

Examining the Main Factors That Causes Photoluminescence Peak to Shift Towards the Smaller Wavelength in Nanoporous Silicon Quantum Dot

Adem Beriso

Madda Walabu University, college of Natural and computational Science, Department of Physics, Bale-Robe, Ethiopia; P.box: 247

S.K.Ghoshal

Universiti Teknolgi Malaysia, Department of Physics, Malaysia

Abstract

Both nanocrystalline and nanoporous silicon show interesting light emission properties. As the system size goes to nanoscale many unusual properties start to emerge. The purpose of this work to examine the main factors that causes photoluminescence peak to shift towards left or to the smaller wavelength of visible spectrum (blue shifted). With connection to this, we also study the light emission of nanoporous silicon cluster (quantum dot) with varying porosity and size of the dot. We examine these properties by using surface state model and our results are in conformity with some other experimental and theoretical findings.

Keywords: Nanoscale; Quantum dot; Porosity; Size; Photoluminescence

Introduction

Photoluminescence

Luminescence is a general term which describes any process in which energy is emitted from a material at different wave lengths that at which it is observed. It has different meanings depending on the field of application. Therefore, there are different types of luminescence; few of them are photoluminescence- by optical radiation, electroluminescence- by electrical field or currents, cathodoluminescence- by electron beams (cathode rays), Chemoluminescence-by the action of chemicals and Sonoluminescence-by the action of sound [1].

In this work we focus on photoluminescence. Luminescence resulting from the optical excitation is called photoluminescence. Photoluminescence (PL) is a process in which a substance absorbs photons (electromagnetic radiation) and then radiates photons back out. Quantum mechanically, this can be described as excitations to a higher energy state and then a return to a lower energy state accompanied by the emission of a photon (see fig.1). This is one of many forms of luminescence (light emission) and is distinguished by photo-excitation (excitation by photons), hence the prefix photo. The period between absorption and emission is typically extremely short, in the order of 10 nanoseconds. Under special circumstances, however, this period can be extended into minutes or hours. Ultimately, available chemical energy states and allowed transitions between states (and therefore wavelengths of light preferentially absorbed and emitted) are determined by the rules of quantum mechanics. A basic understanding and studying the electron configurations of the principles involved can be gained by molecular orbital of simple atoms and molecules [2, 3].

Mechanism of visible light emission from Nanoporous silicon

The recent discovery of bright visible luminescence from Nanoporous Silicon has stimulated research for a better understanding of the basic mechanisms of light emission from Si nanostructures and for a better control of the numerous parameters of Nanoporous silicon formation and further processing in order to give a high quantum efficiency of luminescence [4].

For structures related to porous silicon, Canham showed that the confinement requirements can be obtained by chemical dissolution of porous samples. Related to chemical thinning of crystallites, a blue shift of the fluorescence was also observed. It is suggested that passivation is provided by hydrogenation during the dissolution, but spontaneous oxidation when are exposed to air could not be excluded as a perturbation to the passivation. Some previous works have shown that visible luminescence could be obtained from as-formed high-porosity samples without further chemical dissolution and that an enhanced emission is observed after anodic oxidation. This complementary process has the advantage of bestowing good mechanical properties on the porous layer. In addition, it gives rise to a bright electroluminescence [5].

