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Photoluminescence from Silicon Nanostructures

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***Abstract* – Bulk silicon (Si) and germanium (Ge) have an indirect band gap transitions however when they are miniaturized to Nanometer scale, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) increases, and hence the transition changes to direct due to confinement. The HOMO-LUMO gap determines the excitation of electrons so that the Nano structures will emit light. When the size of quantum dot decreases the surface area to volume ratio increases and localized surface states appears in the forbidden region. Exciton energy states are also exists in the same gap region. We have explicitly integrated these effects in a phenomenological model to obtain an analytical expression for the photoluminescence spectra. We presented also the parameters that tune the photoluminescence intensity of Si nanostructure. Finally we developed a model that could explain experimental results of Si Nano crystal photoluminescence versus size and wavelength by using mat lab programming**

***Keywords* – Photoluminescence, Nanostructures, Quantum Confinement, Recombination.**

I. Introduction

Studying photoluminescence (PL) and understanding its mechanism has tremendous attention to optoelectronic applications. Silicon is the most wide spread semiconductor in modern microelectronics technologies. Its natural abundance, low cost, and high purity, as well as the high electronic quality of silicon interface, have led to its overcoming dominance in microelectronic devices. Nevertheless, the use of silicon in optoelectronic remains highly limited.

Visible photoluminescence property from germanium (Ge) nanostructures at room temperature has been reported over years [1]. Quantum confinement effects play an important role in optical absorption and luminescence semiconductor nanostructures [2], gas evaporation [3], magnetron co sputtering [4], cluster-beam evaporation [5] and so on. In recent years, laser ablation is used for many application system and production of local nanostructures [6].

Si is widely used in semiconductors because, it remains semiconductor at higher temperature than the semiconductor Ge and its native oxide it is easily grown in furnace and forms a better semiconductor /dielectric interface than any other material [7].

The band gap in bulk Ge and Si are connected by indirect transitions, light emission in these materials are naturally phonon mediated process [8]. Si is the leading material concerning high density electronic functionality, its band gap (1.12 eV) is ideal for room temperature operation, In bulk Si competitive non-radiative recombination rates are much higher than the radiative ones and most of the excited electron-hole (e-h) pairs recombine non-radiatively. This yields very low internal quantum efficiency for Si luminescence. What concerns the lasing of Si is, its fast non radiative process such as Auger or free carrier absorption severely prevent population inversion at high pumping rates needed to achieve optical amplification [9]. The alloy composition of Si and Ge remains indirect; there is a little motivation from optoelectronic device considerations to grow the alloy: however, there has been great interest in this alloy since it can be a component of Si-SiGe structures and allow hetero-structure concepts to be realized in Si technology [10].

The main objective of this work is to study photoluminescence properties of Si and Ge nanostructures, to describe formation mechanisms of PL from Si and Ge nanostructures and to study the dependence of PL intensity with different parameters.

II. Optical Properties of Silicon and Germanium Nanostructures

Photoluminescence (PL) is one of the optical properties of semiconductor nanostructures. It is a process in which a substance absorbs photons and then re-radiates photons. Quantum mechanically, this can be described as an excitation to a higher energy state and then return to a lower energy state accompanied by the emission of photon. In other words, it is the emission of light beam from semiconductors mainly when electrons and holes recombine. When electrons in the valence band exposed to a high-power laser will leave their orbits until the average energy drops to the bottom of the conduction band. Usually at this stage attraction of the holes over comes the electrons and they recombine at the same time emits photons of energy equal to band gap energy.

PL extends from 600 nm to 1000 nm [11]. The excitation source is laser with photon energy larger than band gap energy Eg. Electrons and holes relax rapidly by interacting with photon or phonon with lattice vibrations of electrons-phonon coupling 100 fs: much faster than the radiative life time [12].

The photoluminescence from p-Si is at wavelength ranging from the ultraviolet to the infrared [12]. The PL is usually excited by a wavelength shorter than the emission wavelength with excitation wavelengths typically lying between 260nm (for ultraviolet emission and approximately 520nm [13]. PL can be excited through an up conversation process by pumping the p-Si at the infrared wavelengths [14.15].

