THE EFFECT OF OSCILLATOR STRENGTH ON GERMANIUM NANOCRYSTALS (GE-NCS)

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Abstract

Understanding the mechanism of a promising germanium nanocrystal (GeNCs) responsible for photoluminescence at room temperature has attracted much attention for its visible Photoluminescence emission. Estimation of the influence of oscillator strength on the PL spectrum in GeNCs is carried out. A theoretical model using matlab codes is adopted to examine the influence of oscillator strength as a function of size, photon energy and also on the photoluminescence intensity. Results indicated that, oscillator strength of GeNCs behavior is in line with the quantum confinement effects which determine the optical properties of GeNCs. The oscillator strength in nanocrystallites varies with the amount of confinement and also with the surrounding environment via the change in dielectric constant.

ACRONYMS

oD – Zero Dimensional
1D – One Dimensional
2D – Two Dimensional
3D – Three Dimensional
AFM – Atomic Force

[redacted]

KEYWORDS: *mechanism; photoluminescence; oscillator strength; GeNCs; quantum confinement.*

Microscopy
CB – Conduction Band
GENCs –Germanium Nanocrystalline
CVD – Chemical Vapor Deposition
DFT – Density Function Theory
DOS – Density of State
DVDs – Digital Versatile Disks
EG – Energy Gap
FFT – Fast Fourier Transformer
ICs – Integrated Circuits
IR – Infra Red

LED – Light Emitting Diode
PL –Photo Luminescence
PLE – Photo Luminescence Excitation
QCE – Quantum Confinement Effects
QCLCM – Quantum Confinement Luminescence Center Model
QCM – Quantum Confinement Model
QD – Quantum Dot
SC – Semi-Conductor
SS- Surface State
SSM - Surface State Model
STM –Scanning Tunneling Microscopy
TB – Tight Binding
VB – Valence Band
VLSI – Very Large Scale Integration

INTRODUCTION

Several efforts have been made toward matter manipulation at the nanometer scale, motivated by the fact that desirable properties can be generated by just changing the material dimension, morphology and shape (Kanemitsu, 1995). In the last few decades' positive efforts have been made to examine whether Si and Ge can become intrinsically a direct semiconductor when in nanocrystalline clusters. Germanium nanocrystals (GeNCs) have undergone intensive theoretical and experimental research since after the discovery of room-temperature visible luminescence from Si and Ge nanostructures and in small semiconductor structures which make them suitable for application in optoelectronics devices. In spite of these efforts, the origin on the mechanism of the visible luminescence remains unclear. Thus, it has been established that quantum confinement (QC) can modify the energy gap such that visible luminescence is produced as experimentally observed (Ghoshal et al., 2015). Knowledge of the band structures for these nanostructures is essential for understanding the mechanism of this visible luminescence effect.

The radiative recombination of electrons and holes in the quantum confined nanostructures is responsible for visible photoluminescence. However, in spite of intensive experimental and theoretical studies, no conclusive argument has been given on the mechanism for efficient luminescence from nanogermanium and related materials. Many issues like the size-dependent oscillator strength (OS), the density of states, the radiative recombination rate, the absorption coefficient, temperature dependent PL and EL intensity the dielectric function, and the influence of surface passivation on the optical properties are far from being understood. Efficient emission of visible light has been observed from a nanostructure of germanium when it is exposed to ultraviolet light. It has been surmised that these nanostructures and the porous form of them have a direct band gap and emit light from violet to red, depending upon the size of the nanostructures (Ghoshal et al., 2015). With a large surface-to-volume ratio in nano and porous structures, the surface effects become more enhanced. Surface effects, as well as quantum confinement effects, control the optical and the electronic properties of these materials.

