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Size and dimension effect on volume plasmon energy of nanomaterials

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ABSTRACT

The influence of size and dimension on the volume plasmon energy of nanomaterials is examined, and the effect of band-gap variation and lattice contraction is explicitly included in our improvised phenomenological model. The advantage of this improvised model is the ability to predict the volume plasmon energy for low dimensional materials, literally free from any arbitrarily adjustable parameters. We find that the volume plasmon energy increases almost exponentially with decreasing size and this increase is shown to be the most evident for nanoparticles, as compared to nanowires and nanofilms of the same material. This is largely due to the variation in the surface/volume ratio with dimension modulation. More importantly, our improvised model outperforms other reported ones, bringing our predicted results closest to available experiments. In particular, for semiconducting/semi-metal nanoarchitectures, we demonstrate that the rapid increase in volume plasmon energy of nanomaterials is a direct consequence and interplay of band-gap variation and lattice contraction.

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1. Introduction

Nanostructured materials have attracted a lot of attention for the past decade or so [1,2], largely due to the fact that their size-dependent material properties (e.g., their electronic, magnetic, optic, catalytic, mechanical and thermodynamic properties) are significantly different from those of either extreme size (i.e., either in their bulk or their atomic/molecular counterparts) [1]. Deriving a "design-rule" to control and tune such material properties will be highly desirable for new modern technologies. Given that the differences seen in nanomaterial's characteristics essentially arise from an increase in the surface/volume ratio (A/V), we can try to express this dependence in many such properties, to have the form of $1/D$, where D denotes the size of the nanostructure. To add complexity to this dependence, many nanomaterial's characteristics are also greatly influenced by the dimension, d of the nanomaterial, e.g., showing a dependence on the diameter of nanoparticles and nanowires or the thickness of nanofilms. In this letter, we seek to explore both the size- and dimension-dependence of the volume plasmon energy, $E_p(D,d)$, for semiconducting nanomaterials.

For an infinite solid, volume plasmons can be thought of as compressional electron oscillations of the free electron gas density, often in the presence of an external perturbation (e.g., an electric field) [3]. From electron energy loss spectroscopic (EELS) studies, in particular for semiconductors, the volume plasmon energy peak is distinctively separated from that of so-called surface plasmons (which are plasma oscillations that are restricted to surface-region), even for very small semiconducting nanostructures where A/V becomes appreciable [4]. This allows one to study the variation of the volume plasmon energy peak, which reflects the band gap widening in ultra-small, nano-sized semiconducting materials, as a function of its size and dimension [5–8]. Given that the volume plasmon in semiconductors is thought to be closely related to the oscillator strength of inter-band transition beyond the band-gap (E_g), having a size- and dimension-dependent description of a material's volume plasmon could then provide us with some desirable information about its electronic structure near the E_g [9]. Once armed with this fundamental knowledge, it will allow us to design a wide range of practical applications of nanostructured semiconductors, covering from nanoplasmonics technology to nanolasers [10–13]. Specifically, it has already been shown that in some early experimental results, a blueshift of E_p occurs with decreasing size (D), namely, $E_p(D) > E_p(\infty)$, where ∞ denotes the bulk regime [5–8]. It was thought that this blueshift of the energy is associated with changes made to the dispersion relation of the volume plasmon [8] with decreasing size. Therefore, in this letter, we aim to provide an improvised phenomenological (and theoretical) model to investigate $E_p(D,d)$, the size- and dimension-dependent volume plasmon energy of semiconducting nanomaterials.

In order to understand size(only)-dependent volume plasmon energy, $E_p(D)$, different theoretical approaches have been proposed in literature [5,9,14–16]. Unfortunately, a comprehensive

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theoretical model providing a quantitative relationship between D and the $E_p(D)$ shift is presently not well developed and this calls for a more in-depth study [5]. For example, Mitome et al. introduced an approximated function for the $E_p(D)$ shift. It considered that $E_p(D)$ increases in proportion to the inverse square of the size, namely $E_p(D) \propto 1/D^2$ and is thought to be caused by an increase in $E_g(D)$ [9]. However, it was later found that by fitting to experimental results, the exponent may now take values from 0.83 to 1.32 [5,15]. In addition, Sanchez et al. also considered that the changes of $E_p(D)$ to be solely dependent on lattice contraction [16]. while Yamada et al. attributed the blueshift of $E_p(D)$ to the common effect of $E_g(D)$ variation and lattice contraction [14]. All of the above mentioned approaches either contain some arbitrarily adjusted parameters or simply provide only a qualitative analysis. At this point, we would also like to point out that, to date, the dimension-dependence of E_p has not been addressed for nanomaterials with different dimensions (d), $E_p(d)$ and it may present a different behavior as compared to $E_p(D)$ [5,14]. Thus we deem it necessary and important to establish a quantitative (rather than just qualitative) model to predict the effect of both D and d on the volume plasmon energy, $E_p(D,d)$ and then attempt to explain the physical origin of the blueshift seen for E_p in experiments.

2. Model

According to the nearly free electron model, $E_p(\infty)$ can be expressed as follows [17].

$$E_P(\infty) = \hbar\left(\frac{fne^2}{\varepsilon_0 m_0}\right)^{1/2} \tag{1}$$

where $\hbar$, f, n, e, ε_0 and m_0 are the Planck constant, the oscillator strength of each valence electron for the excitation, the valence electron density, the elementary charge, the permittivity of free space and the real mass of an electron, respectively. From these parameters mentioned above, the only ones found to be material-dependent are only f and n. Thus, in order to further establish a theoretical description to explain the experimental results (i.e., to determine the $E_p(D,d)$), the size and dimension effect on $f(D,d)$ and $n(D,d)$ has to be addressed.

