ESTIMATION OF ABSORPTION COEFFICIENT, OSCILLATOR STRENGTH AND DIELECTRIC FUNCTION OF SMALL SILICON NANOCRYSTALLITES

By

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To Marty and Menbere Bashaye.

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Abstract

Even if bulk silicon is poor emitter of light, due to quantum size effect which leads to an increase (the blue shift) of the band gap of the crystallites compared to bulk silicon, silicon nanostructure (porous Silicon, quantum dots, quantum wells and nanoclusters) exhibit strong photoluminescence at room temperature. Nanosilicon research is gaining tremendous attention in recent years towards the possibility of photonic application.

In order to explain optical properties of nanoporous semiconductor i.e the variation of absorption coefficient, dielectric constant and oscillator strength with size of nanoporous semiconductor information about the density of states which depends on the dimensionality of the system is very important. To do so, we obtain the density of states for 3-D, 2-D and 1-D and the dipole matrix element with the help of Kane approximation of momentum matrix element of direct band gap semiconductors. Using the dipole matrix element together with the joint density of states between valence and conduction band states we calculate the optical absorption coefficient, imaginary part of the dielectric function as well as the oscillator strength near the band edge for nanoporous semiconductor thus we find that the optical absorption coefficient and the imaginary part of the dielectric function are explicit function of photon energy and band gap energy but implicit function of the nanoporous semiconductors size through band gap energy. Our results for these optical parameters are in conformity with other observations.

Chapter 1

Introduction

Since the early 60's silicon has been the dominating material of microelectronics because of its excellent mechanical, chemical and electrical properties. The report by Canham, Lehmann and Gisele about the visible and efficient photoluminescence from porous silicon attracted a large attention of researchers which resulted in more than 1500 paper published since 1990. Light emitting silicon nanostructure have since been produced by using a wide range of different techniques. Initial excitement surrounded porous silicon (por -Si) because it represents an inexpensive and easily prepared form of nanostructure silicon. Quantum confinement effects are prominent in por-Si, which has led to a wide range of studies into its optoelectronic properties. While an explanation of Canham's observation of visible light emission[1]has motivated most of the work on por-Si, increasingly interest has developed in por-Si as a bio-compatible material and as a component of chemical and biochemical sensors.

The origin of visible photoluminescence (PL) from nanoscale Si is still the subject of much debate. Views are polarized between quantum confinement and other mechanisms [2]. An explanation based on quantum size effects alone does not explain all observations. Surface passivation, surface states, fabrication wavelength and pore

structure also play a role.

In the coming section what porous semiconductors are, some of their fabrication methods and how the optical properties of nonstructural gets affected by quantum confinement; will be discussed briefly.

1.1 Fabrication of nanocrystallites

The discovery of read PL from porous si has initiated comprehensive research activities, and today there are various fabrication techniques : electrochemical anodization , plasma-enhanced chemical vapor deposition (PECVD) , ion-implantation,and recently, laser pyrolysis technique has been introduced to achieve relatively narrow size distribution of silicon nanocrystals laser pyrolysis[3]. In the coming section we explore three of the fabrication techniques.

1.1.1 Fabrication of porous silicon

Porous Silicon can be produced using electrochemical anodization or photoelectrochemical technique without external bias. Sample of different porosity and thickness can be produced depending upon the preparation conditions(i.e the anodic current density and the anodization time).

Porous silicon layer can be fabricated by anodic etching of p^+ si(100) substrates (0.005 Ω) in a HF ($50^o/_o in H_2O$) ethanol solution (HF:ethanol=2:3-1:1) with a current density of 100 $\frac{mA}{cm^2}$ for 5 min. The porosity can be increased gradually with the anodization time where as the desire thickness of the porous si can be achieved by controlling the etching time[4].

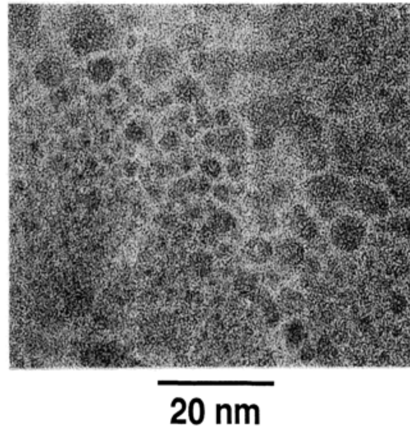

Figure 1.1: TEM image of a free-standing porous Si film

Free-standing porous silicon layers can be prepared using (100)-oriented p-type silicon wafers with resistivity of 0.2,3.5,10,50 and 230 Ωcm. Thin AL films were evaporated on the back of the wafer to form good Ohmic contact, the anodization is carried out in in HF-ethanol solution ($HF : H_2O : C_2H_5OH = 1 : 1 : 2$) at a constant current density of 30 $\frac{mA}{cm^2}$ for 15-60 min. After the anodization, the current density were abruptly increased up to 700 $\frac{mA}{cm^2}$ and the porous silicon layer were removed from the silicon substrate electrochemically. The thickness of porous silicon film prepared in this way is 20-40 μm[5].

Rama-spectroscopy and transmission-electron-microscopy examinations shows that Silicon crystallite spheres with diameters of several nanometers are dispersed in amorphous phase. Fig 1.1 shows a typical TEM image of local structure of porous Silicon film prepared from the 3.5Ωcm waffer. Porous silicon is a mixture of Silicon crystalline spheres and an amorphous phase [6].

In recent year, A Weller *et al* study por-Si prepared by a photoelectrochemical technique without external bias. The holes necessary for etching are created on

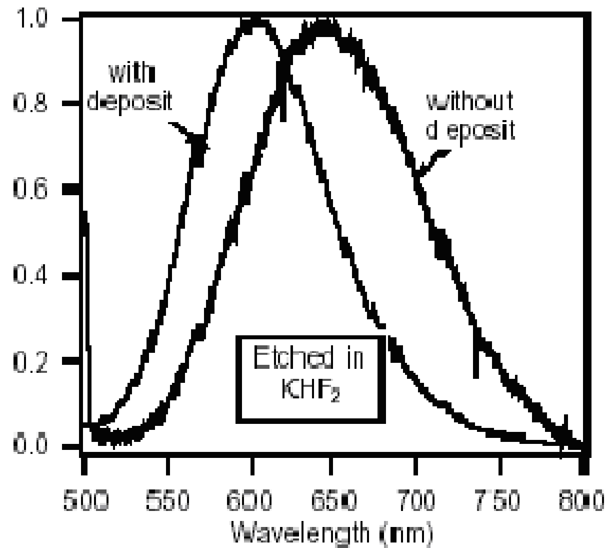

Figure 1.2: Photoluminescence spectrum from porous silicon produced by etching in aqueous KHF_2. A significant blue shift and intensity enhancement is observed in the presence of a deposit of K_2SiF_6.

excitation of an electron from the valence band to the conduction band by a HeNe laser. They have observed a deposit on the external surface when potassium ions are present in the etchant [7].

Laser assisted etching of n-type silicon, without an applied potential, in a variety of etchant produces photoluminescent porous silicon. Porous silicon produced from etchant containing K+, Cs+ or Rib+ can have cubic crystallites of hexafluorosilicate on top of and embedded in the porous silicon film. These are formed during etching from the metal ion and the etch product, SiF_6, via heterogeneous nucleation and growth. The photoluminescence of the hexafluorosilicate coated por-Si on excitation with UV light is blue-shifted (590610 nm), as compared to porous silicon which shows red photoluminescence ($\sim$ 640nm), even though the pure hexafluorosilicates exhibit

no photoluminescence of their own.

Disadvantage of porous silicone; the strong deterioration of the mechanical properties with increasing porosity and its electroluminescence degradation during operation can be avoided by subsequently oxidizing the porous silicon layer using electrochemical anodization.

1.1.2 Ion-implanted silicon nanocrystal

The discovery of red PL from porous Silicon has initiated comprehensive research activities, and today the palette of different approaches extends from porous Silicon over the diverse deposition techniques to ion implantation of semiconductor species into thin SiO_2 layers thermally grown on crystalline Silicon. Because of the robustness of the matrix, the very good control over the fabrication process and its full compatibility with SiO_2 current Silicon technology, ion implantation into thin films is a promising candidate [8]. Ion implanted Silicon nanocrystallite can be obtained by implanting Si or Ge into Si wafers or SiO_2 substrates and by annealing the samples, as shown in fig 1.3.

In contrast to porous silicon, implanted silicon nanocrystallites are very stable and form a reproducible system fully compatible with VLSI technology. The presence of a high-quality SiO_2 matrix guarantees superior oxygen passivation of silicon-related dangling bonds and non-radiative centers. In addition, the interface between the silicon nanocrystallite surface and the SiO_2 matrix can play an active and crucial role in the radiative recombination mechanism. The silicon nanocrystallite region has an effective refractive index, $n_{eff} = 1.71$, larger than that of SiO_2. Fig.(1.3) shows

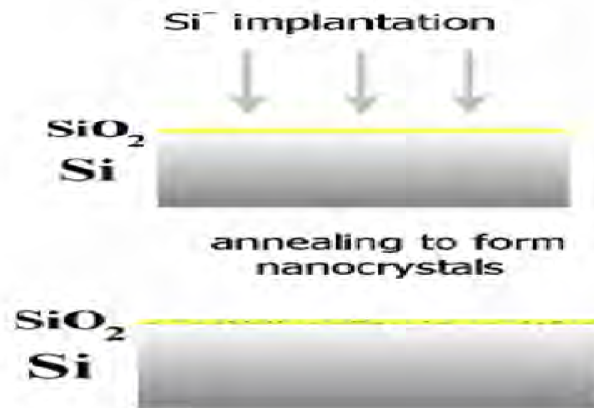

Figure 1.3: Formation of silicon nanocrystallites in a shell SiO_2 by implantation of silicon ions of 270 keV energy into silicon dioxide with subsequent annealing.

the formation of silicon nanocrystallites in a SiO_2 shell by implantation of silicon ions into SiO_2 with subsequent annealing [9].

