The Band Gap in Silicon Nanocrystallites

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The gap in semiconductor nanocrystallites has been extensively studied both theoretically and experimentally over the last two decades. We have compared a recent “state-of-the-art” theoretical calculation with a recent “state-of-the-art” experimental observation of the gap in Si nanocrystallite. We find that the two are in substantial disagreement, with the disagreement being more pronounced at smaller sizes. Theoretical calculations appear to over-estimate the gap. Recognizing that the experimental observations are for a distribution of crystallite sizes, we proffer a phenomenological model to reconcile the theory with the experiment. We suggest that similar considerations must dictate comparisons between the theory and experiment vis-a-vis other properties such as radiative rate, decay constant, absorption coefficient, etc.

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I. INTRODUCTION

Semiconductor nanocrystallites, more popularly known as quantum dots (QDs), have been extensively studied over the past decade and a half. The system is interesting from the point of view of basic physics, with the carriers being confined to an essentially “zero dimensional” structure. The efficient luminescence observed in some of these crystallites makes them promising candidates for opto-electronic devices. Further, the inexorable drive towards device miniaturization makes them technologically significant.

The earliest theoretical works in this field were reported in early 1980’s. For over a decade after, most of the theoretical works reported were based on effective mass theory (EMT) and tight-binding semi-empirical approaches. These works predicted the experimentally observed trends for quantum confinement, i.e. the inverse dependence of enhanced band gap on the nanocrystallite size. These calculations were, however, performed for a single nanocrystallite, whereas experiments are performed on an ensemble of QDs of varying sizes. We have earlier pointed out that the existence of an ensemble of QDs of varying sizes must be taken into account in any theoretical formulation. Though improved theoretical calculations were pursued later, this aspect has largely been ignored.

In a recent work Ogut et al. reported a “state-of-the-art” theoretical calculations based on first principles. This work is claimed to be in excellent agreement with an early experimental work and is claimed to be superior to semi-empirical calculations. We compared their calculations to a later “state-of-the-art” experimental results of Buuren et al. We found that there was a large disagreement between the two. This comparison is presented in Sec. II.

In Sec. III, we proffer a phenomenological scheme for this underestimation of the band gap and suggest a possible reconciliation between the theory and experiment. Conclusions are presented in Sec. IV.

II. COMPARISON : THEORY VS. EXPERIMENT

In a Letter Ogut et al. have employed a carefully argued ab-initio methodology to obtain the size-dependent optical gap of Si QDs with sizes ranging from 1 to 3 nm. These authors choose to compare their calculations with the experimental observations of Furukawa and Miyasato. A little later, Buuren et al. reported state of the art measurements of the band edges of Si quantum dots (QDs) with average diameters ranging from 1 to 5 nm. By adding the measured conduction band (CB) and valence band (VB) shifts to the band gap of bulk Si they obtained the band gap of the Si QDs. Recent PL and extended X-ray absorption data for oxygen terminated silicon nanocrystallites of size less than 4 nm, were found to match these observations. These band gaps are smaller than most reported theoretical calculations. This fact was noted by Buuren et al. who choose to compare their observations with older calculations by Wang and Zunger. We also note that several first principles/LDA calculations on nanocrystalline forms of Si have been reported in the past. It appears that theoretical calculations over-estimate the gap.

A comparison of the “state-of-the-art” theoretical calculations with the “state-of-the-art” experimental observations reveals that the two are in substantial disagreement with each other. This comparison is presented in Fig. I. In fact the Ogut et al. calculation does worse than Wang and Zunger (not shown in Fig. I) and other
semi-empirical theoretical calculations. Perhaps the only commonality between the theory and experiment depicted in the figure may be stated in terms of a bland quantum confinement (QC) dictum: “the band gap increases as the size decreases”.

The disagreement between theory and experiment is enhanced at smaller dot sizes. Were we to make a constant upward shift of 0.72 eV to the data of Buuren et al. such that they match with the theoretical calculation at 3.5 nm then the increasing divergence at smaller sizes is clearly manifested. This is depicted in the inset of Fig. II. On the other hand, we may translate the experimental data horizontally by 1.75 nm and force an agreement with the (extrapolated) theoretical calculations. This would imply that the QD sizes have been seriously underestimated by Buuren et al. While the latter do not discount the possibility of some underestimation, a 1.75 nm error is unlikely.

