Photoluminescence Spectra From The Direct Energy Gap of a-SiQDs

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Abstract. A theoretical model for radiative recombination in amorphous silicon quantum dots (a-SiQDs) was developed. In this model, for the first time, the coexistence of both spatial and quantum confinements were considered. Also, it is found that the photoluminescence exhibits significant size dependence in the range (1-4) nm of the quantum dots. a-SiQDs show visible light emission peak energies and high radiative quantum efficiency at room temperature in contrast to bulk a-Si structures. The quantum efficiency is sensitive to any change in defect density (the volume nonradiative centers density and/or the surface nonradiative centers density) but, with small dots sizes, the quantum efficiency is insensitive to such defects. Our analysis shows that the photoluminescence intensity increases or decreases by the effect of radiative quantum efficiency. By controlling the size of a-SiQDs, we note that the energy of emission can be tuned. The blue shift is attributed to quantum confinement effect. Meanwhile, the spatial confinement effect is clearly observed in red shift in emission spectra. We found a good agreement with the experimental published data. Therefore, we assert that a-SiQDs material is a promising candidate for visible, tunable, and high performance devices of light emitting.

Keyword. photoluminescence, Amorphous silicon, Quantum Dots, Confinement.

1. Introduction
One of the key components needed to induce photoluminescence in silicon is the presence of materials of low dimensional (nanostructures) [1]. Therefore; SiQDs is considered a promising material to open a number of technological relevant and scientifically challenging areas that deal with atomic scales [2]. The structures of quantum dot, in general, used quantum confinement to shift the luminescence of silicon into the visible region [3]. Thus, the effect of quantum confinement is considered to be one of the mechanisms of illumination; however, it differs from other mechanisms by controlling the size that can be tunable[4,5]. Therefore; the spectrum of SiQDs can be tuned continuously across the visible spectrum [6,7], where the wavelength of the emitted light, from green to infrared, is controlled by the size of dots [8,9]. However, in the process of searching for more efficient materials of less dimension, it has been shown that the amorphous silicon dots, a-SiQDs, may be a suitable material for this purpose [10,11]. In fact, there are two
important advantages of bulk amorphous silicon compared to crystalline silicon [4,10]: Firstly, the energy gap of a-Si (1.6 eV) is greater than of c-Si (1.1 eV). Second, the luminescence efficiency in a-Si is higher than c-Si, due to structural disturbance. Thus. This material, a-Si, will be a good candidate for emitters of short wavelength light [12,13].

The efficient visible light emission from a-SiQDs has attracted much interest from researchers both in terms of basic physics and applications to silicon-based devices. It is known that; the radiative recombination processes are involved in this phenomenon, but its mechanism is still a matter of debate. In fact, the mechanism of the photoluminescence is the main issue of the current research [14]. It is studied first by Dunstan and Boulitrop[15], for a bulk a-Si. In the case of a-Si nanostructures, Estes and Moddel[16,17]are developed this model, which is depending on the spatial confinement. Calculations were made using a simple model of radiative recombination in amorphous silicon nanostructure of 2-D, 1-D and 0-D. Their calculations showed a significant size dependence of the photoluminescence. They believed, the spatial confinement effects exist only and no quantum confinement. Also, in 1997 [18], they reported on the influence of doping, temperature, porosity, band gap, and oxidation on the photoluminescence properties of porous a-Si. With the same manner of Estes and Model opinion, a complete analysis of the light emission properties of porous a-Si:H was produced by I. Solomon etal.[19]. The measurements of Light emission and optical absorption energy of a-SiQDs with different sizes revealed that tuning of the light emission is possible by controlling the size of the a-SiQDs. This important performance is achieved by Nae-Man Park etal.[13], who prove the possibility of existence of the quantum confinement in a-SiQDs. They also fabricated an orange light emitting diode (LED) by using a-SiQDs with a mean size of 2 nm [4]. F. Karbassian etal. [20] show that nanocrystals emit light around a wavelength of 550 nm. Multilayer structures have been fabricated to increase the PL intensity by separating luminescent nanocrystal layers with a 5 nm-thick layer of silicon oxynitride. By methods of optical spectroscopy and Raman spectroscopy, N.G. Galkin etal. show that embedded NC form intensive peaks in the reflectance spectra at energies up to 2.5 eV and Raman peaks and a photoluminescence and electroluminescence at room temperature were firstly observed [21]. Theoretically, K. Nishio etal.[10,11] studied the light emission properties of a-SiQDs by using the continuous random network (CRN) model. Their tight-binding calculations, for direct band-to-band recombination, reproduce the peak energies of experimental photoluminescence results, obtained by [13].

