Study of Raman Redshift of Nanoscale Semiconductors

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ABSTRACT

Considering the Lu model and dangling bonds, we derived equations for the optoelectrical properties of semiconductors at the nanoscale. The size and shape-dependent band gap and phonon frequency of nanoparticles are studied. It is reported that the bandgap increases on decreasing the size, while the phonon frequency decreases on reducing the particle size in the nano range. The effect of shape is included in our research. It is projected that the effect is considerable on changing the shape from spherical to film shape. The developed model may provide new insight, into where the experimental findings are missing.

Keywords: Nanomaterials, cohesive energy, dangling bonds, phonon frequency

I. INTRODUCTION

Nanoscience and nanotechnology focus on creating, studying, and utilizing materials that have at least one dimension in the nanometer range, this involves synthesizing characterizing,exploring, and exploiting nanostructured materials [1].One example of nanostructured material is semiconductor nanocrystals which exhibit optical properties that depend on their size and shape and these properties are a result of quantum confinement effects which make semiconductor nanocrystals potentially useful in various optoelectronic devices [2].The electrons and holes in a semiconductor in a nanoscale are restricted due to quantum confinement hence the energy difference between the valence band and covalent band increases the band gap of the semiconductor however regarding the applications in optoelectronic devices the band gap changes the optical and electronic properties of the semiconductor drastically [3].

The quantization effects of zero-dimensional quantum dots and one-dimensional quantum wellsare strong when their sizes range from 1 to 5 nanometers which is similar to the size of the exciton radii.The application of semiconductor nanocrystalline materials in optoelectronic devices is approved as their valence conduction band gap energy varies with the size of semiconductor quantum dots and quantum wells and decreases as their size decreases, this is observed in Si [4-7] and CdSe [8].The energy band gap of nanoparticles influences the properties of a semiconductor such as magnetoresistance,melting point,solid state phase,transition pressure,Debye temperature, and self-diffusion coefficient [9].The changes in the energy band gap of a semiconductor change the physical and chemical properties of that semiconductor when working on a nanometer scale.

In a nanometre scale, the semiconductor is made up of very few numbers of molecules so the number of overlapping energy levels decreases and the width of the band gap gets narrower causing an increase in the energy band gap between the valance and the conduction band and this simply means the band gap increases as the size of the nanoparticle decreases due to electron confinement at the nanoscale [10].

Recent studies indicate that Raman frequency undergoes a red shift when the size of the material decreases. This shift has been observed in both narrow and wide-gaped semiconductor nanocrystals such as Si, InP, and CdSe [11]. Various analytical models have been developed to study the Raman frequency in nanosized semiconductors hence phonon confinement and surface stress are thought to be responsible for the Raman redshift[12].When the size of semiconductor nanocrystals decreases, their surface-to-volume ratio increasesthis leads to phonon confinement and higher energy levels for the atoms on their surface. As a result, the amplitude of atomic vibrations increases causing a decrease in their vibrational frequency [13].

In this model,the theoretical analysis was done on Si and CdSe semiconductors compound nanomaterials and their predictions agree with the experimental analogy that band gap energy increases with a decrease in size. Apart from this, the size-dependent phonon frequency of semiconductor nanocrystals is determined regarding the size-dependent force constant,bond length, and bond energy ofnanocrystals and it predicted that frequency shifts as the size of the crystal decreases.These predictions agree with experimental results [14].

II. MATHEMATICAL ANALYSIS

The cohesive energy of nanowires is given as [15]

$$E(D,d) = E_0 \left(1 - \frac{4d}{3D} \right) \tag{1}$$

where d is the atomic size, D is the cross-sectional size of the nanowire and E_0 is the cohesive energy of bulk material. It has been reported that the strength of a bond in a material can be described by both its cohesive energy and its melting temperature. Furthermore, it is widely accepted that there exists a linear relationship between the cohesive energy and melting temperature for all materials [15]. So the melting temperature of the nanomaterial is

$$T_m(D,d) / T_m(\infty,d) = E_0 \left(1 - \frac{4d}{3D} \right) \tag{2}$$

Where $Tm(\infty)$ is the temperature of the bulk material.Size and temperature-dependent Arrhenius expression for the electrical conductivity is expressed as [16]

$$\sigma(D,d) = \sigma_0 \exp\left(-\frac{E_a(D,d)}{RT} \right) \tag{3}$$

Or, we can write,

$$\sigma_0 \exp\left(-\frac{E_a(D,d)}{RT_m(D)} \right) = \sigma_0 \exp\left(-\frac{E_a(\infty)}{RT_m(\infty)} \right) \tag{4}$$

