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Size effects on the band-gap of semiconductor compounds

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Abstract

Based on a thermodynamic model for size-dependent melting temperature, the size-dependent band-gap of low dimensional semiconductor compounds is modeled without any adjustable parameter. The model predicts an increase of the band-gap of nanoparticles and nanowires for IIB-VIB and IIIB-VB semiconductor compounds, with decreasing their size, which is supported by available experimental and other theoretical results.

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Keywords: Band-gap; Size-dependent; Semiconductor

Semiconductor compounds, with the tenability of their electronic and optical properties by the three-dimensional confinement of carriers, have attracted considerable interest as technologically important materials [1]. Hence, the study of the quantum confinement in these semiconductors has been a subject of intense study. One of the characteristics of the semiconductor nanocrystals is the increase of the valence-conduction band-gap E_g with decreasing of D where D denotes the diameter of nanocrystals [1–33]. Size-dependent band-gap of semiconductor nanocrystals is well known and studied quantum confinement effect [34]. The band-gap of IIB-VIB compound nanoparticles [2–23,31] and IIIB-VB compound nanoparticles [24–31] has been extensively investigated. But the study in nanowires is just beginning [31]. In order to understand the size-dependent band-gap, different theoretical approaches have been adopted and they can be described as $\Delta E_g(D)=E_g(D)-E_g(\infty)$ where $E_g(\infty)$ is the band-gap of bulk size. However, most of them suit only for crystallites larger than several nanometers and are approximate when $D<10$ nm [1,22,35–37]. Then it is necessary to establish a quantitative model that suits full size range of nanocrystals.

In this contribution, a simple model without any adjustable parameters is developed to predict the size-dependent band-gap of semiconductor compounds. The predicted results are consistent with the available experimental and/or theoretical reports in the full size range.

It is well known that the size and temperature dependent of electrical conductivity $\sigma(D,T)$ can be read [38],

$$\sigma(D,T) = \sigma_0 \exp[Q(D)/(k_B T)], \tag{1}$$

where σ_0 denotes a pre-exponential constant, $Q(D)$ is the size-dependent activation energy for electrical migration for nanocrystals, k_B is Boltzmann′s constant and T is temperature. In terms of Eq. (1), $\sigma(D,T)/\sigma(\infty,T)=\exp\{[Q(D)-Q(\infty)]/(k_B T)\}$ if the size effect of σ_0 is negligible. For semiconductors, $(D,T)=\sigma_0\exp[-E_g(D)/(2k_B T)]$ [39]. Thus, $\sigma(D,T)/\sigma(\infty,T)=\exp\{[E_g(\infty)-E_g(D)]/(2k_B T)\}$, which leads to $\Delta E_g(D)=2[Q(\infty)-Q(D)]$. When $D\rightarrow D_0$ (D_0 denotes a critical diameter at which all atoms of a low-dimensional material are located on its surface, which depends on dimension d and atomic diameter h. For particles, $d=0$, for wire $d=1$, for thin film, $d=2$), $Q(D)=0$ and $\Delta E_g(D)=E_g(\infty)$ for $E_g(\infty)=2Q(\infty)$ [39]. The following expression can get,

$$\frac{\Delta E_g(D)}{E_g(\infty)} = \frac{2[Q(\infty)-Q(D)]}{2Q(\infty)} = 1-\frac{Q(D)}{Q(\infty)}, \tag{2}$$

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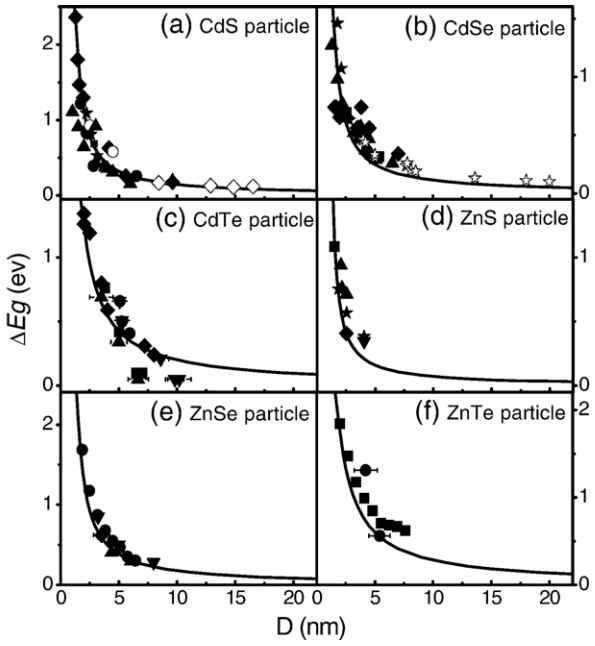

Fig. 1. Comparisons for ΔE_g values of IIB-VIB compounds nanoparticles between the model predictions in term of Eq. (7) and the experimental results. (a) CdS nanoparticles (⬢ [2], ● [3], ▲ [4], ■, ○ [5], ★ [6] and ◇ [7]). (b) CdSe nanoparticles (▲ [8], ★ [9], ☆ [10], ◆ [2] and ■ [11]. (c) CdTe nanoparticles (▲ [12], ■, ▼ [13], ● [14] and ◆[2]). (d) ZnS nanoparticles (■ [15], ▲ [16], ▼ [17] and ◆ [18]). (e) ZnSe nanoparticles (◆ [19], ▼ [20], ▲ [21] and ● [22]). (f) ZnTe nanoparticles (● [22] and ■ [23]). The necessary parameters in the calculations are listed in Table 1.

