Study of Dependence of Optical Parameters on the Size of Nanoporous Silicon Quantum Dot Through Energy Gap

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Abstract

Both nanocrystalline and nanoporous silicon show interesting optical properties. As the system size goes to nanoscale the optical band gap, radiative transitions, oscillator strength, absorption coefficient and dielectric function increase. The nanosilicon shows unusual optical properties which have tremendous importance for nanophotonics and optoelectronic applications. The purpose of this work is to study the optical behavior of nanoporous silicon cluster (quantum dot) with varying porosity and oxygen as well as hydrogen at the surface. In order to clarify the morphological effects such as surface passivation and porosity level of a nanoporous silicon on its optical properties, calculation of optical absorption coefficient, dielectric function and oscillator strength of porous silicon nanoclusters as a function of size (diameter) through energy gap have been discussed. The effects of nanoparticles size along with surface passivation and porosity level on optical band gap have also been investigated and compared with experiment. The porosity and surface effects are incorporated through some empirical parameters c and p in our study.

Keywords: Optical properties; quantum dot; porosity; optical band gap; surface effects

Introduction

Quantum dots (QDs) are highly emissive, spherical nanoparticles with a few nanometers in diameter. They provide a functional platform for a class of materials for use in light emitting diodes, photovoltaic cells, and biosensors [1]. Due to their extremely small size, on the order of a few nanometers, the dots behave similarly to three dimensional quantum wells. When an electron is excited by a photon striking the quantum dot, it behaves as a particle confined in an infinite potential well, since the electron cannot escape from the quantum dot. The hole, created by the excited electron, behaves in the same fashion [2].

Quantum confinement effect on the size of nanostructures

Semiconductor nanocrystals having analogous interior bonding geometries compared to their known bulk counter parts exhibit variations in their optical properties with size variation. The main concern for these changes lies in the variation of density of states as a function of energy, which varies as a function of dimension of nanostructures. From a density of state point of view nanocrystals lie between discrete atomic and bulk limit. In any material there will be a size below which one observes fundamental electronic and optical properties as a function of size. This quantum size effect regime begins when the energy level spacing exceeds K_BT (energy level spacing > K_BT). If we confine the electron-hole pairs (excitations) in a small region, having dimensions of the order of a few nanometers, the properties of the material completely change. Since the order of magnitude of the electron and hole De-Broglie's wavelength (~1nm) is comparable with the confinement dimensions, they behave as a particle in a box. Consequently, the confinement effect in a region of nanometric size is referred to as quantum confinement and it has an effect in widening the band gap nanostructures [3].

One of the most direct effects of reducing the size of materials to the nanometer range is appearance of quantization effects due to the confinement of the movement of electrons, this leads to discrete energy levels depending on the size of the structure. Following this line artificial or natural structure with properties different from the corresponding bulk materials can be created. Control over dimensions as well as composition of structures makes it possible to tailor material properties to specific applications which are influenced by quantum confinement effect (QCE) [3]. Hence, quantum confinement (QC) in semiconductors results from the geometric confinement of electrons, holes or excitons (electron hole bound pair). The normal size of an exciton in a large bulk crystal is expressed as an exciton Bohr radius (BER). When an electron- hole pair is squeezed below the dimensions approaching excitons Bohr radius, quantum confinement effects becomes prominent in the structure and the effective band gap increases. The smaller the nanostructure the larger the effective band gap and the greater the energy of the optical emission which changes the optical and the electronic properties when the sample size is sufficiently smaller than 10nm. This effect can also be understood from the Heisenberg's uncertainty principle according to which energies of an electron or hole increase as their position is confined. As a result the effect of QC is a rearrangement of the density of the electronic states in energy as direct consequence of volume shrinking in one, two, or even three dimensions, which can be obtained, respectively, in quantum wells, wires, and dots. Thus, understanding of the spatial confinement of electrons within the crystallite boundary leads to a larger spacing between band gap to change various properties and physical structure of the material as the size of the nanostructure decreased [4].

Density of states in view of quantum confinement

As a result of quantum confinement in different directions, there is a change in wave function describing the behavior of electrons and holes and consequently the number of states per unit energy, i.e. the density of states changes as a function of energy E of the particle. Generally, the density of states depends on the dimensions of the nanostructure and the corresponding wave vector dispersion [5]. In case of a bulk material, the density of states increases with energy of the particle following a parabolic law. Therefore for a three dimensional bulk material, the DOS is defined as the number of available electronic states per unit volume per unit energy and it is given by:

$$D\ (E) = \frac{\sqrt{2}m_e^{\frac{3}{2}}}{\pi^2\hbar^3}E^{\frac{1}{2}} \tag{1}$$

Where as in the case of two-dimensional nanostructures (quantum well) the carrier movement is restricted to a plane (the two directions are for the movement of particles, while the third direction determines the quantum confinement direction). The DOS is defined as the number of electronic states per unit area per unit energy and it is given by:

$$D\ (E) = \frac{m_e}{\pi^2\hbar^2} \tag{2}$$

Further reduction in the dimension of a system ends up in a quantum wire. Examples of such one-dimensional structures include nanotubes, semiconductors nano-wires and nano-rods. For a quantum wire (particles are free to move in only one direction and the two sides are confined) the DOS is defined as the availability of electronic states per unit length per unit energy and is give by:

$$D\ (E) = \frac{\sqrt{2}m_e^{\frac{1}{2}}}{\pi\hbar}E^{-\frac{1}{2}} \tag{3}$$

Finally, for a zero dimensional system (quantum dot), the confinement is along all three dimensions and the DOS becomes a delta function. In the 0-D (strong confinement) the electrons are confined in their motion in all three directions [6].