In fact, many treatments are used to convert this material into an efficient photo-emitting material. One of these treatments is the concept of the confinement. In this paper, we are trying open new considerations on the mechanism of photoluminescence for a-SiQDs model. In fact, these considerations are consisting the dynamic of the confinements (the spatial and the quantum), which suggests the coexistence of both the spatial and the quantum confinement’s effects in amorphous silicon nanostructure material [22]. To clarify this proposal, we have used the experimental data of \( E g \) vs. \( R_t \) to obtain a theoretical relation via a fitting process [13]. Thus, the comparison between these two confinements is reflected in our results. We have analysis the results of this model by starting the concepts of both confinements with their characteristic lengths, where are considered special features of a-SiQDs model. We were also studying the most important parameters which have affected on the intensity of photoluminescence, for both types of the confinement. Finally, the tuning is one of an applications parameter of this study that is resulting from the controlling of the sphere’s sizes, where the red and blue shifting is discussed.

2. The Model

In previous our paper [22], we had believed that \( a-SiQDs \) changes the nature of amorphous silicon optical band gap from indirect to direct transition material. In fact, these structures, it is note that: the first; zero-phonon optical transitions are allowed, second; oscillator strength of the zero-phonon transition is significantly enhanced [23]. Thus, it is expected, the properties of light emission will be improved [24].

Now, we describe our model with both concepts the spatial and the quantum confinements to produce the photoluminescence from a-SiQDs.

In the spatial confinement, the common model of recombination is used in the amorphous silicon which suggested by Street [25], where the defects provide the dominant recombination centers as illustrated in ‘Figure
which is represented the bulk case of a-Si. The distance from a defect at which the nonradiative and radiative recombination rates are equal, a nonradiative capture radius, \( R_c \), is defined. \( R_c \) is the distance from a defect at which the nonradiative and radiative recombination rates are equal. Thus, the size of capture can be considered as a sphere surrounding the defect [26] as shown in Figure 1b. When the electron-hole pair into the sphere, it recombines nonradiatively; otherwise, it recombines radiatively [19, 26]. In this case, the electron-hole pairs can recombine either radiatively or nonradiatively. Alternatively, the capture radius, \( R_c \), may be seen as the characteristic length explored by a photocreated electron-hole pair before its radiative recombination [19]. The spatial confined for a-Si is represented in Figure 1b.

In view of the fact that the values of \( R_c \) must not adopt as a randomly, that takes the form [16, 17]:

\[
R_c = \left\{ \frac{3}{4\pi N_{nr}} \ln \left( \frac{1}{\eta_0} - 1 \right) \exp \left( \frac{1}{T_0} \right) + 1 \right\}^{\frac{1}{2}}
\]

where \( N_{nr} \) is the volume nonradiative recombination density (cm\(^{-3}\)), \( T_0 \) is an experimentally determined constant and \( \eta_0 \) is the low temperature maximum quantum efficiency limit. We used in this paper the values for bulk a-Si:H [27] \( \eta_0 \sim 0.998 \) and \( T_0 \sim 23K \).

In a-SiQDs structure, we suppose the amorphous silicon nanocrystals are grown in a silicon nitride film by one of the deposition technique as shown in Figure 1c. The probability for a photocarrier of encountering a nonradiative center is no more given by the dark sphere volume but the volume of the intersection of the dark spheres with quantum dots nanostructures [19]. When the characteristic size of the quantum dot is smaller than \( R_c \), hence the nonradiative recombination probability is decreased. Also, from Figure 1c, one can notice that the periodicity due to a superstructure is absent [14], which is called also superlattice. It is important, in this research, to mention that the localization radius in this model has the same meaning of the effective Bohr radius, \( R_o \), which is estimated to be 10Å [16, 17].

![Figure 1](image)

**Figure 1.** a- illustrates the case of bulk a-Si with defects. Dark spheres are represented the nonradiative capture regions. b- the same bulk film with the spatial confinement, the circles are the capture volume with radius, \( R_c \). c- In this case, the spatial confinement is still considered, where a-Si-QDs are etching in the film.
Since quantum dots usually consist of tens to thousands of atoms, geometric considerations promote a very high surface-to-volume ratio, compared to the bulk version of the same quantum dot material [28]. The volume, \( V = \frac{4}{3} \pi R^3 \), and surface area, \( A = 4 \pi R^2 \), of spherical dot are taken as the ordinary geometric expression for this shape. But, the concept of \( R \) is different from one magnitude to another. When the magnitude of \( R \) lies in the range of active quantum dots, \( R \) represents the dot radius, \( R_t \). In this case, the model is treated as the nanostructure material. But, if \( R \) has a magnitude more than this range, then it will be the nonradiative capture radius, \( R_C \) that is considered. It is clear that, the material should be treated as a bulk in this case. As a consequence, \( R_C \) can be used as a probe of \( R_t \) according to its magnitude in this work. Therefore, there are three different cases for the volume and the surface area of spherical dot; where \( R_t \) may be less than \( R_C \), equal to \( R_C \), or more than \( R_C \). In both cases \( R_t \leq R_C \), the characteristic length is considered as the radius of the quantum dot itself. According to this assumption, different cases for capture volume, \( V_C \), and surface capture area, \( A_C \), can be computed as shown in (table 1).

