



Modelling to determine the optical properties of nanosized semiconducting compounds

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Abstract. In the present paper, a theoretical model is used to study the optical properties of nanomaterials. The optical properties of nanosized semiconductors are studied in relation to dimension and size. The model proposed by Guisbiers is extended to study the impact of size and shape on band-gap expansion, dielectric constant, vibrational frequency and electrical susceptibility of nanomaterials. The model is free from any adjustable parameter. We have considered here II–VI and III–V group semiconductors. It is found from model predictions that the energy band gap of the nanosized semiconducting compounds increases as size decreases because of the quantum confinement of electrons and holes as size is reduced to nanolevel. The vibrational frequency, dielectric constant and electrical susceptibility are found to decrease with decrease in the size of the nanosized semiconductors. The results calculated from the present model are found to be in good agreement with the available experimental and simulated data.

Keywords. Shape; dielectric constant; size; vibrational frequency.

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1. Introduction

The structures with sizes between 1 and 100 nm are considered nanomaterials. In comparison with their bulk counterpart, they show a different behaviour as size reduces to nanoscale due to a drastic increase in the surface atoms, and therefore nanomaterials have fascinating thermal, physical and mechanical properties [1, 2]. Due to quantum confinement in nanomaterials with the reduction in size, electrons and holes get confined in nanosized semiconductors leading to an increase in the energy difference between the filled and the empty states [3–5].

It is feasible to modulate the physical properties of nanomaterials by manufacturing them using different methods and techniques. The most important property of the nanosized semiconductors is the energy band gap which plays an important role in explaining electrical and optical properties. To study the properties of nanomaterials like melting temperature, energy band gap, dielectric constant, electric susceptibility, vibrational frequency etc., various theoretical models have been formulated whose predicted results are considered important in manufacturing mechanical and electronic nanodevices. These properties change with shape and size in nanomaterials [6,7].

It is clear from the previous studies that the cohesive energy of the nanomaterials reduces with size reduction to nanoscale because of the increase in the number of dangling bonds. An increase in surface area to volume ratio and quantum confinement results in a decrease in melting temperature with a decrease in size in nanomaterials [8–11]. Due to the polarisable bond present on the surface, the dielectric constant in nanomaterials also decreases with a decrease in size [12,13]. The III–V group semiconducting compounds have a different chemical nature from those of II–VI compounds. Group III–V compounds exhibit quantum size effects in complete analogy with prototypical II–VI semiconducting compounds [14]. These semiconductor compounds are synthesised using different techniques, namely molecular beam epitaxy (MBE), liquid phase epitaxy (LPE), atomic layer deposition (ALD) etc. The maximum quantum size effects are seen in those compounds, which allow larger delocalisation of electrons and holes. In comparison with III–V semiconductor compounds, bare atoms or ions of II–VI group compounds can be used as precursors, which allow the direct reaction of relevant compounds. However, if III–V group semiconducting compounds are treated as precursors, they can directly react with the solvent [15–17].

In the present study, Guisbiers model [8,18,19] is extended to describe the effect of dimension and size on the band gap, vibrational frequency, dielectric constant and electrical susceptibility in II–VI and III–V nanosized semiconducting compounds. The compounds considered in the present study are CdS, CdTe, AlP, AlSb, GaP and GaSb.

2. Mathematical formulation

Using Guisbiers model [8], the cohesive energy of nanomaterials E_{Cn} is expressed as follows:

$$E_{Cn} = E_{Cb} \left(1 - \frac{\alpha_{\text{shape}}}{D} \right), \quad (1)$$

where E_{Cb} is the cohesive energy of the bulk material, $\alpha_{\text{shape}} = AD(\gamma_s - \gamma_l)/V\Delta H_{bm}$ where D is the diameter of the nanomaterial, γ_l and γ_s are the surface energies in the liquid and solid phase of the material, respectively and ΔH_{bm} is the melting enthalpy of the bulk material [18,19]. A/V is the ratio of surface area to volume.

As cohesive energy is directly related to melting temperature from the relation [20]

$$T_{Mb} = \frac{0.032}{k} E_{Cb},$$

in view of eq. (1), the melting temperature of nanomaterials T_{Mn} can be expressed as [8]

$$T_{Mn} = T_{Mb} \left(1 - \frac{\alpha_{\text{shape}}}{D} \right). \quad (2)$$

Here T_{Mb} is the melting temperature of the bulk material.