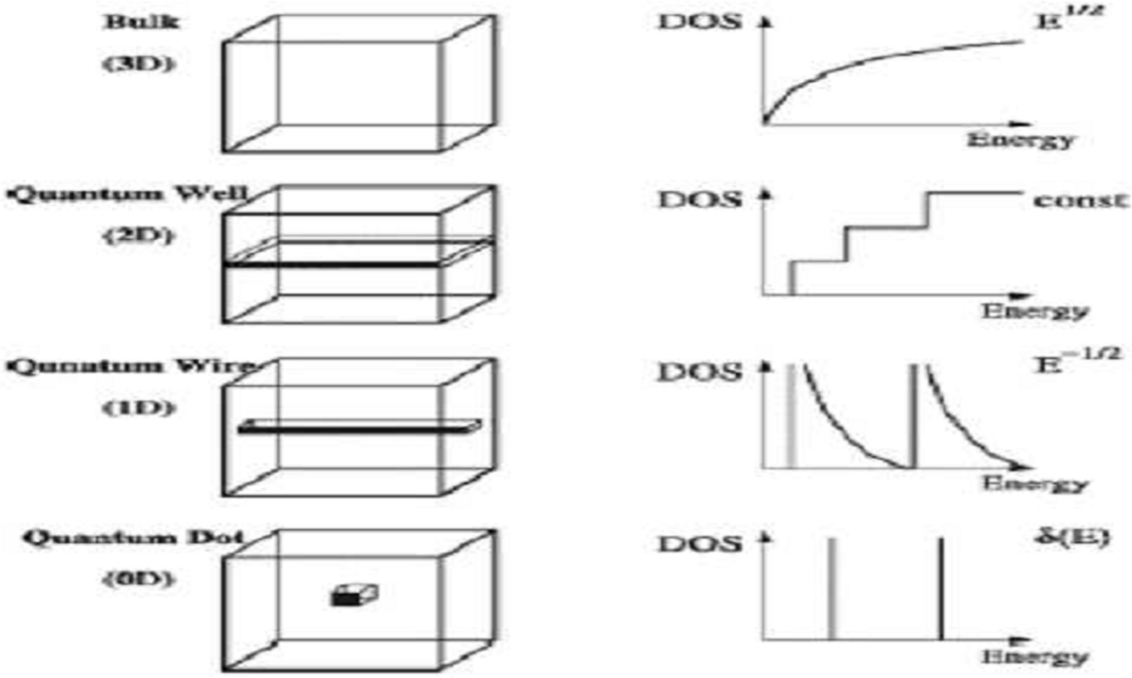

Figure .1. The density of states as a function of energy for a particle confined to move in a bulk, quantum well, quantum wire and quantum dot. As can be seen from the above diagrams the density of states varies as a function of energy from nanoscale to bulk regime. It logically follows that optical and electronic properties drastically change as one goes from bulk to nanoscale, which mainly evolves from quantum confinement effect. As can be seen from the above diagrams the density of states varies as a function of energy from atomic to bulk regime. It logically follows that optical and electronic properties drastically change as one goes from bulk to atomic level (nanoscale), which mainly evolves from quantum confinement effect [6].

Energy gap of nanostructures

The size quantization effect that has been looked into at great lengths only recently leads to an important change in various properties such as electrical property, optical transitions, conductivity, magnetization etc, start to change. These different behaviors of most materials reflect the different character of the band gap, i.e. the difference in energy between the lowest point of empty conduction band and the highest fulfilled point of the valence band [7]. Therefore, downscaling of purely classical bulk material properties can lead to dramatic changes in behavior in the nanoscale. Nevertheless the most exciting effects in the nano realm where quantum physics comes into play and leads to completely new kinds of behavior causes the band gap $(E_g)$to expand which means size quantization effect increases the energetic gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO-LUMO gap), shifting the band gap from 1.12 eV in bulk silicon all the way into nanoclusters as shown in the figure below [8].

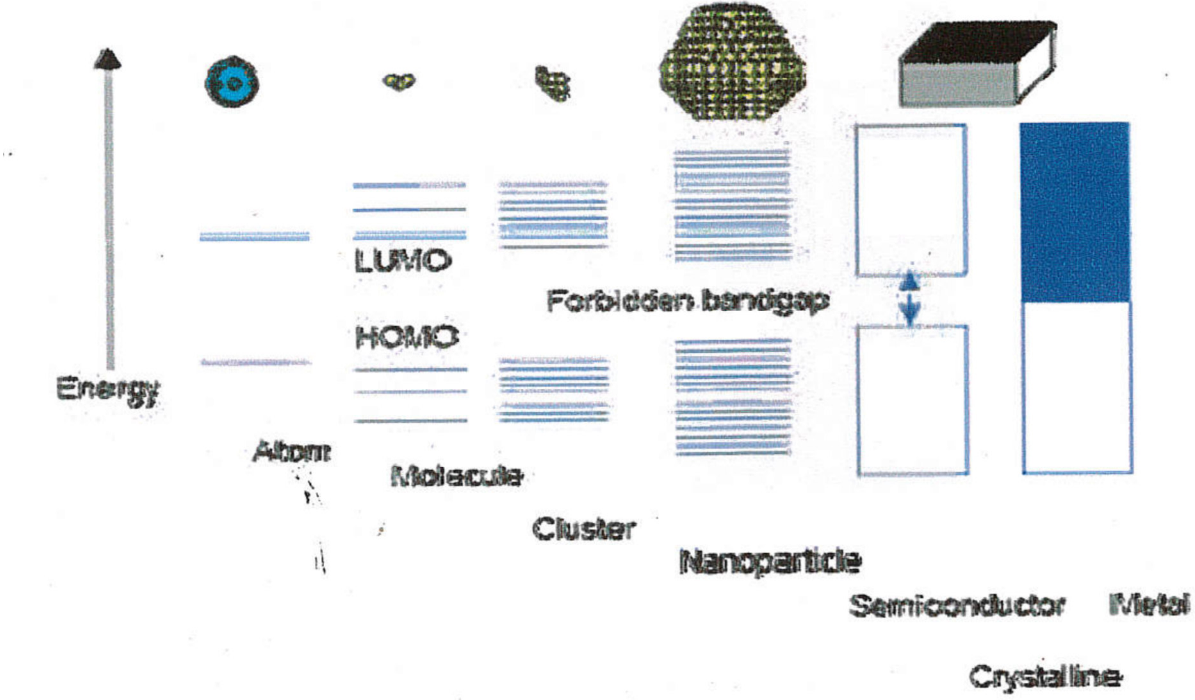

Figure.2. Size quantization effect.Electronic state transition from bulk to small cluster [8].

Thus, the quantum confinement effect is responsible for the increment of the band gap of nanoclusters. In addition to quantum confinement, the size, shape and passivation of hydrogen and oxygen samples affect the band gap of nano-size particles (nano-dots). According to many calculations and observations:

$$E_g^{nano} = E_g^{bulk} + \frac{c}{d^p} \tag{4}$$

Where c is a constant and p ranges from 1.25 to 1.85 and depends on the type of passivation as well as the symmetry of nanoclusters (the value of c and p depend on the nature of the surface as well as the symmetry of nanoclusters). The main concern of this section was to find out the analytic calculations for the band energies using the K.P perturbation method.

Optical parameters

Optical parameters include density of state, absorption coefficient, dielectric constant and oscillator strength. In the coming sections we will see the relation between these optical parameters (optical absorption coefficient, dielectric constant and oscillator strength) with nanoporous silicon quantum dot diameter (size) through energy gap. Varying porosity level and passivating surface of the quantum dot with hydrogen and oxygen will also be considered.

