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EFFECT OF QUANTUM DOT SIZE ON FREQUENCY OF CONFINEMENT POTENTIAL.

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ABSTRACT:
The effect of quantum dot size on frequency of confinement potential was investigated using the modified single band toy model. The three different semiconductor quantum dots considered are Cadmium Selenide (CdSe), Zinc Sulphide (ZnS), and gallium Arsenide (GaAs). The sizes of semiconductor quantum dots considered are the same as the nano-size of the Bohr exciton radius of electron-hole pairs in solids. Due to this fact, they exhibit effects of quantum size as particles in a three dimensional box. The frequency of the confinement potential and confinement energy of electrons in semiconductor quantum dots increases with decrease in the size of the nano-crystal. The graphs of the frequency of confinement potentials as a function of quantum dot size plotted for each of the three different semiconductor quantum dots show an exponential decay curves. This is in agreement with the fact that the lowest possible energy for a quantum dot sample is never zero.

Key words: Quantum dots, confinements, exciton, frequency,

INTRODUCTION

A tremendous amount of research has been devoted to the study of quantum dots in the last decade. These structures provide confinement in all three dimensions. They are distinguished by their discrete energy spectrum and thus share properties of single atoms. Quantum dots (QD) often referred to as "semiconductor nano-particles" are particles with physical dimensions smaller than the exciton Bohr radius and are confined in three spatial directions (Chukwuocha and Onyeaju, 2012). They are sometimes called artificial atom due to its quantum properties (Schaller and Klimov, 2004). The electronic characteristic of these nano-particles are closely related to the size and shape of the individual crystals and has a band gap which is determined by the frequency range of the emitted light. Their dimensions and number of atoms between the atomic-molecular level and bulk material with a band-gap depends in a complicated fashion upon a number of factors, including the bond type and strength with the nearest neighbours (Bera *et al.*, 2010). The QD dependence on size arises mainly from changes of the surface-to-volume ratio with size and from quantum confinement effects (Alivisatos, 1996), and they exhibit different colour of emission with change in size. This is shown in fig. 1.