1.2 Quantum confinement and optical property

Because of its 1.1 eV indirect band gap, silicon is characterized by a very poor optical radiative efficiency and only produces light outside the visible range. Until recent time several attempts to improve this efficiency have been unsuccessful, but in the paste decades room temperature visible photoluminescence has been observed from porous silicon surfaces prepared by chemical dissolution [1]. This observation has stimulated an intense experimental activity leading to promising results. In particular, electroluminescence has been reported during the anodic oxidation of porous silicon films and also during charge carrier's injection in rectifying junctions. The luminescence is often interpreted as resulting from the quantum confinement in small

size crystallites of porous silicon. In effect, even if bulk silicon is poor emitter of light, silicon nanostructure (porous Silicon, quantum dots, quantum wells and nanoclusters) exhibit strong photoluminescence at room temperature. This is due to quantum size effect which leads to an increase (the blue shift) of the band gap of the crystallites compared to bulk silicon. As the size of nanoporous silicon becomes comparable to the Bohar exciton radius in bulk silicon, the quantum confinement widens the band gap. Thus, quantum confinement effect change the indirect band gap nature of bulk Si to direct band gap in nanoporous silicon. Higher energy shift of energy levels with reduction of the size of semiconductor quantum dots by gaining the kinetic energy due to spatial confinement of the electrons by a potential barrier is often referred to as a quantum confinement effect.

The electronic states of silicon nanocrystallites (Si-nc) as compared to that of bulk Silicon are dramatically influenced both by quantum confinement (QC) and by the enhanced role of state- and defects-at the surface. The effect of quantum confinement is a rearrangement of the density of electronic states in energy as direct consequence of volume shrinking in one, two or even three dimensions, which can be obtained, respectively, in quantum wells, wires, and dots. The Modification of material properties, especially optical one, by reducing the dimension makes nanostructuring of a semiconductor an alternative way to look for new material. In recent years spectroscopic studies show that an increase of the band gaps [10] and the oscillator strength with decreasing size of the nanocrystallites. As a result, despite the fact bulk Silicon is a very inefficient light emitter, low dimensional Silicon shows light amplification characteristics, non linear optical effect as well as visible light emission.

1.3 Photoluminescence

Very recently many attempts have been made to produce quasi-direct-gap semiconductor nanostructures made from indirect -gap semiconductors and a great deal of research effort is focused on nanometer size crystallites or quantum dote made from Si or Ge. Strong Photoluminescence at room temperature from Si nanostructures with diameters less than 5 nm has attracted much attention from fundamental physics viewpoint and because of the potential application to optical devices.

There exist two classes of explanation for the origin of visible PL in porous silicon:(1)the quantum confinement model in which luminescence is due to electronic confinement in the columnar like (or dote like) structure of porous silicon, and (2)the chemical model in which the large surface area presented by porous silicon support luminescing siloxenes.

For H-terminated, photoluminescence spectral shows continuous shift of peak energy from the bulk band gap to the visible region with a good agreement with the quantum confinement effect, whereas the photoluminescence spectra of oxidized surface porous silicon are confined to a specific region [11]. Generally, silicon nanocrystallites grown by different methods exhibit strong photoluminescence in the red region and progressively shift towards the blue when the mean size decreases. Depending on the size, the photoluminescence of silicon nanocrystals can be tuned from the near infrared (1.38 eV) to the ultraviolet (3.02 eV) i.e as the size of a silicon nanocrystallite structure decreases, the band gap of the material increases due to the quantum confinement effect [Fig.(1.4)].

Fig. 1.5 shows a room-temperature photoluminescence spectrum obtained from

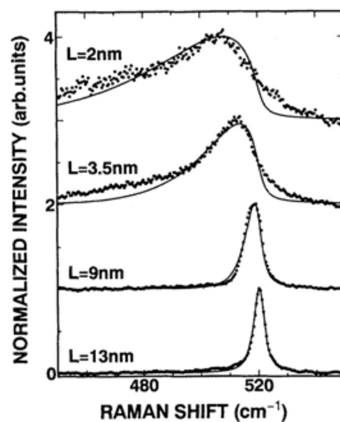

Figure 1.4: Raman spectra of free-standing porous Silicon film compared with the spectra calculated for a sphere with diameter L (solid lines).

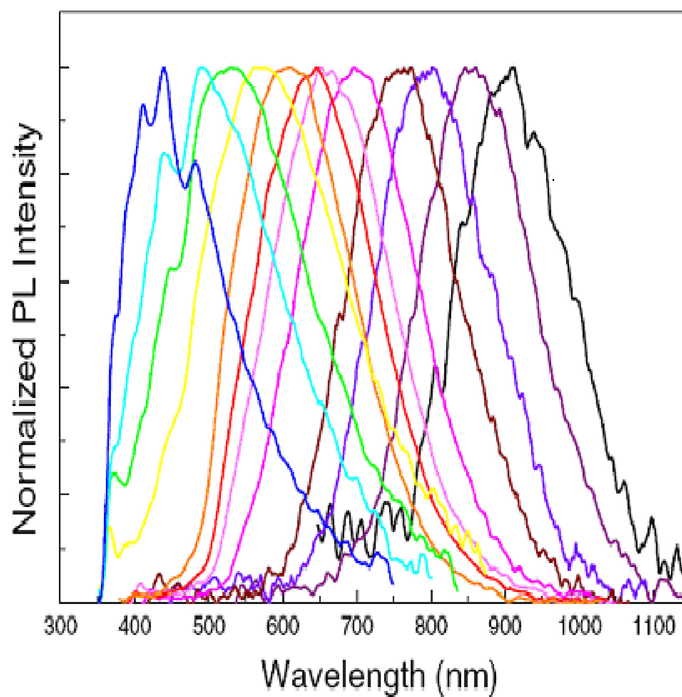

Figure 1.5: Room temperature photoluminescence spectra of silicon nanocrystallites. The peak position can be controlled by the appropriate adjustment of the nanocrystallites size [12].

various sized silicon nanocrystals, where the tuning of the photoluminescence emission from 410 to 900 nm is possible by controlling the size of the silicon nanocrystallite and, as a result, the emission colour can be changed by controlling the size of the nanocrystallite. For example, nanocrystallite sizes corresponding to red, green, and blue emission are 4.6, 3.1, 2.7 nm, respectively [12].

1.4 Objective

1.4.1 General objective

Our main objective here in this thesis is to estimate and study the optical absorption coefficient, dielectric function and oscillator strength of small silicon nanocrystallites.

1.4.2 Specific objective

Specifically, we investigate the effect of size and surface passivation on optical absorption coefficient, dielectric function and oscillator strength in small silicon nanocrystallites by analytically estimating the optical parameter of nanoporous silicon at different size and passivation (i.e oxygen and hydrogen passivation).

1.5 Thesis outline

In this thesis we study the optical properties of nanoporous silicon by estimating optical absorption coefficient, oscillator strength and imaginary part of the dielectric function near the band edge as a function of photon energy and size distribution. The thesis is organized into five chapters. Chapter 2 discusses the density of states of confined systems and variation of the band gap with size of nanoporous silicon. Chapter 3 discusses how the joint density of states and the dipole matrix elements is used to relate the optical absorption coefficient, oscillator strength and imaginary part of the dielectric function with the band gap and photon energy of nanoporous silicon. The dipole matrix elements are found from the Kane approximation of the dipole matrix elements for direct band gap semiconductors. In our calculation we use the size dependent band gap so that the calculated optical parameter are a function of photon energy and size. Chapter 4 contains the result and discussion, and chapter 5 gives the summary and conclusion.

Chapter 2

Density of a states

To study the Optical properties of nanocrystalline quantum structure, one has to know the density of states and the band theory for nanocrystalline quantum structure. In this chapter we are going to see how the density of state and the band theory vary as we go from bulk to silicon nanocristalline quantum structure i.e the electron density of states of a quantum dot (0-D), quantum wire (1-D), quantum well (2-D) and bulk Silicon (3-D).

2.1 Density of states

For a 3-D bulk material, the DOS is defined as the number of available electronic state per unit volume per unit energy E. In an $\hat{n}$ space one accounts for the special filling of states up to a radius $R = R(\hat{n}_x, \hat{n}_y, \hat{n}_z)$, which is determined by the number of available electrons. The number of state G within an energy range of E+dE is obtained from the volume of the spherical shell of the octant, permitting only positive values of $\hat{n}_i$.

$$G_n^{dR} = \frac{1}{8}\frac{4\pi}{3}(R_2^3 - R_1^3)$$

$$G_n^{dR} = \frac{\pi}{6}d^3R = \frac{\pi}{2}R^2dR \tag{2.1.1}$$

$$since, R^2 = \hat{n}_i^2 and K_i = \frac{\pi}{\ell}n_i$$

$$\Rightarrow R = \frac{\ell k}{\pi} \Rightarrow dR = \frac{\ell}{\pi}dk$$

$$G_n^{dR} = \frac{\pi}{2}(\frac{\ell^2k^2}{\pi^2})\frac{\ell}{\pi}dk$$

$$G_n^{dR} = \frac{\ell^3}{2\pi^2}k^2dk$$

Where $\ell^3$is the volume of the semiconductor

$$\Rightarrow G_n^{dR} = \frac{V}{2\pi\pi^2}k^2dk \tag{2.1.2}$$

In an isotropic parabolic band, the dispersion equation of Bloch electron is given by

$$E(k) = E_c + \frac{\hbar^2}{2m_n}k^2 + ...$$

$$\Rightarrow dE = \frac{\hbar^2}{m_e}kdk$$

$$Thus, G_E^{dE} = \frac{V}{2\pi^2}(\frac{2m_e}{\hbar^2})E\frac{1}{2}(\frac{2m_e}{\hbar^2})(\frac{\hbar^2}{2m_n})^{\frac{-1}{2}}E^{\frac{1}{2}}dE$$

$$G_E^{dE} = \frac{V}{2\pi^2}(\frac{2m_e}{\hbar^2})^{\frac{3}{2}}\frac{1}{2}E^{\frac{1}{2}}dE \quad (2.1.3)$$

Dividing by crystal volume and permitting double occupancy i.e. permitting for spin up and down for each state.

$$g(E)dE = \frac{1}{2\pi^2}(\frac{2m_e}{\hbar^2})^{\frac{3}{2}}E^{\frac{1}{2}}dE$$

$$\Rightarrow g(E) = \frac{\sqrt{2}m_e^{\frac{3}{2}}}{\pi^2\hbar^3}E^{\frac{1}{2}} \quad (2.1.4)$$

For two dimensional structure, the carrier movement is restricted to a plane. The DOS is modified to the number of available electronic states per unit area per unit energy[13]. Thus,

$$G_R^{dR} = \frac{1}{8}4\pi R^2 = \frac{\pi}{2}R^2 = \pi R dR$$

Proceeding in the same manner as the above, we will get

$$g = \frac{2m_e}{\pi\hbar^2} \quad (2.1.5)$$

And for one-dimensional structure (quantum wire), the DOS is defined as the availability of electronic states per unit length per unit energy i.e

$$G_R^{dR} = dR \quad (2.1.6)$$

$$But, K = \frac{\pi R}{\ell}, R = \frac{\ell k}{\pi}$$

$$\Rightarrow dR = \frac{\ell}{\pi} dk$$

$$G_k^{dk} = \frac{\ell}{\pi} dk$$

$$But, E = \frac{\hbar^2 k^2}{2m_e}$$

$$\Rightarrow dk = \frac{1}{2} (\frac{2m_e}{\hbar^2})^{\frac{1}{2}} E^{\frac{-1}{2}}$$

$$Thus, G_E^{dE} = \frac{\ell}{\pi} (\frac{2m_e}{\hbar^2})^{\frac{1}{2}} \frac{1}{2} E^{\frac{-1}{2}} dE$$

$$G_E^{dE} = \frac{\ell}{2\pi} (\frac{2m_e}{\hbar^2})^{\frac{1}{2}} E^{\frac{-1}{2}} dE \tag{2.1.7}$$

Therefore, the DOS per unit length per unit energy permitting for spin up and spin down for each state is

$$g = \frac{1}{\pi} (\frac{2m_e}{\hbar^2})^{\frac{1}{2}} E^{-\frac{1}{2}}$$

$$g = \frac{\sqrt{2} m_e^{\frac{1}{2}}}{\pi \hbar} E^{-\frac{1}{2}} \tag{2.1.8}$$

Finally, for a zero dimensional system (0-D), the confinement is along all three dimensions and the DOS becomes a delta function.