Absorption coefficient

The optical absorption coefficient is proportional to the number of optical transitions per unit volume and time elements. Therefore, it can be given by the absorption energy per unit time, $\hbar\omega W(\omega)$, divided by the energy flux ,$\left(\frac{A_o W^2 \varepsilon_o n}{2c\pi}\right)$, i.e.

$$\alpha(\omega) = \frac{\hbar\omega W(\omega)}{A_o^2 \omega^2 \varepsilon_o \frac{n}{2c\pi}} \tag{5}$$

where n is the refractive index of the silicon quantum dot.

The total number of optically induced transitions per unit volume and unit time is given as:

$$W(\omega) = \frac{2\pi}{\hbar}\left(\frac{eA_o}{m_o c}\right)^2 |\hat{e}.M_{cv}|^2 J_{cv} \tag{6}$$

Where, the Joint Density of State, J_{cv} can be expressed as:

$$J_{cv} = \frac{1}{2\pi^2}\left(\frac{2m_r^*}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\hbar\omega - E_g} \tag{7}$$

Here J_{cv} related to energy gap which is a function of size. Therefore, the absorption coefficient near the absorption edge will be:

$$\alpha(\omega) = \frac{4\pi^2 e^2}{\varepsilon_o n c m_o^2 \omega}\{|\hat{e}.M_{cv}|^2 J_{cv}\} \tag{8}$$

Using eq. (7),

$$\alpha(\omega) = \frac{4\pi^2 e^2}{\varepsilon_o n c m_o^2 \omega}\left\{|\hat{e}.M_{cv}|^2 \frac{1}{2\pi^2}\left(\frac{2m_r^*}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\hbar\omega - E_g}\right\}$$

$$\alpha(\omega) = \left\{\frac{2e^2(2m_r^*)^{3/2}}{\varepsilon_o n c m_o^2 \hbar^3 \omega}\right\} |\hat{e}.M_{cv}|^2 \sqrt{\hbar\omega - E_g}$$

The matrix element is given by:

$$|\hat{e}.M_{cv}|^2 = \frac{3}{2}\frac{m_o}{m_e^*}(m_o - m_e^*)\frac{E_g + \Delta_o}{3E_g + 2\Delta_o} E_g \tag{9}$$

Hence,

$$\alpha(\omega) = \frac{3e^2\sqrt{m_o}}{\varepsilon_o n \hbar^2 c}\left(\frac{2m_r^*}{m_o}\right)^{\frac{3}{2}} \frac{m_o - m_e^*}{m_e^*}\frac{E_g + \Delta_o}{3E_g + 2\Delta_o}\frac{E_g}{\hbar\omega}\sqrt{\hbar\omega - E_g}$$

$$\alpha(\omega) = \frac{3e^2\sqrt{m_o}}{\varepsilon_o n \hbar^2 c}\left(\frac{2m_r^*}{m_o}\right)^{\frac{3}{2}} \frac{m_o - m_e^*}{m_e^*}\frac{E_g}{\hbar\omega}\mathrm{f(g)} \tag{10}$$

Where: $\mathrm{f(g)} = \frac{E_g + \Delta_o}{3E_g + 2\Delta_o}\sqrt{\hbar\omega - E_g}$

For $\hbar\omega \approx E_g$

$$\alpha(\omega) = \frac{3e^2\sqrt{m_o}}{\varepsilon_o n \hbar^2 c}\left(\frac{2m_r^*}{m_o}\right)^{\frac{3}{2}} \frac{m_o - m_e^*}{m_e^*}\mathrm{f(g)} \tag{11}$$

From eq. (11) we can see that the optical absorption coefficient is function of photon energy and energy gap. But Zunger et al using tight-binding method, Tripat et al and Ghoshal et al using local pseudopotential method to calculate the bandgap energy as a function of diameter (size) for clean and passivated surface silicon nanoclusters at room temperature as a result even if the optical absorption coefficient is directly a function of energy gap and photon energy it is indirectly a function of silicon nanoclusters diameter (size) through the band gap.

Dielectric function

For semiconductor with optical absorption α, the refractive index is complex and given by

$$\tilde{n} = n_r + ik \tag{12}$$

This complex index of refraction is related to the complex dielectric constant as

$$\tilde{\in} = \in' + i\,\in'' \tag{13}$$

Where: $\in' = \in$

$$\in'' = \frac{\sigma}{\varepsilon_o \omega}$$

From eq. (12) and eq. (13), we will get

$$\in' = {n_r}^2 - k^2$$

$$\in'' = \frac{\sigma}{\varepsilon_o \omega} = 2n_r k$$

But the optical absorption coefficient is given by

$$\alpha = \frac{2\omega k}{c} \Rightarrow k = \frac{c\alpha}{2\omega}$$

$$\in'' = \frac{c\alpha n_r}{\omega} \tag{14}$$

And using eq. (11)

$$\in'' = \frac{3e^2\sqrt{m_o}}{\varepsilon_o \hbar^2 \omega}\left(\frac{2m_r^*}{m_o}\right)^{\frac{3}{2}} \frac{m_o - m_e^*}{m_e^*}\mathrm{f(g)} \tag{15}$$

where, $\mathrm{f(g)} = \frac{E_g + \Delta_o}{3E_g + 2\Delta_o}\sqrt{\hbar\omega - E_g}$

As we can see from eq. (15) the imaginary part of the dielectric function is directly a function of energy gap and photon energy while it is indirect function of silicon nanoclusters diameter (size) through the band gap.

Oscillator strength

The Oscillator strength, the equivalent number of oscillations of the transition between the Valance and conduction bands, is related to the matrix element of the momentum matrix and is given by the equation:

$$f_{cv} = \frac{2|P_{cv}|^2}{m_o \hbar\omega_{cv}} \tag{16}$$

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

$$\Rightarrow f_{cv} = \frac{2|\hat{e}.M_{CV}|^2}{3m_o \hbar\omega_{cv}} \tag{17}$$

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

And in equation (9) we see that

$$\left|\hat{e}.M_\mu V\right|^2 = \frac{3}{2}\frac{m_o}{m_e^*}(m_o - m_e^*)\frac{E_g + \Delta_o}{3E_g + 2\Delta_o}E_g$$

Inserting this equation in to equation (16) and using $m_e^* = 0.4\mathrm{m_o}$ we obtain:

$$f_{cv} = \frac{2}{3m_o\hbar\omega_{cv}}\frac{3}{2}\frac{m_o}{m_e^*}(m_o - m_e^*)\frac{E_g+\Delta_o}{3E_g+2\Delta_o}E_g \tag{18}$$

$$f_{cv} = \frac{3}{2\hbar\omega_{cv}}\frac{E_g+\Delta_o}{3E_g+2\Delta_o}E_g \tag{19}$$

From eq. (19) we can see that the oscillator strength is directly a function of energy gap and photon energy while it is indirect function of silicon nanoclusters diameter (size) through the band gap.

