

SIZE EFFECT ON PHOTOLUMINESCENCE SPECTRA OF SILICON NANOCRYSTALLITES: THEORETICAL MODEL

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Abstract

Bulk silicon, the foundation of our telecommunications and computational infrastructure, possesses an indirect band gap, and as a result, does not exhibit room-temperature visible luminescence. In this paper I have developed a possible model to analyze the room temperature photoluminescence (PL) spectra observed from silicon nanostructures. I have explicitly incorporated the effects of localized surface states along with quantum confinement effects to obtain an analytical expression for the photoluminescence intensity. Normal as well as log-normal crystallite size distributions are considered for PL intensity calculations. Experimental PL data on a variety of nanocrystalline silicon structures with directly measured crystallite size distribution have been analyzed. My model is able to deduce size distribution parameters from PL data that agree well with the experiments.

Keywords: Photoluminescence, Quantum Confinement, Band gap, porous silicon, Surface State, Ensemble

Introduction

A nanocrystal made of semiconductor material is now an interesting means of new electronics and optoelectronics devices, and it has become predominantly significant over last few decades. Properties of materials of nanometric dimensions are appreciably unlike from those of atoms as well as those of bulk materials. Appropriate management of the properties of nanometric scale structure can escort to new science as well as novel devices and technologies. A small nanocrystal of one nanometer diameter will have as much as 30 percent of its atoms on the surface, while a large nanocrystal of 10 nanometers will have around 15 percent of its atoms on the surface. For a spherical nanoparticles of radius R composed of atoms with an average spacing a , the ratio is given by $N_{\text{surf}}/N = 3a/R$. For $R = 6a \approx 1$ nm, half of the atoms are on the surface [i]. The cohesive energy is significantly lowered because atoms on the surface are incompletely bonded. Nanoparticles consequently melt at temperature far below the melting temperature of the corresponding bulk solid.

The effect determined by size is appropriate to the evolution of structural, thermodynamic, electronic, spectroscopic, electromagnetic chemical features of the material. It should be noted that even metals show non metallic band gap when the diameter of the nanocrystal is in the 1-2 nm range [i].

Nanotechnology is the worldwide hot and top issue of science and technology to describe matter and process occurring in it at a nanoscale level called nanoscience) and manipulating materials (atoms and molecules) at nano level to produce nanoscale materials.

Light emission from porous silicon occurs mainly in the visible region of the electromagnetic spectrum. The emission has the unique property that the wavelength of the emitted light can be changed simply by increasing or decreasing the porosity of the material. For example, a highly porous sample (70-80 percent porosity) will emit green/blue light while a less porous sample (40 percent) will emit red light [ii].

1 Optical properties of low dimensional silicon

In bulk crystals the electronic properties (band structure) are determined by the nature of the atoms forming the crystal. We would like to modify the band structure for a variety of reasons, depending upon technology needs. There are three important ways of modifying band structure. These are: making alloys, quantum wells and strain field [iii]. These techniques can be used to modify the properties of the materials by changing gap between the valence and conduction bands. In this paper attention is given for the quantum well together with quantum wire and quantum dot. For example, let's consider electrons confined in the z-direction and are free to move in

the x-y plane. The Schrödinger equation for the quantum well in which the confinement is along the z-axis can be separated into equations in the x and y direction and in the z-direction as follows:

$$\Psi = \Psi_x \Psi_y \Psi_z$$

$$-\frac{\hbar^2}{2m^*} \frac{\partial^2 \Psi_x}{\partial x^2} = E_x \Psi_x$$

$$-\frac{\hbar^2}{2m^*} \frac{\partial^2 \Psi_y}{\partial y^2} = E_y \Psi_y$$

$$\left(-\frac{\hbar^2}{2m^*} \frac{\partial^2 \Psi_z}{\partial z^2} + V(r)\right) \Psi_z = E_z \Psi_z$$