Vibrational frequency ω is related to cohesive energy as $\omega \propto E_C^{1/2}$ [21,22]. So vibrational frequencies of nanomaterial to bulk ω_n/ω_b can be expressed as

$$\frac{\omega_n}{\omega_b} = \left(\frac{E_{Cn}}{E_{Cb}} \right)^{1/2}. \quad (3)$$

Using eq. (1), ω_n/ω_b can be written as

$$\frac{\omega_n}{\omega_b} = \left(1 - \frac{\alpha_{\text{shape}}}{D} \right)^{1/2}. \quad (4)$$

As per the nearly free-electron approach, the band gap E_g of semiconductors can be expressed as $E_g = 2|V|$, where V is the crystalline field which depends on the total number of atoms and interatomic interactions of a solid [23,24]. Using the first-order approximation, on generalising the relation to the nanometre size range, the expression obtained is

$$\frac{\Delta E_{Gn}}{E_{Gb}} = \left| \frac{V_N}{V_B} \right|. \quad (5)$$

The interatomic interaction of the solid (V) is proportional to the atomic cohesive energy (E_C). On expanding this relation to the nanoscale, the expression obtained is as follows:

$$\left| \frac{\Delta V_N}{V_B} \right| = \left| \frac{E_{Cn} - E_{Cb}}{E_{Cb}} \right| \quad (6)$$

Using eqs (1) and (2), the melting temperature of the nanosolid (T_{Mn}) and the energy band gap (E_{Gn}) are related as follows:

$$\frac{\Delta E_{Gn}}{E_{Gb}} = \left(1 - \frac{T_{Mn}}{T_{Mb}} \right). \quad (7)$$

Considering eqs (2) and (7), the expression of the energy band gap is written as follows:

$$E_{Gn} = E_{Gb} \left(1 + \frac{\alpha_{\text{shape}}}{D} \right). \quad (8)$$

The dielectric constant of the bulk material (ϵ_b) is related to electrical susceptibility (χ_b) by the relation [25–27]

$$\epsilon_b - 1 = \chi_b. \quad (9)$$

Both depression in dielectric constant due to electronic polarisation and blue shift in photoluminescence occur because of the increase in the crystalline field due to the contraction of surface bonds and the increase in surface atoms in nanosemiconductors with the decrease in size [25–28]. The electrical susceptibility and band-gap expansion variation with size in CdSe and Si semiconductors are studied by Sun *et al* [28]. In view of the previous studies, the dependence of the electric susceptibility on band gap in III–V and II–VI group semiconductors is expressed by the relation [29]

$$\chi_b \propto (E_{Gb})^{-2}. \quad (10)$$

The relation between the dielectric constant and melting temperature of the nanomaterials and their bulk counterpart using eqs (9) and (10), is expressed as follows:

$$\frac{\epsilon_n - 1}{\epsilon_b - 1} = \left(\frac{E_{Gn}}{E_{Gb}} \right)^{-2}. \quad (11)$$

Considering eqs (10) and (11), the electrical susceptibility and dielectric constant can be written as

$$\frac{\epsilon_n - 1}{\epsilon_b - 1} = \left(1 + \frac{\alpha_{\text{shape}}}{D} \right)^{-2} \quad (12)$$

$$\frac{\chi_n}{\chi_b} = \left(1 + \frac{\alpha_{\text{shape}}}{D} \right)^{-2}. \quad (13)$$

3. Results and discussion

In the present study, Guisbiers’ model is extended to determine the band-gap expansion, vibrational frequency, dielectric constant and electrical susceptibility in nanosized semiconductors with respect to size for spherical nanoparticles and nanowires of CdS, CdTe, AIP, AlSb, GaP and GaSb. The input parameters are listed in table 1. The shape parameter α_{shape} required for the calculations for materials considered is taken from refs [18,29] and listed in table 2. α_{shape} for the nanofilms is calculated as the shape factor for the spherical nanoparticle, cylindrical nanowires and nanofilms are in the ratio 3:2:1 [18].

