UNIT-III

3. Applications: Applications of nanoparticles, quantum dots, nanowires and thin films for photonic devices (LED, solar cells).

Applications of Quantum Dots:

Quantum dots (QD) are semiconductor nanocrystals which exhibit quantum mechanical behaviour. The interesting electronic properties of quantum dots arise from the specific size of their energy band gaps. The high extinction coefficient of a quantum dot makes it perfect for optical uses. Quantum dots of very high quality can be ideal for applications in optical encoding and multiplexing due to their narrow emission spectra and wide excitation profiles. Important applications of Quantum Dots in optical field are given below.

a) Light Emitting Diodes:

Quantum dot light emitting diodes (QD-LED) and 'QD-White LED' are very useful when producing the displays for electronic devices because they emit light in highly specific Gaussian distributions. QD-LED displays can render colours very accurately and use much less power than traditional displays.

b) Photovoltaics:

Quantum dot solar cells are much more cost-effective when compared to silicon solar cells. Quantum dot solar cells can be produced using simple chemical reactions and can help to save manufacturing costs as a result.

Operational efficiency is also greatly improved by using quantum dots. In traditional silicon p-n junction solar cells, when a photon with energy less than the bandgap of silicon hits the solar cell it is transmitted and does not contribute to the power output. This results in a trade-off in design, if the bandgap is lower more incoming photons can excite electrons (meaning a higher current) but the electrons have lower energy (thus lower voltage) and vice versa for a higher bandgap. Theoretical peak solar efficiency for a silicon p-n solar cell is 33.7%.

Quantum dots can offer a significant increase in efficiency, by using dots of varying sizes top of each other with the largest band gaps on top. Incoming photons will be transmitted until reaching a layer with a bandgap smaller than the photon energy. With enough layers each photon will excite an electron with a bandgap close to its own energy and thus waste a small amount of energy. When the number of layers approaches infinity, the efficiency approaches a theoretical thermodynamic limit of 86%.

c) Photodetectors:

Quantum dot photodetectors (QDPs) can be produced from traditional single-crystalline semiconductors or solution-processed. Solution-processed QDPs are ideal for the integration of several

substrates and for use in integrated circuits. These colloidal QDPs find use in machine vision, surveillance, spectroscopy and industrial inspection.

Single electron transfer devices:

The manipulation of single electrons was demonstrated in the seminal experiments by Millikan at the very beginning of the 20th century, but in solid state circuits it was not implemented until the late 1980s. The main reason for this delay is that the manipulation requires the reproducible fabrication of very small conducting particles, and their accurate positioning against external electrodes. The necessary nanofabrication techniques have become available during the past two decades, and have made possible a new field of solid state physics, single-electronics.

Let a small conductor (traditionally called an island) be initially electro neutral, i.e. have exactly as many (m) electrons as it has protons in its crystal lattice. In this state the island does not generate any appreciable electric field beyond its borders, and a weak external force F may bring in an additional electron from outside. (In most single-electron devices, this injection is carried out by tunnelling through an energy barrier created by a thin insulating layer). Now the net charge Q of the island is (-e), and the resulting electric field E repulses the following electrons which might be added. Though the fundamental charge $e \approx 1.6\times10^{-19}$ Coulomb is very small on the human scale of things, the field E is inversely proportional to the square of the island size, and may become rather strong for nanoscale structures. For example, the field is as large as ~140 kV/cm on the surface of a 10-nm sphere in vacuum.

The theory of single-electron phenomena shows that a more adequate measure of the strength of these effects is not the electric field, but the charging energy

$$E_C = e^2/C \quad \text{..... (1)}$$

where C is the capacitance of the island. When the island size becomes comparable with the de Broglie wavelength of the electrons inside the island, their energy quantization becomes substantial. In this case the energy scale of the charging effects is given by a more general notion, the electron addition energy E_a. In most cases of interest, E_a may be well approximated by the following simple formula:

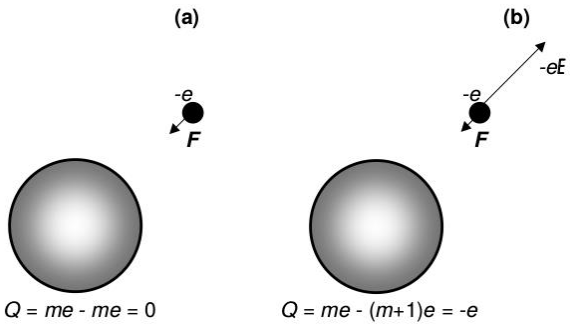
$$E_a = E_C + E_k \quad \text{..... (2)}$$

Here E_k is the quantum kinetic energy of the added electron; for a degenerate electron gas $E_k = 1/g(\varepsilon_F)V$, where V is the island volume and $g(\varepsilon_F)$ is the density of states on the Fermi surface.

If the island size is reduced below ~10 nm, E_a approaches 100 meV, and some single-electron effects become visible at room temperature. However, most suggested digital single-electron devices require even higher values of E_a (~ 100 k_BT) in order to avoid thermally-induced random tunneling events, so that for room temperature operation the electron addition energy E_a has to be as large as a few electron-volts, and the minimum feature size of single-electron devices has to be smaller than ~1 nm.

In this size range the electron quantization energy E_k becomes comparable with or larger than the charging energy E_C for most materials; this is why islands of this small size are called as quantum dots. Their use involves not only extremely difficult nanofabrication technology, but also some major physics problems including the high sensitivity of transport properties to small variations of the quantum dot size and shape.

This is why it is very important to develop single-electron devices capable of operating with the lowest possible ratio E_a/k_BT. As we will see below, some devices may work in the size range where $E_C > E_k$ even at room temperature, thus avoiding complications stemming from the energy quantization effects.



The basic concept of single-electron control: a conducting island (a) before and (b) after the addition of a single electron. The addition of a single uncompensated electron charge creates an electric field E which may prevent the addition of the following electrons.

Devices based on Single electron transfer:

a) Single-Electron Box:

It is an electronic device that is based on single electron transfer. Figure (a) shows the conceptually simplest device, the "single-electron box". The device consists of just one small island separated from a larger electrode ("electron source") by a tunnel barrier. An external electric field may be applied to the island using another electrode ("gate") separated from the island by a thicker insulator which does not allow noticeable tunneling. The field changes the electrochemical potential of the island and thus determines the conditions of electron tunneling.

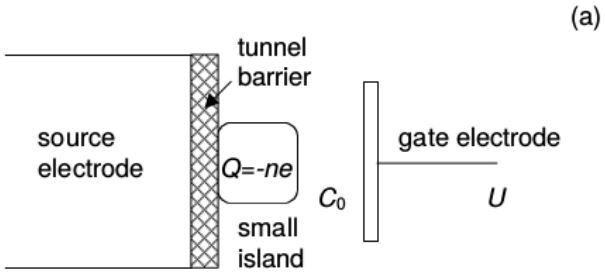
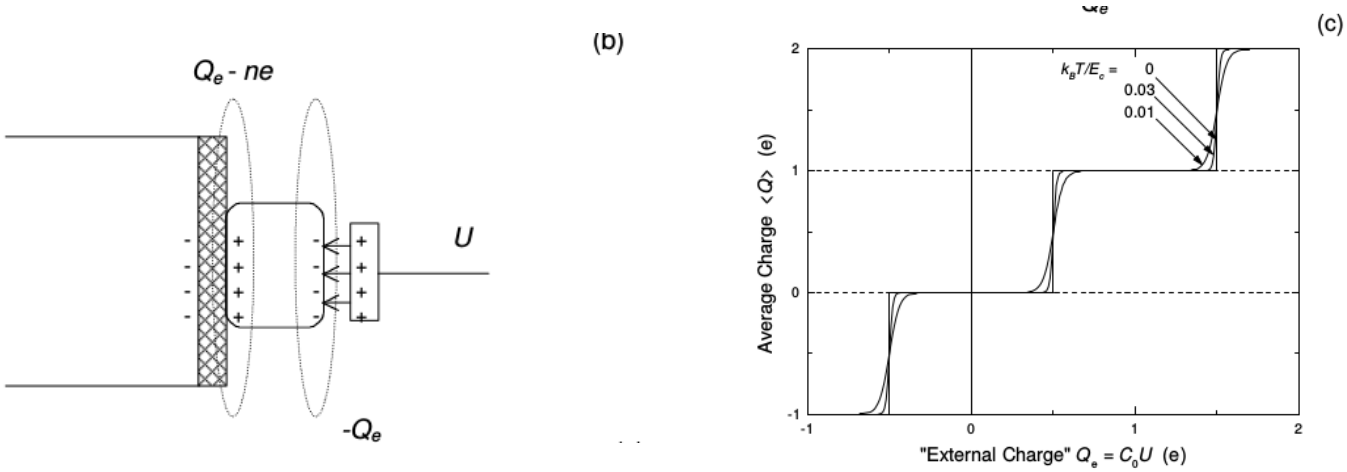


Figure (b) shows a particular geometry in which the "external charge" $Q_e = C_0U$ can be readily visualized, and (c) the "Coulomb staircase", i.e. the step-like dependence of the average charge $Q = -ne$ on the gate voltage, for several values of temperature. The increasing gate voltage U attracts more and more electrons to the island. The discreteness of electron transfer through low-transparency barriers necessarily makes this increase step-like.

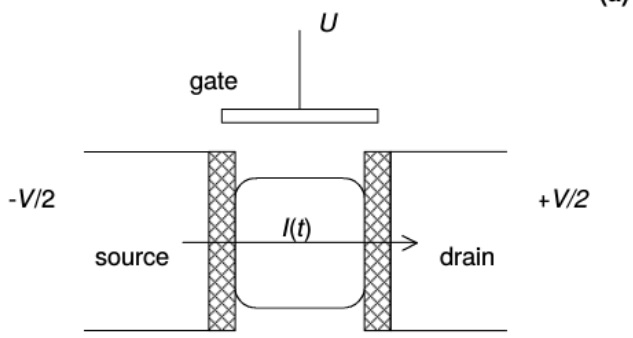


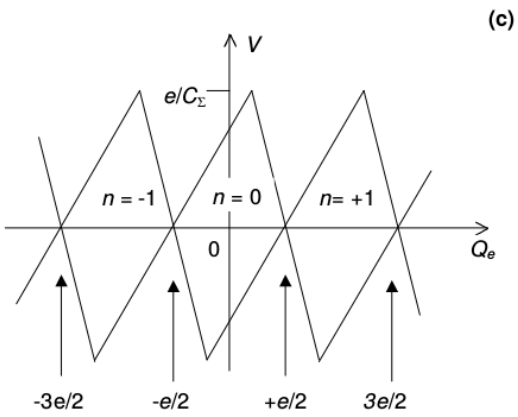
b) Single-electron Transistor:

Schematic diagram of single electron transistor is shown in figure (a). The device is reminiscent of a usual MOSFET, but with two tunnel barriers embedded in a small conducting island, instead of the usual inversion channel. The most important property of the single-electron transistor is that the threshold voltage, as well as the source-drain current in its vicinity, is a periodic function of the gate voltage, with the period given by the equation

$$\Delta Q_e = e \quad \text{and} \quad \Delta U = e/C_0 = \text{const.}$$

If U is changed by $\Delta U = e/C_0$, Q_e changes by *e*, and may be exactly compensated for by one of the electrons tunneling into/from the island. The effect of the gate voltage is equivalent to the injection of charge $Q_e = C_0 U$ into the island and thus changes the balance of the charges at tunnel barrier capacitances C_1 and C_2, which determines the Coulomb blockade threshold V_t .





