

Semiconductor Nanomaterial and its Electronic Structure: A Review

Upamanyu Das
Rajiv Gandhi University

Abstract— After the great success of semiconductor microelectronics in the last century, the nanoscale semiconductor materials emerged as the building blocks of the next generation of electronic, optoelectronic and chemical sensing devices. The main challenges in the field of nanoscale semiconductor electronics is to the rational control as well as manipulation of synthesis to derive materials with one of their dimensions and upscale production of devices. For the reason, in theoretical study of the movement of electron and electronic structure is very much necessary. The article reviews the contribution of various researcher for and their work for explaining the band structure of semiconductor nanomaterials. The development and deployment of these theoretical study play a role in achieving the goals of nanoscience and nanotechnology.

Index Terms— semiconductor nanoparticles, quantum confinement effect

1 INTRODUCTION

Now-a-days, the impact of nanoscience and nanotechnology is spread out all over the globe. This technology involves precise utilization of nanostructured material (NSM) [1]. These NSMs are the ultra-fine material structures having an average phase or grain size on the order of a few nanometres (10-9m). Each nanoparticle in NSMs can be considered as a “nano crystallite” of a typical size of the order of few nanometres, consisting of 100’s to ,000,000’s of atoms. It is a state of matter in the transition region between bulk solid and molecular structure [2-5]. The importance of NSMs is being realized owing to its unique size-dependent characteristics in the sense that materials with similar chemical composition but different dimension behave differently. With size reduction, its physical properties gradually shift from bulk behaviour towards molecular behaviour.

Although NSMs are considered as an invention in the area of modern science, they actually have a long history. NSMs were used by artisans as far back as the 9th century in Mesopotamia for generating a glittering effect on the surface of pots. Egyptians also knew to use the healing powers of gold nanoparticles against wounds and physical ailments. The use of colloidal particles of gold and different materials was known and used by the Romans toward the middle age (for e.g. staining of glass). In modern times, it was the great alchemist Paracelsus who first prepared gold colloid solution (16th century). He called his purple solution of gold Aurum Potable (Latin: potable gold) and believed it cured all manner of physical, mental, and spiritual ailments. But serious study on gold colloids did not start until the mid-19th century by Faraday, who prepared the first pure colloidal gold which he called ‘activated gold’ [6]. He used phosphorus to reduce a solution of gold chloride for the development his colloidal gold. These colloidal solutions were the first, which gives us an idea about size effects. Faraday was

the first started to study the size dependence of the physical properties of a material. He also used gold, but proceeded in the other direction to study the size effect: he started with very small pieces of gold (nanocrystalline gold) in solution and, by pressing them together, made bigger pieces of gold. His amazement at what he observed is clear from the March 11, 1856 entry in his diary [6].

“and then put on the gold above the convex surface of a rock crystal plano convex lens and pressed it by hand steadily, rocking it a little. This pressure converted the violet or dark tint of the place [of contact] to a beautiful green - far more beautiful than any I have seen in a gold leaf beaten - the effect was perfect.”

Faraday was one of the greatest scientists of the 19th century. So, it is not at all surprising that his diary continues with, what we now know to be, a rather accurate explanation of this phenomenon:

“Has the pressure converted the layer of atoms into a continuous layer by expansion and welding, and is that all the difference? I rather think it is. . . So it appears that these different layers are all gold, and owe their different appearances not to composition but to physical differences.”

Faraday discovered that the color (or to be more precise: the electronic structure) of a metal can become size dependent below a certain critical size. What this critical size was, and why it was different for the different metals that he investigated, was something that Faraday could not understand fully. In the early twentieth century, work on the glasses containing Cadmium Sulphide (CdS) showed that there was a red- shift in the absorption threshold with the growth of CdS particle size [7]. So far, it is the first experiment that proved that this size dependence of material properties also applied to semiconductors. It was found that both the absorption and the emission of CdS shifted towards shorter wavelengths for smaller crystallite sizes. Again, a qualitative explanation was sought in terms of the reduced size of the CdS crystal and shifting of absorption peaks.

During the first half of 20th century it was revealed that a

Author is currently Assitant Professor, Department of Phycis, Rajiv Gandhi University, Doimukh- 791112 Arunachal Pradesh, India . E-mail: upam2005@gmail.com

material can become strongly dependent on the size of the material below a certain threshold size. But no adequate explanation of the size effects was at that time. It was the seventies, the impetus progress in the development of analytical skills and the fabrication of low-dimensional semiconductor structures made it possible to understand physical basis of such effects in quantitative qualitative ways.

In the late 1960's researchers reported differences between the absorption spectra of colloidal semiconductor particles and the spectra of the corresponding macro-crystalline materials in 1967, Berry reported that the absorption onset of suspensions of crystals of AgBr [8] and AgI [9] was shifted to shorter wavelengths as compared to the macro-crystalline material, and made the following statement:

"The observed shift of the absorption curve to shorter wavelengths should not be regarded as suggesting a mechanism in which the band gap is widened, but as either a decreased number of absorbing atoms or a decreased efficiency of the phonon-assisted electronic transitions."