Solution in the x-y plane

$$\Psi_x = \frac{1}{\sqrt{L_x}} e^{ik_x x}, E_x = \frac{\hbar^2 k_x^2}{2m^*}$$

$$\Psi_y = \frac{1}{\sqrt{L_y}} e^{ik_y y}, E_y = \frac{\hbar^2 k_y^2}{2m^*}$$

Solution for an infinite barrier case becomes;

$$\Psi_z = \frac{\sqrt{2}}{\sqrt{\omega}} \cos \frac{n\pi z}{\omega}$$

For odd n values

$$\Psi_z = \frac{\sqrt{2}}{\sqrt{\omega}} \sin \frac{n\pi z}{\omega},$$

For even n values

$$E_z = \frac{\pi^2 \hbar^2 n^2}{2m^* \omega^2}$$

Eigen values E_x and E_y are different from E_z in form due to confinement of electrons in the z-direction.

2 Photoluminescence from nanosilicon

Photoluminescence (abbreviated as 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 of the principles involved can be gained by studying the electron configurations and molecular orbital of simple atoms and molecules.

3 Theoretical Model for photoluminescence profile

In order to formulate and describe the PL spectra from nc-Si structures, we consider nc-Si as ensemble of nanometer sized spherical particles having a well defined size distribution. The optical band gap widening in crystallites is considered due to quantum confinement effect (QCE) in nanoparticles. On excitation with high energy photons, photo carriers are generated inside the crystallites (path a) and then a fraction of these photo excited carriers relax none radiatively to the surface states (path c) subsequently, the relaxed carriers recombine to ground state radiatively giving PL (path d). Since the oscillator strength for direct transition between the conduction and valence bands (path b) is smaller than that via surface states, we neglect the contributions due to direct transitions. The oscillator strength in crystallites is taken to depend on the crystal size as inverse power law [v].

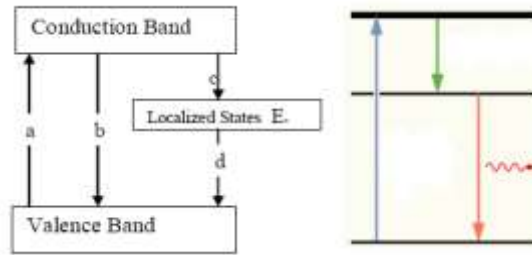


Figure 1: Schematic of possible excitonic recombination paths (a) excitation: excited states (valence band) to excited states (conduction band); (b) deexcitation: conduction to valence band recombination; (c) relaxation: excited states to localized surface states (LSS) and (d) radiative recombination: LSS to ground states (left). Intrinsic surface state emission process (right).

Under the above assumption, the intensity of PL at particular photon energy becomes proportional to the population of occupied surface states and to the oscillator strength. The number of surface states in a crystallites is proportional to the number of atoms on the surface and hence, surface area A of the crystallites [v]. If N_s is the total number of surface states, then

$$N_s \propto A \dots\dots\dots 1$$

If each atom in a crystal contributes at least one photo-excited carrier to the crystallite, the number of photo-excited carriers N_v in a crystal is proportional to its volume.

$$N_s \propto V \dots\dots\dots 2$$

Since the rate of transition of an excited carrier to the localized surface state is proportional to the product of the number of excited photo carriers and the number of available empty surface states in steady state condition, the population N_r of photo carriers in surface states participating in PL process becomes proportional to the product of the above two. i.e

$$N_r \propto AV \dots\dots\dots 3$$

For spherical crystallite with diameter $V \propto L^3$ and $A \propto L^2$. Then we get

$$N_r \propto L^5 \dots\dots\dots 4$$

The rate of radiative transition depends on the oscillator strength f . The oscillator strength in nanocrystalline varies as inverse power law and can be approximated as $f \approx \frac{1}{L^\alpha}$, where the power exponent α depends on the material properties as well as the range of crystallite size being used. Taking the oscillator strength into account, the radiative transition probability in a nanocrystallite of diameter L becomes

$$P(L) \propto N_r f \propto L^{5-\alpha} \dots\dots\dots 5$$

Now, the PL intensity from an ensemble of crystallite having size distribution $\Phi(L)$ will be obtained by summing the contribution from all the crystallites having size L . The PL intensity from crystallites of size L may be given by

