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Quantization in Nanomaterials

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***Abstract*—**This paper is a review of quantization phenomena in nanomaterials. Dimensions of nanomaterial are reviewed and Quantum concept is analyzed. The influence of band structures on the physical properties of quantized structures is studied. Energy level and effective mass calculation through equations are understood. Finally quantized electronic structure of semiconductor is studied.

Keywords—nanomaterial,quantization, emiconductor,quantum ,band structure.

INTRODUCTION

The physical properties of the material significantly depend on their size when reduced to Nano dimension. In bulk system, most of the atoms are the interior atoms, so the properties of the materials are determined by them. But in the case of nanoparticles, the fraction of surface atoms cannot be neglected. The nonmaterial are the elements that have at least one spatial measurements in size range 1 to 100 nanometers. The quantum number determines a set of discrete energies which the electron can have, since the energy is directly related to the electron's momentum. Quantum confinement is responsible for the increase of energy difference between energy states and band gap. Nanomaterials are generally characterised as zero dimensional nanomaterials and one dimensional nanomaterials. Low dimensional structures having quantum confinement of one, two, and three dimensions such as

- quantum wells
- quantum wires
- Quantum dots

To predict the confined energy levels of nanostructures Schrodinger equations are used. In recent years, with the advent of MBE, MOCVD and other experimental techniques, the influence of quantization of band states on the different physical properties of nanostructured materials such as quantum wells, quantum well wires, quantum dots, inversion layers, magnetic quantization, and different field added dimensionally reduced systems. The influence of band structures on the physical properties of quantized structures is becoming increasingly important

INTRODUCTION TO NANOMATERIALS

There are different kinds of materials of different size around us. Some materials are natural e.g. silver, gold, and garnet etc. and some materials are manmade e.g. cement, CD and pigments etc. Human eye can see the materials with naked eye using visible rays 350 nm to 700 nm. Human eye resolution is 0.07mm. If we want to see the material below 0.07 mm size then we have to use different microscopes according to the size of material.

What is Nanoscale?

It can be used to refer to one billionth of any measure.

Nanometer

Nanosecond

Nanogram

Nanomole

The diameter of one human hair is about 10,000 to 80,000 nanometers. The diameter of atom is 0.1 nm to 0.2 nm. A crystal of 0.1 mm size contains approximately 1021 atoms. Nanoscale materials have size less than 100 nm. Nanoscale materials can be seen using light rays of wavelength in the range of 0.1 nm to 10 nm which can be achieved using electrons. So electron microscopy is very important in analysis of nanoscale materials.

Unusual properties are seen at nanometer size. For example- electrons which are delocalized becomes confined so the properties depending on localization of electron will change. Metal becomes non-metal due to this. Similarly reactivity will change due to change of surface to volume ratio. Disorder of dipoles increases with decrease of size which will result in transition from magnetic to nonmagnetic material.

Different size of gold particles appears in different colors which can be explained with the help of nanoscience.

Gold cluster < 1nm Orange gold

Gold nanoparticles: 3 to 30 nm Red color gold

More than 50 nm size: Crimson to blue color gold

Bulk gold film: Yellow color gold.

Different type of microscopes used in nanoscale analysis is

1- TEM- Transmission Electron Microscope(1931)
2- SEM- Scanning Electron Microscope(1937)
3- STM- Scanning Tunneling Microscope(1981)
4- AFM- Atomic Force Microscope(1986)

Nanotechnology gives new array of properties which are not possible with bulk material. Eric Drexler has written a book in 1981 with title “molecular manufacturing” and another book in 1986 with title “Engine of creations”. These books have given the direction to nanoscale manufacturing. Atomic manipulation of Xe atoms is done in 1989 at IBM.

In electronics size is very important. Nanoscale miniaturization will lead to reduction of effective electron path and reduction in electron scattering which will lead to faster operation of electron devices but it will require more complicated manufacturing process and it will lead to increase in the fabrication cost.

Electronic and optical properties of materials can be controlled by controlling their size and shape.

III ENERGY LEVEL IN ATOMS

The sum of the kinetic and potential energies of an electron moving around a nucleus can only assume a set of discrete values for the simplest atom (hydrogen). This is due to wave like properties exhibited by electrons.

The electron wave must repeat itself exactly when followed around any circular path enclosing the nucleus to become stable. It leads to the conclusion that an integral number of wavelengths must fit into the path, and is termed as 'quantization condition'.

