MECHANISMS FOR FORMATIONS OF PHOTOLUMINESCIENCE FROM SILICON AND GERMANIUM NANOSTRUCTURES AND FORMULATING MODELS.

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MECHANISMS FOR FORMATION OF PHOTOLUMINESCIENCE FROM SILICON AND GERMANIUM NANOSTRUCTURE AND FORMULATING MODELS.

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_____

To my father whom I lost when 15 days left for ESLCE and my wife mother whom I lost in this year, with the help of God I able to with stand my condolences and complete this paper and my study.

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Abstract

Bulk silicon (Si) and germanium (Ge) have an indirect band gap transitions however when they are miniaturized to nanometer scale, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) increases, and hence the transition changes to direct due to confinement. The HOMO-LUMO gap determines the excitation of electrons so that the nanostructures will emit light. In this work,quantum confinement effects for Si and Ge,some methods to calculate band structures and formation mechanisms of photoluminescence from Si and Ge nanostructures are presented. We presented the parameters that influence the photoluminescence intensity of Si and Ge nanostructures. Finally we developed a model that could explain experimental results of Si nanocrystal photoluminescence versus size and wavelength by using Matlab program.

Acknowledgement

I am grateful to my advisor, Dr. Tesgera Badassa for his critical and constructive suggestion, well planned follow up, constant support, and friendly approach during this research; he was tireless, programmed, and ready to encourage me at any time when I consult him not only in my thesis work but also in my entire graduate study. As an advisor he put a lot of impression on me that I never forget whenever and wherever in my academic life. My special thanks goes to my wife Kezina A/Zinab and kid Abel Solomon whose continuous support and moral give this fruit. My gratitude's extended to my Friends leta and Zemach who played constructive role for my work to take this position..My gratitude's also goes to Jimma University and Addis Ababa University for their opening this opportunity to study this program.

CHAPTER ONE

1. INTRODUCTION

What is “nano”? Well, without providing a definite answer to this question, nano is a popular (emerging) area of science and technology today. It has attracted the attention of researchers from all walks of life, from physics to chemistry to biology and engineering. Further impetus for this movement comes from the tremendous increase in public and private funding for nano over the last decades. A prime example of this is the new National Nano technology Initiative (NNI) created by former president Bill Clinton of USA.

The mantle of nano has also been adopted by various scientific visionaries. Perhaps the most prominent is Eric Drexler who has founded an institute, called the for insight institute, devoted to exploring his ideas. Concepts being discussed include developing tiny nanorobots that will “Live” inside us and repair our blood vessels when damaged, preventing heart attacks. They will also kill cancer, cure us when we are sick, mend bones when broken, make us smarter and even give us immortality. The nano robots will also serve as tiny factories, manufacturing anything and everything from food to antibiotics to energy. In turn, nanotechnology will provide a solution to all of mankind’s problems whether it is hunger in developing countries or population in developed ones. Drexler therefore envisions a vast industrial revolution of unprecedented size and scale. At the same time, concurrent with this vision of utopian future is a darker side, involving themes where such nanorobots escape from the laboratory and evolve into sentient beings completely out of man kind’s control. Such beings could then sow the

needs to mankings own destruction in the spirit of recent movies and books such as the Terminator The matrix and prey. Now, whether such predictions and visions of the future will ever become reality remains to be seen. However, any such developments will ultimately rely on the scientific research of today, which is on a daily basis, laying down the foundation for tomorrow’s nanoscinece and nano technology.

In to days scientific realm, the word nano describes physical length scales that on the order of a billionth of a meter long. Nanoscale materials therefore lie in a physical size regime between bulk, macro scale, materials (the realm of condensed matter physics) and molecular compounds (the realm of traditional chemistry). This mesoscopic size regime has previously been

unexplored and beckons the researcher with images of scientific wild West with opportunities a bound for those willing to pack their wagons and head in to the scientific and technological hinterland. In this respect nanaoscale physics, chemistry, biology and engineering ask basic, yet unanswered, questions such as how the optical and electrical properties of a given material evolve from those of individual atoms or molecules to those of the parent bulk. Other questions that nanoscience asks include.

4. How does one make a nanometer sized object?
5. How do you make many (identical) nanometer sized objects?
6. How do the optical and electrical properties of this nanoscale object change with size?
7. How does their optical and electrical property change with its “dimensionality”?
8. How do changes behave in nanoscale objects?
9. How does charge transport occur in these materials?
10. Do these nanoscale materials possess new and previously undiscovered properties?
11. Are they useful?

The transition to nanoscience begins at this last point when we ask how these nanoscale materials might be exploited to improve our lives. Venture capital firms and mainstream industry have therefore taken up this challenge with much small start up trying to apply nanoscale materials in products ranging from better sunscreen lotions to fluorescent labels for biological imaging applications to next generation transistors that will one day store the entire content of the library of congress on the head of a pin. More established companies, such as GE, HP, Lucent and IBM, have also started their own in house nano programs to revolutionaries’ consumer lightings, personal computing, data storage and so forth. So whether it be for house hold lighting or consumer electronics, a nano solution exists and there is very likely a company or person pursuing this vision of a nano future.

Studying photoluminescence and understanding its mechanism has tremendous attention due to optoelectronic applications. Silicon is the most wide spread semiconductor in modern microelectronics technologies. Its natural abundance, low cost, and high purity, as well as the high electronic quality of silicon interface, have led to its overcoming dominance in microelectronic devices. Nevertheless, the use of silicon in optoelectronic remains highly limited. This state of affairs has remained, in fact, almost unchanged because of fundamental property of the silicon band structure, “indirect band gap”.

Visible photoluminescence property from germanium (Ge) nano particle at room temperature has been reported over years even though bulk Ge is an indirect band-gap semi conducting materials [1]. Quantum confinement effects play an important role in optical absorption and luminescence in nano-scale particles and structures of semiconductors [2], gas evaporation [3], rf magnetron co sputturing [4], cluster-beam evaporation [5] and so on. In recent years, laser ablation is used for many application system and production of local nanostructures [6].

Si and Ge are the most common metalloids, the conduction and valence bands of Ge are based on a combination of theoretical and experimental results [7]. Si is a tetravalent metalloid and less reactive than its chemical analog carbon, occurs as a pure element in nature and the eighth most common element in universe by mass, more widely distribution in dusts, planetoids and planets as various forms of SiO_2 . It is widely used in semiconductors because, it remains semiconductor at higher temperature than the semiconductor Ge and because of its native oxide it is easily grown in furnace and forms a better semiconductor /dielectric interface than any other material [8].

The threshold of optical absorption at frequency ω_g determines the band gap $E_g = \hbar\omega_g$. In the direct absorption process, a photon is absorbed by the crystal with creation of an electron and hole. In indirect absorption process, the minimum energy gap of the band structure involves electrons and holes separated by substantial wave vector K. Here in a direct photon transition at energy of the minimum gap cannot satisfy the requirement of conservation of wave vector, because photon wave vectors are negligible at the energy range of interest. Optical measurement determines whether the band gap is direct or indirect. The band gap in bulk Ge and Si are connected by indirect transitions, light emission in these materials are naturally phonon mediated process (Spontaneous recombination life times in the millisecond range) [9]. Silicon nano wire (SiNw) growth with hydrogen passivated has been demonstrated and extensive experimental and theoretical studies of electronic optical and mechanical properties have been performed. $SiNw_s$ has a direct band gap, with potential applications in electronic, optoelectronic, and chemical sensors [10]. Si is the leading material concerning high density electronic functionality, its band gap (1.12 ev) is ideal for room temperature operation, and its oxide SiO_2 (allows a processing flexibility to place more than 10^8 transistors on a single chip). However all the single transistors and electronic devices have to transfer information on length scales which are relevant with respect to their nanometer scale. In bulk Si competitive non-radiative recombination rates are much higher than the radiative ones and most of the excited electron-hole (e-h) pairs recombine non-radiatively. This yields very

low internal quantum efficiency for Si luminescence. As what concerns the lasing of Si, fast non radiative process such as Auger or free carrier absorption severely prevent population inversion at high pumping rates needed to achieve optical amplification [11]. The alloy composition of Si and Ge remains indirect, there is a little motivation from optoelectronic device considerations to grow the alloy: however, there has been great interest in this alloy since it can be a component of Si-SiGe structures and allow hetero structure concepts to be realized in Si technology [12].

1.1 Project outline and Objectives

In this work we study optical and electrical properties of Si and Ge nanostructures with more emphasis on optical properties. The paper is organized in five sections apart from introduction; section II deals with quantum confinement and band structures, in this chapter quantum wells, quantum Dots as well as quantum wires and some of the methods of calculating band structures like Tight binding and pseudo potential are discussed. Section III contains optical and electrical properties of Si and Ge nanostructures; here emission and absorption of light, recombination rates and PL of porous Si are presented. Section III is also concerned mainly about photoluminescence from Si which embedded in a dielectric SiO_2 . Sections IV and V talks about the formulation of models and results of this work respectively. The last section gives conclusion and future outlooks.

General and specific objectives:

The general objective of this work is to study photoluminescence properties of Si and Ge nanostructures.

Specific objectives:

- To describe formation mechanisms of PL from Si and Ge nanostructures.
- To study the dependence of PL intensity with different parameters for Si nanocrystals.

Methodology

The methodology applied for this study is Review article with optimal utilization of available resources.

The scope of the study

The study aimed at to be getting acquainted with the fundamental and revised understanding of photoluminescence properties of Si and Ge nanostructures and to come up with formulation of models based on analysis of experimental results. It also emphasizes on the Optical properties of Si and Ge nanostructures particularly Si nanocrystals against different parameters that tune the intensity of the photoluminescence of the system.

CHAPTER TWO

2. QUANTUM CONFINEMENT AND BAND STRUCTURES

2.1 Introduction

Confinement

Quantum wells, wires and dots are often described using the analogy to a particle in a 1D, a 2D box and a 3D box. This is because when the actual physical length scale of the system is smaller than the exciting Bohr radius or corresponding de Broglie wavelength, either or both the electron and hole experience confinement. In turn, the energies of the carrier along that dimension of the material are not longer continuous as in the case where there is no confinement. The appearance of discrete states is one of the fundamental signatures of nanomaterials, since solving the Schrödinger equation of a carrier to find its eigen values and eigen functions involves using boundary conditions, one can also immediately predict that the actual shape of a quantum well, wire or dot will also play a role indictating the ordering and spacing of states. A nanowire will have a similar but different progression of states than a quantum dot (or crystal). The same applies to quantum wells as well as more exotic shapes of nanostructures.

2.1.1 Quantum dots

Quantum dots (QDs) are nanometer scale “boxes” for selectively holding or releasing electrons. They are small physical devices that contain a “tiny droplet” of free electrons, small metal or semiconductor boxes that hold a specified number of electrons (QDs generally look more like pyramid) than actual dots. QDs are going to atoms so small that the addition or removal of an electron will change its properties in significant way.

QDs are semiconductor structures where the electron wave function is confined in all three dimensions by the potential energy barriers that form the QDs boundaries. Specifically, QDs are semiconductor structures that continue the electrons and holes to a volume of order of $20nm^3$.