Equations (7) and (8) are used for studying the energy band gap expansion in spherical nanoparticles, nanowires and nanofilms. Figures 1a–1f show the energy band-gap expansion variation with size in CdS, CdTe, AIP, AlSb, GaP and GaSb spherical nanoparticles (NP) and nanowires (NW). Our calculated results are compared with the available experimental and simulated data [30,33,35,36]. It is seen that band gap increases in nanomaterials with a decrease in size. This is because of the increase in transition energy from the top level of the valence band to the lowest level of the conduction band and the quantum confinement of electrons and holes. The trend is the same for spherical nanoparticles and nanowires.

The present model is based on the consistency between the previous model predictions and the observations, which confirm that both depression in dielectric constant and blue shift in photoluminescence occur due to the contraction of surface bonds and the increase in surface-to-volume ratio in nanosemiconductors. The

agreement of the results obtained from previous studies with experimental data is taken into account to find the relation between dielectric constant and band-gap expansion in III–V and II–VI group semiconductors [25–29]. Kumar *et al* [29] proposed simple relations using the plasma oscillation theory of solids and calculated the values of energy band gap and dielectric constant of II–VI and III–V group semiconductors. The dielectric constant and energy band gap are computed using the model theory in II–VI and III–V group semiconductors and the results are consistent with the model considered in the present study.

Equations (3) and (4) are used to study the variation in relative vibrational frequency of nano to bulk material in nanosized semiconductors, i.e. CdS, CdTe, AIP, AlSb, GaP and GaSb with respect to the size of the nanomaterial. Figures 2a–2h represent the variation of ω_n/ω_b in CdS, CdTe, AIP, AlSb, GaP and GaSb spherical nanoparticles. Experimental data are not available for comparing the results of vibrational frequency. Therefore, we have obtained results for vibrational frequency using eq. (3) of cohesive energy and vibrational frequency [30,33]. The study of the variation of vibrational frequency with size is used to know their applications in developing optoelectronic devices. So the study here is beneficial. The theoretical study predicts that the vibrational frequency decreases with a reduction in the size of the nanomaterial because the surface atoms in nanomaterials increase with size reduction, resulting in phonon confinement and an increase in vibrational amplitude of the atoms.

Equations (12) and (13) are used to study the variation in electrical susceptibility and dielectric constant with size in nanosized semiconductors. In figures 3a–3f,

Table 1. Input parameters.

Semi conductor	E_{Gb} (eV)	Static dielectric constant ϵ_b	Semiconductor	E_{Gb} (eV) [31]	Static dielectric constant ϵ_b [31]
CdS	2.50 [23]	8.70 [30]	AlSb	1.61	12.04
CdTe	1.47 [31]	10.20 [31]	GaP	2.27	11.10
AIP	2.45 [31]	9.80 [31]	GaSb	0.75	15.70

Table 2. Shape parameters [18,32–34].

Semi conductor	α_{shape} (NP) (nm)	α_{shape} (NW) (nm)	Semiconductor	α_{shape} (NP) (nm)	α_{shape} (NW) (nm)
CdS	0.38	0.25	AlSb	0.64	0.32
CdTe	0.78	0.39	GaP	0.54	0.27
AIP	0.38	0.19	GaSb	0.84	0.42