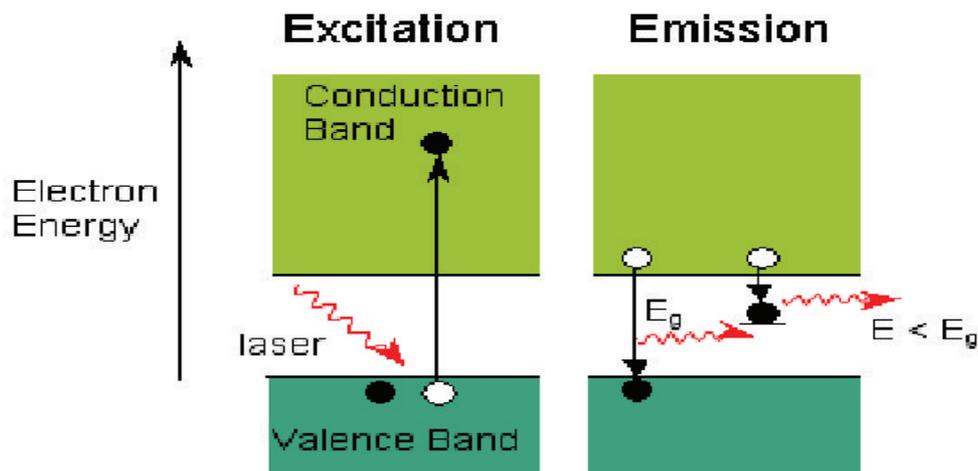


Figure 2. Photoluminescence. On the left a high energy laser photon gets out an electron from its orbit. The electron loses energy until it reaches the bottom of the conduction band. The right hand diagram shows two possible transitions. On the left the electron combines immediately with a hole in the valence band emitting a photon of energy E_g . On the right it gets stuck in a ‘between-gap’ state emitting a lower energy photon [3, 6, 7].

Effect of surface states on photoluminescence

When the valence electrons $3s^23p^2$ of a silicon atom form hybrid orbitals sp^3 to make bonds with neighboring atoms, their energy levels split into bonding and antibonding states. The valence electrons have accommodated in the bonding state, so the anti-bonding state is empty. Since in a crystal many atoms make bonds with each other to arrange themselves periodically, these energy levels have broadened to make bands: the valence band and the conduction band, respectively. These are electronic states in a bulk crystal. However, on the surface there exist dangling bonds (unpaired hybrid orbitals), which are similar to the hybrid orbitals of isolated atoms, whose energy levels will be located between the bonding and antibonding states, or within an energy gap (see figure 3).

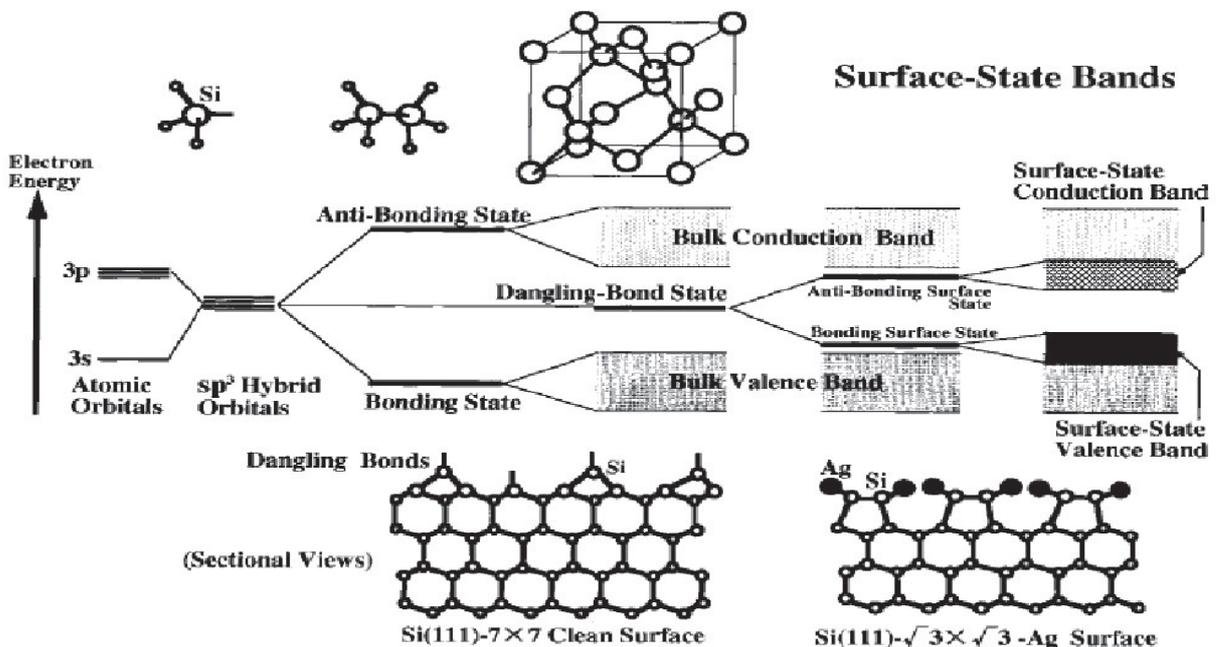


Figure.3. A schematic energy diagram for atoms and molecules, and also the bulk and the surface of a silicon crystal [8].