Germanium has an indirect band gap of 0.664 eV at room temperature, putting germanium emission at high efficiency compare to silicon (Sun, 2010). The technical importance of germanium is growing, with applications for optoelectronic, detectors, solar cells, transistors and photovoltaic devices (Saba et al., 2014). Bulk germanium (Ge) band gap materials do not show luminescence. Miniaturization to nanometer scale not only widens the energy band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) due to the size confinement effect but also causes a transition to direct band gap. Bulk Germanium has large wavelength (1550nm) out of visible range and emits 10% efficiency at its direct band gap, but germanium nanocrystals (GeNCs) has shorter wavelength and higher light emissions abilities covering the entire visible and wavelength ranges because of quantum confinement effect (Sun, 2010). The reduction of crystallite sizes to nanometer scale can drastically modify the electronic, phononic, and photonic behaviors in bulk Ge (Pedro et al., 2007). GeNCs with combined effects of quantum confinement effect, doping and strain could be very promising high-efficiency light emitters covering the entire visible and wavelength ranges (Haiyan et al., 2011). GeNCs have low band gaps, larger dielectric constant, high mobility of electrons and holes and unprecedented dimensions.

In bulk Ge, the resulting non-radiative recombination rates are much higher than the radiative ones and most of the excited electron hole (e-h) pairs

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recombine non-radiatively. In this work, a theoretical approach is adopted to find the influence of oscillator strength on the optical behavior of nanogermanium using a matlab programming.

STATEMENT OF THE RESEARCH PROBLEM

Germanium nanostructures have attracted attentions toward the quantum mechanical nature of its phenomenon since after the discovery of room temperature visible photoluminescence in GeNCs. Still the mechanism of visible PL of the Nanoscale Ge is far from being understood, despite of several proposed model to explain the luminescence, including quantum confinement, surface states, defects in the chemical and oxides complexes. The measures of the relative strength of the electronic transitions within atomic and molecular systems are essential in determining the level of the energy emissions in nanocrystals. In spite of many efforts made toward the understanding of this effect, the issue of relative oscillator strength in GeNCs is not yet understood.

OBJECTIVES OF THE STUDY

- To determine the relative strength of electronic transition against size, photon and band gap energies of GeNCs.
- To estimate the influence of oscillator strength on the PL spectrum in GeNCs.

SIGNIFICANT OF THE STUDY

The discovery of room temperature visible photoluminescence (PL) from porous silicon and Ge/Si nanostructure and possibility of tuning the optical response of germanium nanosized material by modifying their size has invited several attentions in these special kinds of nanoclusters and in small semiconductor structures. The influences of oscillator strength (OS) on the optical nature of nanometer germanium which modify virtually all the properties of its contents form the basic significant aspect of the study.

INTERNATIONAL JOURNAL – ERT
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SCOPE OF THE STUDY

Scope of this study includes:

- Usıng quantum gap energy model to fit the experimental findings.
- Gather experimental data from literatures and fit with the model to get the empirical fitting parameters.
- Simulate the analytical expression of oscillator strength by Matlab program to get size, band gap and photon energy dependent oscillator strength (OS) and PL intensity.
- Analyze the data obtained to understand the mechanism of PL emission and the influence of OS.

DEFINITION OF KEY TERMS

OSCILLATOR STRENGTH: The measure of relative strength of electronic transition in an atom or molecule is known as oscillator strength.

DENSITY OF STATE: Is essentially the number of different state at a particular energy level that electrons are allowed to occupy (i.e. the number of electron states per unit volume per unit energy).

PHOTOLUMINESCENCE INTENSITY: Is light emission from any form of matter after the absorption of photons (electromagnetic radiation). It is one of many forms of luminescence (light emission) and is initiated by photoexcitation (i.e photons that excite electrons to a higher energy level in an atom).

PHOTON ENERGY: Is the energy carried by a single photon. the amount of energy is directly proportional to the photon's electromagnetic frequency and inversely proportional to the wavelength.

NANOTECHNOLOGY: Nanotechnology is a catchall phrase for materials and devices that operate at the nanoscale. Nanometer is the master unit for nanoscience and nanotechnologies.

BULK GERMANIUM: Germanium (Bulk) is a chemical element with symbol Ge, atomic number 32 and atomic weight of 72.64g.

BAND GAP ENERGY: Is an energy range in a solid where no electron states can exist.

