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Theoretical prediction for the band gap of semiconductor nanoparticles as function of bond number

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HIGHLIGHTS

- Only bond number is required in the established model of Eq. (10).
- The success of Eq. (10) is found for both Si and II-VI compound nanoparticles.
- Eq. (10) can be expected for any other nanostructures in full size range.

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ABSTRACT

Taken bond number as the only parameter, an unified model for the size-dependent band gap $E_g(D)$ of semiconductor nanoparticles is established in this work, with D being the particle size. As expected, the band gap increases with size dropping, and the success of the model is confirmed not only by the results of single elemental Si nanoparticles but also by the II-VI semiconductor compounds nanoparticles even in full size range. Based on the bond number of cubooctahedron which is used to describe the shape of the nanoparticles in this work, a good agreement between the model predictions and experimental, first-principle calculation results is obtained. Since there is no other adjustable parameter, the established model presents a possible way to predict the band gap of other nanostructure as long as its bond number is known.

1. Introduction

Up to now, there still have a lot of attractive attention for the semiconductor nanomaterials to researchers due to their special properties [1–3]. It has been widely accepted that they have great potential application in many fields, such as for solar cells [4], novel ultra small electronic logic and memory devices in the electronic industry [5,6], and even for a single-atom transistor [7]. Since the higher surface/volume ratio, many kinds of optical or electrical properties of nanomaterials are different from that of the bulk counterpart. One of the important things is that the band gap E_g has been found to have great relationship with size [8–12], and usually there is a larger value for nanostructures if compared with bulk materials. This greatly enhances the application of semiconductor nanomaterials owing to the widened band gap. For example, many different types of Si photon nanodevices are have been widely produced and used, while the bulk silicon is limited in the application due to its indirect and small band gap feature [10–12]. Moreover, in order to satisfy the requirement for the high effect transistors in the graphene-based electronic devices, the band gap opening in graphene has been successfully realized by controlling the size of graphene [13,14]. Thus, it becomes necessary for quantitatively determining the size-related band gap of the semiconductor nanostructures, which will be the good guidance for their applications in industry.

The fact of the size-related band gap has been greatly supported by many researches, including experimental measurements [15–29], first principle calculations [30–35] and theoretical deduction [1,9,36–40], etc. Through the band energy level analysis, one can get the value of band gap by means of X-ray photoemission spectroscopy [15,19], or by X-ray absorption spectroscopy [16–18,20,22], and or by photoluminescence [24,28]. Density Function Theory (DFT) calculation is another valid and popular method to obtain the band gap of semiconductor nanostructures. Especially for the small clusters including several hundreds or decades atoms, the detail about the size-related band gap is clearly

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obtained [31–35]. We should note that the theoretical prediction for band gap of semiconductor nanostructures still has its own merit. This is because the theoretical model of band gap could in advance give a valuable guidance for the application or design of semiconductor nanostructures. According to the quantum confinement theory, Buhro et al. [36] built a inverse proportional relationship between band gap E_g and size D (that is $\Delta E_g(D) \propto D^{-\lambda}$) as a first-order approximation, where λ is the index and could be 1 or 2, and $'\Delta'$ means the difference between $E_g(D)$ and bulk band gap $E_g(\infty)$. The reasonable estimation of Buhro's model is evident mainly for the larger size, while the inevitable divergence will exist when the size of nanostructure becomes more and more smaller. Since the energy is a basic property for materials, the thermodynamic analysis for the size-dependent band gap is another useful way to estimate band gap [1,37]. With the supporting of melting point model, Jiang et al. [40] get the good prediction for band gap. And Sun et al. also work the band gap out well based on the bond order-length-strength (BOLS) theory [38,39]. All the evidences suggested that the band gap E_g of nanostructures has a larger value, and will increases with size dropping.

Even though some theoretical models have been established, an unified model for size-dependent band gap $E_g(D)$ which has the ability to predict the band gap in full size range, is still lack. However, it maybe the possible way if we introduce the parameter of bond number. This is because one hand the bond number could be calculated well for a certain nanostructure without any limitation on the size. On the other hand, we have successfully applied the bond number into the melting model which is directly related with cohesive energy [41]. What's more important, the fact of the close relationship between band gap and cohesive energy implies that one could use the bond number as one of the parameters presented in the band gap model. Thus, based on the inherent relation with cohesive energy, an unified model for the size-dependent band gap $E_g(D)$ of semiconductor nanoparticles is constructed in this work. The comparison of model predictions with experimental and first principle calculation results is made. Their good agreement confirms the validity of the established model even in full size range. And also the established model shows it can be applied simultaneously for the single crystal nanoparticles and compound ones.

