Quantum confinement

When the size or dimension of a material is continuously reduced from a large or macroscopic size, such a metre or centimetre, to a very small size, the properties remain the same at first, and then small changes begin to occur, until finally when the size drops below100 nm, dramatic changes in properties can occur.

Nano Materials have properties that are different from those of bulk materials.

Most Nano structure materials are Crystalline in nature and they posses unique properties.

In Nano Crystals, the Electronic energy levels are not continuous as in the bulk but are discrete (finite density of states), because of the confinement of the electronic Wave function to the physical dimensions of the particles. This phenomenon is called Quantum confinement and therefore Nano Crystals are also referred to as quantum dots (QDs).

2-D or Quantum Wells: The carriers act as free carriers in a plane. First observed in semiconductor systems

1-D or Quantum Wires: The carriers are free to move down the direction of the wire

0-D or Quantum Dots: Systems in which carriers are confined in all directions (no free carriers)

One of the most direct effects of reducing the size of materials to the nanometer range is the appearance of quantization effects due to the confinement of the movement of electrons. This leads to discrete energy levels depending on the size of the structure as it is known from the simple potential well treated in introductory quantum mechanics. Following these line artificial structures with properties different from those of the corresponding bulk materials can be created. Control over dimensions as well as composition of structures thus makes it possible to tailor material properties to specific applications.

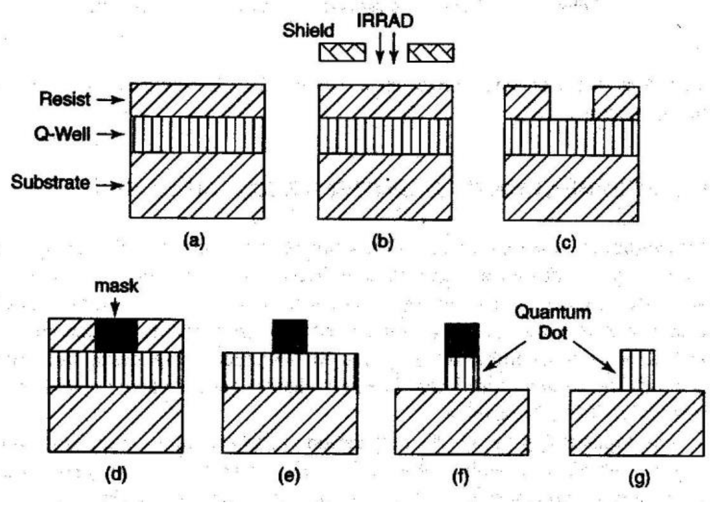
Preparation of Quantum nanostructures

i. Bottom-up approach:

Collect, consolidate and fashion the individual atoms and molecules into the structure. This is carried out by sequence of chemical reactions controlled by catalysts.

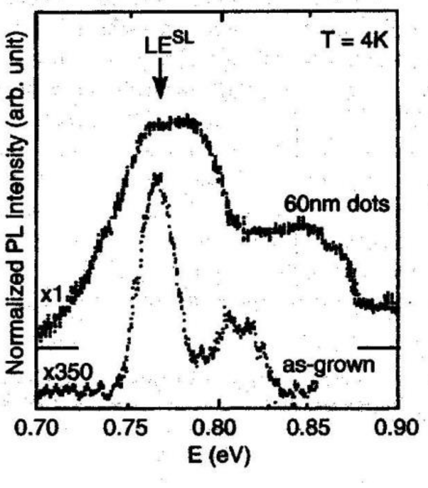
ii. Top-down approach:

A large scale objects or pattern and gradually reduces its dimension or dimensions. This is accomplished through lithography. Radiation is shines through a template to a surface coated with radiation sensitive resist. The resist is then removed and surface is chemically treated to produce nanostructure.



- Step 1: Place radiation sensitive resist on the surface of sample
- Step 2: Selectively irradiate sample by an electron beam in the region where nanostructure will be located. This is done by using a radiation mask. The radiation chemically modifies the exposed area of resist so that it becomes soluble in a developer.
- Step 3: The application of developer to remove the irradiated portion of resist
- Step 4: Insertion of etching mask to the hole in the resist
- Step 5: Lifting off the remaining parts of the resist
- Step 6: Areas of quantum well not covered by the etching mask are chemically etched away to produce quantum structure
- Step 7: Etching mask is removed to produce desired quantum structure (wire or dots)

The advantage of fabricating quantum dots arrays, it produces greatly enhanced photo luminescent output of light. The photoluminescence spectrum obtained from quantum dot is found to be 100 times stronger than spectrum obtained from initial multiple quantum wells. The main peak was featured to a localized exciton.