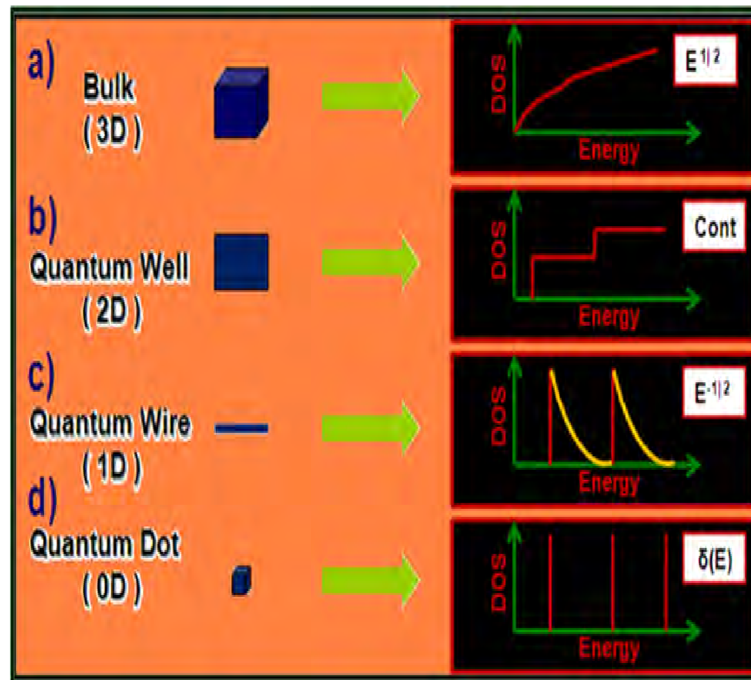

Figure 2.1: Density of states for various geometries of semiconductor materials:(a)3-D, (b)quantum well, a 2-D structure, (c)quantum wire, a 1-D structure, and (d)quantum dot, a 0-D entity.

Transformation from a 3-D system to a 2-D thin film changes the DOS from a continuous parabolic dependence to a step like dependence. This is due to the quantization of carrier motion in the thickness direction. Consequently, the optical absorption edge is shifted to higher energy with respect to the bulk and above the absorption edge; the spectrum is stepped rather than smooth.

2.2 Energy gap of nano-structures

Most of material properties, such as the dielectric function and optical transitions, depend on energy-gap between the conduction band and the valance band of the material thus altering the energy gap may significantly alter the materials optical properties, more interestingly in the last decade it was proposed that the band gap is a function of porous silicon nanoclusters diameter (size) which eventually lead to the fact that altering the energy gap may significantly alter the materials optical properties. In this topic our main objective will be to investigate how the the material properties specially optical one are related to the size of porous silicon nanocluster.

As we all know because of its 1.1 eV indirect band gap silicon is characterized by a very poor optical radiative efficiency and only produces light outside the visible range. But after many investigations it has been observed that quantum confined nano-silicon structures are direct band gap material which show zero phonon transition reflected in the Raman spectra. This is due to quantum size effect which leads to an increase (the blue shift) of the band gap of the crystallites compared to bulk silicon. As the size of nanoporous silicon becomes comparable to the Bohar exciton radius in bulk

silicon, the quantum confinement widens the band gap. Thus, quantum confinement effect change the indirect band gap nature of bulk Si to direct band gap in nanoporous silicon which lead to a vary good optical radiative efficiency. However, this can not be explained only by quantum confinement effects also effects such as structural changes, lattice contractions and surface passivation can change the band-gap of the material.

And several models have been proposed in order to describe band structure of clean, oxygen and hydrogen passivated sample, for instance tight-binding method, pseudopotential method and the effective mass approximation(EMA)are few of them. In there remarkable work Zunger *et al* [14]using tight-binding method, Tripathy *et al* [15] and Ghoshal *et al* [16] using local pseudopotential method calculated the band gap energy as a function of diameter (size) for clean surface silicon nanoclusters at room temperature and found approximately the gap as:

$$E_g^{nano}(d) = E_g^{bulk} + \frac{3.73}{d^{1.37}}(eV) \quad (2.2.1)$$

where: $E_g^{nano}(d), E_g^{bulk}$ and d in (nm) are the band gap energy of silicon nanocrystal, bulk silicon band gap energy at room temperature and diameter (size) of the silicon nanocrystallite respectively. Tripathy *et al* also calculated band gap energy for hydrogen passivated silicon nanocrystals using local pseudopotential method at room temperature as:

$$E_g^{nano}(d) = E_g^{bulk} + \frac{4.042}{d^{1.353}}(eV) \quad (2.2.2)$$

Where the calculated band-gap energy for oxygen-passivated silicon nano-crystals using the local pseudo-potential method is given by:

$$E_g^{nano}(d) = E_g^{bulk} + \frac{3.82}{d^{1.33}}(eV) \tag{2.2.3}$$

For all these materials, the variation of the band gap follows roughly the same kind of law.

$$E_g^{nano}(d) = E_g^{bulk} + \frac{c}{d^{\alpha}}(eV) \tag{2.2.4}$$

Further more, from this expression it is evident that the energy necessary to generate an electron-hole pair increases by decreasing the size of the system and we can also see that surface passivation plays an important role in increasing the band-gap of the nano-crystals. In general, fig. 2.2 illustrates the calculated band-gap variation as a function of diameter.

In the next chapter we will discuss how the optical properties of nano-silicon namely dielectric function, Oscillator strength and optical absorption coefficient depends on the size(Diameter) of porous silicon nanocluster through the band gap using Optically band-to-band transitions together with Kane estimate of the dipole matrix elements for direct band gap.

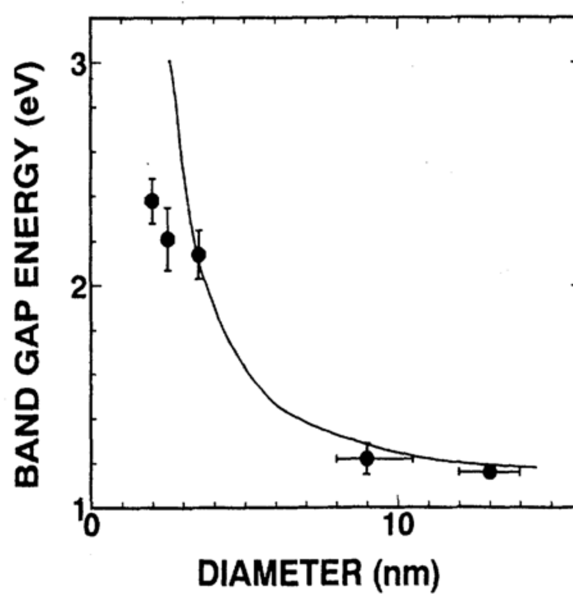

Figure 2.2: *Band gap as a function of size (Diameter).*

Chapter 3

Calculation of optical absorption coefficient, dielectric function and oscillator strength

Optically band-to-band transitions are resonance transitions and provide the most direct information about the band structure of semiconductors. Nanosize Silicon structure of size below 10 nm are approximately direct gap semiconductor. In this chapter our Main objective is to calculate the optical absorption coefficient, oscillator strength and the dielectric function as a function of energy gap and photon energy and indirectly a function of silicon nanoclusters diameter (size) through the band gap. In doing so we will use Optically band-to-band transitions together with Kane estimate of the dipole matrix elements for direct band gap.

3.1 Dipole matrix element

Because of its 1.1 eV indirect band gap, silicon is characterized by a very poor optical radiative efficiency and only produces light outside the visible range. Until recent time several attempts to improve this efficiency have been unsuccessful, but in the

past decade there are many investigations where it is observed that quantum confined nano-silicon structures are direct band gap material which show zero phonon transition reflected in the Raman spectra. This is due to quantum size effect which leads to an increase (the blue shift) of the band gap of the crystallites compared to bulk silicon. The effect of quantum confinement is a rearrangement of the density of electronic states in energy as direct consequence of volume shrinking in one, two or even three dimensions, which can be obtained, respectively, in quantum wells, wires, and dots. As the size of nanoporous silicon becomes comparable to the Bohar exciton radius in bulk silicon, the quantum confinement widens the band gap. Thus, quantum confinement effect change the indirect band gap nature of bulk Si to direct band gap in nanoporous silicon.

In bulk silicon optical transition are indirect where as in nanosize silicon structure optical transition are direct. Therefore, we are going to consider direct transitions which involve a direct optical excitation from the valence to the conduction band, using only photons in direct band gap silicon nanocrystallites.

Consider electro-magnetic filed of sufficiently short wavelength which initiates electronic transitions from valance band to conduction band :

$$\overrightarrow{E} = A_0 \hat{e} \exp\{i(k_0 \cdot r - \omega t)\} \tag{3.1.1}$$

Where:

A_o- Amplitude

$\hat{e}$- Electronic polarization vector and

k_0-Wave vector of the light travelling in r-direction.