Quantum dots come in to play for several reasons. They have absorption and emission spectra which are tunable, size dependent. Different quantum dots can be made to absorb anywhere from the UV in to infrared.

Modern semiconductor processing techniques permit the artificial creation of quantum confinement (QC) (quantum confinement in all three spatial dimensions) of only few electrons. Such a finite fermions QD system has much in common with the atoms, yet they are man made structures, designed and fabricated in the laboratory.

The generalization of the Schrödinger equation in three dimensions is:-

$$\frac{-\hbar}{2\mathrm{m}}\nabla^2\Psi(r) + V(r)\psi(r) = E \quad \Psi(r) \quad . \qquad (2.1.1)$$

The solution of the differential eq. (2.1.1) for a particle in 3D in a finite trap of volume L^3 with impermeable walls with V(r) =0 is given as:-

$$\Psi_n(x,y,z) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \qquad (2.1.2)$$

and the corresponding energy eigen value will be

$$En = \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \qquad (2.1.3)$$

¿

Eqs. (2.1.2) and (2.1.3) are applicable to electron and hole states in semiconductor “quantum dots”. A “hole’ (missing electron) in a full energy band behaves very much like an electron except that it has a positive charge, and tends to float to the top of the band, i.e. the energy of the hole increases oppositely to the energy of an electron. To create an electron hole pair in semiconductors requires energy at least equal to the energy gap E_g of the semiconductor.

2.1.2 Quantum wires (nanowires)

Nanowires (also called quantum wires) are 1D molecular structure with electrical and/or optical properties. In order to have enhanced physical properties, the wires must be of small diameter, must have high aspect ratio (i.e the ratio of length to thickness, and must be uniformly oriented. Nanowires are relatively easy to produce and can have different shapes. They are often thin and short “threads” but can also have other manifestations. The propagation of electromagnetic energy has been demonstrated along a noble metal stripes with band of a few microns, Propagation has also

been demonstrated along nanowires with sub wavelength cross selection and propagation length of a few micron. Metal nanowires can be optimized for particular wave length of interest, and non regular cross-sections and coupling between closely spaced nanowires allows a tunneling of optical response.

Devices using these low dimensional materials have not been made to any great extent. This is because the historical development of nanostructures seems to have skipped nanowires, moving from wells to dots first. More recently, though, researchers have learned how to make a symmetric nanowire using a number of approaches including vapor-liquid-solid (VLS) and solution-liquid-solid (SLS) growth. The move to applications has occurred quickly with the key selling point being that, in addition to exhibiting quantum confinement effects, nanowires are at the same (as their name implies) wires. This means that making electrical connections to the outside world and assembling actual devices may be a lot easier than with other nanostructures such as quantum dots.

Crossed nanowire junctions have been made, using p-type and n-type wires. These junctions serve as diodes in one case, memory elements in another and even electroluminescent devices. A schematic diagram of such a nanowire device is provided below. Ultimately, though, the trick is to lean reproducible fashion.

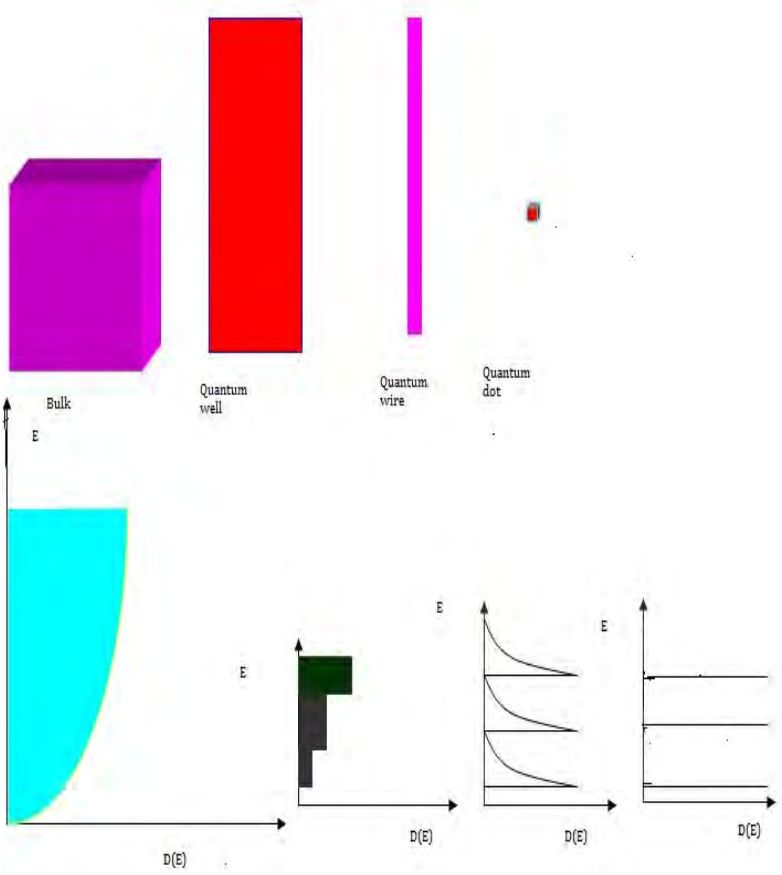

Figure 2.1: Change in density of state as the number of confining dimension increases

Nanowires have also been used as sensors by monitoring charges in the conductance experienced when different compounds or gases are adsorbed to the wire's surface. In this respect, nanowires may one day be packaged as efficient sensors for minute amounts of toxic gases, chemical weapons, and explosives.

The term quantum wire describes a carrier confined in two dimensions say Y and Z to a small dimension d (wire cross-section d) and free to move along the length of the wire X (qualitatively this situation resembles the situation of the carrier moving along a carbon nanotube, or silicon nanowire, although the details of the bound state wave functions are different).

The solution of eq. (2.1.1) in the case of quantum wire of a square cross-section is

$$\Psi_{nn}(x,y,z)=\frac{2}{d}\sin\left(\frac{n_y \Pi y}{d}\right)\sin\left(\frac{n_z \Pi z}{d}\right)\ \exp(ik_x x) \qquad (2.1.4)$$

and the corresponding energy is

$$En = \frac{\hbar^2 \pi^2}{2md^2}(n_y^2 + n_z^2) + \frac{(\hbar^2 k_x^2)}{(2\mathrm{m})}$$

¿ (2.1.5)

2.1.3 Quantum wells (QW)

A physical situation that often arises in semiconductor devices is a carrier confined in one dimensions, say Z to a thickness d and free in two dimensions say X and Y this is called 2D bands or quantum wells. In this case the solution of eq. (2.1.1) will have form.

$$\Psi_n(x,y,z) = \left(\frac{2}{d}\right)^{1/2} \sin \frac{n_z \Pi z}{d} \quad \exp(ik_x x) \exp(ik_y y) \qquad (2.1.6)$$

and the energy of the carrier in the n^{th} band [4, 9] is

$$E_n = \frac{\hbar^2 \pi^2}{2md^2} n^2 z + \frac{\hbar^2 k_x^2}{2\mathrm{m}} + \frac{\hbar^2 k_y^2}{2\mathrm{m}} \qquad (2.1.7)$$

2.1.4 Density of state in low dimension structures

An important manifestation of this sub band structure is the density of states (DOS) of electronic bands. The DOS figures importantly in both electrical and optical properties of any system. The density of state is the number of orbital per unit energy range. Therefore we can express the density of state for different quantum confinements as:

3. For a bulk system D(E) = $\frac{dN}{dE}$ where $N = 2\frac{4\pi\kappa^3}{\left(\frac{2\Pi}{L}\right)^3}$

$$\mathrm{D}(\mathrm{E}) = \frac{V}{2\Pi^2}\left(\frac{2\mathrm{m}}{\hbar^2}\right)^{3/2} E^{1/2} \qquad (2.1.8)$$

4. For quantum well

5. Conduction band D(E) = $\sum_i \frac{m*\delta(E-Ei)}{\Pi\hbar^2}$ (2.1.9)

Where δ is Heaviside step function δ =1, if E>E_i

δ = 0 otherwise and E_i are the sub energy band levels.

Valence D(E) = $\sum_i \sum_{j=1}^{2} \frac{m*\delta(E_{ij}-E)}{\Pi\hbar^2}$ (2.1.10)

6. For quantum wire

$N=\frac{KL}{\Pi}$

D (E) = $\frac{1}{2\Pi}\sqrt{\frac{2m}{\hbar^2}}\ E^{-1/2}$ (2.1.11)

7. For quantum dot; The density of state is delta function

D (E) = δ (E-Ei) (2.1.12)

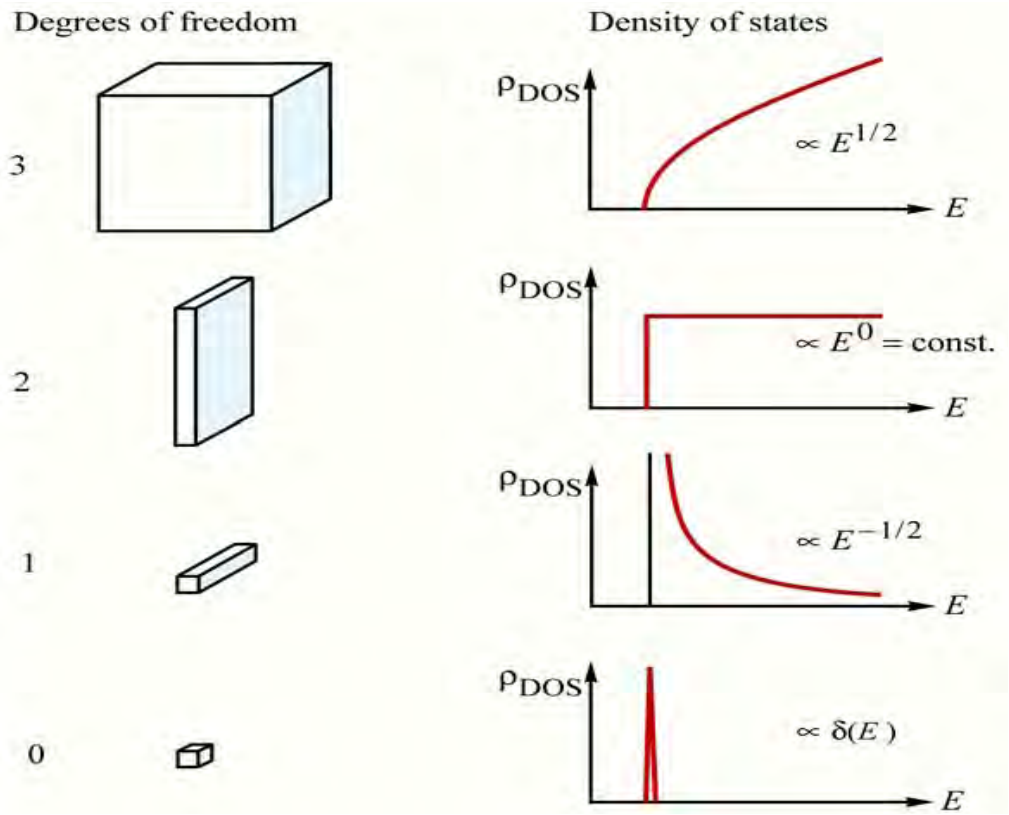

Figure 2.2: Electronic density of states of semiconductors with 3, 2, 1 and 0 degrees of freedom for electron propagation.