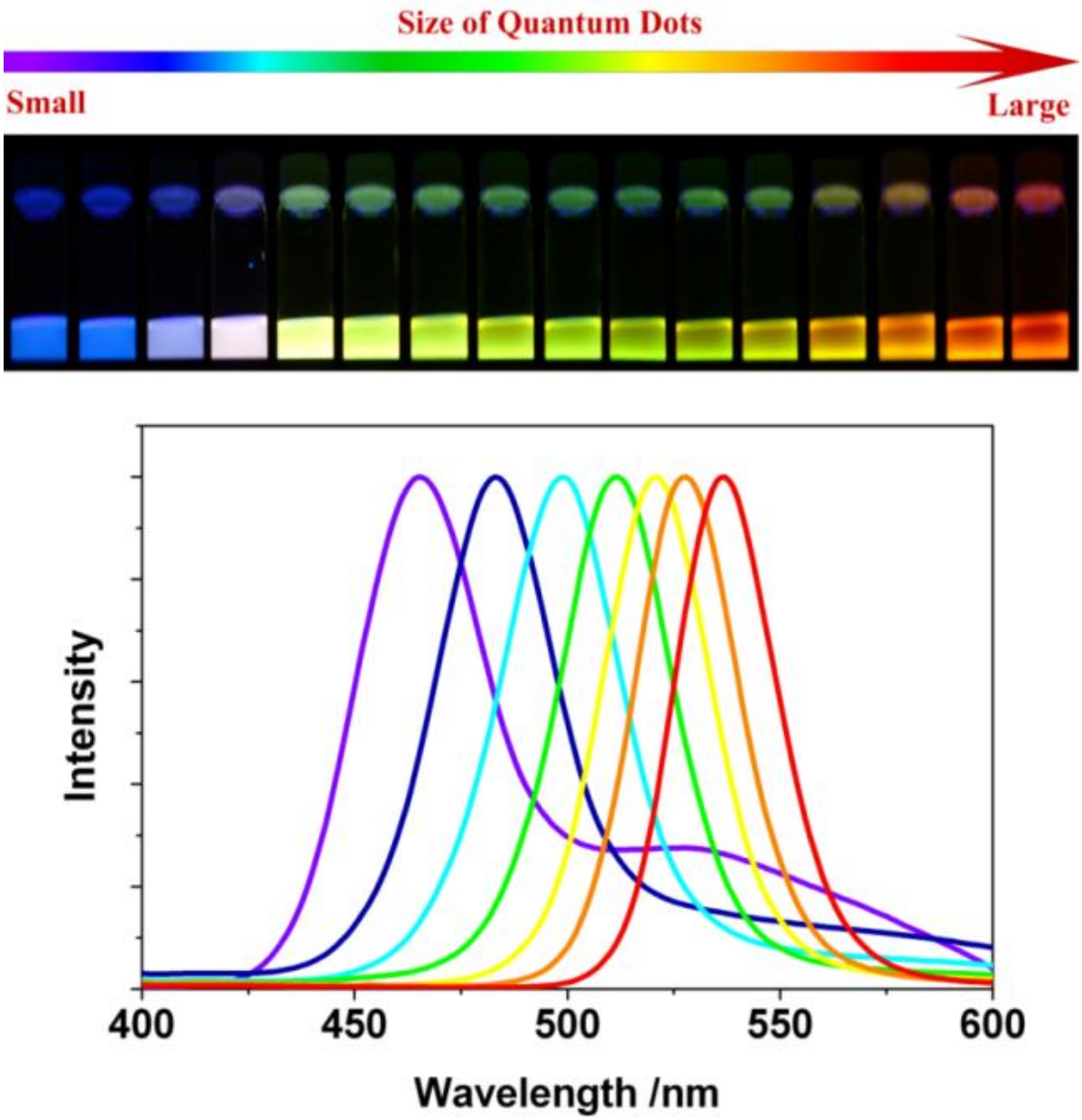

Fig 1**.** Top: Sixteen emission colours from small (blue) to large (red) CdSe quantum dots excited by a near-ultraviolet lamp; Bottom: Photoluminescence spectra of some of the CdSe Quantum dots (Bera *et al.*, 2009).

Quantum confinement effect is the key reason behind quantum dot colouration, and it is directly related to the energy levels of quantum dots. The band gap energy that determines the energy and the colour of the fluorescent light is inversely proportional to the square of the quantum dot size. These effects is said to arise from the spatial confinement of electrons within the crystallite boundary, and it is the key feature in emerging electronic devices. Quantum confinement effects endow QD with singular photochemical properties that are not available on the bulk material. This generally results from an increase in the band-gap energy and a decrease in the size

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of the QD (Anderson *et al.*, 2002). Optical properties of QD can be enhanced by doping the QD produced. These properties can be varied by changing the amounts and the positions of dopants in the dots (Yang *et al.*, 2005). Many simulation techniques have been used to compute the confinement energy or the electronic properties of the dots. For example; Kuo et al. (2001) used the stabilization method (sm) to show the accurate dynamic behaviour of the tunnelling rate and the intra-band absorption of a single QDs, Filikhin et al (2008) also used the single sub-band approach for the confinement energy in InAs/GaAs QD and the effect of strain and piezoelectricity. Botha (2007) studied the electronic structure and transport properties in a type II heterostructures using the multiband k.p Riccati equation. Recently, Chukwuocha et al. (2012) employed the Bruce equation to study the size dependence off confinement energy on QD, in this study however; the modified single band toy model of Zhang et al. (2009) was used to compute the frequency of the confinement potential on the QD of CdSe, ZnS and GaAs. This article is organized as follows: Section 2 consist of a review of the theoretical framework, Single band toy model of quantum confinement is presented in section 3, the numerical results is in section 4, discussion of results is in section 5, and conclusion is in section 6.