2. Model

In light of the nearly-free-electron theory, we can get the bulk band gap $E_g(\infty)$ based on the first Fourier coefficient, which can be expressed as $E_g(\infty) = 2|V(\infty)|$ for simplicity [40], where $V(\infty)$ means the first Fourier coefficient of crystalline field. If using this relation into the nanoscale, there is $\Delta E_g(D)/E_g(\infty) = |\Delta V(D)/V(\infty)|$, where $\Delta E_g(D) = E_g(D) - E_g(\infty)$ and $\Delta V(D) = V(D) - V(\infty)$, and $E_g(D)$ and $V(D)$ separately denote the band gap and the Fourier coefficient of crystalline filed in nanoscale. It should be noted that $V(\infty)$ and the bulk cohesive energy $E_c(\infty)$ have the similar means because both of them are greatly controlled by both of the atom number and the interaction energy between atoms in a system. Thus, an approximate relation, i.e., $E_c(\infty) \propto V(\infty)$ is put forward and then $E_c(D) \propto V(D)$ could also be seen. Then, with these relations, $E_g(D)$ could have the following expression,

$$\frac{E_g(D)}{E_g(\infty)} = 1 + \left|\frac{\Delta V(D)}{V(\infty)}\right| = 1 + \left|\frac{E_c(D) - E_c(\infty)}{E_c(\infty)}\right| = 2 - \frac{E_c(D)}{E_c(\infty)} \tag{1}$$

Eq. (1) presents a possible way to obtain $E_g(D)$ value if the size-dependent cohesive energy $E_c(D)$ is resolved, since the corresponding bulk values of both $E_g(\infty)$ and $E_c(\infty)$ are usually constants. Just because there exists a direct relationship between cohesive energy and bond number, the construction of a new relationship between band gap and bond number becomes feasible. As expected, there is $E_c(\infty) = \varepsilon_i(\infty) \times B_t$ where $\varepsilon_i(\infty)$ and B_t denote the single bond energy and the bond number of bulk materials, respectively [42]. Then a similar expression, i.e., $E_c(D) = \varepsilon_i(D) \times B_a$ can be read with $\varepsilon_i(D)$ meaning the average single bond energy and B_a the bond number in a nanostructure. So, one can obtain the model of $E_c(D)/E_c(\infty) = [\varepsilon_i(D) \times B_a]/[\varepsilon_i(\infty) \times B_t]$, through which the size-dependent cohesive energy could be resolved. If $\varepsilon_i(D) \approx \varepsilon_i(\infty)$ is taken for approximation, $E_c(D)$ can be determine by the following expression,

$$E_c(D)/E_c(\infty) = B_a/B_t \tag{2}$$

In Eq. (2), it is clear $E_c(D)$ can be determined directly by bond number, however, the bond relaxation is ignored in full size range. This is not always reasonable because the bond deficit on surface becomes more and more important when the size decreases to nanoscale [41]. This inevitably leads to the bond relaxation with the evidence of $\varepsilon_i(D) \neq \varepsilon_i(\infty)$. To further modify the model of Eq. (2), the bond relaxation is taken into consideration. Through introducing the surface energy γ which arises from the bond deficit on the surface, and considering its role on the $E_c(D)$ by using surface/volume ratio δ, $E_c(D)$ could be written,

$$E_c(\mathrm{D}) = \delta(E_c(\infty) + \gamma) + (1 - \delta)E_c(\infty) \tag{3}$$

In Eq. (3), the determination on γ has been given in Ref. [43], that is, $\gamma/E_c(\infty) = -[1 - (Z_s/Z_b)^{1/2}]$, where Z_s is the mean coordination number of the surface atoms and Z_b is the coordination number of bulk interior atoms. In terms of the two boundary conditions, one is a system with all atoms standing on the surface (i.e. having $\delta \to 1$) and another is bulk system with $\delta \to 0$ respectively, and by inserting this expression for γ into Eq. (3) yields two limits cases for $E_c(D)/E_c(\infty)$. Then there are,

$$E_c(D)/E_c(\infty) \approx (Z_s/Z_b)^{1/2} \quad (\delta \to 1) \tag{4.1}$$

$$E_c(\mathrm{D})/E_c(\infty) \approx 1 - \left[1 - (Z_{sb}/Z_b)^{1/2}\right]\delta \quad (\delta \to 0) \tag{4.2}$$

where Z_{sb} means the surface coordination number of bulk system. Letting N_s, N_i and N be the number of surface atoms, inner atoms and total atom number, respectively, the common relationship is

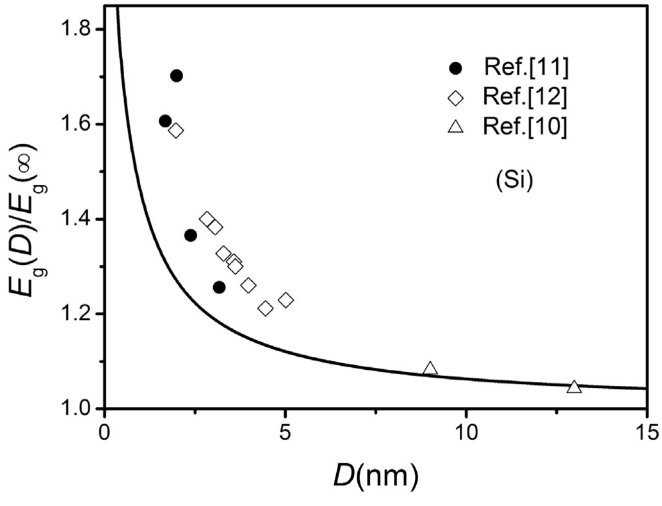

Fig. 1. The model predictions of $E_g(D)$ for Si nanoparticles by Eq. (10) denoted as the solid line, and D is determined by $n = (D/h_0 - 1)/2$ with $h_0 = 0.235$ nm [45] for Si crystal. The symbols are the relevant experimental [10,11] and first-principle calculation [12] results of band gap of Si nanoparticles.

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