Table 1. The different cases of the capture volume, \( V_C \), and the surface capture area.

| \( R_t \) | \( V_C \) | \( A_C \) |
|---|---|---|
| \( R_t < R_C \) | \( \frac{4}{3} \pi R_t^3 \) | \( \frac{4\pi R_t^2}{3} \) |
| \( R_t = R_C \) | \( \frac{4}{3} \pi R_t^3 \) | \( 0 \) |
| \( R_t > R_C \) | \( \frac{4\pi R_t^2}{3} \) | \( 0 \) |

From table (1), it can be said that when \( R_t \leq R_C \), the material behaves as quantum dots nanostructure. While when \( R_t > R_C \), follows the bulk \( a\)-Si. Figure 2 describes the different cases of capture volume \( V_C \) and surface capture area \( A_C \) according to the relation between \( R_C \) and \( R_t \).

Figure 2. According to the relation between \( R_C \) and \( R_t \), the different cases of the capture volume, \( V_C \), and the surface capture area, \( A_C \), as indicated in table 1. In front of the circle is the quantum dot with radius \( R_t \), while behind the circle is the capture region with radius \( R_C \). In each case, this region has different size because it has different nonradiative center density.

According to the Anderson-Mott picture of amorphous semiconductors [29], a rigid-band model is assumed [15,16]. The Mott-Davis model is suggested to satisfy this purpose. In this model, radiative recombination take place via tunneling between the deepest accessible energy conduction and valence states in the respective band tail [10,15,16,19], without Stokes Shift [16,17]. Radiative transition to/or from defect levels near midgap is not considered here [16,17] because this transition is not occurred at only one band. The surfaces do not additional radiative recombination paths are assumed [17], since, in general, the surface transitions is nonradiative process. On the other hand, nonradiative recombination occurs through a tunnel to a nonradiative defect center when this center is within the capture volume, \( V_C \) [16,19]. We have assumed that the surface is additional nonradiative states due to excess dangling bond. It is important to note that; in \( a\)-SiQDs structure, carriers will find deeper energy paths within the volumes of spheres. While in bulk, carriers may recombine through only a few low energy tail or defect [16].
The carriers at the spatial confinement have smaller volumes, this led to increasing the average luminescence energy and efficiency [16,17]. The quantum confinement is making to convert an indirect optical transition into a direct one [14]. Radiative recombination becomes more efficient since the electron and hole wavefunctions overlap, leading to a faster recombination for size decreasing of nanocrystal [1]. In fact, studying the effect of quantum confinement in a-Si as a function of dimension can yield important informations about the physical processes which are related to the carrier mobility [13]. Recombination at interface states or other defect states away from the quantum dots form competitive nonradiative recombination paths [1].

The net effect of the quantum confinement is a reduction of carrier mobility and a widening of mobility gap [16,30]. By using the best fitting for the experimental data that is achieved by Dunstan et al.,[13], this effect is done in the a-SiQDs model. According to the theory of effective mass, an infinite potential barrier is assumed, therefore, the energy gap, $E_{QD}$, for three-dimensionally confined a-SiQDs model is expressed as [4, 12, 13],

$$E_{QD} = E_{g(bulk)} + \frac{C}{R_{i}^{2}}$$

(2)

Where $E_{g(bulk)}$ is the bulk of the a-Si band gap that takes the value (1.56 eV) obtained from the best fit for the experimental data which is mentioned above. This value is very close to the values reported in literature for bulk a-Si [31]. $R_{i}$ is the radius of the dot and $C$ is the confinement parameter. This parameter is about (2.4 eV nm$^{-2}$).

Since the density of states function in amorphous silicon is changed as the energy depth increase [31], the density of states function for a-SiQDs model is still under debate and search [10]. Therefore, some assumptions must be taken in account for this model: the electronic states are assumed to be the same as those of bulk a-Si [16,17], where the estimation for a-SiQDs is often carried out in an analogous manner [11]. The exponential band tails are supposed to be independent of size [10,16,17]. This led to estimate the probability that no band tail states exist in volume comparable with a-SiQDs [10,11]. Also, for simplicity, Fermi energy level is considered constant throughout the structure and is located near midgap [16].