In 1968, Stasenko presented experiments on the thin films of CdS [10], motivated by the prediction from Sandomirskii (1963) that for very thin semiconductor films the band gap is inversely proportional to the square of the film thickness [10]. The results were in good agreement with the theoretically predicted shift of the bandgap and he reported: "Such a forbidden-energy gap increase is connected with quantum effects" It was realized in the early 1980's that these quantum effects are not only responsible for the different properties of the nanostructured materials as compared to the macro crystalline material, but also for some the peculiar behavior of particles. Some 15 years after the firm statement by Berry, it was shown that the mechanism that he ruled out (widening of the band gap) is in fact responsible for his observations. In the last two-decade researcher successfully explain most of the properties in lowdimensional systems.

Among the massive number of materials available in the today's world, people able to develop and analysis large variety of materials at nanoscale regime as

- Metals: gold [Au], silver [Ag], palladium, platinum, cobalt.
- Semiconductors: Elemental (Si, Ge), II-VI (ZnS, CdS, CdTe, ZnSe),III-V(GaAs, GaN, InP, GaAs), IV-VI(PbS, PbTe, PbTe) systems
- Oxides: ZnO , TiO₂,Ga₂O₃, Al₂O₃,MgO etc.

All of these materials show extensively new verities of properties, which make them as candidate for today's technology base world. Metal nanoparticles (Ag, Au etc) exhibit plasmon absorbance bands in the visible spectral region that are controlled by the size of the particles [11]. Numerous studies reported on the labeling for bioassays and staining of biological tissues using those metal nanoparticles as means to analyze and visualize biological processes [12-18]. Among the Oxides materials, the well-known nanocrystalline film of titanium dioxide was shown to be utilized for dye-sensitized solar cells [19, 20]. Now a day, effort is being put worldwide to develop and assemble quality semiconductor nanostructures for variable application in industries.

2 SEMICONDUCTOR NANOSTRUCTURE MATERIALS

A typical semiconductor has an electrical conductivity between that of a conductor and an insulator (10³ ohm-1cm-1 to 10⁻⁸ ohm-1cm-1) There are four major types of semiconductor materials as listed below -

2.1 ELEMENTAL SEMICONDUCTORS:

The elemental semiconductor materials comprise of elements from group IV of the periodic table. The materials crystallized into possess narrow indirect band gaps. Silicon (Si) and Germanium (Ge) are typical of such kind.

2.2 BINARY COMPOUNDS SEMICONDUCTOR:

Binary compounds semiconductor: These kinds of semiconductors are compounds of two different group elements. These kinds of semiconductors are compounds of two different group elements. The choices are -

- Column III with column V (III-V's): A_{III}B_V
Example: GaAs, GaN, InP etc
- Column II with column VI (II-VI's): A_{II}B_{VI}
Example: ZnS, CdS, ZnO etc
- Column IV with Column VI (IV-VI's): A_{IV}B_{VI}
Example: PbS, PbSe, PbTe etc

The energy band gap of II-VI systems is found wider while for the IV-VI system it is found narrower.

	III	IV	V	VI
	B 5	C 6	N 7	O 8
II	Al 13	Si 14	P 15	S 16
	Zn 30	Ga 31	Ge 32	As 33
	Cd 48	In 49	Sn 50	Sb 51
	Hg 80	Tl 81	Pb 82	Bi 83
				Po 84

Fig 1: Part of a periodic table

2.3 TERNARY ALLOY SEMICONDUCTOR:

These are alloys of two binary compound semiconductors. Ternary alloys have two elements from one column and one from another. Depending on the substitution sites (cationic/anionic) can have two options:

$$A_{III(x)} B_{III(1-x)} C_V = [A_{III} C_V]_{(x)} + [B_{III} C_V]_{(1-x)}$$

$$A_{III} B_{V(y)} C_{V(1-y)} = [A_{III} B_V]_{(y)} + [A_{III} C_V]_{(1-y)}$$

Some of the commonly used ternary semiconductor alloys are Aluminium gallium arsenide (Al_xGa_{1-x}As), Indium gallium arsenide (In_xGa_{1-x} As), Aluminium indium antimonide (Al_x-In_{1-x}Sb), Gallium arsenide nitride (Ga_xAs_{1-x}N), Aluminium

gallium phosphide ($\text{Al}_x\text{Ga}_{1-x}\text{P}$), Indium gallium nitride ($\text{In}_x\text{Ga}_{1-x}\text{N}$), Indium arsenide antimonide ($\text{In}_x\text{As}_{1-x}\text{Sb}$)

2.4 QUATERNARY ALLOYS SEMICONDUCTOR:

Quaternaries alloys are consisting of 4 elements. It may be mixer of four binary semiconductor or three binary semiconductors. Some such semiconductors are: Aluminium gallium indium phosphide (AlGaInP); Aluminium gallium arsenide phosphide (AlGaAsP); Indium gallium arsenide phosphide (InGaAsP); Aluminium indium arsenide phosphide (AlInAsP); Aluminium gallium arsenide nitride (AlGaAsN); Indium gallium arsenide nitride (InGaAsN); Indium aluminium arsenide nitride (InAlAsN)

Although nanostructured materials are objects made out of metallic, semiconductor or insulating materials, in the last two decades, there has been much research on nanoparticles made out of semiconductor system, especially on II-VI semiconductor types, e.g. CdSe, CdTe, CdS, ZnS, etc. Any of these semiconductor materials containing grain size or clusters below 100 nm or layer, filament of that dimension is considered as semiconductor nanostructure. It is a state of matter in the transition region between bulk solid and molecular structure. The NSMs materials have unique characteristics in the sense that materials with similar chemical composition but different dimension behave differently. The properties gradually change from bulk behavior to molecular behavior with decreasing particle size. It is due to the quantum mechanical phenomenon which dominates in low dimensional structures which results and are associated with:

- Enhancement in band gap and evolution of discrete energy levels.
- Extremely high surface to volume ratio ($\gg 1$) compared to bulk which is about 10% for 100 Å particles and 90% for 10 Å particles.
- Enhancement in excitonic binding energy with respect to bulk as a result of which the exciton absorption can be visible at the room temperature
- Enhancement in the oscillator strength with respect to bulk

Since in a NSM, most of the atoms are displayed on the surface than the core, surface reactivity increases at large. It has been reported that their optical, electronic, magneto-optical and catalytic properties can be uniquely vary with size [21-23]. It is expected that the size dependent properties of the nanocrystals is just enormous. To name a few are microelectronics, electro-optics, nonlinear optics, catalysis, photography, electrochemistry and many more.

The specific properties of NSMs materials can have two different possible origins. First, Size effects, which result from the spatial confinement of carrier motion in a

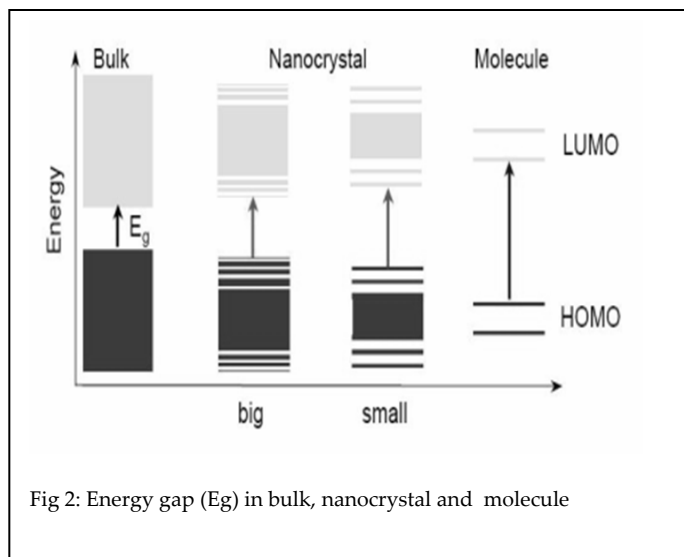


Fig 2: Energy gap (E_g) in bulk, nanocrystal and molecule

low-dimensional system. An example is the confinement of electron wavefunctions inside a region whose size is smaller than the electron mean free path. This class of effects may give birth to completely new properties. Second one is the surface effects, which are a consequence of the significant volume fraction of matter located near surfaces, interfaces, or domain walls.

3. QUANTUM EFFECTS IN SEMICONDUCTOR NANOSTRUCTURES:

In the early eighties, quantum confinement effect on small particles in suspension was first reported in the early 1980s by Ekimov[25] , Efros [26] and Papavassiliou [27]. Later, Brus et al. [28,29] laid out the proper framework for understanding such effects from the view point of molecular quantum physics. This quantum confinement is observed in semiconductor crystals with sizes of few nanometer due finite size of the crystal, which limits the motion of electrons, holes, and excitons (a quasi-particle a electron-hole pair interacting each other via

$$a_0 = \frac{4\pi\epsilon_0\epsilon_r\hbar}{e^2} \left[\frac{1}{m_e^*} - \frac{1}{m_h^*} \right] \quad (1)$$

Where, ϵ_r relative dielectric constant (high frequency), m_e^* effective mass of electron, m_h^* effective mass of hole.

coulomb potential) can be restricted along one or more direction . The excitons correspond to a hydrogen like bound state of an electron-hole pair and characterized by an exciton Bohr radius defined as [30] -

This exciton Bohr radius a_B is considerably larger the respective value for a hydrogen atom ($\sim 0.53\text{\AA}$). For most of the semiconductors it is $\sim 1-10$ nm.

The excitonic Bohr radius is a useful parameter in quantifying the quantum confinement effect in NSMs. We can say "Quantum confinement effects" arise when the size of a nano-

• Upamanyu Das is currently working as Asst. Professor in Rajiv Gandhi University, Arunachal Pradesh, India. Email: upam2005@gmail.com

crystal is comparable to the length parameters i.e., the deBroglie wavelength λ and exciton Bohr radius (a_B) of the carriers (electrons, holes, excitons). When the radius of a particle approaches the excitonic Bohr radius the movement of carriers (excitons, electrons, holes) is confined and coulomb interaction is increased, thereby increasing excitonic binding energy. This leads to drastic changes in the electronic structure of NSMs. The changes include shift of the energy levels to higher energy, the development of discrete feature of the spectra and the development of strong oscillator strength between selective transitions.

The first explanation for the quantum confinement effect in nanocrystals was Effective Mass Approximation (EMA) given by Efros and Efros [26]. This approach, based on the 'particle in a box model' and the effective masses of the electron (m_e^*) and the hole (m_h^*), with parabolic bands EMA is based on the following assumptions-

- (1) The crystal structure of the Quantum dot (nanoparticle) is same as that of the bulk material
- (2) The Quantum dot or nanoparticle is assumed to be spherical in shape with a radius 'R'
- (3) The potential barrier at the surface of the QD is infinite.