The characteristics of PL changes as the wavelength of emission changes from ultraviolet wavelength to infrared

wavelength. A specific characteristic normally applied to a discrete set of wave lengths in to three bands to describe these characteristics. The main characteristic of each of wavelength bands called the "red" "blue" and "infrared" bands. Normally it is very difficult to compare one's own result of luminescence investigations with those of another author due to the use of relative units for intensity. To overcome this problem, integral features of spectra such as peak areas can be given in terms of efficiency [16].

The PL peak energy as a function of diameter of Si nanoclusters can be obtained by fitting the relationship between PL peak energy and diameter of Si nanoclusters, the dependence of the associated energy-gap E (eV) on the diameter (d) nm of the Si nanoclusters can be expressed as [17]:

$$E(ev) = 1.17 + \frac{11.6}{d^2} \quad (1)$$

Eq (1) can be substituted in the QC model to get the luminescence intensity.

The photoluminescence arising from implanted Si nanocrystals in SiO_2 has been attributed by some investigations to quantum confinement [18], [19], while others have concluded that surface states present in the inter-facial layer between the Si nanocrystals and the surrounding oxide matrix play an important role in the emission porous [16]. more recently, oxidation effects photoluminescence from Si nanocrystals fabricated by laser ablation have been reported [16].

III. Methods and Formulation of Models

The methodology applied for this study is Review article with optimal utilization of available resources and matlab program. The procedure is using experimental result we develop an equation to express the result and plot the graph using matlab program. Finally we compare the them and draw conclusions.

There exist two classes of explanation for the origin of the visible PL, the quantum conferment effects and the surface state effects. Here we consider the Quantum confinement model effects for our system.

This model is based on the electronic confinement in dot like structure of Si. The development of this model is based on the effective mass approximation theory. In this model, the luminescence process is attributed to an energy shift of carriers (electrons and holes) and is proportional to L^{-2} L being the Si-nc diameter [20], [21], [22], [23].

Assuming that a Gaussian size distribution about the mean diameter L_0 for the nanocrystallites:

$$I(L) = \frac{1}{\sqrt{2\Pi\sigma^2}} \exp - \frac{(L - L_0)^2}{2\sigma^2} \quad (2)$$

The number of electrons in a column diameter L participating in the PL process is proportional to L^2 . The heights of the columns depend only on the growth time and are approximately the same. Hence

$$N_e \sim L^2 \Rightarrow N_e = bL^2 \quad (3)$$

For P-Si sample consisting of varying column diameters the probability distribution of electrons participating in the PL process is:

$$I_e(L) = \frac{1}{\sqrt{2\Pi\sigma^2}} N_e(L) \exp(-\frac{(L - L_0)^2}{2\sigma^2} \quad (4)$$

$$I_e(L) = \frac{1}{\sqrt{2\Pi\sigma^2}} bL^2 \exp(-\frac{(L - L_0)^2}{2\sigma^2} \quad (5)$$

where b is a suitable normalization constant. The luminescence intensity can be determined by the Fourier transform of eq (1) to the energy axis as:

$$I(\Delta E) = \int I(L)\sigma(L) - \frac{C_1}{L^2})dL \quad (6)$$

$$I(\Delta E) = \frac{1}{\sqrt{2\Pi\sigma^2}} \int \delta(\Delta E - \frac{C_1}{L^2})L^2 \exp(-\frac{(L - L_0)^2}{2\sigma^2} dL \quad (7)$$

The Dirac delta function facilitates a straight forward integration.