The electron's wavelength (λ) is inversely proportional to its momentum (p) as defined by De Broglie's relation of the wave-

particle duality:

$$\lambda = h/p \qquad (2.1)$$

Where h is called Planck's constant and it has the value 6.6×10^{-34} Js. The quantization condition fixes the electron momentum to one of a set of discrete values depending on the number of wavelengths fitting the circular path. The quantum number determines a set of discrete energies which the electron can have, since the energy is directly related to the electron's momentum.

IV EFFECTIVE MASS:

The concept of mass of the carriers occupies a central position in the whole field of solid-state electronics. This mass is different than that of free electron mass and is called the effective mass of the carrier whose expression changes under different physical conditions. The effective carrier mass, in general, can be expressed as

$$\textit{effective carrier mass along a particular direction}\left(m^*\right) = \frac{\textit{momentum}\left(p\right)\ \textit{along this direction}}{\textit{velocity}\left(v\right)\ \textit{along the same direction}} \qquad \text{eqn. (2.2)}$$

From eqn. (2.1) we can write,

$$p = \frac{h}{\lambda} = \left(h/2\pi\right)\left(\frac{2\pi}{\lambda}\right) \qquad (2.3)$$

The term $\left(h/2\pi\right)$ is called $\hbar$ and is called the normalized Planck's constant or the Dirac's constant and the term $\left(\frac{2\pi}{\lambda}\right)$ is known as the carrier wave vector $\left(\vec{k}\right)$. Therefore the eqn. (2.3) can be expressed as,

$$\vec{p} = \hbar\vec{k} \qquad (2.4)$$

The velocity as written in eqn (2.2) must be the group velocity $\left(\frac{\partial\omega}{\partial k},\ \textit{where the frequency}\ \omega = \frac{E}{\hbar}\ \textit{in which E is the total energy of the carrier}\right)$ and not at all the phase velocity. Therefore the velocity of the carrier is $\frac{\partial\omega}{\partial k}$. Thus the mass of the carrier should, in general, be written as

$$m^* = \frac{\hbar k}{\frac{\partial \omega}{\partial k}} = \frac{\hbar k}{\frac{1}{\hbar}\frac{\partial E}{\partial k}} \qquad (2.5)$$

Therefore the effective mass of the carriers can be expressed as,

$$m^* = \hbar^2 k \frac{\partial k}{\partial E} \qquad (2.6)$$

From eqn. (2.6), we observed that effective mass changes with the slope of the E-k curve. This E-k relation is called the dispersion relation which changes from semiconductor to semiconductor, and consequently the m^* also changes. The momentum effective mass is the most fundamental. Acceleration effective mass $m_f^* = \hbar^2 \Big/ \frac{\partial^2 E}{\partial k^2}$.

This is also called the curvature effective mass. These two definitions yield the same result when E∝k2 i.e. E-k relation is parabolic. For any deviation from the parabolicity these two definitions of the effective mass will not converge to the same expression. The effective momentum mass of the carriers as given by eqn. (2.6) affects all the properties of semiconductors such as electronic heat capacity, diffusivity to mobility ratio, the Hall co-efficient, all types of transport co-efficient and changes with electron concentration and other externally controllable parameters.

V FERMI-DIRAC STATSTICS

The Fermi-Dirac statistics expresses the probability with which the electron will occupy the energy level E and is extremely important in the whole field of solid-state electronics.
This equation is called the functional equation and can be satisfied if and only if we substitute f(E) as

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

where EF is the fermi energy (a quantity defined later on), kB in the Boltzman constant (8.62 x 10-5 eV/K) and T is the absolute temperature in Kelvin (K) .

The total energy E of a conduction electron is given by

E = Kinetic energy + Potential energy

$= \frac{p^2}{2m_c^*}$ + P.E. (where m_c^* is the effective mass of the electron in the conduction band)

$= \frac{p^2}{2m_c^*}$ (assuming the energy is measured from the edge of the conduction band EC)

Since we have already proved that $p = \hbar k$ therefore we can write that $$E = \frac{\hbar^2 k^2}{2m_c^*} \quad (2.8)$$

This indicates a parabolic dependency between the energy and wave vector as shown in the fig below and is termed as electron parabola. In this figure the horizontal line EC indicates the edge of the conduction band, the horizontal line EV is called edge of valence band, the dotted horizontal line near EC is called the donor level ND, the dotted horizontal line near EV is called the acceptor level NA. Ed is called the donor energy level, Ea is the acceptor energy level. The energy is measured from the edge of the conduction band EC in the vertical upward direction. The band gap Eg is defined as Eg= EC - EV. For positive band gap EC > EV, for negative band gap EC < EV and for zero band gap EC =EV.

Below the line EV the heavy hole, light hole and split-off hole parabolas have been drawn, since, only three types of holes exist experimentally. The effective masses of the three types of holes are mhh,, mlh, and msoh respectively.