The real space stationary Schrödinger equation for an electron in a bulk crystalline solid with a spatially periodic potential is

$$\left[\frac{-\hbar^2}{2m^*} \nabla^2 + V(r) \right] \psi_r(r) = E_k \psi(r) \quad (2)$$

Where the first term represents the kinetic energy operator for the electron and $V(r)$ is the periodic potential energy experienced by the electron

The potential V may include the ionic potential with respect to lattice translations such that

$$V(r) = V(r + T) \quad (3)$$

where, T , is lattice translational vector

The Bloch theorem indicates that an eigenfunction of the Schrodinger equation for a periodic potential is the product of a plane wave $e^{ik \cdot r}$ times a function $U_k(r)$ which has the same periodicity as periodic potential $V(r)$. Thus, we get

$$\psi_r(r) = e^{ik \cdot r} U_k(r) \quad (4)$$

$$\text{with } U_k(r) = U_k(r + T) \quad (5)$$

Assuming a parabolic band, the eigenvalues of Equation (2) for the eigenfunctions $\psi_k(r)$ can be given by

$$E(k) = \frac{\hbar^2 k^2}{2m} \quad (6)$$

where, m^* being the effective mass of electron and hole. An excited state of a nanocrystal can be considered quantum mechanically as electron-hole-pair states inside a spherical potential. In the envelope function approximation, the eigen-

state is composed of an envelope function $\psi(r)$ and a periodic part U_k of Bloch function $\Psi_k(r)$, i.e.

$$\psi_k(r) = U_k(r) \psi(r) \quad (7)$$

For non-interacting electron-hole pairs, the envelop function consists of independent contributions from electrons and holes and can be written as

$$\psi(r_e, r_h) = \phi_e(r_e) \phi_h(r_h) \quad (8)$$

The periodic part is assumed to be the same in the barrier (well), so -

$$U_k(r)_{\text{barrier}} = U_k(r)_{\text{well}} = U_k(r) \quad (9)$$

The Hamiltonian operator for the envelope function in single parabolic potential approximation and without coulomb interaction is given by -

$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 + V_e(r_e) + V_h(r_h) \quad (10)$$

Such that the confining potential $V(r)$ becomes

$$\begin{aligned} V_i(r_i) &= 0 \text{ for } r_i < R \quad (i = e, h) \\ V_i(r_i) &= \infty \text{ for } r_i > R \quad (i = e, h) \end{aligned} \quad (11)$$

The normalized wave functions ϕ_i for electron and hole can be obtained by solving the Schrodinger equation using the wave function Eq. (8) and Hamiltonian eq.(10) with boundary conditions eq. (12) [Davydov 1987]. This results in

$$\phi_{nlm}^i(r) = Y_{lm} \sqrt{\frac{2}{R^3}} \frac{J_l(\chi_{nl} \frac{r}{R})}{J_{l+1}(\chi_{nl})} \quad (12)$$

with $l \leq m \leq l$ and $l = 0, 1, 2, 3$

Here, J_l are Bessel functions and Y_{lm} are spherical harmonics.

The energy eigenvalues can be derived by applying the boundary condition that the wavefunction has to vanish at the QD matrix interface, i.e

$$J_l(\chi_{nl} \frac{r}{R})|_{R=r} = 0 \quad (13)$$

This gives the eigenvalues -

$$E_{nl}^e = \frac{\hbar^2}{2m_e} \frac{\chi_{nl}^2}{R^2} \quad (\text{for electron}) \quad (14 a)$$

$$E_{nl}^h = \frac{\hbar^2}{2m_h} \frac{\chi_{nl}^2}{R^2} \quad (\text{for hole}) \quad (14 b)$$

Where, χ_{nl} is the n^{th} zero of spherical Bessel function or order l , m_e , m_h are the effective masses of electron and hole respectively; R is the radius of the nanocrystal

Thus, labeling the quantum number $l = 0, 1, 2, \dots$, the first roots are

$$\chi_{1s} = 3.1416 ; \chi_{1p} = 4.493 ;$$

$$\chi_{1d} = 6.2822 ; \chi_{2s} = 7.725 \text{ etc.}$$

The lowest quantized energy state with $n=1$ and $l=0$ is given by

$$E_{10}^e = \frac{\hbar^2 \pi^2}{2m_e R^2} \quad \text{for electron} \quad (15a)$$

$$E_{10}^h = \frac{\hbar^2 \pi^2}{2m_h R^2} \quad \text{for hole} \quad (15b)$$

Using these results we can calculate the energy levels of electron and hole using the values of χ_{nl} as

Table 1: values of χ_{nl}

$l \rightarrow$	1	2	3	4
0	3.142	6.283	9.425	12.556
1	4.4493	7.725	10.904	14.066
2	5.764	9.095	12.323	
3	6.988	10.417	13.698	
4	8.183	11.705		
5	9.356	12.967		
6	10.513	14.207		
7	11.657			
8	12.791			
9	13.916			

So, the enhancement in band gap due to quantum confinement

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \quad (16)$$

It theory also implies that the energy discretization scales with the square of the inverse radius (R)

