THE PHOTOLUMINESCENCE MECHANISM STUDY IN SILICON NANOCRYSTALS: A QUANTUM CONFINEMENT EFFECT (QCE) MODEL INVESTIGATION

Gezahegn Assefa¹ and Mengesha Ayene²
¹,²Department of Physics, Wollo University, Dessie, Ethiopia

Abstract
Studies on the photoluminescence (PL) emission intensity from many of the silicon-based nanostructured systems has attracted extensive interest to identify its mechanism, in particular, in nanocrystalline Silicon (nc-Si). Despite many recent successes in the field of silicon nanostructures, until now, the origin and properties of the PL are not completely understood. Currently, the underlying mechanisms behind the PL are a major source of debate and dispute among scientist communities. The present paper successfully describes the PL mechanism of nanostructured systems from the Quantum Confinement Effect (QCE) model approach. The selected model (QCE model) assigns the PL to quantum size effects in nc-Si core of the nanostructures. It is widely investigated that one of the fundamental parameters describing the PL mechanisms of nc-Si is the radiative recombination rate. The present investigation revealed that the rate of radiative recombination depends on the diameter d of the spherical nano-crystallites; in particular, the finding clearly confirmed that the radiative recombination rate increases with the decrease in the size of the nc-Si. Certainly, these findings from the QCE model are useful to enhance the PL intensity in nc-Si and possibly useful to tune the PL emission intensity into the visible range.

Keywords: silicon nano-crystals, quantum dots, photoluminescence, quantum confinement effect model, radiative recombination rate.

I. INTRODUCTION

The availability of the raw materials and its good mechanical and thermal properties make silicon the semiconductor material of choice the device technology today. The bulk of the Si-wafer is, for example, provides good mechanical support for the fabricated electronic devices, which reside in the region near the wafer’s surface. Metal oxide semiconductor field effect transistors (MOSFETs) can be fabricated from SiO₂. MOSFETs are building blocks of complementary metal oxide semiconductor (CMOS) circuits.

Bulk silicon is characterized by fully filled valance band and entirely empty conduction bands, which are separated by a forbidden range of energies. The gap between valance and conduction band is of fundamental importance. Most properties, such as intrinsic conductivity, electronic transitions or optical transitions depend on it. The properties of the material significantly change with the change of the gap. Since bulk silicon has indirect band gap, the optical process should conserve via a phonon interaction. Although broad spectrum of phonons is available, only those phonons with the required momentum change are functional. Because the indirect transition is a two-step process, it has low transition probabilities. In addition, bulk crystalline silicon is a centro-symmetric crystal that does not show photoluminescence (PL), i.e., it emits light in the infrared region and at a very low efficiency [1, 2]. Optical absorption in semiconductor nanocrystals is different from that of the bulk system. They show much change in their electronic properties down to a very small size, about 10 nm and below [3]. The origin of such alteration of electronic properties is
however still not clear.

The band gap of bulk silicon ($\approx 1.12 \text{ eV}$) is ideal for room temperature operations; however, the discovery of visible PL at room temperature from porous silicon (P-Si) [4] has generated much attention in monocrystalline silicon (nc-Si) because of the possibility of wide application in optoelectronic devices [2].

Recent experimental researches on nc-Si has shown that the band transforms from indirect to direct and the band gap energy is blue shifted into the range of visible light owing to the quantum confinement effect (QCE) [1, 2]. Understanding the role of QCE in altering optical properties of semiconductor materials with reduced dimensions is a problem of both the technological and fundamental interest. There is a great deal of experimental and theoretical evidences that supports the important role played by QCE, in producing PL [5]. Recently it has been noticed that the electron-hole exchange interaction play a vital role in the description of the basic optical properties of nanocrystalline assemblies [6].

Nanocrystal quantum dots (NC-QDs) are chemically synthesized semiconducting particles that show discrete atomic-like electronic level structure and optical transition. NC-QDs usually consist of a crystalline semiconductor core, often no longer than just a few nanometers in diameter and a surrounding shell. The shell provides the confining effect for the core electrons. They are building blocks for a range of photonic applications. Their absorption and emission wavelengths can be tuned by controlling their size as well as their constituent materials. Recently, efforts have been made to design NC-QDs that emit light in the near infrared spectral range [7] due to their importance in optical networking applications and many other optoelectronic uses.

