-20 degrees.

2. Scanner. The movement of the tip or sample in the x , y , and z -directions is controlled by a piezo-electric tube scanner, similar to those used in STM. For typical AFM scanners, the maximum ranges are 80 mm x 80 mm in the x - y plane and 5 mm for the z -direction.

3. Feedback control. The forces that are exerted between the tip and the sample are measured by the amount of bending (or deflection) of the cantilever. By calculating the difference signal in the photodiode quadrants, the amount of deflection can be correlated with a height. Because the cantilever obeys Hooke's Law for small displacements, the interaction force between the tip and the sample can be determined.

A summary of the different modes of operation is found in Table 4.6

Table 4.6 AFM Modes of operation

Mode of Operation	Force of Interaction
Contact mode	strong (repulsive) - constant force or constant distance
Non-contact mode	weak (attractive) - vibrating probe
Tapping mode	strong (repulsive) - vibrating probe
Lateral force mode	frictional forces exert a torque on the scanning cantilever

Applications

The AFM is useful for obtaining three-dimensional topographic information of insulating and conducting structures with lateral resolution down to 1.5 nm and vertical resolution down to 0.05 nm. These samples include clusters of atoms and molecules, individual macromolecules, and biological species (cells, DNA, proteins). Unlike the preparation of samples for STM imaging, there is minimal sample preparation involved for AFM imaging. Similar to STM operation, the AFM can operate in gas, ambient, and fluid environments and can measure physical properties including elasticity, adhesion, hardness, friction and chemical functionality. A concise applications listing is given below.

- Metals: tooling studies, roughness measurements, corrosion studies...
- Solid powder catalysts: aggregate structural determination,

- Polymers: determination of morphology and surface properties, kinetic studies, aging phenomena, surface treatment modifications, adhesion force measurement and indentation,
- Biological samples, biomaterials: macromolecules association and conformation studies, adsorption kinetic of molecules on polymer surfaces,
- Nano- and microparticle structures, Langmuir-Blodgett Film studies...

Advantages

The AFM has several advantages over the scanning electron microscope (SEM).

- Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a true three-dimensional surface profile.
- Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample.
- While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms.
- In principle, AFM can provide higher resolution than SEM. It has been shown to give true atomic resolution in ultra-high vacuum (UHV).

Disadvantages

- A disadvantage of AFM compared with the scanning electron microscope (SEM) is the image size. The SEM can image an area on the order of millimetres by millimetres with a depth of field on the order of millimetres. The AFM can only image a maximum height on the order of micrometres and a maximum scanning area of around 150 by 150 micrometres.
- Another inconvenience is that at high resolution, the quality of an image is limited by the radius of curvature of the probe tip, and an incorrect choice of tip for the required resolution can lead to image artifacts.
- Traditionally the AFM could not scan images as fast as an SEM, requiring several minutes for a typical scan, while an SEM is capable of scanning at near real-time (although at relatively low quality) after the chamber is evacuated.
- AFM images can be affected by hysteresis of the piezoelectric material.

4.0.3 Scanning Near-Field Optical Microscopy