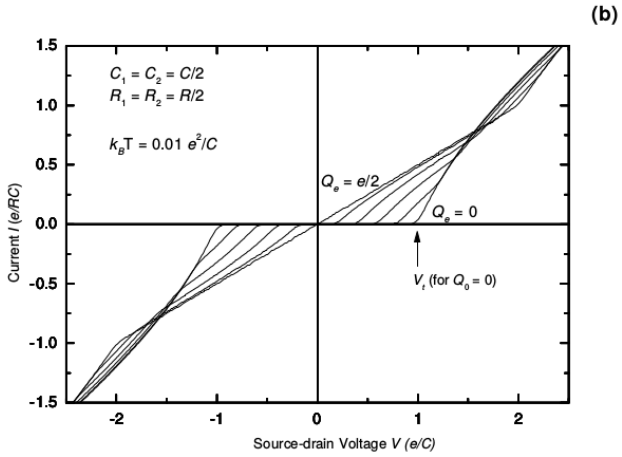


Figure (b) shows source-drain dc I-V curves of a symmetric transistor for several values of the Q_e, i.e. of the gate voltage of a capacitively-coupled single-electron transistor, and figure (c) shows the Coulomb blockade threshold voltage V_t as a function of Q_e at $T \rightarrow 0$. Materials and fabrication methods of some of the single electron transistors are given table 1.

Table 1. Some high-E_a single-electron transistors.

Materials (Island; Barrier)	Fabrication Method	Highest E_a (meV)
Al; AlO_x	Evaporation through an e-beam-formed mask	23
CdSe; organics	Nanocrystal binding to prepatterned Au electrodes	60
Al; AlO_x	Evaporation on a Si_3N_4 membrane with a nm-scale orifice	92
Ti; Si	Metal deposition on prepatterned silicon substrates	120
Carboran molecule	E-beam patterned, thin-film gate; STM electrode	130
Si; SiO_2	E-beam patterning + oxidation of a SIMOX layer	150
Nb, NbO_x	Anodic oxidation using scanning probe	1,000

c) SET Oscillators:

SET oscillations imply that the Ohmic resistor provides a continuous transfer of charge, i.e. is capable of transferring sub-single-electron amounts of electricity in order to recharge the island capacitance in time intervals between the subsequent tunnelling events. This assumption is supported by the observation that the macroscopic diffusive conductors do not exhibit shot noise at voltages $V > k_BT/e$, as should happen at the discrete transfer of electrons. The theoretical explanation of the continuous conduction in such conductors is based on the extended character of the electron. For the implementation of a narrowband SET oscillator, however, the Ohmic resistor has to combine the continuous transfer of charge with very high resistance (~1 MΩ or higher) and very small stray capacitance ($\sim C << e^2 / k_BT$).

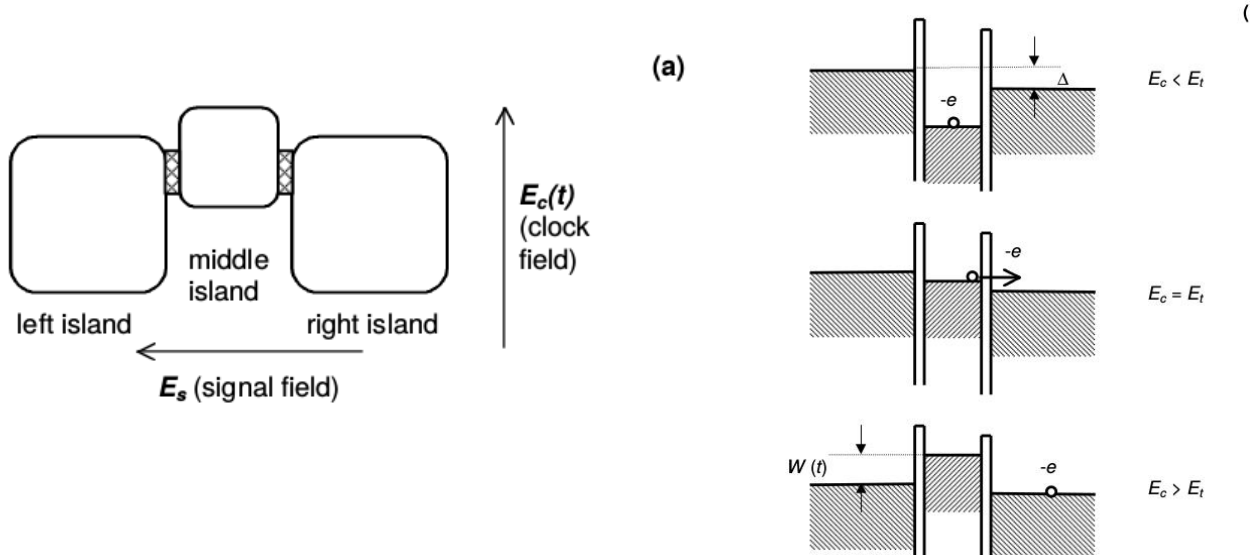
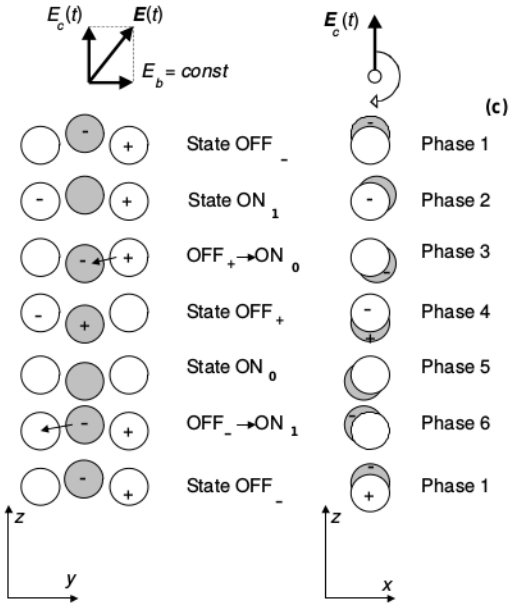


Figure (a) shows the schematic diagram of a SET oscillator, figure (b) shows the energy diagram at 3 values of the clock field $E_C(t)$. Energy difference Δ between the edge islands is proportional to the signal field E_S , while the energy shift W(t) of the middle island is determined by the clock field. A shift register using a variety of SET Parametron cells ("single-exciton parametrons") which do not require the initial charging is shown in figure (c).



CNT based transistors:

A **carbon nanotube field-effect transistor (CNTFET)** refers to a field-effect transistor that utilizes a single carbon nanotube or an array of carbon nanotubes as the channel material instead of bulk silicon in the traditional MOSFET structure.

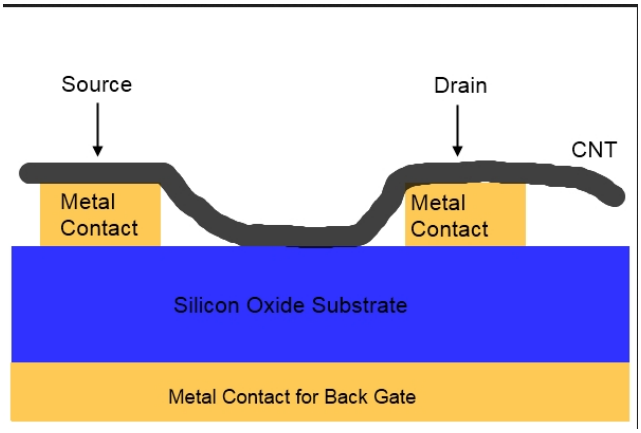
A carbon nanotube's bandgap is directly affected by its chirality and diameter. If those properties can be controlled, CNTs would be a promising candidate for future nano-scale transistor devices.

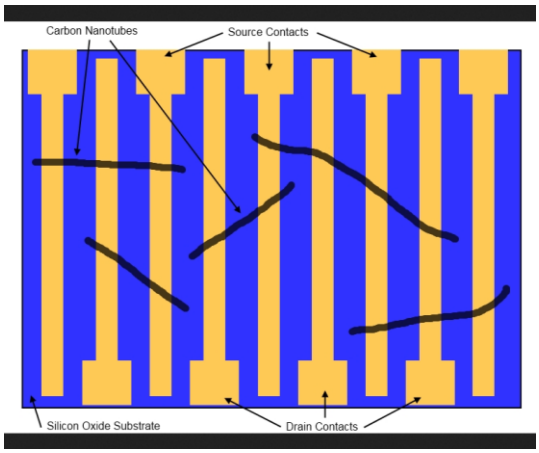
Moreover, because of the lack of boundaries in the perfect and hollow cylinder structure of CNTs, there is no boundary scattering. CNTs are also quasi-1D materials in which only forward scattering and back scattering are allowed, and elastic scattering mean free paths in carbon nanotubes are long, typically on the order of micrometers. As a result, quasi-ballistic transport can be observed in nanotubes at relatively long lengths and low fields.

Because of the strong covalent carbon–carbon bonding in the sp^2 configuration, carbon nanotubes are chemically inert and are able to transport large amounts of electric current. In theory, carbon nanotubes are also able to conduct heat nearly as well as diamond or sapphire, and because of their miniaturized dimensions, the CNTFET should switch reliably using much less power than a silicon-based device.

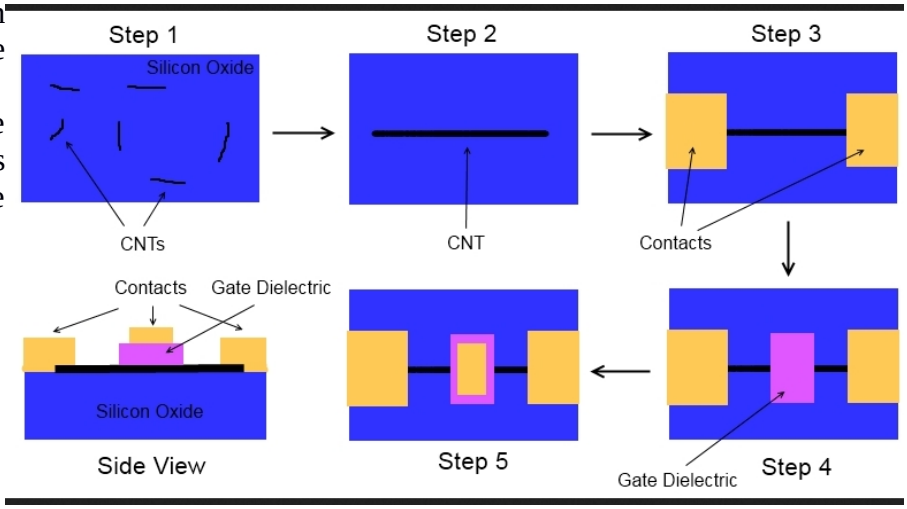
Types of CNTFET devices and their fabrication is given below:

a) Back-gated CNTFETs: They involve pre-patterning parallel strips of metal across a silicon dioxide substrate, and then depositing the CNTs on top in a random pattern. One metal strip is the "source" contact while the other is the "drain" contact. The silicon oxide substrate can be used as the gate oxide and adding a metal contact on the back makes the semiconducting CNT gateable. The structure of back-gated CNT FET is shown below.