2.2 Band structures of Si and Ge nanostructures

Luminescence is the emission of light by electrical or optical excitations. To get luminescence spectrum in the visible range of the HOMO-LUMO gap has a great influence, which is related to the band gap energy of the bulk structure. Therefore we need to study some of the methods for calculating band structures.

In semiconductors the Fermi energy lays in the gap between two bands i.e. there is an upper most completely filled band called valence band (VB), the unoccupied band is called the conduction band CB, the two bands are separated by an energy gap E_g. In fact nobody can tell either by experiment or calculations exactly what the upper edge of the conduction band looks like. The calculations need assumptions that might be enough to determine the band structures. The tight binding approximation and the pseudo potential method approximation are typical ones.

2.2.1 Tight binding approximations

This is also called the linear combination of atomic orbital (LCAO), in this approximation we assume that the valence wave functions of crystal atoms are slightly perturbed form of their free state, and we limit on the nearest neighbor approximation and most essential of the free atoms.

Si: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Ge: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p6\ 4s^2\ 3d^{10}\ 4p^2$

The valence electrons are made up of either s-type or p-type orbital. While this conclusion is strictly true for the elements in atomic form, it turns at that even in the crystalline semiconductors the electrons in the valence and conduction band retains this s-type or p-type character even though they are free Bloch electrons.

The tight binding methods (TBM) uses atomic functions as basis set for the Bloch functions. The periodic part of the Bloch function is represented by some combinations of atomic orbital centered at the lattice point is.

If $\Psi_n(r-R)$ represents such an orbital centered at R, we could write a Bloch function of the form:

$$\Psi_n(r) = \sum \varphi_n(r-R) \text{ exp (ik.Rn)} \qquad (2.2.1)$$

The periodic part of the Bloch function is expanded in terms of atomic-like orbital of the atoms of the unit cell.

The elements Si and Ge have valence electrons described by s-or p-type atomic orbital.

We assume the solution of the atomic problem

$$H_{at}\Psi_n = E_n\Psi_n \qquad (2.2.2)$$

is already known for the atom forming the crystalline material. This solution leads to the description of the electronic structure of various atoms constructing a Bloch state given by

$$\Psi_k(r) = \sum_{n,R} \text{ exp (ik.R) } \Psi_n(r-R_n) \qquad (2.2.3)$$

But this state does not describe the new problem of the crystalline material where now we have

$$H_{cryst} = H_{at} + \Delta V(r) \qquad (2.2.4)$$

Where $\Delta v(r)$ is additional perturbation coming in due to interaction of neighboring atoms. The new wave functions are now chosen as the more general wave functions

$$\Psi_k(r) = \sum_R \exp(ik.R)\varphi(r-R) \qquad (2.2.5)$$

Where φ (r) is not atomic functions, but can be constructed out of the atomic functions. Expanding φ (r) in terms of atomic eigen functions $\Psi_n(r)$ we have

$$\Psi(r) = \sum_{n=1}^{N} b_n \Psi_n(r) \qquad (2.2.6)$$

The Schrödinger equation is now

$$H\Psi_k = E(k)\Psi_k \qquad (2.2.7)$$

Using eqs. (2.2.5) and (2.2.6) for the eigen function Ψ_k in eq. (2.2.7) and multiplying by $\Psi *_m(r)$ and integrating over space we get

$$\int d^3r \quad \Psi *_m(r) \quad [H_{at} + \Delta v(r)] \quad \sum_{R,n} \exp(ik.R)\Psi_n(r-R) = \text{E(k)} \sum_{R,n} \exp(\text{ik.R}) \qquad (2.2.8)$$

Since the atomic wave functions are orthogonal

We have

$$\int d^3r \quad \Psi *_m(r) \quad \Psi_n(r) \quad = \delta_{mn} \qquad (2.2.9)$$

However the atomic wave functions centered at different sites are not orthogonal i.e

$$\int d^3r (\quad \Psi *_m(r) \quad) \Psi_n(r-R) \neq \delta_{mn} \quad \text{for} \quad R \neq 0$$

In the summation over lattice vectors we separate the terms R=0 and R 0 to get

$$(E(k) - \text{Em}) b_m = -(E(k) - E_m) \sum_{n=1}^{N} [\left(\sum_{R \neq 0} \right) \int d^3r \Psi *_m(r) \Psi_n \text{ (r-R)exp(ik.R)]b}_n$$

$$+ \sum_{n=1}^{N} [\int d^3r \Psi *_m(r) \Delta v(r) \Psi_n(r)] b_n$$

$$+ \sum_{n-1}^{N} [\int d^3r \Psi *_m(r) \Delta v(r) \Psi_n(r)] b_n$$

$$+\sum_{n-1}^{N}\left[\sum_{R\neq 0}\int d^3r\,\Psi *_m(r)\Delta v(r)\Psi_n(r-R)\right]\ \exp(ik.R)]b_n \qquad (2.2.10)$$

Where we have used

$$\int d^3r\Psi *_m(r)H_{at}\Psi_n(r)=E_m\delta_{mn}$$

It can be pointed out that the atomic energies E_m may correspond to the isolated atomic energies. This is due to the modification arising from the neighboring atoms. We have an approximation.

$$\int d^3r\Psi *_m(r-R)\exp(ik.R)\approx 0$$

The approximation assumes that there is negligible overlap between neighboring atomic wave functions i.e. the atomic waves functions are tightly bound to the atom,which

$$\int d^3r\Psi *_m(r)H\Psi_n(r)=E_m+\int d^3r\Psi *_m(r)\Delta v(r)\Psi_n(r)$$

is called the on-site matrix element. For most potentials the on site integral

$$\int d^3r\Psi *_m(r)\Delta v(r)\Psi_n(r)\approx 0 \text{ For } m\neq n$$

In semiconductors we have two atoms per basis and for each atom we need to include at least the outer shell S,P_x,P_y,P_z functions. Thus the secular equation of the tight binding is quite difficult to solve.

To get some physical insight in to the problem consider a band structure arising from a single atomic s-level where b_s=1. In this case eq. 2.2.10 becomes.

$$(E(k)-E_s)=-(E(k)-Es,\sum_{R\neq 0}\int d^3r\Psi_s*(r)\Psi_s(r-R)\ \exp(ik.R)+\int d^3r\Psi_s*(r)\Delta v(r)\Psi_n(r)$$

$$+\sum_{R\neq 0}\int d^3r\Psi_s*(r)\Delta v(r)\Psi_s(r-R)\exp(ik.R) \qquad (2.2.11)$$

Now let's denote

$$\alpha(R)=\int d^3r\Psi_s*(r)\psi_s(r-R)$$

$$\beta_s=-\int d^3r\Psi_s*(r)\Psi_s(r)$$

$$\gamma(R)=-\int d^3r\Psi_s*(r)\Delta v(r)\Psi_s(r-R)$$

From orthogonal, $\alpha(R)=0$, this gives

$$E=E_s-B_s-\sum_R\gamma(R)\exp(ik.R) \qquad (2.2.12)$$

The off-site integrals (R) drop rapidly as the separation R increases [33].

2.2.2 The pseudo potential method (PPM)

The PPM is a powerful to solve for the band structure of semiconductors and often used as a bench mark for comparison of other techniques.

It makes use of information that the valence and conduction band state are orthogonal to the core states. The back ground periodic potential is replaced by a new potential that are softer than all electron potentials called “pseudo potential” which is obtained by subtracting out the effects of core levels. The pseudo potential includes relevant information to give the valence and conduction band structure. Here we seek a function which oscillates rapidly inside the core, but runs smoothly as a plane wave in the remainder of the open space.

Suppose we take

$$\Psi_v(k,r)=\varphi_v(k,r)-\sum_c <\Psi_c/\Psi_v>\Psi_c \qquad (2.2.13)$$

The Schrödinger equation for the valence and conduction band states is

$$\left[\frac{-\hbar^2}{2m}\nabla^2+v(r)\right]\Psi_v(k,r)=E_v\Psi_v(k,r) \qquad (2.2.14)$$

With the orthogonal condition $\Psi_c/\Psi_v>=0$ where Ψ_c are the core states

$$H\Psi_v(k,r)=E_v\Psi_v(k,r)$$

Plugging eq 2.2.13 in eq 2.2.14 we have

$$H[\Psi_v(k,r)-\sum_c <\Psi_c/\Psi_v>\Psi_c]=E_v[\Psi_v-\sum_c <\Psi_c/\Psi_v>\Psi_c]$$

$$H[\Psi_v(k,r)-\sum_c [E_c(R)-E_c]<\Psi_c/\Psi_v>\Psi_c]=E_c\Psi_v(k,r)$$

Where E_c is the core energy levels

The Schrödinger equation $\Psi_v(k,r)$ has the same eigen value is the origin $\Psi_v(k,r)$ together with the orthogonal condition, but with new back ground potential. The original potential V(r) is replaced by the operator.

$$V(r)\Psi_v(k,r)\rightarrow v(r)\Psi_v(k,r)+\sum_c [E_v(k)-E_c]<\Psi_c/\Psi_v>\Psi_c \qquad (2.2.15)$$

Denoting, $V_R = \sum_c [E_V(K) - E_C] \langle \psi_c / \psi_v \rangle$ we can write the effective potential as $v_p = v_R + V(r)$

where v_R is the actual potential and V_p is the new potential operator which involves subtraction of the core energies weighted out with $\varphi_v(k,r)$ from the eigen values $E_v(k,r)$ is called the pseudo potential. The pseudo potential v_p is a non-localized eigen value dependent operator. The problem is simplified due to the realization that the pseudo potential is smoother than the original starting potential. Since the term $-E_C \langle \psi_c / \psi_v \rangle$ is a position term which subtracts the strong core effects near the atomic sites leaving the potential region b/n the atoms unchanged. The pseudo potential plus

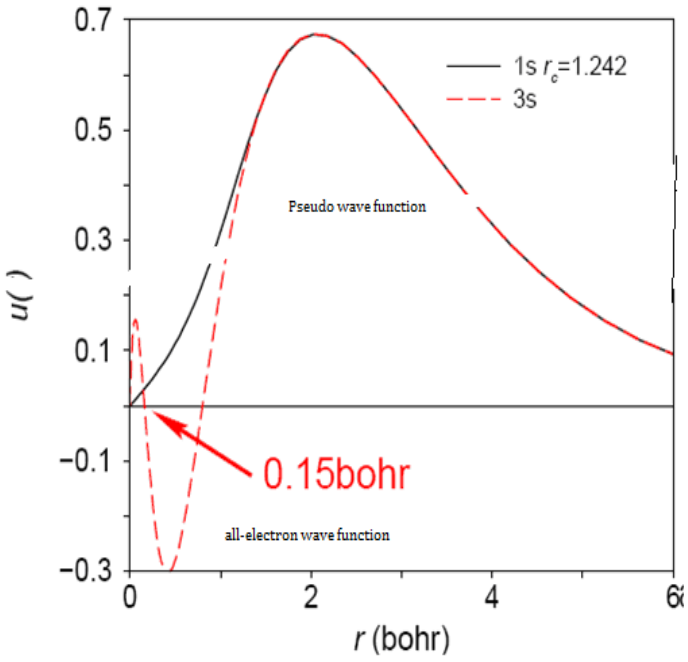

Figure 2.3: The actual potential and the pseudo potential with their corresponding wave functions [11]

a weak back-ground potential as far as the valence and conduction band states are concerned.