The mechanism responsible for nanosilicon light emission is the matter of great controversy; however, there are different models to explain luminescence from nanosilicon. They can be grouped into three categories. These are the quantum recombination model, the surface state model, and the molecular recombination model [8].

This paper mainly focused on the model of optical transition and formulation of the problem; finally, to discuss how the radiative recombination rate relates to the size of the QD. We use the empirical pseudopotential approach to calculate the Hamiltonian and the optical transition probabilities of silicon nanocrystal. Because in our calculation the wavefunctions of the nc-si can be composed of energy band states of the bulk, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) states, and by assuming that the electronic properties are mostly rely on the valence electrons rather than the core electrons and section four gives the conclusion.

II. MODEL OF OPTICAL TRANSITION AND FORMULATION OF THE PROBLEM

2.1 Model of optical transition

In this paper, the focus is on the quantum confinement model to explain PL emission intensity. NC-QDs usually consist of a crystalline semiconductor core, often no longer than just a few nanometers in diameter and a surrounding shell. The shell provides the confining effect for the core electrons. It has considered that the photoemission occurs inside the NC-QDs with energy gap larger than the bulk silicon due to the QCE.

For PL from these systems, Qin an d Jia [9] suggested a quantum confinement luminescence center (QCLC) model, which claimed that the photoexcitation of electron-hole pairs occurs mainly in NC-QDs. The recombination process is takes place in the luminescence centers (LC). Defining the geometry of NC-QDs is very essential before any theoretical calculations are performed.

In order to formulate and describe the PL phenomena from nc-Si structures, consider nc-Si as ensemble of nanometric size spherical particles (quantum dots), having a well defined size distribution. The optical band gap widening in the crystallites is considered due to QCE in NC-QDs. We assume that both photo excitation and photo emission processes for electron-hole pairs occur in the nanosilicon particles.
Path A: On excitation with high energy photons, photo carriers are generated inside the quantum dots and then relaxed.

Path B: The relaxed carriers recombine radiatively to ground states giving PL emission.

2.2 Radiative Recombination Rate
Optical transition between the LUMO and the HOMO is induced due to the illumination of light.

Since light is an electromagnetic field (EMF) and is assumed to be of the form:

\[ E(t) = E(e^{-i\omega t} + e^{i\omega t}) \]  \hspace{1cm} (2.1)

The wave function of the transition between HOMO-LUMO states of N identical atoms are Bloch wave functions of the form:

\[ \psi_h = \frac{1}{\sqrt{N}} e^{i k \cdot r} U_h(k) \]  \hspace{1cm} (2.2)

\[ \psi_l = \frac{1}{\sqrt{N}} e^{i k' \cdot r} U_l(k') \]  \hspace{1cm} (2.3)

Where, \( \Omega \) refers to the volume element over which the integration is carried out.

Throughout this paper, we shall confine our discussion to the so-called one-particle picture. Thus, we define the total Hamiltonian (\( \hat{H}_t \)) of the system as:

\[ \hat{H}_t = \hat{H}_0 + \hat{H}_l \]  \hspace{1cm} (2.4)

Where, \( \hat{H}_0 = \frac{p^2}{2m} + V(r) \), where \( V(r) \) is Coulomb interaction potential and \( \hat{H}_l \) is the interaction Hamiltonian of the electromagnetic field with the electronic state in the nearly free electron model.

The quantum mechanical Hamiltonian of the system have the form:

\[ \hat{H}_l = \frac{1}{2m} (P + \frac{e}{c} A)^2 + V(r), \]  \hspace{1cm} (2.5)

Where, \( P = -i\hbar \) is the linear momentum operator and \( A \) is the vector potential of the electromagnetic field.