Results and Discussions

In the above section we have seen how the optical absorption coefficient, the dielectric function and oscillator strength are related to size of nanoporous silicon quantum dot through energy gap. The aim of this work also extends to the dependence of energy gap of nanoporous silicon quantum dot on the size of the dot. Here in addition to their size dependence we also take into account the effect of porosity level and surface passivation. Therefore, in this chapter we investigate the results based on our expressions. The plots are generated from the relations we obtain in equations (4), (11), (15) and (19) using MATLAB programs.

According to many calculations and observations, the optical energy gap (eq. 4) is given as:

$$E_g^{nano} = E_g^{bulk} + \frac{c}{d^p} \tag{20}$$

where E_g^{nano} and E_g^{bulk} are the band gap energies of silicon nanoporous quantum dot and bulk silicon respectively, d is the size of silicon nanoporous quantum dot and the values of c and p depend on the nature of the surface as well as the symmetry of nanoclusters.

For pure sample at room temperature eq. (20) becomes:

$$E_g^{nano} = E_g^{bulk} + \frac{3.73}{d^p} \tag{21}$$

And, for hydrogen and oxygen passivated respectively it becomes:

$$E_g^{nano} = E_g^{bulk} + \frac{4.042}{d^p} \tag{22}$$

$$E_g^{nano} = E_g^{bulk} + \frac{3.82}{d^p} \tag{23}$$

In addition to varying size of nanoporous silicon quantum dot, varying porosity level of the material and see its effect on energy gap and optical parameters (absorption coefficient, dielectric function and oscillator strength) of nanoporous silicon quantum dot is the main objective of this thesis. Therefore, let us take two different values for p ($p = 1.32$ and $\alpha = 1.42$).

Now using eq. (21), eq. (22) and eq.(23) together with effective mass of hole, $m_h^* = 0.54m_o$, effective mass of electron, $m_e^* = 0.4m_o$, bulk silicon spin-orbit splitting, $\Delta_o = 0.044$ eV, effective refractive index of porous silicon nanoclusters (quantum dot) with size (1-10nm) from eq. (11) as:

$$\alpha = 5.15 \times 10^5 \times (E_g)\left(\frac{E_g+0.044}{3E_g+0.088}\right)\sqrt{3 - E_g}\,\mathrm{eV}^{-1/2}\mathrm{cm}^{-1} \tag{24}$$

Where the imaginary part of the dielectric function from eq. (15), becomes:

$$\varepsilon'' = 10.22 \times (E_g)\left(\frac{E_g+0.044}{3E_g+0.088}\right)\sqrt{3 - E_g}\,\mathrm{eV}^{-1/2} \tag{25}$$

And finally the oscillator strength from eq. (19) for photon energy, $\hbar\omega_{cv} = 3\mathrm{eV}$, becomes:

$$f = \left(\frac{1}{2}\right)\left(\frac{E_g+0.044}{3E_g+0.088}\right)E_g \tag{26}$$

In the next sections based on the above derived expressions (eqs. 20-26) we will plot them using MATLAB programs and understand them in detail.

Dependence of optical energy gap on level of porosity as well as size of nanoporous silicon quantum dot

In this section we describe analytically the behavior of optical energy gap of nanoporous silicon quantum dot as a function of its level of porosity and size. Taking $E_g^{bulk} = 1.12eV, c = 4.5$ and 6.2 and $p = 1.32$ and1.42, where c and p are called porosity parameters and varying d from 1nm to 10nm in eq. (20), the following figures (figure 3 and figure 4) can be obtained. As we can see from these figures, the energy gap of silicon nanoporous quantum dot increases as its size decreases. In addition, the variation of energy gap was also observed by varying porosity level and we found that energy gap decreases with increasing the value of p and it increases with increasing value of c (see figures 3 and 4 carefully). Our results are in good agreement with recent experimental and theoretical findings.

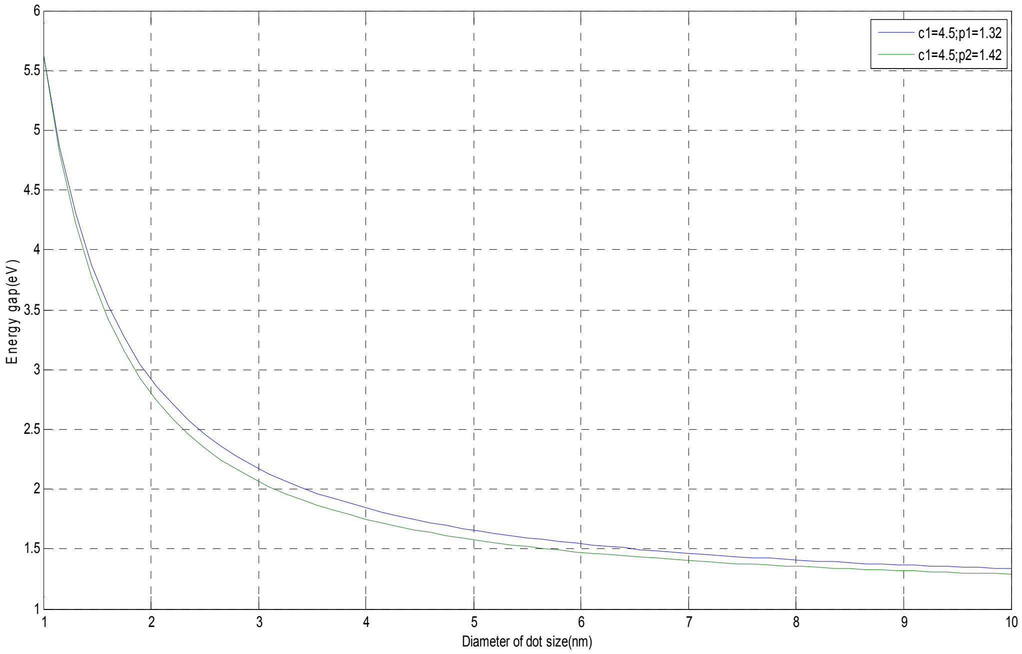

Figure.3. Variation of optical energy gap with porous silicon nanoclusters (quantum dot) diameter. The upper line (blue) is for $\mathrm{p} = 1.32(10\% \text{ to } 20\% \text{ porosity})$ and the lower line (green) is for $\mathrm{p} = 1.42(30\% \text{ to } 40\% \text{ porosity})$. For both lines $\mathrm{c} = 4.5$.

