Radiative lifetime and internal quantum efficiency of silicon nanostructures: Model Calculation

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Abstract

Nanosilicon (nanocrystal and porous) research is gaining tremendous attention in recent years. Improving efficiencies in radiative recombination of nano-scale materials enhance potential applications as optoelectronic devices with new operational capabilities. In this work we investigate the influence of quantum confinement and excitation laser pump flux on the radiative lifetime and internal quantum efficiency of silicon nanocrystals. Our work presents a new phenomenological approach that explain the size and laser pump flux dependence of radiative lifetime and internal quantum efficiency of silicon nanocrystals. To investigate the mechanism of the photoluminescence we perform computer simulation. The results show that, miniaturizing the size and increasing laser pump flux strongly alters radiative lifetime and internal quantum efficiency of silicon nanocrystal. Our results have in well agreement with many other theoretical and experimental findings. Our model confirms that the radiative lifetime and internal quantum efficiency of silicon nanocrystals enhance due to pump flux and quantum confinement.

Keywords: Radiative lifetime, internal quantum efficiency, pump flux.

Resumen

La investigación de Nanosilicones (nanosilicones y porosos) está adqiriendo una enorme atención en los últimos años. Mejorando la eficiencia en la recombinación radiactiva de los materiales nano-escala para mejorar las aplicaciones potenciales como dispositivos optoelectrónicos con nuevas capacidades operacionales. En este trabajo investigamos la influencia del confinamiento cuántico y el flujo de excitación láser de bombeo en el tiempo de vida de la radiación y la eficiencia interna cuántica de los nanocristales de silicio. Nuestro trabajo presenta un nuevo enfoque fenomenológico que explica el tamaño y la dependencia del flujo de bombeo láser del tiempo de vida de la radiación y la eficiencia cuántica interna de los nanocristales de silicio. Para investigar el mecanismo de la fotoluminiscencia realizamos simulación por computadora. Los resultados muestran que, minimizando el tamaño e incrementando el flujo de bombeo del láser fuertemente altera el tiempo de vida radiactivo y la eficiencia interna cuántica de nanocristales de silicio. Nuestros resultados tienen en buen acuerdo con muchos otros resultados teóricos y experimentales. Nuestro modelo confirma que el tiempo de vida de la radiación y la eficiencia cuántica interna de los nanocristales de silicio para mejorar debido al flujo de bombeo y el confinamiento cuántico.

Palabras clave: Tiempo de vida radiactivo, eficiencia cuántica interna, flujo de bombeo.

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I. INTRODUCTION

Silicon is the most widespread semiconductor in modern microelectronics technologies. Its natural abundance, low cost and high purity, as well as the high electronic quality of the si/sio$_2$ interface, have led to its over whelming dominance in micro-electronic devices [1]. Nevertheless bulk Silicon does not have lasing action because the fast non-radiative processes such as Auger or free-carrier absorption strongly prevent population inversion at the high pumping rates needed to achieve optical amplification [2].

In silicon nanocrystals (Si-nc) the spatial confinement by Potential barriers prevents the diffusion of excitons to non-radiative centers and the radiative recombination is a much more efficient process than bulk silicon. Nanoscale silicon crystal exhibits efficient photoluminescence at visible energy above the silicon band gap of 1.12eV.

Radiative lifetime and internal quantum efficiency are among the parameters that describe the luminescence property of a given crystallite. The radiative lifetime τ_{rad} is the lifetime of an excited electron in the prescence of light emission transition and is the reciprocal of probability for radiative de-excitation rate ($\tau_{rad}{}^{-1} = \Gamma_{rad}$), and an internal

quantum efficiency $\eta = \frac{\Gamma_{rad}}{\Gamma_{exp}}$ is the "weight" of the radiative channel in the recombination process [1] or the measure of the fraction of total de-excitation which are radiatively recombine. Where Γ_{exp} is the experimental decay rate which comprises the radiative (Γ_{rad}) and non-radiative (Γ_{nr}) de-excitation paths ($\Gamma_{exp} = \Gamma_{rad} + \Gamma_{nr}$). An internal quantum efficiency of a nanocrystal is only limited by its internal property.