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RESERCH METHODOLOGY

Quantum confinement effects and the surface state effects are the two reasons for the explanation of visible photoluminescence in the quantum GeNCs. Here, we consider the models of quantum confinement, oscillator strength and PL intensity to investigate the photoluminescence in GeNCs. The quantum confinement model is based on the electronic confinement in nanostructure. 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. The size dependence of optical band gap of quantum crystals according to quantum confinement model is

$$E_g^{nano}(d) = E_g^{bulk} + \frac{\beta}{d^{\alpha}}\ (ev). \qquad (2.1)$$

Where E_g^{nano} : $Energy\ gap\ of\ nanostructures(ev)$.

$E_g^{bulk}\ Energy\ gap\ of\ bulkstructures(ev).\ d\ is\ the\ diameter\ of\ nanostructures(nm).$

$\beta\ and\ \alpha\ are$ quantum confinement effect $of\ nanostructures$[3,4].

RESERCH DESIGN AND PHYLOSOPHY

OSCILLATOR STRENGTH

In quantum mechanics, oscillator strength is used as a measure of the relative strength of the electronic transitions within atomic and molecular systems. Oscillator strength is particularly useful as a method of comparing transition "strengths" between different types of quantum mechanical systems. The Oscillator strength, the equivalent number of oscillations of the transition between the valance and conduction bands, it related to the matrix element of the momentum matrix P_{cv} and is given by the equation.

$$f_{cv} = \frac{2|Pcv|^2}{m_0 \hbar w_{cv}} \qquad (2.2)$$

Where $P_{cv} = |\hat{e}.\ M_{cv}|$

$$\Rightarrow F_{Cv} = \frac{2|\hat{e}.M_{cv}|^2}{3m_0 \hbar w_{cv}} \qquad (2.3)$$

The factor $\frac{1}{3}$ in the above equation is due to averaging with $|M_x|^2 = |M_y|^2 = |M_z|^2 = \frac{|M|^2}{3}$.

$$|\hat{e}.\mathrm{M}_{\mu\nu}|^2 = \frac{3}{2}\frac{m_0}{2m_e^*}(m_0 - m_e^*)\frac{Eg+\Delta_0}{3E_g+2\Delta_0}E_g \quad (2.4)$$

Inserting equation (2.4.) in to equation (2.1) and using m_e^* =0.4m_o we obtain:

$$f_{c\nu} = \frac{2}{3m_0\hbar w_{c\nu}}\frac{3m_0}{2m_e^*}(m_0 - m_e^*)\frac{E_g+\Delta_0}{3E_g+2\Delta_0}E_g \quad (2.5)$$

$$f_{c\nu} = \frac{3}{2m_0\hbar w_{c\nu}}\frac{E_g+\Delta_0}{3E_g+2\Delta_0}E_g \quad (2.6)$$

On the basis of these derived expression of (Oscillator strength) optical parameters, we estimate them using **(mat lab)** programs (Anley Gesese, 2009). The plot and detaıl explanatıon wıll be avaılable ın the next sectıon.

INSTRUMENTS OF DATA COLLECTION

The quantum confinement in different directions also changes the wave functions describing the behavior of electrons and holes that modifies the density of states. The orientation dependent parameters are found to be ꞵ =1.15 and ∂ = 3.80 eV. This is obtained by fitting the model with experimental values of size dependent band gap of Germanium Nanocrystal as shown in figure 2.1. The band gap energy is found to increase as the NWs diameter is decreased. Using quantum electronic gap expression (Eq.2.1) as shown in Figure 2.1. A model expression (Eq.2.6) is used to generate PL spectra and expression (Eq. 2.5) using these quantum confinement parameters with the correction of ±0.5 for further analyses. PL spectra as well as the oscillator strength variation are simulated using a **matlab** programming.