In this work, in contrast to Dunstan and Boulitrop, the entire density of states are considered, including both exponential band- tail and quadratic band states as potential luminescence sites [16,17]. The amorphous-silicon density-of states function (cm$^{-3}$eV$^{-1}$) for conduction band is given by[16]:

$$N_{CO}(E) = \begin{cases} 
N_{CO} \exp \left( \frac{E}{E_{CO}} \right) & \text{for} \ E \leq E_{C} \equiv 0 \\
N_{CO} \left( \frac{2}{E_{CO}} \right)^{\frac{3}{2}} (E - E_{C})^{\frac{3}{2}} & \text{for} \ E > E_{C}
\end{cases}$$

(3)

Where $E_{C} \equiv 0$ is the conduction -band energy at which the band and tail state densities are equal, $N_{CO}$is the effective density of states (cm$^{-3}$) at $E_{CO}$ and $E$ is the energy relative to $E_{C}$.

$E_{CO}$ the slope of the band tail energy, which is defined as the characteristic energy which describes the width of the Urbach edge, therefore; $E_{CO}$ is a measure of the width of the localized state distribution [32], which is given by [33]:

$$E_{CO} = kT$$

(4)

The valence –band has a similar form for $N_{v}(E)$, where $E$ is valence band energy relative to the energy $E_{V} \equiv 0$ at which the band and tail state densities are in equal. As in conduction band, $E_{VO}$ is obtained by [33]:

$$(E_{VO})^{2} = (E_{VO})^{2}_{T=0} + (kT)^{2}$$

(5)

Where the second term is represented the room temperature energy.

The process of thermalization is considered as a characteristic feature of amorphous semiconductors [25]. Accordingly, photoluminescence carriers are presumed quickly thermalize down or above (for conduction or valence band, respectively) through localized states in the band tails [16, 19, 32]. These carriers reach to the deepest energy states before recombination within some distance $R$ [16, 19]. It must be mentioned, the deepest state for conduction band means the lowest state and the highest state for valence band [19].

The carriers’ separation arises from the diffusion of carriers in the extended states during the thermalization process [19]. It could be considered as the initial distance of electron-hole pairs may have spatial distribution even immediately after photoexcitation [34].
When the density of states drops \( (E_C V_C)^{-1} \) at energy in the conduction band tail, this energy is equal to [26]:

\[
\Delta E_C = E_C \ln(V_C N_{\text{eo}}) \tag{6}
\]

which is defined as the thermalization energy for electrons that lie below the conduction band mobility edge. While the energy for holes that lies above the valence band mobility edge is named the thermalization energy. The valence band had the same expression.

Now, it is easy to calculate the total number of states which are contributed in these transitions for both conduction and valence bands.

For an electron injected at an energy \( \Delta E_C \) above \( E_C \), the total number of accessible conduction–band states below \( \Delta E_C \) and within the capture volume, \( V_C \), is given by [16]:

\[
n_C = V_C \int_{\Delta E_C}^{0} N_C(E) dE \tag{7}
\]

The function of probability density for conduction band, \( P_{C(\text{lowest state})}(E) \), which is gives the probability that the lowest-energy conduction band state within the capture volume lies between \( E \) and \( E + dE \). It is then the probability that \( n_C - 1 \) states lie above the energy \( E \) times the probability that \( n_C^{th} \) state is between \( E \) and \( E + dE \), which is denoted by \( \int_{\text{lowest state}}^{E} N_C(E) dE \).

Assuming that these \( n \) states are independent \( P_C(E) \) is thus:

\[
P_C(E) = P_{C(\text{lowest state})}(E) P_{C(n-1\text{states})}(E) \tag{8}
\]

\[
P_C(E) = V_C N_C(E) \left( \int_{-\Delta E_C}^{0} N_C(E) dE \right)^{n_C-1} \tag{9}
\]

A similar expression applied for the probability density function of highest-energy valence-band hole states, \( P_V(E) \).

The normalized luminescence photon flux spectrum, \( P(h\nu) \), is the convolution of probability density function of deepest energy conduction \( P_C(E) \) and valence \( P_V(E) \) band states within the capture volume [15,16,17,19].

\[
P(h\nu) = P_C(E) P_V(E) \tag{10}
\]

\[
P(h\nu) = \int_{\Delta E} N_C(E) P_V(h\nu - E_{g} - E) dE \tag{11}
\]

It should be noted that the two \( E \) values are in different reference frames [16], \( E_g \) is the band gap energy of \( a-Si \) (1.6 eV) in the case of spatial confinement, but it’s value is already different as the size of dots in the case of quantum confinement [35].

Since the luminescence spectrum is a function of the capture volume, it should be spatially averaged and multiplied by photon energy to obtain the net intensity spectra for \( a-SiQDs \), which was computed numerically [16]:

\[
I_{\text{OD}} = 3 h\nu \eta_{\text{OD}} P(h\nu) \tag{12}
\]

Where \( h\nu \) is the excitation energy, \( \eta_{\text{OD}} \) is the internal radiative quantum efficiency.