Putting $y = \frac{C_1}{L^2}$ and apply the properties of Dirac delta function, the above integral will be transformed in the form.

$$I(\Delta E) = \frac{1}{2} \frac{bC^{3/2_1}}{\sqrt{2\Pi\sigma^2}} \int [\sigma(\Delta E - y) y^{-5/2}]^2 \exp(-\frac{(-L_{0^2})}{2\sigma^2} (L_0 \sqrt{\frac{C_1}{y}} - 1)^2$$

The above integral gives the intensity as a function of ΔE

$$I(\Delta E) = \frac{bC^{3_1}}{\sqrt{8\pi\sigma^2}} \Delta E^{-5/2} \exp(-\frac{-L_{0^2}}{2\sigma^2} \left[(\frac{\Delta E_0}{\Delta E})^{1/2} - 1 \right]^2 \quad (8)$$

Where ΔE is the energy shift due to the confinement given by

$$\Delta E = h\nu - (E_g - E_b) \quad (9)$$

E_g being the bulk band gap of Si or Ge and E_b is the exciton binding energy, and $\Delta E_0 = \frac{C_1}{L_{0^2}}$, being the nanocrystal mean diameter and δ standard deviations. The values of E_g ranges from 1.11eV to 1.17 eV for Si, depending on temperature; however, we took 1.12ev for Si and 0.7ev for Ge which is actually reported in most standard experiments at room temperature, while the value of E_b varies with nanocrystal radius of the sample ranging exponentially from 0.05ev (r-5nm) to 0.24ev (r-1nm).

According to the QC model, the emission wavelength and intensity depends on nanocrystal diameter, size distribution and concentration. This model can explain the general tendency of most experimental results such as the blue shift of the luminescence spectrum with decrease of the Si-nc size. The QC model is highly predictive when the nanoclusters are associated from the matrix (ex: Si-nc isolated from SiO_2). Consequently this model does not give a satisfactory explanation for the evolution of the luminescence spectra for some experimental parameters such as the PL for sample temperature below look, as well as oxidation or oxygen passivation of samples containing

Si-nc. Due to this reason we used another model for terminated Si-nc [24].

In this chapter we will study the results of PL intensities for Si nanostructures as a function of different parameters. We used the quantum confinement model and develop matlab program to compute the PL intensity as a function of different parameters and we fit most of our results with experimental results reported in many experimental researchs.

IV. Results and Discussion

4.1 Dependence of PL intensity on wavelength for different δ s

Fig.1 Shows the PL intensity as a function of wave length for both Si and Ge nanostructures. As we can see from the figure, the PL intensity for both nanostructures seems to be almost similar since they have band structure except a light change in the band gap energy. The standard deviation from the mean crystallize (which in fact contains the dependence of PL intensity on size influence on the intensity.

Putting different values of sigma suppresses the nature of the luminescence intensity that would have been on the smaller value of sigma in the spectrum of luminescence intensity versus wavelength. This is as expected because the PL intensity depends on the emitted photon energy, not to the number of emitted photons.

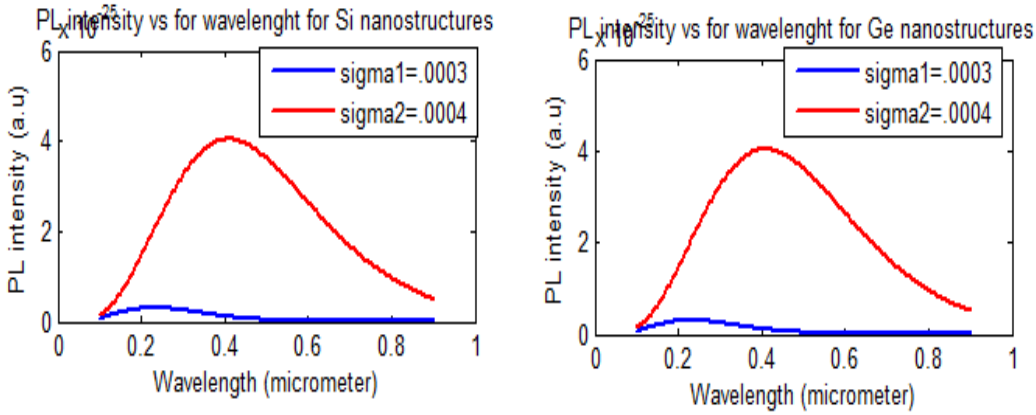

Fig.1. PL intensity versus wavelength for Si and Ge nanostructures[26]

4.2 Photoluminescence properties of silicon nanocrystal as function of size.

Table 1: Characteristics parameters and PL properties of the different nc-Si samples Studied [24].[25]. The values derived from Gaussian fits to the experimental Data.