Radiative lifetime and internal quantum efficiency have strong size dependent properties, hence tuning the size of nanocrystals strongly affect their magnitude, and thus the ability to vary these parameters is a key to realize nanostructures with novel properties. When the size of Si-nc is comparable to its characteristics bohr exciton radius (4.9nm), the probability for radiative de-excitation rate and quantum efficiency of the nanocryatal increases, as a result photo-luminescence (PL) intensity that we get from the nanocrystallite increases appreciably. The quantum yield of the PL of Si-nc is larger by several orders of magnitude than the bulk silicon due to quantum confinement, so starting from the bulk, it is expected that the photoluminescence yield will increase when one goes to nanostructure.

In systems of Si-nc, one can additionally take the advantage of high quality oxide to passivate the surface and therefore eliminate many nonradiative channels, such as dangling bonds and defect centers. This further enhance the quantum efficiency by reducing the total decay rate, however in order to compete with direct band gap quantum dots as CdSe and InAs, the emission intensity of Si-nc must be enhanced by three order of magnitude [2]. Thus, improvement of light emission efficiency of silicon quantum dots remains a challenge for optoelectronic technologies.

II. MODEL CALCULATION

The rate of spontaneous transition from an excited electron-hole state $|c>$ to the ground state $|v>$ can be derived from Fermi's golden rule in the first order approximation theory in the following form

$$\Gamma = \frac{2\pi e^2 {A_0}^2 cos^2\theta}{\hbar m^2 c^2} |< c|P|v >|^2 \delta(E_c - E_v - \hbar\omega), \quad (1)$$

where e is the electron charge, m the electron rest mass, $\hbar$ Planck's constant, c the speed of light, A_0 is the amplitude of light, θ is the angle between $A\ and\ P$, and $|< c|P|v >|$ the matrix element of the momentum.

Several excitation process are possible between different sub-bands for a given optical excitation energy. Based on the band structures of quantum dots [3], we approximate the difference in energy levels between the final and initial states of an excited electron by

$$E_C - E_V = E_g(d) + E\left(\frac{1}{{n_i}^2}\right) + \frac{\hbar^2 k^2}{2\mu}. \quad (2)$$

The first term $E_g(d)$ represents the size dependent energy gap of nanostructure, the second term $E\left(\frac{1}{{n_i}^2}\right)$ is the sum of all atomic like energy levels of nanostructures which have large value of energy as compared to the difference in energy between two successive levels, and $\frac{\hbar^2 k^2}{2\mu}$ is the parabolic approximation of closely spaced energy levels.

In terms of oscillator strength which is the measure of strength of quantum mechanical transition between two atomic levels, the probability for radiative de-excitation rate Γ_{rad} lead us to the expression

$$\Gamma_{rad} = \frac{e^2 {A_0}^2 cos^2\theta\omega}{8\pi^2 mc^2} V_{nc} \sum f_{v\to c} \int \delta(E_c - E_v - \hbar\omega) d^3k. \quad (3)$$

It is found experimentally that the oscillator strength in nanocrystals is dependent on the crystallite size as the inverse power law $f \sim d^{-\beta}$ where d is the diameter of the spherical nanocrystallites and the value of β is $5 \le \beta \le 6$ [4]. The power exponent β depends on the material property as well as the range of the crystallite size being used.

If there exist more than one photo-excited carrier in a quantum dot at a time, Auger recombination or free carrier absorption can quench the luminescence of the quantum dot, therefore we assume there exist only one photo-excited carrier in one life time of excited electron.

For spherical nanocrystals with diameter d the volume is related to the diameter by

$$V_{nc} = \frac{\pi}{6} d^3. \quad (4)$$

Integration followed by substitution of the size depen-dence of oscillator strength (f) and the volume of nano-crystallite (V_{nc}) in to Eq. (3) yields the size and excitation energy dependence of radiative de-excitation rate ${\tau_{rad}}^{-1}$

$${\tau_{rad}}^{-1} = \frac{\Gamma_0(\omega)}{d^{\beta-3}} \sqrt{\hbar\omega - \left(E_g(d) + E\left(\frac{1}{{n_i}^2}\right)\right)}. \quad (5)$$

Where $\Gamma_0(\omega) = C_0 \left(\frac{e^2 {A_0}^2 cos^2\theta}{48mc^2} \left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}}\right)\omega$, C_0 is the proportionality constant that depend on the material property as well as range of nanocrystallite size being used.