THEORETICAL FRAMEWORK

The Brus equation is used to describe the emission energy of QD semiconductor nanocrystal in terms of the band gap energy (E_g), Planck's constant (h), the radius of the dot (r), and also the reduced mass of the electron (m_e^*), and that of the hole (m_h^*) (Kippeny et al., 2002). The radius of the QD affects the wavelength of the emitted light due to quantum confinement, and this describes the effect of changing radius of the dot on the wavelength of light emitted ($\Delta E = \frac{hc}{\lambda}$, where c is the speed of light in m/s). The Brus equation which was based on effective mass approximation given by:

$$E_g(qd) = E_{bulk} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{4\pi\varepsilon_o\varepsilon_r R^2}$$

(1). Kayanuma who later modified the Brus equation quantified the size dependence band gap energy of quantum dots as (Kayanuma, 1998)

$$E_g(qd) = E_{bulk} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{4\pi\varepsilon_o\varepsilon_r R^2} - 0.248E_{Ry}^* \quad (2).$$

Where $E_g(qd)$ is band gap energy of the dot, E_{bulk} is band gap energy of bulk semiconductor, R is radius of the dot, h is Planck's constant, e is electronic charge, ε_o is permittivity of vacuum, ε_r is relative permittivity and E_{Ry}^* is Rydberg energy.

Ignoring the last two terms on the right hand side which are the columbic interaction exciton energy and the spatial correlation effect respectively, the overall Brus equation for calculating the emission energy is given as:

$$\Delta E(R) = E_g(bulk) + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \quad (3)$$

Where,

$\Delta E(R)$ = Emission energy

$E_g(bulk)$ = Band gap energy of the bulk semiconductor

$\frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$ = Ground state confinement energy of the semiconductor QD.

Single Band Toy Model of Quantum Confinement

The basis for the single band toy model is provided by considering the total Lagrangian of a couple systems aside the unperturbed cohesive energy term given by (Zhang *et al.*, 2009)

$$\left(E_c - \frac{\hbar^2}{2m^*}\nabla^2\right)\psi(r) + a_c.Tr(\varepsilon)\psi(r) = E\psi(r) \quad (4)$$

Here, m^* is the effective mass of the electron and hole, ε is the elastic strain tensor, E_c is the energy of the band gap edge for the conduction of the valence band, E is the electronic spectrum of energies, $\varepsilon = \frac{1}{2}(\nabla U + \nabla^T U)$ (where U is the strain energy for linear elastic deformation and ∇^T is the local strain tensor), $\psi(r)$ is the wave function, a_c is the deformation potential constant.

Since Equation (4) do not give an accurate solution for the ground state energy for a low dimensional quantum dot, there is need to modify the single band toy model. We construct a model that will be suitable for a small quantum dot of GaAs. Assuming that a well known strain field exist that interacts with the electronic structure and perturbs it. The motion of the confined electron in a spherical quantum dot confined by a radial potential of the form $\frac{1}{2}m_e^*\omega_o^2 r^2$ (where m_e^* is the effective mass of the electron, r is the position of the quantum dot and ω_o is the frequency of the quantum dot confinement potential) with the application of external magnetic field is given by:

$$\left[E_c - \frac{1}{2}m^*(p - e/c\,A)^2\right]\psi(r) + \frac{1}{2}m^*\omega_o^2 r^2\psi(r) = E\psi(r) \quad (5)$$

where

$$E_c = E_{c,v}^o + a_c r \in_h, \quad (6)$$

E_c is the energy of the conduction-band state, $E_{c,v}^o$ is the energy of the band edge for conduction or valence band and $\in_h$ is the hydrostatic strain, a_c is the deformation potential constant and r is the radius of quantum dot (Lam and Ng, 2010). The assumption made in obtaining the general solution for the modified single band toy model is based on space quantization of the orbital angular momentum, in which the direction of the orbital angular momentum vector is quantized with respect to the direction of the external magnetic field B.