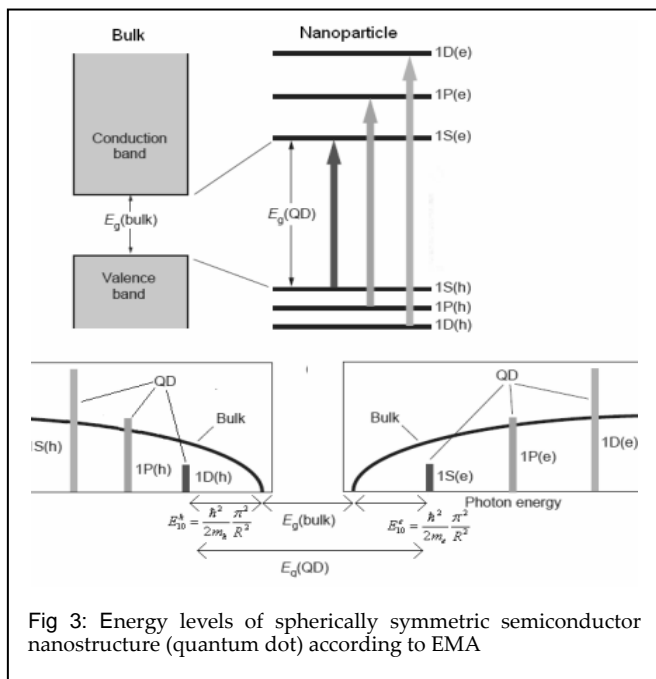


Fig 3: Energy levels of spherically symmetric semiconductor nanostructure (quantum dot) according to EMA

The quantum mechanical picture of a particle in a spherical potential as given above deals with the envelope function. The Bloch part assumed to be a simple direct bandgap semiconductor with parabolic and isotropic bands. In reality, the Bloch part, for example, for semiconductor materials with indirect band gap and for anisotropic crystal structures (e.g. zinc-blende, wurtzite, perovskite etc) needs modification for a better understanding of the optical behavior of QDs

Though EMA described by addressed quite well about the quantum confinement effect, however Efros and Efros has excluded the columbic interaction between hole and electrons present in the Quantum Dot. Brus et al (1983) have considered Coulomb interaction between the localized carriers which has modified the single-particle picture to a great extent. The modified Hamiltonian with the Coulomb interaction between the electron and hole inside the QD can be expressed as

$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{\epsilon_2 |r_e - r_h|} + V_e(r_e) + V_h(r_h) \quad (17)$$

Where, ϵ_2 is the dielectric constant of the QD. $|r_e - r_h|$ is the difference in the coordinates defining the columbic interaction between the electron and hole.

Using perturbation approach Brus [28, 29] developed the expression for the lowest excited state energy as -

$$E_{gn} = E_{gb} + \left(\frac{\hbar^2 \pi^2}{2R^2} \right) \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - 1.8 \frac{e^2}{\epsilon_2 R} \quad (18)$$

Using variational calculations Kayanuma give the expression for the lowest excited state energy as [31],

$$E_{gn} = E_{gb} + \left(\frac{\hbar^2 \pi^2}{2R^2} \right) \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - 1.786 \frac{e^2}{\epsilon_2 R} - 0.248 E_{RY}^* \quad (19)$$

where, $E_{RY}^* = \frac{e^4}{2\epsilon\hbar^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right)^{-1}$ exciton binding energy

Later on Kayanuma identified two limiting cases depending upon the ratio of the radius of the quantum dot to the Bohr exciton radius, of the bulk solid [32]. For $R/\alpha_B \gg 1$, the exciton can be pictured as a particle moving inside the quantum dot with only little increment in confinement energy. This is the weak confinement regime. In the strong confinement regime $R/\alpha_B \ll 1$ and independent particle confinement effects comes to the forefront. It was pointed out that in this regime, the electron and the hole should be viewed as individual particles in their respective single particle ground states with negligible spatial correlation between them owing to the increased kinetic energy term. Kayanuma[31] further found that the strong confinements are observable upto $R \cong 2 \alpha_B$. In this regime EMA is valid to a great extent in the where the effective mass approximation is relatively more valid, though quantitatively EMA fails to account for the observed changes.

The equation (19) gives a good fit of the experimentally observed relation between E and R for the case of weak confinement regime. But it is unable to observed phenomena explain the strong confinement regime where the EMA with infinite

barriers breaks down. Thus, for larger sizes of the nanocrystallites, the infinite potential effective mass approximation (IP-EMA) gives a good description of the band gap variation with size. However, it grossly overestimates the change, ΔE_g , in the bandgap for smaller nanocrystals. In the infinite potential EMA (IP-EMA) model, it was essentially neglects any possibility extending of the wavefunction beyond the surface of the nanocrystals as a consequence of the assumption of a rigid wall (infinite potential). This model ignores the tunneling possibility of the electrons and the holes of the surface atom to outside the nanocrystal.

To overcome the shortcomings of the IP-EMA, Kayanuma and Momiji [33] used the finite potential to account for the experimental data for small CdS crystallites. The confining potentials V_e , for the electron and V_h , for the hole, satisfy the relation $E_g + V_e + V_h = E_{1g}$, where E_{1g} is the band gap energy of the surrounding material. The resulting problem was solved by variational principle in the Hylleraas coordinate system. In addition to spherical clusters, Kayanuma and Momiji also treated cylindrical shaped microcrystallites in EMA model. Lo and Sollie (1991), Tran Thoai et al (1990) and Hu et al (1990) used variational calculation in finite potential well to improve further the EMA model.

Although the finite potential effective mass of the electron describes quite well using a single conduction band, the top level of the valence band in these semiconductor systems is degenerate and the description of the hole effective mass

requires more number of bands. In this context, the multi-band effective mass approximation (MBEM) theory [34] represents a substantial improvement over the single band, infinite potential EMA model. For CdSe nanocrystals, the size dependence up to 10 excited states in the absorption spectra are successfully described by the uncoupled multi-band EMA [34,35]. This includes the valence band degeneracy, but does not couple the valence and conduction bands. Banin et al [36] have used the multi-band EMA including the valence and the conduction band coupling. They use an eight band Luttinger-Kohn Hamiltonian to calculate the quantum size levels in InAs. Such improvements over the over simplified IP-EMA model was found to satisfactory.