Increasing the excitation laser pump flux to a certain saturation value (to the extent of increasing laser pump flux has no significant effect in increasing the radiative de-excitation rate and PL intensity) enhances the radiative de-excitation rate and PL intensity of Si-nc. For a given photon flux ϕ, the number of photo-excited carriers in a given nanocrystal could be more than one within one life time of excited electron, therefore the rate equation describing the time evolution of the concentration of photo-excited cariers in a given nanocrystal is given by

$$\frac{dN^*}{dt} = \sigma_0 \phi (N - N^*) - \frac{N^*}{\tau}. \quad (6)$$

Where N^* is the number of excited atoms, N is the number of atoms in a given nanocrystal, σ_0 is atomic cross section and τ^{-1} is the experimental decay rate.

Under steady state conditions, an analysis of the two level system yields

$$N^* = N\left(\frac{\sigma_0\phi}{\sigma_0\phi+\Gamma_{exp}}\right), \tag{7}$$

and

$$N^*\Gamma_{rad} = N\left(\frac{\sigma_0\phi}{\sigma_0\phi+\Gamma_{exp}}\right)\Gamma_{rad}. \tag{8}$$

After certain re-arrangement, the internal quantum efficiency ($\eta = \frac{\Gamma_{rad}}{\Gamma_{exp}}$) is

$$\eta = \left(\frac{N^*}{N-N^*}\right)\left(\frac{\Gamma_{rad}}{\sigma_0\phi}\right). \tag{9}$$

For any pump flux regime the number of ionized atoms are much smaller than the total number of atoms in a nanocrystal, therefore $N - N^* \approx N$.

Now the internal quantum efficiency can be re-written as

$$\eta \approx \left(\frac{N^*}{N}\right)\left(\frac{\Gamma_{rad}}{\sigma_0\phi}\right). \tag{10}$$

The number N of silicon atoms constituting the nanoparticle is related to its diameter d (nm) by

$$N = 26.2d^3. \tag{11}$$

Therefore the size and pump flux dependence of the internal quantum efficiency is

$$\eta \approx \left(\frac{N^*\Gamma_0(\omega)}{26.2\sigma_0\phi}\right)\left(\frac{1}{d^\beta}\right)\sqrt{\hbar\omega - \left(E_g(d) + E\left(\frac{1}{n_i{}^2}\right)\right)}. \tag{12}$$

Maximizing the size and pump flux dependence of internal quantum efficiency that we obtain in Eq. (12), we can get the diameter associated with the peak value of internal quantum efficiency $\left(d_\eta{}^{max}\right)$ of silicon nano-crystal for a given excitation energy as

$$d_\eta{}^{max} = 2.578\left(\frac{1+\frac{1.39}{2\beta}}{\hbar\omega-\left(1.17+E\left(\frac{1}{n_i{}^2}\right)\right)}\right)^{\frac{1}{1.39}}. \tag{13}$$

III. RESULTS AND DISCUSSION

A. Results of η versus Size of nanocrystals

As we can see in Eq. (10) the internal quantum efficiency of a nanocrystal is directly proportional to the product of effective carrier concentration in a nanocrystal and probability for radiative de-excitation rate, however a single extra free charge carrier can effectively switch a silicon nanocrystal in to "dark" state, in which radiative recombination is unlikely [5]. Due to this phenomena, when the carrier concentration in a nanocrystal increases the probability for radiative de-exciattion rate decreases as a result the internal quantum efficiency goes to zero. On the other hand the internal quantum efficiency is inversely proportional to the number of atoms in the nanocrystal and excitation pump flux, as we expect.

For spherical nanocrystal with diameter d, the internal quantum efficiency has inverse power relation with the diameter as shown in Eq. (12). The power exponent can be determined by material property and range of the nanocrystal being used. This result confirms that the increase in overlap of electron and hole wave functions as consequence of size reduction increases the radiative recombination rate in Si-nc and the improvement in radiative de-excitation channel enhances the internal quantum efficiency drastically.