The number of optically induced transitions at the same k (neglecting the wave vector of the photons) between band μ and ν is proportional to the square of momentum matrix elements given by

$$e \cdot M_{\mu\nu}(k) = \langle \varphi_\mu | \hat{e} \cdot \rho | \varphi_\nu \rangle$$

$$e \cdot M_{\mu\nu}(k) = e \cdot \int_\nu \varphi_\mu^*(k,r)(-i\hbar\nabla)\varphi_\nu(k,r)dr$$

With the integration extending over the crystal volume v, the proportionality factor for a special transition is

$$\mathbf{P}_{\mu\nu} = \frac{2\pi}{\hbar}(\frac{eA_0}{m_0 c})^2 \delta(E_\mu(k) - E_\nu(k) - \hbar\omega) \tag{3.1.2}$$

Hence, the probability of an electron to make a transition from band μ to band ν state, $P_{\mu\nu}$ is given by

$$P_{\mu\nu} = \frac{2\pi}{\hbar}(\frac{eA_0}{m_0 c})^2 |\hat{e} \cdot M_{\mu\nu}(k,r)|^2 \delta(E_\mu - E_\nu - \hbar\omega) \tag{3.1.3}$$

After integration over all states and all bands between which the given photon can initiate transitions, we obtain the total number of optically induced transition per unit volume and unit time as:

$$W(\omega) = \sum_{\mu\nu} \int_k P_{\mu\nu} |\hat{e} \cdot M_{\mu\nu}(k)|^2 dk$$

$$W(\omega) = \frac{2\pi}{\hbar}(\frac{eA_0}{m_0 c})^2 \sum_{\mu\nu} \int_k |\hat{e} \cdot M_{\mu\nu}(k)|^2 \delta(E_\mu(k) - E_\nu(k) - \hbar\omega) dk \tag{3.1.4}$$

The momentum matrix elements can be approximated from the kane-estimate using:

$$|\hat{e} \cdot M_{\mu\nu}|^2 = (\frac{m_0}{\hbar})^2 P^2 \tag{3.1.5}$$

Where P is the momentum matrix parameter which can be approximated from K.P perturbation theory and Kane has estimated that:

$$P^2 = (\frac{1}{m_e^*} - \frac{1}{m_0})\frac{3}{2}\hbar^2 \frac{E_g - \triangle_0}{3E_g + 2\triangle_0} E_g$$

$$P^2 = \frac{3}{2}\hbar^2 (\frac{m_0 - m_e^*}{m_0 m_e^*})\frac{E_g - \triangle_0}{3E_g + 2\triangle_0} E_g$$

Where:

$\triangle_0$-Spin-orbit splitting energy

m_e^*-Effective mass of electron in the conduction band

E_g-Band gap

m_0 -Electron rest mass

with known $m_e^*, E_g, \triangle_0$ and m_0 the matrix element will be

$$|\hat{e} \cdot M_{\mu\nu}|^2 = \frac{3}{2}\frac{m_0}{m_e^*}(m_0 - m_e^*)\frac{E_g + \triangle_0}{3E_g + 2\triangle_0} E_g \tag{3.1.6}$$

So far we have seen how the matrix element is related to the band gap. However, in there remarkable work Zunger *et al* [14]using tight-binding method, Tripathy *et al* [15]and Ghoshal *et al* [16] using local pseudopotential method calculated the band gap energy as a function of diameter (size) for clean and passivated surface silicon

nanoclusters at room temperature this finding enable as to express the matrix element, the Joint Density of State and more importantly the optical absorption coefficient, imaginary part of the dielectric function and the oscillatory strength in terms of silicon nanoclusters diameter (size). To illustrate these in the next section we are going to see how the joint density of state is related to energy gap, photon energy and indirectly related to silicon nanocrystal size using the matrix element and the total number of optically induced transitions per unit volume and unit time.

3.2 Joint density of state

For photon energy slightly exceeding the band gap, transitions between the different valence bands into different E(k) values of the conduction band are possible near k=0, the fundamental absorption edge ($k \approx 0$).

In the previous section we see that the total number of optically induced transitions per unit volume and unit time which are initiated with the given photon energy $\hbar\omega$ is given by

$$W(\omega) = \frac{2\pi}{\hbar}(\frac{eA_0}{m_0 c})^2 \sum_{\mu\nu} \int_k |\hat{e} \cdot M_{\mu\nu}(k)|^2 \delta(E_\mu(k) - E_\nu(k) - \hbar\omega) dk$$

The matrix element vary little with in the Brillouin zone; therefore, we can pull out the matrix element in front of the integral.

$$W(\omega) = \frac{2\pi}{\hbar}(\frac{eA_0}{m_0 c})^2 \sum_{\mu\nu} |\hat{e} \cdot M_{\mu\nu}(k)|^2 \int_k \delta(E_\mu(k) - E_\nu(k) - \hbar\omega) dk \qquad (3.2.1)$$

The integral identifies the sum over all possible transitions which can be initiated by photons with certain energy, and it is commonly referred to as the joint density of states.

$$J_{\mu\nu}(\omega) = \frac{2}{(2\pi)^D} \int \delta(E_\mu(k) - E_\nu(k) - \hbar\omega) dk$$

Nano-sized semiconductor still has 3-D structure of a direct band continuum of states thus D=3:

$$J_{\mu\nu}(\omega) = \frac{2}{(2\pi)^3} \int \delta(E_\mu(k) - E_\nu(k) - \hbar\omega) dk$$

$$since \int g(x)\delta(f(x))dx = g(x_0)\frac{1}{|\frac{df(x)}{dx}|_{x=x_0}}$$

$$J_{\mu\nu}(\omega) = \frac{2}{(2\pi)^3} \int \frac{ds}{|\nabla_x(E_\mu(k) - E_\nu(k))|_{E_\mu - E_\nu = \hbar\omega}}$$

Where ds is a surface element of k-space with the surface depicted by

$$E_\mu(k) - E_\nu(k) = \hbar\omega$$

This yield,

$$J_{\mu\nu} = \frac{2}{(2\pi)^3} \frac{d(\frac{4}{3}\pi k^3)}{d(\hbar\omega)} \tag{3.2.2}$$

The transition between the top of one valence band to the bottom of the lowest conduction band when both lie at k=0 is responsible for the direct optical absorption

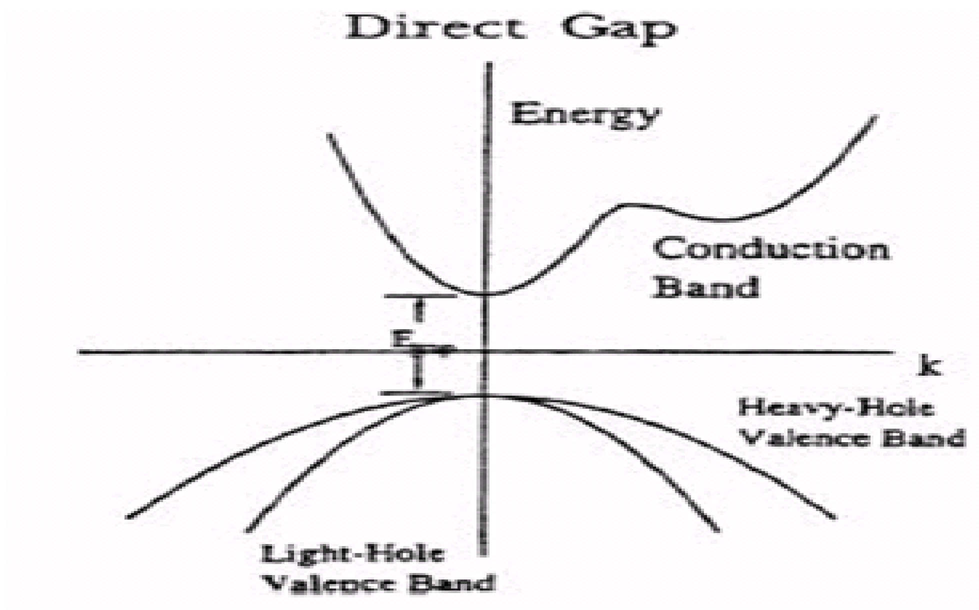

Figure 3.1: Direct transition between valence band conduction band.

edge. The joint density of state is estimated from a parabolic approximation of both bands:

$$\hbar\omega = E_\mu(k) - E_\nu(k)$$

$$\hbar\omega = E_g + \frac{\hbar^2 k^2}{2m_e} + \frac{\hbar^2 k^2}{2m_h}$$

$$\hbar\omega = E_g + \frac{\hbar^2 k^2}{2m_r^*}$$

With E_g as the band gap energy and m_r^* as a reduced carrier mass.

$$\frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

$$k = \sqrt{(\hbar\omega - E_g)\frac{2m_r^*}{\hbar^2}} \tag{3.2.3}$$

Substituting eq.(3.2.3) into eq.(3.2.2) the Joint Density of State becomes

$$J_{c\nu} = \frac{1}{2\pi^2}(\frac{2m_r^*}{\hbar^2})^{\frac{3}{2}}\sqrt{\hbar\omega - E_g} \tag{3.2.4}$$

Thus, the total number of optically induced transitions per unit volume and unit time (i.e eq.(3.2.1))can be rewritten as

$$W(\omega) = \frac{2\pi}{\hbar}(\frac{eA_0}{m_0 c})^2|\hat{e} \cdot M_{c\nu}(k)|^2 J_{c\nu} \tag{3.2.5}$$

Where:

$$J_{c\nu} = \frac{1}{2\pi^2}(\frac{2m_r^*}{\hbar^2})^{\frac{3}{2}}\sqrt{\hbar\omega - E_g} \tag{3.2.6}$$

Here the Joint Density of State is related to energy gap which is a function of size. Thus, in the next sections we will calculate the optical absorption coefficient using this joint density of State and the momentum dipole matrix element this will enable as to relate the calculated optical absorption coefficient directly to the band gap and photon energy which in turn makes it indirect function of silicon nanoclusters size (diameter) through the band gap.

