

CHAPTER - 5

NANO TECHNOLOGY

5.1 Introduction

Manufactured materials are made from atoms. The properties of those materials depend on how these atoms are arranged. If one rearranges the atoms in coal, he gets diamond and if one arranges the atoms in sand he gets computer chips. Theoretical analysis makes it clear that one can do a lot more. One of the basic principles about matter is positional control. The control may be either macroscopic or microscopic level but the results could be much lighter, stronger and more precise. A new technology creates a new science called *nanotechnology* which is about rearranging atoms whichever way we want. Nanotechnology is an umbrella term that covers many areas of research dealing with objects that are measured in nanometers. It is a sub classification of technology in physics, chemistry, biology and engineering fields [Figure 5.1]. *Nanoscience* is the study of the fundamental principles of atoms, molecules and structures with at least one dimension roughly between 1 and 100 nanometers. The fundamental goal of nanoscience or nanotechnology is to understand the evolution with decreasing crystal size of molecular properties from bulk properties.

Nanoscience and nanotechnologies incorporate exciting areas of research and development at the interface between physics, chemistry, biology, computer science, bioinformatics, molecular and Information Technology. Figure 5.1 depicts the convergence of nanotechnology from all existing various boundary areas. In this, convergence refers to the multiple ways in which nanotechnologies will combine in the future with other developments in new technology (reflecting its genuinely interdisciplinary nature). Convergence probably presents some of the biggest uncertainties, with respect to what is genuinely plausible and when new technologies might actually come into use.

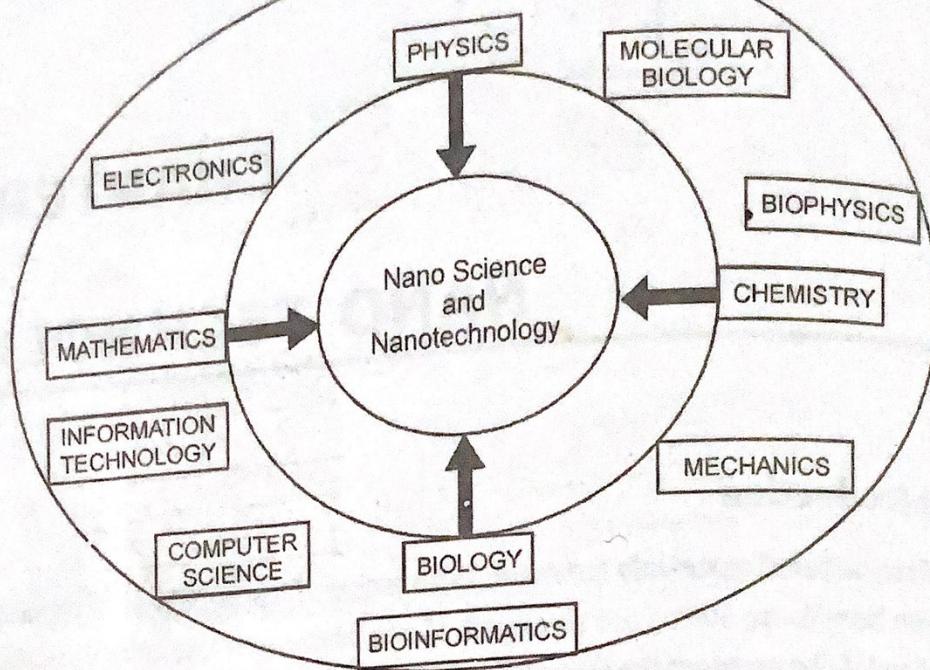


Figure 5.1: Convergence towards nanoscience

Nanoparticles have existed for billions of years: Geckos hang upside down on the ceiling by nanotech effect; on each tow they have millions of tiny hairs, and each hair has a minute force which holds on to the ceiling. Terpene: hydrocarbons in the essential oils and resins of trees (turpentine) and volcanic ash contains nanoparticles. A human hair is approximately 80,000nm wide, and a red blood cell approximately 7000nm wide.

Figure 5.2 shows the nanometre in context. Atoms are below a nanometre in size, whereas many molecules, including some proteins, range from a nanometre upwards. The conceptual underpinnings of nanotechnologies were first laid out in 1959 by the physicist *Richard Feynman*, in his lecture ‘There’s plenty of room at the bottom’ (Feynman 1959). Feynman explored the possibility of manipulating material at the scale of individual atoms and molecules, imagining the whole of the Encyclopaedia Britannica written on the head of a pin and foreseeing the increasing ability to examine and control matter at the nanoscale.

The term ‘nanotechnology’ was not used until 1974, when *Norio Taniguchi*, a researcher at the University of Tokyo, Japan used it to refer to the ability to engineer materials precisely at the nanometre level. The primary driving force for miniaturization at that time came from the electronics industry, which aimed to develop tools to create smaller (and therefore faster and more complex) electronic devices on silicon chips.