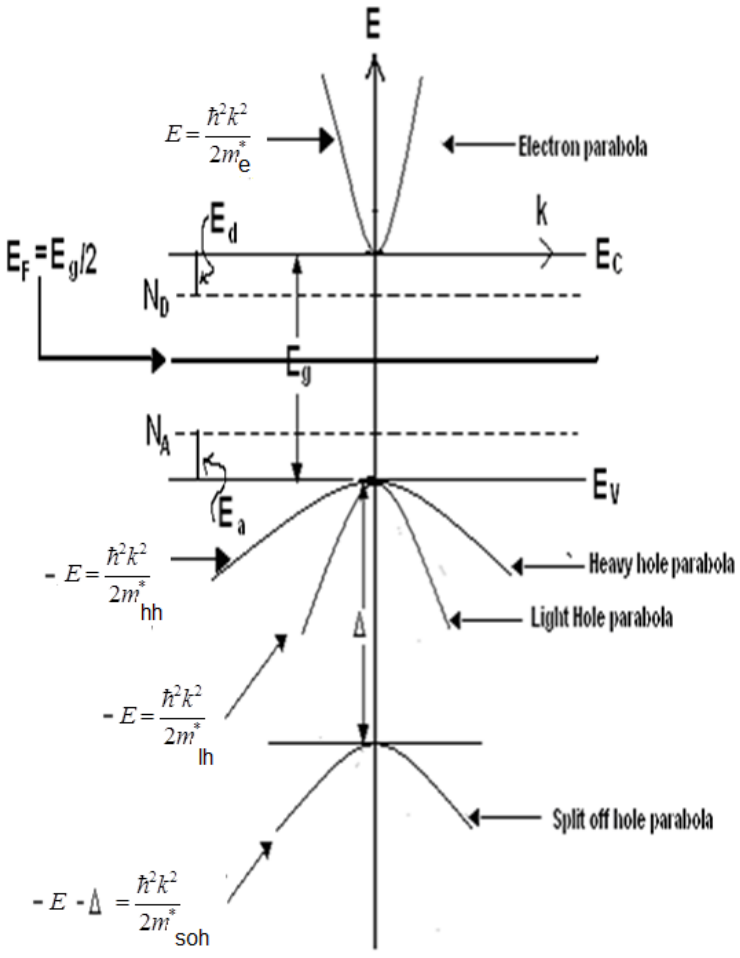

Figure 2.1 Typical model of an energy band structure of the crystalline material (Δ is called spin orbit splitting constant of valance band) Semiconductors (Eg ≤ 2.34eV)

VI QUANTIZED ELECTRONIC STRUCTURE

Quantum confinement leads to collapse of the continuous energy bands of bulk material into discrete, atomic like energy levels. The discrete structure of energy states leads to a discrete absorption spectrum, which is in contrast to the continuous absorption spectrum of a bulk semiconductor as shown in Fig.3.1

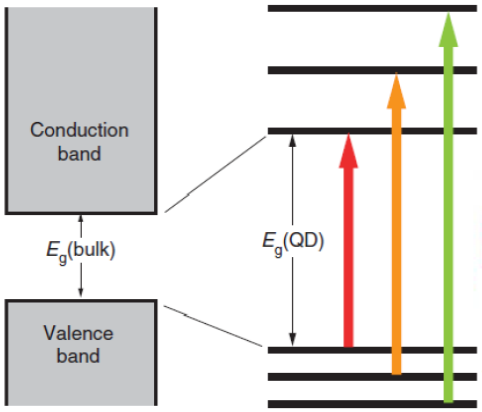

Fig. 3.1: A schematic of the discrete energy level of a semiconductor.

In semiconductors, the quantization effect that enhances the optical gap is routinely observed for clusters ranging from 1 nm to almost 10 nm. Metal particles consisting of 50 to 100 atoms with a diameter between 1 and 2 nm start to lose their metallic behavior and tend to become semiconductors.

Low dimensional structures having quantum confinement of one, two, and three dimensions (such as quantum wells, wires, and dots) have, attracted much attention in uncovering new phenomena and their interesting applications in nanotechnology.

Table 3.1 *Classification of quantum confined structures.*

Structure	Quantum confinement	Number of free dimension
Bulk	0	3
Quantum well/superlattices	1	2
Quantum wire	2	1
Quantum dot/Nanocrystals	3	0

In general, quantum wires, wells and dots are grown by advanced epitaxial techniques in nanocrystals produced by chemical methods or by ion implantation, or in Nano devices made by state of- the-art lithographic techniques.