Sample Identifier	Average size (nm)	Width of size distribution (nm)	PL. Max. (eV)	PL Max. (nm)	PL width (nm)
A	3.44	1.02	1.82	680	190
B	3.46	0.63	2.03	610	165
C	3.88	0.61	1.75	710	155
D	4.05	0.62	1.65	750	150
E	4.45	0.78	1.55	800	145
K	2.8	0.86	1.95	635	115
L	3.2	1.08	1.71	725	145
M	3.6	1.16	1.44	860	170
N	4.8	1.16	1.35	900	200

Table 2. Modified model result: Characteristics parameters and PL properties of the different nc-Si samples.

Sample Identifier	Average size (nm)	PL. Max. (eV) Experimental	PL. Max. (eV) result for our model	PL. Max. (nm) Experimental	PL. Max. (nm) result for our model
A	3.44	1.82	1.7021	680	728.496
B	3.46	2.03	1.6969	610	730.728
C	3.88	1.75	1.6025	710	773.774
D	4.05	1.65	1.5709	750	789.339
E	4.45	1.55	1.5709	800	822.318
K	2.8	1.95	1.9166	635	646.965
L	3.2	1.71	1.7705	725	700.352
M	3.6	1.44	1.6625	860	745.848
N	4.8	1.35	1.4629	900	847.613

4.3 Strong confinement energies.

where $R \leq a_B$, strong confinement regime, the confinement effect dominates and the electron and hole will be viewed as individual particles predominantly in their respective ground states with only little spatial correlation between them[13].In this confinement regime, unlike the weakly confined exciton we can take the effect of confinement potential V(r_e, r_h) in to account. Hence, the Hamiltonian of an exciton strongly confined in QD of radius is given by:

$$H = \frac{P^{2e}}{2m_e} + \frac{P^{2h}}{2m^h} - \frac{e^2}{\varepsilon(r_e - r_h)} + V(r_e - r_h) \qquad (10)$$

where r_e, r_h are the position of electron and holes respectively, and V(r_e, r_h)=}0 if

$r_e, r_h < R$ } ∞ otherwise

So, the poison of the lowest exciton energy state has expressed [30] as

$$E_{lsls} = E_{g_{bulk}} + \frac{\pi\hbar^2}{2\mu R^2} - 1.786\left(\frac{a_B}{R}\right)E^{RY} - 0.248E^{Ry}$$

where the second term corresponds to the sum of the single particle ground state energies (kinetic energies), the third term the coulomb attraction and the last term one for spatial correlation between the two particles.

On the other hand, using the band gap energy expression for the lowest exciton energy we find:

$$E_{lsls} = E_{g_{QD}} - 1.786\left(\frac{a_B}{R}\right)E^{RY} - 0.248E^{Ry}$$

From such expression, we understood that the exciton binding energy should be

$$b = 1.786\left(\frac{a_B}{R}\right)E^{RY} + 0.248E^{Ry}$$

Now, using quantum confinement model we obtain the following band gap energy expression:

$$E^{QD_g} = E_{g_{bulk}} + \frac{B}{d^\gamma} - 1.786\left(\frac{a_B}{R}\right)E^{RY} - 0.24E^{Ry}$$

We use this expression for the photoluminescence spectra. Now, taking the oscillator strength into account, the radiative transition probability in quantum dot of diameter d becomes

$$p(d) \sim fN_r \sim d^2$$

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

$$I(d) \sim p(d)\, n(d) \qquad (11)$$

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

$$E_{PL} = E_{g_{bulk}} + \Delta E - E_b - E_s$$

According to quantum confinement model that band gap up shift can be modeled as $\Delta E = \frac{B}{d^\gamma}$, where β and γ are constants due to quantum confinement effect,their magnitude strongly depend up on the band gap calculation method being employed.