3.3 Calculation of linear optical absorption

The optical absorption coefficient is proportional to the number of optical transitions per unit volume and time elements. Therefore, it can be given by the absorption

energy per unit time, $\hbar\omega W(\omega)$, divided by the energy flux , $\frac{(A_o W^2 \varepsilon_o n_r)}{2c\pi}$, i.e.

$$\alpha(\omega) = \frac{\hbar\omega W(\omega)}{A_o^2 \omega^2 \varepsilon_o \frac{n_r}{2c\pi}}$$

Using eq.(3.2.5), the absorption coefficient near the absorption edge will be

$$\alpha(\omega) = \frac{4\pi^2 e^2}{\varepsilon_o n_c m_o^2 \omega}\{\mid \hat{e}\cdot M_{cv} \mid^2 J_{cv}\}$$

Using eq.(3.2.6)

$$\alpha(\omega) = \frac{4\pi^2 e^2}{\varepsilon_o n_c m_o^2 \omega}\{\mid \hat{e}\cdot M_{cv} \mid^2 (\frac{1}{2\pi^2}(\frac{2m_r^*}{\hbar^2})^{\frac{3}{2}}\sqrt{\hbar\omega - E_g})\}$$

$$\alpha(\omega) = \{\frac{2e^2(2m_r^*)^{\frac{3}{2}}}{\varepsilon_o n c m_o^2 \hbar^2 \omega}\} \mid \hat{e}\cdot M_{cv} \mid^2 \sqrt{\hbar\omega - E_g}$$

Introducing the value of $\mid \hat{e}\cdot M_{cv} \mid^2$ from eq.(3.1.6),

$$\alpha(\omega) = \frac{3e^2\sqrt{m_o}}{\varepsilon_o n\hbar c}(\frac{2m_r^*}{m_o})^{\frac{3}{2}}\frac{m_o - m_e^*}{m_e^*}\frac{E_g + \Delta_o}{3E_g + 2\Delta_o}\frac{E_g}{\hbar\omega}\sqrt{\hbar\omega - E_g}$$

$$\alpha(\omega) = \frac{3e^2\sqrt{m_o}}{\varepsilon_o n\hbar c}(\frac{2m_r^*}{m_o})^{\frac{3}{2}}\frac{m_o - m_e^*}{m_e^*}\frac{E_g}{\hbar\omega}f(g) \qquad (3.3.1)$$

Where:$f(g) = \frac{E_g+\Delta_o}{3E_g+2\Delta_o}\sqrt{\hbar\omega - E_g}$

For $\hbar\omega \approx E_g$

$$\alpha(\omega) = \frac{3e^2\sqrt{m_o}}{\varepsilon_o n\hbar c}(\frac{2m_r^*}{m_o})^{\frac{3}{2}}\frac{m_o - m_e^*}{m_e^*}f(g) \qquad (3.3.2)$$

From eq.(3.3.2) we can see that the optical absorption coefficient is function of photon energy and energy gap. But Zunger *et al* using tight-binding method, Tripathy *et al* and Ghoshal *et al* using local pseudopotential method calculate the band gap energy as a function of diameter (size) for clean and passivated surface silicon nanoclusters at room temperature as a result even if the optical absorption coefficient is directly a function of energy gap and photon energy it is indirectly a function of silicon nanoclusters diameter (size) through the band gap. In the next section we are going to see how the imaginary part of the dielectric function is directly related to energy gap and photon energy while it is indirect function of silicon nanoclusters diameter (size) through the band gap.

3.4 Dielectric function

For semiconductor with optical absorption α, the refractive index is complex and given by

$$\tilde{n} = n_r + ik \tag{3.4.1}$$

This complex index of refraction is related to the complex dielectric constant as

$$\tilde{\varepsilon} = \varepsilon' + i\varepsilon'' \tag{3.4.2}$$

Where:

$\varepsilon' = \varepsilon$

$\varepsilon'' = \frac{\sigma}{\varepsilon_o \omega}$

From eq.(3.4.1)and eq.(3.4.2), we will get

$$\varepsilon' = n_r^2 - k^2$$

$$\varepsilon'' = \frac{\sigma}{\varepsilon_o \omega} = 2n_r k$$

But the optical absorption coefficient is given by

$$\alpha = \frac{2\omega k}{c} \Rightarrow k = \frac{c\alpha}{2\omega}$$

$$\varepsilon'' = \frac{\alpha c n_r}{\omega} \tag{3.4.3}$$

And using eq.(3.3.2)

$$\varepsilon'' = \frac{3e^2\sqrt{m_o}}{\varepsilon_o \hbar^2 \omega}\left(\frac{2m_r^*}{m_o}\right)^{\frac{3}{2}}\left(\frac{m_o - m_e^*}{m_e^*}\right) f(g) \tag{3.4.4}$$

$$Where, f(g) = \frac{E_g + \Delta_o}{3E_g + 2\Delta_o}\sqrt{\hbar\omega - E_g}$$

Now the imaginary part of the dielectric function is directly a function of energy gap and photon energy while it is indirect function of silicon nanoclusters diameter

(size) through the band gap. In the next section we are going to see how the oscillator strength is directly related to energy gap and photon energy while it is indirectly a function of silicon nanoclusters diameter (size) through the band gap.

3.5 Oscillator strength

The Oscillator strength, the equivalent number of oscillations of the transition between the valance and conduction bands, is related to the matrix element of the momentum matrix P_{cv} and is given by the equation:

$$f_{cv} = \frac{2|Pcv|^2}{m_0 \hbar \omega_{cv}} \tag{3.5.1}$$

Where $P_{cv} = |\hat{e} \cdot M_{cv}|$

$$\Rightarrow f_{cv} = \frac{2|\hat{e} \cdot M_{cv}|^2}{3 m_0 \hbar \omega_{cv}} \tag{3.5.2}$$

The factor $\frac{1}{3}$ in the above equation is due to averaging with $|M_x|^2 = |M_y|^2 = |M_z|^2 = \frac{|M|^2}{3}$. And in equation(3.1.6) we see that

$$|\hat{e} \cdot M_{\mu\nu}|^2 = \frac{3}{2} \frac{m_0}{m_e^*} (m_0 - m_e^*) \frac{E_g + \triangle_0}{3E_g + 2\triangle_0} E_g \tag{3.5.3}$$

Inserting equation(3.5.3) in to equation(3.5.1) and using $m_e^* = 0.4 m_o$ we obtain :

$$f_{cv} = \frac{2}{3m_0\hbar\omega_{cv}}\frac{3}{2}\frac{m_0}{m_e^*}(m_0 - m_e^*)\frac{E_g + \triangle_0}{3E_g + 2\triangle_0}E_g \tag{3.5.4}$$

$$f_{cv} = \frac{3}{2m_0\hbar\omega_{cv}}\frac{E_g + \triangle_0}{3E_g + 2\triangle_0}E_g \tag{3.5.5}$$

On the basis of these derived expression of optical parameters we estimate them using $matlab/fortran$programs. In the next chapter we will plot them and understand in detail.

Chapter 4

Results and Discussions

Here in this chapter we are going to examine analytically how the optical absorption coefficient, imaginary part of the dielectric function and the oscillatory strength near the band edge varies with the crystal size and photon energy by making them implicit function of porous silicon nanocluster size through the band gap energy.

In the previous chapter the optical absorption coefficient, the imaginary part of the dielectric function and the oscillatory strength near the band edge were related to the band gap energy and photon energy using Kane estimate of the dipole matrix elements for direct band gap. Therefor, if we incorporate the fact that the band gap varies as a function of size in to this expression the derived optical parameter which were explicit function of band gap and photon energy now will become implicit function of porous silicon nanocluster size through the band gap energy. Moreover, the expression of the band gap as a function of porous silicon nanocluster size were given by many researchers in there remarkable work for instance, Zunger *et al* using tight-binding method, Tripathy *et al* and Ghoshal *et al* using local pseudopotential method calculated the band gap energy as a function of diameter (size) for clean surface silicon nanoclusters at room temperature and found approximately the band

gap as:

$$E_g^{nano}(d) = E_g^{bulk} + \frac{3.73}{d^{1.37}}(eV) \tag{4.0.1}$$

where: $E_g^{nano}(d), E_g^{bulk}$ and d in (nm) are the band gap energy of silicon nanocrystal, bulk silicon band gap energy at room temperature and diameter (size) of the silicon nanocrystallite respectively. Tripathy *et al* also calculated band gap energy for hydrogen passivated silicon nanocrystals using local pseudopotential method at room temperature as:

$$E_g^{nano}(d) = E_g^{bulk} + \frac{4.042}{d^{1.353}}(eV) \tag{4.0.2}$$

Where the calculated band-gap energy for oxygen-passivated silicon nano-crystals using the local pseudo-potential method is given by:

$$E_g^{nano}(d) = E_g^{bulk} + \frac{3.82}{d^{1.33}}(eV) \tag{4.0.3}$$

now using eq.(4.0.1), eq.(4.0.2)and eq.(4.0.3) together with effective mass of hole, $m_h^* = 0.54m_o$, effective mass of electron, $m_e^* = 0.4m_o$, bulk silicon spin-orbit splitting, $\Delta_o = 0.044eV$ and effective refractive index of porous silicon nanocluster, $n_r = 1.7$ we can finally get the optical absorption coefficient for porous silicon nanoclusters (4-10nm) from eq.(3.3.2) as:

$$\alpha(\omega) = 2.744 \times 10^6 \times (\frac{E_g}{\hbar\omega})(\frac{E_g + 0.044}{3E_g + 0.088})\sqrt{\hbar\omega - E_g}eV^{-\frac{1}{2}}cm^{-1} \tag{4.0.4}$$

Where the imaginary part of the dielectric function from eq.(3.4.4) become:

$$\varepsilon''(\omega) = 92 \times (\frac{E_g}{\hbar\omega})(\frac{E_g + 0.044}{3E_g + 0.088})\frac{\sqrt{\hbar\omega - E_g}}{\hbar\omega} eV^{\frac{1}{2}} \tag{4.0.5}$$

And finally the oscillatory strength from eq.(3.5.5) become:

$$f_{cv} = (\frac{3}{2m_0\hbar\omega})(\frac{E_g + 0.044}{3E_g + 0.088})E_g \tag{4.0.6}$$

As we can see from the above equations, due to the fact that the band gap varies as a function of size [(eq.(4.0.1-4.0.3)] the optical absorption coefficient, imaginary part of the dielectric function and the oscillatory strength which were explicit function of photon energy and band gap energy now become implicit function of porous silicon nanoclusters size through band gap energy.

On the basis of these derived expression of optical parameters we estimate them using matlab/fortran programs. In the coming sections we will plot them and understand in detail.