Since \( P \) and \( A \) in quantum mechanics do not generally commute, the total Hamiltonian becomes:

\[ \hat{H}_t = \hat{H}_0 - \frac{i e\hbar}{2mc} (A \cdot \nabla + \nabla \cdot A) + \frac{e^2 A^2}{2mc^2} \]  \hspace{1cm} (2.6)

Since, \( \frac{e^2}{2mc^2} \ll \frac{e^2}{2mc} \),

we neglect second term of equation (2.6) and using the fact that \( \nabla \cdot A = 0 \), equation (2.6) can be written as:

\[ \hat{H}_l = - \frac{i e\hbar}{2mc} (A \cdot \nabla) \]  \hspace{1cm} (2.7)

The matrix element of the transition from HOMO-LUMO state is given by:

\[ \hat{H}_{hl}(r) = \int \psi_h^*(r) \hat{H}_l \psi_l (r) dr \]  \hspace{1cm} (2.8)

Substituting equation (2.5) into (2.6) and using the fact that the Bloch functions in the Brillion zone in two different bands is orthogonal and \( k = k' \) for direct transition, then the matrix element becomes:

\[ \hat{H}_{hl}(r) = - \frac{i e\hbar}{2mc^2} \int U_h^*(k) A \cdot \nabla U_l (k') dr \]  \hspace{1cm} (2.9)

The momentum operator for the transition between HOMO and LUMO state is given by:
\[ P_{hl} = -\frac{ih}{\hbar} \int U_h(k) \nabla U_l(k') \, dr \]  
\begin{align*}
\text{(2.10)}
\end{align*}

Therefore, equation (2.7) can be rewritten as:
\[ \overline{H}_{hl}(r) = \frac{e}{2mc^2} \mathbf{A} \cdot \mathbf{P}_{hl} \]  
\begin{align*}
\text{(2.11)}
\end{align*}

The oscillator strength \( f_{hl} \) which is the measure of the radiative probability of a quantum mechanical transition between two atomic levels is related to the momentum matrix element as:
\[ f_{hl} = \frac{2}{m \hbar \omega} |\mathbf{P}_{hl}|^2 \]  
\begin{align*}
\text{(2.12)}
\end{align*}

Where, \( \omega_{hl} \) is the frequency of the external EMF with energy equal to the HOMO-LUMO energy gap.

The emission and absorption of light by a charged carrier, where an electron or hole is essentially a scattering phenomenon between initial state \( \text{ele} \) and final state \( \text{ele} \). The light (EMF) is the time dependent perturbation, which induces this event. The transition rate, \( \left( \frac{1}{\tau_{hl}} \right) \) from the initial state to final state is given by the Fermi’s Golden rule as:
\[ \frac{1}{\tau_h} = \frac{2\pi}{\hbar} \sum_h |H_{hl}|^2 \delta(E_{hl} \pm \hbar \omega) \]  
\begin{align*}
\text{(2.13)}
\end{align*}

Where, \( E_{hl} = (E_h - E_l) \) is the energy gap between the HOMO-LUMO states.

The Delta function now explicitly contains the photon energy with the minus sign representing absorption and the plus sign representing emission. Substituting equation (2.9) into equation (2.11), we obtain:
\[ \frac{1}{\tau_h} = \frac{2\pi e^2 A^2 \cos^2 \theta}{\hbar m^2 c^2} \sum_h |P_{hl}|^2 \delta(E_{hl} \pm \hbar \omega) \]  
\begin{align*}
\text{(2.14)}
\end{align*}

Where, \( \theta \) is the angle between the vector potential and the momentum operator.