$$I(L) \propto P(L)\Phi(L) \dots\dots\dots 6$$

The emitted photon energy from nanocrystallite will be lower than the band gap energy of the crystallite by an amount of localization energy E_s of the surface states and the exciton binding energy E_b . Both, in general are function of crystal size. The emitted photon energy from crystallite will then be given as

$$E_{pl} = E_g + \Delta E - E_s - E_b \dots\dots\dots 7$$

Where ΔE is the amount of band gap up shift due to QCE in the nanocrystalites and E_g is the band gap corresponding to the bulk crystalline material or

$$\Delta E = E_{pl} - (E_g - E_s - E_b) \dots\dots\dots 8$$

According to QCE in the nanocrystallite of diameter L , band gap up shift can be modeled as $\Delta E = \frac{C}{L^n}$, where C and n are constants due to QCE; their magnitudes strongly depend on the band gap up shift calculation method being employed. One can transform Eq.(6) from L to ΔE dependency as:

$$I(\Delta E) \propto \int I(L)\delta(L - \Delta E)dL \dots\dots\dots 9$$

$$I(\Delta E) \propto \int L^{5-\alpha} \Phi \delta(L - \Delta E)dL \dots\dots\dots 10$$

If we take a normal distribution function for crystallite size in nc-Si, then

$$\Phi(L) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(L - L_o)^2}{2\sigma^2}\right] \dots\dots\dots 11$$

Where L_o and σ are the mean crystallite size and standard deviation, respectively, for nanocrystalline ensemble. Putting Eq.(11) in to Eq.(10), we get

$$I(\Delta E) \propto \int \frac{L^{5-\alpha}}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(L - L_o)^2}{2\sigma^2}\right] \delta(L - \Delta E)dL \dots\dots\dots 12$$

$$I(\Delta E) \propto \frac{1}{\sigma\sqrt{2\pi}} \int L^{5-\alpha} \exp\left[-\frac{(L - L_o)^2}{2\sigma^2}\right] \delta(L - \Delta E)dL \dots\dots\dots 13$$

$$\Delta E = \left(\frac{C}{L^n}\right) \Rightarrow dL = -\frac{1}{C^n} \left(\frac{C}{\Delta E}\right)^{\frac{n+1}{n}} d\Delta E \text{ then,}$$

$$I(\Delta E) \propto \frac{1}{C^n \sigma \sqrt{2\pi}} \int \left(\frac{C}{\Delta E}\right)^{5-\alpha} \exp\left[-\frac{(L - L_o)^2}{2\sigma^2}\right] \delta(L - \Delta E) \left(\frac{C}{\Delta E}\right)^{\frac{n+1}{n}} d\Delta E \dots\dots\dots 14$$

$$I(\Delta E) \propto \frac{1}{C^n \sigma \sqrt{2\pi}} \int \left(\frac{C}{\Delta E}\right)^{5-\alpha} \exp\left[-\frac{(L - L_o)^2}{2\sigma^2}\right] \delta(L - \Delta E) \left(\frac{C}{\Delta E}\right)^{\frac{n+1}{n}} d\Delta E \dots\dots\dots 15$$

Using the properties of Dirac's delta function

$$I(\Delta E) \propto \frac{1}{C^n \sigma \sqrt{2\pi}} \left(\frac{C}{\Delta E}\right)^{\frac{6-\alpha+n}{n}} \exp\left[-\frac{\left(\left(\frac{C}{\Delta E}\right)^{\frac{1}{n}} - L_o\right)^2}{2\sigma^2}\right] \dots\dots\dots 16$$

It is also common to obtain a log-normal size distribution of particle size given by

$$\Phi(L) = \frac{1}{\sigma\sqrt{2\pi}L} \exp\left[-\frac{(\ln(L) - \ln(L_o))^2}{2\sigma^2}\right] \dots\dots\dots 17$$

$$I(\Delta E) \propto \frac{1}{C^n \sigma \sqrt{2\pi}} \left(\frac{C}{\Delta E}\right)^{\frac{5-\alpha+n}{n}} \exp\left[-\frac{\left(\ln\left(\frac{C}{\Delta E}\right)^{\frac{1}{n}} - \ln(L_o)\right)^2}{2\sigma^2}\right] \dots\dots\dots 18$$