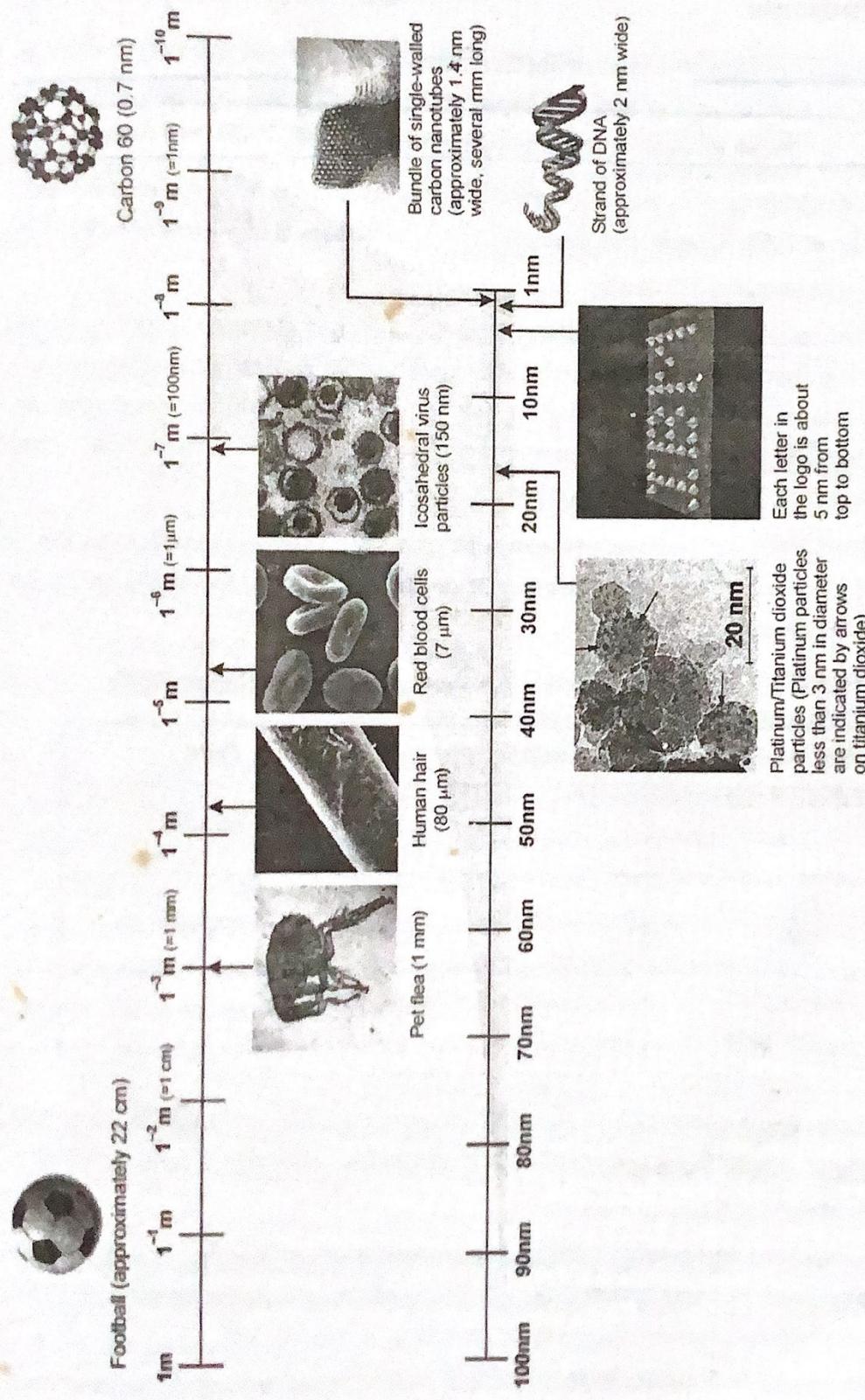


Figure 5.2: Length scale showing the nanometre in context. The length scale at the top ranges from 1m to 10^{-10}m , and illustrates the size of a football compared to a carbon 60 (C_{60}) molecule, also known as a buckyball. For comparison the world is approximately one hundred million times larger than a football, which is in turn one hundred million times larger than a buckyball. The section from 10^{-7}m (100nm) to 10^{-10}m (1nm) is expanded below. The lengthscale of interest for nanoscience and nanotechnologies is from 100nm down to the atomic scale - approximately 0.2nm .

5.2 Nanoscale

Nanotechnology is a field of applied science that ~~throws~~ light on the design, synthesis, characterization and the application of materials and devices on the nanoscale. A nanoscale is an object having nanometer size (1-100 nm range).

A nanometer (nm) is one-billionth (10^{-9}) of a meter or 10 \AA , so particles having a radius of about 1000 \AA can be considered and is derived from the Greek word for dwarf, 'nano'.

A nanometer is about the width of six bonded carbon atoms and our fingernails grow approximately one nm per second. Nanoparticles are generally considered to be a number of atoms or molecules bonded together with a radius of 100 nm. Nanomaterials, are grown either by way of a top-down approach (a bulk material is reduced in size to nanoscale pattern) or a bottom-up approach (grown atom by atom).

Table 5.1 gives a variation between molecules, nanoparticles and bulk materials. A cluster of 1 nm radius has approximately 25 atoms, but most of the atoms are on the surface of the cluster.

Table 5.1: Distinction between molecules, nanoparticles and bulk

No. of atoms	Radius (nm)	Type
1 10	1	Molecules
10^2 10^6	10	Nanoparticles
10^7 onwards	< 100	Bulk

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.

Nanotechnologies are the design, characterisation, production and application of structures, devices and systems by controlling shape and size at nanometer scale.

5.3 Nanophase materials

In a nanostructure, electrons are confined in the nanoscale dimension(s), but are free to move in other dimension(s). Nanophase materials or simply *nano materials* are the nanostructured materials having a characteristic length less than 100 nm. These are recently developed new materials having so many new properties. These have a three dimensional structure with a domain size smaller than 100 nm. These are characterized by a large number of grain boundary interfaces in which local atomic arrangements are different from those of the crystal lattice. A cluster of nanoparticles contains less than 10^4 molecules or atoms corresponding to a diameter of only a few nanometers.

Thus one can conclude that particle's size in nano materials is about 1 nm. With these small sized particles one can get the different properties (electronic, optical, electrical, magnetic, chemical and mechanical) which are different from the bulk materials. Having a size between the molecular and bulk solid state structures, the nano particles have hybrid properties. They have nonlinear optical and magnetic properties.

The change in geometry continued to small sizes containing only a few atoms, at which point all traces of the bulk arrangement will be lost. It is clear that at these sizes the clusters are no longer fragments of the bulk structure. Therefore the metal aggregates cannot be simply treated as minute elements of the block of a metal, as implied by the term divided metals. Because the conduction band present in the bulk metal will be absent and instead there would be discrete states at the band edge. Electrons will therefore undergo quantum confinement in very small metal particles, showing quantum dots, further a high proportion of the atoms in small metal nanoparticles will be present at the surface. There is remarkable increase in the surface to bulk ratio, with decrease in size. For instance, nanoparticles of 10 nm diameter would have approximately 10% of surface atoms, while in 1 nm size-particle there will be 100% surface atoms.

Starting from the bulk, the first effect of reducing particle size is to create more surface sites. This changes the surface pressure and results in a change in the inter-particle spacing. The change in the inter-particle spacing and the larger surface to volume ratio in particles has concomitant effect on the material properties. Variations in surface free energy change the chemical potential. This affects the thermodynamical properties of which the simplest example is melting point of Au particle as a function of size decreases. The variation in inter-particle spacing and geometry also result in a variation in electronic properties with size. For small particles, the electronic states

are not continuous but discrete, due to confinement of the electron wave function. As the size decreases, the electronic bands become narrower and the delocalized electronic states are transformed to more localized molecular bonds. The electronic property accessible for experimental measurements is the ionization potential. The ionization potentials at smaller sizes are higher than the bulk work function and showed considerable fluctuations as a function of size. Photo electronic spectroscopy is used to probe the changes in electronic energy levels with size for free cluster. A negative charge created on the clusters by exposing them to low energy electronic energy levels with size for free cluster. The anionic clusters are then crossed with a fixed frequency laser beam and the resulting photo detached electrons are analysed. Therefore, the spectra are finger prints of the ground and excited states of neutral cluster. They provide information on vertical and adiabatic electron affinities and the low lying electronic states.

Further, the large surface to volume ratio and the variations in geometry and electronic structures have a strong effect on catalytic properties. The reactivity of small clusters found to vary by order of magnitude, when the cluster size is changed by only few atoms. Another classic example is that storage ability of hydrogen in metals. Most metals do not absorb hydrogen, and even among those that do, hydrogen is absorbed dissociative on surfaces with hydrogen to metal ratio of one. This limit can be significantly enhanced in small sizes. It is found that small positively charged clusters of Pd, Pt and Ni generated in molecular beams containing two to sixty atoms, can absorb up to eight hydrogen atoms per metal atom. The number of absorbed hydrogen atoms decreases with increasing cluster size and approaches one for clusters containing around 60 atoms. This shows that small particles may be useful for hydrogen storage devices. The fundamental challenges in nanostructure materials are,

- Ability to control the scale (size) of the system
- Ability to obtain the required composition; not only the average composition but also the details such as defects, concentration gradients etc.
- Understand the influence of the size of building blocks in nano structured materials as well as the influence of microstructure on the physical, chemical and mechanical properties of the material.