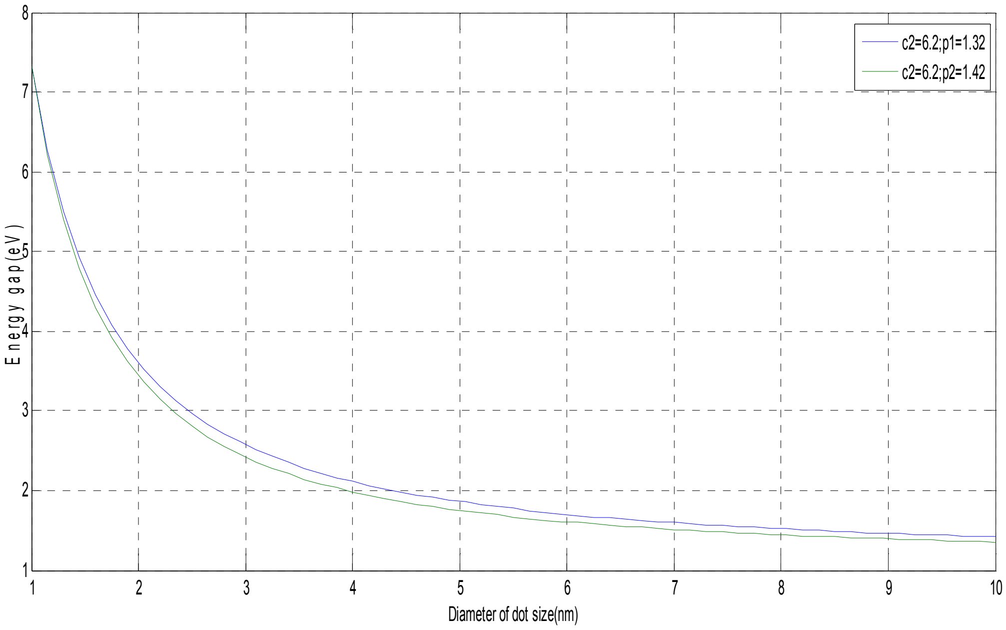

Figure.4. Variation of optical energy gap with porous silicon nanoclusters (quantum dot) diameter. The upper line (blue) is for $\mathrm{p} = 1.32(10\% \text{ to } 20\% \text{ porosity})$ and the lower line (green) is for $\mathrm{p} = 1.42(30\% \text{ to } 40\% \text{ porosity})$. For both lines $\mathrm{c} = 6.2$.

Optical absorption coefficient

In this section we explain how optical absorption coefficient varies by taking size of nanoporous silicon quantum dot, its porosity level and surface passivation into account. Using eqs. (20-24) the plot of optical absorption coefficient verses effective size (1-10nm) for clean, hydrogen and oxygen passivated porous silicon nanoclusters (quantum dot) at a given photon energy (3eV) and $\mathrm{p} = 1.32$ is shown in fig. 5 whereas for other value of alpha (p) ,i.e., when $\mathrm{p} = 1.42$ the plot is shown in fig.6.

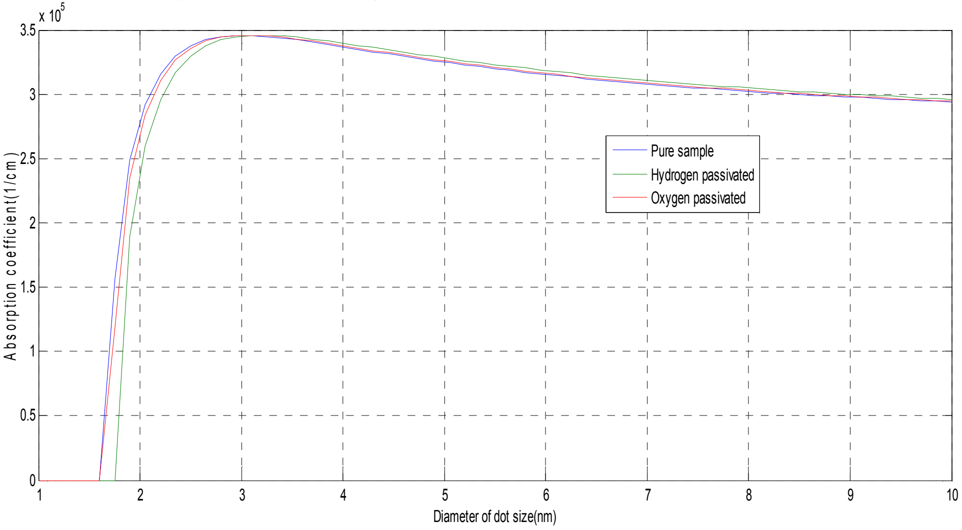

Figure.5. Optical absorption coefficient as a function of porous silicon nanoclusters (quantum dot) size at a given photon energy $\hbar\omega = 3eV$. For pure and passivated samples $\mathrm{p} = 1.32$ (10% to 20%).

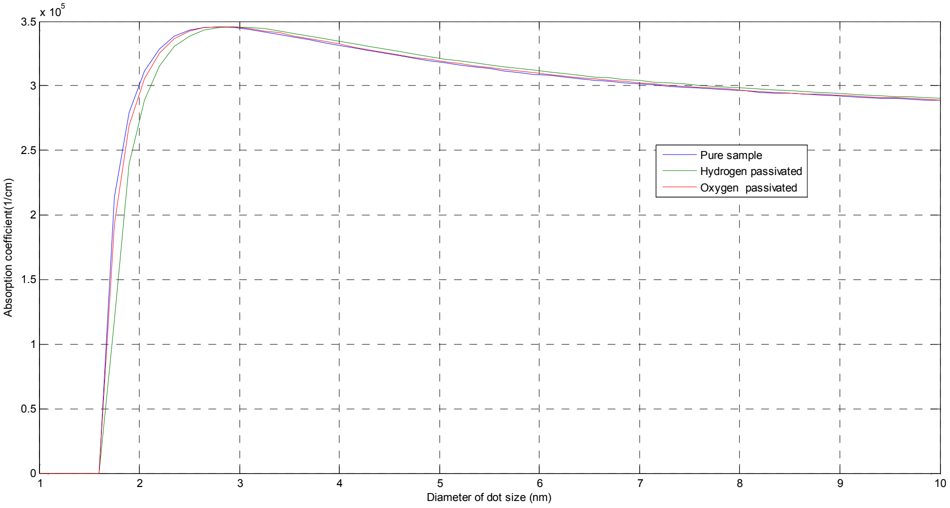

Figure.6. Optical absorption coefficient as a function of porous silicon nanoclusters (quantum dot) size at a given photon energy $\hbar\omega = 3eV$.For pure and passivated samples $\mathrm{p} = 1.42$ (30% to 40%).