In fact, the dangling-bond state on a clean Si (111) surface is known to lie around the middle of the bandgap [8]. In addition, surface to volume ratio increase as the crystallite size decreases hence; the influence of surface states on the photoluminescence from smaller crystallites will be highly enhanced. Therefore, the role of surface states, especially for low crystallite size should be included into account during the study of photoluminescence mechanism. Wolkin et al. obtained photoluminescence spectra at room temperature by using a pulsed excitation

nitrogen laser (337nm) and/or a continuous excitation HeCd laser (325nm) [9]. Accordingly, figure 4 (a) shows the photoluminescence spectra of five types of Oxygen-free porous silicon samples with different porosities.

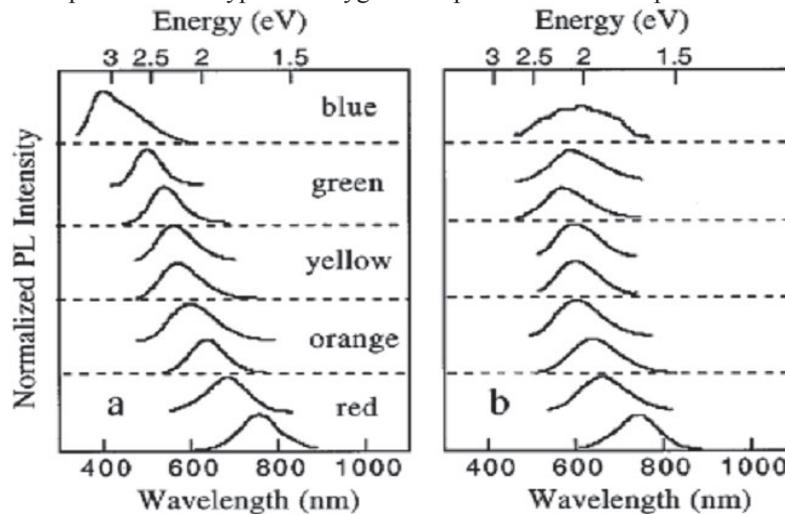


Figure 4. Room temperature photoluminescence spectra from porous silicon samples with different porosities kept under Ar atmosphere (a) and after exposure to air (b) [8].

Stable red, orange, yellow, green and blue spectra have observed as increasing the order of porosity. The results have obtained and measured during the samples kept in the Ar environment. Where as, figure 4 (b) shows how the spectra were modified after the samples had been exposed to air for 24 h and they observed that oxidation introduces states in the band gap which pin the transition energies. In addition, below about 3nm in size, oxide passivated nanocrystals are luminescence at lower energy than hydrogen passivated nanocrystals [10]. Calculation shows that the size of the bandgap and the corresponding spatial pattern of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), depend upon the electronegativity of the passivating layer at such small size. In oxide, terminated nanocrystals, the HOMO is sketch to the surface and resides in weakened Si-Si back bonds on interfacial Si atoms directly bonded to oxygen. Therefore, we realized that as the silicon exposed to air oxygen make a bond with the dangling bond and the SiO₂ layer cover the surface as shown in figure 5, the same is true when the dangling bond makes a bond with Hydrogen, and surface states appears in the band gap. Consequently, the photoluminescence peak shifted (modified) due to surface states. Therefore, surface passivation has remarkable effect on photoluminescence intensity.