A wide range of synthetic procedures are used in preparation of nanomaterials

such as

- Gas phase evaporation method
- Reduction of metal ions
- Decomposition of organometallic compounds and cluster complexes
- Metal atom vapour synthesis
- Metal vapour deposition into polymer
- Encapsulation in inert gas matrices
- Sol-Gel processing: single-phase materials, multiphase materials, hybrids

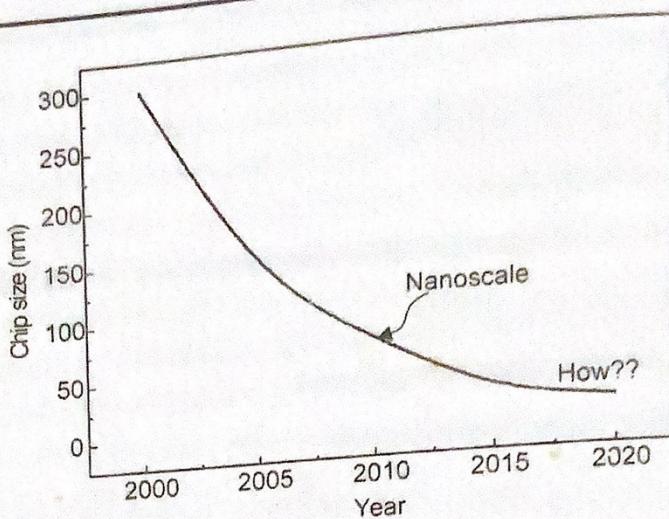
Scanning Tunneling Microscope (STM) is a technology evolved to allow the manipulation of individual atoms and molecules. What makes nanostructures unique and interesting? For bulk materials (e.g., a Cu wire, a cup of water), their intrinsic physical properties, such as density, conductivity and chemical reactivity, are independent of their sizes. For example, if a one-meter Cu wire is cut into a few pieces; those intrinsic properties of the shorter wires remain the same as in the original wire. If the dividing process is repeated again and again, this invariance cannot be kept indefinitely. Certainly, we know that the properties are changed greatly when the wire is divided into individual Cu atoms (even more at the level of electrons, protons and neutrons). Significant property changes often start when we get down to the nanoscales. The following phenomena critically affect the properties of nanostructural materials:

5.4 Moore's law

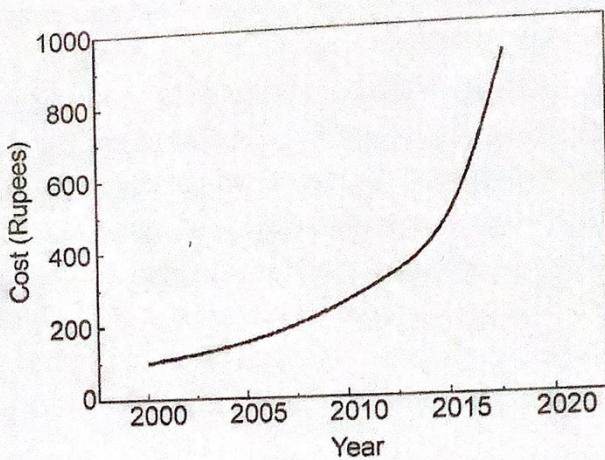
Gordon Moore, one of the founders of the Intel Corporation, came up with two empirical laws to explain the amazing development in integrated circuit electronics. Moore's first law (called Moore's law) says that the amount of space required to install a transistor on a chip shrinks by roughly half every 18 months. This means that the space that could hold one transistor 15 years ago can hold approximately 1000 transistors today. Figure 5.3 shows Moore's law in a graphical way.

Moore's second law predicts that the cost of building a chip manufacturing plant doubles with every other chip generation or roughly every 36 months. Microprocessors and memory circuits follow Moore's law.

5.8



(a) Moore's first law



(b) Moore's second law

Figure 5.3

5.5 Semiconducting nanoparticles

Because of their role in quantum dots, nanoparticles made of the elements, which are normal constituents of semiconductors, have been the subject of much study, with particular emphasis on their electronic properties. The title of this section, "semiconducting nanoparticles", is somewhat misleading. Nanoparticles made of cadmium, germanium, or silicon are not themselves semiconductors. A nanoparticle of Si can be made by laser evaporation of a Si substrate in the region of a helium gas pulse. The beam of neutral clusters is photolyzed by a UV laser producing ionized clusters whose mass to charge ratio is then measured in a mass spectrometer. The

most striking property of nanoparticles made of semiconducting elements is the pronounced changes in their optical properties compared to those of the bulk material. There is a significant shift in the optical absorption spectra toward the blue (shorter wavelength) as the particle size is reduced.

In a bulk semiconductor a bound electron-hole pair, called an *exciton*, can be produced by a photon having an energy greater than that of the band gap of the material. The band gap is the energy separation between the top filled energy level of the valence band and the nearest unfilled level in the conduction band above it. The photon excites an electron from the filled band to the unfilled band above. The result is a hole in the otherwise filled valence band, which corresponds to an electron with an effective positive charge. Because of the Coulomb attraction between the positive hole and the negative electron, a bound pair, called an *exciton*, is formed that can move through the lattice. The separation between the hole and the electron is many lattice parameters. The existence of the exciton has a strong influence on the electronic properties of the semiconductor and its optical absorption. The exciton can be modeled as a hydrogen-like atom and has energy levels with relative spacings analogous to the energy levels of the hydrogen atom but with lower actual energies. Light-induced transitions between these hydrogen-like energy levels produce a series of optical absorptions that can be labeled by the principal quantum numbers of the hydrogen energy levels. We are particularly interested in what happens when the size of the nanoparticle becomes smaller than or comparable to the radius of the orbit of the electron-hole pair. There are two situations, called the *weak-confinement* and the *strong-confinement regimes*. In the weak regime the particle radius is larger than the radius of the electron-hole pair, but the range of motion of the exciton is limited, which causes a blue shift of the absorption spectrum. When the radius of the particle is smaller than the orbital radius of the electron-hole pair, the motion of the electron and the hole become independent, and the exciton does not exist. The hole and the electron have their own set of energy levels.

5.6 Nanocomposites

Nanocomposites are special type of materials originating from suitable combination of two or more such nanoparticles by some appropriate techniques, resulting in materials having unique physical properties. Novel properties of Nanocomposites can be derived from the successful combination of the features of parent constituents into a single material. These properties obtained by nanomaterials are consequences of their finite smaller size, dimensionality, organization and interaction with each other as well as

the surrounding environment. These properties include enhanced quantum electronic and optical nonlinearities as a consequence of the spatial, quantum and dielectric confinement of electrons, holes and excitons with respect to the nanoscale of the materials. Nanosize metal particles pose a number of unsolved problems and require new approaches for their synthesis, stabilization and characterization.