Quantum Effects

The so-called quantum size effect describes the physics of electron properties in solids with great reductions in particle size. Quantum effects can begin to dominate the behavior of matter at the nanoscale affecting the optical, electrical and magnetic behavior of materials. Materials reduced to the nanoscale can suddenly show very different properties compared to what they show on a macroscale. For instance, opaque substances become transparent (copper); inert materials become catalysts (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon).

Surface area

Another important aspect of nanomaterials is surface area. When compared to the same mass of material in bulk form, nanoscale materials have a relatively larger surface area. This can make materials more chemically reactive (in some cases materials that are inert in bulk form are reactive when produced in their nanoscale form), and affect their strength or electrical properties.

Size and dimensionality effects

One of the most direct effects of reducing the size of materials to the nanometer range is the appearance of quantization effects due to the confinement of the movement of electrons. This leads to discrete energy levels depending on the size of the structure. Following these line artificial structures with properties different from those of the corresponding bulk materials can be created. Control over dimensions as well as composition of structures thus makes it possible to tailor material properties to specific applications.

Nanostructures possess large fraction of surface atoms per unit volume. For a cube of n unit cells the percentage of atoms on the surface.

n=2, percentage of atoms on the surface:	51.1%
n=3,	38.7%
n=50,	2.9% and
n=100,	1.5%

A charge carrier in a conductor or semiconductor has its forward motion in an applied electric field periodically interrupted by scattering off phonons and defects. An electron or hole moving with drift velocity ***v*** will exterience a scattering event at every **τ** seconds and a travel distance ***l*** called the mean free path between collisions, where

$$l = v\tau$$

This is called the ***intraband scattering*** because the charge carrier remains in the same band after scattering. Mean free path in metal depends on the impurity level. In normal metal the mean free path is in nanometer range whereas it is much longer in pure samples. Various types of defects in a lattice can interrupt the forward motion of conduction electrons and hence the mean free path. Examples of zero dimensional defects are missing atoms (vacancy) and extra atoms (interstitial atom) located between standard lattice sites. A vacancy-interstitial pair is called Frenkel defect. The scattering of electrons limits the electrical conductivity.

Another size effects arise from the level of doping of semiconductor. A quantum nanostructure is typically characterized by very small number or concentration of electrons that can carry current. This leads to single electron tunneling.

Quantum confinement in semiconductors

In an unconfined (bulk) semiconductor, an electron-hole pair is typically bound within a characteristic length called the Bohr exciton radius. If the electron and hole are constrained further, then the semiconductor's properties change. This effect is a form of quantum confinement, and it is a key feature in many emerging electronic structures. The quantum confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron. The word confinement means to confine the motion of randomly moving electron to restrict its motion in specific energy levels (discreteness) and quantum reflects the atomic realm of particles. So as the size of a particle decrease till we a reach a nano scale the decrease in confining dimension makes the energy levels discrete and this increases or widens up the band gap and ultimately the band gap energy also increases.

Quantum confinement is responsible for the increase of energy difference between energy states and band gap. A phenomenon tightly related with the optical and electronic properties of the materials.

Conduction electrons and dimensionality

Consider electronic systems that exist in three dimensions of large macroscopic size. Conduction electrons are delocalized and move freely throughout the entire conducting medium such as copper wire (dimension of wire is much larger than atomic spacing). When dimension of wire becomes so small and it approaches atomic spacing dimensions, the electrons experience confinement. The quantum well experience confinement in one dimension, quantum wire in two dimensions whereas quantum dots in all three dimensions.

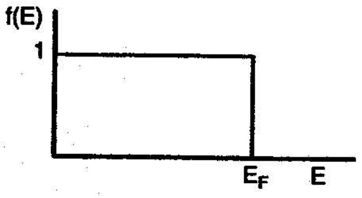
Fermi gas and density of states

The properties of good conductors are explained by treating valence electron of metal dissociate themselves from atoms and become delocalized conduction electron that can move freely through the background of positive ions. These electrons acts like a gas called the fermi gas in their ability to move with very little hindrance throughout the metal.