Equation (2.12) can be written in terms of the oscillator strength in equation (2.10) as:
\[ \frac{1}{\tau_h} = \frac{\pi e^2 A^2 \omega_{hl} \cos^2 \theta}{mc^2} \sum_h f_{hl} \delta(E_{hl} \pm \hbar \omega) \]  
\begin{align*}
\text{(2.15)}
\end{align*}

Considering the continuum limit, the total recombination rate can be taken as the integral over the frequency
\[ \frac{1}{\tau_h} = \frac{\pi e^2 A^2 \omega_{hl} \cos^2 \theta}{mc^2} \int \sum_h f_{hl}(E_{hl}) \delta(E_{hl} \pm \hbar \omega) d\omega \]  
\begin{align*}
\text{(2.16)}
\end{align*}

In the volume there may be many states but only those states whose energy difference matched with the frequency of the external EMF would contribute for the transition and for PL. So this would happen for the frequency \( \omega = \omega_{hl} \) and the corresponding energy is \( E_{hl} = \hbar \omega_{hl} \). In addition, using the property of the delta function, equation (2.14) can be written as:
\[ \frac{1}{\tau_h} = \frac{\pi e^2 A^2 \omega_{hl} \cos^2 \theta}{mc^2} \sum_h f_{hl}(\omega_{hl}) \]  
\begin{align*}
\text{(2.17)}
\end{align*}

Where, \( \sum_h f_{hl}(\omega_{hl}) \) is the total oscillator strength.

It is found experimentally that the oscillator strength in the nano-crystallites is dependent on the size as the inverse power law [10, 11].
\[ f_{hl} = \frac{1}{d^\beta} \]  
\begin{align*}
\text{(2.18)}
\end{align*}

Where, \( d \) is the diameter of the spherical crystallites and the power exponent \( \beta \) depends on the material property as well as range of the crystallite size being used, and its value is \( 5 < \beta < 6 \).

If we assume that each atom in the crystallites contributes at least one photo excited carrier, the number of photo-excited carriers \( N_P \) in the dot is proportional to its volume.
\[ N_P \sim \Omega \]  
\begin{align*}
\text{(2.19)}
\end{align*}

Where, \( \Omega = \frac{1}{6} \pi d^3 \) is the volume of spherical quantum dots of diameter \( d \).
Therefore, we can write equation (2.17) as:

\[ N_p \sim d^3 \quad (2.20) \]

Assuming \( N_p \) transitions over the volume of the quantum dot corresponding to each photocarriers in the volume and for every transition the oscillator strength is proportional to \( d^{-\beta} \), so the total oscillator strength over the volume is proportional to \( N_p d^{-\beta} \). i.e.

\[ \sum \left(f_{hi} \omega_{hi}\right) \sim N_p d^3 \sim d^{3-\beta} \quad (2.21) \]

Hence, equation (2.15) is reduced to:

\[ \frac{1}{\tau_h} \sim \frac{\pi e^2 A^2 \omega_{hi} \cos^2 \theta}{mc^2} d^{3-\beta} \quad (2.22) \]

Taking an arbitrary proportionality constant, \( \eta \), which can be determined by considering different properties of the quantum dots, equation (2.20), can be rewritten as:

\[ \frac{1}{\tau_h} = \eta \frac{\pi e^2 A^2 \omega_{hi} \cos^2 \theta}{mc^2} d^{3-\beta} \quad (2.23) \]

On considering all other parameters as a constant except the size of the Si-QD, it is possible to write equation (2.21) as:

\[ \frac{1}{\tau_h} = \frac{\Theta}{d^{\beta-3}} \quad (2.24) \]

Where, \( \Theta = \eta \frac{\pi e^2 A^2 \omega_{hi} \cos^2 \theta}{mc^2} \), is a parameter that can be determined by studying electronic states; intensity of the incident light and the dielectric function of the amorphous matrix on which the quantum dots are embedded.

**III. RESULTS AND DISCUSSION**

The calculated radiative recombination rate, represented in equation (2.22), clearly shows that it depends on the size of NC-QDs. The transition rate is calculated by combining the experimental and theoretical facts. The transition rate means in other word is the recombination rate, because the higher the number of transition per time is the higher the number of recombination per time (i.e. high recombination rate). High recombination rate ascribes high PL intensity. In order to obtain an insight of the size effects of on the PL of Si-QDs, we use the recombination rate as a measure. The PL emission in visible range is observed when optical transitions between HOMO-LUMO gaps are induced. The photoexcitation is due to the illumination of light, and the photoemission occurs when the photocarriers (electrons and holes) recombine radiatively. That is the recombination process is either radiative or non- radiative depending on the recombination rate. If the recombination rate is relatively high, an excited electron-hole can recombine via radiative emission process. If the recombination rate is low the recombination is non-radiative.