Different approaches that are commonly used to attain nanocomposites are:

- Polymeric nanocomposites
- Organic –inorganic systems
 - One dimensional inorganic structures
 - 3D inorganic structures
 - Layered structures
- Inorganic – inorganic systems
 - Nanocomposites in stable colloidal form
 - Nanocomposites with improved physical properties

5.6.1 Synthesis of Nanoparticles

If you take a sheet of paper and tear it in half and tear it pieces in half and so on, you will soon find that it becomes increasingly difficult to produce smaller pieces. Similarly, it is quite difficult if not impossible to produce nanomaterials by breaking down larger particles. How then can we go about producing nano sized particles? Just as a wall be built up by piling bricks one over the other, particles may be created by assembling together their building blocks which may be atoms or molecules. This can be done much more easily than trying to break down a large particle into a nano particle. Nano particles are synthesized by bringing together atoms or molecules which are initially apart to form a larger cluster of atoms. This is similar to how crystals grow in a solution. However, things are not that simple and these particles quickly grow to be too large. It is thus important to arrest or limit the growth of these particles when they have grown to the desired size. There are a wide variety of techniques that are capable of creating nanostructures with various degrees of quality, speed and cost. These manufacturing approaches fall under two categories: '*bottom-up*', and '*top-down*'. In recent years the limits of each approach, in terms of feature size and quality that can be achieved, have started to converge. A diagram illustrating some of the

types of materials and products that these two approaches are used for is shown below in Figure 5.4.

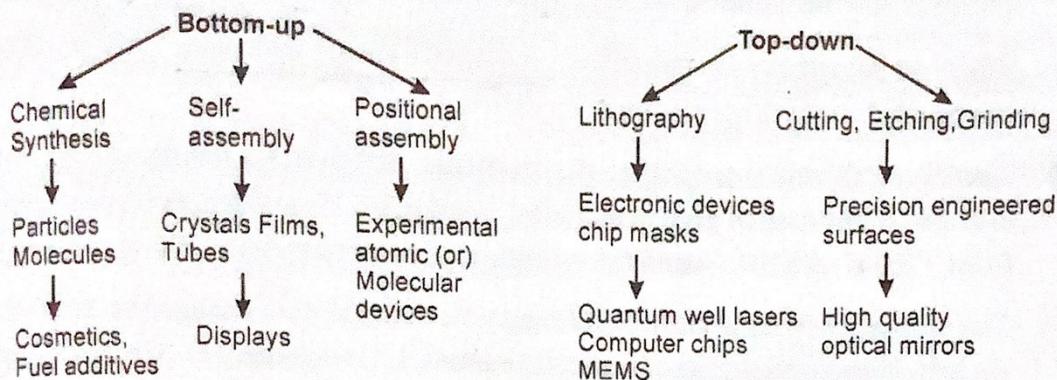


Figure 5.4: The use of bottom-up and top-down techniques in manufacturing

5.7 Properties of nanomaterials

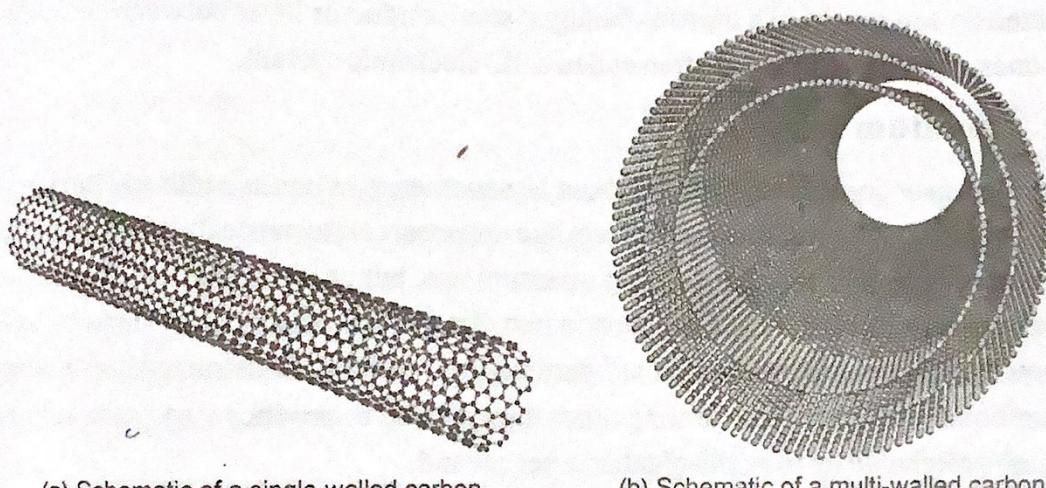
Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms, and at 3 nm 50% of its atoms. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles.

What makes nanoparticles very interesting and endows them with their unique properties is that their size is smaller than critical lengths that characterize many physical phenomena. Generally, the physical properties of nanomaterials can be characterized by some critical length, a thermal diffusion length or a scattering length, for example. The electrical conductivity of a conductor is strongly determined by the distance that electron travels between collisions with the vibrating atoms or the impurities of the solid. This distance is called mean free path or the scattering length. If the sizes of particles are less than this characteristic length, it is possible that new physics may occur. Perhaps a working definition of a nanoparticle is an aggregate of atoms between one and 100 nm viewed as a sub division of a bulk material, and of dimension less than the characteristic length of some phenomena. The interesting properties of nanoparticles are mainly due to their reduction in size.

- i) As the size is reduced from the bulk the electronic bands in metals become narrower and the value of ionization potential is raised. *surface functional*
- ii) When we have metals in nanophase, the metals absorb hydrogen. This property can be used for hydrogen storage in metals.
- iii) The thermodynamic properties are drastically different for nanoparticles. For example in the case of gold in nanophase condition, its melting point decreases from 1200 K to 800 K when the particle size decreases from 300 Å to 20 Å.
- iv) The properties of nano particles of magnetic materials are changed so that they are behaving as other kind of magnetic materials. For example Fe, Co and Ni are ferromagnetic in the bulk state. But they are changed into superparamagnetic to the nanophase. Similarly Na, K and Rb are paramagnetic in the bulk state. But they are changed into ferromagnetic in the nanophase. Further the magnetic nanomaterials are used to nonvolatile magnetic storages and permanent magnets.
- v) Regarding mechanical properties, they are inferior with respect to elastic strength. But the plastic behaviour is increased. In some nanophase materials, it is found that there is decrease in hardness with decreasing grain size when the grain size is less than 10 nm. But for many nanocrystalline pure metals (10 nm) the hardness is about 2 – 7 times greater than that of large grained ($> 1 \mu\text{m}$) metal.
- vi) These have high solid state phase transition pressure, lower Debye temperature and high self diffusion coefficient, high catalytic activity and lower ferroelectric phase transition temperature.

Nanotube is a one dimensional fullerene with a cylindrical tube. **Carbon nanotubes** (CNTs) are molecular scale-tubes of graphite carbon or allotropes of carbon with a nanostructure that can have a length-to-diameter ratio greater than 10^6 and were discovered in 1991 by Sumio Iijima. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science, as well as extensive use in architectural fields. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Inorganic nanotubes have also been synthesized.

Nanotubes are members of the *fullerene* structural family, which also includes the spherical buckyballs. The cylindrical nanotube usually has at least one end capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is in the order of a few nanometers (approximately 1/50,000th of the width of a human hair), while they can be up to several millimeters in length (as of 2008). Nanotubes are categorized as *single-walled nanotubes* (one tube) and *multi-walled nanotubes* (several concentric tubes). Both of these are typically a few nanometres in diameter and several micrometres (10^{-6} m) to centimetres long.



(a) Schematic of a single-walled carbon nanotube (SWNT)

(b) Schematic of a multi-walled carbon nanotube (MWNT)

Figure 5.5

Carbon nanotubes are the strongest and stiffest materials on earth, in terms of tensile strength and elastic modulus respectively. Bulk carbon nanotubes have already been used as composite fibers in polymers to improve the mechanical, thermal and electrical properties of the bulk product. Carbon nanotubes have also been successfully used in the construction of handlebars for mountain bikes. The handlebar, created by Easton, which has won awards for its incredible strength and light weight.