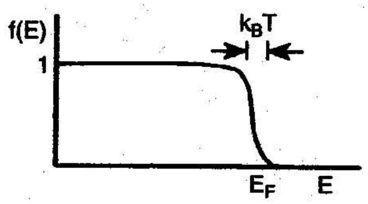
In quantum mechanical description the component on electron's momentum along x direction is P_x ($P_x=\hbar k_x$. Each electrons has unique value of wave vector component along x,y and z directions forms a lattice in k space called reciprocal lattice. At absolute zero temperature, the electrons of fermi gas occupy all the lattice points in reciprocal lattice out to a distance k_F from origin k=0 and corresponding value of energy is called Fermi energy (E_F).

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

Assume sample in cubical form of dimension L. The distance between two adjacent electrons in k space is 2π/L. At absolute zero of temperature all conduction electrons are equally spread out inside a sphere of radius k_F and of volume $4/3\pi K_F^3$ in k space. The probability distribution is shown below:



The deviations from equal density occur near fermi energy E_F at higher temperature.



The number of conduction electrons with particular energy depends on the value of energy and also on the dimensionality of the space. The number of electrons (dN) with energy E within narrow range of energy $dE=E_2-E_1$ is proportional to density of states (dN/dE) at that value of energy. The density of stated for various dimensions are listed below:

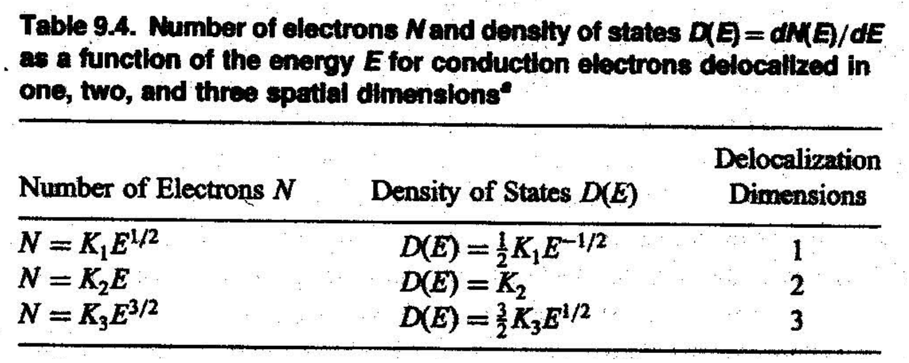


Table 9.4. Number of electrons N and density of states $D(E) = dN(E)/dE$ as a function of the energy E for conduction electrons delocalized in one, two, and three spatial dimensions[a]

Number of Electrons N	Density of States $D(E)$	Delocalization Dimensions
$N = K_1E^{1/2}$	$D(E) = \frac{1}{2}K_1E^{-1/2}$	1
$N = K_2E$	$D(E) = K_2$	2
$N = K_3E^{3/2}$	$D(E) = \frac{3}{2}K_3E^{1/2}$	3

The density of states decreases with increasing energy for one dimension, is constant for two dimensions and increases with increasing energy for three dimensions. The densities of states are very important in determining the electrical, thermal and other properties of metal and semiconductors.

Partial confinement

The confinement of electrons in various dimensions leads to discrete energies irrespective of the dimensionality and shape of potential well. Also, the Fermi gas model leads to energies and density of states that differed quite significantly for delocalized electrons. This means that the electronic and other properties changes dramatically with dimensionality changes. The energy dependence of number of electrons and density of states for various confinement (quantum dots with full confinement, the quantum wires and well with partial confinement and bulk material with no confinement) is listed below:

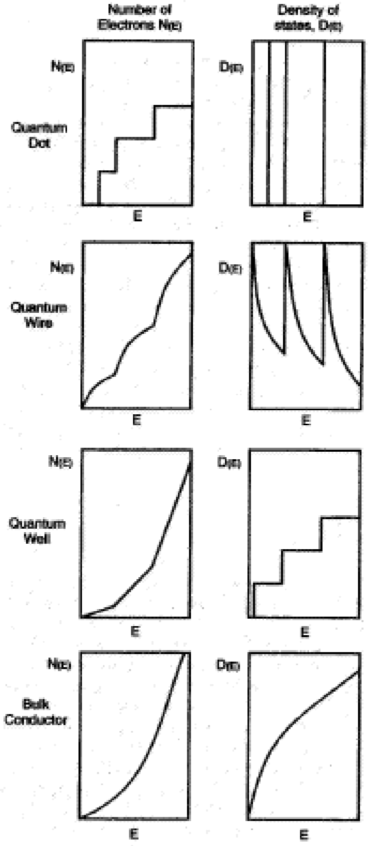
The summations are over various confinement levels *i*.