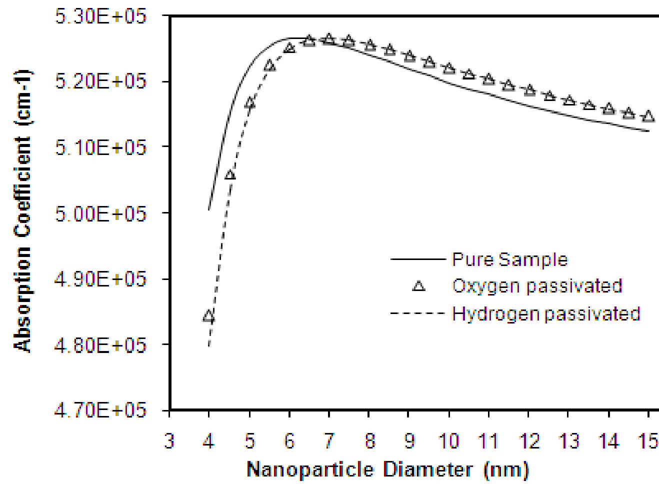

Figure 4.1: *Optical absorption coefficient as a function of porous silicon nanocluster size at a given photon energy* $\hbar\omega = 2.2\ eV$.

4.1 Optical absorption

Here we describe how the optical absorption coefficient of nanoporous silicon varies with photon energy and size of the nanocrystals, including the effect of surface passivation. With the help of eq.(4.0.4) and eq.(4.0.1-4.0.3) the plot of optical absorption coefficient verses effective size(4-15 nm) for clean, hydrogen and oxygen passivated porous silicon nanoclusters at a given frequency (2.2eV) is shown in fig.4.1 where as, the plot of optical absorption coefficient as a function of photon energy (1.5 - 6 eV) for clean, hydrogen and oxygen passivated porous silicon nanoclusters of effective size (8 nm) and (5.5 nm) is shown in fig.4.2 and fig.4.3 respectively.

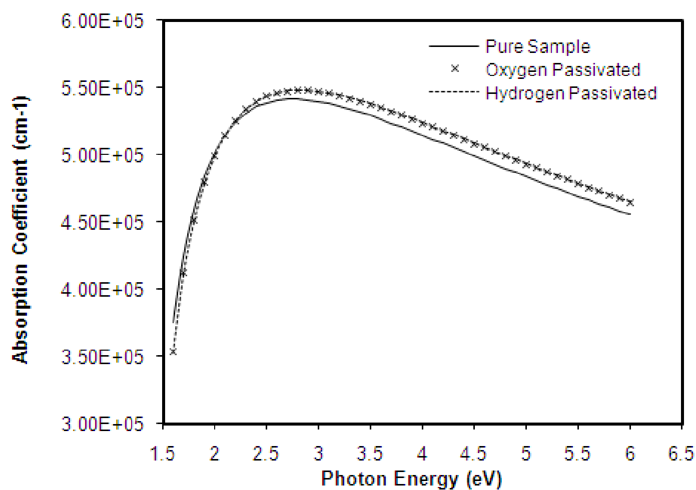

Figure 4.2: *Optical absorption coefficient as a function of photon energy for effective porous silicon nanocluster size d = 8 nm.*

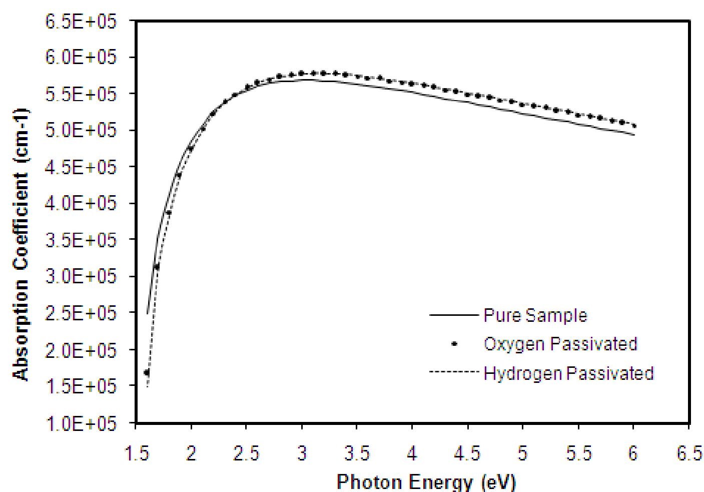

Figure 4.3: *Optical absorption coefficient as a function of photon energy for effective porous silicon nanocluster size d = 5.5 nm.*

We have demonstrated that the optical absorption coefficient of nanoporous silicon strongly depend not only on the size of the nanoparticle, i.e on the quantum confinement, but also on the surface passivation. What we find in fact is that when the size of the cluster is very small ($< 6nm$) the surface effects dominates due to large volume fraction of the near surface region over the crystalline core thus in these limit the absorption increases with increasing size. But as we increases the size further the surface effect play vary little role on the absorption and it is found that the optical absorption coefficient decreases for increasing nanoparticle diameter and photon energy. Furthermore, as we can see from the above figures the optical absorption coefficient increases on passivating the surface of the cluster with hydrogen and oxygen respectively i.e clusters with no bond distortion and with its dangling bonds completely passivated possess a large optical absorption coefficient. So the optical absorption coefficient of nanoporous silicon strongly depend not only on the size of the nanocrystals, i.e on the quantum confinement, but also on the surface passivation.

In fig.4.4 our results and in fig.4.5 the experimental optical absorption spectrum of PS measured in Ref. [17] as well as the result of theoretical calculations, obtained by solving the Bethe-Salpeter equation (BSE) and at the level of quesiparticle random-phase approximation (QP-RP) level [18], are reported. The agreement is excellent, with the experimental peak position and width very well described by the BSE calculation. In fig.4.6 our results and in fig.4.7 the result done by Haybertsen *et al* [19], are reported. Our results are in good agreement with these results as well.

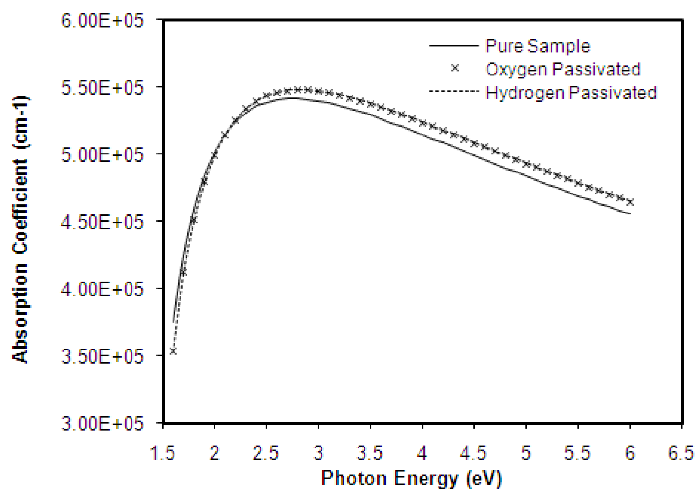

Figure 4.4: *Optical absorption coefficient as a function of photon energy for effective porous silicon nanocluster size d = 8 nm.*

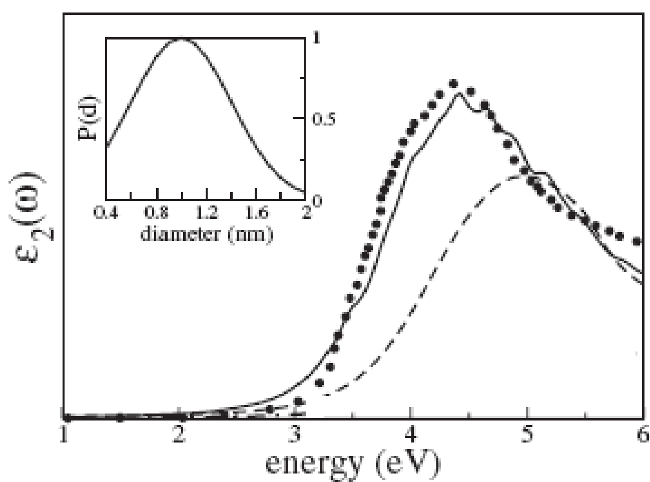

Figure 4.5: *BSE (solid line) and QP-RPA (dashed line) [17] absorption coefficient of PS compared with the experiments (dots) [18].*

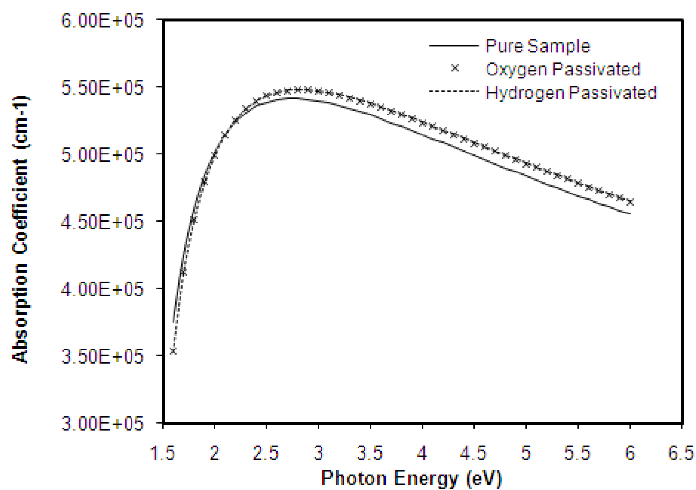

Figure 4.6: *Optical absorption coefficient as a function of photon energy for effective porous silicon nanocluster size d = 8 nm.*

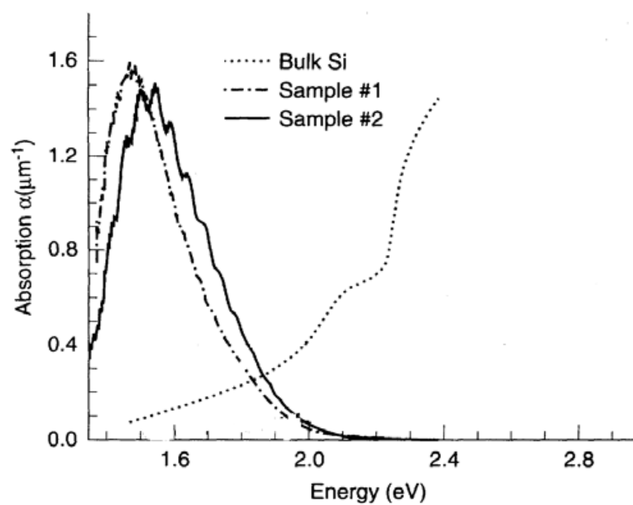

Figure 4.7: *optical absorption of porous si films absorption coefficient measured at 300K for samples 1 and 2 [19].*

4.2 Imaginary part of the dielectric function

With the help of eq.(4.0.5) and eq.(4.0.1-4.0.3) a similar effect is found for the imaginary part of the dielectric function. The plot of imaginary part of the dielectric function verses effective size(4-15 nm) for clean, hydrogen and oxygen passivated porous silicon nanoclusters at a given frequency (2.2 eV) is shown in fig.4.8 where as the plot of imaginary part of the dielectric function as a function of photon energy (1.5 - 6 eV) for clean, hydrogen and oxygen passivated porous silicon nanoclusters of effective size (8 nm) and (5.5 nm) is shown in fig.4.9 and fig.4.10 respectively.