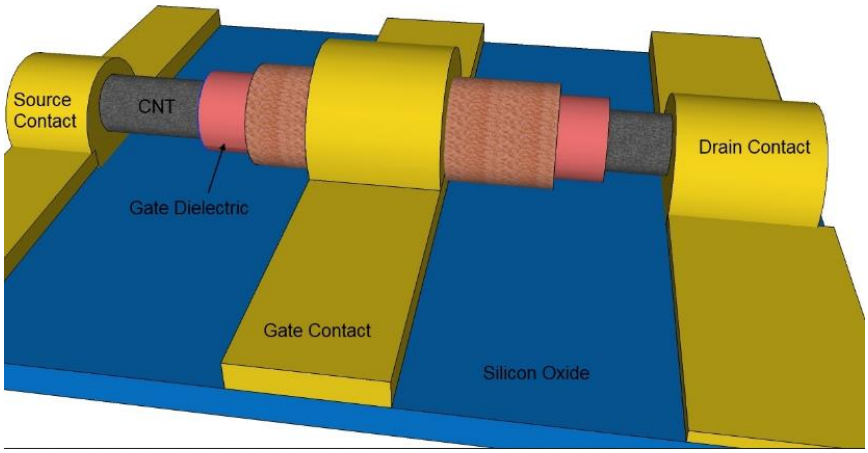


b) Top-gated CNTFETs: Individual nanotubes are located via atomic force microscope or scanning electron microscope. After an individual tube is isolated, source and drain contacts are defined and patterned using high resolution electron beam lithography. A high temperature anneal step reduces the contact resistance by improving adhesion between the contacts and CNT. A thin top-gate dielectric is then deposited on top of the nanotube, either via evaporation or atomic layer deposition. Finally, the top gate contact is deposited on the gate dielectric, completing the process as shown in the figure.

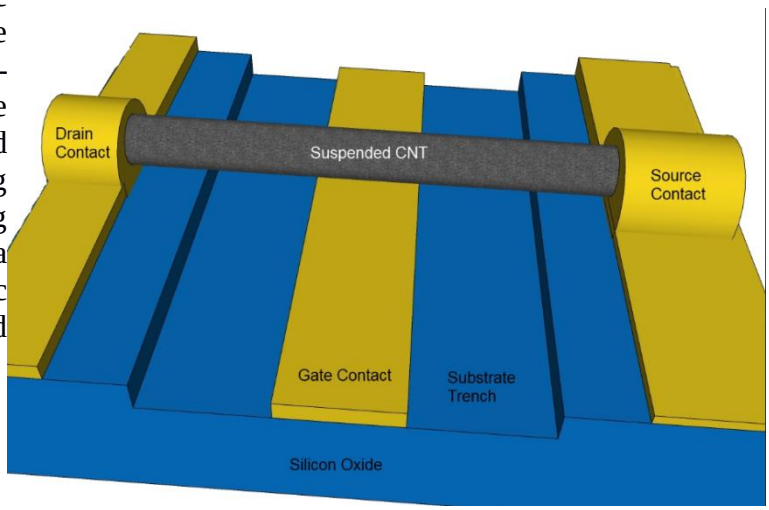


c) Wrap-around gate CNTFETs: Wrap-around gate CNTFETs, also known as gate-all-around CNTFETs and are a further improvement upon the top-gate device geometry. In this device, instead of gating just the part of the CNT that is closer to the metal gate contact, the entire circumference of the nanotube is gated. This should ideally improve the electrical performance of the CNTFET, reducing leakage current and improving the device on/off ratio.

Device fabrication begins by first wrapping CNTs in a gate dielectric and gate contact via atomic layer deposition. These wrapped nanotubes are then solution-deposited on an insulating substrate, where the wrappings are partially etched off, exposing the ends of the nanotube. The source, drain, and gate contacts are then deposited onto the CNT ends and the metallic outer gate wrapping.

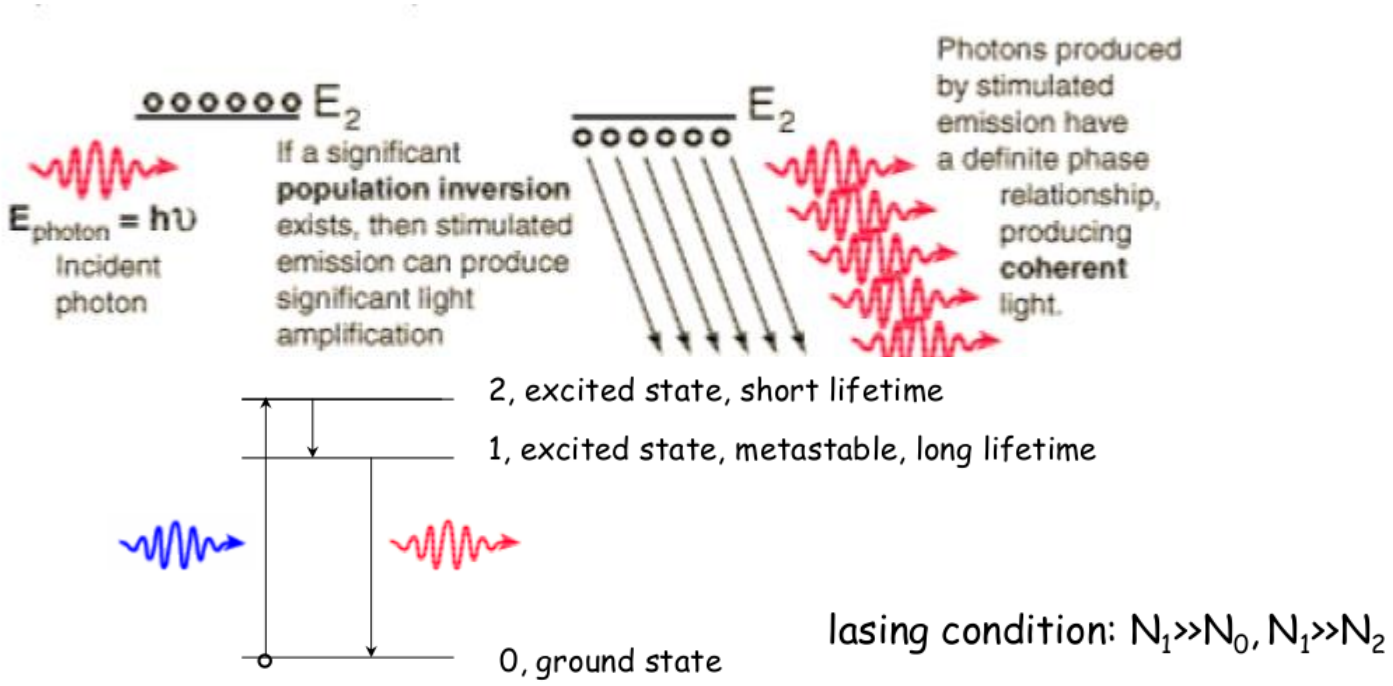


d) Suspended CNTFETs: Another CNTFET device geometry involves suspending the nanotube over a trench to reduce contact with the substrate and gate oxide. This technique has the advantage of reduced scattering at the CNT-substrate interface, improving device performance. There are many methods used to fabricate suspended CNTFETs, ranging from growing them over trenches using catalyst particles, transferring them onto a substrate and then under-etching the dielectric beneath, and transfer-printing onto a trenched substrate as shown in figure.



Nanomaterial Devices: Quantum dots heterostructures lasers,

A **quantum dot laser** is a semiconductor laser that uses quantum dots as the active laser medium in its light emitting region. Due to the tight confinement of charge carriers in quantum dots, they exhibit an electronic structure similar to atoms. Lasers fabricated from such an active media exhibit device performance that is closer to gas lasers, and avoid some of the negative aspects of device performance associated with traditional semiconductor lasers based on bulk or quantum well active media. Improvements in modulation bandwidth, lasing threshold, relative intensity noise, linewidth enhancement factor and temperature insensitivity have all been observed. The quantum dot active region may also be engineered to operate at different wavelengths by varying dot size and composition. This allows quantum dot lasers to be fabricated to operate at wavelengths previously not possible using semiconductor laser technology.
Laser process is briefly discussed here:



- Visible diode lasers:
  - 670 nm, 630 nm (commercial)
  - green, blue, violet in laboratory (ZnSe, GaN)

✓ Optical memories (spot size $\propto \lambda$)

✓ Replace in many applications gas lasers (HeNe)

- Bar-code scanners
- Measurement applications
- Printers
- Medical applications

✓ HeNe-laser survives in applications where good beam quality essential

Important semiconductor laser materials

Compound	Wavelengths (nm)	Notes
GaN	<400 →	1995
ZnSe	460-530	first demonstrated 1991
AlGaInP	630-680	
$Ga_{0.5}In_{0.5}P$	670	active layer between AlGaInP layers; long room-temperature lifetime
$Ga_{1-x}Al_xAs$	620-895	x=0 to 0.45; lifetimes very short for wavelengths below 720 nm
GaAs	904	
$In_{0.2}Ga_{0.8}As$	980	strained layer on GaAs substrate
$In_{1-x}Ga_xAs_yP_{1-y}$	1100-1650	InP substrate
$In_{0.73}Ga_{0.27}As_{0.58}P_{0.42}$	1310	major fiber-communication wavelength
$In_{0.58}Ga_{0.42}As_{0.9}P_{0.1}$	1550	major fiber-communication wavelength
InGaAsSb	1700-4400	possible range, developmental, on GaSb substrate
PbEuSeTe	3300-5800	cryogenic
PbSSe	4200-8000	cryogenic
PbSnTe	6300-29000	cryogenic
PbSnSe	8000-29000	cryogenic

optical switching and optical data storage. Magnetic quantum well; magnetic dots - magnetic data storage.

Microelectromechanical systems (MEMS)

Microelectromechanical systems (**MEMS**, also written as *micro-electro-mechanical*, *Micro Electro Mechanical* or *microelectronic and microelectromechanical systems* and the related *micro mechatronics*) is the technology of microscopic devices, particularly those with moving parts. It merges at the nano-scale into nanoelectromechanical systems (NEMS) and nanotechnology.

MEMS are made up of components between 1 and 100 micrometres in size (i.e., 0.001 to 0.1 mm), and MEMS devices generally range in size from 20 micrometres to a millimetre (i.e., 0.02 to 1.0 mm), although components arranged in arrays (e.g., digital micromirror devices) can be more than $1000mm^2$. They usually consist of a central unit that processes data (the microprocessor) and several components that interact with the surroundings such as microsensors. Because of the large surface area to volume

ratio of MEMS, forces produced by ambient electromagnetism (e.g., electrostatic charges and magnetic moments), and fluid dynamics (e.g., surface tension and viscosity) are more important design considerations than with larger scale mechanical devices. MEMS technology is distinguished from molecular nanotechnology or molecular electronics in that the latter must also consider surface chemistry.