Equations (16) and (18) give general expression for PL intensity profile from nc-Si ensemble. It is clear from the above expression that the PL profile will depend strongly on the QC parameters C and n. Therefore, care must be taken in using the correct QC model for band gap up shift estimation. The oscillator strength and the exciton binding energy E_b both are complicated functions of size of the nanocrystallites and surrounding media. Hence, the PL from the silicon nanostructures is a complex process. The main aim here is to compare the experimental observation on PL intensity variation with my model calculation.

In my model I vary crystallite size, photon energy and distribution of sizes.

4 Results and Discussion

In this section, I present the main results that are obtained based on my model calculation. In order to obtain an insight in to the effects of various parameters influencing the PL luminescence spectra profile in nc-Si, I computed the PL spectra using relevant numbers in equations (16).

The radiative transition in silicon based nanostructures may be with or without phonon mediation depending upon the crystallite size. The power exponent α of oscillator strength is large for zero phonon case and small for phonon assisted case. Following careful calculations of Proot et al [vi] for crystalline silicon, we take $n = 1.39$ and $C = 4.122$ eV when L_0 is in units of nm. We take a constant value of 0.07 eV for E_b , which is a fairly good average value for the range of crystallite sizes from 2.5 nm to 5 nm. A study of resonant PL from PS has shown phonon assisted radiative transition for crystallite size greater than about 2nm [vii]. Therefore, surface localization energy E_s is taken to be of the order of phonon energies, which is about 0.05 eV. We take E_g as 1.12 eV for c-si at room temperature and for spherical nanocrystallites with $L > 2.0$ nm, the oscillator parameter α can be taken 3.

The PL spectra were simulated using equation (16) with the typical values of L_0 and σ found in the light emitting nc-Si samples. The calculated PL spectra for fixed $L_0 = 3.2$ nm and variable values of σ from 0.16 nm to 0.54 nm are shown in figure 2. As σ increases, the PL spectrum broadens as well as shifts toward low emission energies accompanied by a decrease in relative PL intensity. This implies that the amount of size dispersion affects both the PL peak energy and width. This is in agreement of with the experimental results of Wolkin et al.

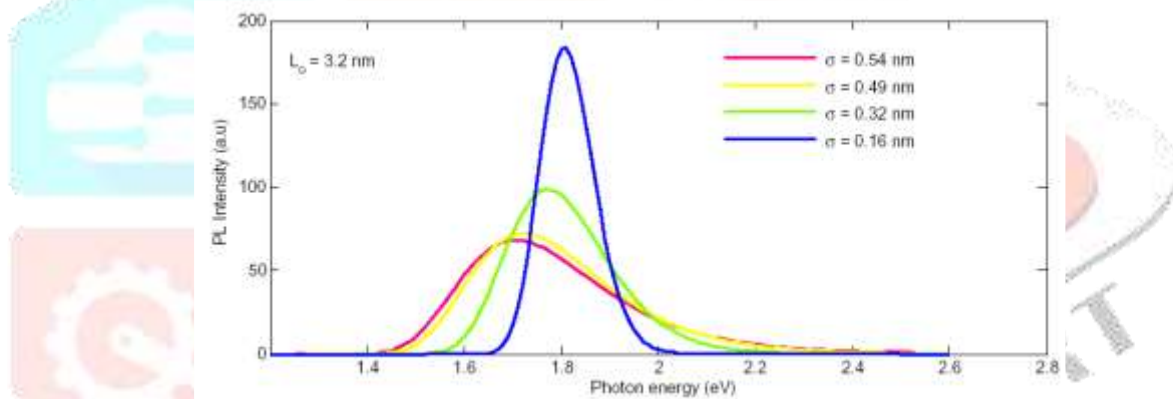


Figure 2: PL spectra computed for silicon nanocrystal having normal crystal size distribution around average mean crystallite diameter, $L_0 = 3.2$ nm at different standard deviation σ .