Table 9.5. Number of electrons $N(E)$ and density of states $D(E) = dN(E)/dE$ as a function of the energy E for electrons delocalized/confined in quantum dots, quantum wires, quantum wells, and bulk material[a]

			Dimensions	
Type	Number of Electrons $N(E)$	Density of States $D(E)$	Delocalized	Confined
Dot	$N(E) = K_0 \sum d_i \Theta(E - E_{iW})$	$D(E) = K_0 \sum d_i \delta(E - E_{iW})^2$	0	3
Wire	$N(E) = K_1 \sum d_i (E - E_{iW})^{1/2}$	$D(E) = \frac{1}{2} K_1 \sum d_i (E - E_{iW})^{-1/2}$	1	2
Well	$N(E) = K_2 \sum d_i (E - E_{iW})$	$D(E) = K_2 \sum d_i$	2	1
Bulk	$N(E) = K_3 (E)^{3/2}$	$D(E) = \frac{3}{2} K_3 (E)^{1/2}$	3	0

[a] The degeneracies d_i of the confined (square or parabolic well) energy levels depend on the particular level. The Heaviside step function $\Theta(x)$ is zero for $x < 0$ and one for $x > 0$; the delta function $\delta(x)$ is zero for $x \neq 0$, infinity for $x = 0$, and integrates to a unit area. The values of the constants K_1, K_2, and K_3 are given in Table A.3 of Appendix A.

The plots of energy dependence of N(E) and density of states D(E) for four types of nanostructure is shown below:



The number of electrons N(E) increases with energy E. However the density of state that describes the number of states available in the system and is essential for determining the carrier concentration and energy distribution varies dramatically for each of three nanostructure types. These variations have definite effect on their properties. This can be used to predict the properties of nanostructure or type of nanostructure from properties.

The properties dependent on density of states

- The specific heat of solid (the amount of hear required to raise the temperature by 1^0C) dependence on the lattice vibrations that in turn depends on the phonon density of states.
- The component of susceptibility (X=M/H, the measure of magnetization or magnetic moment per unit volume) called the *pauli susceptibility* is proportional to electronic density of state at the Fermi level.
- When a good conductor is bombarded with fast electrons to remove an electron from inner core energy level, the electrons from the conduction band can fall into the vacant level (hole). This will leads to the emission of radiation and the intensity of radiation dependent on the density of states of conduction electron.
- The other properties that depend on the density of states are the optical absorption determination of dielectric constant, the superconducting energy gap, Josephson junction tunnelling in superconductors etc.

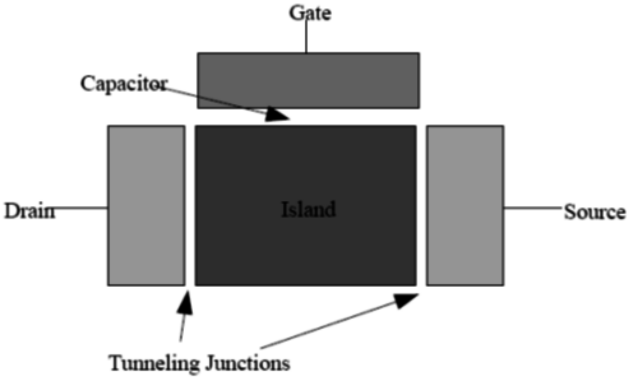
Excitons

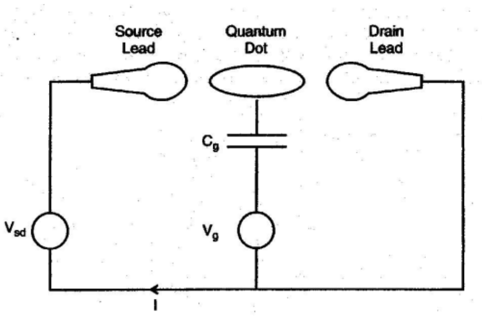
An **exciton** is a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and in some liquids. An exciton can form when a photon is absorbed by a semiconductor. This excites an electron from the valence band into the conduction band. In turn, this leaves behind a positively charged electron hole. The electron in the conduction band is then effectively attracted to this localized hole by the repulsive Coulomb forces from large numbers of electrons surrounding the hole and excited electron. This attraction provides a stabilizing energy balance.