For bulk \( a-Si \), the internal radiative quantum efficiency is determined by solving the nearest neighbor distribution function for randomly dispersed sea of electrons and holes or defects [25,19]. This distribution function is applied to nonradiative tunneling of an electron to a defect [36], then it can be given:-

\[
\eta = e^{\left(\frac{h\nu R_{\text{eff}}}{kT}\right)} \tag{13}
\]

where \( N_{\text{nr}} \) is the volume nonradiative recombination center density \( \left( \text{cm}^{-3} \right) \).

But, for \( a-SiQDs \) model the equation (13) is taken for different situations depending on the size of the dot. Meanwhile, no change occurs in case \( R_t > R_C \), but \( R_C \) is replace by \( R_t \) for the case \( R_t \leq R_C \). Thus, equation (13) become:

\[
\eta = e^{\left(\frac{h\nu R_{\text{eff}}}{kT}\right)} \tag{14}
\]
Besides the effect of volume nonradiative recombination center density, the effect of the surface nonradiative recombination center density, \( N_{\text{nr}} \) (cm\(^{-2}\)) is also considered. Therefore, the equation (14) is replaced by:

\[
\eta_{\text{OD}} = e^{\frac{3\pi R_0^2 N_{\text{nr}}}{2}} e^{8\pi R_0^2 N_{\text{nr}}}
\]

where the number of surface atoms is a large proportion of the total number of atoms [28]. In fact, the above expression simply gives the probability of not finding a nonradiative recombination center within the capture volume but the surface capture area does not exist [16].

In this model, the quantum efficiency is defined as the ratio of the light-color volume, which is shown in Fig.(1c), to the whole volume [19]. The quantum efficiency is improved by breaking the bulk momentum space selection rule (quantum confinement effects) [3] and by reducing the efficiency of the nonradiative channels for the recombination because of the localization of the carriers (effects both spatial and quantum confinement) [3, 5].

3. The Results and Discussion

In this paper, we are dealing with the term of the characteristic length at more position. Generally, this term is separated between two cases, processes, values, etc. Therefore; we will be analysis as its positions in this section.

In the case of the spatial confinement for the bulk material, the characteristic length is the capture radius, \( R_C \), where the tunneling process of the carriers is assumed. From ‘equation (1)’, there are two quantities which are essentially affected on the value of the capture radius, \( R_C \). The first is the temperature energy, that is estimated by the room temperature \( (T=300K) \). The other quantity is the volume nonradiative center density, \( N_{\text{nr}} \). The capture radius versus nonradiative center density is illustrated in ‘figure 3’.

![Figure 3](image)

Figure 3. The capture radius is represented the characteristic length for bulk a-Si as a function of volume nonradiative center density.

It is clear from ‘figure 3’ that the value of capture radius, \( R_C \) is decreasing, (and so on the capture volume \( V_C \)), when the volume nonradiative center density is increasing. Since free carriers can move around and access a larger volume of amorphous silicon, they stand a greater chance of finding nonradiative recombination centers or very deep tail states [16]. With taking into account the carriers have enough thermal energy to diffuse a considerable distance before being trapped and recombined.

In the case of the spatial confinement for quantum dot nanostructures, the characteristic length is submitted to the relation between the quantum dot radius, \( R_q \), and the capture radius, \( R_C \). In fact, this relation may be explained, because of the tunneling rate is proportional to \( \exp(-R/R_0) \) [26]; therefore, the tunneling is almost considered the shorter distance. As a consequence, the characteristic length is the quantum
dot radius, $R_t$ when $R_t \leq R_C$. But, it is remained as the capture radius, $R_C$ in case $R_t > R_C$ which is represented the bulk material.

As an electron shows properties of a particle and a wave, if the size is small, the electron energy spectrum is quantized [1]. Therefore; the magnitude order of the electron and the hole de Broglie’s wavelength is comparable with the confinement dimension [37]. Thus, the characteristic length in the case of the quantum confinement is the de Broglie wavelength, $\lambda_B$. We are computed $\lambda_B$ for $a$-$SiQDs$ from [38,39,40]-

$$\lambda_B = \frac{h}{P} = \frac{h}{m^* v_{th}}$$

where $v_{th}$ is the thermal velocity, and $P$ is the momentum, which its magnitude is about (4.4 nm). In general, the characteristic length in this case is considered as a criterion for the confinement. When the wavelengths of the emitting energy are larger than the $\lambda_B$, the confinement is described as a weak. While it is considered a strong if the wavelengths are smaller than $\lambda_B$.

It is useful to mention this; the total number of states is included both radiative and nonradiative states. ‘figure 4’ illustrates the number of nonradiative states as a function of the quantum dot size. In fact, this figure is confirming that; first, the contribution of the valence band states in the tunneling processing are more than for the conduction band states. Second; the carriers are tunnelling nonradiatively in the valence band which is more than the case in conduction band. Third, the number of nonradiative states, in both bands, is decreasing when the size is decreasing. This means the transitions, in only one band, is decreased when the size is decreased. In a very small size, the number of nonradiative states is closing to zero. In this case, the small sizes almost have the radiative states. We can say the transitions between the two bands are occurred more in the small size.