From Eqs (1), (2), (3), and (4), we get

$$\frac{\Delta E_g(D,d)}{E_g(d)} = \frac{\Delta E_a(D,d)}{E_a(d)}$$

Lu *et al* [17] developed a model for melting temperature given as

$$\frac{T_m(D,d,\lambda)}{T_m(\infty)} = \left[1 - \frac{1}{12D/D_0 - 1} \right] \exp\left[1 - \frac{2\lambda s_b}{3R(12D/D_0 - 1)} \right] \tag{5}$$

R and S_b are the gas constant and bulk solid-vapour transition entropy and $D_0 = 2(3-f)h$ is a critical size and h is the degree of freedom at which all the atoms of the crystal are located on the surface [18].

Using equations (4) and (5) the size-dependent expression for the band gap of semiconducting nanowires is obtained as

$$\frac{\Delta E_g(D,d,\lambda)}{E_g(\infty)} = 1 - \left[1 - \frac{1}{12D/D_0 - 1} \right] \exp\left[1 - \frac{2\lambda s_b}{3R(12D/D_0 - 1)} \right] \tag{6}$$

We have the relation between phonon frequency and temperature,

$$\frac{\omega^2(D,d)}{\omega^2(\infty)} = \frac{T_m(D,d,\lambda)}{T_m(\infty)} \tag{7}$$

Thus, the phonon frequency of Nano solids can be related to the phonon frequency of the electrons in atoms its bulk counterparts are written as

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$$\frac{\omega(D,d,\lambda)}{\omega(\infty)} = \left[\left[1 - \frac{1}{12D/D_0 - 1} \right] \exp\left[1 - \frac{2\lambda s_b}{3R(12D/D_0 - 1)} \right] \right]^{1/2} \quad (8)$$

Eqs. (6) and (8) are used to calculate the bandgap energy and phonon frequency of Si and CdSe semiconductors atthe nanoscale in different dimensions.

Table 1. Input parameters used in calculations [13, 17]

Nanoparticles	$\omega(\infty)\,cm^{-1}$	$S_b(\infty)\,Jgatom^{-1}\,K^{-1}$	$h(nm)$	$\Delta E_g(D)$ ev
Si	520	6.7	0.553	1.1
CdSe	212	6.62	0.608	1.7
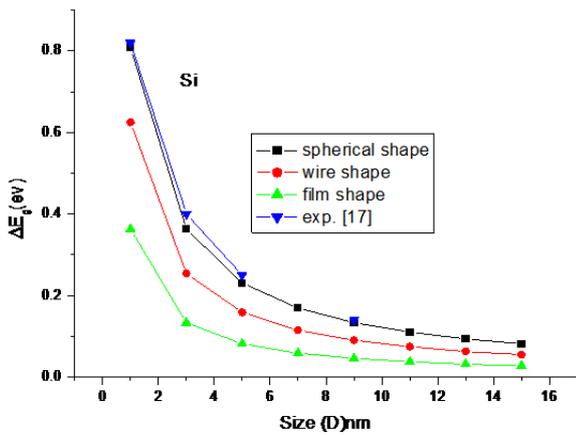
Figure 1: Variation of energy band gap Si nanoparticle with size and shape along with experimental data [17].
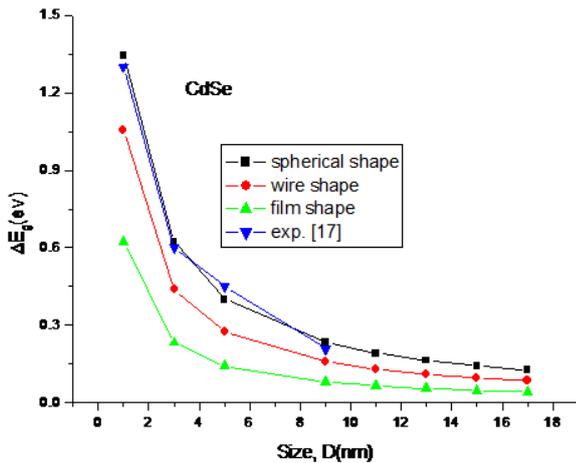
Figure2: Variation of energy band gap CdSe nanosphere with size and shape along with experimental data [17].
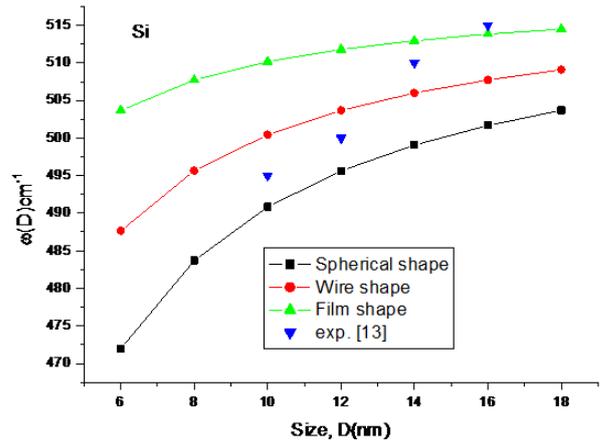
Figure 3: Variation of phonon frequency of Si nanoparticle with size and shape along with experimental data [13].
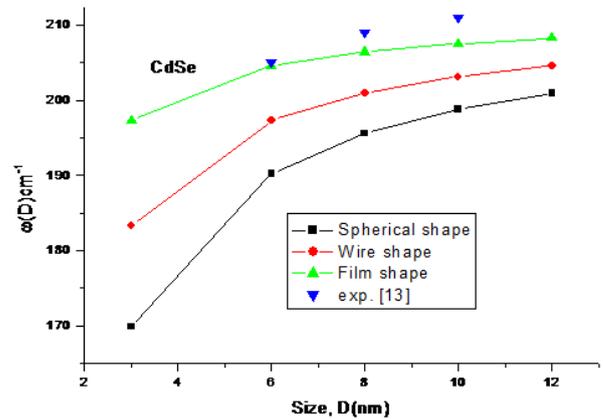
Figure 4: Variation of phonon frequency of CdSe nanoparticle with size and shape along with experimental data [13].