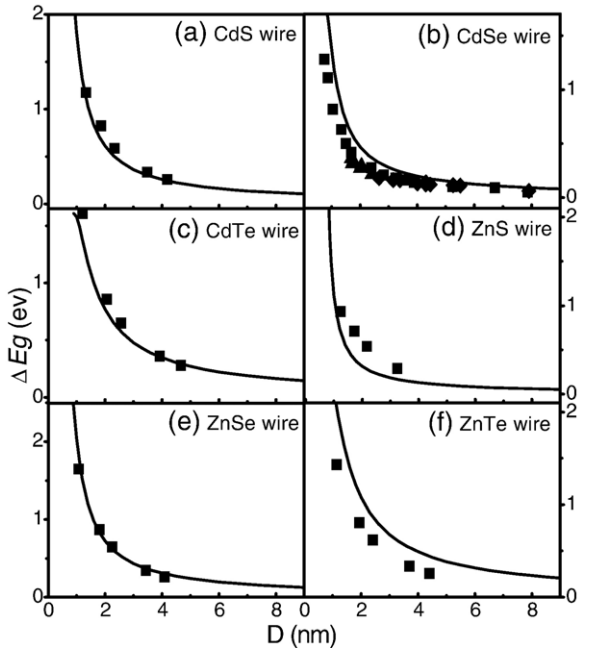

Fig. 2. Comparisons for ΔE_g values of IIB-VIB semiconductor compounds nanowires between the model predictions in term of Eq. (7) and the experimental and theoretical results. CdS nanowires (■ [31]). (b) CdSe nanowires (◆ [31], ■ [32] and ▲[33]). (c) CdTe nanowires (■ [31]). (d) ZnS nanowires (■ [31]). (e) ZnSe nanowires (■ [31]). (f) ZnTe nanowires (■ [31]). The necessary parameters in the calculation are the same as these in Table 1.

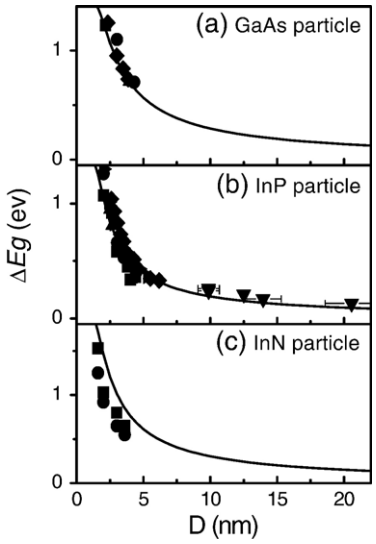

Fig. 3. Comparisons for ΔE_g values of IIIB-VB compounds nanoparticles between the model predictions in term of Eq. (7) and the experimental and other theoretical results. (a) GaAs nanoparticles (▲ [24], ■ [25], ● [26] and ◆ [30]). (b) InP nanoparticles (● [27], ■ [28], ▲ [29] and ▼, ◆, ► [30]). (c) InN nanoparticles (■ [31]). The necessary parameters in the calculation are the same as these in Table 1.

here D has a usual meaning of diameter for a nanoparticle or a nanowire, and denotes its thickness for a film. D_0 can read [40,41],

$$D_0 = 2(3-d)h, \tag{3}$$

To establish $Q(D)$ function, the value of σ at melting temperature T_m is understandably assumed to be size independent, or $\sigma\,[D, T_m(D)] = \sigma[\infty, T_m(\infty)]$. Thus, $\sigma[D, T_m(D)] = \sigma_0(D)$

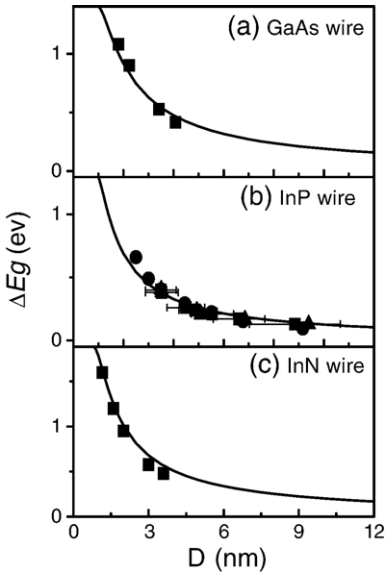

Fig. 4. Comparisons for ΔE_g values of IIIB-VB compound's nanowires between the model predictions in term of Eq. (7) and the experimental and theoretical results. (a) GaAs nanowires (■ [31]), (b) InP nanowires (■, ●, ▲[30]) (c) InN nanowires (■ [31]). The necessary parameters in the calculation are the same as these in Table 1.