Since the valence energies lie above the core energies, the pseudo potential is positive so that $v(r)+v_R$ provides at least a partial calculation to provide a weak enough potential to do nearly free electron calculation for $\varphi_v(k,r)$ the so called pseudo wave function, treating the pseudo potential as a weak perturbations. The pseudo potential for a problem is not unique not exact, but it may be very good on

the empty core model (ECM) we take the unscreened potential to the zero in side some radius R_e [34, 35].

$$V(r)=0 \quad , \qquad \text{for } r<R_e$$

$$V(r)=\frac{-e^2}{r} \quad , \qquad \text{for } r>R_e$$

2.3 Excitons

Reflectance and absorption spectra often shows structure for photon energies just below the energy gap, where we might expect the crystal to be transparent. This structure is just caused by the absorption of a photon with creation of a bound electron-hole pair. An electron and hole may be bound together by their attractive coulomb interaction; just an electron is bound to a proton to form a neutral hydrogen atom. The bound electron-hole pair is called an exciton.

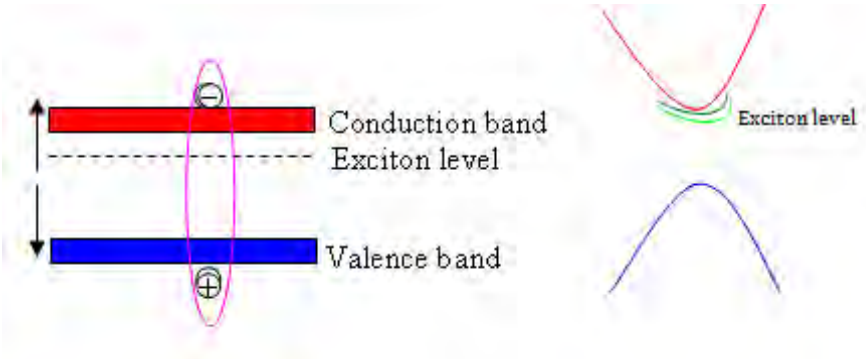

Figure 2.4: Exciton levels for transition from VB to CB [9].

An exciton can move through the crystal and transport energy: it does not transport charge because it is electrically neutral. Excitons can be formed in every insulating crystal. When the band gap is indirect, excitons near the direct gap may be unstable with respect to the decay in to free electron and free hole. All exciton s are unstable with respect to the ultimate recombination process in which electron drops in to the hole.

We have seen that a free electron and a free hole are created whenever a photon of energy greater than the energy gap is absorbed in a crystal. The threshold of this process is $\hbar w > E_g$ in a direct process. In an indirect process, the threshold is lower by the phonon energy $\hbar$ n. But in the formation of excitons the energy is lowered with respect to these thresholds by the binding energy of the exciton.

The binding energy of excitons can be measured in three ways:

- In optical transitions from the valence band, by the difference between the energy required to create an exciton and the energy to create a free electron and free hole.
- In recombination luminescence by comparison of the energy of the free electron-hole pair recombination line with the energy of the exciton recombination line.
- By photo-ionization of exciton s, to form free carriers. [9].

CHAPTER THREE
OPTICAL AND ELECTRICAL PROPERTIES OF SILICON AND GERMANIUM NANOSTRUCTURES

3.1 Porous silicon preparation

The discovery of bright visible luminescence from porous silicon has stimulated research for a better understanding of the basic mechanisms of light emission from silicon nanostructure and for a better control of the numerous parameters of porous silicon formation and further processing in order to give a high quantum efficiency of luminescence.

Rather simple considerations show that two conditions are required or efficient visible light emission from silicon structures: **I**, a confinement of carriers in to nanometer-sized silicon cells in order to get enough confinement to bring optical transitions in the visible range: **II**, an enhancement of the luminescence quantum efficiency, which can take its origin from an increase in the radiative recombination rate because of the breaking of momentum conservation or from a reduction of the non radiative processes by a passivation of the confined zone surfaces.

The P-Si is generally formed by electro chemical etching followed by photo assisted stain etching of 6Ω cm p-type Si wafers at current densities of 8-50m A/cm^2 using 10%-25% HF: ethanol solutions. Stain etching, accomplished under illumination with a 500/μ halogen lamp, was used to further increase the porosity [19]. All samples were rinsed in ethanol and immediately transferred in to an air environment. Special care was taken that the samples never be exposed to air. The blue sample was the only one measured under vacuum. A second set of identical samples were rinsed in ethanol and then exposed to air. A strong photoluminescence (PL) can be achieved under optical transition.

3.1.1 Emission and absorption of light

The emission and absorption of light in semiconductors is very analogous to the same process that we quite familiar within atoms. An electron in an excited state of energy E_1 makes a transition downwards to an empty state (energy E_0) and emits a photon: an electron in a lower state (Energy E_0)

absorbs a photon and makes a transition to higher state (energy E_1). The energy conservation equation is Ephoton = $\hbar w = \Delta Electron = E_1 - E_0$

The band gap of insulators is what makes them relatively transparent if the incoming light has a frequency $w < \frac{E_g}{\hbar}$, then it can not be absorbed by the electrons filling the valence band. The very low absorption of wide-gap insulators is generally due to impurities, so light penetrate relatively deeply in to them [19].

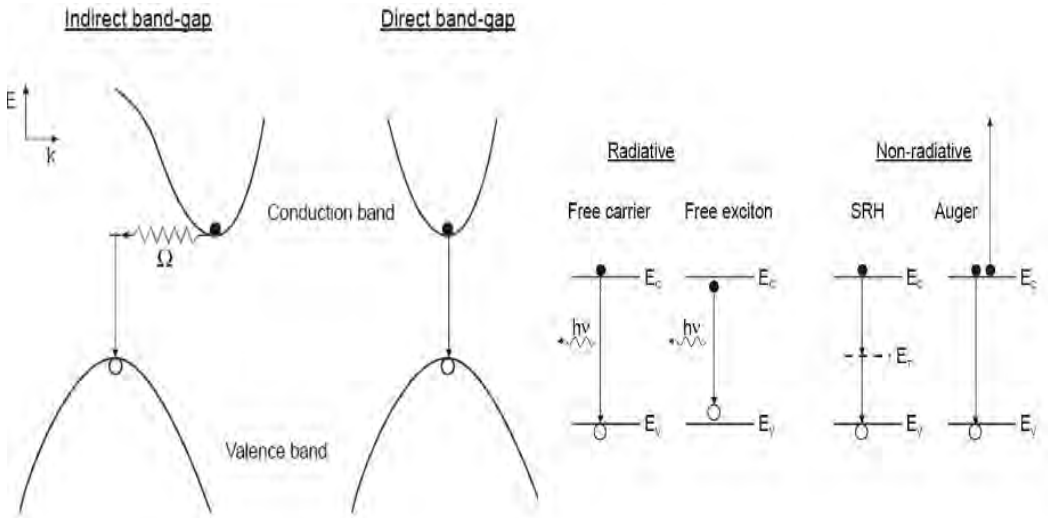

Figure 3.1: Direct and indirect band transitions [20].

Besides to Si and Ge, most semiconductors are in fact indirect band gap materials with the band structure, lattice constant, chemical species, bond length, electro negativity, stiffness and elasticity. Conventionally the band structure of semiconductor is represented by the dispersion relation E_n (k) where En is the energy of an electron (or a hole) at the band edge with a wave vector k in the first Brillion zone. The indirect gap also affects absorption of incident radiation. Photo excitation of carriers can occur both by absorption or emission of photons in indirect semiconductors. The absorption coefficient α has a quadratic dependence on photon energy and has two branches.

In direct semiconductors no phonon assistance is needed and α shows a parabolic dependence with incident photon energy.

The net result is that when band-to-band absorption occurs in direct semiconductors, the incident radiation is absorbed in a much shallower depth than in indirect semiconductors the forbidden gap can also mediate an electron-hole pair recombination.

In indirect semiconductors, phonon assistance may still be required making gap state mediated radiative recombination potentially less efficient than a direct transition [21].

Here we derive the standard exponential attenuation law of light being absorbed by a solid. Picture an incident beam of light with an initial intensity of I_0 picture. Next a bulk solid which can be divided in to very small "slices" or "scabs" of thickness of the solid is x.

Next, each slab absorbs some light and transmits the rest.In each slab a fraction (1-f) of impinging light is transmitted. Here $0 \leq f \leq 1$. So initially we have I_0 . After the first slab your have a residual intensity of $I=(1-f)^2 I_0$ and so on.

The general expression for the residual intensify offer n slabs is therefore

$$I=(1-f)^n I_0$$

To derive the exponential attenuation law, re-arrange this in to the following.

$$\frac{I}{I_0}=(1-f)^n$$

This is the fraction of the incident intensity that makes it through n slabs. Re call now that $x=n\Delta x$

giving $\frac{I}{I_0}=(1-f)^{x\Delta x}$

Next, to simplify the notation let $p=(1-f)$ yielding

$$\frac{I}{I_0}=p^{x\Delta x} \quad ,$$

where $0<p<1$. This can be rearranged as

$$\frac{I}{I_0}=(p^{\Delta x})^x=\left(\frac{1}{p}\right)^{(\frac{1}{\Delta x})-x} \quad ,$$

where note that $1/p>1$. Now note that p is a constant. In addition, Δx is a constant therefore, can the whole thing some other constant, say y.

$$\frac{I}{I_0}=y^{-x} \quad ,$$

where recall that y can be expressed alternatively as $y=e^{lny}$. This gives

$$\frac{I}{I_0} = (e^{\ln y})^{-x}$$

Next, since y is a constant, so is lny. Call it α giving $\frac{I}{I_0} = e^{-\alpha x}$,

where $\alpha > 0$. This leads to popular expression for the exponential attenuation of light in solid

$$\frac{I}{I_0} = e^{-\alpha x} \quad , \qquad (3.1.1)$$

where α is called the absorption coefficient

3.2 Luminescence

Luminescence is light that usually occurs at low temperature and thus form a cold body radiation, which distinguishes it from incandescence. It is a general term which describes any process in which energy is emitted from a material at different wave length [22].

Optoelectronic devices work by exciting electron-hole pairs; when a pair recombines it emits light. This is called luminescence. It results when there is a significant over lap (indirect and reciprocal space) in the electron-hole pair wave functions. When ever there is such overlap, luminescence is possible; however the strength of the luminescence that is light emission rate quantum efficiency depends on the extent of this overlap and the transition probability [21].

There are different types of luminescence; here we mention photoluminescence and electro luminescence. Electro-luminescence is the excitation of carriers by electric current or strong electric field, often practical method; and photoluminescence is the excitation of carriers by light it self, it is usually caused by optical radiation [18, 22).