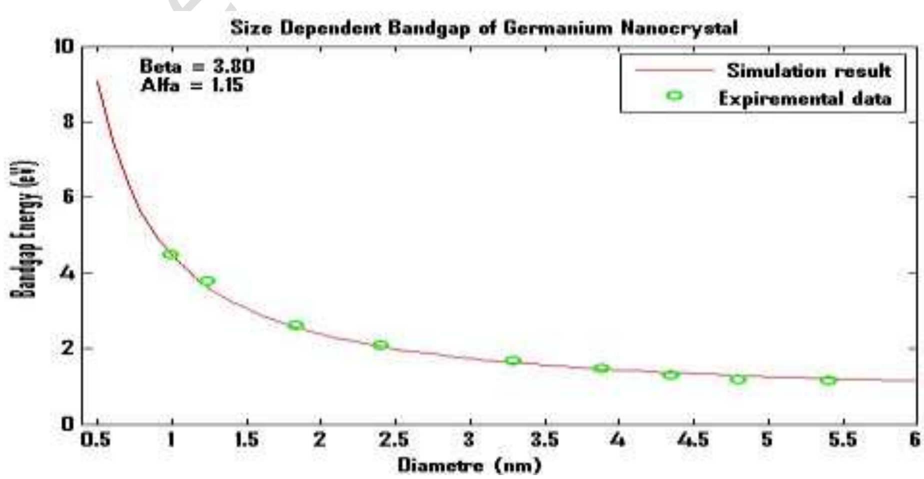

Figure 2.1: Band gap variations of GeNCs with diameter (nm)

OSCILLATOR STRENGTH CALCULATION

Calculated oscillator strength using derived equation (2.5) above, at 3.0 eV photon energy.

$$Where:\ E_g = 0.66\ ev\ (Band\ gap\ energy).$$
$$m_o = 9.11 * 10^{-31} kg\ (Electron\ rest\ mass).$$
$$\Delta_o = 0.29\ ev\ (spin - obit\ splitting\ energy).$$
$$\hbar w_{cv} = 3.0\ ev\ (photon\ energy).$$

$$f_{cv} = \frac{(3)}{2(9.11 * 10^{-31} * 3.0)} * \frac{(0.66 + 0.29)}{3[0.66 + (2 * 0.29)]} * (0.66)$$
$$f_{cv} = 1.8637795 * 10^{28}.$$

DATA ANALYSIS TECHINQUE

PHOTOLUMINESCENCE INTENSITY

The photoluminescence intensity profile for nanostructures is gives as,

$\boldsymbol{I = 1/(\sigma\sqrt{2\pi})\ (\beta/\Delta E)^{\wedge}[(6 - \alpha + \gamma)/\gamma]\ \exp\{-[(\beta/\Delta E)^{\wedge}(1/\gamma) - L_o\ ]^{\wedge}2/(2\sigma^{\wedge}2\ )\}}$ (2.7)

Where L_0 and σ are the mean crystallite size and standard deviation, respectively, for the NWs ensemble.

It is clear from the above expression that the PL profile will depend strongly on the QC parameters β and γ. Therefore, good care should be taken in using the correct QC model for band gap up shift estimation. The oscillator strength is complicated functions of the size of nano crystallites and their surrounding media. We took γ = 1.939, β = 3.80eV and E_g =0.66eV for Ge at room temperature. The localization energy Es has taken to be the order of phonon energies, which is about 0.05 eV for optical phonons and energy separation (ΔE) = 0.8500 eV.

PHOTON ENERGY

$$\boldsymbol{E(^{pe)} = \frac{1.24}{\lambda(\mu m)}(ev).} \qquad (2.8)$$

Where : $E^{(pe)} is$ photon energy in eV. $\lambda\ is$ wave length in μm.

RESULTS AND DISCUSSION

The plots of oscillator strength verses size, band gap energy and photon energy are presented in Fig.3.1, 3.2 and 3.3. These plots were simulated using eqn. 2.5, 2.7 and 2.1, respectively. It is found that the oscillator strength decreases with increasing size, band gap energy and photon energy. The results suggested that the relative strength of electronic transitions appreciated when the material is very small.