In this section, we will discuss the experimental results in terms of size effects in the frame work of the quantum confinement model. In this theory, the PL energy is blue shifted with respect to the band gap of bulk silicon (Eo=1.17ev) and obeys a power law with an exponent equal to -1.39 for particle diameter d measured in nanometers.We transform eq.(6.1) from d to ΔE dependence [19]as

$$I(\Delta E) = \int I(d)n(d)\delta\left(\Delta E - \frac{\beta}{d^\gamma}\right)dd \qquad (12)$$

Taking $n(d) = \frac{1}{\delta\sqrt{\pi}}\exp\left(-\frac{(d-d_0)}{2\delta^2}\right)^2$ where d_0 and δ are the mean dot and standard deviation respectively. So, we obtained an expression for the photoluminescence intensity as

$$I(\Delta E) = \frac{1}{\delta\sqrt{\pi}}\left(\frac{\beta}{\Delta E}\right)^{2\gamma}\exp-\left\{\frac{\left(\frac{\beta}{\Delta E}\right)^{1\gamma} - d_0}{2\delta^2}\right\}^2 \qquad (13)$$

Eq.(13) gives general expression for photoluminescence intensity from Silicon quantum dots ensemble. It is clear from the above expression that the photoluminescence intensity depends strongly on the quantum confinement parameters β and γ .We took, $\gamma = 1.39$, $\beta = 3.73$ and $E_{g_{bulk}} = 1.12eV$ at room temperature[5]

4.4 Photoluminescence intensity versus size (Silicon nanocrystal).

Different experiments have performed on silicon nanocrystals to see the effect of quantum confinement and surface states. Fig. 2 and Fig.3 shows the photoluminescence spectra of different samples studied with their size distribution as measured by time-of-flight mass spectroscopy (TOFMS) together with results of our model i.e. normalized photoluminescence intensity versus dots size, for experimental and results of our model for two set of samples

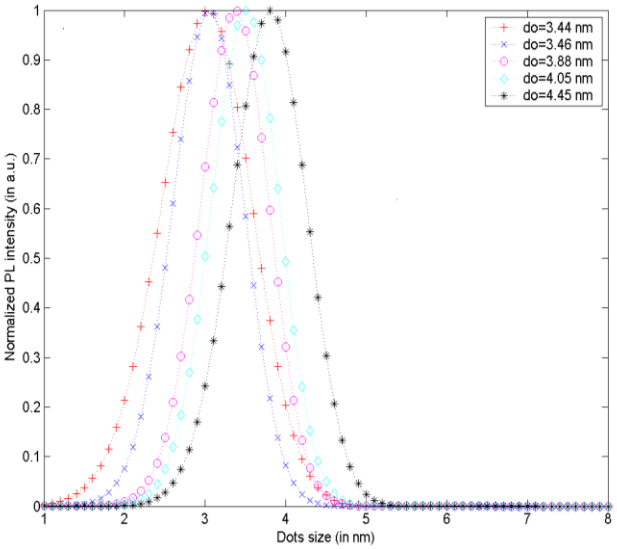

Fig.2. Normalized PL intensity versus nano cluster size (A-E)