Carbon nanotubes have also been proposed as a possible gene delivery vehicle and for use in combination with radiofrequency fields to destroy cancer cells. Carbon nanotubes are said to have the strength of diamond, and research is being made into weaving them into clothes to create stab-proof and bulletproof clothing. The nanotubes would effectively stop the bullet from penetrating the body but the force and velocity of the bullet would be likely to cause broken bones and internal bleeding.

5.8 Quantum well

When layered in particular ways, doped silica can trap conduction electrons in a membrane so thin that, from one face to the other, their behavior as tiny quantum wave packets takes precedence over their behavior as particles. This structure is called a quantum well. From there, confining the electrons along a second dimension produces a quantum wire, and finally, with three dimensions, a quantum dot."

Here electrons are confined in one dimension (1D), free in other 2D. It can be realized by sandwiching a narrow-bandgap semiconductor layer between the wide-gap ones. A quantum well is often called a 3D electronic system.

5.9 Quantum wires

A strip of conducting material about 10 nanometers or less in width and thickness that displays quantum-mechanical effects like universal conductance fluctuations called quantum wires. It is another form of quantum dot, but unlike the three-dimension "dot," a quantum wire is confined only in two dimensions - that is it has "length," and allows the electrons to propagate in a "particle-like" fashion. Constructed typically on a semiconductor base, and (among other things) used to produce very intense laser beams, switchable up to multi-gigahertz per second.

Real quantum wires include polymer chains, nanowires and nanotubes. A single walled nanotube can have a diameter of 2 mm and a length of 100 μm , form a narrow dimensional structure called a *nanowire*.

5.10 Quantum dots

Quantum dots are semi-conducting crystals of nanometre dimensions. In other words nanocrystals (NCs), nanometer-size crystals of cadmium-based semiconductors are also referred to as quantum dots (QDs). Due to their incredibly small size (ranging from <1.5 to >8 nanometers), these usually non-fluorescing compounds develop intense, long-lasting colors excitable by UV and visible light LEDs, lasers, etc. The colors produced are a function of the particle size (blue to red and infrared, depending on the diameter of the nanocrystals) with the smallest NCs fluorescing in the blue and green. The fluorescence is due to a phenomenon called *quantum confinement*. Quantum confinement is the confinement of electrons in the nanoscale dimensions result in quantization of energy and momentum, and reduced dimensionality of electronic states.

When electrons and holes (exciton pairs) generated by photons are confined within a space, or quantum box, smaller than the Bohr exciton radius (i.e., the normal, off-the-shelf, preferred, bulk material electron-to-hole distance of an exciton pair), the semiconductor's band gap widens and its fluorescence shifts towards the blue. The smaller that box, the bluer the fluorescence. Conversely, the looser the confinement, the bigger the quantum box, the redder the fluorescence.

Eventually, one enters the infrared and the invisible. The fluorescence is generated when electron and hole recombine. The restricted confinement requires additional energy and this causes the wavelength shift.

Quantum dots are in fact very small physical cavities in which a finite number of particles, for example electrons, are trapped. These dots are commonly engineered by the current silicon technology. The physics behind quantum dot is very simple — quantum mechanics QM which is the most fundamental (and well accepted) theory currently known to mankind. QM governs the dynamics of everything in the microscopic world. Quantum dot is a physical (approximately) realization of the textbook example of the so-called particle-in-a-box which illustrates the quantization of energy when a particle is placed inside a (sufficiently small) box.

It has become recognized in recent years that the electronic and optical properties of metals and semiconductors change dramatically as the particulates of the materials are reduced to approach the nanometer size range of dimensions. At such size levels, the physical dimensions of the material may have a critical effect on the electronic or optical behaviour of the material. The restriction of the electronic wave function to smaller and smaller regions of space within a particle of material (the resonance cavity) is referred to as "quantum confinement".

In short, semiconductor structures in the nanometer size range, exhibiting the characteristics of quantum confinement, are commonly referred to as "quantum dots" when the confinement is in three dimensions, "quantum wires" when the confinement is in two dimensions, and "quantum wells" when the confinement is in one dimension.

Films of NCs in polymers or coatings on indium tin oxide (ITO) glass can produce electroluminescent devices. NCs are being used in solar cell research. Some manufacturers are talking about adding these crystals to fabrics for brighteners and intense colorants.

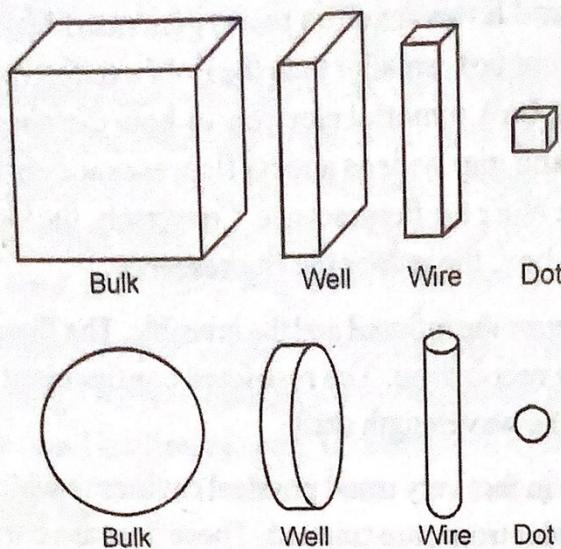


Figure 5.6: Generation of rectangular and curvilinear nanostructures

Despite the existence of ongoing work in the area of quantum dots for over a decade, the field remains one of the most interesting and cutting-edge areas of science.

5.11 Nanolithography

The word “lithography” originally referred to making objects from stones. A *lithograph* is an image (usually on paper) that is produced by carving a pattern on the stone, inking the stone, and then pushing the inked stone onto the paper.

Many types of small-scale lithography operate in very much this way. Indeed, the common methods used to make current computer chips normally use optical (or) x-ray lithography, in which a master mask is made using chemical methods and light passes through that mask to produce the actual chip structures. It works just like a silk screen for a T-shirt.

Nanoscale lithography really can't use visible light because the wavelength of visible light is at least 400 nanometers, so structures smaller than that are difficult to make directly using it. This is one of the reasons that continuing Moore's law into the nanoscale will require entirely new preparation methods.

Despite this, there are several techniques for doing small-scale lithography. One of the most straight forward and elegant is *micro-imprint lithography*, largely developed by George Whitesides and his research group at Harvard. This method works in the same way as the rubber stamps that are still found in post offices. A pattern is inscribed onto a rubber surface (in this case actually a rubber-like silicon/oxygen polymer), and that rubber surface is then coated with molecular ink. The ink

can then be stamped out onto a surface: this is paper in the post office, but it could be a metal, polymer, oxide, or any other surface in small-scale stamps. Small-scale stamping is more complex, but it is very inexpensive and can be used to make numerous copies. Originally, the stamps worked at the larger micron (1000-nanometer) scale, but recent improvements are bringing it to the nanoscale.

The technique of nanolithography is the patterning a thin film where the line resolution is below 100 nm. There are several primary techniques that are used for patterning in the nanoscale regime.

