Analytical Model of Photoluminecsence from silicon nanocrystals embedding in amorphous matrix

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In this work, we propose a model to calculate photoluminescence spectrum of silicon nanocrystals embedded in amorphous matrix. Our model considers that the nanocrystals are surrounding by a non-abrupt transition region and immersing in optically active matrix. The transition region plays a key role in the photoluminescence with a quantum confinement. Results show that the proposed model ameliorate well the photoluminescence peak position.

Keywords; Silicon nanocrystals; photoluminescence; SiN matrix.

I. INTRODUCTION

Since the discovery of efficient visible light photoluminescence (PL) in porous silicon [1], there has been renewed interest in the emission properties of all kinds of quantum-sized structures. The most natural explanation of the strong PL is the quantum confinement effect (QCE) [2], which seems to be confirmed by the calculated radiative lifetimes [3], [4], and by the existence of phononstructures [5] in the excitation spectrum of the photoluminescence, showing full similarity with bulk crystal.

Embedding in amorphous matrix, Silicon nanocrystals (Si-nc) have attracted a special attention: many researchers have investigated the light emission from a silicon nanostructure embedded in silicon oxide films due to its easy processing, robustness and stability in comparison with porous materials and its full compatibility with mainstream complementary metal oxide semiconductor [1]. However, this material has a low efficiency of carrier injection because of a relatively high potential barrier of 9 eV. Recently, in order to increase the injection efficiency of carriers, silicon nitride (SiN_x) films having an embedded silicon nanostructure have been studied extensively [6], as they have a lower potential barrier (5 eV)

than silicon oxide [7]. Fabricated via plasma enhanced chemical vapor deposition (PECVD), the photoluminescence was tuned from the near infrared to the ultraviolet just by adjusting the composition of the process gases [6-8]. Recently, hydrogenated amorphous silicon containing silicon nanocrystals has been investigated as a possible candidate for the production of inexpensive solar cells [9].

Several techniques have been invented to produce amorphous matrix embedding silicon nanocrystals (Si-nc). Some of these techniques are plasma assisted chemical vapor deposition [10-11], size selected cluster deposition [12], sputtering [13], laser ablation [14-15], catalytic chemical vapor deposition (Cat-CVD) [7], and ion implantation into matrices [16].

Despite the great number of papers devoted to the study of light emission from silicon nanostructures, the origin of room temperature PL from Si-nc have not yet completely understood. It generally accepted that the quantum confinement effect in the nanocrystallites opens up the band gap as well as relaxes the selection rules for radiative transitions giving rise to above band gap PL in the visible region for crystallite sized below 5 nm [2]. However, QCE alone cannot explain the PL. The puzzling problem is the large difference between luminescence energies and calculated band gap. This difference corresponds to a huge stokes shift (~1 eV for crystalline diameter d~1.5 nm).

Many different finding have been reported to explain the PL phenomenon: some of these are the gap states due to the voids and defects observed by wolkin et al [17], siloxane model and derivative materials [18], the interface state postulated by Koch et al [19], curved surfaces of Si-nc shape, [20] and temperature effect [21].

Allan et al [5] have demonstrated, from both empirical tight binding and first principle locale density calculations that some states exist under the form of "self-trapped excitons" at the interface between the Si-nc and the amorphous matrix supposed sharp. Daldasso et al [22] present an experimental – theoretical study of light emitting from Si-nc embedded in Silicon dioxide (SiO_2). They provide evidence that the Silicon/Silicon dioxide interface is not sharp but a transition region (SiO_x) composed of amorphous Silicon (Si) and a strained SiO_2 surrounding the Si-nc. Their experimental investigation shows that the transition region participates to the light emission process. Ab-initio density functional calculations indicate that the strained SiO_2 layer around the Si-nc introduces optically active state.

The present contribution propose a model to calculate the PL intensity from Si-nc embedding in SiN_x matrix. Indeed, we find first, the transition region thickness enveloping Si-nc. Then, we confirm that the QCE alone cannot explain the light emitting phenomenon. The nanostructures shape, the transition region surrounding Si-nc contribute also to the PL.