We have verified that the optical absorption coefficient of nanoporous silicon quantum dot strongly depends not only on the size of the nanoparticles (quantum confinement), but also on the surface passivation and porosity level. We observed that the effect of both size of the nanoparticles (quantum confinement) and the surface passivation on the optical absorption coefficient is dominant at very small size ($\sim 1.5 - 2.5$nm). The reason for these two effects to be dominant at very small size is due to large volume fraction of the near surface region over the crystalline core (surface effect) and position of carriers is largely confined (quantum confinement effect). In this very small region optical absorption coefficient increases rapidly with increasing size. But as we keep on increasing the size, both the surface and the quantum confinement effects play very little role on the absorption coefficient and it is found that optical absorption coefficient decreases for increasing nanoparticles diameter. By careful observation and comparison of two figures (fig.5 and fig.6), the effect of porosity level can also be notified. Approximately in the region 1.5nm to 2.5nm the slop of figure for the optical absorption coefficient is large for large porosity level but its slop is small after this region when compared to the figure with low porosity level and our results are in conformity with other observations.

Imaginary part of the dielectric function

With the help of eq. (25) and eqs. (21-23) a parallel effect is also found for the imaginary part of dielectric function as that of absorption coefficient. The plot of imaginary part of dielectric function verses effective size (1-10nm) for clean, hydrogen and oxygen passivated porous silicon nanoclusters at a given porosity level, $p = 1.32$ and the photon energy (3eV) is shown in figure 7 and when we change only the porosity level to the value 1.42, the plot is shown in figure 8.

As the case of absorption coefficient, imaginary part of dielectric function also strongly depends on the size of nanoparticles. In the very small size ($\sim 1.5 - 2.5$nm) the effect of surface passivation and quantum confinement are strongly dominant due to the reasons mentioned under the optical absorption coefficient section. As we can see from figures 7 and 8, in this region imaginary part of dielectric function increases with increasing size of nanoparticles but as we continue to increase the size of nanoparticles imaginary part of dielectric function decreases. This is because for large size both surface and quantum confinement effects play very little role on imaginary part of dielectric function. When we compare figures 7 and 8, the effect of porosity level can also be understood. Approximately in the region 1.5nm to 2.5nm the slop of figure for the imaginary part of dielectric function is large for large porosity level but its slop is small after this region when compared to the figure with low porosity level. Turning point of the figure with higher porosity level takes place before the figure with lower porosity level. This point also works for the absorption coefficient figures.

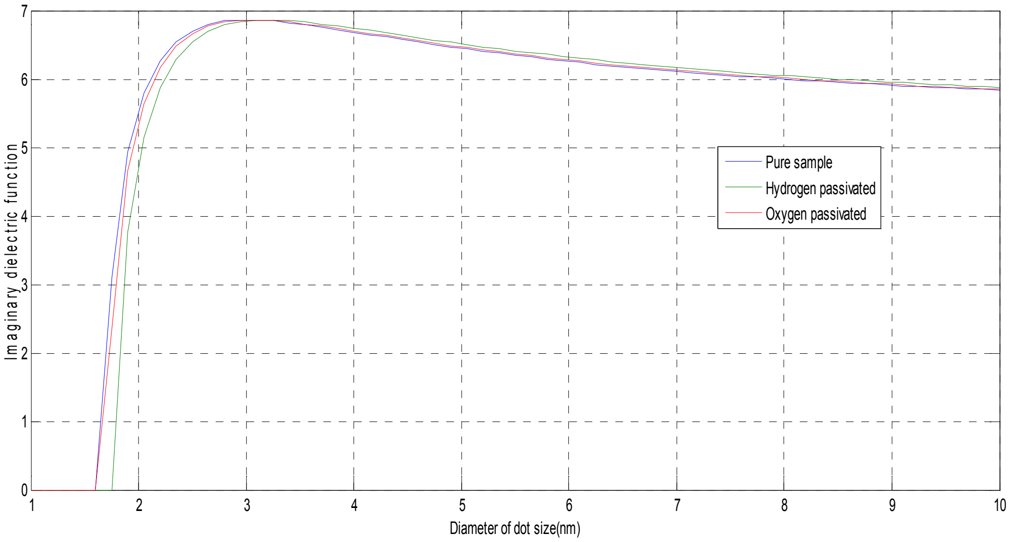

Figure.7. Imaginary part of dielectric function as a function of porous silicon nanoclusters (quantum dot) size at a given photon energy $\hbar\omega = 3eV$.For both pure and passivated samples $p = 1.32$ (10% to 20% porosity).

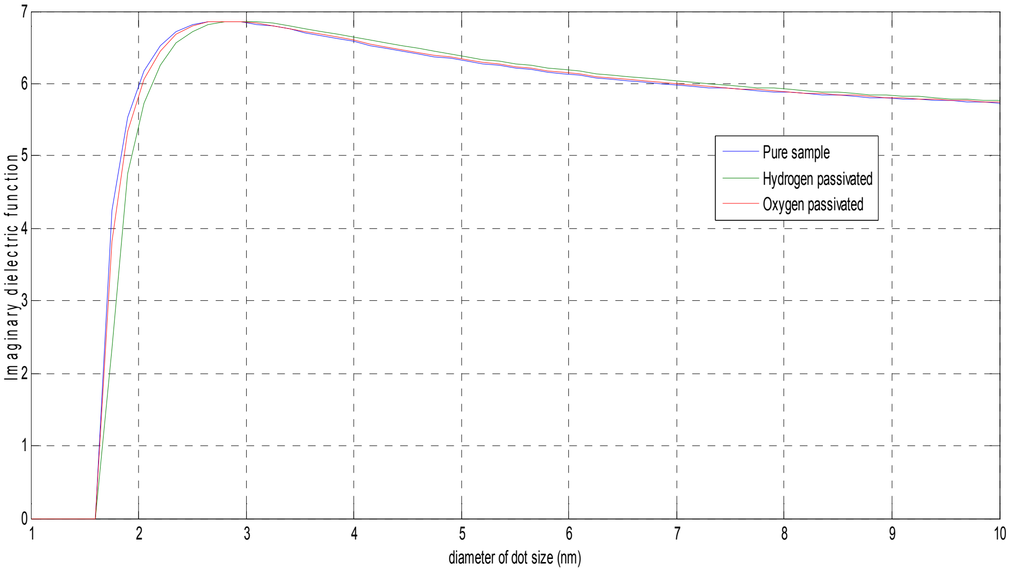

Figure.8. Imaginary part of dielectric function as a function of porous silicon nanoclusters (quantum dot) size at a given photon energy $\hbar\omega = 3eV$.For both pure and passivated samples $p = 1.42$ (30% to 40% porosity).

Oscillatory strength

Finally using eq. (26) and eq. (21-23) the plot of the oscillatory strength verses effective size (1-10nm) for clean, hydrogen and oxygen passivated nanoporous silicon quantum dot at a given porosity level, $p = 1.32$ and the photon energy (3eV) is shown in figure 9 and when we change only the porosity level to the value 1.42, the plot is shown in figure 10.