Mean crystallite size L_0 being the dominant parameter governing the quantum confinement effect

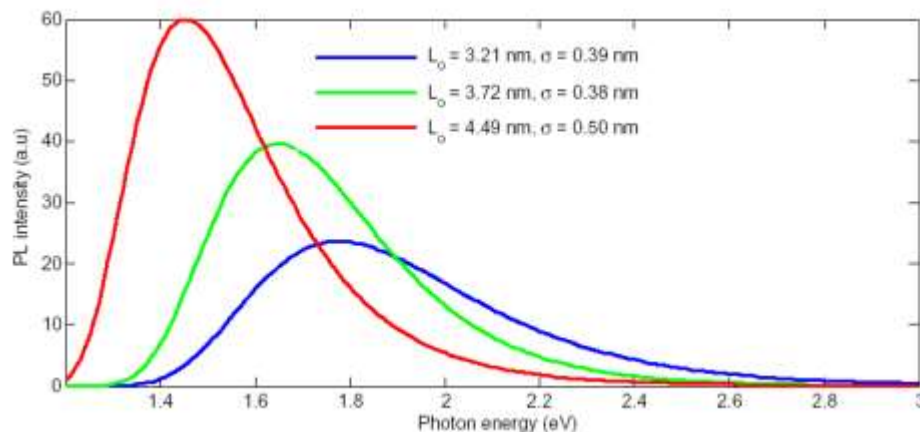


Figure 3: PL spectra computed by our model for Si nanocrystallites having normal size distribution with different average mean crystallite diameters L_0 and standard deviations σ .

(QCE), the effect of L_0 on the PL peak energy is strong. In figure 3, calculated PL spectra are shown for three different values of L_0 and σ . Our model depicts the shift of PL peak position (from 1.79 eV to 1.45 eV) with the increasing mean crystal size (L_0) and σ .

dispersion (σ) from 3.21 nm to 4.46 nm and 0.39 nm to 0.50 nm respectively. The PL spectra computed by our model shown in figure 3 is in conformity with experimental PL spectra shown in figure 4 (fig. 5 of ref.iv), in which the PL intensity peak energy shift from 1.78 eV to 1.5 eV with the increasing mean crystal size from 3.65 nm to 4.95 nm.

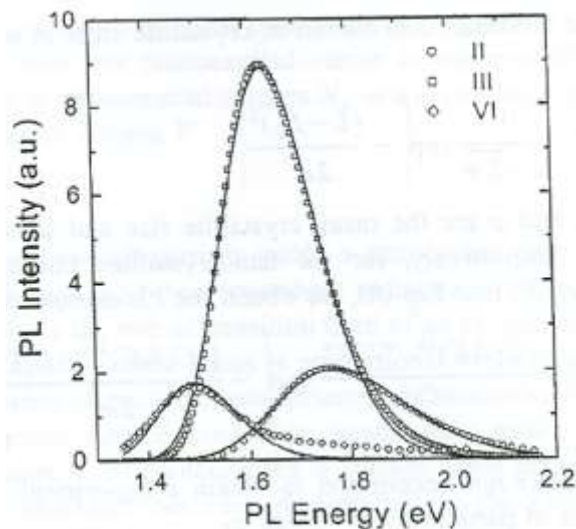


Figure 4: Experimental PL spectra (points) on size selected cluster beam deposited nc-Si films having different crystallite size (II = 3.65 nm, III = 3.92 nm and VI = 4.95 nm) distribution. Solid lines are fit to the experimental data using L_0 and σ as free parameters.

5 Conclusion

Quantum confinement effects, localized surface states and exciton binding energy are used in my model to depict photoluminescence spectra and the enhancement of surface band gap from silicon nanocrystallites. The mean diameter of Si nanocrystallites has been revealed to have a consequence on the PL intensity and band gap energy.

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