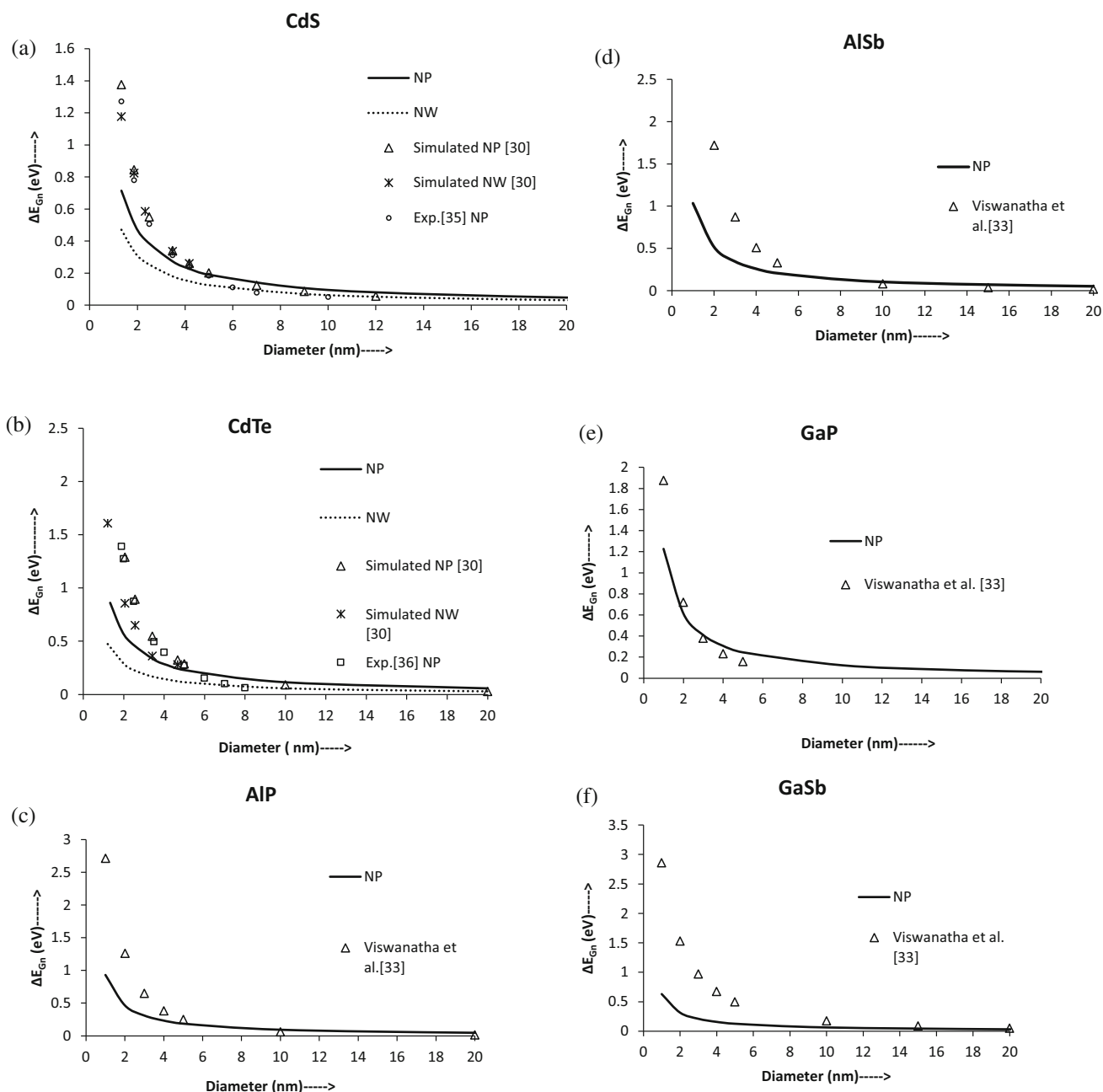


Figure 1. Variation in band-gap expansion with size in (a) CdS, (b) CdTe, (c) AIP, (d) AlSb, (e) GaP and (f) GaSb.

variation of electrical susceptibility with size is depicted for CdS, CdTe, AIP, AlSb, GaP and GaSb spherical nanoparticles. Figures 4a–4f represent the variation of dielectric constant in CdS, CdTe, AIP, AlSb, GaP and GaSb spherical nanoparticles. The values of electrical susceptibility and dielectric constant of CdS, CdTe, AIP, GaP, AlSb and GaSb nanoparticles are computed for comparison using the relation $(\epsilon - 1) \propto (E_G)^{-2}$ from the stimulated and experimental data [30, 33]. The present calculated results for electrical susceptibility as

well as dielectric constant are in good agreement with the experimental and simulated results obtained from band-gap values [30, 33].

It is seen that both electrical susceptibility and dielectric constant decrease as size decreases to nanoscale. This is because of the size effects. The lower coordination number and high surface-to-volume ratio decrease the cohesive energy, which encourages quantum entrapment and perturbed Hamiltonian that limits the band gap [11].