$\exp\{-Q(D)/[k_B T_m(D)]\} = \sigma_0(\infty)\exp\{-Q(\infty)/[k_B T_m(\infty)]\}$. Since the exponential coefficient $Q(D)$ plays an essential role in the size of $\sigma(D,T)$ function, $\sigma_0(D) \approx \sigma_0(\infty)$ is assumed as a first order approximation. As result, there is,

$$Q(D)/Q(\infty) = T_m(D)/T_m(\infty). \quad (4)$$

As it has been established that the size-dependent of $T_m(D)$ has the following form [40],

$$\frac{T_m(D)}{T_m(\infty)} = \exp\left(-\frac{2S_{vib}(\infty)}{3R(D/D_0-1)}\right), \quad (5)$$

$S_{vib}(\infty)$ is the bulk vibrational melting entropy and R is the ideal gas constant. Transformation from semiconductor to metals for the electronic state of semiconductors leads to a large contribution on bulk overall melting entropy $S_m(\infty)$ [42]. If the corresponding $S_{vib}(\infty)$ is unavailable, a rough estimation on $S_{vib}(\infty)$ is shown as follows [42],

$$S_{vib}(\infty) \approx S_m(\infty) - R. \quad (6)$$

The following expression can get,

$$\frac{\Delta E_g(D)}{E_g(\infty)} = 1 - \exp\left(-\frac{2S_{vib}(\infty)}{3R(D/D_0-1)}\right). \quad (7)$$

Comparisons for the ΔE_g values of IIB-VIB compound's nanoparticles between the predictions of Eq. (7) and the experimental results and/or other theoretical results are shown in Fig. 1, the results imply that the ΔE_g increases with the decreasing nanoparticle size. The predicted results are in good agreement with the experimental results in full size range of IIB-VIB compound's nanoparticles. Note that there exists a little deviation, which could be partly induced by measuring uncertainties of $\Delta E_g(D)$ values.

Fig. 2 indicates the comparisons for the ΔE_g values of IIB-VIB compound's nanowires between the prediction in terms of Eq. (7) and the experimental results and/or theoretical results. The trend is similar to the nanoparticles. But its value is smaller than that of nanoparticles. It is because the quantum confinement in the wire is weakened to the expected extent by the loss of one confinement dimension [30].

Figs. 3 and 4 present the comparisons for the ΔE_g values of IIIB-VB compound's nanoparticles and nanowires, respectively, between the model predication of Eq. (7) and the available experimental or theoretical results. They also show that the ΔE_g increases with the decreasing size and the model prediction results are in agreement with the experimental and other theoretical results. By the way, the ΔE_g values of the nanoparticles are also larger than those of the nanowires (Table 1).

Considering the mathematical relation of $\exp(-x) \approx 1-x$ when x is small enough as a first order approximation, Eq. (7) can be rewritten as,

$$\frac{\Delta E_g(D)}{E_g(\infty)} = \frac{2\Delta S_{vib} D_0}{3RD}, \quad (7)$$

Table 1
The relevant data used in the calculations of Eq. (7)

	$E_g(\infty)$ eV	S^a_{vib} J/g-atom K	S_m J/g-atom K	a [44] nm	h^b nm
CdS	2.5 [44]	8.314	16.628 [47]	0.582	0.18
CdSe	1.74 [45]	6.596	14.91 [47]	0.608	0.189
CdTe	1.61 [13]	12.056	20.37 [47]	0.648	0.201
ZnS	3.68 [44]	2.186	10.5 [47]	0.541	0.168
ZnSe	2.822 [44]	6.806	15.12 [47]	0.567	0.176
ZnTe	2.394 [44]	12.266	20.58 [47]	0.61	0.189
GaAs	1.424 [44]	23.186	31.5 [47]	0.565	0.175
InP	1.344 [44]	15.626	23.94 [47]	0.586	0.182
InN	1.9 [46]	21.296	29.61 [48]	0.498	0.155

[a] $S_{vib} = S_m - R$. [b] $h = \{[3V/(4\pi)]^{1/3}\}/2$ with $V = a^3$ denoting the volume of one cell where a is the crystal lattice constant.

or,

$$\frac{\Delta E_g(D)_{wire}}{\Delta E_g(D)_{particle}} = \frac{D_{0_{wire}}}{D_{0_{particle}}} = 0.67, \quad (8)$$

$\Delta E_g(D)_{wire}$ and $\Delta E_g(D)_{particle}$ are size-dependent of the band-gap of nanowire and nanopaticle, respectively; $D_{0_{wire}}$ and $D_{0_{particle}}$ are their critical diameters, respectively. The similar result also can be found in the work of Nanda et al. [43]. As shown in these results, the complicated ΔE_g can still be analyzed and predicated by this simple model when the relative thermodynamic parameters are clear.

In summary, a simple and unified model of the size-dependent band-gap for semiconductor compounds has been established. It predicates that the band-gap increases with the decreasing size and the predicted results are consistent with the available experimental and theoretical evidences for IIB-VIB and IIIB-VB compound's nanoparticles and nanowires.

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