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SIZE-DEPENDENT BAND-GAP AND DIELECTRIC CONSTANT OF SI NANOCRYSTALS

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Based on the consideration on size-dependent temperature $T_m(D)$ where D denotes the diameter of nanoparticles and nanowires or the thickness of thin films, the size-dependent band-gap $\Delta E_g(D)$ and dielectric constant $\varepsilon(D)$ of low dimensional materials are modeled without any adjustable parameter. The model predicts an increase of the band-gap and a decrease of dielectric constant with drop of Si nanocrystals' size. The predicted results correspond to experimental and computer simulation results of Si nanocrystals.

Keywords: Band-gap; dielectric constant; size-dependent; Si.

1. Introduction

With the size reduction, the physical properties of nanocrystals will change dramatically, which has led to new technological applications of media with tunable properties. With the decreasing of D where D denotes diameter of nanoparticles, or diameter of nanowires or thickness of thin films, the most common findings of Si nanocrystals are (1) the increase of the band-gap E_g (D) which is an important parameter in dealing with the semiconductors and (2) drastic reduction in dielectric constant $\varepsilon(D)$. The physics and chemistry of a

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material are notably altered on changing E_g (D), as much of the materials' behavior depends on it. Reduction in $\varepsilon(D)$ causes an increase in Coulomb interaction energy between electrons, holes and ionized impurities, and therefore can significantly modify the optical absorption and transport phenomenon of nanometric device.[1]

It was found that E_g and ε values are functions of D[2-9] and $\varepsilon(D)$ function is related to the E_g (D) function. Once E_g (D) function is known, $\varepsilon(D)$ function is also can be determined. Therefore, it is important to determine E_g (D) function. In order to understand the size-dependent band-gap, different theoretical approaches have been adopted and it can be described as $\Delta E_g(D) = E_g(D)-E_g(\infty)$ where ∞ and Δ denote the bulk size and the change. However, most of them are exact only when $D > 10$ nm.[10-14] Thus, it is necessary to establish a quantitative model, which is applicable in a full size range of Si nanocrystals.

In this contribution, a simple equation without any parameters is developed to predict the size-dependent band-gap $\Delta E_g(D)$ and the model that is established is extended to predict the size effect on $\varepsilon(D)$ of Si films. The model predictions agree well with known experimental and computer simulation results.

2. Model

According to the Arrhenius relationship,

$$\sigma(D,T) = c\exp[Q(D)/(k_BT)]. \tag{1}$$

where c denotes a pre-exponential coefficient, $Q(D)$ is the size-dependent activation energy for electrical migration for nanocrystal, k_B is Boltzmann′s constant and T is absolute temperature.[15] According to Eq. (1), there is $\sigma(D,T)/\sigma(\infty,T) = \exp\{[Q(D)-Q(\infty)]/(k_BT)\}$, where the coefficient c is assumed to be a size-independent amount. As presented in Ref. 16, $\sigma(D,T) = c\exp[-E_g(D)/(2k_BT)]$ for semiconductors. Considering the relationship above, $\sigma(D,T)/\sigma(\infty,T) = \exp\{[Q(\infty)-Q(D)E_g(\infty)-E_g(D)]/(k_BT)\}$ where $\Delta E_g(D) = 2[Q(\infty)-Q(D)]$. Let D_0 represent the critical diameter at which all atoms of low-dimensional material are located on it′s surface, there is, [17]

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

where d and h denote the dimension and the atomic diameter and $d = 0$, 1 and 2 for particles, wires and films, respectively. It is clear, as D approaches D_0, $Q(D) = 0$ and $\Delta E_g(D) = E_g(\infty)$ since $E_g(\infty) = 2Q(\infty)$,[16] the following expression can be gotten,

$$\frac{\Delta E_g(D)}{E_g(\infty)} = \frac{2[Q(\infty)-Q(D)]}{2Q(\infty)} = 1-\frac{Q(D)}{Q(\infty)}\quad . \tag{3}$$

It is known that[18] $\sigma[D,T_m(D)] = \sigma[\infty,T_m(\infty)]$ where T_m is the melting temperature. Taking this consideration into Eq. (1), $\sigma[D,T_m(D)]=c\exp\{-Q(D)/[k_BT_m(D)]\}= c\exp\{-Q(\infty)/[k_BT_m(\infty)]\}$. Thus,

$$Q(D)/Q(\propto) = T_m(D)/T_m(\propto)\,. \tag{4}$$

As it has been established that the size-dependent $T_m(D)$ function has the following form,[17]

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

$S_{vib}(\infty)$ is the bulk vibrational melting entropy and R is the ideal gas constant.

Accdoding to Eqs.(3), (4) and (5), the size-dependent bandgap can be gotten,

$$\frac{\Delta E_g(D)}{E_g(\infty)} = 1 - \exp\left(-\frac{2Svib(\infty)}{3R(D/D_0 - 1)}\right) . \quad (6)$$

According to Tsu *et al*[19] related the dielectric susceptibility ($\chi = \varepsilon$-1) change $\Delta\chi(D)/\chi(\infty) = -2\Delta E_g(D)/E_g(\infty)$,the size-dependent dielectric constant can be found,

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

3. Results and Dscussion

Comparisons between the model predictions in term of Eq. (6) and the experimental and other simulant results for $\Delta E_g(D)$ values of Si nanoparticles and wires are shown in Fig. 1. It implies that $\Delta E_g(D)$ increases with the decreasing size. The predictions are in good agreement with the experimental results in full size range of Si nanocrystals. Note that there exists a little deviation, which could be partly induced by measuring uncertainties of $\Delta E_g(D)$ values. Furthermore, the change of $\Delta E_g(D)$ function of wires with D is weaker than that of nanoparticles. These differences should be attributed to the different surface/volume ratios A/V = 4/D, 6/D for wires and nanoparticles with d = 1, 0, respectively.