In QWs, the restriction of the motion of the carriers in the two directions may be viewed as carrier confinement by two infinitely deep 1D square potential wells, leading to quantization [known as quantum size effect (QSE)] of the wave vectors along the two directions, allowing 1D electron transport representing new physical features not exhibited in bulk semiconductors.

The allowable energy levels, motion, and optical properties of the electrons are strongly affected by the quantum-mechanical effects. These artificially synthesized quantum structures find major application in high-performance transistors such as the microwave high-electron-mobility transistor (HEMT), and in high-performance solid-state lasers such as the semiconductor quantum-well laser.

Zero-dimensional materials: Nanocrystals absorb light then re-emit the light in a different colour. The size of the nanocrystal (at the Angstrom scale) determines the colour. A quantum dot is a semiconductor whose excitations are confined in all three spatial dimensions. As a result, they have properties that are between those of bulk semiconductors and those of discrete molecules.

In an unconfined (bulk) semiconductor, an electron-hole pair is typically bound within a characteristic length called the Bohr excitation 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. Specifically, the effect describes the phenomenon results from electrons and electron holes being squeezed into a dimension that approaches a critical quantum measurement. For 0-D nanomaterials, where all the dimensions are at the nanoscale, an electron is confined in 3-D space. Quantum confinement is responsible for the increase of energy difference between energy states and band gap. Quantum dots offer great potential in the form of QLEDs which are made out of networks of quantum dots and can also build on, yet dramatically improve, existing LED technologies.

Quantum dots are essentially nanometer-size crystals of semiconductor materials (e.g., silicon or germanium) for which the electronic properties are strongly dependent on their size.

Wavelengths in quantum dots can be controlled in nanocrystalline materials. The energy separation between valence and conduction bands can be altered in nanocrystalline quantum dots by changing the size of the nanoparticles. Resulting energy levels can thus be varied.

One-dimensional nanomaterials: The diameters of the nanostructures are comparable to the sizes of biological and chemical species being sensed, and thus intuitively represent excellent primary transducers for producing signals that ultimately interface with macroscopic instruments.

The size-tunable colours of semiconductor nanocrystals, together with their highly robust emission properties, are opening up opportunities for labelling and optical-based detection of biological species that offer advantages compared with conventional organic molecular dyes widely used today.

The underlying mechanism for nanowire sensors is a field effect that is transduced using field effect transistors (FETs), the ubiquitous switches of the microelectronics industry. The electronic characteristics of nanowires are well controlled during growth in contrast to carbon nanotubes. Si nanowires can be prepared as single-crystal structures with diameters as small as 2-3 nm.

The Einstein relation for the diffusivity (D) to the mobility (μ) ratio (DMR) of the carriers in electron devices is very useful since the diffusion constant can be obtained from this ratio by knowing the experimental values of the mobility. It is more accurate than any of the individual relations for the diffusivity or the mobility, which is the two widely, used quantities of carrier transport of modern semiconductor devices. The classical value of the DMR is equal to $(k_B T/e)$, (k_B, T, and e are Boltzmann constant, temperature and the magnitude of the carrier charge respectively) which represents the well-known Einstein relation. The relation is valid for both the electrons and the holes. In this conventional form it appears that, the DMR increases linearly with T and is independent of carrier concentration. This relation holds only under the condition of carrier non-degeneracy although its validity has been suggested erroneously for degenerate materials. Besides, the performance of the electron devices at the device terminals and the speed of operation of modern switching transistors are significantly influence by the degree of carrier degeneracy present in these devices. The simplest way of analyzing such devices taking into account of the degeneracy of the band is to use the appropriate Einstein relation to express the performance at the device terminal and switching speed in terms of the carrier concentration.

The photo-current density depends on the density-of-states function which significantly affects the different physical properties of electronic materials having various band structures. Photoemission from electronic materials having degenerate electron concentration is essentially determined by their respective energy band structures. It has different values in different materials and varies with the electron concentration, with the magnitude of the reciprocal quantizing magnetic field under magnetic quantization, with the quantizing electric field as in inversion layers, with the nano-thickness as in quantum wells, wires and dots and also with superlattice period as in the quantum confined superlattices of small gap compounds with graded interfaces having various carrier energy spectra.