For ground state energy, the equation for the modified single band toy model becomes

$$E_C - E_g = \frac{m^{*3}r^6(\omega_c^2 - \omega_o^2)^2}{8\hbar^2} \quad (7)$$

where E_g is Band gap energy of the bulk semiconductor, ω_c is Cyclotron frequency, and m^* is the exciton reduced mass given as $\frac{m_e^* m_h^*}{(m_e^* + m_h^*)}$ with m_e^* as the effective mass of excited electron and m_h^* the effective mass of excited hole. For a zero magnetic field, $\omega_c^2 = 0$. and equation (7) becomes:

$$E_C = E_g + \frac{4\pi^2 m^{*3}r^6\omega_o^4}{8h^2} \quad (8).$$

$\frac{4\pi^2 m^{*3}r^6\omega_o^4}{8h^2}$ = Ground state confinement energy of the semiconductor quantum dot.

Comparing the ground state energies in equations (3) and (8), we have:

$$\omega_o = \frac{h}{\sqrt{2\pi}m^*R^2} \quad (9).$$

Equation (9) is the frequency of the confinement potential.

RESULTS

The material parameters utilized for the computation of the confinement energies at various radii is given in tables **1**, **2** and **3**.

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Table 1: Material parameters used for the computation of the confinement energies at various radii which is less than the Bohr radius a_B (Sinclair and Dagatto, 2009).

Quantum Dots	m_e^*	m_h^*	E_{bulk} **at 300k**	a_B **(Bohr Radius)**
CdSe	0.13 m_o	0.45 m_o	1.74 eV	6 nm
ZnS	0.34 m_o	0.23 m_o	3.68 eV	5 nm
GaAs	0.063 m_o	0.51 m_o	1.424 eV	10 nm

Table 2: Deformation potential of zincblende II-IV wide band gap semiconductors (Calderon, 2002)

Compound	a **(eV)**	b **(eV)**
CdSe	-3.664	-0.80
CdTe	-4.520	-1.10
ZnS	-4.000	-0.62
ZnSe	-4.530	-1.14
ZnTe	-5.800	-1.80
GaAs	-8.930	-1.76

Table 3: Hydrostatic strain as it varies with different quantum dot sizes (Gamalath and Fernando, 2013):
For Cadmium Selenide (CdSe)

R(nm)	0.90	1.20	1.44	1.92	2.40	2.96	3.50	4.20	4.80
$\in_h$	o.487	0.485	0.481	0.480	0.475	0.472	0.466	0.460	0.459

For Zinc Sulphde (ZnS):

R(nm)	0.75	1.25	1.75	2.25	2.75	3.25	3.75	4.00	4.50
$\in_h$	0.489	0.484	0.480	0.475	0.470	0.468	0.464	0.460	0.459

For Gallium Aresenide (GaAs):

R(nm)	1.50	2.00	2.50	4.00	5.50	6.60	7.00	7.50	8.00
$\in_h$	0.480	0.475	0.474	0.460	0.458	0.455	0.451	0.442	0.438

Tables 4, 5 and 6 shows the Confinement Potential Frequency as it varies with dot sizes for CdSe, ZnS, and GaAs respectively. These values are gotten using equation (9) above.

Table 4: The Confinement potential Frequency and Diameter of Dot for Cadmium Selenide

Diameter of Dot (nm)	**Confinement Potential Frequency (THz)**
1.80	3,553.80
2.40	1,999.20
2.88	1,388.30
3.84	780.90
4.80	499.80
5.92	328.60
7.00	235.00
8.40	163.20
9.60	125.00

Table 5: The Confinement Potential Frequency and Diameter of Dot for Zinc Sulphide.