Here we found that oscillator strength increases as the size of nanoparticles decreases and we also observed that the oscillator strength increases on passivating the surface of the cluster with oxygen and hydrogen respectively. So the oscillator strength of nanoporous silicon quantum dot strongly depends both on the size of the nanoparticles (on quantum confinement), and on the surface passivation (surface effect). Furthermore, we also found that oscillator strength decreases as the porosity level increases (compare figures 9 and 10 with each other).

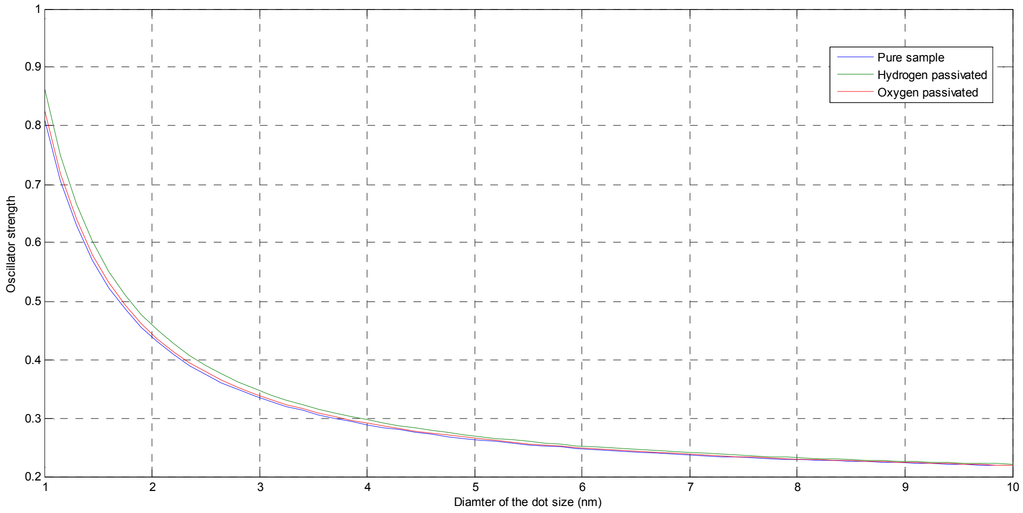

Figure. 9. Oscillator strength as a function of porous silicon nanoclusters (quantum dot) size at a given photon energy $\hbar\omega = 3eV$.For both pure and passivated samples $p = 1.32$ (10% to 20% porosity).

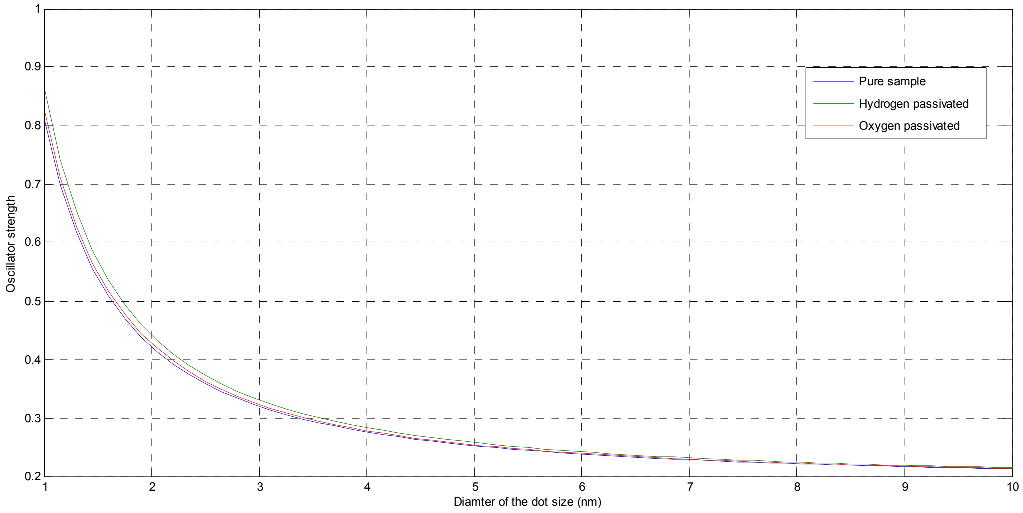

Figure. 10. Oscillator strength as a function of porous silicon nanoclusters (quantum dot) size at a given photon energy $\hbar\omega = 3eV$.For both pure and passivated samples $p = 1.42$ (30% to 40% porosity).

Conclusion

In this work our main aim was to calculate analytically the optical properties of porous silicon nanocluster (quantum dot). In order to characterize the optical properties, the density of states which depend on the dimensionality of the system is necessary. With help of joint density of states and momentum matrix elements we derive the expression for optical absorption coefficient, dielectric constant and oscillator strength. These optical parameters are implicit function of nanoporous silicon quantum dot diameter through energy gap. We found that energy gap and optical parameters (optical absorption coefficient, dielectric constant and oscillator strength) of nanoporous silicon quantum dot depends not only on the size (diameter) dot (quantum confinement effect) but also on the surface passivation (surface effect) and porosity level. The energy gap of silicon nanoporous quantum dot increases as its size decreases. In addition, the variation of energy gap was also observed by varying porosity level and we also found that energy gap decreases with increasing the value of p and it increases with increasing the value of c. The dependence of both absorption coefficient and dielectric constant on size, surface passivation and porosity level is in a similar way. In the very small size region $(\sim 1.5 - 2.5\text{nm})$ both absorption coefficient and dielectric constant increase rapidly with increasing size because in this very small size region the effects of surface passivation and quantum confinement are strongly dominant for the reason that at very small size large volume fraction of the near surface region over the crystalline core (surface effect) and position of carriers is largely confined (quantum confinement effect). Approximately in the region 1.5 to 2.5nm the slope of the figures for the optical absorption coefficient and dielectric constant is large for large porosity level but its slop is small after this region when compared to the figure with low porosity level. Moreover, in this very small region the effect of passivating the surface of the cluster with oxygen has greater effect on these optical parameters than passivating the surface of the cluster with hydrogen but after this small region the effect of hydrogen takeover the effect of oxygen and our results are in conformity with experimental findings. We also observed that oscillator strength increases as the size of the nanoporous silicon quantum dot decreases and it increases on passivating the surface of the cluster with oxygen and hydrogen respectively. Furthermore, we also found that oscillator strength decreases as the porosity level increases and the agreement between our results and the experimental findings is not bad.

Appendices

A: MATLAB program to plot optical band gap energy Vs dot size taking porosity parameters into account.