II. A MODEL FOR PHOTOLUMINESCENCE PROFILE

In order to formulate and describe the PL spectra from Si-nc structures, we consider Si-nc as an ensemble of nanometer sized spherical particles having a well Gaussian or log-normale size distribution [23], surrounding by a transition region. Figure.1 show a transition region between Si-nc and the amorphous matrix.

The optical band gap widening of the crystallites is considered due to QCE in nanoparticles. The magnitude of band gap widening is determined using the analytical expression for band gap obtained from the tight binding method [2].

Figure 1. Transition region surrounding Si-nc

Under excitation with appropriate energy photons, a fraction of photocarriers generated recombine inside a nanocrystal and the rest at a transitive region.

The oscillator strength that is the dimensionless quantity expressing the strength of transition in crystallites from one quantum state to another in Si atom, when absorbing light. It exhibits extremely sharp dependence on the size. It is

expected that a small fraction of the nanocrystals may be responsible for the disproportionally large portion of the output radiation.

Under the above assumption, the PL intensity at particular photon energy becomes proportional to the population in the nanocrystal and it transition region, and to the oscillator strength.

The number of states in the transition region is proportional to its volume V_T.

If N_{VT} is the total number of states in the transition region, then:

$$N_{VT} \alpha V_T = \frac{4}{3}\pi(R^3 - r^3) \qquad (1)$$

Further, by assuming that each atom in a crystallite contributes to the carrier generation, at least one, the number of photoexcited carriers N_V in a crystallite is proportional to its volume V.

$$N_V \alpha V = \frac{4}{3}\pi r^3 \qquad (2)$$

The photoexcited carriers inside a nanocrystal relax to the surface states, and recombine radiatively in the transition region assumed to be optically active [24]. Since the migration rate from of an excited carrier to the transition region is proportional to the product of the number of excited photocarriers and the number of available empty transition region states, the population N_r of photocarriers in a transition region participating in PL process becomes proportional to the product of N_{VT}, and N_V:

$$N_r \sim V.V_T \alpha A.r^3.(R^3 - r^3) \qquad (3)$$

The radiative rate transitions depends on the oscillator strength (OS) [25] as:

$$OS \sim \left[\frac{1}{1-(0.86r/a)^2} \cdot \frac{sin(0.86\pi r/a)^2}{0.86\pi r/a}\right] \qquad (4)$$

Where a is the lattice constant taken 5.66Å for Si

Taken the oscillator strength into account, the radiative transition probability in a nanocrystallite becomes:

$$P(r) \sim N_r.OS$$

$$\sim r^3.(R^3 - r^3)\left[\frac{1}{1-(0.86r/a)^2} \cdot \frac{sin(0.86\pi r/a)}{0.86\pi r/a}\right]^2 \quad (5)$$

Equation 5 depend very strongly, only on the smallest dimension of Si-nc. For d>a this dependence approaches r^{-6}. As a result even a small fraction of nanocrystals being abnormally short can be responsible for the large change in the emission spectrum. In the other hand, if $0.86\pi\, r/a$ is

small, the dependence became proportional to r⁻⁴, the increase of OS persist but moderately (figure.2).
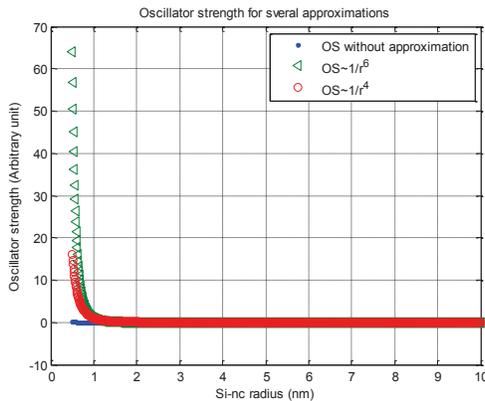
Figure 2. Oscillator strength shape with several approximations

Zooming the oscillator strength curve without approximation (figure.3):
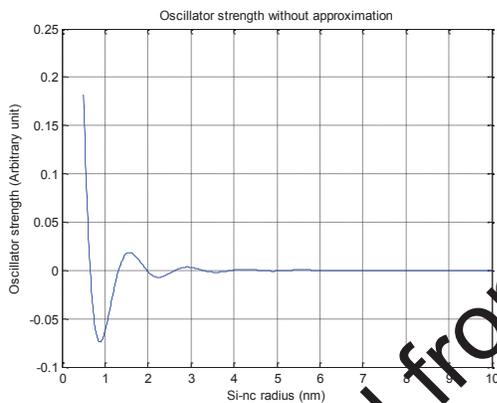
Figure 3. Oscillator strength shape