Luminescence is further broken down in to two categories according to the speed of recombination. Direct electron-hole recombination is usually relatively fast; the lifetime depends on the number of final states available.
The excited electron first makes a second transition to such a state, whose energy normally lies in the gap. Then it makes a second transition to finally recombine with the hole in the valence band. Often

one of these transitions is non-radiative.By this is meant that the energy given of f_1 in the transition appears as heat, not light.

$$f(E)=\frac{1}{\exp\left(\frac{E-\mu}{K_B T}\right)+1} \tag{3.3.1}$$

The concentration of electrons in the conduction band is [5]

$$n(T)=\int_{E_g}^{\infty} D_c(E) f_e(E)\, dE \tag{3.3.2}$$

$$n(T)=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\int E^{1/2}\left[1+\exp\left(\frac{E-\mu}{K_B T}\right)\right]^{-1} dE \tag{3.3.3}$$

$$f(E)=1-\frac{1}{\exp\left(\frac{E-\mu}{K_B T}\right)+1} \tag{3.3.4}$$

And the concentration of holes in the valence band is

$$P(T)=\int_{\infty}^{E_v} D_v(E) f_h(E)\, dE \tag{3.3.5}$$

$$p(T)=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\int E^{1/2}\left[1+\exp\left(\frac{\mu-E}{K_B T}\right)\right]^{-1} dE \tag{3.3.6}$$

3.2.1 Recombination rates

The recombination rate for electron hole pairs is given by

$$\frac{dN(t)}{dt} = -\alpha_r N(t) P(t)$$

N (t) is the number of electrons and P (t) is the number of holes, α_r is a constant that we could calculate, given our knowledge of transitions between quantum states. It is an integrated involving the electric field and the initial and final state wave functions.

In addition to this here is a thermal generation rate for e-h pairs.

$$\left(\frac{dN(t)}{dt}\right)\text{themal} = \alpha_r N^{(2)}{}_i$$

Now let us say that we are in thermal equilibrium in an intrinsic semiconductor. This is a steady state and N (t) =P (t) so

$$\left(\frac{dN(t)}{dt}\right)total = \alpha_r N^{(2)}{}_i - \alpha_r N(t) P(t) = \alpha (N^{2}{}_i - N^2(t)]$$

$N(t) = N_i$,a constant. Thus N_i has the meaning of the number of carriers in a intrinsic semiconductor in thermal equilibrium. It is a strong function of temperature. In thermal equilibrium in general, we have

$$\left(\frac{dN(t)}{dt}\right)total = \alpha_r N_i^{(2)} - \alpha_r N(t) P(t) = 0$$

So N (t) = Ni^2 ; the product of electron and hole concentrations (in equilibrium) is always the same, it does not depend on doping, which is some what surprising. Note that in an n-type material, we would have N (t)>>P (t) and vice-versa for p-type.

Now let us think about a situation where we shine a pulse of light on a p-type sample. N (0) will depend on the strength of the pulse and then it will relate back to its equilibrium value $N_c = \frac{N^{(2)}{}_i}{Nv}$.

We have n (t) <<P (t), but P (t) is not much changed from its base value, so let

P (t) = N_v

$$N(t) = N_c + \left[N_0 - N_c\right]\exp^{\frac{-t}{(\tau)}}$$

Where $i = \frac{1}{\alpha_r N_v}$, for p-type, and $i = \frac{1}{\alpha_r N_c}$ for n-type [18].

3.3 Photoluminescence

Studying photoluminescence and understanding its mechanism has tremendous attention due to op to-electronic applications. Photoluminescence (PL) is a process in which a substance absorbs photons (electro-magnetic radiation) and then re-radiates photons. Quantum mechanically, this can be described as an excitation to a higher energy state and then return to a lower energy state accompanied by the emission of photon. In other words, it is the emission of light beam from semiconductors mainly when electrons and holes recombine. When electrons in the valence band exposed to a high-powered laser they will leave their orbits until the average energy drops to the bottom of the conduction band. Usually at this stage attraction of the holes over comes the electrons and they recombine at the same times emits photons of energy equal to band gap energy.

Luminescence resulting from optical excitation is called photoluminescence (PL). Typically for Si nanocrystal (Si-nc) PL extends from 600nm to 1000 nm [23]. The excitation source is laser with photon energy larger than band gap energy Eg. Electrons and holes relax rapidly by interacting with photon or phonon with lattice vibrations $\rightarrow$ electrons $\rightarrow$ phonon coupling ~ 100 fs: much faster than the radiative life time.

3.3.1 The photoluminescence of porous silicon

The photoluminescence from p-Si is at wavelength ranging from the ultraviolet to the infrared [33]. The PL is usually excited by a wave length shorter than the emission wave length with excitation wavelengths typically lying between 260nm (for ultraviolet emission and approximately 520nm [26]. Alternatively PL can be excited through an up conversation process by pumping the p-Si at the infrared wavelengths [27, 28].

The characteristics of PL changes as the wavelength of emission changes from ultraviolet wavelengths to infrared wavelengths. A specific characteristic normally applied to a discrete set of wave lengths in to three bands to describe these characteristics. The main characteristic of each of wavelength bands called the “red” “blue” and “infrared” bands. Normally it is very difficult to compare one’s own result of luminescence investigations with those of another author due to the use

of relative units for intensity. To overcome this problem, integral features of spectra such as peak areas can be given in terms of efficiency.

The spectra shown in this work are mapped on an energy scale, and therefore a peak area is proportional to the emitted energy, not to the number of emitted photons. The efficiency η_p is defined as the ratio of the light out put power to the in put power, which is the light in put power in the case of PL or electrical out put power in the case of EL.

In the literature terms the external quantum efficiency η_E or internal quantum efficiency η_I is the ratio of emitted photons to the number of photons directly absorbed by the luminescence centers. These efficiencies fulfill the equation $\eta_p < \eta_E < \eta_I$. In the PL η_p and η_E differ by of the energy of exciting to the emitted photons and both are similarly suitable to characterize the achieved intensity. However in the case of EL and high applied voltages the use of η_E could give rise to misunderstanding [29]

3.4 Silicon nanocrystals in Sio_2

In the past decades, there has been considerable interest in semiconductor nanostructures, especially porous Si and Si nanocrystals [30, 31] because of their potential applications towards Si-based optoelectronic devices. Si nanocrystals have been fabricated by a variety of methods and include such techniques as co-sputtering chemical vapor deposition, molecular beam epitaxy, gas evaporation, laser ablation and so on. Nanometer-sized crystallites exhibit unique electrical, optical, magnetic and thermal properties which are not observed in bulk materials. Although a considerable amount of research has been performed by many researcher worlds wide, the mechanism responsible for photoluminescence from these Si nanostructures is still unclear. While P-Si exhibit luminescence properties, its stability was a deriving force for the investigation of other structures, where Si nanocrystals would be better passivity.

One way to from Si nanocrystals embedded in SiO_2 is to create an excess Si concentration in the oxide by Si implantation and to induce nanocrystal formation and growth by subsequent high temperature annealing [32].

The optimum passivation time that varies with the quality of SiO_2 (fused silica, wet and dry SiO_2 grown process) and the Si implantation depth profile. The effect of passivation time for the SiO_2 samples implanted with Si ions varies with energy. Passivation can also induce a blue shift or a red shift of the PL spectrum. The PL spectrum has been red shifted after passivation of the sample

implanted to high excess Si concentration, while no spectrum shift has been observed at low excess Si concentration. On the other hand the PL intensity decreases (increase) with a red shift (blue shift) of the PL spectrum.

When a larger concentration of Si is implanted, the luminescence signal decreases with the Si concentration. However; the effects of Si-nc size, shape and distribution on the PL spectra remains complex due to the presence of several radiative transition process [23].

Many different investigation have shown a flat interface between Si and SiO_2 is formed, this extremely sharp (at single atom level) and extremely stable with the external agents. For this reason si-nc embedded in SiO_2 matrix has been used to form light emitting systems with superior properties with respect to p-Si which is formed by Si nanostructures with time dependent surface passivation. The quality and stability of the Si/SiO_2 interface in si-nc embedded in SiO_2 is what renders this system superior.

The role of the interface on the electronic and optical properties of Si-nc has been recently addressed in various experimental and theoretical studies. The oxidation introduces defect level in the Si-nc band-gap which pin their emission energy. The defect levels are due to the formation of Si-O double bond. Similar results can be obtained also for O connecting two Si atoms (single bond) at the Si-nc surface the assistance of Si-O vibrations at the interface has been proposed the dominant path for recombination [34].

Si-ncs embedded in a SiO_2 matrices are currently attracting great interest as a candidate system to solve the physical instability of the bulk Si, due to its indirect energy band gap to act as an efficient light emitter; the emission is shifted in the visible region due to Quantum confinement (QC) effects. The radiative recombination of e-h pairs generated inside a nanocrystal embedded in SiO_2 is also very efficient at room temperature. Amorphous Si nanocrystals have also considerable attention as light emitting material. The electrical properties are strictly related to the peculiar structure of the active layer, consisting of a very high density of partially interconnected and very small amorphous clusters. Due to a strong dependence of current, the electronic conduction can not be explained by a model based on tunneling mechanism [37].

EL is a very important feature for any long optoelectronic technology. Its characterization and optimization are essential for the development of all Si light emitting diodes (LEDS) and eventually of a Si laser. EL has been first reported in amorphous Si because of the difficulty of electrical

pumping of the Si-nc embedded in a consulting matrix (SiO_2). However; when (SiO_2) is thin enough and appropriate setup is used, EL can also be observed in si-nc produced by ion implantation and plasma enhanced chemical vapor deposition PECVD with low activation voltage.

The electrical carrier injection is usually performed by means of a structure resembling metal-oxide-semiconductor (MOS) device. Transparent thin electrodes are deposited on to the Si-nc/ SiO_2 layer. The size of this electrode is kept small to concentrate the injected electrons [23].

Si nanoclusters embedded in SiO_2 matrices hinder the attainability of stable efficient electrically driven light emitting devices owing to a huge barrier mismatch between Si and SiO_2 . The EL emission crystalline Si nanoclusters must be grown or past-annealed at high temperature to participate the crystalline Si nanoclusters. The PL peak energy as a function of diameter of Si nanoclusters can be obtained by fitting the relationship between PL peak energy and diameter of Si nanoclusters, the dependence of the associated energy-gap E(ev) on the diameter (d) nm of the Si nanoclusters can be expressed as [44,45].

$$E(ev) = 1.17 + \frac{11.6}{d^2} \qquad (4.2.1)$$

Eq (4.2.1) can be substituted in the QC model to get the luminescence intensity

The photoluminescence arising from implanted Si nanocrystals in SiO_2 has been attributed by some investigations to quantum confinement [36, 37], while others have concluded that surface states present in the inter-facial layer between the Si nanocrystals and the surrounding oxide matrix play an important role in the emission porous ([38,39] , more recently, oxidation effects photoluminescence from Si nanocrystals fabricated by laser ablation have been reported [39]

3.5 Photonic applications

The aim of recent investigations are towards the development of photonic applications in which multi-layer porous silicon structures are used to fabricate Bragg reflections, Fabry-perot filters and micro-cavities [40]. The fabrication and optical characterization of dielectric porous silicon multi-layers with periodic variation of refractive index as a function of depth is possible through etch process. These complex multi-layers structures have used to create interference filters and/or narrow band reflections formed by dielectric films. Bragg reflectors and Fabry-perot devices fabricate on the bases of these multi-layers that help to tune and narrow down the p-emission band. Other applications of porous silicon multi-layers include planer wave-guides in infrared and visible region.