Diameter of Dot (nm)	Confinement Potential Frequency (THz)
1.50	3,762.10
2.50	1,354.40
3.50	691.00
4.50	418.00
5.50	279.80
6.50	200.40
7.50	150.50
8.00	132.30
9.00	104.50

Table 6: The Confinement Potential Frequency and Diameter of Dot for Gallium Arsenide.

Diameter of Dot (nm)	**Confinement Potential Frequency (THz)**
3.00	2,301.20
4.00	1,294.40
5.00	828.40
8.00	323.60
11.00	171.20
13.20	118.90
14.00	105.70
15.00	92.00
16.00	80.90

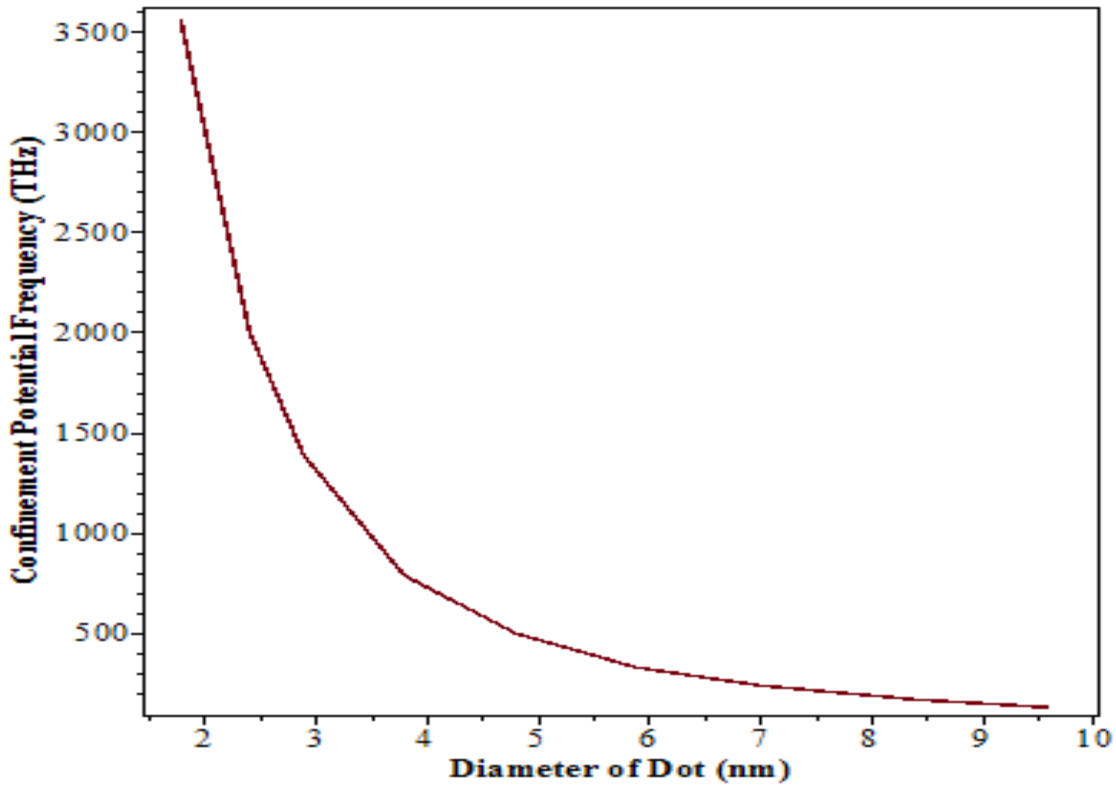

Fig 2: Confinement Potential Frequency as a function of Dot Size (in diameter) for Cadmium Selenide (CdSe).