From the graph of internal quantum efficiency versus size of nanostructure, we can see that as the size of the nanodot gets smaller and smaller the internal quantum effiency increases appreciably and the slope of internal quantum efficiency graph gets steeper and steeper, which indicates that changing the size a little, strongly alters the internal quantum efficiency of the smallest nanocrystal than larger one.

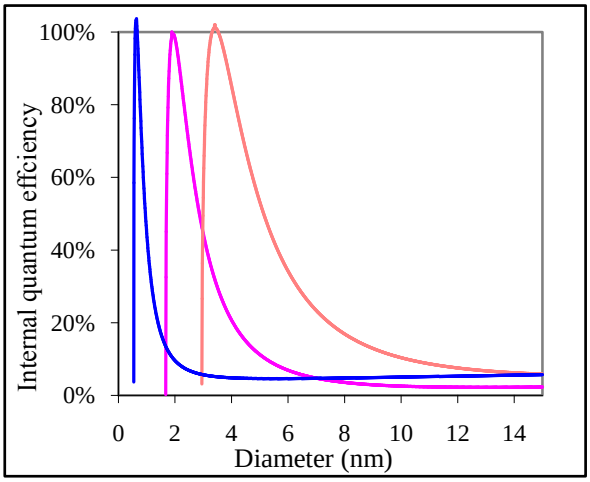

FIGURE 1. The size dependent internal quantum efficiency shift towards the small nanocrystals as the pump flux increase.

We can also see that when the excitation energy increases the internal quantum efficiency graph shift towards smaller nanocrystals, this is due to the fact that smaller nanocrystals which were not active emitters at low excitation energy becomes active emitters when the energy increase and give larger PL energy. However at very high pump flux (blue curve), the population of nanocrystals with internal

quantum efficiency near and at the peak values falls rapidly and very small portion of the nanocrystal will have significant internal quantum efficiency, the rest have nearly zero internal quantum efficiency. This phenomenon decrease PL intensity obtained from nanocrystal and can be explained in terms of Auger recombination which switch on at high pump flux regime.

B. Results of η Versus Wavelength

On the other hand, the normalized internal quantum efficiency versus wavelength graph shows that PL energy and wavelength that we obtain from smaller dots blue shifted with respect to PL spectra from larger dots due to the effect of quantum confinement. When the size of the dot decreases the band gap stretches and photo-excited carriers in the dot at least gain energy in the order of the band gap, therefore PL energy one can get from smaller dots larger, and thus we can tune the emission spectral range across the visible by using proper sized Si-nc.

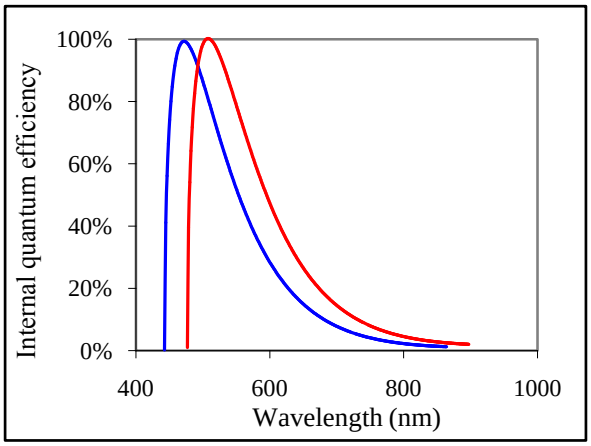

FIGURE 2. The blue shift in wavelength of internal quantum efficiency in the visible region of electromagnetic spectrum when the excitation pump flux increases and size of nanocrystals decrease.

C. Results of τ_{rad} Versus Wavelength

Our result shows that the size dependent radiative lifetime that we obtain in Eq. (5) has a power relation with the diameter of spherical nanocrystal. The power exponent can be determined by material property and range of the nanocrystal being used. These results confirm that miniaturizing the size of nanocrystals increases the overlapping of electron and hole wave functions in position space. This overlapping increases the oscillator strength and radiative lifetime.

Additionally increasing the laser pump flux alters the radiative lifetime drastically as shown in Fig. 3.