The other approach which is widely used to explain the band structure of nanostructures is Linear combination of atomic orbital theory- molecular orbital theory (LCAO). This is based on a bottom up approach where the combination of atomic orbital and molecular orbital (LCAO-MO) is considered. In this method, nanoparticles are considered as large molecules and the overall wave function in a nanoparticle can be constructed from the wave function of individual atomic orbital. It provides a more detailed basis for predicating the evolution of the electronic structure of clusters, from atoms and/or molecules to nanoparticles to bulk materials.

The simplest case is that of a molecule consisting of only two atoms, where

two atomic orbitals combine to make a bonding and an anti-bonding molecular orbital

(MO). When only the low-energy (bonding) MO is filled with electrons, it is called the Highest Occupied Molecular Orbital (HOMO). In that case, the high-energy (anti-bonding)

level is empty and referred to as the Lowest Unoccupied Molecular Orbital (LUMO). As the number of atoms increase, the discrete energy band structure changes from large energy steps to small energy steps that are to a continuous energy

band. The energy difference between the top of the HOMO and bottom of the LUMO (equals to the band gap E_g) gets decreased, and the bands split into discrete energy levels of reduced mixing of atomic orbitals for a small number of atoms. Therefore, the small size of the nanoparticles results in quantized electronic band structures intermediate between the atomic/molecular and bulk crystalline molecular orbitals.

When the molecule becomes larger, more energy levels arise, and the energy spacing between the HOMO and LUMO becomes smaller.

In this model, a nanoparticle (quantum dot) can be regarded as a very large molecule or cluster consisting of a few hundred or thousand atomic valence orbitals, forming as many MOs. Still, there exist discrete energy levels at the edges of the "bands", and the spacing between the HOMO and LUMO levels (i.e. the bandgap) becomes smaller when the it increases in size. This explains both quantum confinement effects from a molecular point-of-view. Finally, when the semiconductor becomes even larger, the energy-spacing between the MO levels becomes so small that the different energy levels cannot be distinguished experimentally and it is considered as a band of continuous energy levels in a bulk semiconductor.

This LCAO-MO approach provides the tight-binding model (Slater and Koster [37]) which is an efficient scheme to calculate the electronic structure of periodic solids. As this method is computationally much less demanding compared to other methods such as the plane-wave methods, it has been extensively employed to calculate electronic structures of various metals, semiconductors, clusters and a number of complex systems such as alloys and doped systems.

The tight-binding electronic parameters, namely the orbital energies and the hopping strengths, were determined by fitting the ab initio band dispersions to the band dispersion obtained from the tight-binding Hamiltonian, given by

$$H = \sum_{i_1\sigma} \epsilon_{l_1} a_{i_1\sigma}^+ a_{i_1\sigma} + \sum_{ij} \sum_{l_1, l_2, \sigma} (t_{ij}^{l_1 l_2} a_{i_1\sigma}^+ a_{i_2\sigma} + h.c.) \quad (20)$$

where, the electron with spin σ is able to hop from orbital labeled l_1 with onsite energies equal to ϵ_{l_1} in the i th unit cell to those labeled l_2 in the j th unit cell with a hopping strength $t_{ij}^{l_1 l_2}$, with the summations l_1 and l_2 running over all the orbitals considered on the atoms in a unit cell, and i and j over all the unit cells in the solid. To calculate the eigen value spectra of nanocrystals, we need to know the ϵ 's for the various orbitals and the t 's for the interactions. These are evaluated by performing a TB-fit with a prudent choice of the basis orbitals and the interactions, to the band structure of the bulk solid obtained from first principle calculations such as pseudo-potential methods.

Lippens and Lannoo [38] was the first to use 'Tight Binding Method' to calculate the variation band gap with size for CdS and ZnS nanocrystals. They use sp^3s^* orbital basis with only the nearest neighbor interactions as suggested by the work of Vogl et al.[39] for bulk semiconductor materials. The calcula-

tions were carried out for clusters ranging in size from 17 atoms (3 shells) to 2563 atoms (15 shells). They took the valence band to be parabolic but non-parabolicity is considered for the conduction band. Wang and Herron (1996) successfully calculate the energy levels of the CdS clusters (~20Å) using tight binding model considering non-parabolic valence and conduction band. Sarma et al studied in details of band gap enhancement of the semiconductor quantum dot based on TB model and gives the expression for band gap enhancement as [40-42].

$$\Delta E_g = \frac{1}{aD^2 + bD + c} \quad (21)$$

Here, D is the diameter of quantum dot. The a, b and c parameters are dependent on the system. The values a, b, c of some systems are listed in the Table 2

Table 2: values of a, b, c

semiconductor	a nm ⁻¹ eV ⁻¹	b nm ⁻¹ eV ⁻¹	c nm ⁻¹ eV ⁻¹
ZnS	0.2349	0.1418	0.2562
ZnO	0.2174	0.0392	0.2134
ZnSe	0.0845	0.1534	0.2128
CdS	0.1278	0.1018	0.1821
CdSe	0.0397	0.1723	0.1111
GaAs	0.1969	0.2631	0.0728
GaP	0.0359	0.1569	0.1564
InAs	0.0374	0.2569	0.1009
InAs	0.0461	0.3153	0.0623

They have developed a method for estimating the diameters and diameter- distribution from the UV spectra [42].