Commercial application presently hindered by scattering loss and absorption in the porous medium. The fabry-perot devices help to fabricate porous silicon micro-cavities, which act as confinement region for emitted photons and modify the photon density of states that finally lead to alterations of spontaneous emission characteristics. The effect of micro-cavity is manifested in many ways: (i) A 16-fold increase in intensity (ii) strong narrowing of emission band, (iii) decrease in the luminescence decay time constant, and (iv) strong directional emission from the micro-cavity. These features are evidence through angular resolved photoluminescence measurements and time resolved excitation spectroscopy. Porous silicon Schottky diodes have studied with yielding efficiencies [47]. These types of diodes are used to achieve porous silicon light emitting diodes (LEDS) with improved performance. The current voltage characteristics proved to be independent of the type of metal used for the electrical contact. Devices based on Si homo junctions have fabricated for providing more adequate carrier injection mechanism for efficient electro luminescence (EL) and shower degradation. Micro-cavity (LEDS) is very useful to achieve efficient EL. In 1996 attempt was made to integrate a porous silicon LED with Si electronics and it was possible to turn the LED on and off by applying small current pulse to the base of the transistor. Finally, arrays of such integrated structures fabricated.

Nano-silicon is a good candidate for developing two dimensional photonic crystals (2D-PC) by anodic electro chemical dissolution method. This method is technologically friendly, simpler, cheaper, and faster and water scalable. These 2D-PC made from porous silicon has air columns in the Si – material that acts as macro-pores. They can fill with active materials to form either enhanced

LEDS or nonlinear media. Another application of porous silicon is in fabricating porous silicon Fibonacci quasi crystals. In these structures, the localization of light waves helps for many nonlinear applications. Researches observed that the electric field intensity of optical modes shows local field enhancement effect, which s due to the weak localization of modes. This investigation is very important from fundamental physics point of view as the time resolved propagation. Measurements on porous silicon Fibonacci quasi-crystals demonstrate the presence of localized photon states.

CHAPTER FOUR
FORMULATION OF MODELS FOR PHOTOLUMINESCENCE

There exist two classes of explanation for the origin of the visible PL and EL in P-Si, the quantum conferment effects and the surface state effects. Here we consider the Quantum confinement model effects for our system.

4.1 The quantum confinement model (QCM)

This model is based on the electronic confinement in dot like structure of Si. The development of this model is based on the effective mass approximation theory. In this model, the luminescence process is attributed to an energy shift of carriers (electrons and holes) and is proportional to L^{-2} L being the Si-nc diameter [43, 42]. We model a nanostuctured QD by a sphere of diameter, so that its HOMO-LUMO gap is [41].

$$E_g^n = E_g^b - \frac{c_1}{L_1^{\alpha_1}} \qquad (5.1.1)$$

Quantum wire can be modeled as a cylinder with HOMO-LUMO gap

$$E_g^n = E_g^b - \frac{c_2}{L_2^{\alpha_2}} \qquad (5.1.2)$$

The energy in QW is parabola, thus we can model it as a hemisphere so that its HOMO-LUMO gap is

$$E_g^n = E_g^b - \frac{c_3}{L_3^{\alpha_3}} \qquad (5.1.3)$$

Where E_g^n, E_g^b are the energy gaps of the confined and bulk structures respectively in their geometric domain: L_1,L_2 and L_3 are the diameters the sphere the cylinder, and the hemisphere which we model the QD, quantum wire and QW and C_1,C_2 and C_3 and α_1, α_2 and α_3 are constants that can be found by empirical fit.

A natural choice to find QDs size is to associate the effective size with the diameter of the sphere which has the mass density ℓ of bulk Si and contains the same number of Si atoms as the QD in question. Then the diameter is

$$L(N_{si})=\left(\frac{3}{4\Pi\ell}\right)^{1/3} N^{1/3} si \approx 3.3685 N^{1/3} si\text{Å} \qquad (5.1.4)$$

Assuming that a Gaussian size distribution about the mean diameter L_0 for the nanocrystallites:

$$I(L)\approx\frac{1}{\sqrt{2\Pi\delta}}\exp-\frac{(L-L_0)^2}{2\delta^2} \qquad (5.1.5)$$

The number of electrons in a column diameter L participating in the PL process is proportional to L^2 . The heights of the columns depend only on the growth time and are approximately the same. Hence

$$N_e \sim L^2 \Rightarrow N_e = bL^2$$

For P-Si sample consisting of varying column diameters the probability distribution of electrons participating in the PL process is:

$$I_e(L)=\frac{1}{\sqrt{2\Pi\delta}} N_e(L)\exp(-\frac{(L-L_0)^2}{2\delta^2} \qquad (5.1.6)$$

$$I_e(L)=\frac{1}{\sqrt{2\Pi\delta}} bL^2\exp(-\frac{(L-L_0)^2}{2\delta^2} \qquad (5.1.7)$$

where b is a suitable normalization constant. The luminescence intensity can be determined by the Fourier transform of eq (5.1.7) to the energy axis as:

$$I(\Delta E)=\int I(L)\delta(\Delta E-\frac{C_1}{L^2})dL \qquad (5.1.8)$$

$$I(\Delta E)=\frac{1}{\sqrt{2\Pi\delta}}\int \delta(\Delta E-\frac{C_1}{L^2})L^2\exp(-\frac{(L-L_0)^2}{2\delta^2}dL \qquad (5.1.9)$$

The Dirac delta function facilitates a straight forward integration.

Putting $y=\frac{C_1}{L^2}$ and apply the properties of Dirac delta function, the above integral will be transformed in the form.

$$I(\Delta E)=\frac{1}{2}\frac{bC^{3/2_1}}{\sqrt{2\Pi\delta}}\int[\delta(\Delta E-y)\,y^{-5/2}]^2\exp(-\frac{(-L_{0^2})}{2\delta^2}(L_0\sqrt{\frac{C_1}{y}}-1)^2$$

The above integral gives the intensity as a function of ΔE

$$I(\Delta(E)=\frac{bC^{3_1}}{\sqrt{8\Pi\delta}}\Delta E^{-5/2}\exp(-\frac{-L_{0^2}}{2\delta^2}\left[(\frac{\Delta E_0}{\Delta E})^{1/2}-1\right]^2 \qquad (5.1.10)$$

Where ΔE is the energy shift due to the confinement given by

$$\Delta E=h\nu-(E_g-E_b) \qquad (5.1.11)$$

E_g being the bulk band gap of Si or Ge in this sample and E_b is the exciton binding energy, and

$\Delta E_0=\frac{C_1}{L_{0^2}},$ being the nanocrystal mean diameter and δ standard deviations. The values of

E_g ranges from 1.11ev to 1.17ev for Si, depending on temperature; however, we took 1.12ev for Si and 0.7ev for Ge which is actually reported in most standard experiments at room temperature, while the value of E_b varies with nanocrystal radius of the sample ranging exponentially from 0.05ev (r-5nm) to 0.24ev (r-1nm).

According to the QC model, the emission wavelength and intensity depends on nanocrystal diameter, size distribution and concentration. This model can explain the general tendency of most experimental results such as the blue shift of the luminescence spectrum with decrease of the Si-nc size. The QC model is highly predictive when the nanoclusters are associated from the matrix (ex: Si-nc isolated from SiO_2). Consequently this model does not give a satisfactory explanation for the evolution of the luminescence spectra for some experimental parameters such as the PL for sample temperature below look, as well as oxidation or oxygen passivation of samples containing Si-nc. Due to this reason we used another model for terminated Si-nc [42].

CHAPTER FIVE

RESULTS AND DISCUSSION

In this chapter we will study the results of PL intensities for Si and Ge nanostructures as a function of different parameters. We used the ideas and expressions of our models and develop matlap program to compute the PL intensity as a function of different parameters and we fit most of our results with experimental results reported in many experimental researchers.

5.1 Dependence of PL intensity on wave length for different δ s

Fig 5.1 Shows the PL intensity as a function of wave length for both Si and Ge nanostructures. As we can see from the figure, the PL intensity for both nanostructures seems to be almost similar since they have band structure except a light change in the band gap energy. The standard deviation from the mean crystallize (which in fact contains the dependence of PL intensity on size influence on the intensity.

Putting different values of sigma suppresses the nature of the luminescence intensity that would have been on the smaller value of sigma in the spectrum of luminescence intensity versus wavelength. This is as expected be cause the PL intensity depends on the emitted photon energy, not to the number of emitted photons.

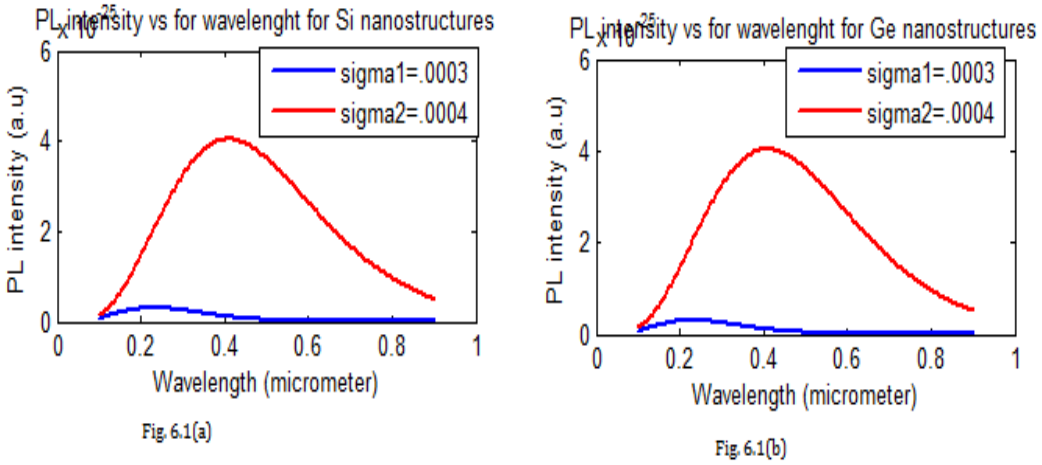

Figure 5.1: PL intensity versus wavelength for Si and Ge nanostructures[15]

5.2 Photoluminescence properties of silicon nanocrystal as function of size.

Table 1. Characteristics parameters and PL properties of the different nc-Si samples studied [21] .