Figure 3

```
d=1:0.15:10;
c1=4.5, p1 = 1.32, p2 = 1.42;
eg1 =1.12+4.5./(d.^1.32);
eg2 =1.12+4.5./(d.^1.42);
Plot (d, eg1, d, eg2);
Legend (‘c1=4.5;p1 = 1.32’, (‘c1=4.5;p2 = 1.42’);
xlabel (‘Diameter of dot size (nm)’), ylabel (‘Energy gap (eV)’)
```

Figure 4

```
d=1:0.15:10;
c2=6.2, p1 = 1.32, p2 = 1.42;
eg3 =1.12+6.2./ (d. ^1.32);
eg4 =1.12+6.2./ (d. ^1.42);
Plot (d, eg3, d, eg4);
Legend (‘c2=6.2;p1 = 1.32’, (‘c2=6.2;p2 = 1.42’);
xlabel (‘Diameter of dot size (nm)’), ylabel (‘Energy gap (eV)’)
```

B: MATLAB program to plot absorption coefficient Vs dot size taking surface passivation and porosity level into account.

Figure 5

```
d= 1:0.15:10;
Pure sample= 3.73;
Hydrogen passivated= 4.042;
Oxygen passivated= 3.82;
eg1= 1.12+3.73./ (d. ^1.32);
eg2= 1.12+4.042./ (d. ^1.32);
eg3= 1.12+3.82./ (d. ^1.32);
ac1=5.15e5.*eg1.*((eg1+0.044). / (3*eg1+0.088)).*sqrt(3-eg1);
ac2=5.15e5.*eg2.*((eg2+0.044). / (3*eg2+0.088)).*sqrt(3-eg2);
ac3=5.15e5.*eg3.*((eg3+0.044). / (3*eg3+0.088)).*sqrt(3-eg3);
Plot (d, ac1, d, ac2, d, ac3);
Legend (‘Pure sample’, ‘Hydrogen passivated’, ’Oxygen passivated’);
xlabel (‘Diameter of dot size (nm)’), ylabel (‘ Absorption coefficient (1/cm)’);
```

Figure 6

```
d= 1:0.15:10;
Pure sample= 3.73;
Hydrogen passivated= 4.042;
Oxygen passivated= 3.82;
eg1= 1.12+3.73./ (d. ^1.42);
eg2= 1.12+4.042./ (d. ^1.42);
```

```
eg3= 1.12+3.82./ (d. ^1.42);
ac1=5.15e5.*eg1.*((eg1+0.044). / (3*eg1+0.088)).*sqrt(3-eg1);
ac2=5.15e5.*eg2.*((eg2+0.044). / (3*eg2+0.088)).*sqrt(3-eg2);
ac3=5.15e5.*eg3.*((eg3+0.044). / (3*eg3+0.088)).*sqrt(3-eg3);
Plot (d, ac1, d, ac2, d, ac3);
Legend (‘Pure sample’, ‘Hydrogen passivated’, ’Oxygen passivated’);
xlabel (‘Diameter of dot size (nm)’), ylabel (‘ Absorption coefficient (1/cm)’);
```

C: MATLAB program to plot imaginary part of dielectric function Vs dot size taking surface passivation and porosity level into account.

Figure 7

```
d= 1:0.15:10;
Pure sample= 3.73;
Hydrogen passivated= 4.042;
Oxygen passivated= 3.82;
eg1= 1.12+3.73./ (d. ^1.32);
eg2= 1.12+4.042./ (d. ^1.32);
eg3= 1.12+3.82./ (d. ^1.32);
ε1 = 10.22.*eg1.*((eg1+0.044). / (3*eg1+0.088)).*sqrt(3-eg1);
ε2 = 10.22.*eg2.*((eg2+0.044). / (3*eg2+0.088)).*sqrt(3-eg2);
ε3 = 10.22.*eg3.*((eg3+0.044). / (3*eg3+0.088)).*sqrt(3-eg3);
Plot (d,ε1, d, ε2, d, ε3);
Legend (‘Pure sample’, ‘Hydrogen passivated’, ‘Oxygen passivated’);
xlabel (‘Diameter of dot size (nm)’), ylabel (‘Imaginary dielectric function’);
```

Figure 8

```
d= 1:0.15:10;
Pure sample= 3.73;
Hydrogen passivated= 4.042;
Oxygen passivated= 3.82;
eg1= 1.12+3.73./ (d. ^1.42);
eg2= 1.12+4.042./ (d. ^1.42);
eg3= 1.12+3.82./ (d. ^1.42);
ε1 = 10.22.*eg1.*((eg1+0.044). / (3*eg1+0.088)).*sqrt (3-eg1);
ε2 = 10.22.*eg2.*((eg2+0.044). / (3*eg2+0.088)).*sqrt (3-eg2);
ε3 = 10.22.*eg3.*((eg3+0.044). / (3*eg3+0.088)).*sqrt (3-eg3);
Plot (d,ε1, d, ε2, d, ε3);
Legend (‘Pure sample’, ‘Hydrogen passivated’, ‘Oxygen passivated’);
xlabel (‘Diameter of dot size (nm)’), ylabel (‘Imaginary dielectric function’);
```

D: MATLAB program to plot oscillator strength Vs dot size taking surface passivation and porosity level into account.

Figure 9

```
d=1:0.15:10;
Pure sample=3.73;
Hydrogen passivated=4.042;
Oxygen passivated=3.82;
eg1=1.12+3.73./(d.^1.32);
eg2=1.12+4.042./(d.^1.32);
eg3=1.12+3.82./(d.^1.32);
 f1=(1./2).*((eg1+0.044)./(3*eg1+0.088)).*eg1;
f2=(1./2).*((eg2+0.044)./(3*eg2+0.088)).*eg2;
 f3=(1./2).*((eg3+0.044)./(3*eg3+0.088)).*eg3;
plot(d,f1,d,f2,d,f3);
Legend('Puresample','Hydrogenpassivated','Oxygenpassivated');
xlabel('Diamter of the dot size (nm)'),ylabel('Oscillator strength');
```

Figure 10

```
 d=1:0.15:10;
Pure sample=3.73;
Hydrogen passivated=4.042;
Oxygen passivated=3.82;
eg1=1.12+3.73./(d.^1.42);
```

```
eg2=1.12+4.042./(d.^1.42);
eg3=1.12+3.82./(d.^1.42);
 f1= (1. /2).*((eg1+0.044)./(3*eg1+0.088)).*eg1;
f2= (1. /2).*((eg2+0.044)./(3*eg2+0.088)).*eg2;
 f3= (1. /2).*((eg3+0.044)./(3*eg3+0.088)).*eg3;
Plot (d, f1, d, f2, d, f3);
Legend ('Puresample','Hydrogenpassivated','Oxygenpassivated');
xlabel('Diamter of the dot size (nm)'),ylabel('Oscillator strength');
```

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