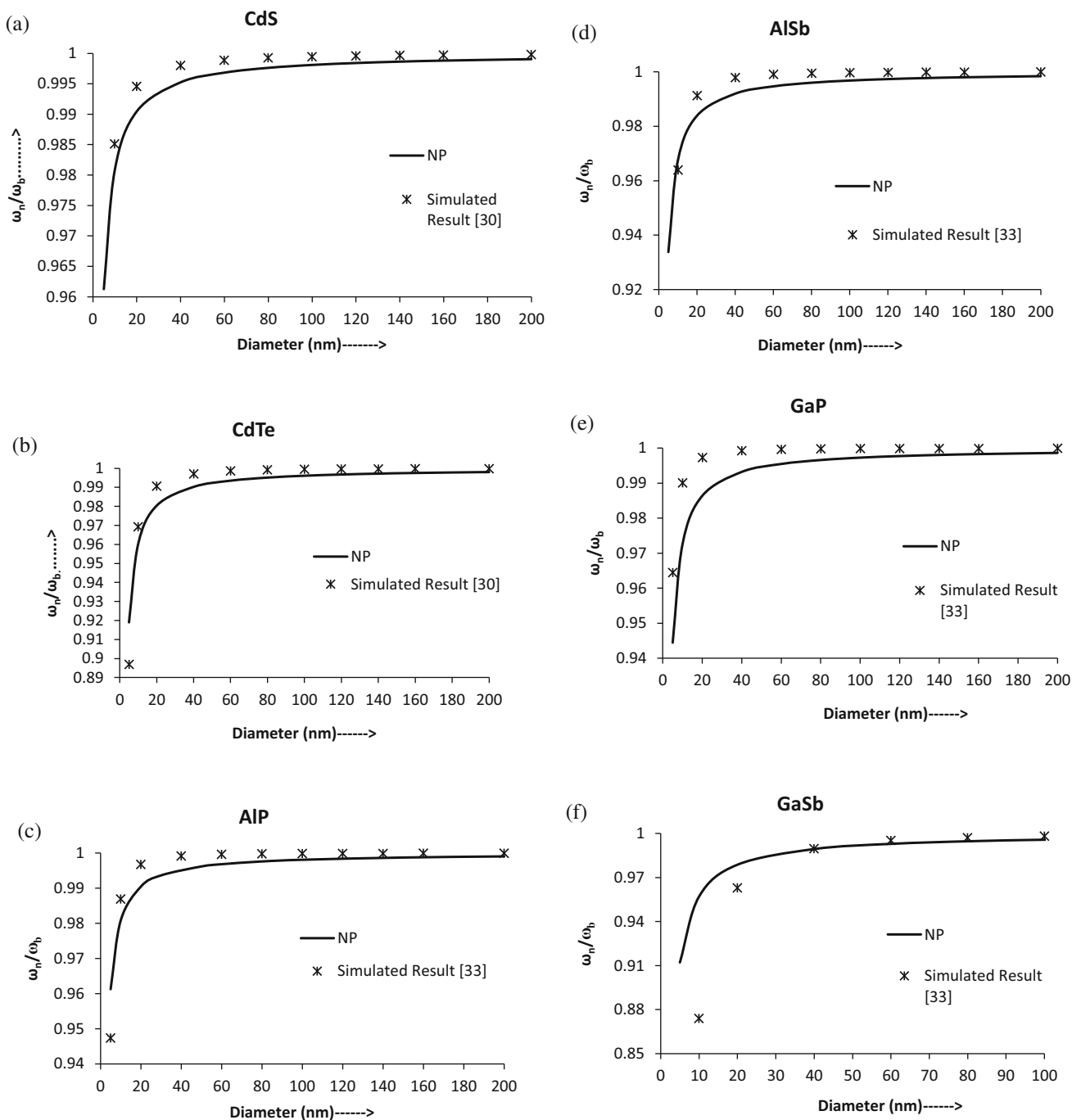


Figure 2. Vibrational frequency vs. size in (a) CdS nanoparticle, (b) CdTe nanoparticle, (c) AIP nanoparticle, (d) in AlSb nanoparticle, (e) in GaP nanoparticle and (f) GaSb nanoparticle.

Figures 5a and 5b show the variation in electrical susceptibility and dielectric constant with size in CdS for spherical nanoparticles, cubic nanoparticles, cylindrical nanowires, parallelepiped nanowires and nanofilms. The values of shape factor for different shapes of CdS nanomaterial are taken from ref. [18]. Shape plays an important role in nanomaterials as variation in

surface-to-volume ratios results in a drastic change in physical properties. It is seen that the variation in dielectric constant with size is maximum in cubic nanoparticles and minimum in nanofilms.