Sample identifier	Average size (nm)	Width of size distribution(nm)	PL Max. (eV)	PL Max. (nm)	PL width (nm)
A	3.44	1.02	1.82	680	190
B	3.46	0.63	2.03	610	165
C	3.88	0.61	1.75	710	155
D	4.05	0.62	1.65	750	150
E	4.45	0.78	1.55	800	145
K	2.8	0.86	1.95	635	115
L	3.2	1.08	1.71	725	145
M	3.6	1.16	~1.44[a]	~860[a]	~170[a]
N	4.8	1.16	1.35[a]	900[a]	~200[a]

a- values derived from Gaussion fits to the experimental data

Table 2. Modified model result: Characteristics parameters and PL properties of the different nc-Si samples.

Sample identifier	Average size (nm)	PL Max. (eV) Experimental	PL Max. (eV) results of our model	PL Max. (nm) Experimental	PL Max. (nm) results of our model
A	3.44	1.82	1.7021	680	728.496
B	3.46	2.03	1.6969	610	730.728
C	3.88	1.75	1.6025	710	773.774
D	4.05	1.65	1.5709	750	789.339
E	4.45	1.55	1.5079	800	822.318
K	2.8	1.95	1.9166	635	646.965
L	3.2	1.71	1.7705	725	700.352
M	3.6	1.44	1.6625	860	745.848
N	4.8	1.35	1.4629	900	847.613

5.2.1 Strong confinement energies.

where R≤ a_B , strong confinement regime, the confinement effect dominates and the electron and hole will be viewed as individual particles predominantly in their respective ground states with only little spatial correlation between them[13].In this confinement regime, unlike the weakly confined exciton we can take the effect of confinement potential V(r_e, r_h) in to account. Hence, the Hamiltonian of an exciton strongly confined in QD of radius is given by:

$$H=\frac{P^{2_e}}{2\mathrm{m}_e}+\frac{P^{2_h}}{2\mathrm{m}^h}-\frac{e^2}{\varepsilon(r_e-r_h)}+V(r_e-r_h)$$

where r_e, r_h are the position of electron and holes respectively, and

V(r_e, r_h)=}0 if $r_e, r_h < R$

} ∞ otherwise

So, the poison of the lowest exciton energy state has expressed [15] as

$$E_{lsls}=E_{g^{bulk}}+\frac{\pi\hbar^2}{2\mu\mathrm{R}^2}-1.786\left(\frac{a_B}{R}\right)E^{RY}-0.248\,E^{Ry}$$

where the second term corresponds to the sum of the single particle particle ground state energies (kinetic energies), the third term the coulomb attraction and the last term one for spatial correlation between the two particles.

On the other hand, using the band gap energy expression for the lowest exciton energy we find:

$$E_{lsls}=E_{g^{QD}}-1.786\left(\frac{a_B}{R}\right)E^{RY}-0.248\,E^{Ry}$$

From such expression, we understood that the exciton binding energy should be

$$b=1.786\left(\frac{a_B}{R}\right)E^{RY}+0.248\,E^{Ry}$$

Now, using quantum confinement model we obtain the following band gap energy expression:

$$E^{QD_g} = E_{g^{bulk}} + \frac{B}{d^{\gamma}} - 1.786\left(\frac{a_B}{R}\right)E^{RY} - 0.24\,E^{Ry}$$

We use this expression for the photoluminescence spectra. Now, taking the oscillator strength into account, the radiative transition probability in quantum dot of diameter d becomes

$p(d) \sim fN_r \sim d^2$ Now, the photoluminescence intensity from an ensemble of quantum dot size having size distribution n(d) will be given by

I(d)~p(d) n(d) ……..(5.1)

The emitted photon energy from the quantum dot should be lower than the band gap energy of the quantum confinement model by an amount of the localization binding energy E_s of the surface states and the exciton binding energy E_b .Hence the emitted photon energy from the quantum dot will be

$$E_{PL} = E_{g^{bulk}} + \Delta E - E_b - E_s$$

According to quantum confinement model that band gap up shift can be modeled as $\Delta E = \frac{B}{d^{\gamma}}$, where β and γ are constants due to quantum confinement effect,their magnitude strongly depend up on the band gap calculation method being employed.

In this section, we will discuss the experimental results in terms of size effects in the frame work of the quantum confinement model. In this theory, the PL energy is blue shifted with respect to the band gap of bulk silicon (Eo=1.17ev) and obeys a power law with an exponent equal to -1.39 for particle diameter d measured in nanometers.We transform eq.(6.1) from d to ΔE dependence [19]as

$$I(\Delta E) = \int I(d)\,n(d)\,\delta\left(\Delta E - \frac{\beta}{d^{\gamma}}\right)dd \quad \ldots\ldots\ldots\ldots \quad (5.2)$$

Taking $n(d) = \frac{1}{\delta\sqrt{\pi}}\exp\left(-\frac{(d-d_0)}{2\delta^2}\right)^2$ where d_0 and δ are the mean dot and standard deviation respectively. So, we obtained an expression for the photoluminescence intensity as

$$I(\Delta E) \sim \frac{1}{\delta\sqrt{\pi}}\left(\frac{\beta}{\Delta E}\right)^{2\gamma}\exp-\left\{\frac{\left(\frac{\beta}{\Delta E}\right)^{1\gamma} - d_0}{2\delta^2}\right\}^2 \quad \ldots\ldots\ldots\ldots\ldots \quad (5.3)$$

Eq.(5.3) gives general expression for photoluminescence intensity from Silicon quantum dots ensemble. It is clear from the above expression that the photoluminescence intensity depends strongly on the quantum confinement parameters β and γ .We took, $\gamma = 1.39$, $\beta = 3.73$ and $E_{g^{bulk}} = 1.12\,ev$ at room temperature[5]

5.2.2 Photoluminescence intensity versus size (Silicon nanocrystal).

Different experiments have performed on silicon nanocrystals to see the effect of quantum confinement and surface states. Figure 6.2 and Figure 6.3 shows the photoluminescence spectra of

different samples studied with their size distribution as measured by time-of-flight mass spectroscopy (TOFMS) together with results of our model i.e normalized photoluminescence intensity versus dots size, for experimental and results of our model for two set of samples

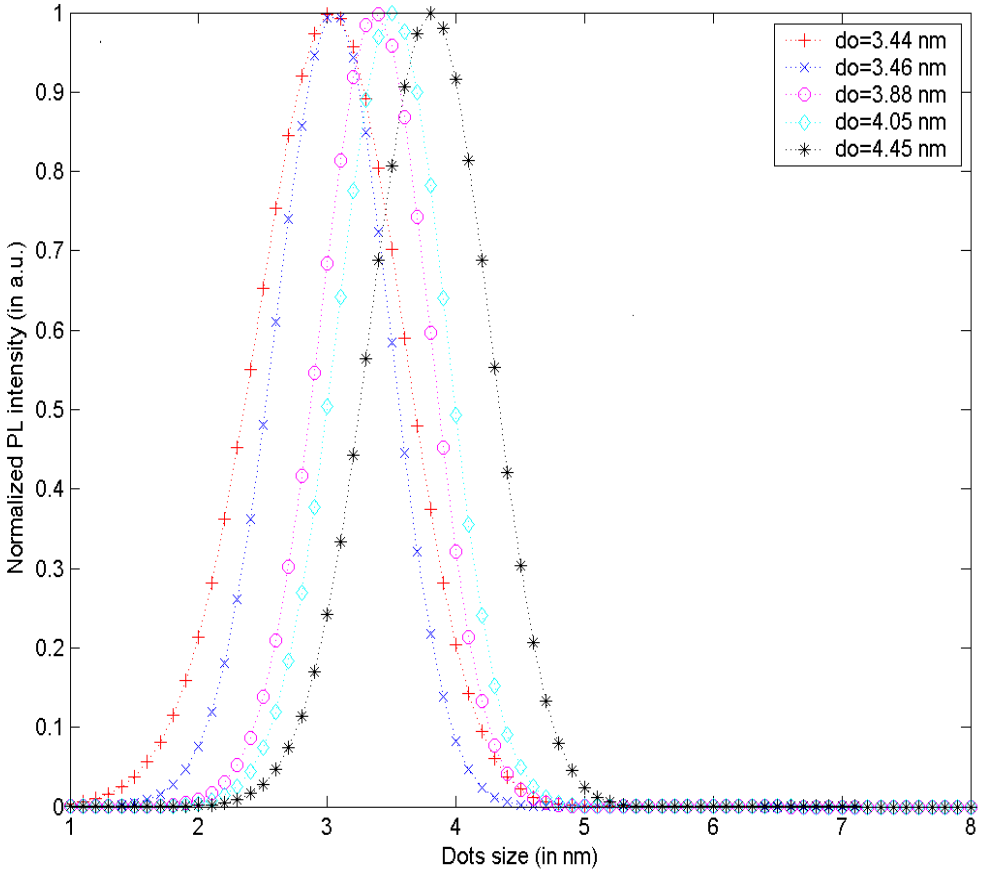

Figure 5.2 Graph of normalized PL intensity versus Dots size (A-E)

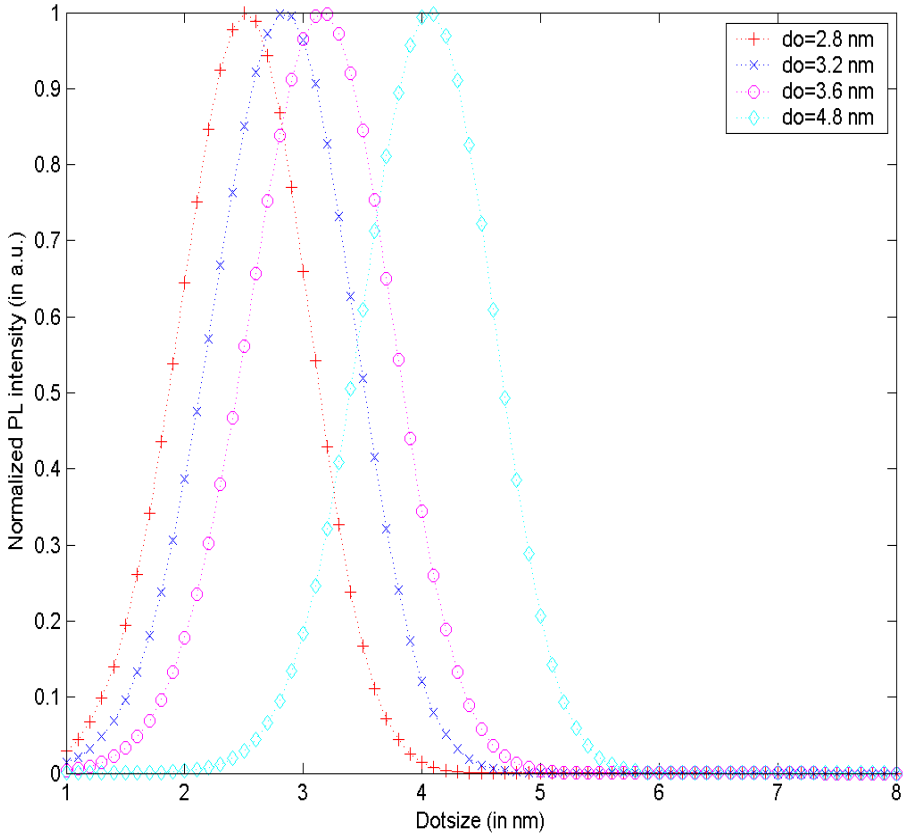

Figure 5.3 Graph of normalized PL intensity versus Dots size (K-N)

5.3 Photoluminescence intensity versus wave length (Silicon nanocrystal)

The photoluminesnce spectra of different samples studied with their size distributions as measured by time-of-flight mass spectroscopy (TOFMS) together with results of our model. From such plots, we understand that as the average size of the sample decreases the optical band gap increases so that the photoluminescence peak shifts to the shorter wavelength range of visible spectrum. Since, the luminescence energy is directly proportional to the optical band gap and inversely proportional to wavelength. Therefore, as the optical band gap increases the luminescence energy increases or wavelength decreases mostly to the shortest wavelength of visible spectrum.