Einevol (1989) used both EMA and TB model and gives a new model known as Effective bond order model (EBOM). In the method he used effective mass model (k.p) for the conduction band and tight-binding methods for the valence bands to determine the energy states in low dimensional structures. Later, Ramakrishna and Friesner [43] used the Empirical pseudo-potential method to calculate the band structure of CdS and GaP nanocrystals upto 30Å radius in the zinc-blende phase. The calculated variation agrees quite well with the experimental data points. Lin-Wang Wang, Alex Zunger and coworkers [44-49] also employed the semi-empirical pseudo-potential method in semiconductor nanostructures. They calculate the electronic structure of Si [44], CdSe [46] and InP [47] quantum dots. Quantitative theoretical approaches have been employed during the two decades to improve the model to determine the exact electronic structures of semiconductor nanoparticles, by using different perturbations and boundary condition in the Hamiltonian. Sercel and Vahala (1990) have

introduced non-parabolic bands in the k.p perturbation theory and calculated quantum-dot band structure of GaAs(AlGaAs) and InAs(GaSb) systems.

Each of the above models has its own advantage and limitation. In fact, the EMA and EBOM overestimate confinement energies, but the TB model to gives an underestimated picture. It is also recognizing that the methods break down for the smallest nanoparticles (<1nm), because of possible surface and interface along with structural changes.

CONCLUSION

In this review, work of various researchers on electronic structure of semiconductor nanomaterial is discussed. In last four-decade, people have attempted to find out the exact Hamiltonian as well as the potential function for the electron confined in the nanostructure material. For spherical semiconductor nanostructure material (semiconductor nanoparticle) the theoretical results approximately similar with the experimental results. However, semiconductor nanostructure with different shape and size lot of work is to be done to find an suitable potential function.

REFERENCES

- [1] R. Birringer and H. Gleiter, "Encyclopedia of Material Science and Engineering Suppl.", Ed. by R. W. Cahn Vol. 1, p.339 (Pergamon, New York, 1988),
- [2] L. E. Brus, *Quantum Crystallites and Nonlinear Optics*, Appl. Phys. A 53, 465 (1991)
- [3] Y. Wang, N. Herron, "Nanometer-sized semiconductor clusters: materials synthesis, quantum size effects, and photophysical properties, J. Phys. Chem. 95, 525 (1991)
- [4] A. P. Alivisatos, *Semiconductor clusters, nanocrystals and quantum dots*, Science 271, 933 (1996)
- [5] H. Weller, Quantized Semiconductor Particles: A novel state of matter for materials science, Adv. Mater. 5, 88 (1993)
- [6] Faraday's diary, Vol. VII, The Royal Institution of Great Britain, Ed. by T. Martin, Bell and Sons: London, page 63 (1936)
- [7] Some modern absorption glasses, G. Jaeckel, Z. Tech. Physik, 7 (1926) 301
- [8] C. R. Berry, Effects of Crystal Surface on the Optical Absorption Edge of AgBr, Phys. Rev. 153, 989 (1967)
- [9] C. R. Berry, Structure and optical absorption of silver iodide microcrystals, Phys. Rev. 161, 848 (1967)
- [10] A. Ya Shik, L. G. Bakueva, S. F. Musikhin, S. Rykov, *A Physics of Low-Dimensional Systems*, ed. by I Il'in, A Ya Shik (a) V.B. Sandomirskii, Sov. Phys. JETP 16, 1630 (1963) (b) A.G. Stasenko, Sov. Phys. Sol. State 10, 186 (1968)
- [11] S. Thomas, S. K. Nair, E. M. A. Jamal, S H Al-Harhi, M. R. Varma, M. R. Anantharaman, *Size-dependent surface plasmon resonance in silver silica nanocomposites*, Nanotechnology 19, 075710, (2008)
- [12] Cap-shaped gold nanoparticles for an optical biosensor, M. Himmelhaus, H. Takei, Sensors and Actuators B, 63,24 (2000)
- [13] D. J. Maxwell, J. R. Taylor, S. Nie, *Self-Assembled Nanoparticle Probes for Recognition and Detection of Biomolecules*, J. Am. Chem. Soc. 124, 9606 (2002)
- [14] C. A. Mirkin, R. L. Letsinger, R. C. Mucic, J. J. Storhoff, *A DNA-based method for rationally assembling nanoparticles into macroscopic materials*, Nature 382, 607 (1996)
- [15] J.-M. Nam, S. J. Park, C. A. Mirkin, *Bio-Barcodes Based on Oligo-*