The radiative recombination rate is the most important property in the description of the PL in NC-QDs. The radiative recombination rate in NC-Si may be with or without phonon mediated depending upon the crystallites size and the nature of the NC-Si (presence of impurity states). The QCE changes the energy level spectrum in the bulk material into a discrete atomic like spectrum. This may lead to the enhancement of the oscillator strength of the electron-hole pairs (excitons).

The strong QCE in the NC-Si implies that for the excitons created in the NC-Si, there is an increase in the radiative recombination rate. As a result, the quantum efficiency of the system increases. On the other hand non-radiative recombination in the non-radiative nc-Si decreases and the quantum efficiency of this process goes decreases. Since the power exponent of the oscillator strength is greater than 3 as obtained experimentally by Ranjan et. el [13], our calculation shows that the radiative recombination rate increases as the size of the NC-QDs deceases.

Our work is qualitatively in a good agreement with the work of Delerue et. al [12] as they obtained the emitted photon energy depends on the size of particles as

\[ E = 1.17 + \frac{3.73}{d^{1.39}} \]
This verifies that for silicon quantum dots having the same properties, the radiative recombination rate increases as the size of the dot decreases. This shows that there exists a strong PL form lower sized nc-Si particles.

IV. CONCLUSIONS

In this work, the effect of radiative recombination rate on the PL of nc-Si using the QCE method of approach was discussed. The role of QCE is to treat the nc-Si as the atomic like structure. The model enables us to observe clearly the PL from nc-Si. It is a simple approach to understand the variation of PL of nanocrystals with size and provides a very good comparison for experimental results.

The wavefunction used for the HOMO-LUMO state consists of components of the bulk states in the Brouillon zone, so it is convenient for the analysis of the transition property. Thus, this method is suitable for studying the PL emission intensity caused by the QCE. The combination of experimental and theoretical results enables us to develop a picture of nc-Si luminescence. The strong PL of nc-Si is due to exciton confinement energy, the type of recombination process (radiative or non-radiative) and the optical transition oscillator strength (which is inversely proportional to the exciton lifetime). The increase in radiative recombination rate, because of decrease in the size, shifts the PL emission spectrum from infrared (Bulk) to visible region.

In conclusion, the research result presents a new approach for the PL mechanism of nc-Si. In addition, the theoretical result confirms that low dimensional crystallites manifest for stronger PL emission.
REFERENCES

[1] Pavesi and Guardini, Brazilian Journal of Physics 26, No-1(1996)
[2] A. A. Guzelian, U. Banin, A. V. Kadavanich, X. Peng, and A. P. Alivisatos, Appl. Phys. Lett. 69:10, 1432, (1996)
[3] C.N.R.Rao, A.Muller and A.K.Cheetham, The Chemistry of Nanomaterials: Synthesis, Properties and Applications. Vol-2 WILEY (2001)
[4] L.T Canham, App Phys.lett.57, No-10, 1046 (1990)
[5] K.Nisho, J.Koga,T.Yamaguchi and F.Yenezawa, Phys.Rev B 67, 195304 (2003)
[6] A.L.Efros, M.Rosen, M.Kenko, M.Nirmal, D.J.Norris and M.Bawendi, Phys. Rev. B 54, 4843(1996)
[7] N.Tessler, V. Medvedev, M. Kazes, S.-H. Kan, and U. Banin, Science, 295, 1506 (2002),
[8] Lei Lin,C.S. Jayanthi and Shi-Yu Wu, Appl. Phys, 90, 4143 (2001)
[9] G.G.Qin and Y.Q.Jia, Solid state Communication, 86, 559 (1993)
[10] V. Ranjan,Vijay A. Singh ,George C. John, Phys.Rev.B 58 ,1158-1161(1998)
[11] M.S.Hybertsen, Phys.Rev.Lett.72.1514(1994)
[12] C.Delerue, G.Allan, and M. Lannoo, Phys Rev.B 48, 11024(1993)