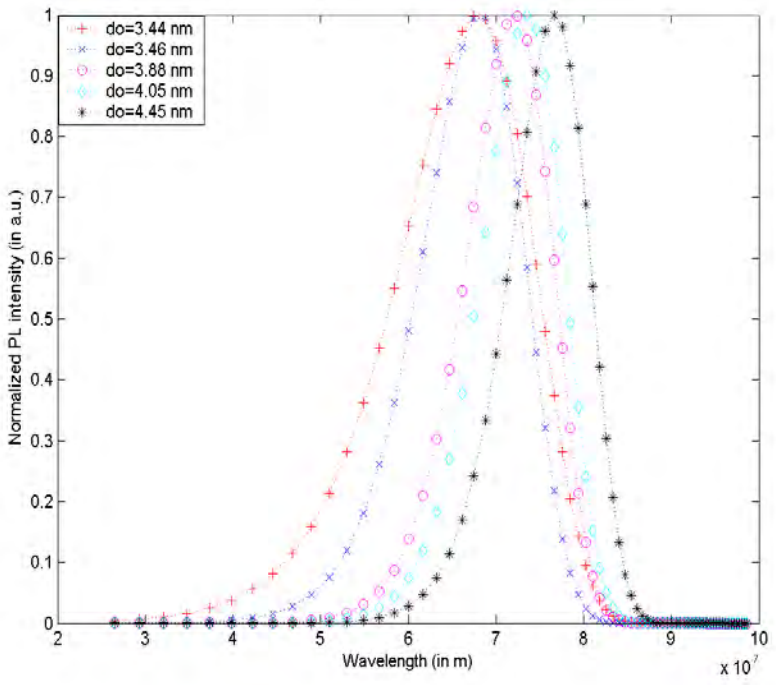

Figure 5.4 Graph of normalized PL intensity versus wavelength (A-E)

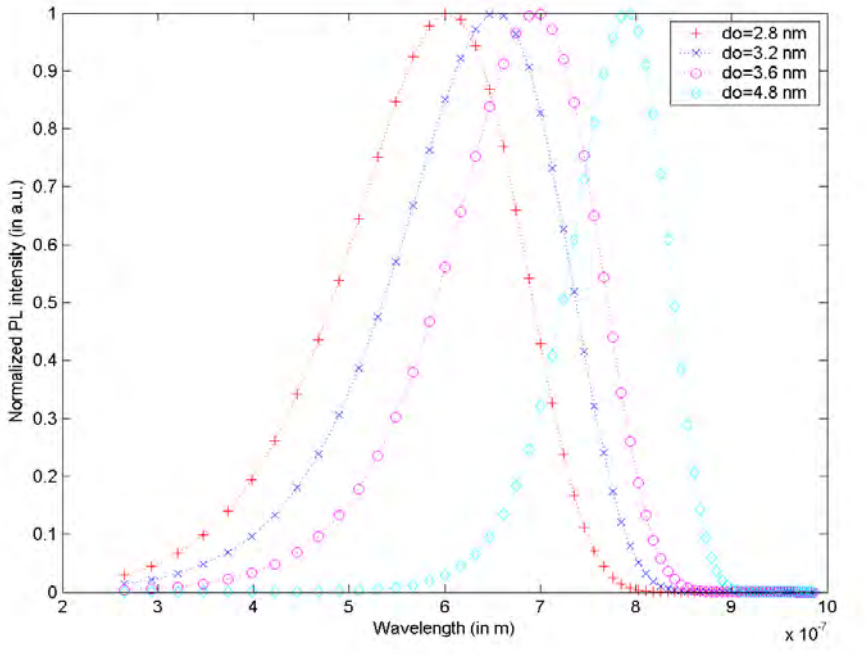

Fig 5.5 Graph of normalized PL intensity versus wave length (K-N)

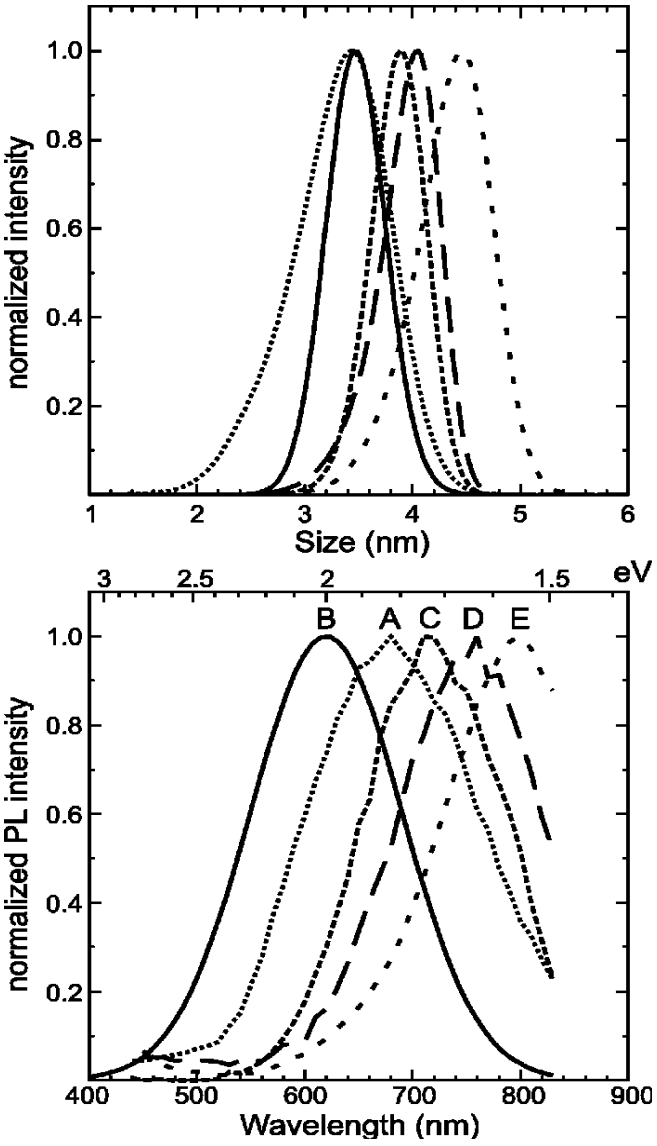

Figure 5.6 Experimental Results for comparison (A-E) samples

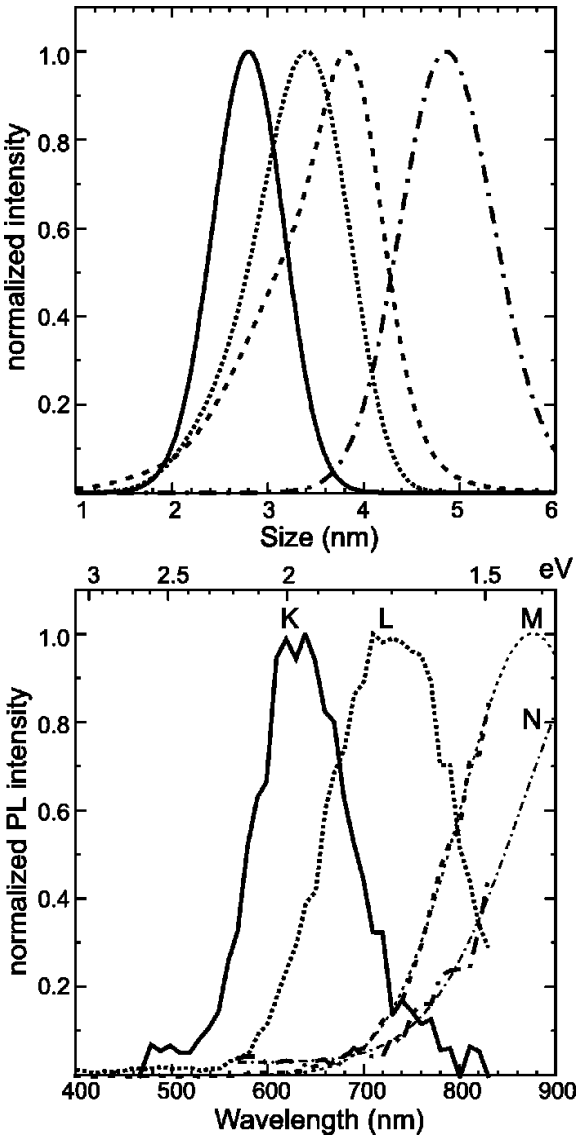

Figure 5.6 Experimental Results for comparison(K-N) samples

Chapter 6

Conclusion and future outlook

QC effect is more prominent in Si and Ge nanostructures, its effect is the enhancement of radiative recombination rate of excitons with decreasing the cluster size, it also increases the band gap. PL and EL spectrum are caused by optical and electrical excitations respectively, has the same luminescence center, and occurs at the same energy; however,the EL spectra has more narrow Gaussian sub peaks and red shifted than the PL spectra.A blue shift to the luminescence is observed with decreasing nanocrystal size. Visible light emission in Si becomes possible with radiative recombination rates. The light generated by e-h recombination in Si and Ge nanostrcutures is quantified by quantum efficiency.

Generally the HOMO-LUMO gap determines the energy of emitted photon spectrum, the intensity of this spectrum depends on the size of the nanocluster and the energy Shift due to confinement.
We have measured the photoluminescence properties of silicon nanocrystals as a function of their size. Our results can be well understood in the quantum confinement model. Since the experimental variation of the PL position is close to the theoretical behavior and since the internal PL yields of the nanocrystals are close to 100%. The PL shift with aging of the samples under normal atmosphere is also consistent with this model.

Future outlook

Study on the light emission properties (PL and EL) are the interesting application of Si and Ge nanostructures; detailed explanation on PL has not been done so far.
Electropho-toluminescence (EPL) and photoelectroluminescence (PEL) are also used nowadays, the future work will aim at studying the detail properties and applications of EL, PEL and EPL and enhancing the stability of EL intensity, increasing the QE both in PL and EL,and minimizing the EL degradation. Controlling Auger recombination, which is bad for luminescence and enhancing radiative recombination, will be the future work. EL and PL spectrum from Si and Ge nanostructures occurs at the same energy, but EL is red shifted and has narrow Gaussian sub peaks, it is thought that non-radiative recombination (Auger decay) which is bad for quantum efficiency is responsible for this effect; However, adequate explanation for it still do not exist, so this will be one of the future work for researches on EL and PL spectrum from Si/Ge nanostructures.

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