- nucleotide-Modified Nanoparticle*, J. Am. Chem. Soc. 124, 3820 (2002)
- [16] S. G. Penn, L. He, M. J. Natan, *Nanoparticles for bioanalysis*, Current Opinion Chem. Biol. 7, 609 (2003)
- [17] J. J. Storhoff, R. Elghanian, R. C. Mucic, C. A. Mirkin, R. L. Letsinger, *One-Pot Colorimetric Differentiation of Polynucleotides with Single Base Imperfections Using Gold Nanoparticle Probes*, J. Am. Chem. Soc. 120, (1998) 1959.
- [18] T. A. Taton, C. A. Mirkin, R. L. Letsinger, *Scanometric DNA Array Detection with Nanoparticle Probes*, Science 289, 1757 (2000)
- [19] M. Grätzel, *Solar cells to dye for*, Nature 421, 586 (2003)
- [20] M. Gratzel, *Dye-sensitized solar cells*, J. of Photochemistry and Photobiology C: Photochemistry Reviews 4, 145, (2003)
- [21] A. P. Alivisatos, *Perspectives on the Physical Chemistry of Semiconductor Nanocrystals*, J. Phys. Chem. 100, 13226 (1996)
- [22] M. G. Bawendi, M. L. Steigerwald, L. E. Brus, *The Quantum Mechanics of Larger Semiconductor Clusters ("Quantum Dots")*, Annu. Rev. Phys. Chem. 41, 477 (1990)
- [23] Surface electron transfer processes, by R. J. D. Miller, G. L. McLendon, A. J. Nozik, W. Schmickler, F. William, p31, VCH:New-York (1995)
- [24] Clusters & Colloids, ed. G. Schmid, VCH: New-York (1994)
- [25] A. I. Ekimov, A. A. Onushchenko, *Quantum size effect in the optical-spectra of semiconductor micro-crystals*, Sov. Phys. Semicond. 16, 775 (1982)
- [26] A. L. Efros, A. L. Efros, *Interband absorption of light in a semiconductor sphere*, Sov. Phys. Semicond. 16, 772 (1982)
- [27] G. C. Papavassiliou, *Luminescence spectra and Raman excitation profiles in small CdS particles*, J. Solid State Chem. 40, 330 (1981)
- [28] Brus, L. E. *A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites*. J. Chem. Phys. 1983, 79, 5566–5571.
- [29] L. E. Brus, *Electron-electron and electron-hole interactions in small semiconductor crystallites –the size dependence of the lowest excited electronic state*, J. Chem. Phys. 80, 4403 (1984)
- [30] S.V. Gaponenko, *Optical Properties of Semiconductor Nanocrystals*, Cambridge University Press, USA (1998)
- [31] Wannier exciton in microcrystal, Y. Kayanuma, Solid state comm. 59, 406 (1986)
- [32] Y. Kayanuma, *Quantum-size effects of interacting electrons and holes in semiconductor microcrystals with spherical shape*, Phys. Rev. B 38, 9797 (1998)
- [33] Y. Kayanuma and H. Momiji, *Incomplete confinement of electrons and holes in microcrystals*, Phys. Rev. B 41, 10261 (1990).
- [34] D. J. Norris, S. C. B. Murray, and M. G. Bawendi, *Measurement of the size dependent hole spectrum in CdSe quantum dots*, Phys. Rev. Lett. 72, 2612 (1994).
- [35] D. J. Norris and M. G. Bawendi, *Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots*, Phys. Rev. B 53, 16338 (1996).
- [36] U. Banin, C. J. Lee, A. A. Guzelian, A. V. Kadavanich, A. P. Alivisatos, W. Jaskolski, G. W. Bryant, A. L. Efros, M. Rosen, *Size-dependent electronic level structure of InAs nanocrystal quantum dots: Test of multiband effective mass theory*, J. Chem. Phys. 109, 2306 (1998).
- [37] J. C. Slater and G. F. Koster, *Simplified LCAO Method for the Periodic Potential Problem*, Phys. Rev. B 94, 1498 (1954).
- [38] *Calculation of the band gap for small CdS and ZnS crystallites*, P. E. Lippens and M. Lannoo, Phys. Rev. B 39, 10935 (1989)
- [39] *A Semi-empirical tight-binding theory of the electronic structure of semiconductors*, P. Vogl, H. P. Hjalmarson, J. D. Dow, J. Phys. Chem. Solids 44, 365 (1983).
- [40] S. Sapra, T. Saha- Dasgupta, D. D. Sarma, *Electronic structure of and quantum size effect in III-V and II-VI semiconducting nanocrystals using a realistic tight binding approach*, R. Viswanatha, Phys. Rev. B 72, 045333 (2005)
- [41] *Evolution of the electronic structure with size in II-VI semiconductor nanocrystals*, S. Sapra, D. D. Sarma: Phys. Rev. B 69, 125304 (2004)
- [42] R. Viswanatha, D. D. Sarma, *Study of the Growth of Capped ZnO Nanocrystals: A Route to Rational Synthesis*, Chem. Eur. J. 12, 180 (2006)
- [43] Exciton spectra of semiconductor clusters, M. V. Rama Krishna and R. A. Friesner, Phys. Rev. Lett. 67, 629 (1991)
- [44] L. W. Wang and A. Zunger, *Solving Schrödinger's equation around a desired energy: Application to silicon quantum dots*, J. Chem. Phys. 94, (1994) 2158
- [45] L. W. Wang and A. Zunger, *Local-density-derived semiempirical pseudopotentials*, Phys. Rev. B 51, 17398 (1995)
- [46] L. W. Wang and A. Zunger, *Pseudopotential calculations of nanoscale CdSe quantum dots*, Phys. Rev. B 53, 9579 (1996)
- [47] H. Fu and A. Zunger, *InP quantum dots: Electronic structure, surface effects, and the red shifted emission*, Phys. Rev. B 56, 1496 (1997).
- [48] H. Fu, A. Zunger, *Local-density derived semiempirical nonlocal pseudopotentials for InP with applications to large quantum dots*, Phys. Rev. B 55, (1997) 1642