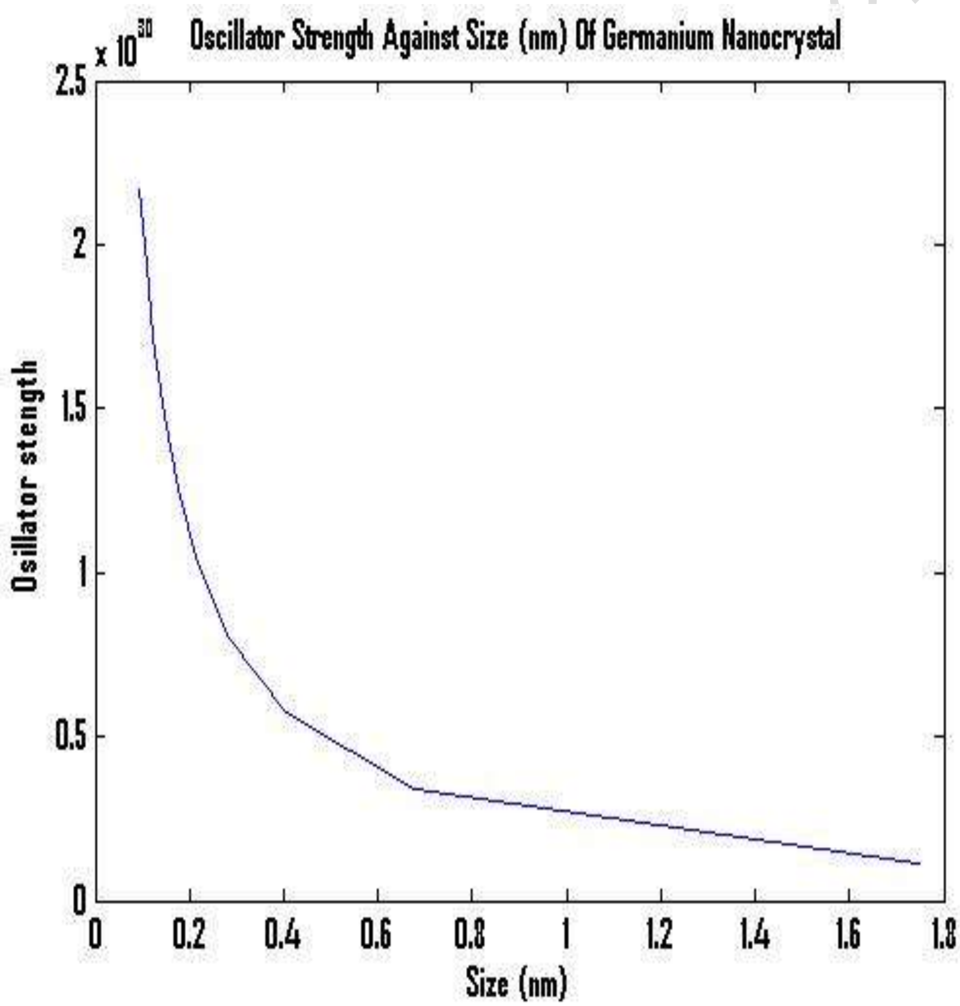

Figure 3.1: Oscillator strength of germanium Nanocrystal against size (nm)