Materials for MEMS manufacturing:

The fabrication of MEMS evolved from the process technology in semiconductor device fabrication, i.e. the basic techniques are deposition of material layers, patterning by photolithography and etching to produce the required shapes

i) Silicon: Silicon is the material used to create most integrated circuits used in consumer electronics in the modern industry. The economies of scale, ready availability of inexpensive high-quality materials, and ability to incorporate electronic functionality make silicon attractive for a wide variety of MEMS applications. Silicon is very reliable as it suffers very little fatigue and can have service lifetimes in the range of billions to trillions of cycles without breaking.

ii) Polymers: MEMS devices can be made from polymers by processes such as injection molding, embossing or stereolithography and are especially well suited to microfluidic applications such as disposable blood testing cartridges.

iii) Metals: Metals can also be used to create MEMS elements because they exhibit very high degrees of reliability. Commonly used metals include gold, nickel, aluminium, copper, chromium, titanium, tungsten, platinum, and silver.

iv) Ceramics: The nitrides of silicon, aluminium and titanium as well as silicon carbide and other ceramics are increasingly applied in MEMS fabrication due to advantageous combinations of material properties.

MEMS Fabrication:

MEMS can be created by Deposition processes such as Physical vapor deposition (PVD), Sputtering, chemical vapor deposition (CVD), LPCVD (Low Pressure chemical vapor deposition) and PECVD (Plasma-enhanced chemical vapor deposition).

MEMS can also be created by patterning or lithography techniques such as Electron beam lithography, Ion beam lithography, Ion track technology, X-ray lithography and Diamond patterning.

MEMS can also be created by Etching processes such as Isotropic etching, Anisotropic etching, (Hydrofluoric Acid) HF etching, Electrochemical etching, Vapor etching, Plasma etching and Reactive ion etching (RIE).

Applications of MEMS:

- Used in Inkjet printers
- Used in Accelerometers in modern cars
- MEMS Accelerometers and MEMS gyroscopes in remote controlled helicopters, planes and multirotors (also known as drones), used for automatically sensing and balancing flying characteristics of roll, pitch and yaw.
- MEMS microphones in portable devices, e.g., mobile phones, head sets and laptops
- Used in Silicon pressure sensors e.g., car tire pressure sensors, and disposable blood pressure sensors

- Bio-MEMS applications in medical and health related technologies
- Used in Digital micromirror device (DMD) chip in a projector based on DLP technology
- Used in Micromachined ultrasound transducers

Nanoelectromechanical systems (NEMS):

Nanoelectromechanical systems (**NEMS**) are a class of devices integrating electrical and mechanical functionality on the nanoscale. NEMS form the logical next miniaturization step from so-called microelectromechanical systems, or MEMS devices. NEMS typically integrate transistor-like nanoelectronics with mechanical actuators, pumps, or motors, and may thereby form physical, biological, and chemical sensors. The name derives from typical device dimensions in the nanometer range, leading to low mass, high mechanical resonance frequencies, potentially large quantum mechanical effects such as zero point motion, and a high surface-to-volume ratio useful for surface-based sensing mechanisms. Uses include accelerometers, or detectors of chemical substances in the air.

NEMS Fabrication:

Two complementary approaches to fabrication of NEMS can be found. The top-down approach uses the traditional microfabrication methods, i.e. optical, electron beam lithography and thermal treatments, to manufacture devices. While being limited by the resolution of these methods, it allows a large degree of control over the resulting structures. In this manner devices such as nanowires, nanorods, and patterned nanostructures are fabricated from metallic thin films or etched semiconductor layers.

Bottom-up approaches, in contrast, use the chemical properties of single molecules to cause single-molecule components to self-organize or self-assemble into some useful conformation, or rely on positional assembly. These approaches utilize the concepts of molecular self-assembly and/or molecular recognition. This allows fabrication of much smaller structures, albeit often at the cost of limited control of the fabrication process.

A combination of these approaches may also be used, in which nanoscale molecules are integrated into a top-down framework. One such example is the carbon nanotube nanomotor.

Materials used for NEMS:

i) Carbon allotropes: Many of the commonly used materials for NEMS technology have been carbon based, specifically diamond, carbon nanotubes and graphene. This is mainly because of the useful properties of carbon based materials which directly meet the needs of NEMS. The mechanical properties of carbon (such as large Young's modulus) are fundamental to the stability of NEMS while the metallic and semiconductor conductivities of carbon based materials allow them to function as transistors.

ii) Metallic carbon nanotubes: Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. They can be considered a rolled up graphene. Metallic carbon nanotubes have also been

proposed for nanoelectronic interconnects since they can carry high current densities. This is a useful property as wires to transfer current are another basic building block of any electrical system.

Key hurdles currently preventing the commercial application of many NEMS devices include low-yields and high device quality variability. Before NEMS devices can actually be implemented, reasonable integrations of carbon based products must be created.

Applications of NEMS: NEMS are used in

- Nanoelectromechanical relay
- Nanoelectromechanical systems mass spectrometer
- nanoresonators
- integrated peizoresistive detection devices
- ultrasharp tips for atomic force microscopy
- nonvolatile NEMS memory
- Carbon nanotube single electron transistors
- relays and switches with nanotubes
- protein concentration detectors
- pH sensors

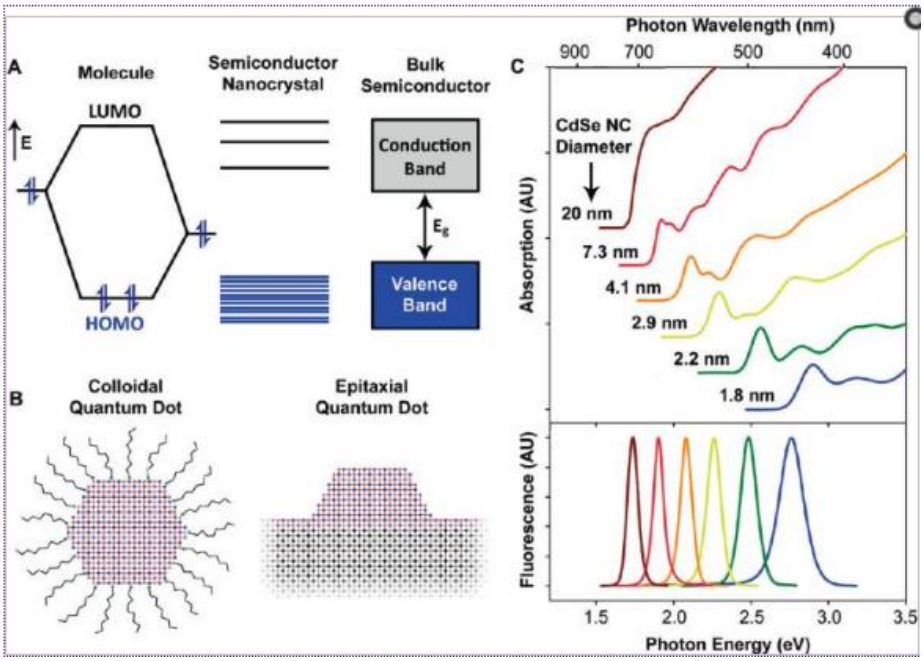
Nanoparticles **have one dimension that measures 100 nanometers or less. The properties of many conventional materials change when formed from nanoparticles. This is typically because nanoparticles have a greater surface area per weight than larger particles which causes them to be more reactive to some other molecules.**

Nanoparticles are used, or being evaluated for use, in many fields.

UNIT-IV

4. Nanoelectronics: Introduction, Electronic structure of Nanocrystals, Tuning the Band gap of Nanoscale semiconductors, Excitons, Quantum dot,

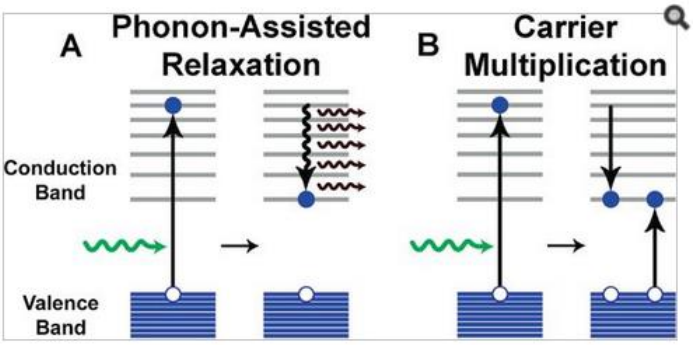
Semiconductor nanocrystals aretiny crystalline particles that exhibit size-dependent optical and electronic properties. With typical dimensions in the range of 1-100 nm, these nanocrystals bridge the gap between small molecules and large crystals, displaying discrete electronic transitions reminiscent of isolated atoms and molecules, as well as enabling the exploitation of the useful properties of crystalline materials.

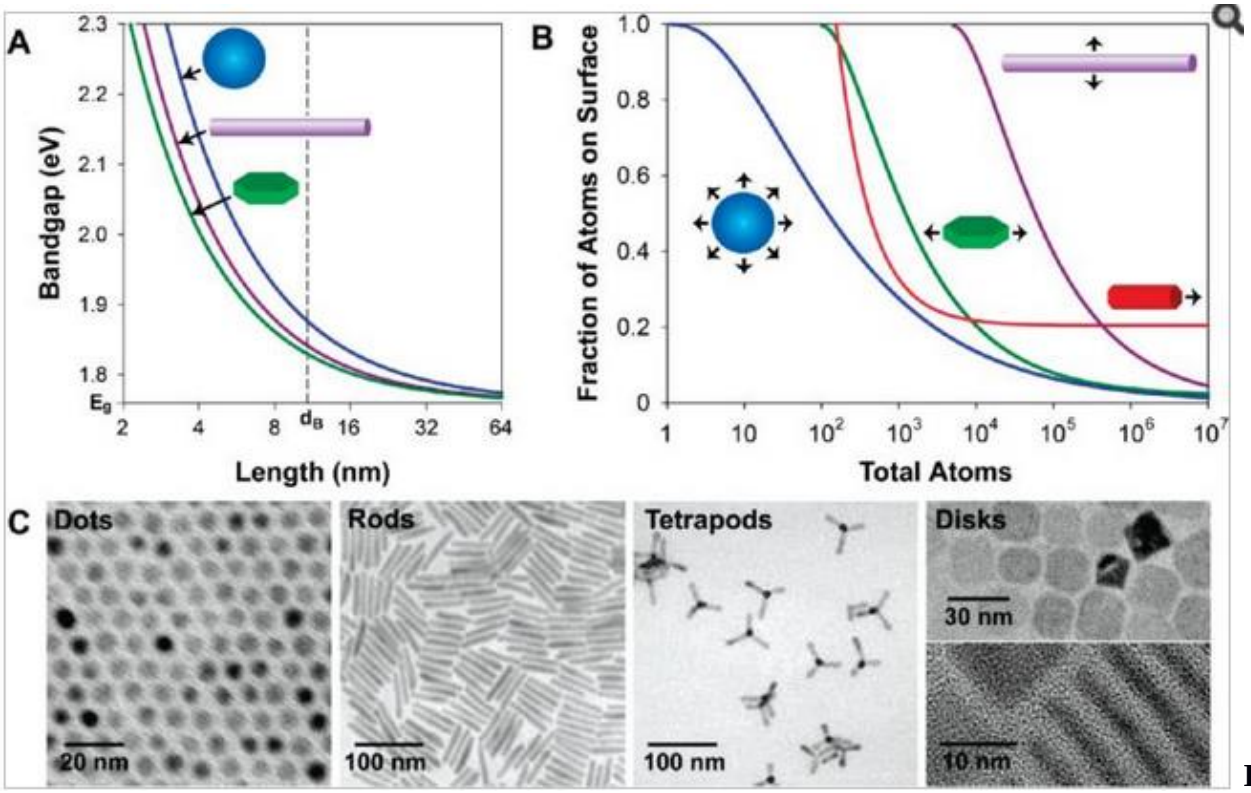


Bulk semiconductors are characterized by a composition-dependent band gap energy (E_g), which is the minimum energy required to excite an electron from the ground state valence energy band into the vacant conduction energy band. With the absorption of a photon of energy greater than E_g , the excitation of an electron leaves an orbital hole in the valence band. The negatively charged electron and positively charged hole may be mobilized in the presence of an electric field to yield a current, but their lowest energy state is an electrostatically bound electron-hole pair, known as the exciton. Relaxation of the excited electron back to the valence band annihilates the exciton and may be accompanied by the emission of a photon, a process known as radiative recombination.