Figure 5c depicts the variation in dielectric constant of III–V group semiconductors and II–VI group

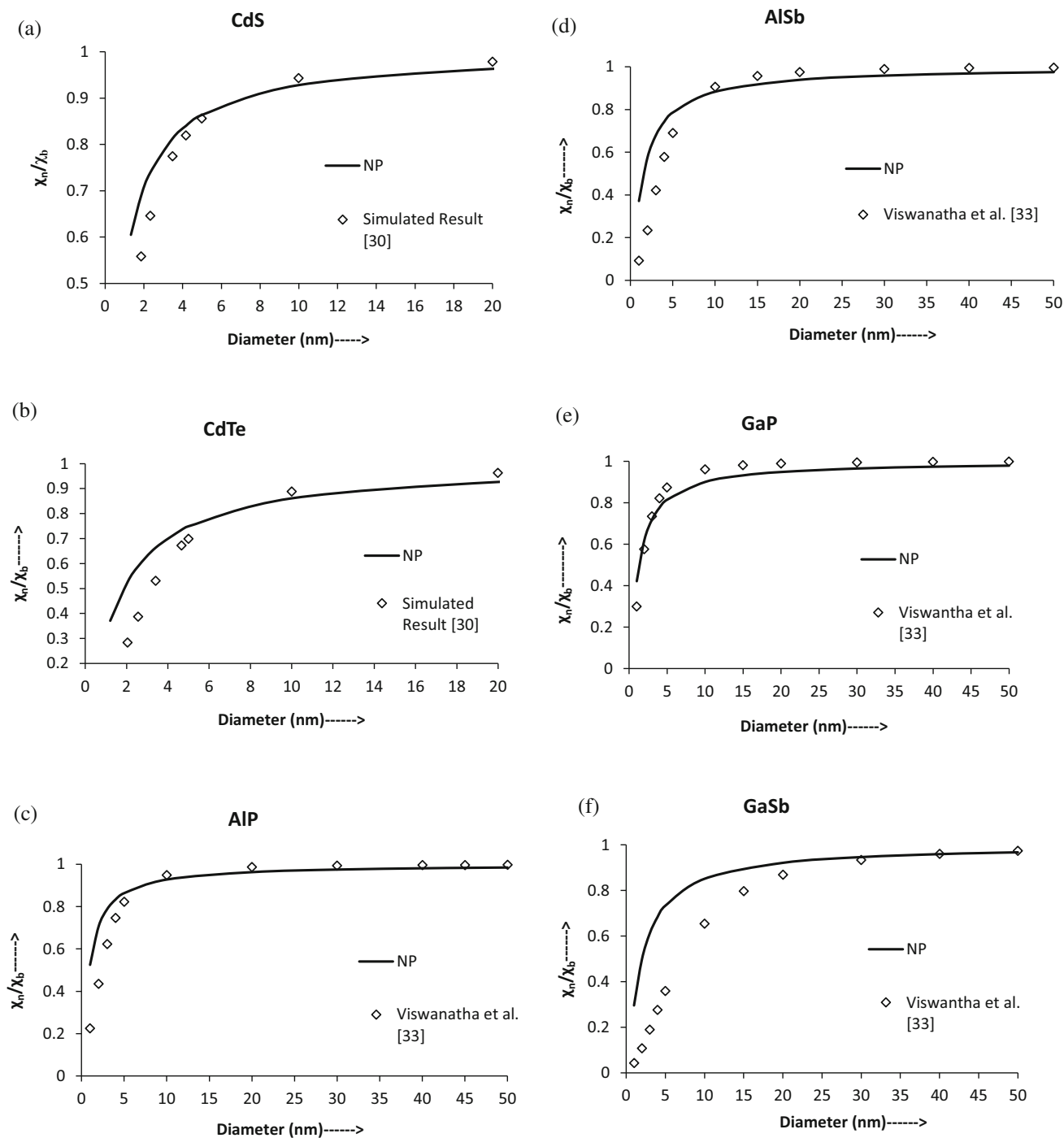


Figure 3. Electrical susceptibility vs. size in (a) CdS nanoparticle, (b) CdTe nanoparticle, (c) AIP nanoparticle and (d) AlSb nanoparticle, (e) GaP nanoparticle and (f) GaSb nanoparticle.

semiconductors with the variation in energy band gap as the size of the nanosolid increases from 5 nm to 200 nm. The nature of the graph depicts that the

dielectric constant of semiconductors increases as particle size increases. However, the energy band gap decreases with the increase in particle size.