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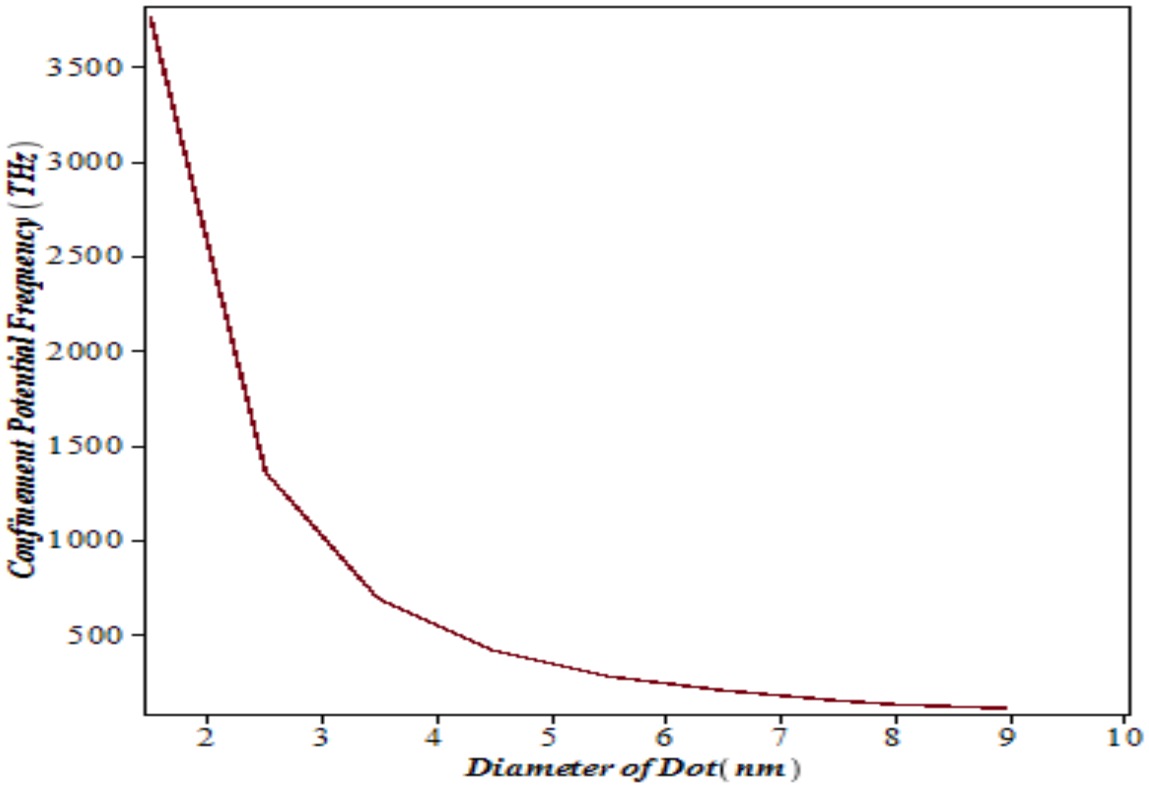

Fig 3: Confinement Potential Frequency as a function of Dot Size (in diameter) for Zinc Sulphide (ZnS).