The exciton has a finite size within the crystal defined by the Bohr exciton diameter (a_B), which can vary from 1 nm to more than 100 nm depending on the material. If the size of a semiconductor nanocrystal is smaller than the size of the exciton, the charge carriers become spatially confined, which raises their energy. Therefore, the exciton size delineates the transition between the regime of bulk crystal properties and the quantum confinement regime, in which the optical and electronic properties are dependent on the nanocrystal size. Nanocrystals with dimensions smaller than a_B demonstrate size-dependent absorption and fluorescence spectra with discrete electronic transitions.

By confining the exciton of a semiconductor, the band gap may be tuned to a precise energy depending on the dimensionality and degree of confinement. Figure below depicts the shift of the band gap of CdSe nanocrystals confined in three dimensions (quantum dots), two dimensions (quantum wires or rods), or one dimension (quantum wells or disks). An increase in the number of confined dimensions yields a stronger degree of electronic confinement and thus a wider range of tunability in the band gap, although exceptions to this trend have been reported for CdTe nanocrystals. Quantum dots have attracted broad attention due to their wide optical tunability and utility for biolabeling, whereas elongated structures have been shown to emit linearly polarized light with a wide energy separation between the absorption and emission maxima (Stokes shift), which can reduce light reabsorption for light emission applications. Quantum wells are well-established components of optoelectronic devices, and their colloidal "disk" analogues have recently been described, which may have novel piezoelectric applications if they can be confined in polar lattice directions.

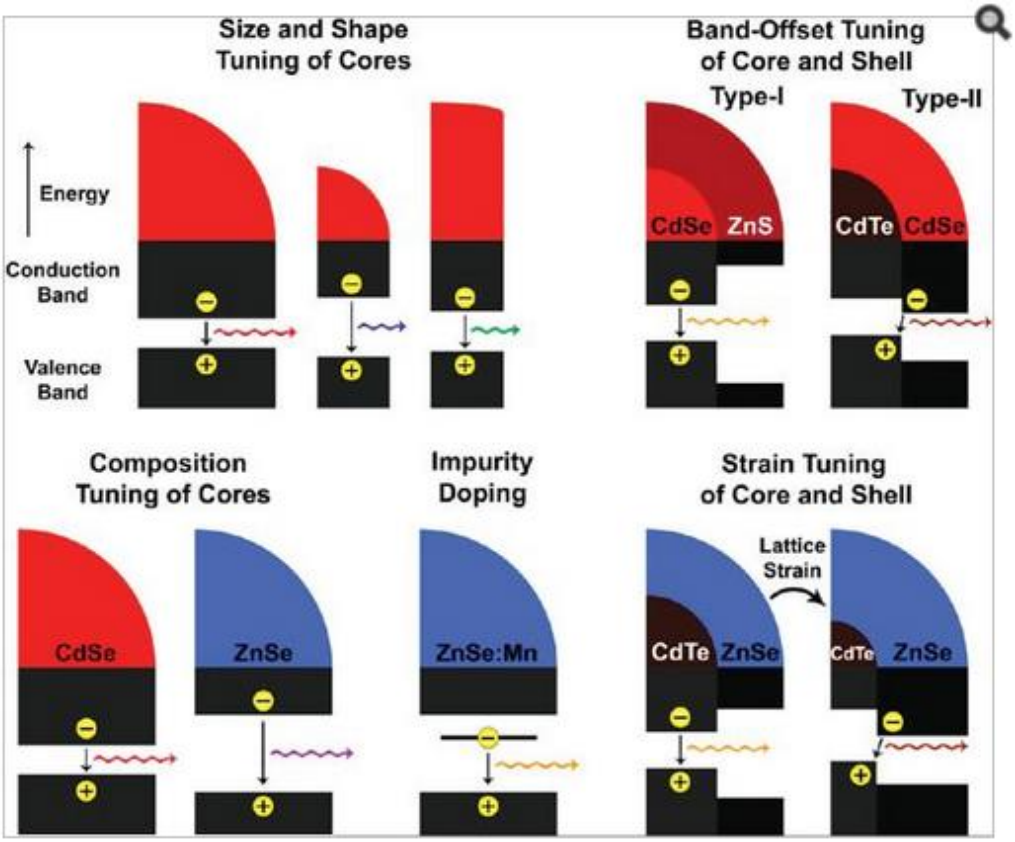




Band Gap and Wave Function Engineering:

In comparison with bulk semiconductors, nanocrystals have a diverse and growing range of parameters that can modulate their electronic band gaps including size, shape, and composition. Quantum confinement can shift the band gap of most semiconductors by over 1 eV, giving an enormous range of continuous tunability through size and shape for a single material composition. The use of quantum confined structures also allows the independent tuning of size and band gap through the implementation of homogeneously alloyed materials such as $CdSe_yTe_{1-y}$, and $Cd_xZn_{1-x}S$. A chemically related process to alloying is impurity doping, which creates an intraband electronic energy level that

allows lower energy light emission from the defect state to the ground state. Doped nanocrystals can have interesting properties for biolabeling and device applications, such as large Stokes shifts, paramagnetic properties, and improved lasing. At the present, however, the synthesis of these doped nanocrystals is still a challenge due to the chemical dissimilarities between the dopants and their crystalline matrices. More recently, the manipulation of nanocrystal heterostructures has given rise to complex control over charge carrier wave functions, resulting in new optical properties.



The above figure shows the Impact of shape on the electronic and surface properties of semiconductor nanocrystals. (A) Band gaps of CdSe quantum wells, wires, and dots are plotted against the length of the confined dimension. The bulk band gap and exciton diameter are noted on the axes. (B) Fractions of atoms on the nanocrystal surface are plotted against the total number of atoms. The wires (purple) are 1 μm in length, the disks (green) are 20 nm in length, and the rods (red) are 4 nm in diameter. (C) Transmission electron micrographs depicting CdSe dots, rods, tetrapods, and disks.

Type-II Quantum Dotss

In 2003, Bawendi and co-workers developed (core)shell semiconductor heterostructures in which the conduction and valence bands of the core and shell material are staggered, resulting in the segregation of the electron and the hole between the core and shell materials. 38 For example, (core)shell (CdTe)CdSe particles have a minimum conduction band energy in the CdSe shell, whereas the maximum energy of the valence band is in the CdTe core (Figure 6). These energy band offsets segregate the electron to the shell and the hole to the core, and carrier recombination can occur across the interface at a lower energy than the band gaps of either of the constituent semiconductor materials.

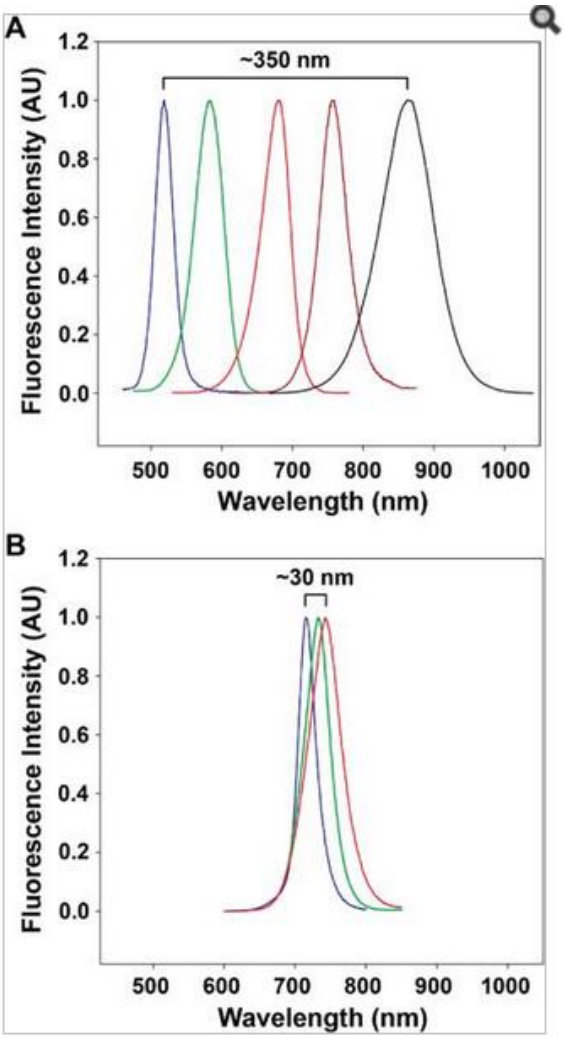
During the course of shell growth, the wavelength of emission shifts strongly to the red, adding a new dimension to band gap engineering. The reduced spatial overlap between the electron and hole also results in a major reduction in band edge oscillator strength and a significant increase in excited state lifetimes. This band alignment is designated as “type-II” in order to distinguish it from “type-I” band alignments like those of (CdSe)ZnS in which the electron and hole overlap in space in the core material. Type-II materials may be greatly beneficial for photovoltaic devices, especially with the development of anisotropic materials in which the segregation of charges is directional, which may enhance directional charge transport in future electronic devices. 39 The use of type-II nanocrystals is also a means by which to independently control which charge carrier is accessible to the surface for charge transfer applications. It is also possible to sequester both charge carriers in the shell material in inverted type-I alignments, which resemble a quantum well in which one-dimensional confinement is present in the radial direction. The capacity to transition between core and shell localization has recently been exploited by Klimov and co-workers to tune the interactions between charge carriers and core-localized magnetic atoms of (ZnSe:Mn)CdSe quantum dots.

Figure: (A) Electronic energy states of a semiconductor in the transition from discrete molecules to nanosized crystals and bulk crystals. Blue shading denotes ground state electron occupation. (B) Comparison of a colloidal quantum dot and an islandlike, self-assembled quantum dot epitaxially deposited on a crystalline substrate. (C) Absorption (upper) and fluorescence (lower) spectra of CdSe semiconductor nanocrystals showing quantum confinement and size tunability. AU = arbitrary units.