As shown in fig.4.8 and fig.4.9, similar to the optical absorption coefficient, imaginary part of the dielectric function is strongly dependent not only on the size of the nanocrystals, i.e on the quantum confinement, but also on the passivation. In Fig.4.10 our results and in fig.4.11 the result of theoretical calculations, obtained by solving the real-time real-space higher-order finite-difference method Yoshiyuki Kurokawa *et al* [20], are reported and the agreement is excellent. In fig.4.12 our results and in fig.4.13 the result by Mark S. Hybertsen* *et al* [21], are reported. Our results are in good agreement with these results as well.

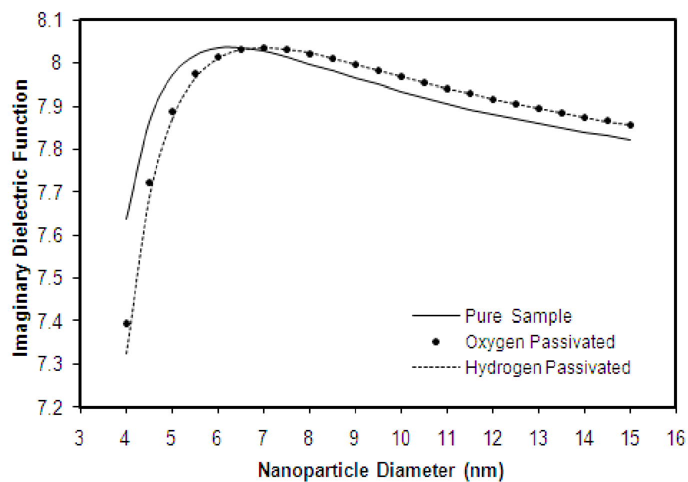

Figure 4.8: *Imaginary parte of the dielectric function as a function of porous silicon nanocluster size at a given photon energy* $\hbar\omega = 2.2\ eV$.

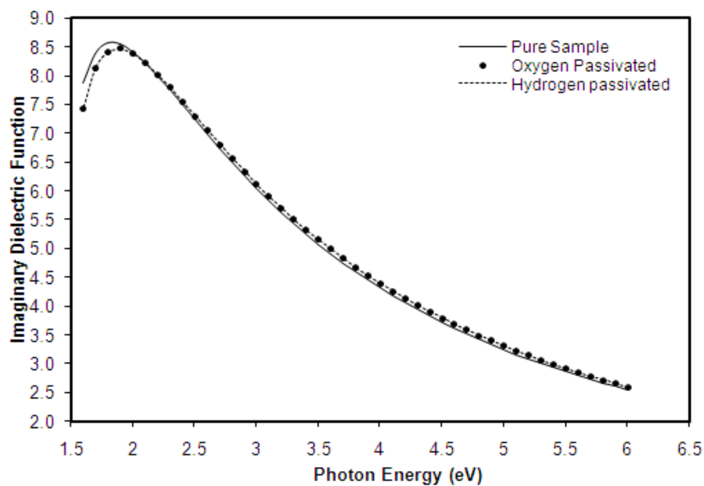

Figure 4.9: *Imaginary parte of the dielectric function as a function of photon energy for effective porous silicon nanocluster size d = 8 nm.*

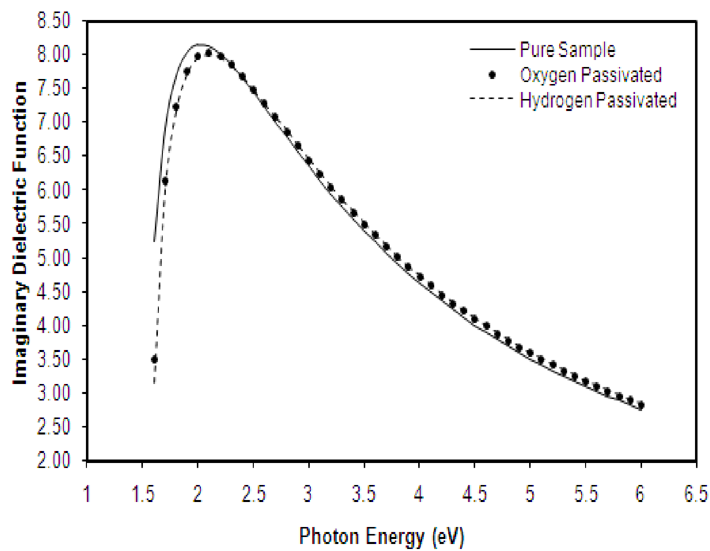

Figure 4.10: *Imaginary parte of the dielectric function as a function of photon energy for effective porous silicon nanocluster size d = 5.5 nm.*

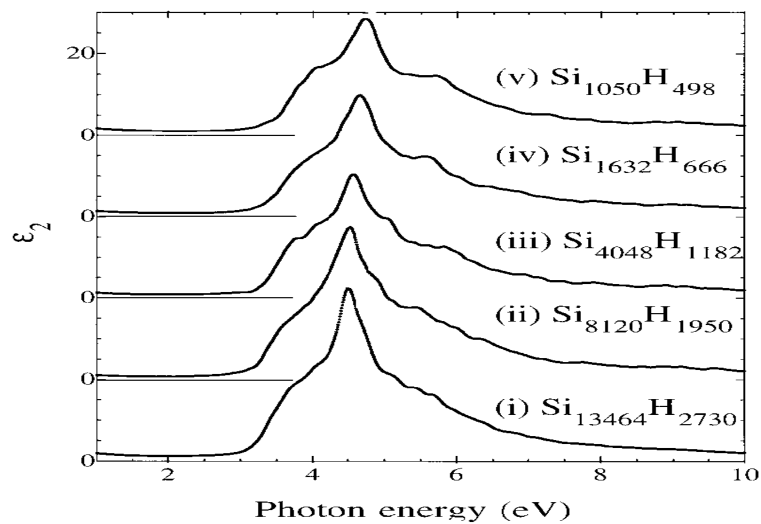

Figure 4.11: *Imaginary part of the dielectric function of hydrogenated Si (i) Si13464H2730, (ii) Si8120H1950, (iii) Si4048H1182, (iv) Si1632H666, and (v) Si1050H498 [20].*

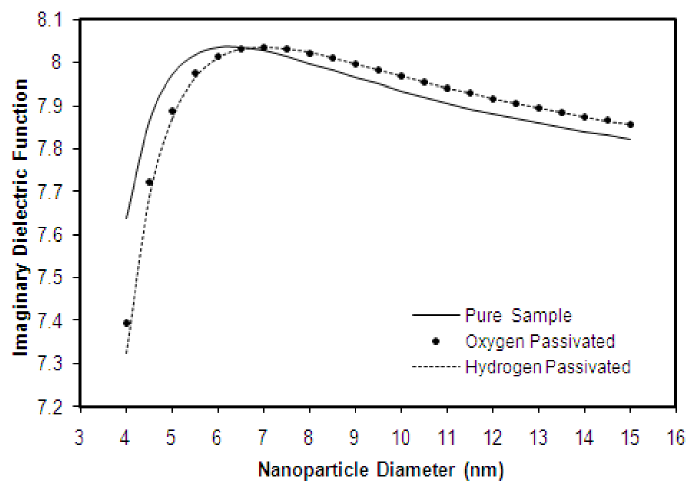

Figure 4.12: *Imaginary parte of the dielectric function as a function of porous silicon size at a given photon energy*$\hbar\omega = 2.2\ eV$.

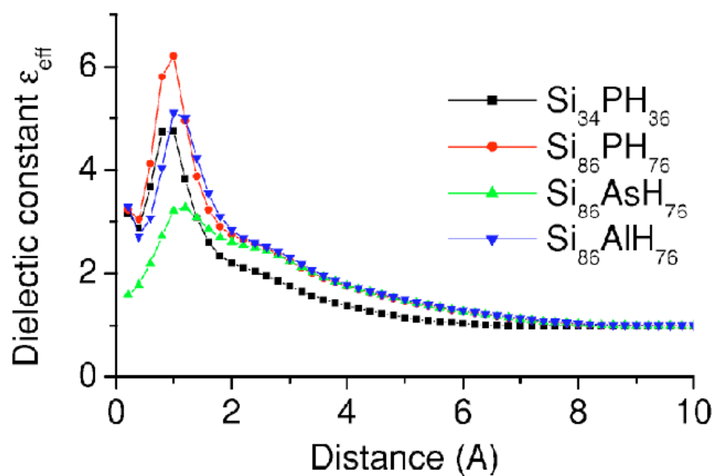

Figure 4.13: *The effective radially dependent dielectric constant for each doped nanocrystal. The lines are guides through the data points [21].*

4.3 Oscillatory strength

And finally using eq.(4.0.6) and eq.(4.0.1-4.0.3) the plot of the oscillatory strength verses effective size(4-15 nm) for clean, hydrogen and oxygen passivated porous silicon nanoclusters at a given photon energy (2.2eV) is shown in fig.4.14 where the plot of the oscillatory strength as a function of photon energy (1.5 - 5 eV) for clean, hydrogen and oxygen passivated porous silicon nanoclusters of effective size (8 nm) and (5.5nm) is shown in fig.4.15 and fig.4.16 respectively.

It is found that the oscillator strength decreases for increasing nanoparticle diameter size and photon energy for pure clusters. Furthermore, the oscillator strength increases on passivating the surface of the cluster with hydrogen and oxygen respectively. So the oscillator strength of nanoporous silicon strongly depend not only on the size of the nanocrystals, i.e on the quantum confinement, but also on the surface passivation. It is found that the cluster with no bond distortion and with its dangling bonds completely passivated possess a large oscillator strength. A computer simulation using tight-binding scheme and empirical pseudo-potential Hamiltonian is performed by S.K. Ghoshal *et al* [22] to study optical properties of silicon quantum dots as shown in fig.4.18 and our results are in agrement with these results.