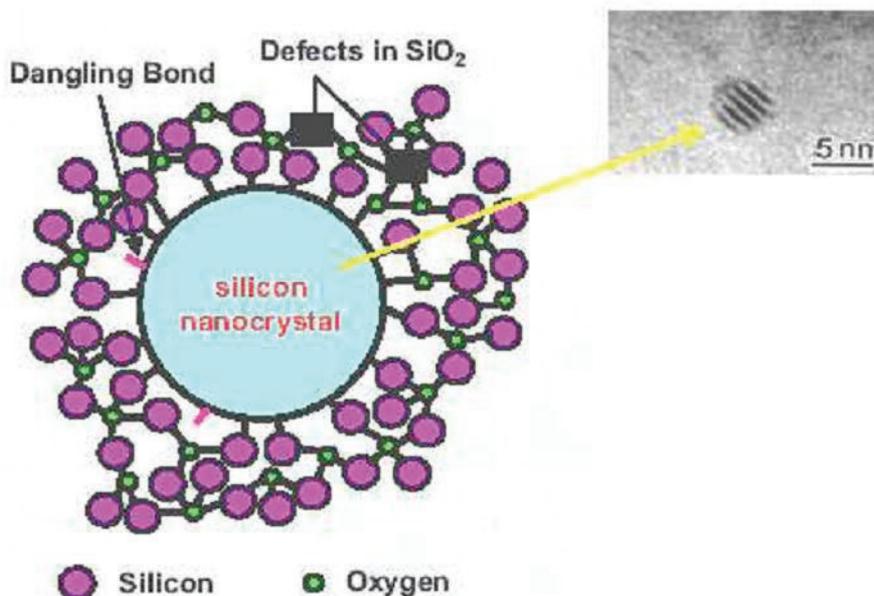


Figure 5. Silicon nanocrystals embedded in SiO₂ [8, 13].

We formulate a model for photoluminescence intensity by taking the effect of surface and exciton states into account in the coming section. In addition, we give a quantitative expression for the photoluminescence intensity.

Formation of a model to generate photoluminescence spectra

The study of silicon quantum dot is a very active field of research due to the interesting fundamental physical properties and the promising applications in advanced electronic and optoelectronic devices [2]. The optical properties have studied intensively for frequencies near the fundamental energy gap of the dots with respect to photoluminescence [11]. Here we are going to formulate and describe the photoluminescence spectra from silicon quantum dot. To do so, let us consider silicon quantum dot as an ensemble of having a well-defined size distribution function $n(d)$. On excitation with high-energy photons, photocarriers have generated inside the crystallites and then a fraction of these photoexcited carriers relax non-radiatively to the surface states. Subsequently, the relaxed carriers recombine to ground states radiatively giving photoluminescence. So, the intensity of photoluminescence at particular photon energy becomes proportional to the population of occupied surface states and the oscillator strength (the equivalent number of oscillations of the transition between the Valance and conduction bands). The number of surface states N_s in a quantum dot is proportional to the number of atoms on the surface and hence, surface area A of the quantum dot. Additionally, if we assume that each atom in a quantum dots contributes at least one photoexcited carrier to the quantum dot, the number of photoexcited carriers N_v in the quantum dot is proportional to its volume, V . The rate of transition from an excited carrier to the localized surface states is proportional to the product of the number of excited photocarriers and the number of available empty surface states in steady state condition, the population N_r of photocarriers in surface states participating in photoluminescence processes becomes proportional to the product, i.e.

$$N_r \sim AV \quad (1)$$

For a quantum dot of diameter d we have $V \sim d^{3-\beta_1}$ and $A \sim d^{2-\beta_2}$. So we get

$$N_r \sim d^{5-(\beta_1+\beta_2)} \quad (2)$$

Where β_1 and β_2 are porosity parameters. In the strong confinement regime, blue shift in band gap energy is quite significant compared to weak confinement limit. Along with the blue shift of the band gap and excitonic levels, particle size reduction also causes an enhancement in the oscillator strengths (f). This can be understood as follows: optical transition probability in a bulk semiconductor is proportional to the probability of finding an electron and a hole in the same unit cell of the crystal. Hence, the oscillator strength of the exciton f_{ex} is inversely proportional to a^3B . In the case of quantum dot transition probability is proportional to the spatial restriction of carrier motion in the quantum dot volume due to externally imposed quantum confinement, i.e.[12].