Figure: Impact of shape on the electronic and surface properties of semiconductor nanocrystals. (A) Band gaps of CdSe quantum wells, wires, and dots are plotted against the length of the confined dimension. The bulk band gap and exciton diameter are noted on the axes. (B) Fractions of atoms on the nanocrystal surface are plotted against the total number of atoms. The wires (purple) are 1 μm in length, the disks (green) are 20 nm in length, and the rods (red) are 4 nm in diameter. (C) Transmission electron micrographs depicting CdSe dots, rods,[13] tetrapods,[14] and disks.

Schematic illustration of electronic energy relaxation and carrier multiplication in quantum dots. (A) Electrons excited to energies greater than the band edge efficiently relax to the band edge through the release of phonons, or quanta of lattice vibration. (B) Alternatively, excited state electrons with kinetic energy greater than the band gap can transfer their energy to a second electron via impact ionization, yielding two excitons.

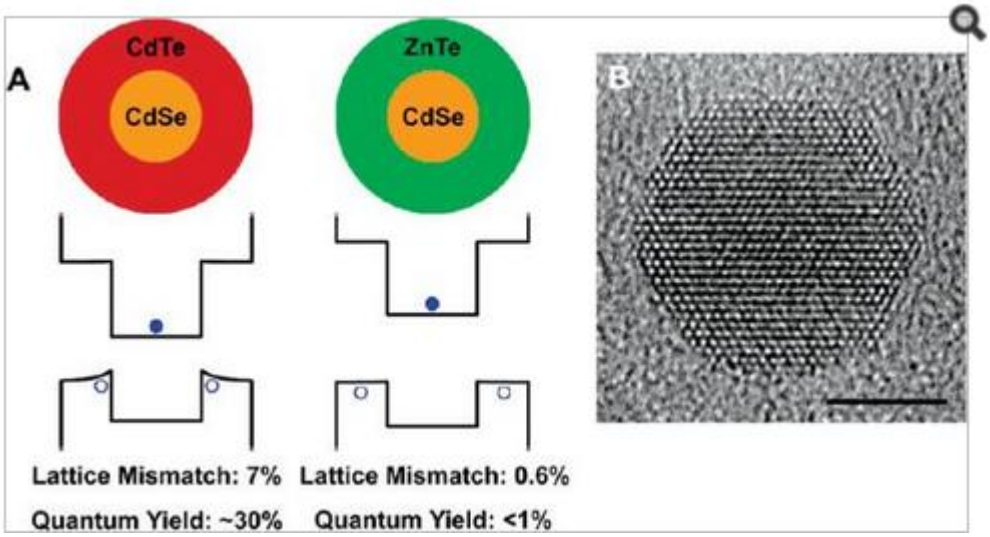
Mechanisms of band gap engineering in semiconductor nanocrystals through size, shape, composition, impurity doping, heterostructure band offset, and lattice strain. See text for discussion.



Fluorescence spectra of strain-tunable (CdTe)ZnSe quantum dots. (A) Fluorescence from 1.8 nm CdTe cores strongly red-shifts when capped with 0-6 monolayers of ZnSe shell (from blue to black) due to strain-induced changes in the core and shell lattices. (B) Fluorescence from 6.2 nm CdTe cores only exhibits a small red-shift when capped with 0-5 monolayers of ZnSe shell (from blue to red) due to strain relaxation through lattice defect formation.

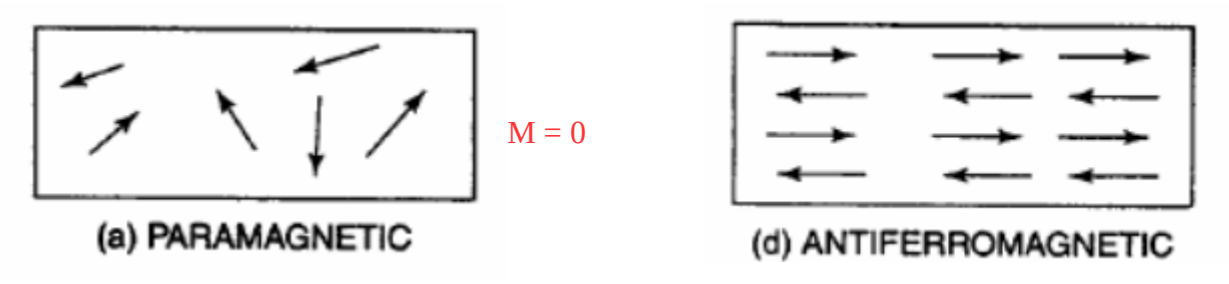
Band-edge warping induced by lattice strain. (A) Energy band levels of quantum confined, strained (core)shell (CdSe)CdTe and (CdSe)ZnTe nanocrystals show that band warping is only significant in the highly strained structure (CdSe)CdTe, resulting in efficient recombination efficiency. (B) Representative transmission electron micrograph of a highly strained (CdSe)ZnS shows direct evidence of lattice warping at core-shell interfaces. Scale bar is 5 nm.

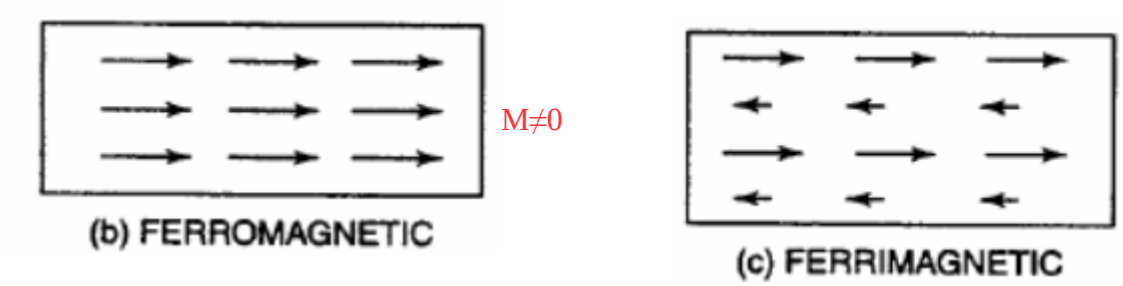
Nanostructured ferromagnetism, Effect of bulk nanostructurin



g of magnetic properties, Dynamics of nanomagnets, Nanocarbon ferromagnets, Giant and colossal magneto-resistance,

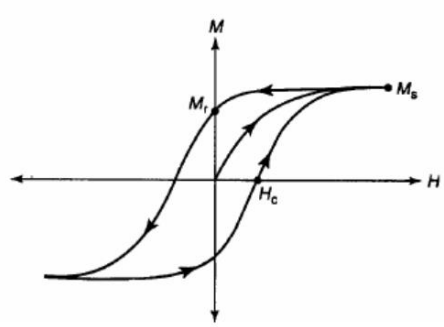
Atoms in the various transition series of the periodic table have unfilled inner energy levels in which the spins of the electrons are unpaires, giving the atom a net magnetic moment.





Effect of bulk nanostructuring on magnetic properties: The amount of energy loss meaning the amount of heat generated is proportional to the area of loop

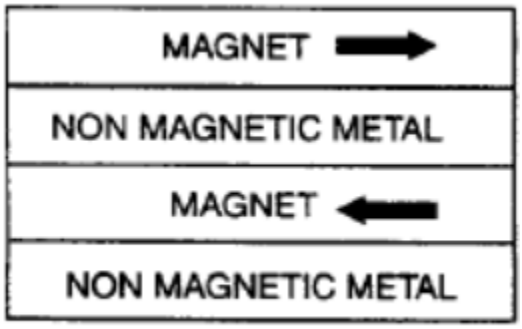
Soft magnet H_C ->0
Hard magnet H_C> 0



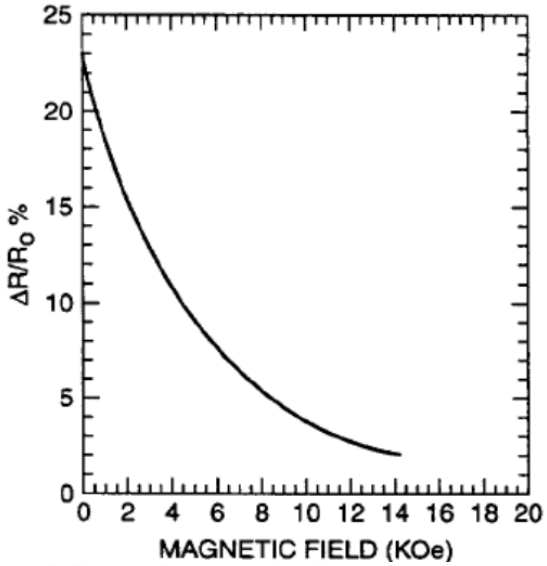
Nanocarbon ferromagnets:

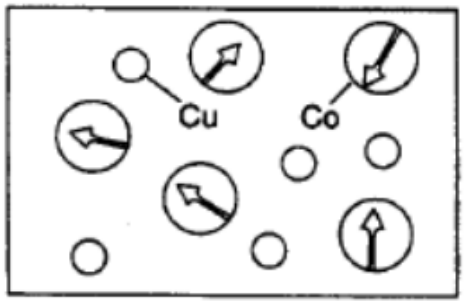
Giant and colossal magnetoresistan:
Metal:
1. The conduction electrons being forced to move in helical trajectories about an applied magnetic field.
2. Field curves the electron trajectory within a length of its mean free path
3. Cu at 4 K with H=10 T , resistance R increases 10 times

Giant magnetoresistance (GMR):
Alternate layers of FM and Non-FM



(a)





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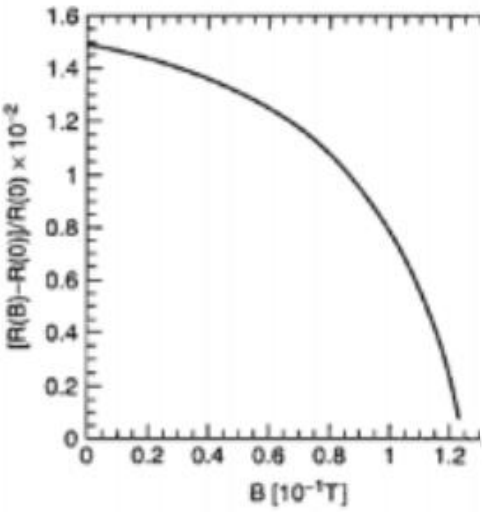