Electron beam lithography

X-ray lithography

Scanning probe microscope lithography

Nano imprint lithography

Dip pen nanolithography

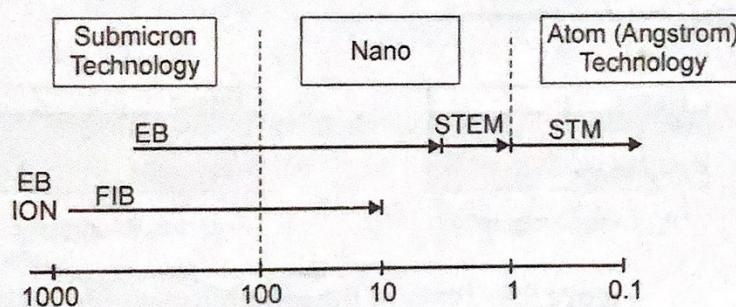


Figure 5.7: Focused Ion Beam (FIB)

Lithography involves the transfer of a pattern to a photosensitive material by selective exposure to a radiation source such as light. A photo sensitive material is the one that experiences a change in its physical properties when exposed to a radiation source. If we selectively expose a photosensitive material to radiation by masking some of the radiation, the pattern of the radiation is transferred to the material exposed.

5.11.1 Electron beam Lithography

Although optical lithography is most common, there exist other lithographic techniques, as depicted in figure 5.8. Electron lithography offers high resolution because of the small wavelength of electrons (≤ 0.1 nm for 10–50 keV electrons). The resolution of an electron lithographic system is not limited by diffraction, but rather by electron scattering in the resist (Figure 5.8 & Figure 5.9) and by the various aberrations of the electron optics.

The advantages of electron lithography are:

1. Generation of micron and submicron resist geometries
2. Highly automated and precisely controlled operation
3. Greater depth of focus
4. Direct patterning without a mask

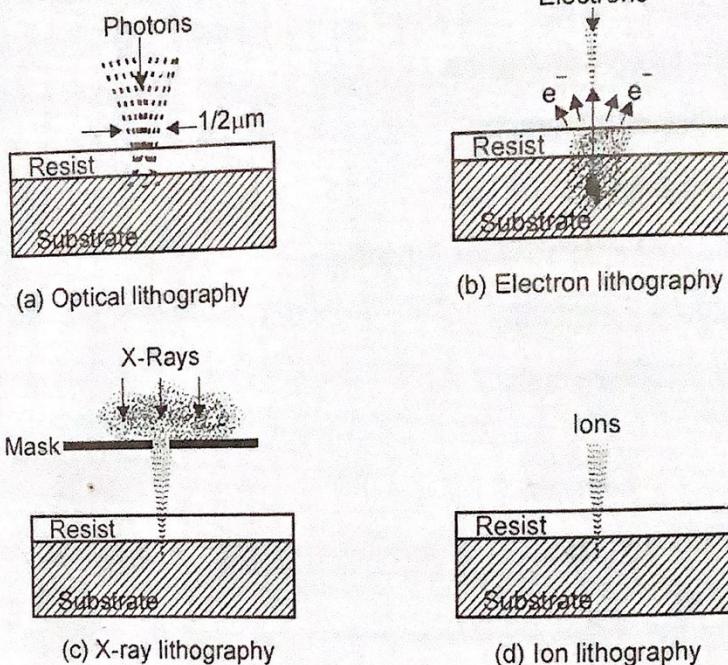


Figure 5.8: Types of lithographic methods

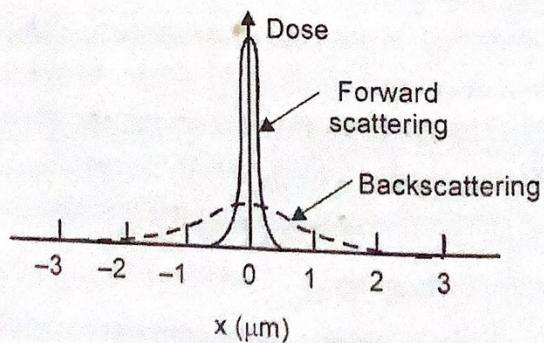
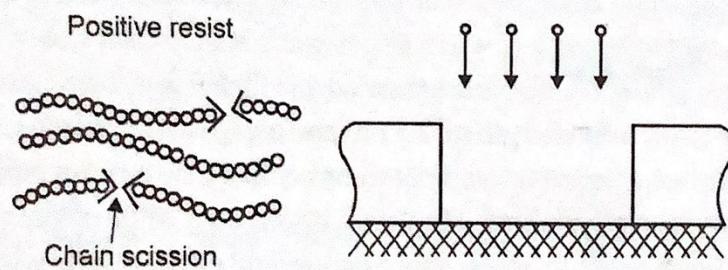


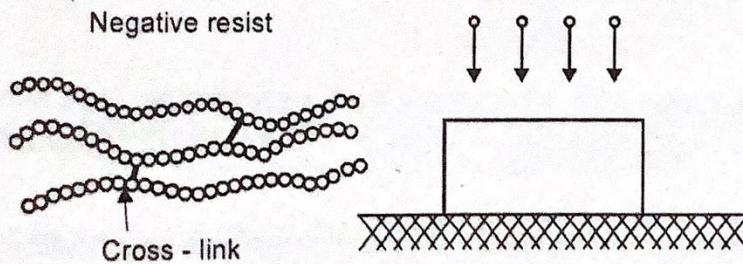
Figure 5.9: Dose distribution for forward scattering and backscattering at the resist - substrate interface

The biggest disadvantage of electron lithography is its low throughput (approximately 5 wafers / hour at less than $0.1\mu\text{m}$ resolution). Therefore, electron lithography is primarily used in the production of photomasks and in situations that require small number of custom circuits.

There are two basic ways to scan an electron beam. In raster scanning, the patterns are written by an electron beam that moves through a regular pattern. The beam scans sequentially over the entire area and is blanked off where no exposure is required. On the contrary, in vector scanning, the electron beam is directed only to the requested pattern features and hops from features to features. Time is therefore saved in a vector scan system.



(a) Schematic of the chemical reaction of a positive resist



(b) Schematic of the chemical reaction of a negative resist used in electron beam lithography

Figure 5.10

Electron resists are polymers. For a positive electron resist, the polymer-electron interaction causes chain scission, that is, broken chemical bonds (Figure 5.10(a)). The irradiated areas can be dissolved in a developer solution that attacks low-molecular-weight material. Common positive electron resists are poly (methyl methacrylate), abbreviated PMMA, and poly (butene-1 sulfone), abbreviated PBS. Positive electron resists typically have resolution of $0.1\mu\text{m}$ or better. When electrons

impact a negative electron resist, polymer linking is induced (Figure 5.10 (b)). Poly (glycidyl methacrylate-co-ethyl-acrylate), abbreviated COP, is a common negative electron resist. Like a negative photoresist, COP swells during developing, and resolution is limited to about 1 μm .

Electron beam lithography is usually done with SEM and scanned at a controlled rate over the surface of some type of resist material. The scan rate is adjusted to deliver dose to a selected area of the resist. The e^- beam interacts with the material sufficiently to remove the resist material.