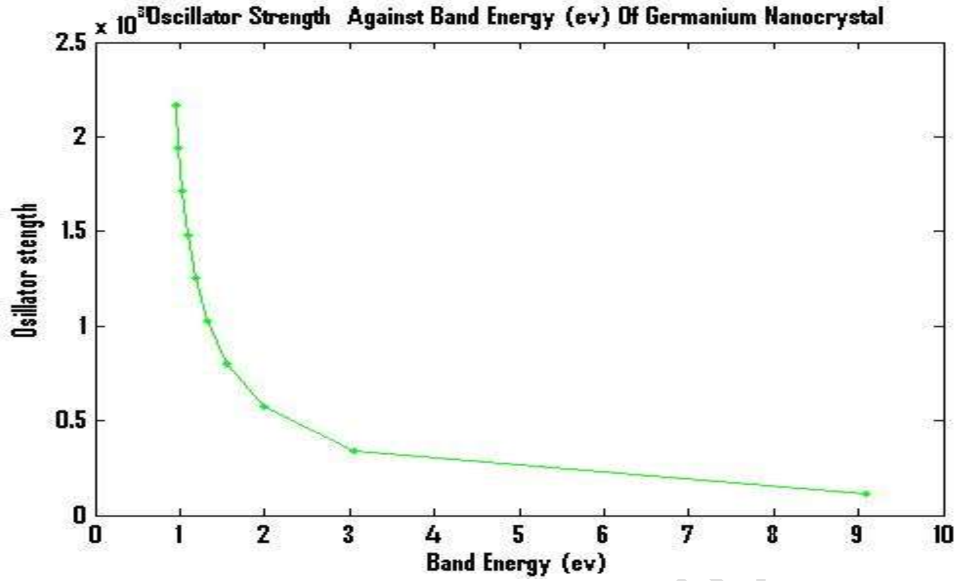

Figure 3.2: Oscillator strength against band energy (eV) of germanium nanocrystal

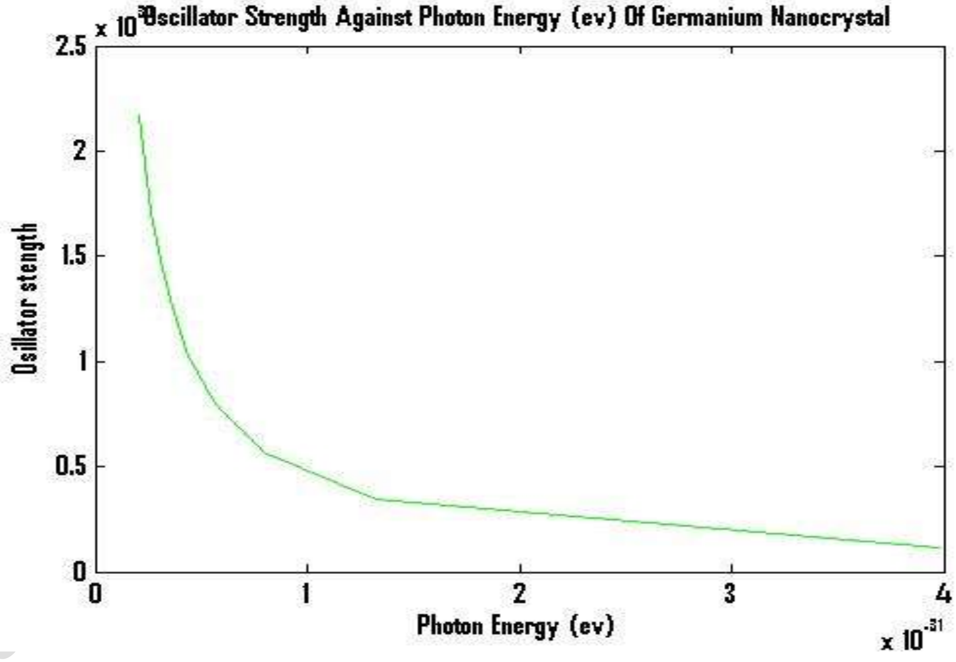

Figure 3.3: Oscillator Strength against photon energy (eV) of germanium nanocrystal

PL line shape is also alerted significantly by the oscillator strength as seen in Fig. 3.4. Here, α is the measure of oscillator strength and appears as an exponent in Eq. (2.6). Fig. 3.4. Shows the effects of variations in the reasonable values of α on the PL intensity profile for fixed values of L_o and σ. It is found that the PL peak shifts towards higher energy (blue, green and red) as the alpha measures increases. Actually, the oscillator strength in Nano crystallites varies with the amount of confinement and also with the surrounding environment via the change in dielectric constant. The higher the dielectric constant of the surrounding environment, the lower is the oscillator strength and vice versa. Therefore, PL spectra will blue-or-red-shift depending up on the surrounding medium around the crystallites. Hence the study of the effects of the dielectric constant should be adopted in the future study.