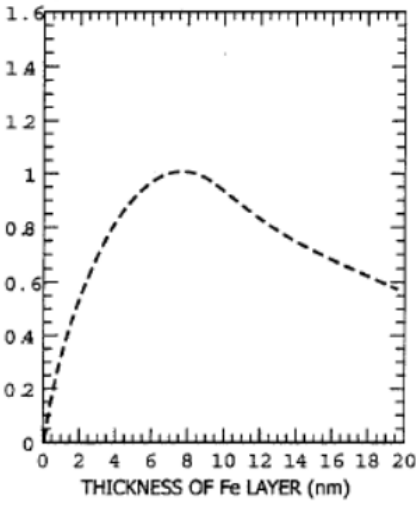

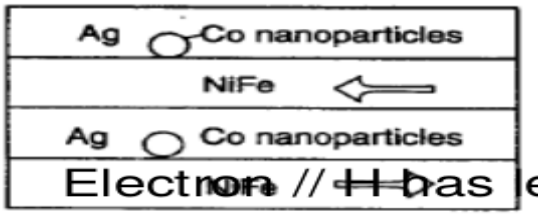

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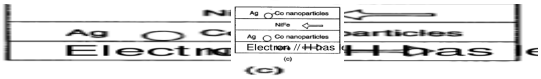
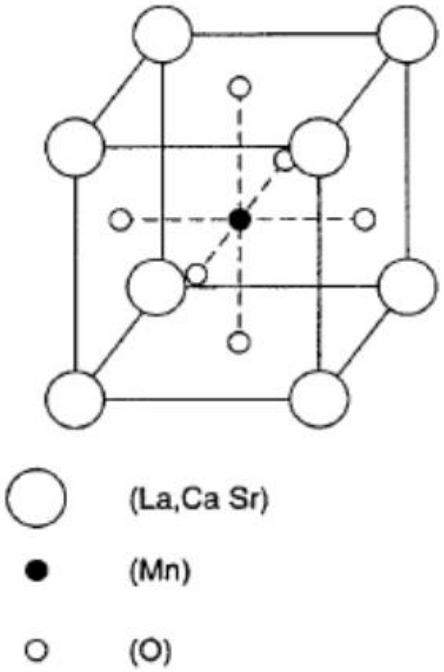
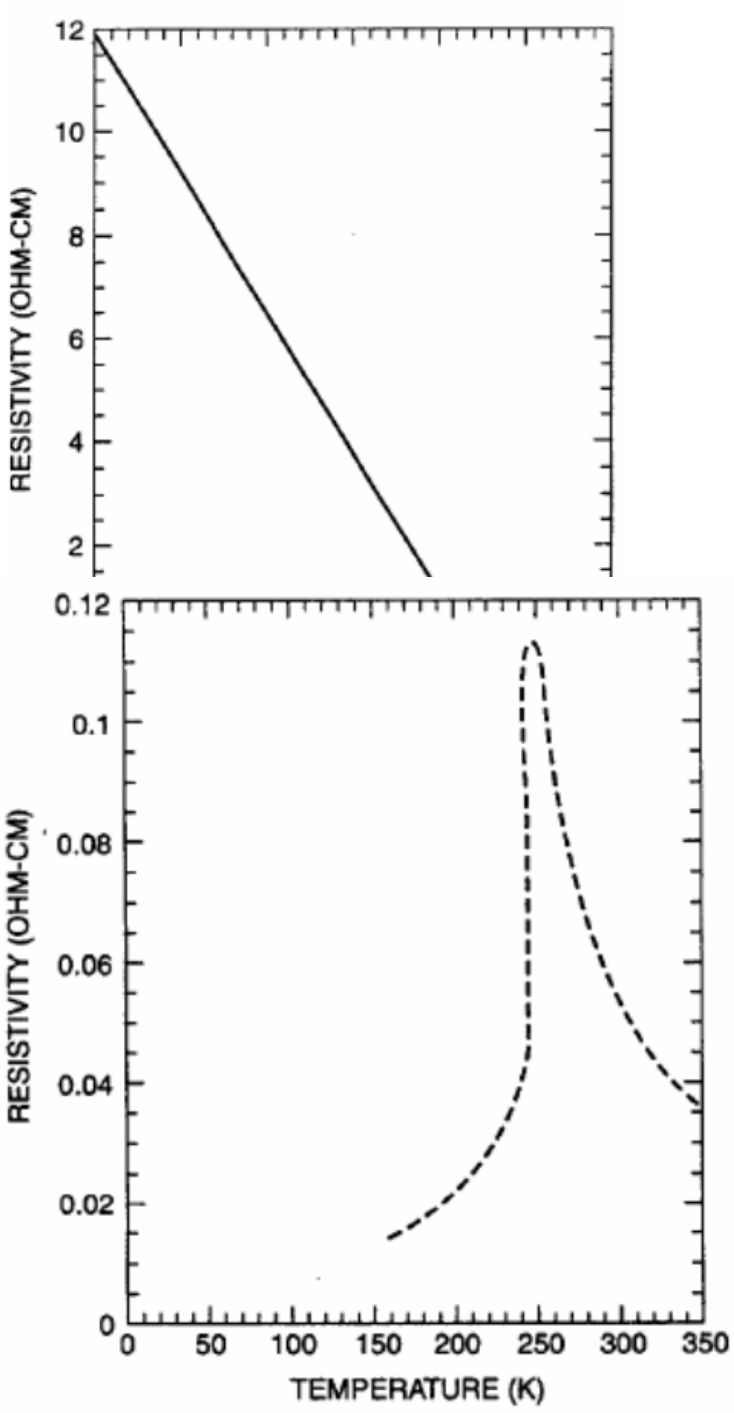


Materials have been discovered having larger magnetoresistive effects than the layered materials, and this phenomenon in them is called collosal magnetoresistance.

Ex: $LaMnO_3$

The perovskite like material $LaMnO_3$ has manganese in the Mn3+ valence state. If the La3+ is partially replaced with ions having a valence of 2+, such as Ca, Ba, Sr, Pb, or Cd, some Mn3+ ions transform to Mn4+ to preserve the electrical neutrality. The result is a mixed valence system of Mn3+/Mn4+, with the presence of many mobile charge carriers. This mixed valence system has been shown to exhibit very large magnetomoment.





Introduction of spintronics, Spintronics devices and applications:

Spintronics (a portmanteau meaning **spin transport electronics**, also known as **spin electronics**, is the study of the intrinsic spin of the electron and its associated magnetic moment, in addition to its fundamental electronic charge, in solid-state devices[4].

Spintronics fundamentally differs from traditional electronics in that, in addition to charge state, electron spins are exploited as a further degree of freedom, with implications in the efficiency of data storage and transfer. Spintronic systems are most often realised in dilute magnetic semiconductors (DMS) and Heusler alloys and are of particular interest in the field of quantum computing.

The spin of the electron is an intrinsic angular momentum that is separate from the angular momentum due to its orbital motion. The magnitude of the projection of the electron's spin along an arbitrary axis is ...., implying that the electron acts as a Fermion by the spin-statistics theorem. Like orbital angular momentum, the spin has an associated magnetic moment, the magnitude of which is expressed as....
In a solid the spins of many electrons can act together to affect the magnetic and electronic properties of a material, for example endowing it with a permanent magnetic moment as in a ferromagnet.

In many materials, electron spins are equally present in both the up and the down state, and no transport properties are dependent on spin. A spintronic device requires generation or manipulation of a spin-polarized population of electrons, resulting in an excess of spin up or spin down electrons. The polarization of any spin dependent property X can be written as....

A net spin polarization can be achieved either through creating an equilibrium energy split between spin up and spin down. Methods include putting a material in a large magnetic field (Zeeman effect), the exchange energy present in a ferromagnet or forcing the system out of equilibrium. The period of time that such a non-equilibrium population can be maintained is known as the spin lifetime.

UNIT-V

5. Nanobiotechnology and Medical applications: Introduction, Biological building blocks- size of building blocks and nanostructures:

Cell is the basic unit of life. All organisms are composed of one or more cells. Humans are made up of many millions of cells. All cells, regardless of their function or location in the body, share common features and processes. Cells are comprised almost entirely of just four basic types of molecules. Additional biomolecules can be made by combining these four types. Since they are present in living things these building blocks are called biomolecules. As an example, many proteins are modified by the addition of carbohydrate chains. The end product is called a glycoprotein.

All living things, including the cells that make up a human body are comprised of a small subset of different biomolecules. There are four main classes, as described below:

1. **Carbohydrates**
    - Carbohydrates are comprised of carbon (C), hydrogen (H), and oxygen (O) molecules.
    - Sugars are common carbohydrates.
    - Carbohydrates serve several functions inside cells:
        - Major energy source
        - Provide structure
        - Communication
        - Cell adhesion
        - Defense against and removal of foreign material
        - Examples of carbohydrates include the sugars found in milk (lactose) and table sugar (sucrose), Glucose, Glycogen, etc.
2. **Proteins**
    - Proteins are comprised of amino acids.
    - Proteins serve several functions inside living things:
        - Structure of hair, muscle, nails, cell components, and cell membranes
        - Cell transport
        - Biological catalysts or enzymes
        - Maintaining cell contact
        - Control cell activity
        - Signaling via hormones
    - Examples: Glycine, Insulin, etc.
3. **Lipids**
    - A wide variety of biomolecules including fats, oils, waxes and steroid hormones.
    - Lipids do not dissolve in water (they are hydrophobic) and are primarily comprised of carbon (C), hydrogen (H), and oxygen (O).
    - Lipids serve several functions in living things:
        - Form biological membranes

- Fats may be stored as a source of energy
- Oils and waxes provide protection by coating areas that could be invaded by microbes (i.e. skin or ears)
- Steroid hormones regulate cell activity by altering gene expression

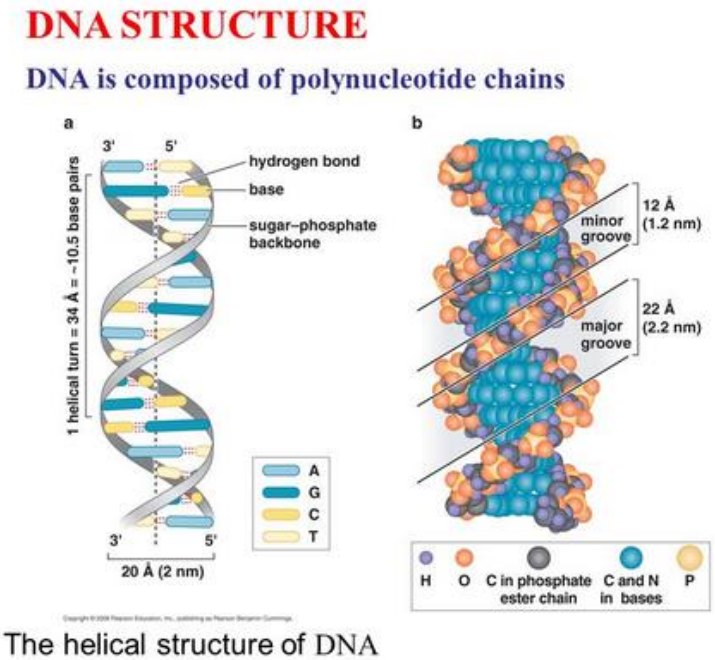
- Examples: Triacylglycerol, Cholesterol, etc.

4. **Nucleic Acids**
    - All of the information needed to control and build cells is stored in these molecules.
    - Nucleic acids are comprised of nucleotides which are abbreviated A, C, G, T, and U.
    - There are two main types of nucleic acid, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA):
        - DNA
            - DNA has double helix structure comprised of nucleotides A, C, G, and T.
            - DNA is located in the nucleus of the cell.
            - DNA is the storage form of genetic information.
        - RNA
            - RNA is typically single stranded and comprised of nucleotides A, G, C, and U.
            - RNA is copied from DNA and is the working form of the information.
            - RNA is made in the nucleus and mRNA is exported to the cytosol.

DNA double nanowires:

Deoxyribonucleic Acid (DNA)

DNA is composed of two long strings (polymers) of nucleotides twisted around each other to form the spiral or helical structure shown below. The twisted molecules are arranged in a particular manner, with specific nucleotides always found across from each other. The nucleotide containing adenine (A) always pairs with the nucleotide containing thymine (T). Likewise, guanine (G) always pairs with cytosine (C). The polymers that form DNA can be extremely long, reaching millions of nucleotides per each individual DNA molecule. DNA is located in the nucleus of cells. All of the nucleated cells in the human body have the same DNA content regardless of their function.