Now, the PL intensity from an ensemble of crystallite having size distribution $\varphi(r)$ may be obtained by summing the contributions from all the crystalites having size r. the PL intensity from crystallites of size r may be given by:

$$I(r) \sim P(r) * \varphi(r) \qquad (6)$$

We need to manipulate the PL intensity variation with energy and not with the Si-nc radius. Why we will substitute the Si-nc radius with a formula contain energy so:

The emitted photon energy from a nanocrystal will be lower than the band gap energy of the crystallite (E_{bulk}) in a bulk form by an amount (ΔE). This amount is a function of diameter r [2] as:

$$E(R) = E_{bulk} + \frac{h^2\pi^2}{2r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.78.e^2}{\varepsilon_r r} + 0.284E_R$$

(7)

Where m_e, m_h, E_R, and ε_r are, respectively, electron masses, hole masse, the Rydberg energy, and dielectric permitivity for bulk silicon

$$E_R = \left(\frac{13.606 m_0}{\varepsilon_r^2\left(\frac{1}{m_e^*} + \frac{1}{m_n^*}\right)}\right) \text{ en eV}$$

$\frac{1.78.e^2}{\varepsilon_r r}$ is the Coulomb term and $0.284 E_R$ gives the spatial correlation energy and is a minor correction.

Equation (7) can be written as [20]:

$$E(R) = E_{bulk} + C/(r^n) \qquad (8)$$

Where C is the confinement factor, r is the silicon nanocrystal radius, and n is constant depend on the used method.

Park et al [7] found E_{bulk} = 1.56 eV and c = 2.40 nm², whereas Kim et al. [27] used E_{bulk} = 1.16 eV and C = 11.8 nm²
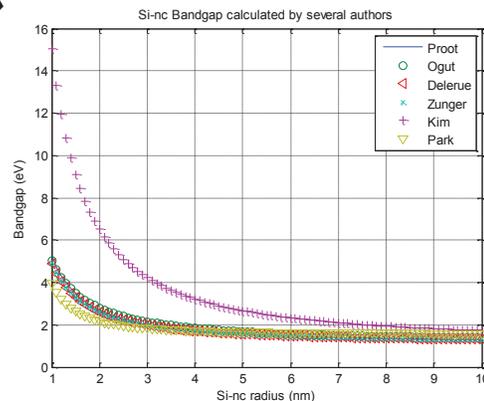
Figure 4. Silicon band gap increasing with radius decreasing calculated by several authors [5,27-30]

Figure.4 show the silicon band gap calculated by several authors. From radius 6 nm, we obtain the band gap energy for silicon in bulk form. At below of this value, we have an enlargement of bandgap due to the QCE producing direct radiative transitions between the conduction and valence bands.

The PL is then determined by transforming equation 6 to the energy axis as commonly done:

$$I(\Delta E) = \int I(r)\delta(\Delta E - C/r^n)dr$$

$$\sim (R^3 - r^3). \left[\frac{sin\left(\frac{0.86\pi r}{a}\right)^2}{\left(1 - \frac{0.86\pi r}{a}\right)*0.86\pi r/a} \right] \varphi(r). \delta \left(\Delta E - \frac{c}{C^n}\right) dr$$

(9)

The Dirac delta function (δ) facilitates a straightforward integration [31].

The simplest idea is to assume that the crystallites are spherical with a Gaussian diameter's distributions, represented by:

$$\varphi(r) = \frac{1}{\sigma\sqrt{2\pi}} exp\left[-\frac{(r-r_0)^2}{2\sigma^2}\right] \qquad (10)$$

Where r_0 and σ are the mean crystallite size and standard deviation respectively for the Si-nc ensemble.