![Figure 4](image-url)

**Figure 4.** The number of nonradiative states versus the quantum dot size for conduction and valence bands.

As a consequence, the ratio of the carriers which are ready to tunnelling radiatively in the conduction band is higher than in the valence band. Therefore, the contribution of the radiative transitions for conduction band is more than the radiative transitions for valence band. This distinct in the ‘figure 5’, where the probability density function is plotted versus the quantum dot size. In fact, this result is in agreement with analysis the number of nonradiative states in both conduction and valence band.
In fact, these results represent the internal quantum efficiency only and do not reflect losses associated with light escaping the structure. Since, the effective index of refraction is considerably lower than that for bulk a-Si, hence a greater fraction of the luminescent light may escape as the angle for total internal reflection larger than for the bulk case [16, 17].

Both surface and volume nonradiative recombination center densities affect on the quantum efficiency value. Besides of that; the value of quantum efficiency is also affected by the quantum dot size. One of the methods for improving the quantum efficiency is to reduce nonradiative defect [5]. Therefore, the expression of ‘equation (15)’, as mentioned previously, simply gives the probability of not finding a nonradiative recombination center within the capture volume and on the surface capture density. From ‘figure 6a’, one can see the effect of structure size on the quantum efficiency for a-SiQDs structure with different values of the volume nonradiative center density. We found, the quantum efficiency is increased when the volume nonradiative center density is decreased at each fixing value of the surface nonradiative density. This dip in efficiency is due to combination of relatively large surface area and relatively large volume of the structure so that carriers are exposed to a maximal number of nonradiative sites [16,17]. Actually, this behavior is reasonable and logical because of the decreasing in the carriers which are recombined radiatively. In fact, at low densities of the volume nonradiative center \( (10^{15} - 10^{17}) \text{ cm}^{-3} \) the quantum efficiency value is sensitive to the changing in magnitude of surface nonradiative density. Whereas the degree of the sensitivity is less at high densities \( (10^{19} - 10^{21}) \text{ cm}^{-3} \), therefore, we can note that; the changing is not great. At small sizes, the near unity quantum efficiency of the quantum dots results simply from there being very few states, and hence a small probability of a nonradiative recombination center, within these sizes. When the dot size is increased, the states, generally, are increasing at each size. This leads to increase the probability of existence nonradiative states, which have the nonradiative recombination centers. As a consequence, in this case, the quantum efficiency value is comedown.

The surface nonradiative density is played a very important role in the magnitude of the quantum efficiency, as we noted in previous section. The reason of this relate to the atoms of surface atoms which have a large proportion in the quantum dot. In fact, it is considered to be a very effective in the value of quantum efficiency [41]. The surface nonradiative density versus the quantum dot size is indicated in ‘figure 6b’. To consider the effect of surface nonradiative density, we have fixed the volume nonradiative density. Whenever the density of the volume nonradiative is increased, the sites of nonradiative centers is increased too because the combination of surface area with the volume of the structure. Therefore; the value of quantum efficiency is comedown by increasing the density of the volume nonradiative.
Figure 6. The quantum efficiency versus the quantum dot size with different values of a- the volume nonradiative recombination center density (10^{15} \text{ cm}^{-3} - 10^{21} \text{ cm}^{-3}) for the surface nonradiative recombination center density 10^{10} \text{ cm}^{-2} value. b- the surface nonradiative recombination center density (10^{10} \text{ cm}^{-2} – 10^{21} \text{ cm}^{-2}) for the volume nonradiative recombination center density 10^{16} \text{ cm}^{-3} value.

‘figure 7’ shows the quantum efficiency versus the volume nonradiative center density for all the sizes of spheres in this work. In the ‘figure 7a’, the surface nonradiative density is assumed to be 10^{10} \text{ cm}^{-2}. It is appeared from this figure, the quantum efficiency value for all sizes has not affected by the increasing the density until closing the value 10^{17} \text{ cm}^{-3}, where the quantum efficiency value at near unity. In other words, the quantum efficiency is independent on the density in this range. But, the quantum efficiency is starting of the decreasing after the density of value 10^{17} \text{ cm}^{-3}. Then, the dip is very clear appeared at high density, where the number of sites nonradiative is increased. On the other hand, the size of the quantum dot plays an important role in the value of quantum efficiency. As we see in this figure; its value increases with the reducing the size. The reason of this refers to increasing the number of the carriers which are recombined radiatively. Also, this means, the probability of not finding nonradiative center has been highly when the size is smaller.