The excitons radius can be taken as an index of extent of confinement experienced by a nanoparticles. If the dimension of nanoparticles (d) is greater that radius of exciton (a_{eff}), it is the weak confinement region, And if d< a_{eff}, it is strong confinement region. And if d>>$a_{eff,}$ no confinement.Under weak confinement conditions, the excitons can undergo unrestricted translational motion. But for strong confinement this translational motion is restricted. There is an increase in overlap of electron and hole wavefunctions with decrease in particle size and thereby enhanced electron hole interaction. An optical index of confinement is the blue shift (shift to higher energies) of optical absorption edge and exciton energy with decrease in nanoparticles size.

Single Electron tunnelling

Single electron transistor is a new type of switching device that uses controlled electron tunnelling to amplify current. Single electron devices differ from conventional devices in the sense that the electronic transport is governed by quantum mechanics. One electron is sufficient to define logic state. A conventional field-effect transistor is a switch that turns on when electrons are added to a semiconductor and turns off when they are removed. These on and off states give the ones and zeros that digital computers need for calculation. Interestingly, these transistors are almost completely classical in their physics. However, if one makes a new kind of transistor, in which the electrons are confined within a small volume and communicate with the electrical leads by tunneling, all this changes. One then has a transistor that turns on and off again every time one electron is added to it, we call it a single electron transistor (SET).





The source supply electron and drain removes electrons for use in external circuit. The voltage causes current 'I' to flow by means of electrons tunnelling into and out of QD. The current flow equals the applied source drain voltage V_{sd} divided by resistance and the value of resistance depends on the tunnelling of electron from source to QD and QD to drain. The resistance of the active region of QD can be controlled using a gate voltage as shown which in turn regulates the current flow between source and drain terminals. The device then function as voltage controlled or field effect controlled transistor (FET).

In a single electron transistor, a drain and source electrode are connected through a tunneling junction to an island, which is also capacitively connected to a gate. When all the biases are zero, electrons do not have enough energy to tunnel through the junction.
Consider spherical potential well. The electrostatic energy E of spherical capacitor of charge Q is changed by amount,

$\Delta E \sim eQ/C$ (1)

When an single electron is added or subtracted, corresponding change in potential,

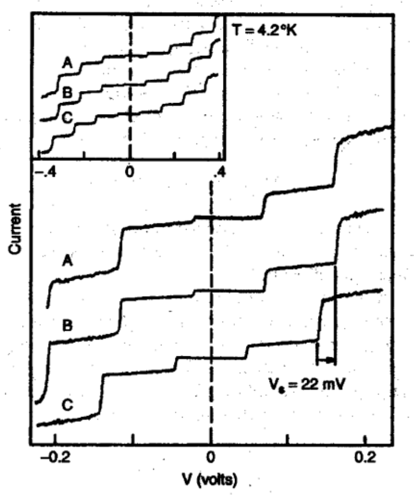
$\Delta V \sim \Delta E / Q = e/C$ (2)

The two quantum conditions for observation of discrete nature of single electron charge transfer to a quantum dots are:

- The capacitor single electron charging energy $e^2/2C$ must exceed thermal energy K_BT
- The uncertainty principle satisfied by the product of capacitor energy ($e^2/2C$) and time (R_TC) required for the charging the capacitor,

$$\Delta E\ \Delta t = \frac{e^2}{2C}(R_TC) > h$$

When this condition is met and voltage changes by the value of eq (2), the I-V characteristics are shown by,



In these conditions, $e^2/2C$ is the electrostatic energy needed for one electron of the "source" electrode to tunnel across the metal island and reach the "drain" electrode. If this energy barrier is appreciably higher than the thermal fluctuation energy K_BT, the island remains sensitive to the addition of just one extra electron to the millions it already contains, and precisely one extra electron can be added in certain polarization conditions of the SET device. If there is not enough electron energy, the transfer will be blocked. This phenomenon is called the **Coulomb blockade.** As the bias voltage between source and drain is increases, an electron can pass through the island when the energy in the system reaches the coulomb energy. The charging energy of the island may be modified, however, by means of a third "gate" electrode coupled to the island through a capacitor, and the effect of the energy barrier can be cancelled.