Ab-initio calculations are computationally demanding at large QD sizes. As we have pointed out the disagreement between theory and experiment is pronounced at smaller dot sizes. It should be possible to re-examine or repeat the ab-initio calculation in this computationally feasible intermediate regime.

III. PHENOMENOLOGY

The observation of visible photoluminescence (PL) in a variety of semiconductor nanocrystallites has fueled a large body of research work in the past decade. PL has acquired the role of central characterizing tool in this field. The photoluminescence spectra from such systems are broad, and often asymmetric about the peak energy. The growth of the QDs is a stochastic process. In an earlier work we have argued that one needs to consider the distribution of crystallite sizes to compare with the experimental spectral shape.

A Gaussian size distribution was used in those works. For semiconductor nanostructures, the log-normal size distribution has considerable experimental and theoretical support. Specifically, Yorikawa and Muramatsu presented an explanation of PL spectra based on the log-normal distribution of porous silicon QD size. The experimental work reported by Buuren et al. also shows a log-normal distribution.

We consider the log-normal size distribution, $P(d)$, of diameter $d$ centered around a mean diameter $d_0$,

$$P(d) = \frac{1}{\sqrt{2\pi\sigma_d}} \exp\left[\frac{-(\ln d - \mu)^2}{2\sigma^2}\right]$$  \hspace{1cm} (1)

$$d_m = \exp(\mu - \sigma^2)$$  \hspace{1cm} (2)

$$d_0 = \exp\left(\frac{\sigma^2}{2} + \mu\right)$$  \hspace{1cm} (3)

where $d_m$ is the dot size for which the maxima occurs in the log-normal distribution and $\{\mu, \sigma\}$ are some characteristic constants.

The number of electrons in a dot of diameter $d$ participating in a PL process is proportional to $d^3$. Thus, for an ensemble of QDs, the probability distribution of electrons participating in the PL process is

$$P_e(d) = \frac{1}{\sqrt{2\pi\sigma_d}} bd^3 \exp\left[\frac{-(\ln d - \mu)^2}{2\sigma^2}\right]$$  \hspace{1cm} (4)

where $b$ is a suitable normalization constant.

In general, the optical band gap is attributed to the energy upshift of the electron and yield

$$E = E_\infty + \frac{C}{d^n}$$  \hspace{1cm} (5)

where $E$ is the enhanced gap, $E_\infty$ is the bulk silicon gap (1.17 eV), $C$ is an appropriately dimensioned constant and $n$ is the exponent with $n \in [1, 2]$.

Hence the energy upshift, $\Delta E$, due to confinement in QD is

$$\Delta E = \frac{C}{d^n}$$  \hspace{1cm} (6)

$$\Delta E_0 = \frac{C}{d_0^n}$$  \hspace{1cm} (7)

where $\Delta E_0$ is a mean upshift, which is related to the mean diameter $d_0$ of QD.
Now, convoluting the upshift (eqn. (6)) with the log-normal size distribution (eqn. (4))

\[ P(\Delta E) = \int_0^{\infty} \delta(\Delta E - \frac{C}{d^n}) \frac{d^2}{\sqrt{2\pi\sigma}} \exp \left[ -\frac{(\ln d - \mu)^2}{2\sigma^2} \right] d(d) \]  

The above integral can be easily solved using the property of Dirac delta function, which yields

\[ P(\Delta E) = \frac{b}{\sqrt{2\pi\sigma nC}} \left( \frac{C}{\Delta E} \right)^{(3+n)/n} \exp \left[ -\{ (1/n) \log(C/\Delta E) - \mu \}^2 \right] \]  

For the PL peak, we equate the derivative of the eqn. (8) to zero. The shift in the PL peak position, \( \Delta E_p \), is given by

\[ \Delta E_p = C \exp \left[ -\{ (3 + n)\sigma^2 + \mu \} n \right] \]  

\[ = C \frac{d_m}{d_0} \left( \frac{d_m}{d_0} \right)^{n[2n+5]/3} \]  

We employ eqn. (11) in eqn. (8) to get

\[ E = E_\infty + \Delta E_p \]  

\[ = E_\infty + \frac{C}{d_0^3} \left( \frac{d_m}{d_0} \right)^{n[2n+5]/3} \]  