Figure 7. The effect of structure sizes (from 1 to 4 nm) on the quantum efficiency as a function of (a) the volume nonradiative recombination center density, the surface nonradiative recombination center density is
fixed at value $10^{10}$. of (b) the surface nonradiative recombination center density, the volume nonradiative recombination center density is established at a value $10^{16}$cm$^{-3}$.

From equation (12), we can distinguish the parameters which are contributed on the photoluminescence intensity magnitude. These parameters are the quantum efficiency, the photon flux (more details of photon flux in previous paper Ref. [35] and the magnitude of the excited photon energy. According in pervious paper [35], they are four regions, each region has a practically behavior differs from another region. We are chosen from each region only one size for both cases of spatial and quantum confinements. These sizes are $(3.6)\,\text{nm}, (2.8)\,\text{nm}, (2)\,\text{nm}, (1.2)\,\text{nm}$ for the four regions respectively. In all figures in this section, the photoluminescence intensity is represented as a function of the photon energy.

Here, we indicate the role of every parameter, which affected on the photoluminescence intensity as mentioned above. The effect of quantum efficiency is shown clearly when the intensity magnitude is increasing or decreasing by changing the volume nonradiative density and/or the surface nonradiative area. We note from all figures that, as a general sequence, the intensity magnitude is decreasing with the increase of volume nonradiative density. But, this magnitude is more comedowns when the surface nonradiative area is increased. The reason for this behavior related by the increase of the number of nonradiative recombination centers.

The effect of photon flux shows the behavior of the intensity, where this behavior has only one style although the intensity magnitude is decreasing or increasing [35]. This leads us to think, the period of optical transitions in the various sizes of quantum dots has the same procedure, and thus the photoluminescence spectrum has the same shape. In amorphous semiconductors, Urbach edge (the exponential part of the absorption edge) is due to optical transitions involving localized states. In fact, the width of the Urbach edge is determined by the Urbach energy, therefore; this energy is a measure of the width of the localized states distribution [32]. Because of this energy is depended on the temperature energy, thus, In this work, the magnitude of Urbach energy, for both conduction and valence bands, is estimated at room temperature.

Since the photoluminescence dynamics of $a$-SiQDs is determined by the recombination of carriers localized in the band tail state, therefore; the broad photoluminescence spectra of $a$-SiQDs is due to various of the radiative transition energy in the band tail state within a quantum dot [24]. However, the full width at half maximum ($FWHM$) of this spectra can be estimated from the Urbach energy [19]. In the case of spatial confinement, the spectra exhibit a line width of approximately $0.22\,eV$ for all the dot sizes. While in the case of quantum confinement, the broadening of spectra is increasing from $0.22\,eV$ to $0.225eV$ with decreasing the dot size, in which exhibits the Gaussian-like shape in both cases. We can explain the first case as; a significant shift of the mobility edge to higher energies being not or less affected [19], whereas the second case suggests; the dot structure affects the distribution of localized states in the band states [32]. In other words, the size effect is inducing a broadening of Urbach energy. It is useful to mention that; besides of the linewidths of spectra are varied by the quantum dot size, they are also varied by local environment [6].

In all figures of photoluminescence intensity, there are differences in the maximum magnitude of the photoluminescence intensity between the spatial and the quantum confinements, where the magnitude for the quantum confinement is higher than for the spatial confinement. The reason of that retain to enhancement of radiative recombination for the case of quantum confinement. Since the emission occurs from the lowest energy states in the conduction band to highest energy states in the valence band [6], the energy of the electron-hole pair, then the number of available states, is increased because the increasing of the excited photon energy [3], that is considered one of the consequences the quantum confinement effects.

Figure 8 a and b illustrates the photoluminescence intensity for the first region, a bulk-like region at the spatial and the quantum confinements respectively. At high densities ($10^{20}, 10^{21})\,\text{cm}^{-3}$ this behavior does not affected by the change of surface nonradiative density. This improves, at this region, the behavior of the intensity to be close to the bulk mode when the radius becomes larger. In other words, the nanostructure mode is appeared partially upon the volume nonradiative density. Also, the intensity magnitude is decreasing with the increasing of surface nonradiative area because the nonradiative centers are increasing.
Figure 8. The photoluminescence intensity as a function of photon energy for the bulk-like region for 3.6 nm size, \(N_{\text{snr}}=10^{10}\,\text{cm}^{-2}\) a- at the spatial confinement b- at the quantum confinement.

In ‘figure 9’, the spectra of photoluminescence intensity at the large-dot region is indicated. While this spectra at the medium-dot region is shown in ‘figure 10’. Finally, the spectra at the small-dot region is indicated in ‘figure 11’.