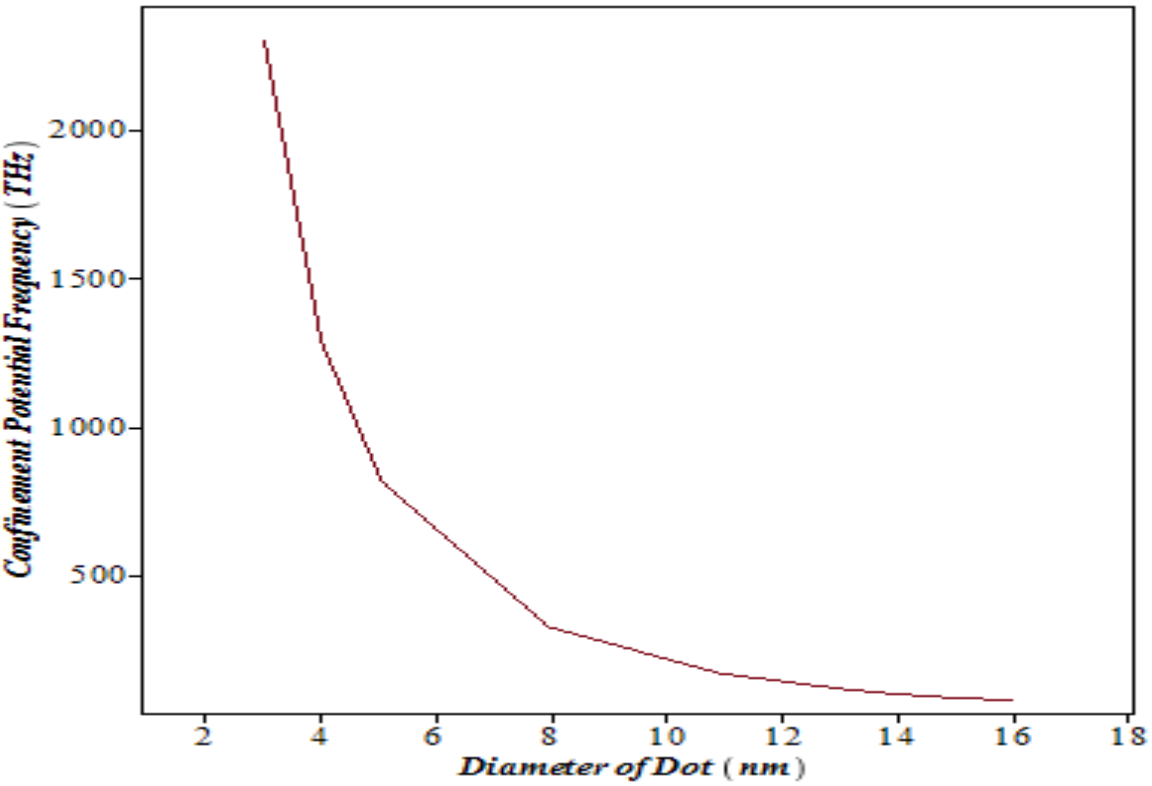

Fig 4: Confinement Potential Frequency as a function of Dot Size (in diameter) for Gallium Arsenide (GaAs).