Putting equation (10) into equation (9), we obtain the PL expression as:

$$I(\Delta E) = \frac{1}{c\sigma}\left(\frac{C}{\Delta E}\right)^{\frac{4-n}{n}} . \frac{sin(0.86\pi r/a)}{\left(1 - \frac{0.86\pi r}{a}*0.86\pi r/a\right)} . \left(3d^2 \left(\frac{C}{\Delta E}\right)^{\frac{1}{n}} + \right.$$

$$\left. 3d\frac{C}{\Delta E}^{\frac{2}{n}} + d^3\right) exp\left[-\frac{\left\{\left(\frac{C}{\Delta E}\right)^{\frac{1}{n}} - r_0\right\}^2}{2\sigma^2}\right] \qquad (11)$$

Where d is the transition region size.

For a log-normale size distribution of particles sizes:

$$\varphi(r) = \frac{1}{\sigma\sqrt{2\pi}r} exp\left[-\frac{\{Ln(r)-Ln(r_0)\}^2}{2\sigma^2}\right] \quad (12)$$

The PL intensity expression transforms to:

$$I(\Delta E) = \frac{1}{c\sigma}\left(\frac{C}{\Delta E}\right)^{\frac{3-n}{n}} . \frac{sin(0.86\pi r/a)}{\left(1 - \frac{0.86\pi r}{a}*0.86\pi r/a\right)} . \left(3d^2 \left(\frac{C}{\Delta E}\right)^{\frac{1}{n}} + \right.$$

$$\left. 3d\frac{C}{\Delta E}^{\frac{2}{n}} + d^3\right) exp\left[-\frac{\left\{Ln\left(\frac{C}{\Delta E}\right)^{\frac{1}{n}} - Ln(r_0)\right\}^2}{2\sigma^2}\right] \qquad (13)$$

We clearly observe from equations (11) and (13) that PL intensity, strongly depends on QCE (c and n parameters), the transition region size (d), and the crystallite size distribution (OS formula).

III. SIMULATION

Our investigation calculate transition region thickness enveloping Si-nc embedding in SiN$_x$ matrix, and then highlights the PL.

However imaging Si nanocrystals embedding in amorphous matrix and building reliable size histograms is a difficult task because of the small difference of atomic number and density between Si and SiN$_x$ matrix. To solve this problem we have proposed a method used OTSU algorithm based on very simple idea, find the threshold of sample image that minimizes the weighted within-class variance of histograms. The algorithm assumes that the image to be thresholded contains two classes of pixels or bimodal histograms, and then calculates the optimum threshold separating those two classes: the object (Si-nc) and the content (amorphous matrix) to calculate the size distribution.

A. Transition region thickness of Si-nc

In order to evaluate the transition region thickness between Si-nc and SiN$_x$ matrix, we consider that the image histogram have a trimodal gray level distribution. Our aim is to separate the Si-nc from the matrix, and to isolate the transition region surrounding Si-nc from the matrix.
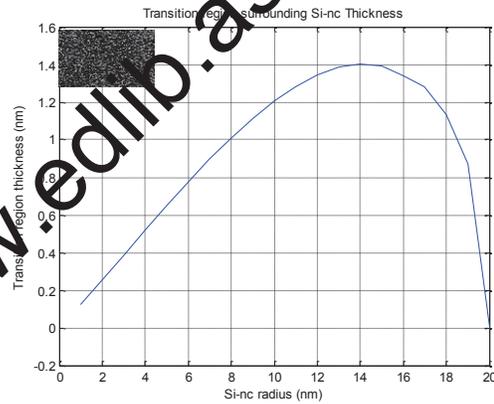
Figure 5. The thickness of the transition region surrounding Si-nc

Figure.5 shows the thickness of the transition region enveloping Si-nc formed by defects (Si-Si and N-N bonds, and Si and N dangling bonds.), in which this thickness increase with Si-nc radius increasing for small nanostructures ($r \leq 14$ nm). This is can be explained by the defects formed on the curved surface of smaller Silicon quantum dots [20, 32]. For Si-nc radius ≥ 15 nm, the shape of the nanostructures at the interface became facet and not curved. With a suitable annealing, the most part of the defects are removed from the interface Si-nc/matrix minimizing hence the thickness of the transition region [20].