5.11.2 X-ray Lithography

X-ray lithography employs a shadow printing method similar to optical proximity printing. The x-ray wavelength (0.4 to 5 nm) is much shorter than that of UV light (200 to 400 nm). Hence, diffraction effects are reduced and higher resolution can be attained. For instance, for an x-ray wavelength of 0.5 nm and a gap of 40 μm , l_m is equal to 0.2 μm . X-ray lithography has a higher throughput when compared to e-beam lithography because parallel exposure can be adopted. However, on account of the finite size of the x-ray source and the finite mask-to-wafer gap, a penumbral effect results which degrades the resolution at the edge of a feature. As shown in Figure 5.11, the penumbral blur, on the edge of the resist image is given by:

$$\delta = ag / L \quad \dots(5.1)$$

where a is the diameter of the x-ray source, g is the gap spacing, and L is the distance from the source to the x-ray mask. If $a = 3 \text{ mm}$, $g = 40 \mu\text{m}$, and $L = 50 \text{ cm}$, δ is on the order of 0.2 μm .

An additional geometric effect is the lateral magnification error due to the finite mask-to-wafer gap and the non-vertical incidence of the x-ray beam. The projected images of the mask are shifted laterally by an amount d , called runout:

$$\delta = rg / L \quad \dots(5.2)$$

where r denotes the radial distance from the center of the wafer. For a 125-mm wafer, the runout error can be as large as 5 μm for $g = 40 \mu\text{m}$ and $L = 50 \text{ cm}$. This runout error must be compensated for during the mask making process.

Electron beam resists can be used in x-ray lithography because when an x-ray photon impinges on the specimen, electron emission results. One of the most attractive x-ray resist is DCOPA (dichloropropyl acrylate and glycidyl methacrylate-co-ethyl acrylate), as it has a relatively low threshold ($\sim 10 \text{ mJ/cm}^2$).

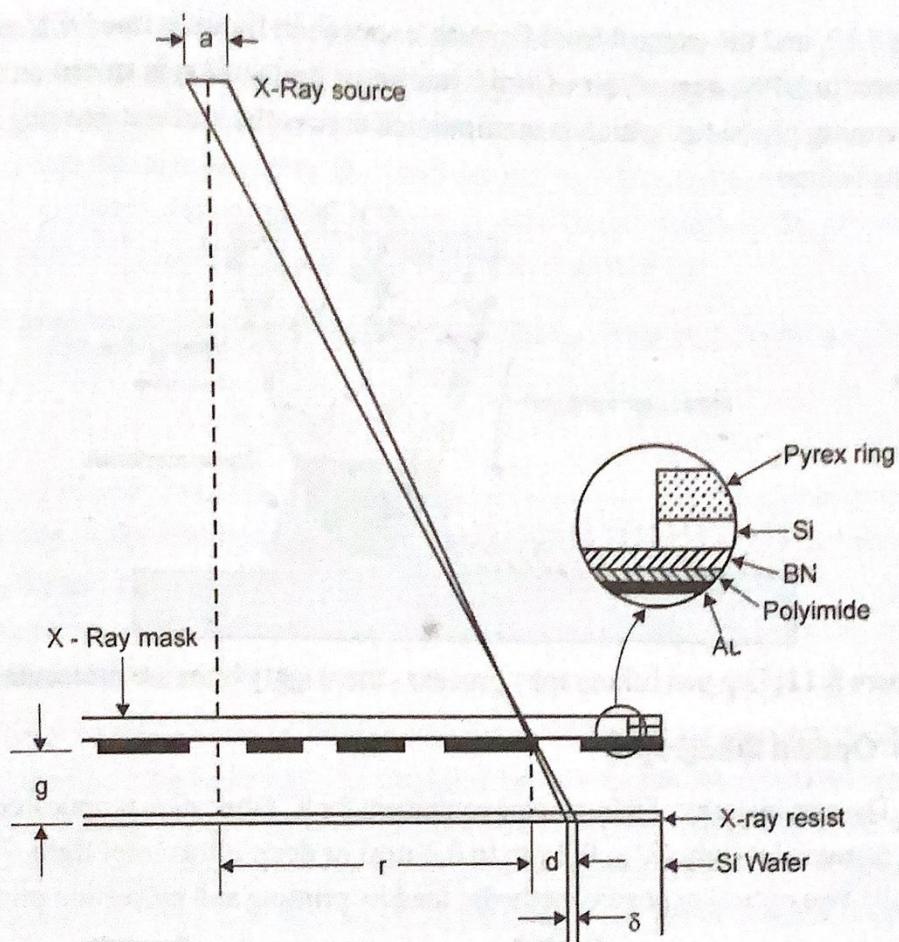


Figure 5.11: Geometric effects in X-ray lithography.

Insert shows the X-ray mask structure

Here the mask is made of an x-ray transparent material with a pattern of high Z material either etched or deposited on it. The mask is held in proximity to the wafer and exposed to x-rays. The mask is the limiting factor in x-ray lithography. The resolution of the pattern is depending on the variations in the mask. Another concern in the pattern accuracy is the accuracy of the pattern created on the mask.

5.11.3 Dip Pen Nanolithography

One way to construct arbitrary structures on surfaces is to write them in exactly the same way that we write ink lines using a fountain pen. To make such lines at the nanoscale, it is necessary to have a nano-pen. Fortunately, AFM tips are ideal nano-pens. *Dip pen nanolithography* (DPN) is named after the old-fashioned dip pen that was used in schoolrooms in the 19th century. The principle of DPN is shown in

figure 5.12, and the excerpt from Feyman's speech in figure is one DPN-assembled structure. In DPN, a reservoir of "ink" (atoms or molecules) is stored on the top of the scanning probe tip, which is manipulated across the surface, leaving lines and patterns behind.

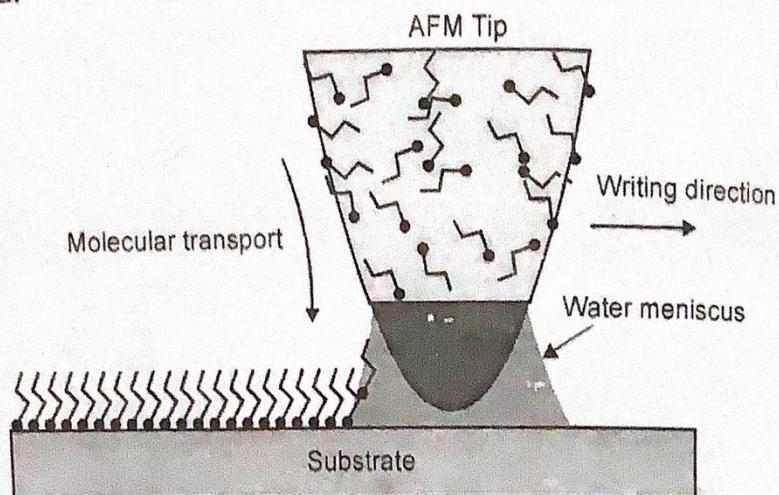
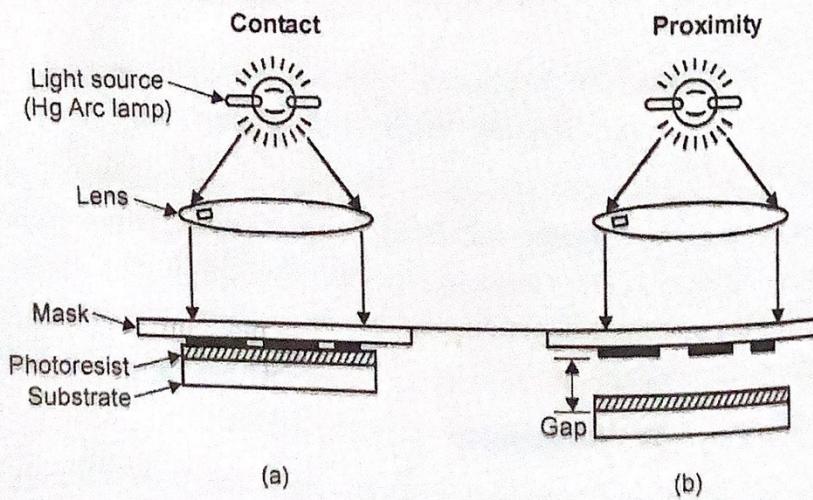