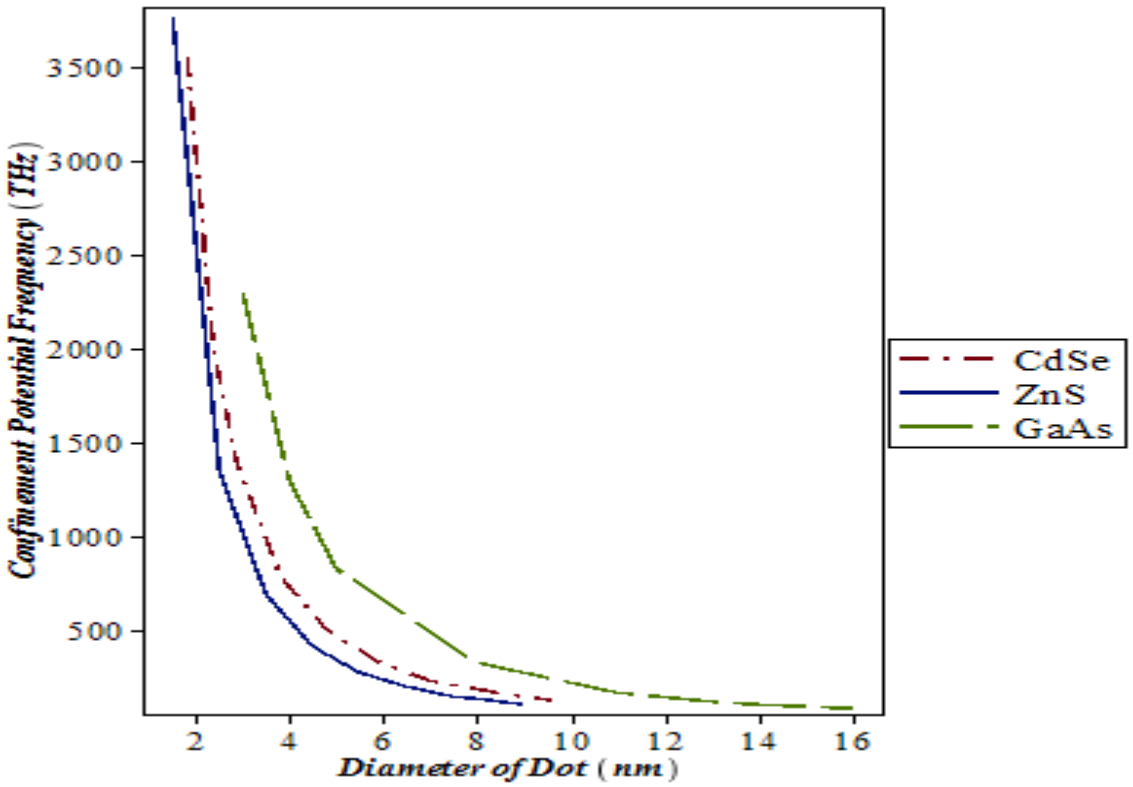

Fig 5: Confinement Potential Frequency Vs Diameter of Dot for (CdSe), (ZnS), and (GaAs).

DISCUSSION OF RESULTS

The graphs of confinement potential frequency against diameter of dot for Cadmium Selenide (CdSe), Zinc Sulphide (ZnS), and Gallium Arsenide (GaAs) semiconductor QD in figures (2), (3), and (4) respectively show an exponential dependence of confinement on the size of the dot. Thus, as the size of the dot is increased, the confinement potential frequency decreases exponentially, but never reaches zero. This finding is in agreement with the theoretical observation of Chukwuocha *et al.* (2012).The Sizing curves of the confinement potential frequency plotted for the three different QD is shown in fig. (5). the confinement region is subdivided into strong confinement regime and weak confinement regime (Harbold, 2005).

The frequency of the confinement potential increases as the confinement effect get stronger (as the diameter of the dot decreases) and the confinement effect dominates. The sharp increase in confinement potential frequency in figure (2) for CdSe begins when the dot size is 3.84nm; and this corresponds to a confinement frequency of about 780.9THz. In fig. (3), the strong confinement frequency limit of 691.0THz is observed when the size of ZnS QD is about 3.50nm. Similarly, in fig. (4), as the size of GaAs reduces to about 5.00nm, its corresponding confinement potential frequency increases sharply to about 828.4THz. The three QDs discussed above are compared in figure (5). It can be seen that the confinement potential frequency is strongest in Cadmium Selenide, followed by Zinc Sulphide and then Gallium Arsenide. These exponential

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decay curves are asymptotic to the horizontal axis.

Pellegrini *et al.* (2005) investigated the matrix influence of size dependent band gap of quantum structures on confinement potentials, using colloidal CdSe. It was observed that the prediction from the finite depth well model used is in strong agreement with their experimental data obtained. This is a strong indication that the confinement potential dimensionalities depends on the size of quantum structures.

The effect of QD size on the frequency of confinement potential has been studied successfully. The results obtained have been analyzed and compared with already existing experimental results. The most obvious evidence of quantum confinement in semiconductor quantum dot is the shift in the optical absorption and emission spectra with size, and this is a consequence of the particle-in-a-box model. The modified single band toy model obtained for the three different semiconductor quantum dots exhibit the size dependence predicted by Brus equation. This is in good agreement with the experimental observation of the size dependence on the band gap energy and confinement potential frequency. The decrease in the frequency of the confinement potential as a function of the quantum dot size suggests that quantum confinement effect exist in the dot considered (i.e. CdSe, ZnS, and GaAs). The degree of confinement among the three quantum dots considered is found to be strongest in Cadmium Selenide, followed by Zinc Sulphide and Gallium Arsenide.

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