Single-electron transistor (SET) is a key element of current research area of nanotechnology which can offer low power consumption and high operating speed. The single electron transistor is a new type of switching device that uses controlled electron tunneling to amplify current.

Why single electron is better than MOSFET?

SET has tunnel junction and a small conducting island (eg. QD). The tunnelling electrons are transferred one by one through the island from source to drain due the effect of coulomb blockade. In the case of MOSFET, it is a p-n junction which has a channel region. Number of electrons is transferred through the channel at a time and hence many electrons participate to the drain current. The consumption of less power across each transistor is the advantage of SET devices over MOSFET.

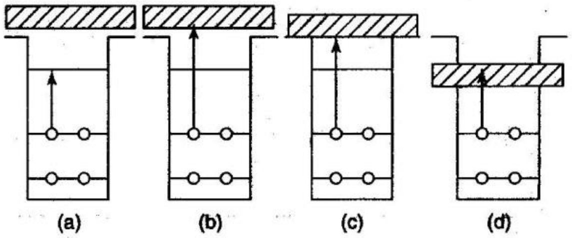
Applications

1. Detection of Infrared Radiation

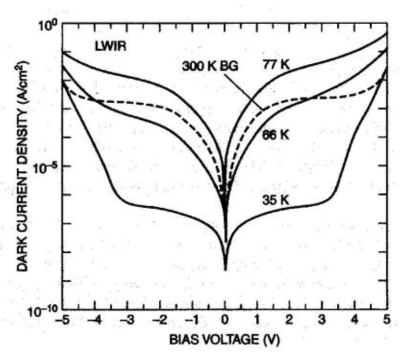
Most of the semiconductor optoelectronic devices utilize transitions between the state in the conduction band and the state in the valence band, so called interband transitions. The operating wavelength of such devices is mainly determined by the band gap of the material employed and is therefore limited to the near-infrared and visible part of the electromagnetic spectrum. However, if one wishes to access longer wavelengths, a different approach is required: the transitions within the same band (intraband transitions) have to be used. Intraband optical transitions in bulk are not allowed and nanostructures have to be used instead.

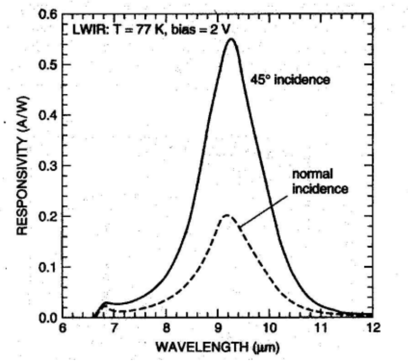
The quantum nanostructures can also be used to detect infrared signals at room temperature. The quantum well infrared photodetector consists of a periodic array of quantum wells subjected to an electric field perpendicular to the plane of the wells. Carriers from the ground state are excited to a higher state by absorbing incident photons. If the higher state is in the continuum or close to it, the excited carrier can be included in the transport and contributes to photocurrent. By exciting electrons over an electrically induced energy barrier, both the range of detectable wavelengths and the sensitivity of the device can be controlled.

The sketches of 4 types of detectors are shown in figure. The sensor works when an infrared signal excites conduction-band electrons in a deep electron reservoir to conduction band and the resultant electric current flow is measure of incident radiation intensity. Figure (a) represents transition from bound state to bound state and takes place within quantum well. (b) represents transition from bound state to continuum. In (c) continuum begins at top of well so the transition is from bound state to quasi-bound state. Where as in (d) transition is from bound state to mini-band (as continuum lies below top of well).



The responsivity of detector is the electric current generated per watt of incoming radiation. The plot of dark-current density (before radiation) Vs bias voltage is shown in figure. The dependence of this detectors responsivity on wavelength is also given. The responsivity reaches maximum at 9.4µm and it is sensitive over the range of wavelength 8.5-10 µm.





2. Quantum dot laser

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. 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.