The helical structure of DNA

Protein nanoparticles:

Natural biomolecules such as proteins are an attractive alternative to synthetic polymers which are commonly used in drug formulations because of their safety. In general, protein nanoparticles offer a number of advantages including biocompatibility and biodegradability. They can be prepared under mild conditions without the use of toxic chemicals or organic solvents. Moreover, due to their defined primary structure, protein-based nanoparticles offer various possibilities for surface modifications including covalent attachment of drugs and targeting ligands.

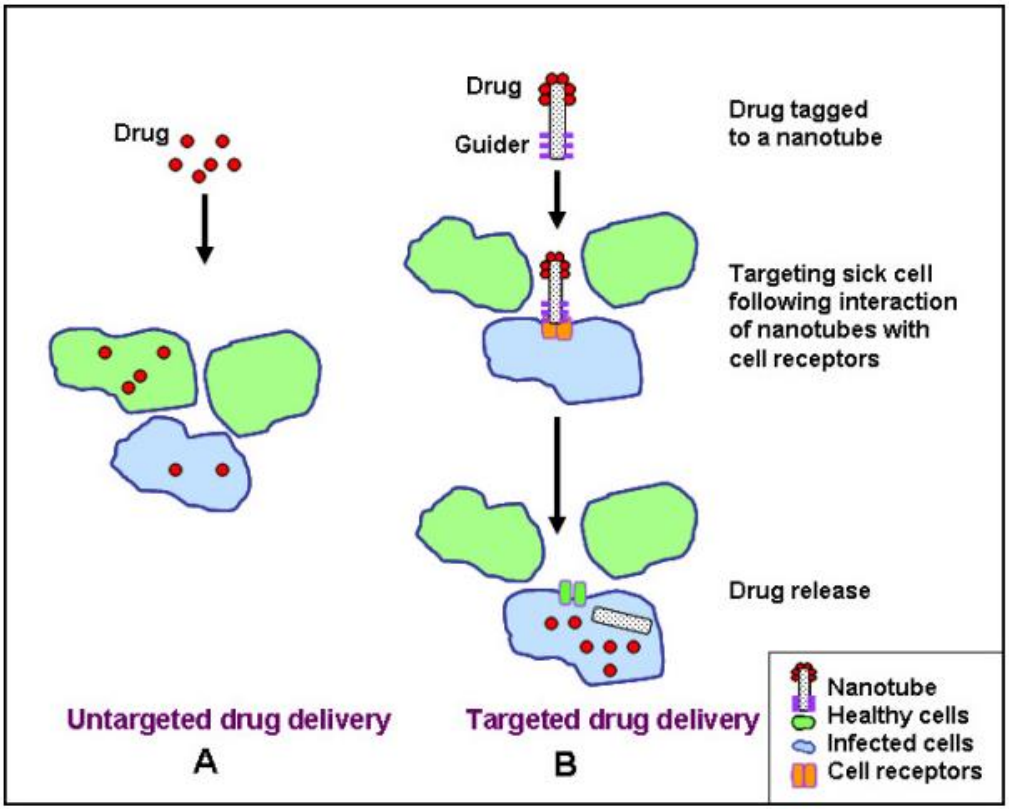
Proteins are a class of natural molecules that have unique functionalities and potential applications in both biomedical and material sciences. They are deemed as ideal materials for nanoparticle preparation because of their amphiphilicity which allows them to interact well with both the drug and solvent. Nanoparticles derived from natural proteins are biodegradable, metabolizable, and are easily amenable to surface modifications to allow attachment of drugs and targeting ligands. They have been successfully synthesized from various proteins including water-soluble proteins (e.g., bovine and human serum albumin) and insoluble proteins (e.g., zein and gliadin).

Table 1: Marketed nanosystems for cancer treatment.

Product name	Drug	Type of nanocarrier	Company
Daunoxome	Daunorubicin citrate	Liposome	Gilead Science, Cambridge, UK
Doxil	Doxorubicin HCl	Liposome	Johnson and Johnson, NJ, USA
Myocet	Doxorubicin	Liposome	Sopherion Therapeutics, NJ, USA
Caelyx	Doxorubicin HCl	Pegylated liposome	Johnson and Johnson, NJ, USA
Transdrug	Doxorubicin	Poly(alkylcyanoacrylate) nanoparticles	BioAlliance, Paris, France
Genexol-PM	Paclitaxel	Methoxy-PEG-polylactide nanoparticles	Samyang, South Korea
Oncaspar	Pegaspargase	PEG-asparaginase nanoparticles	Enzon, NJ, USA
Abraxane	Paclitaxel	Albumin-bound nanoparticles	American Bioscience, CA, USA

Nanomaterials in drug delivery and therapy:

Nanoparticles used as drug delivery vehicles are generally < 100 nm in at least one dimension, and consist of different biodegradable materials such as natural or synthetic polymers, lipids, or metals. Nanoparticles are taken up by cells more efficiently than larger micromolecules and therefore, could be used as effective transport and delivery systems. For therapeutic applications, drugs can either be integrated in the matrix of the particle or attached to the particle surface. A drug targeting system should be able to control the fate of a drug entering the biological environment. Nanosystems with different compositions and biological properties have been extensively investigated for drug and gene delivery applications.



An effective approach for achieving efficient drug delivery would be to rationally develop nanosystems based on the understanding of their interactions with the biological environment, target cell population, target cell-surface receptors, changes in cell receptors that occur with progression of disease, mechanism and site of drug action, drug retention, multiple drug administration, molecular mechanisms, and pathobiology of the disease under consideration. It is also important to understand the barriers to drug such as stability of therapeutic agents in the living cell environment. Reduced drug efficacy could be due to instability of drug inside the cell, unavailability due to multiple targeting or chemical properties of delivering molecules, alterations in genetic makeup of cell-surface receptors, over-expression of efflux pumps, changes in signalling pathways with the progression of disease, or drug degradation. For instance, excessive DNA methylation with the progression of cancer causes failure of several anti-neoplastic agents like doxorubicin and cisplatin. Better understanding of the mechanism of uptake, intracellular trafficking, retention, and protection from degradation inside a cell are required for enhancing efficacy of the encapsulated therapeutic agent.

Nanoparticles can be used in targeted drug delivery at the site of disease to improve the uptake of poorly soluble drugs, the targeting of drugs to a specific site, and drug bioavailability. A schematic comparison of untargeted and targeted drug delivery systems is shown in Figure. Several anti-cancer drugs including paclitaxel, doxorubicin, 5-fluorouracil and dexamethasone have been successfully formulated using nanomaterials. Polylactic/glycolic acid (PLGA) and polylactic acid (PLA) based nanoparticles have been formulated to encapsulate dexamethasone, a glucocorticoid with an intracellular site of action. Dexamethasone is a chemotherapeutic agent that has anti-proliferative and anti-inflammatory effects. The drug binds to the cytoplasmic receptors and the subsequent drug-receptor complex is transported to the nucleus resulting in the expression of certain genes that control cell proliferation. These drug-loaded nanoparticles formulations that release higher doses of drug for prolonged period of time completely inhibited proliferation of vascular smooth muscle cells.

Nanomedicine:

Nanomedicine is a branch of medicine that applies the knowledge and tools of nanotechnology to the prevention and treatment of disease. Nanomedicine involves the use of nanoscale materials, such as biocompatible nanoparticles and nanorobots, for diagnosis, delivery, sensing or actuation purposes in a living organism.

Nanomedicine is the medical application of nanotechnology. Nanomedicine ranges from the medical applications of nanomaterials and biological devices, to nanoelectronic biosensors, and even possible future applications of molecular nanotechnology such as biological machines. Current problems for nanomedicine involve understanding the issues related to toxicity and environmental impact of nanoscale materials (materials whose structure is on the scale of nanometers, i.e. billionths of a meter).

Functionalities can be added to nanomaterials by interfacing them with biological molecules or structures. The size of nanomaterials is similar to that of most biological molecules and structures; therefore, nanomaterials can be useful for both in vivo and in vitro biomedical research and applications. Thus far, the integration of nanomaterials with biology has led to the development of diagnostic devices, contrast agents, analytical tools, physical therapy applications, and drug delivery vehicles.

Targeted gold nanoparticles for imaging and therapy:

In vivo imaging is another area where tools and devices are being developed. Using nanoparticle contrast agents, images such as ultrasound and MRI have a favorable distribution and improved contrast. In cardiovascular imaging, nanoparticles have potential to aid visualization of blood pooling, ischemia, angiogenesis, atherosclerosis, and focal areas where inflammation is present.

The small size of nanoparticles endows them with properties that can be very useful in oncology, particularly in imaging. Quantum dots (nanoparticles with quantum confinement properties, such as size-tunable light emission), when used in conjunction with MRI (magnetic resonance imaging), can produce exceptional images of tumor sites. Nanoparticles of cadmium selenide (quantum dots) glow when exposed to ultraviolet light. When injected, they seep into cancer tumors. The surgeon can see the glowing tumor, and use it as a guide for more accurate tumor removal. These nanoparticles are much brighter than organic dyes and only need one light source for excitation. This means that the use of fluorescent quantum dots could produce a higher contrast image and at a lower cost than today's

organic dyes used as contrast media. The downside, however, is that quantum dots are usually made of quite toxic elements, but this concern may be addressed by use of fluorescent dopants.

Tracking movement can help determine how well drugs are being distributed or how substances are metabolized. It is difficult to track a small group of cells throughout the body, so scientists used to dye the cells. These dyes needed to be excited by light of a certain wavelength in order for them to light up. While different color dyes absorb different frequencies of light, there was a need for as many light sources as cells. A way around this problem is with luminescent tags. These tags are quantum dots attached to proteins that penetrate cell membranes. The dots can be random in size, can be made of bio-inert material, and they demonstrate the nanoscale property that color is size-dependent. As a result, sizes are selected so that the frequency of light used to make a group of quantum dots fluoresce is an even multiple of the frequency required to make another group incandesce. Then both groups can be lit with a single light source. They have also found a way to insert nanoparticles into the affected parts of the body so that those parts of the body will glow showing the tumor growth or shrinkage or also organ trouble.

Nanoparticles have high surface area to volume ratio. This allows for many functional groups to be attached to a nanoparticle, which can seek out and bind to certain tumor cells. Additionally, the small size of nanoparticles (10 to 100 nanometers), allows them to preferentially accumulate at tumor sites (because tumors lack an effective lymphatic drainage system). Limitations to conventional cancer chemotherapy include drug resistance, lack of selectivity, and lack of solubility. Nanoparticles have the potential to overcome these problems

Gold nanoparticles have the potential to join numerous therapeutic functions into a single platform, by targeting specific tumor cells, tissues and organs. Gold nanoparticles tagged with short segments of DNA can be used for detection of genetic sequence in a sample. Multicolor optical coding for biological assays has been achieved by embedding different-sized quantum dots into polymeric microbeads. Nanopore technology for analysis of nucleic acids converts strings of nucleotides directly into electronic signatures.