III. RESULTS AND DISCUSSIONS

Bandgap variation with size and phononfrequency variation with the size of Si and CdSe semiconducting nanoparticles are analysed by using equations (6) and (8) respectivelyin spherical, wire, and film shapes. The input parameters are tabulated in Table 1. The graphical representation of bandgap variation with size and phonon frequency variation with the size of Si andCdSe semiconducting nanospheres are shown in Figure 1-4 along with the available experimental/

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simulation data [13, 17]. In semiconductors, the energy band gap between the valence band and conduction band gaps tends to increase as the diameter of the nanowire decreases this is due to the principle of quantum confinement, which restricts the spatial movement of electrons in the conduction band and holes in the covalent band. This confinement is caused by the potential barrier on the surface or the potential well of the quantum box. On top of this, Quantum mechanics explains that when the nanowire diameter decreases, the quantum well becomes narrower.

However, the impact of the size on the energy band gap is less pronounced in nanowires and even less in Nanofilms. This trend can be explained by the fact that the surface-to-volume ratio increases as the size decreases, this decrease in size particles results in cohesive energy which in turn leads to an increase in energy band gap. The widening of the band gap shows a slow increase at first but then it accelerates rapidly as the size decreases. The graphical representation of the relationship between shape, size, and the expansion of the band energy indicates that shape is also a significant factor at the nanoscale and the ratio of volume to surface area varies with shape and size so this influences the number of surface atoms at the nanoscale which in turn affects the cohesive energy.

As a result, the band gap energy changes at the nanoscale, and this is explained by Quantum mechanics in which this phenomenon suggests that as the particle size approaches the nanoscale the number of overlapping orbitals or energy levels decreases and the thickness of the bands become thinner which in turn causes energy band gap between valence and conduction bands to widen. This gives an elaboration of why the energy band gap is higher in semiconductor compound nanomaterials than in their corresponding bulk counterparts.

For Raman Red shift phonon frequencydecreases as the size decreases and the predicted outcomes match the experimental data at the nanometre scale confirming the validity of the theory. As the size of the semiconductor nanocrystals decreases the surface-to-volume ratio increases leading to phonon confinement and higher energy levels for surface atoms. This results in an increase in atomic vibrational amplitude and a decrease in vibrational frequency. Once the size becomes smaller than 5 nm which is comparable to the exciton radius of the semiconductor nanocrystals the confinement effect becomes more pronounced causing a rapid decrease in $\omega(\infty)$ as shown in Figure 3-4.

IV. CONCLUSION

A basic framework has been developed for determining the band gap energy and phonon frequency of semiconductor nanomaterials with arious sizes and shapes, including spherical nanosphere,nanowires, and nanofilms. The theory suggests that as the size of semiconductor nanomaterial is reduced the band gap increases while phonon frequency decreases. Again this model's predictions for energy band gap and phonon frequency align well with existing experimental/ simulation data.

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