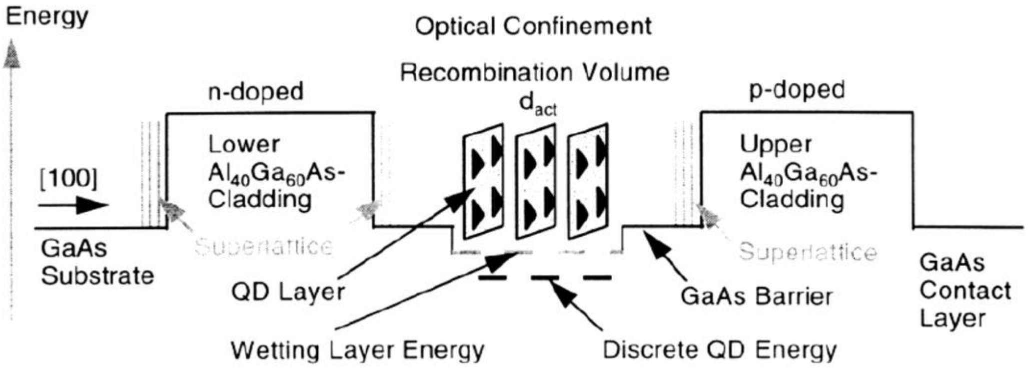
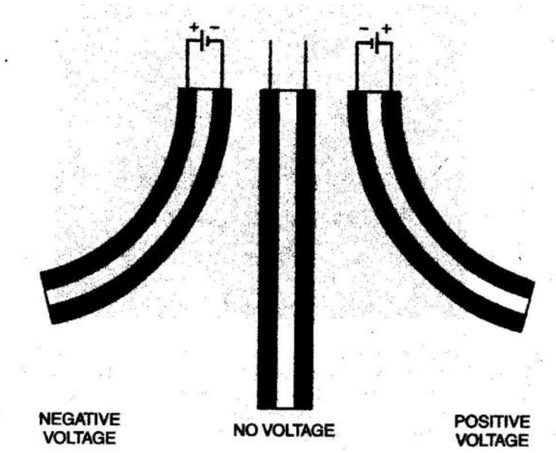


Figure shows schematic view of the band structure of a typical quantum dot laser. An ideal QD laser consists of a 3D-array of dots with equal size and shape (middle of the figure), surrounded by a higher band-gap material which confines the injected carriers. The whole structure is embedded in an optical waveguide consisting of lower and upper cladding layers (n-doped and p-doped shields).

Nanodevices and nanomachines

Actuators are devices that convert electrical energy to mechanical energy. An actuator based on deformation of carbon nanotubes under electrical charge is shown in figure. The actuators consist of 3 fibers aligned with their axes parallel and in contact. The outer two tubes would be metallic and inner tube insulating. The sheets are placed on 1.0M NaCl electrolytic solution. Application of few volts produced a deflection and could be reversed by changing polarity of voltage. Application of ac voltage produced oscillations in the cantilever. It works based on the effect of charging on individual carbon nanotubes.



The challenges of constructing Nano devices are:

1. Problem of communicating with and sensing motion of nanoscale devices
2. Little knowledge about the mechanical behavior of object with nearly 10% of atoms on the surface

However there are noteworthy advantages of NEMS devices that make it worthwhile in their development. The small effective mass of the nanosized beam renders its resonant frequency exteremely sensitive to to slight changes in its mass.e.g. The frequency can be affected by adsorption of small number of atoms on the surface which could be basis of high sensitivity sensor.

A weight on a spring would oscillate indefinitely with same amplitude if there is no friction. However there are air resistance and internal spring friction which dissipate energy resulting in damped oscillations and the damping force is proiportional to velocity of oscillating mass. The equation of motion of spring is,

$$M\frac{d^2x}{dt^2}+b\frac{dx}{dt}+Kx=0$$

Where K is the spring constant and b is the damping factor.

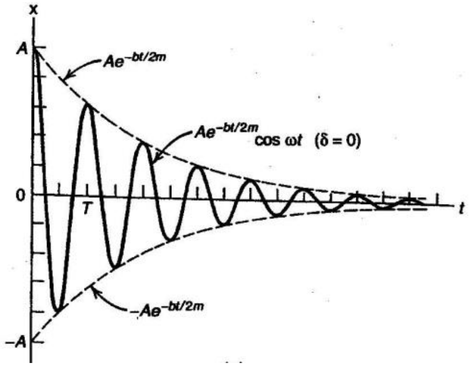
The solution to this equation for a small damping factor is,