B. Transition region effect in the PL spectrum

In order to obtain an insight into the effect of various parameters influencing the PL spectral profile in Si-nc, we compute the PL spectra using relevant numbers in equations (11) and (13). It is sufficient to show the results using a Gaussian crystallite size distribution.

The radiative transition in silicon nanocrystal and in transition region may be with or without phonon mediation.

We take a complete formulate of oscillator strength to take into account all effect of phonon assisted and dependence of size. The n and C value depend on the models employed for the band gap calculations. Following careful calculations of Proot et al for Si-nc, we take n = 1.39 and c = 4.122 eV [28].

The application of the developed model requires physical understanding of the parameters used for studied system.

The presence of surrounding media for the crystallites further complicates the analysis of observed PL data. The degree of localization of surface states depends on the amount of disorders in surface atoms of crystallites.

Our sample was measured by the scanning electron microscopy (SEM). It contain Si-nc embedded in SiN_x matrix, having a size distribution characterized by mean and standard deviation 2.55 nm and 1.44 nm respectively (figure.6).
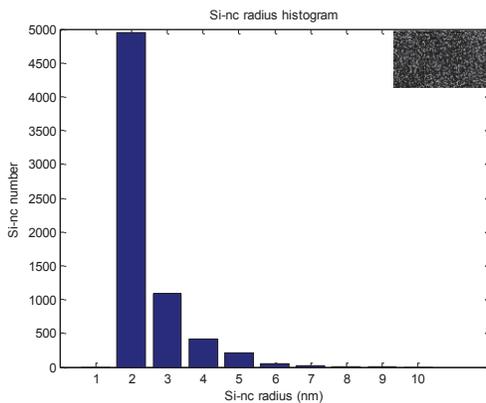
Figure 6. size distribution histograms for Si-nc embedded in SiN_x matrix, and the SEM image corresponding (mean size = 2.55 nm, and standard deviation = 1.44 nm)
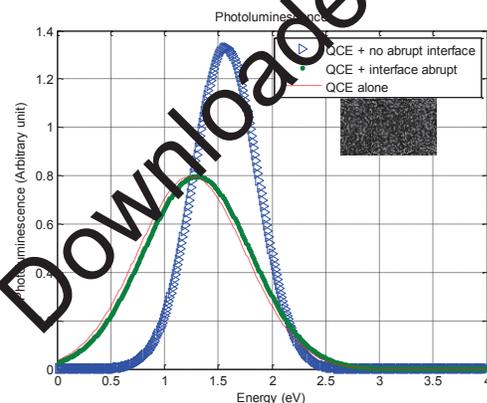
Figure 7. PL spectra computed with (a)QCE (b)QCE and surfaces states in abrupt interface and (c) QCE and surfaces states in transition region surrounding the Si-nc. For Si-nc having Gaussian distribution (mean = 2.55 nm and standard deviation = 0.16 nm).

Figure.7 show the PL intensity simulated by three methods giving respectively 1.25 eV, 1.3 eV and 1.57 eV as PL peak: the first consider that the QCE is alone responsible of light emitting , the second suggest that the surface surrounding the Si-nc contribute in the PL phenomenon. The third that is the aim of our study introduce all the transition region surrounding the nanostructures.

The average radius of the silicon crystallites was estimated to be 2.55 nm. The observed PL characteristics peaks do not seem to have originated solely from these clusters. According to Proot et al. [28], the luminescence energy from silicon nanocrystals can be expressed as:

$$E(d) = 1.13 + 4.122/(d^{1.39}) \qquad (16)$$

Where d is nanocrystal diameter (d = 2*r)

Therefore, the 2.55 nm crystallites radius would result in a luminescence at E = 1.55 eV.

The stokes shift is negligible when we have introducing the transition region surrounding the nanostructures (the simulated value is 1.57 eV whereas the bandgap calculated by Proot et al [28] is 1.55 eV) because we have taking into account other parameters can be responsible of PL. we see also that the PL intensity simulated is more important in this case due to the transition region defects surrounding the Si-nc supposing optically active.

IV. CONCLUSION

We have presented an analytical expressions for PL, by combining both quantum confinement effect, and localized states in the transition region surrounding Si-nc to describe PL peak position. The role of transition region has been clearly demonstrated and explicitly included in the present model minimizing hence the stock shift.

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