$$f \sim \frac{1}{d^{3-\beta_3}} \quad (3)$$

β_3 also defined in the same way as β_1 and β_2 . Now, taking the oscillator strength into account, the radiative transition probability in a quantum dot of diameter d becomes

$$P(d) \sim f N_r \sim d^{2+\beta_3-(\beta_1+\beta_2)} \quad (4)$$

Now, the photoluminescence intensity from an ensemble of quantum dot size d having size distribution $n(d)$ will be given by

$$I(d) \sim P(d)n(d) \quad (5)$$

The emitted photon energy from the quantum dot should be lower than the band gap energy of 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 quantum dot will be:

$$E_{pl} = E_g^{bulk} + \Delta E - E_g - E_s \quad (6)$$

According to quantum confinement model the band gap up shift can be modeled $\Delta E = \beta/d^Y$ where β and Y are constants due to quantum confinement effect, their magnitudes strongly depend up on the band gap calculation method being employed. We transform Eq.(5) from d to ΔE dependence as

$$I(\Delta E) = \int I(d)n(d)\delta\left(\Delta E - \frac{\beta}{d^Y}\right) dd \quad (7)$$

Taking

$$n(d) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\left(\frac{d-d_0}{2\sigma}\right)^2\right)$$

Where d_0 and σ are the mean dot size and standard deviation respectively. So, we obtained an expression for the photoluminescence intensity as:

$$I(\Delta E) \sim \frac{1}{\sigma\sqrt{2\pi}} \left(\frac{\beta}{\Delta E}\right)^{\frac{2}{\gamma}} \exp \left[-\frac{\left\{ \left(\frac{\beta}{\Delta E}\right)^{\frac{1}{\gamma}} - d_0 \right\}^2}{2\sigma^2} \right] \quad (8)$$

Eq. (8) gives general expression for photoluminescence intensity from silicon quantum dots ensemble. It is clear from the above expression is that the photoluminescence intensity depends strongly on the quantum confinement parameters β and γ . We took $\gamma = 1.39$ and 1.42 to plot two graphs for these two values of γ in the discussion part below. $\beta = 3.73\text{eV}$ and $E_g^{bulk} = 1.12\text{ eV}$ at room temperature. The localization binding energy E_s has taken to be the order of phonon energies, which is about 0.05eV for optical phonons. It is important to note that earlier researchers have taken oscillatory strength as proportional to $\frac{1}{d^\gamma}$ but we used $\frac{1}{d^{2-\gamma}}$.

Model, Results and Discussions

Under the section of Formation of a model to generate photoluminescence spectra above we have found the expression for photoluminescence intensity from silicon quantum dots ensemble. In this section we investigate the results based on our expressions. The plots are generated from the relation we obtain in equation (8) using MATLAB program.

Photoluminescence intensity

The plot of the normalized PL intensity verses effective size (1-6nm) at the given values of $\gamma = 1.32$ and 1.42 are shown in figures 6 and 7 respectively. In these two figures we want to observe the effect when the porosity level changes. As we can see from the two figures the effect of porosity level on the photoluminescence peak shifts towards left or to the smaller wavelength of visible spectrum (blue shifted) is not so much pronounced. The plot of the normalized PL intensity verses effective size (1-6nm) at the given value of $\gamma = 1.32$ and for values of mean sizes of the same material indicated in figures 6 and 7 is shown in figure 8. Here we want to see the effect of mean size of quantum dots on photoluminescence peak shifts.

When we looked at the figures below, we realized that the photoluminescence peak shifts towards left or to the smaller wavelength of visible spectrum (blue shifted) as the dot size decreases, which is expected. We found that width of size distribution and the average size of quantum dots are the main factors that cause such shifts and our results are in conformity with different experimental and theoretical results.