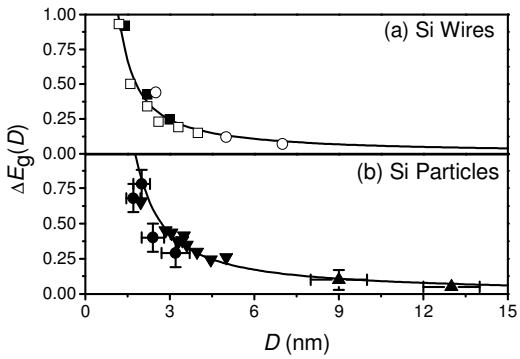

Fig. 1. $\Delta E_g(D)$ functions of Si nanoparticles and wires. The solid lines denote the model predictions in terms of Eq. (6). For Si wires shows in Fig. 1. a. $D_0 = 4h$ = 0.94 nm in terms of Eq. (2) with d = 1 and other related parameters are listed in table 1. The symbol ■[2], ○[3] and ○[4] is the corresponding simulation result. Si particles shown in Fig. 1. b, $D_0 = 6h$ = 1.41 nm in terms of Eq. (2) with d = 0 is used. $\Delta E_g(D)$ for ▲[5], ▼[6] and ●[7] denote the corresponding experimental results.

Table 1. Necessary parameters used in Eqs. (6) and (7).

	$E_g(\infty)$ (eV)	$\varepsilon(\infty)$	S_{vib}(Jg-atom^{-1}K^{-1})	h (nm)[a]
Si	1.12[1]	11.4[20]	6.72[21]	0.235

[a] $h = \sqrt{3}a/4$ for the zinc blende structure with the lattice constant a = 0.543nm nm for Si.[22]

Fig. 2. shows the comparisons between the model predictions in term of Eq. (7) and the experimental and other theoretical results for $\varepsilon(D)$ values of Si films. It predicts that $\varepsilon(D)$ function decreases as D decreases. The model prediction corresponds to the theoretical and the experimental evidences.

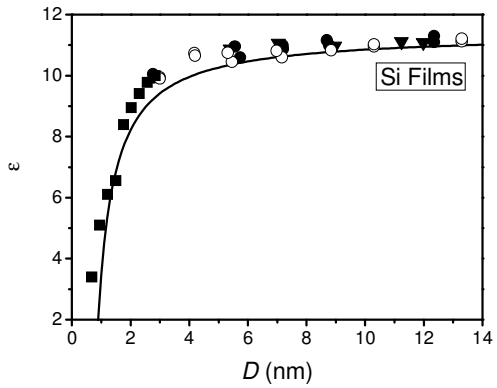

Fig. 2. $\varepsilon(D)$ function of Si films. The solid line denotes the model prediction in terms of Eq. (7) where $D_0 = 2h$ = 0.47 nm with d =2 in terms of Eq. (2). The $\varepsilon(D)$ for ■[8], ●, ○ and ▼[9] denote the corresponding simulation and experimental results.

Considering the mathematical relation of exp $(-x) \approx 1-x$ when x is small enough as a first order approximation, Eqs. (6) and (7) can be rewritten as,

$$\Delta E_g(D)/E_g(\infty) \approx 2\Delta S_{vib} D_0/3RD \,. \tag{8-1}$$

$$(\varepsilon(D)-1)/(\varepsilon(\infty)-1) \approx 1-2\Delta S_{vib} D_0/3RD. \tag{8-2}$$

Hence $\Delta E_g(D)/ E_g(\infty) = C/D$ and $(\varepsilon(D)-1)/(\varepsilon(\infty)-1)=1- C/D$ where $C = 2\Delta S_{vib} D_0/3R$. The change of $\Delta E_g(D)$and $\varepsilon(D)$ functions indicate that the most important size effect for low-dimensional materials is related with the surface/volume radio, namely $1/D$. This is also consisted with other results.

According to Eq. (8-1), it also can be found that,

$$\Delta E_g(D)_{wire} / \Delta E_g(D)_{particle} = D_{0wire}/ D_{0particle} = 0.67. \tag{9}$$

$\Delta E_g(D)_{wire}$ and $\Delta E_g(D)_{particle}$ are size-dependent of nanowire and nanopaticles' band-gap and D_{0wire} and $D_{0particle}$ are their critical diameters, respectively. The same value also can be found in Nanda's work.[23] As shown in these figures, the complicated $\Delta E_g(D)$ and $\varepsilon(D)$

functions can be analyzed and predicated by using this simple model without any free parameter as long as the relative thermodynamic parameters are known.

4. Conclusion

In summary, simple and unified models for the size-dependent band-gap and dielectric constant of Si nanocrystals have been established. They predicate that the band-gap increases with the decreasing size and the dielectric constant decreases as D droping. The predicted results are consistent with the available experimental and computer simulation results.

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