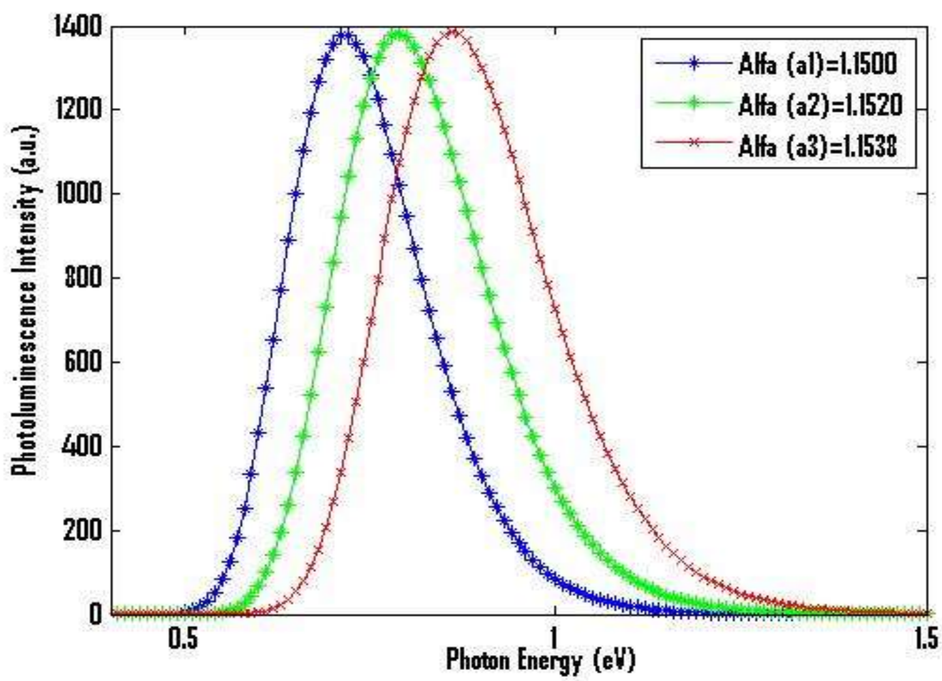

Figure 3.4: Photoluminescence Intensity (a.u) Vs. Photon Energy (eV)

DISCUSSION

It is clear that the PL depend strongly on the quantum confinement (QC) parameters β, γ and $size\ L_O$. The quantum confinement in different directions also changes the wave functions describing the behavior of electrons and holes that modifies the density of states. Good care should be taken in using the correct quantum confinement (QC) model for band gap up shift estimation. The oscillator strength is complicated functions of the size of nano crystallites and their surrounding media for the crystallites further complicates the analysis of observed PL data. The degree of localization of surface state [manifested by E_s] depends on the amount of disorder-ness in surface atoms of crystallites. The different surface passivation will give rise to a variable amount of disorder. Therefore, the localization energy E_s will depend on the type of surface passivation (Ashagrie Mekuriaw et al., 2008). It has been shown that the hydrogen and deuterium termination of surface atoms in PS gives a PL spectrum having a shift of about 0.14 to 0.18eV in PL peak energy for the same crystallite sizes (T. Matsumoto, 1997).

CONCLUSION AND FURTHER OUTLOOK

The effects of oscillator strength for GeNCs are investigated using a model that integrates the effect of quantum confinement and surface states.

The variation of oscillator strength as a function of GeNCs size, band gap energy and photon energy is presented, and has shown to have great influence on the oscillator strength of the nanocrystals.

The measure of oscillator strength on PL intensities has also been examined. All our results are in consistent with other experiments and theoretical findings.

It is observed that quantum confinement effect is more prominent in GeNCs that enhance the radiative recombination rate. The density of states, the radiative recombination rate, the absorption coefficient, temperature dependent PL and EL intensity, the dielectric function, the influence of surface passivation on the optical properties is interesting to look at. Since, the oscillator strength in nanocrystallites varies with the amount of confinement and also with the surrounding environment via the change in dielectric constant. Hence the study of the effects of the dielectric constant should be adopted in the future study.

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