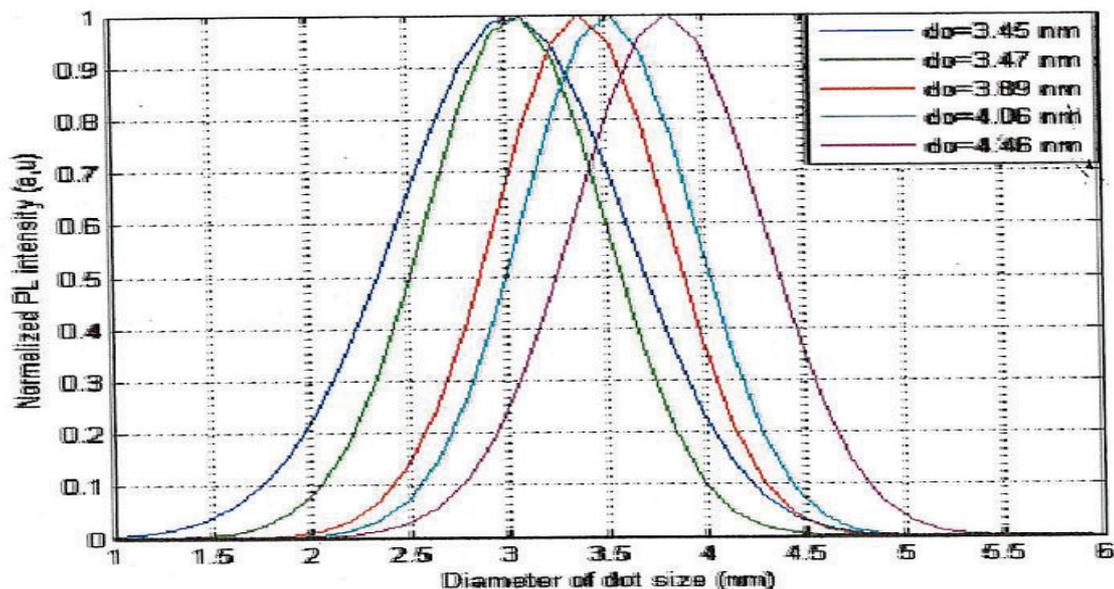


Figure. 6. Normalized PL intensity versus size of nanoporous silicon cluster (quantum dot) for $\gamma = 1.32$ (10% to 20% porosity).