$$X(\omega) = A\exp\left(\frac{-bt}{2M}\right)\cos(\omega t + \delta)$$

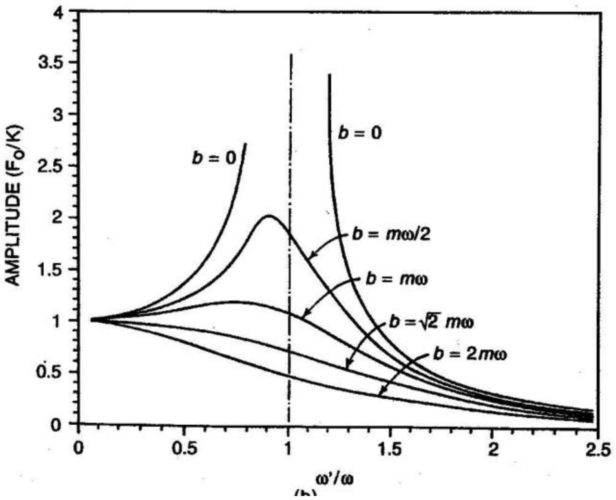
With frequency given by,

$$\omega = \left[\left(\frac{K}{M}\right) - \left(\frac{b}{2M}\right)^2\right]^{-1/2}$$

This describes a system oscillating at a fixed frequency ω with an amplitude exponentially decreasing in time.



For a clamped vibrating beam major source of damping is due to air resistance which is proportional to area of the beam. For the nano sized beam area is smaller so that it dissipates very little energy over vibrational cycle.

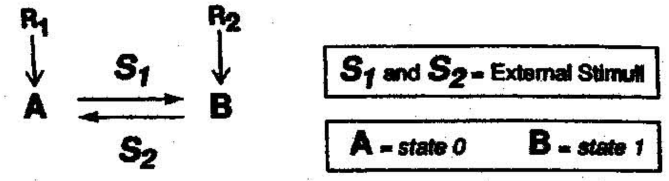


If an external oscillating force $F_0 \cos(\omega' t)$ applied to a damped harmonic oscillator, a large increase in amplitude occurs when the frequency of applied force equals natural resonant frequency of oscillator called **resonance**. The increase is magnitude depends on the damping factor b. Smaller the damping factor, narrower the resonance peak and greater the increase in amplitude. The quality factor ($Q=\omega_0/\Delta\omega$) is the energy stored divided by elergy dissipated per cycle. Where, ω_0 is the resonant frequency and $\Delta\omega$ is the width of resonance at half height. Nano sized cantilevers have very high Q value and dissipate little energy as they oscillate. Such devices are highly sensitive to external damping which is essential in making sensing devices. High Q values means less thermomechanical noise means significantly less random mechanical fluctuations. NEMS oscillators have Q values about 1000 times that of high Q electrical devices. The NEMS devices require very little power to drive then. E.g. a picowatt power can drive NEMS device with low signal to noise ratio.

Molecular and supermolecular switches

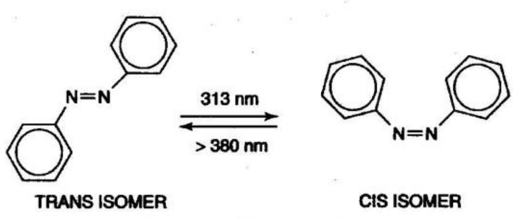
One of the main drivers for nanotechnology research is to uncover ways to produce nanoscale electronic circuits and components. The computing industry demands ever smaller, faster, and more efficient processors, and we are beginning to encounter limits to just how small the necessary components can be made.

One of these molecular devices, on which significant progress has been made in recent years, is the molecular switch. Although a very simple device, a suitable molecular switch could be the basis for more complicated molecular machines. A molecular switch usually consists of a single molecule which can shift controllably between two stable states. The trigger used to switch between the states can be an electrical current, a change in temperature or chemical environment, or even light. The two states must be thermally stable and be able to switch back and forth many times.



The schematic representation of elements of molecular switch is shown in figure. An external stimulus s_1 changes the molecule from state 0 to 1 and s_2 returns the molecule to 0 state.

An example of molecular switch is provided by azobenzene molecule which has two isomeric forms. However the cis form of azobenzene is not thermally stable and slight warming cause it return to trans form. So, optical methods cannot be used for switching. The electrochemical oxidation and reduction can overcome the thermal instability.



In order to build up miniaturized devices, one of the key challenges is to control molecular function at surfaces. Switches represent a prototype of such functional molecules. In particular, azobenzene undergoing trans-cis isomerization of the N=N double bond has been well investigated in solution as well as in the gas phase.