Eq. (13) represents the final form for estimating a more realistic size dependence of the optical gap. The exponent \( n = 1.22 \) and \( C = 3.9 \) in appropriate units, for the results of Ogut et al. shown in fig. (1). Kanemitsu et al.\(^3\) obtained the size distribution of oxidized Si nanocrystallites produced by laser breakdown of silane gas. The optimum log-normal fit on these experimental data yield \( d_m/d_0 \in [0.7, 0.95] \). We have used three values 0.7, 0.8 and 0.9 of the ratio \( d_m/d_0 \) in eqn. (13) and depicted them alongside the data from Ogut et al. and Buuren et al. in fig. (2). We see that our calculation with the value 0.7 brings Ogut et al.’s result in complete agreement with Buuren et al.’s result. Further our phenomenological model produces more pronounced downshift at smaller sizes. This is once again in agreement with the experimental trend. The asymmetric distribution of the dot size with stretched tailing towards larger QDs is responsible for the lower \( d_m/d_0 \) ratio, though the skewness may not be as pronounced as \( d_m/d_0 = 0.7 \). Thus, for more asymmetric log-normal distribution one obtains more prominent downshift at smaller sizes.

**IV. CONCLUSION**

We find that a recent “state-of-the-art” theoretical calculation\(^1\) for optical gap is in large disagreement with a closely following “state-of-the-art” experimental work. The comparison is even worse for smaller crystallite sizes. The experimental work reported a log-normal size distribution for nanocrystallite samples, whereas the theoretical work was performed on a single crystallite. This theoretical calculation showed a very good agreement with a decade old experimental work, whereas other semi-empirical works were shown to be in poor agreement. To the contrary, we find that the semi-empirical works were in better agreement with Buuren et al.’s experimental work.

Ab-initio calculations are computationally demanding at large QD sizes. As we have pointed out the disagreement between theory and experiment is pronounced at smaller dot sizes. It should be possible to re-examine or repeat the ab-initio calculation in this computationally feasible intermediate regime.

We have used the methodology discussed in earlier works\(^2\) with a log-normal distribution. We have shown that Ogut et al.’s results can be in better agreement with experimental works if size distribution is explicitly taken into account. In our formulation the downshift of optical gap is larger for smaller crystallite sizes, making this exercise even more relevant to the present case.

We caution however that the disagreement between the theory and the experiment may not be solely related to a distribution of crystallite sizes. Other factors could be crucial. These are: (i) partial passivation, (ii) passivation with species other than hydrogen, (iii) surface reconstruction, (iv) flattening of the dot, and (v) size underestimation by the microscopic techniques. Some of these factors have been mentioned by Buuren et al.\(^1\).

There has been a growing realization that the existence of an ensemble of QDs of varying sizes must be taken into account in order to explain experimental observations. Tentative attempts have been made to understand the radiative rate, decay constant, absorption data, etc. based on these considerations. Perhaps any theoretical calculation on a single nanocrystallite should be supplemented with effective size averaging before a comparison with experiment is made.
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FIGURE CAPTION

FIG. 1. The figure compares the “state-of-the-art” experimental band gap obtained by Buuren et al. [Ref. 8] with the “state-of-the-art” theoretical one obtained by Ogut et al. [Ref. 6]. The two are in considerable disagreement. In the inset we have up-shifted the data from Ref. 8 by 0.72 eV to ensure an agreement with Ref. 6 at 3.5 nm size. The discrepancy between the theory and the experiment appears pronounced at smaller sizes. The dashed line is our fit to the calculations of Ref. 6 \( (E_g(d) = 1.1 + c/d^{1.22}) \). The ‘+’ symbols are data arrived at by using a relationship between CB and VB edges by Buuren et al. [see Ref. 8].

FIG. 2. The figure depicts the theoretical data of Ref. 6 and the experimental data of Ref. 8. It also shows the band gap of crystallites if a log-normal size distribution is incorporated in Ogut et al.’s calculation. Of the four lines depicted in the figure the lowest one (dashed line) and the subsequent two (dotted and dashed lines) corresponds to log-normal distributions with : \( d_m/d_0 = 0.7, 0.8 \) and 0.9 respectively. The topmost dotted line is the fit to the data of Ref 6 as mentioned in Fig 1 and the text. We notice that the downshift of the band gap is larger for smaller crystallite sizes. We also notice that \( d_m/d_0 = 0.7 \) shows excellent agreement with the experimental results of Buuren et al. [Ref. 8].
Size (nm)

1 1.5 2 2.5 3 3.5

$E_g$ (eV)

1 1.5 2 2.5 3 3.5 4 4.5 5

Buuren

Ogut