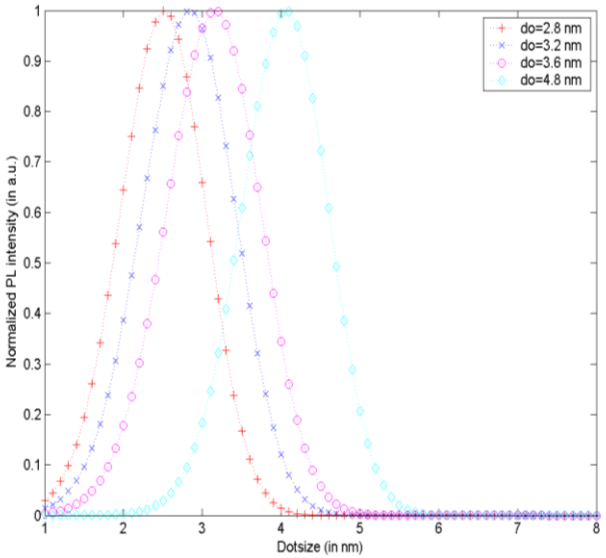

Fig.3. Normalized PL intensity versus nano cluster size (K-N)

4.5 Photoluminescence intensity versus wavelength for Si nanostructures

The photoluminescence spectra of different samples studied with their size distributions as measured by time-of-flight mass spectroscopy (TOFMS) together with results of our model. From such plots, we understand that as the average size of the sample decreases the optical band gap increases so that the photoluminescence peak shifts to the shorter wavelength range of visible spectrum. Since, the luminescence energy is directly proportional to the optical band gap and inversely proportional to wavelength. Therefore, as the optical band gap increases the luminescence energy increases or wavelength decreases mostly to the shortest wavelength of visible spectrum.

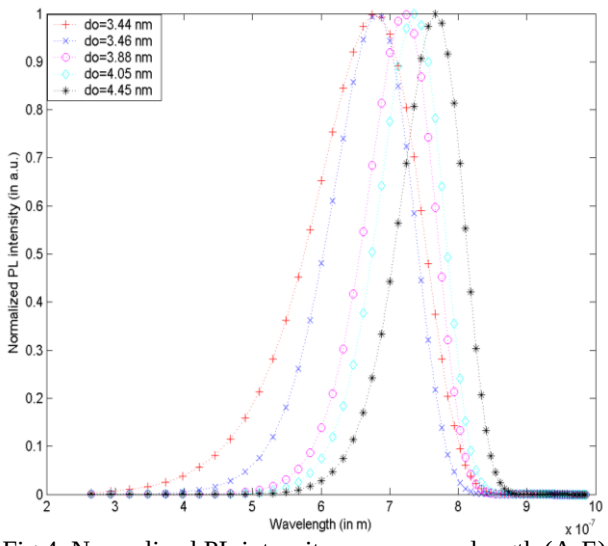

Fig.4. Normalized PL intensity versus wavelength (A-E)

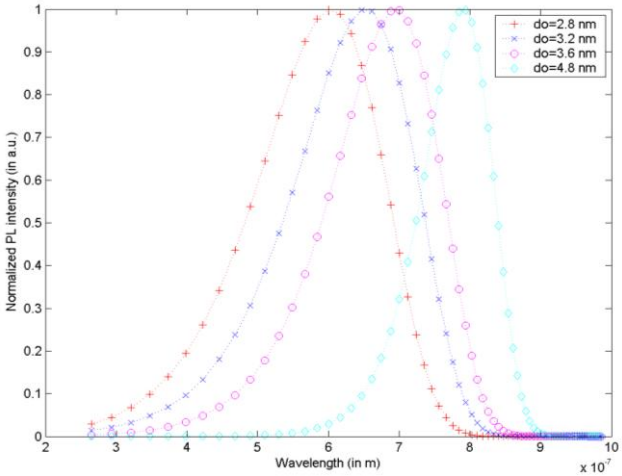

Fig.5. Normalized PL intensity versus wave length (K-N)

V. CONCLUSION

As the size of the quantum dot decreases the effect, become more robust. Our observation is in agreement with many experimental and theoretical observations. Based on our study, taking the effect of existence of exciton energy states in the forbidden region on optical band gap describes better the experimental photoluminescence data from silicon quantum dots developed by several experimental techniques. Therefore, our study shows that the importance of exciton energy levels for predicting the photoluminescence data from silicon quantum dots using quantum confinement and surface states models together. Hence, the result we obtained could apply for controlled light emitting properties in photonic material production.

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