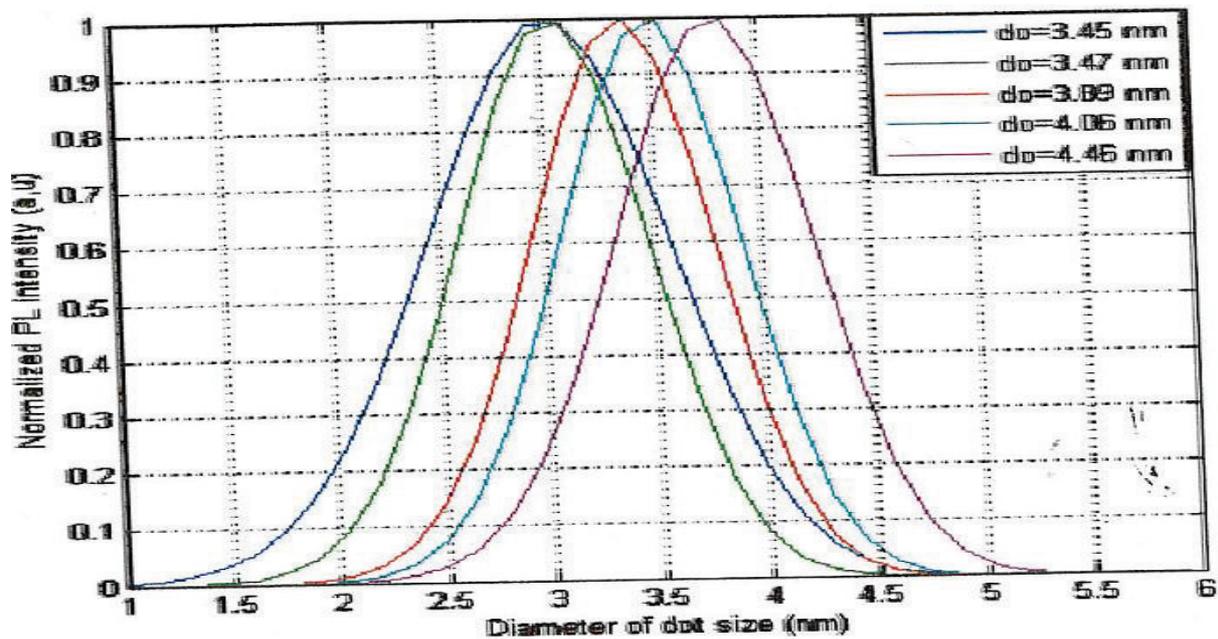


Figure 7. Normalized PL intensity versus size of nanoporous silicon cluster (quantum dot) for $\gamma = 1.42$ (30% to 40% porosity).

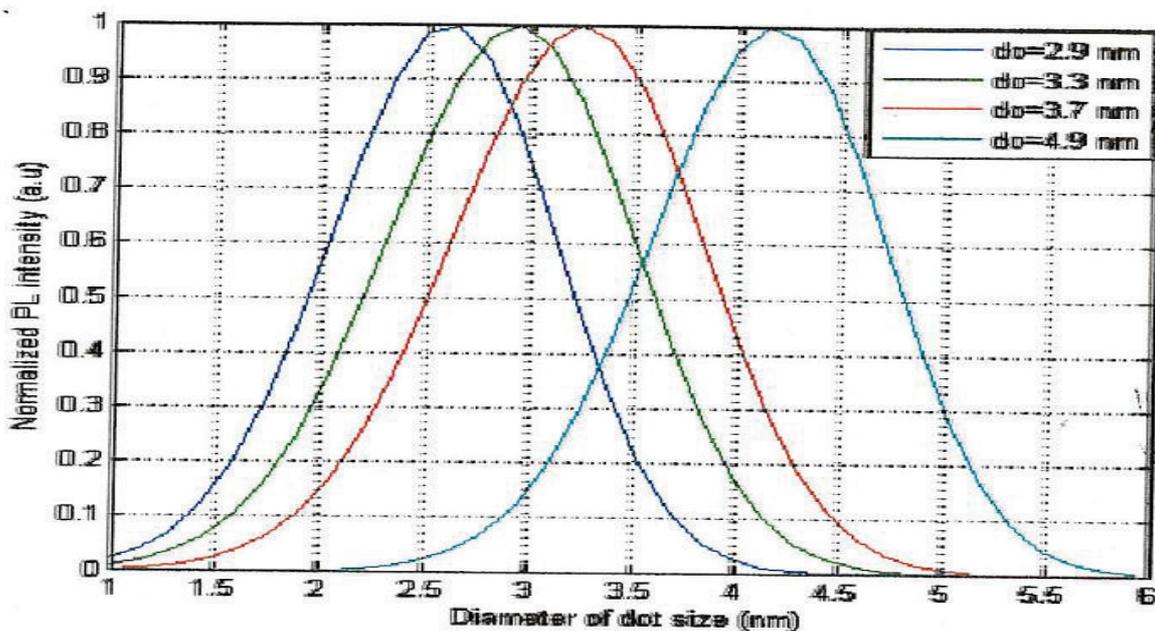


Figure 8. Normalized PL intensity versus size of nanoporous silicon cluster (quantum dot) for $\gamma = 1.32$ (10% to 20% porosity).

Conclusion

From the expression we obtain for PL intensity, we found that width of size distribution and the average size of quantum dots are the main factors that cause the photoluminescence peak shifts towards left or to the smaller wavelength of the visible spectrum (blue shifted) and our results are in conformity with other experimental and theoretical results. Bulk silicon has a problem for light emitting applications due to its indirect band gap, while nanostructuring of silicon comprises porous silicon, quantum dots, quantum wells and nanoclusters that can exhibit strong photoluminescence at room temperature which is observed only after a drastic reduction of silicon size and this has been related to quantum confinement effect and surface passivation that alters indirect band gap to direct band gap. Although quantum confinement alone cannot explain the whole physics of nanostructures but gives explanation for the observation of luminescence. In case of porous silicon the varying porosity along with

crystallites size play role in deciding PL.

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