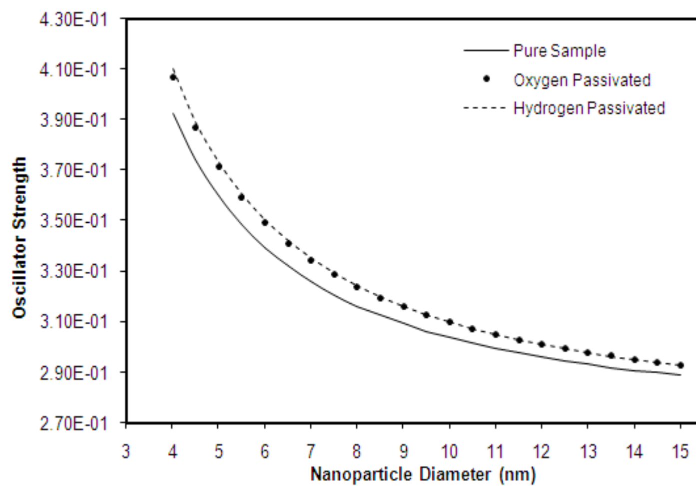

Figure 4.14: *Oscillatory strength as a function of porous silicon nanocluster size at a given photon energy* $\hbar\omega = 2.2eV$.

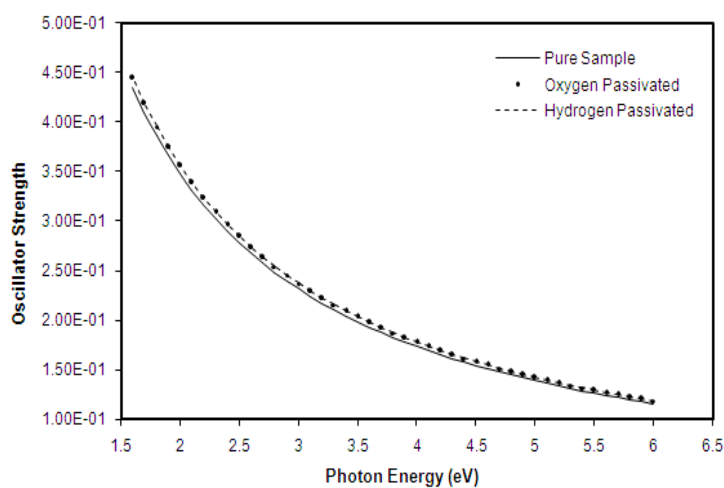

Figure 4.15: *Oscillatory strength as a function of photon energy for effective porous silicon nanocluster size* $d = 5nm$.

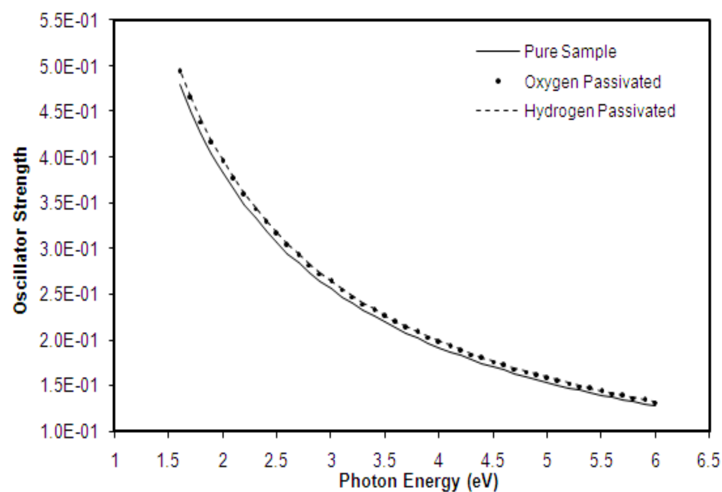

Figure 4.16: *Oscillatory strength as a function of photon energy for effective porous silicon nanocluster size d = 8nm.*

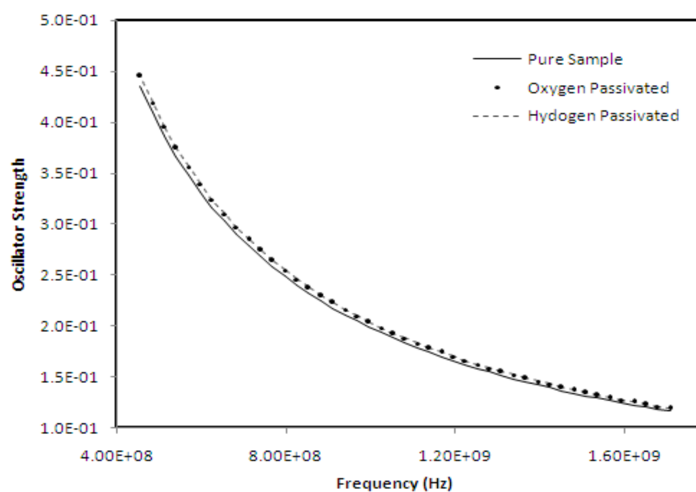

Figure 4.17: *Oscillatory strength as a function of frequency for effective porous silicon nanocluster size d = 8 nm.*

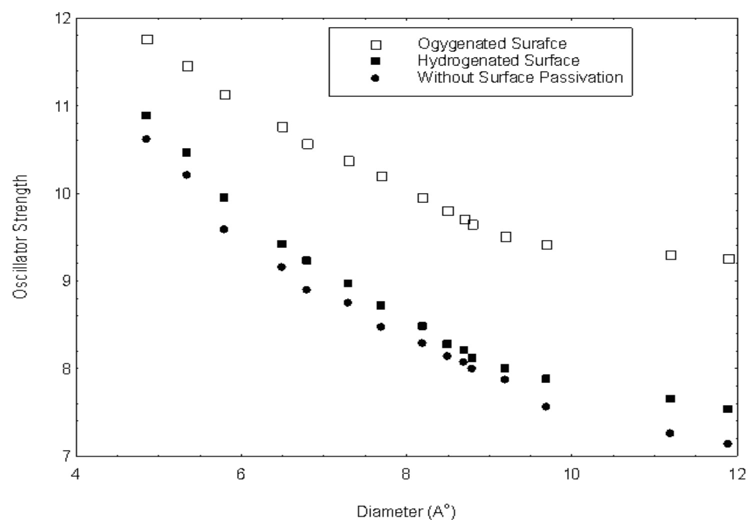

Figure 4.18: *Size dependent Oscillator Strength from non-orthogonalized tight binding.Filled circles (bottom) for pure clusters (free surface), filled square (middle) for hydrogenated surface and open square (top) for oxygenated surface [20].*

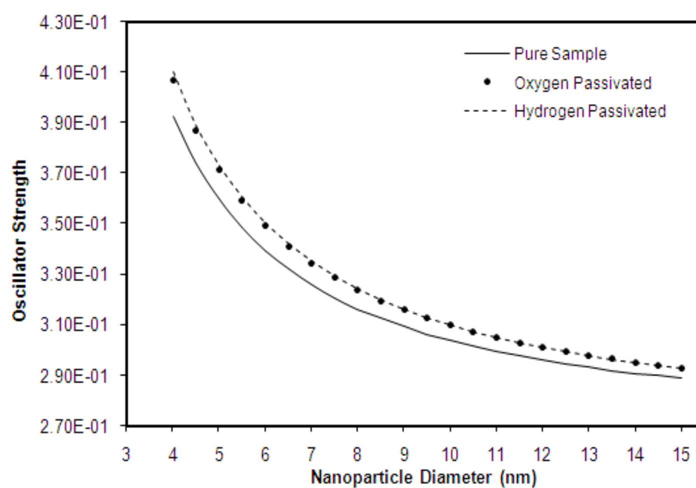

Figure 4.19: *Oscillatory strength as a function of porous silicon nanocluster size at a given photon energy* $\hbar\omega = 2.2eV$.

Chapter 5

Summary and Conclusions

In this thesis our aim is to study optical properties of nanoporous silicon. To do so we drive a formula for optical absorption coefficient, oscillator strength and imaginary part of the dielectric function near the band edge as a function of nanoporous silicon diameter(size) through the band gap. These parameters provide information directly on absorption and photoluminescence spectra.

Silicon is characterized by a very poor optical radiative efficiency and only produces light outside the visible range. But in the past decade room temperature visible photoluminescence has been observed from porous silicon surfaces prepared by chemical dissolution [1]. The luminescence is interpreted as resulting not only from the dimensions of the nanocrystals, i.e from the quantum confinement which leads to an increase of the band gap, but also from the surface passivation. In effect, even if bulk silicon is poor emitter of light, silicon nanostructure (porous Silicon, quantum dots, quantum wells and nanoclusters) exhibit strong optical properties at room temperature. Furthermore, beside their importance in making biological, chemical, optical

sensors and memory devices, their ability to be easily integrated into silicon wafer makes them at the top of the material menu.

Optically band-to-band transitions are resonance transitions and provide the most direct information about the band structure of semiconductors. We have seen how the density of states which depends on the dimensionality of the system is very helpful in analyzing optically band-to-band transitions. With the help of Kane estimate of the dipole matrix elements for direct band gap semiconductor we obtain the joint density of states between valence and conduction band states which is vary essential to calculate the optical absorption coefficient, the imaginary part of the dielectric function and the oscillator strength near the band edge for porous silicon nanocrystals as a function of band gap and photon energy. But our aim is to examine the variation of the optical absorption coefficient, oscillator strength and dielectric function as a function of photon energy and silicon nanocluster diameter, thus using the relation between the band gap and size of silicon nanoclusters, we examine the variation of the optical absorption coefficient, oscillator strength and dielectric function as a function of silicon nanocluster diameter and photon energy with hydrogen and oxygen passivation at the surface.

We have demonstrated that quantum dots with sizes less than a certain diameter ($d < 6nm$) the increases of optical absorption coefficient and dielectric function occurs with an increasing dot size. But for quantum dots with sizes greater than a certain diameter ($d > 6nm$) the increases of optical absorption coefficient, the oscillator strength and dielectric function occurs with decreasing dot size.Furthermore, the optical absorption coefficient, oscillator strength and dielectric function increases on

passivating the surface of silicon nanoclusters with hydrogen and oxygen respectively, i.e nanoclusters with no bond distortion and with its dangling bonds completely passivated possess large optical absorption coefficient, oscillator strength and dielectric function. We have concluded that the optical absorption coefficient, the oscillator strength and imaginary part of the dielectric function of nanoporous silicon strongly depend not only on the size of the nanocrystals, i.e on the quantum confinement, but also on the surface passivation. Our results are in qualitative agreement with other observations as well as with experimental results.

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