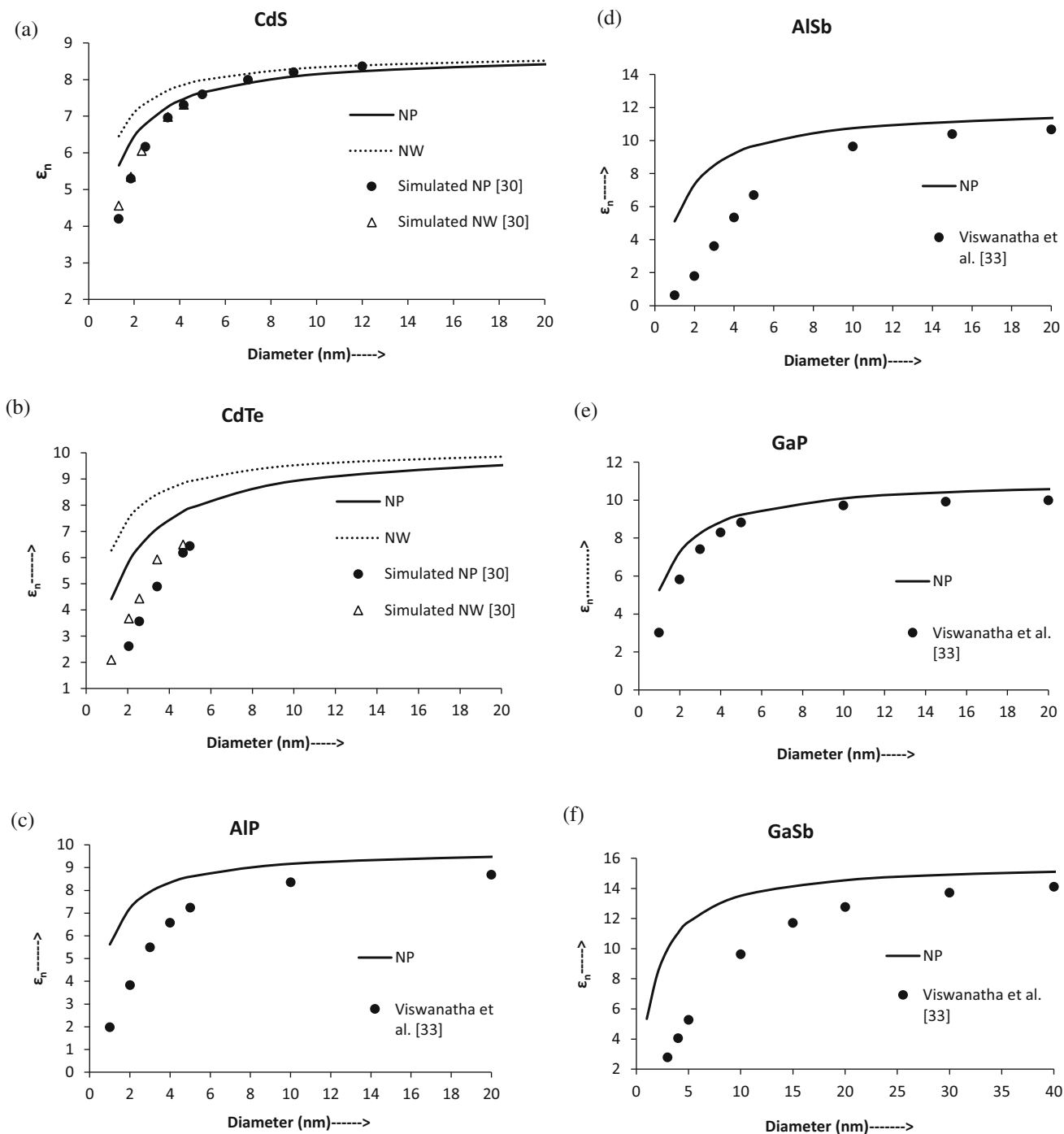


Figure 4. Dielectric constant vs. size in (a) CdS nanoparticles, (b) CdTe nanoparticles, (c) AIP nanoparticles, (d) AlSb nanoparticles, (e) GaP nanoparticles and (f) GaSb nanoparticles.

4. Conclusion

The model predicts the variation well in optical properties with size, shape and dimension of semi-conducting nanomaterial. From the present study, it is obvious that both the size and shape play

significant roles to explain the physical properties of nanomaterials having sizes below 10 nm. It can be concluded that the present study may be useful in predicting the optical properties of nanomaterials for which experimental data are not known yet.