Figure 5.12: Dip pen lithography process - the wiggly lines are molecular "ink"

5.11.4 Optical lithography

The vast majority of lithographic equipment for IC fabrication is optical equipment using ultraviolet light ($\lambda \approx 0.2 \mu\text{m}$ to $0.4 \mu\text{m}$) or deep ultraviolet light. There are basically two optical exposure methods: shadow printing and projection printing.



(a) Contact printing, (b) Proximity printing.

Figure 5.13

In shadow printing, the mask and wafer may be in direct contact, as in contact printing, or in close proximity, as in proximity printing (Figure 5.13). Contact printing

yields very high resolution ($\sim 1 \mu\text{m}$), but suffers from major drawback caused by dust particles or silicon specks accidentally embedded into the mask, thereby causing permanent damage to the mask and defects in the wafers. Proximity printing is not as prone to particle damage. However, the small gap between the mask and wafer (typically $10 \mu\text{m}$ to $50 \mu\text{m}$) introduces optical diffraction at the feature edges on the photomasks and the resolution is typically degraded to the 2 to $5 \mu\text{m}$ regime.

The minimum line-width that can be printed, l_m , in shadow printing is roughly given by

$$l_m = (\lambda g)^{1/2} \quad \dots(1)$$

where λ is the wavelength of the exposure radiation and g is the gap between the mask and the wafer and includes the thickness of the resist. For typical values of λ ($\sim 0.4 \mu\text{m}$) and g ($\sim 50 \mu\text{m}$), l_m is on the order of $4.5 \mu\text{m}$. Equation (1) imparts that the minimum linewidth can be improved by reducing the wavelength λ (that is, going to deep UV spectral region) or the gap g .

In order to circumvent problems associated with shadow printing, projection printing exposure tools have been developed to project an image of the mask patterns onto a resist-coated wafer many centimeters away from the mask. The small image area is scanned or stepped over the wafer to cover the entire surface. Figure 5.14 depicts the various ways to project and scan the image. The resolution of a projection system is given by

$$l_m = \lambda / NA \quad \dots(2)$$

where λ is the wavelength of the exposure radiation and NA is the numerical aperture given by

$$NA = \bar{n} \sin \theta \quad \dots(3)$$

where \bar{n} denotes the refractive index of the imaging medium ($\bar{n} = 1$ in air) and θ is the half angle of the cone of light converging to a point image at the wafer as shown in Figure 5.14. The depth of focus, Δz , can be expressed as

$$\Delta z = \pm \frac{l_m}{2 \tan \theta} \approx \pm \frac{l_m}{2 \sin \theta} = \pm \frac{\bar{n} \lambda}{2 (NA)^2} \quad \dots(4)$$

Resolution can be enhanced by reducing λ and this explains the trend towards shorter wavelength in optical lithography. Typically, scanning projection systems are

capable of about $1 \mu\text{m}$ resolution, while step-and-repeat projection systems can accomplish deep sub-micrometer spatial resolution demanded by modern integrated circuits, especially when coupled with deep UV radiation sources.

Clean Room

An IC fabrication facility requires a clean room, particularly in lithography areas. Dust particles settling on semiconductor wafers and lithographic masks can cause defects in the devices. In a clean room, the total number of dust particles per unit volume must be tightly controlled along with other parameters, such as temperature, humidity, pressure and so on.

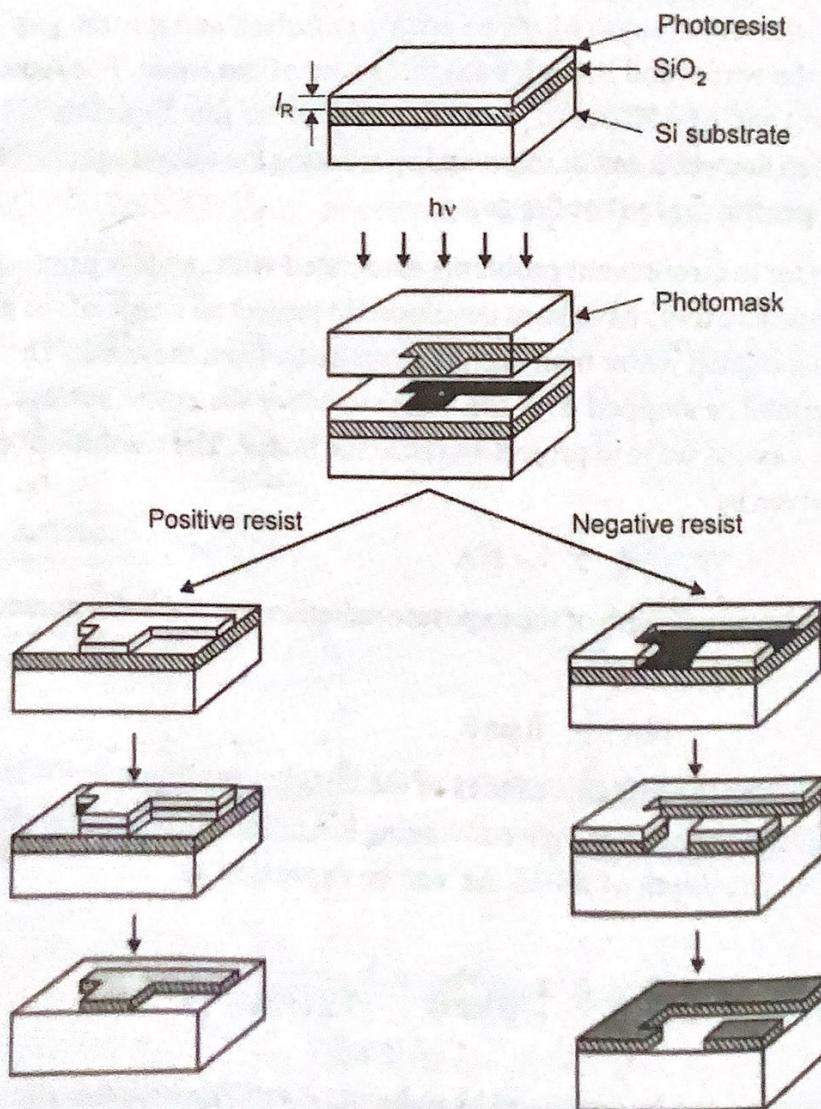


Figure 5.14: Optical lithographic transfer process