Figure 9. The photoluminescence intensity as a function of photon energy for the large-dot region, for 2.8 nm size, \(N_{\text{snr}}=10^{10}\,\text{cm}^{-2}\) a- at the spatial confinement b- at the quantum confinement

Figure 10: The photoluminescence intensity as a function of photon energy for the medium-dot region, for 2 nm size, \(N_{\text{snr}}=10^{10}\,\text{cm}^{-2}\) a- at the spatial confinement b- at the quantum confinement
One of the major outcomes of this study is the realization, the crystallinity is not necessary for visible light emission from nanostructures. Such these structures yield emission energy tunable from near-infrared to the visible range [42]. In fact, the wavelength of the emitted light is controlled by the size and the composition of the dots [9]. In this work, we illustrate the effect of both cases of confinement (the spatial and the quantum) on the emitted light from α-SiQDs.

‘Figure 12a’ illustrates the energy can be shifted toward a larger wavelengths (red shifting) of all sizes are used for the spatial confinement case. In this figure indicates nominally (2.0 – 1.6)eV peak energies in the orange-red room temperature photoluminescence band with decreasing the dot size. In fact, the mechanism of the orange-red photoluminescence originating from the long-lined surface states [43]. This led us to suggest that; the optical transitions occur under the condition \( E \geq E_g \), where \( E \) is the excitation energy, and the excitation states decrease when the dot size is decreasing. [41,44]. While It is clear in ‘figure 12b’ that; the energy can be shifted toward a smaller wavelengths (blue shifting), which indicates the peak energy as a function of dot size. Also, the peak energies have the range 2 eV to 4 eV in the (red to blue) room temperature photoluminescence band with reducing the size of dot. The mechanism of the red-blue photoluminescence relates to the quantum confinement effects. This mechanism can be explained as follow; since the energy levels are shifting to higher magnitude with the dot size decreasing, the energy gap is changed from size to another. Under the condition \( E \geq E_g \), each size have a privacy feature in its transition energy, which takes a high magnitude whenever the dot size is deceased. The explaining of red shifting and blue shifting will present with more details in Ref [22].

**Figure 11.** The photoluminescence intensity as a function of photon energy for the small-dot region, for 1.2 nm size, Nsnr=10^{10} cm^{-2} a- at the spatial confinementb- at the quantum confinement.

**Figure 12.** a- The peak energy as a function of the dot size at the spatial confinement. b-The peak energy as a function of the dot size at the quantum confinement.
‘figure 13’ shows the emission color that could be changed by controlling the dot size, where the tuning of the photoluminescence emission from (0.7 – 0.3) μm. For example, the dot size corresponding to red, green, and blue emission color were (3.6, 2.2, and 1.2) nm respectively. In fact, the tuning of emission color and efficient emission can be achieved by quantum confinement effects [4, 45, 46, 47], where quantum confinement effects make silicon a likely candidate for full-color displays [4].

![Figure 13](image_url)

**Figure 13.** The photoluminescence as a function of photon energy for all used sizes at the quantum confinement.

The results of photoluminescence $a$-Si$QDs$ model are reviewed with the parameters that affect the photoluminescence’s value. In this section, progress the development of amorphous silicon photoluminescence is introduced by ‘figure 14’. This is done, first, by considering the Dunstan and Boulitrop model (Fig.14), that has peak energy at about 1.4eV for $a$-$Si$. The second curve represents porous $a$-$Si$, this material attracted more attention after Canham's discovery in 1990, its peak energy is about 1.75eV. The model of $a$-$SiQDs$ for Estes and Moddel, with a size 2.5nm, has its peak energy at 1.75eV. This model depends on the spatial confinement. But, the peak energy shifts to 2 eV when the model considers the quantum confinement rather than the spatial confinement for a 2nm size as Nishio et al. model. For the same size and with the consideration of both confinements (the spatial and the quantum) in our work, the peak energy has the value 2.2eV.

![Figure 14](image_url)

**Figure 14:** Progress the development of photoluminescence a-$Si$ models.
It is clear from the development steps of $a$-$Si$ models that the photoluminescence is shifting into the visible region. In fact, this improvement means that; the amorphous silicon material can be considered as a good candidate as a light-emitting material. ‘figure 15’ indicates the agreement between our results and the experimental data of Park et al [13]. This agreement leads to the assumption of the coexistence of the spatial and the quantum confinement in this model.

Figure 15. The comparison between our results with the experimental data.

4. Conclusion
In this work, a simple theoretical model for photoluminescence in $a$-$Si$QDs is designed, which considers the coexistence of both confinements (the spatial and the quantum). At room temperature, the radiative quantum efficiency is very sensitive to the change in the volume nonradiative density or/and the surface nonradiative density, while it is insensitive at small dot size. The photoluminescence intensity increases or decreases due to the effect of the quantum efficiency, while its shape style reflects the behavior of photon flux. By controlling the sizes of $a$-$Si$QDs, the emission spectra can be tuned from red to blue (visible region). But, its noted that: blue shifting come from the effect of quantum confinement which is differ from the effect of spatial confinement that is result in the red shifting.

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