This method can predict the confined energy levels of nanostructures by solving Schrodinger equation assuming the barriers have an infinite confining potential. The “effective mass” solutions of the Schrödinger equation for electrons confined in a quantum dot or NCs, quantum wire and quantum well are,

Quantum dot or Nanocrystals:

$$E_{n,m,l} = \frac{\pi^2\hbar^2}{2m^*}\left(\frac{n^2}{L_z^{\,2}} + \frac{m^2}{L_y^{\,2}} + \frac{l^2}{L_x^{\,2}}\right), \psi = \phi(z)\phi(y)\phi(x)$$

Quantum wire:

$$E_{n,m}(k_x) = \frac{\pi^2\hbar^2}{2m^*}\left(\frac{n^2}{L_z^{\,2}} + \frac{m^2}{L_y^{\,2}}\right) + \frac{\hbar^2 k_x^{\,2}}{2m^*}, \psi = \phi(z)\phi(y)\exp(ik_x x)$$

Quantum well:

$$E_n(k_x k_y) = \frac{\pi^2\hbar^2 n^2}{2m^* L_z^{\,2}} + \frac{\hbar^2}{2m^*}\left(k_x^{\,2} + k_y^{\,2}\right), \psi = \phi(z)\exp\left(ik_x x + ik_y y\right)$$

where n, m, l = 1, 2 … the quantum confinement numbers, Lx, Ly and Lz are the confining dimensions, (exp ikxx+ ikyy)is the wave function describing the electronic motion in x and y direction, similar to free electron wave functions

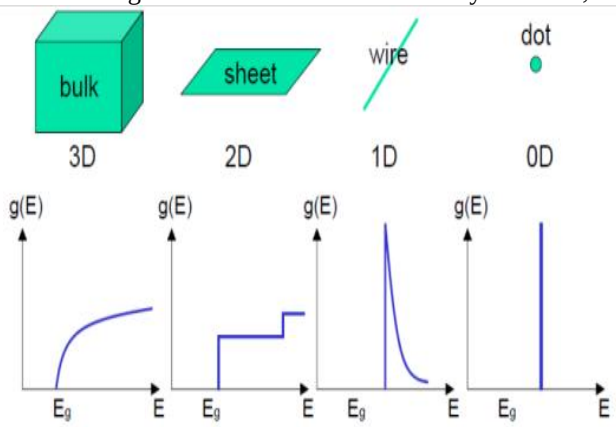

Fig. 3.2 *Density of electron states of a semiconductor as a function of dimension. The optical absorption spectrum is roughly proportional to the density of states.*

The in-plane effective electron mass (mi) in narrow Ga0.47In 0.53As/InP quantum wells is strongly dependent on the quantization energy.

III-V materials are being increasingly used in integrated optoelectronics, passive filter devices, distributed feedback lasers and Bragg reflectors.

In recent years, with the advent of MBE, MOCVD and other experimental techniques, the influence of quantization of band states on the different physical properties of nanostructure materials such as quantum wells, quantum well wires, quantum dots, inversion layers, magnetic quantization, and different field added dimensionally reduced systems. The influence of band structures on the physical properties of quantized structures is becoming increasingly important.

REFERENCES:

1- Bhattacharya P. (2008), " Semiconductor optoelectronic devices", Pearson education, pp 1-155
2- Buczko R(1992) "Valance band quantization in a spherical quantum dot"Acta Physica Polonica A, Vol. 82(5), pp 789-792.
3- John Sanjeev (1987) "Localization and density of states for an electron in a quantized elastic continuum",Physical Review B, Vol. 35(17),pp 9291-9294.

4- Lundstrom M. and Guo J.(2006), "Nanoscale transistors",Springer, pp 1-80

5- Ovsyuk N.N. and Sinyukov M.P. (1980) "Effect of quantization on electrical reflection spectra in the surface region of a semiconductor", JETP lett, Vol. 32(5),pp. 366-370.

6- Paitya N. and Ghatak K. P. (2013) "Quantization and Carrier Mass" Reviews in Theoretical Science Vol. 1(2), pp. 1–141.

7- Piper L. F. J.(2008), "Observation of quantized subband states and evidence for surface electron accumulation in CdO from angle-resolved photoemission spectroscopy" Physical Review B, Vol. 78(12),pp 165127-1-165127-5.

8- Schmidt K. H.et. al. (1997), "Size quantization effects in InAs self-assembled quantum dots", Appl. Phys. Lett., Vol. 70 (13), pp 1727-1729.

9- Wetzel C. et. al (1996) "Electron effective mass and nonparabolicity in Ga 0.47In 0.53As/InP quantum wells" Physical Review B, Vol. 53(3),pp 1038-1041.

10- Zhang Li et. al. (2013), "Weak localization effects as evidence for bulk quantization in Bi2Se3 thin films" Physical Review B, Vol. 88(12),pp 121103-1-121103-4.

11- https://en.wikipedia.org/wiki/Potential_well