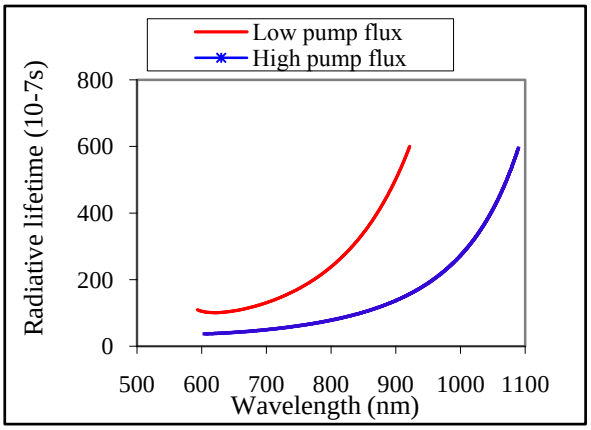

FIGURE 3. The decrease in radiative lifetime as the excitation laser pump flux increases and size decreases.

From the graph of radiative lifetime versus wavelength of emmited photons, one can basically understand that the radiative lifetime gets smaller and smaller as one goes to smaller size of quantum dots due to quantum confinement effect. In addition, we can see the advantage of increasing pump flux on the radiative lifetime. Increasing pump flux up to saturation value significantly enhance the radiative de-excitation rate, and thus it alters the radiative lifetime strongly.

D. Results of d_η^{max} Versus Excitation Energy

Eq. (13) shows that for a given excitation frequency one can optimize the internal quantum efficiency and PL intensity from ensembles of nanocrystal with a given mean diameter.

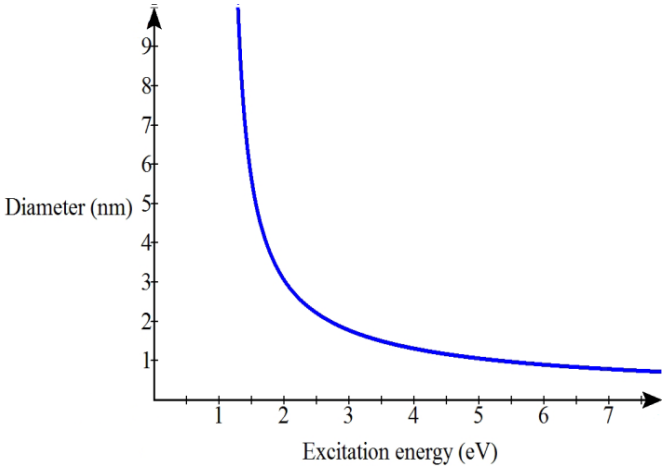

FIGURE 4. The diameter of nanocrystals associated with peak values of internal quantum efficiency decrease as the excitation energy increase.

The graph in Fig. 4 shows the relationship between the diameters associated with peak values of internal quantum efficiency and excitation energy. From this, one can see that those nanocrystals with energy gap closer to excitation energy show maximum internal quantum efficiency, thus to optimize the internal quantum efficiency at given excitation energy it is worth to use appropriate excitation frequency depending up on the energy gap of dominant size distribution in the ensemble of nanocrystals.

IV. CONCLUSION

Our work presents a new approach for the size and pump flux dependence of radiative lifetime and internal quantum efficiency of Si-nc. In silicon nanostructure the phonon assisted indirect band gap transition changes to direct band gap transition and the probability of finding defect and impurity states in the band also minimize, as a result of these the probability for radiative de-excitation rate and quantum efficiency of the nanocryatal increases appreciably. In addition to this, controlling the excitation laser pump flux is also a key to control the luminescence property of a nanocrystal.

Therefore our results confirm that miniaturizing the size of nanocrystal below its characteristics bohr exciton radius, and increasing laser pump flux enhances the radiative lifetime and internal quantum efficiency of Si-nc drastically, hence the ability to tuning the size of nanocrystals is a key to realize nanostructures with novel properties.

It is very important to note that our model is able to predict with what excitation frequency one can optimize quantum efficiency and PL intensity from ensembles of nanocrystal with a given mean diameter.

For the future, it is also worth to look at temperature and pressure dependence optical parameters for other silicon nanostructures (quantum wire, quantum well and etc). We can also extend our model for detailed temperature dependent calculations.

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