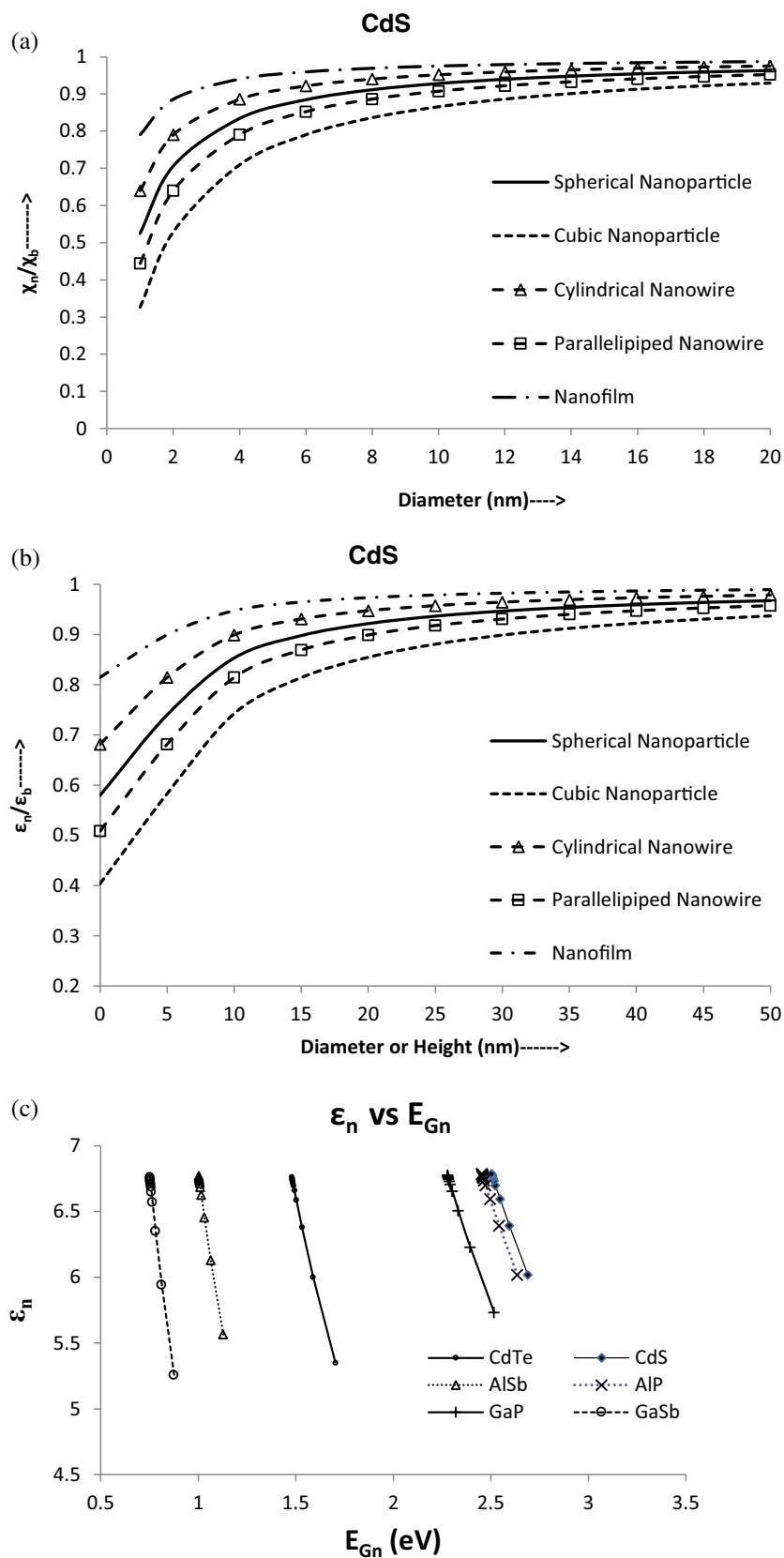


Figure 5. (a) Relative change in electrical susceptibility in CdS nanomaterials with size and shape, (b) relative change in dielectric constant in CdS nanomaterials with size and shape and (c) variation in dielectric constant with energy band gap variation in nanosemiconductors.

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