From quantum mechanics [9], $f(\infty)$ can be expressed as,

$$f(\infty) = \frac{2m_0 E_g(\infty)}{e^2\hbar^2}|d_{oc}|^2 \tag{2}$$

where d_{oc} is an atomic dipole matrix element for the excitation and it could be considered as a size-independent parameter [9]. Thus f is then taken to be proportional to E_g and thus generalizing the proportionality relationship to include both size and dimension dependence, it reads.

$$\frac{f(D,d)}{f(\infty)} = \frac{E_g(D,d)}{E_g(\infty)} \tag{3}$$

Now, from our previous work on $E_g(D,d)$ [18], we can rewrite Eq. (3) formally as,

$$\frac{f(D,d)}{f(\infty)} = \frac{E_g(D,d)}{E_g(\infty)} = 2-\exp\left[-\frac{2S_{vib}(\infty)}{3R[D/2(3-d)h-1]}\right] \tag{4}$$

Where $S_{vib}(\infty)$ is the bulk vibrational melting entropy and R is the ideal gas constant. h is bond length and $d=0$ for nanoparticles, $d=1$ for nanowires and $d=2$ for nanofilms [19]. n is then determined by the electron density of the atoms and the lattice parameter [16]. For a fixed amount of matter, we may take the electron density of the atoms as a constant and size-independent [16]. Again, generalizing the proportionality relationship to include both size and dimension dependence, $n(D,d)$ is inversely proportional to the respective volume, $v(D,d)$, and can thus be expressed as [1,14],

$$\frac{n(D,d)}{n(\infty)} = \frac{v(\infty)}{v(D,d)} = \frac{1}{1+3\frac{\Delta a(D,d)}{a(\infty)}} \tag{5}$$

where a is the lattice constant, and with $\Delta a(D,d)$ defined as the corresponding change in $a(\infty)$. It has been established by Jiang et al. [20] that the size-dependent fractional change in the lattice parameter $\frac{\Delta a(D,d)}{a(\infty)}$ can be written as,

$$\frac{\Delta a(D,d)}{a(\infty)} = \pm\frac{2}{3D}\sqrt{2\kappa(3\text{-}d)h^2 S_{vib}(\infty)H_m(\infty)/(RV_s)} \tag{6}$$

where κ is the compressibility modulus of the material, $H_m(\infty)$ being the melting enthalpy of bulk crystals, respectively, and where the positive (negative) sign denotes the positive (negative) stresses induced by lattice expansion (contraction) [21].

Combining Eqs. (4), (5) and (6) with Eq.(1), the complete expression of $E_p(D,d)$ which now depends on both the dimension and size, can then be written as,

$$\frac{E_p(D,d)}{E_p(\infty)} = \left\{2-\exp\left[-\frac{2S_{vib}(\infty)}{3R\left[\frac{D}{2(3-d)h}-1\right]}\right]\right\}^{1/2} \times\left[\frac{1}{1\pm\frac{2}{D}\sqrt{2\kappa(3-d)h^2 S_{vib}H_m(\infty)/(RV_s)}}\right]^{1/2} \tag{7}$$

3. Results and discussion

For all nanostructures considered in this letter, the relevant data used in the calculation of Eq. (7) are listed in Table 1. Fig. 1 shows the comparisons between the model prediction in terms of Eq. (7) (labeled as the solid line 1) and experimental results and other theoretical calculations for $E_p(D,d)$ of Ge nanoparticles (in Fig. 1a) and nanowires (in Fig. 1b). As shown in Fig. 1, $E_p(D,d)$ increases with a corresponding decrease in size and a dramatic increase in $E_p(D,d)$ is observed for the size range of $D>20$ nm. Beyond $D>20$ nm, $E_p(D,d)$ decreases rather gently until it approaches the bulk value for large D. This trend can be easily explained that, with the reduction of D, more atoms are found to be located on the surface and thus, A/V increases with decreasing D. With the increasing of A/V, an increase in $E_g(D,d)$ [18]. coupled with a lattice contraction [20,21] is found. Both the increase in $E_g(D,d)$ and lattice contraction will then modify the volume plasmon dispersion relations, causing the observed blueshift of $E_p(D,d)$ [9,14,16]. To illustrate the individual effects of the two factors outlined above, we show in Fig. 1a and b the dashed lines (labeled as '2') as the variation of $E_p(D,d)$ under the sole influence of increasing $E_g(D,d)$, and the dot lines (labeled as '3') as that of $E_p(D,d)$ under the sole influence of lattice contraction. We can clearly see that if one is to consider these two effects separately,

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

	h(nm)	v_s(cm^3/g atom) [22]	H_m(KJ/g atom) [22]	S_{vib}(J/g atom K) [23]	k(10^{-10} Pa^{-1})
Ge	0.245[a]	13.64	36.94	4.62	0.768 [22]
Si	0.235[a]	12.06	50.55	6.72	0.306 [22]
Bi	0.407 [20]	21.3	11.3	3.78	0.330 [20]

[a] $h=\sqrt{3}a/4$ for the diamond structure with $a=0.566$ nm for Ge and 0.543 nm for Si [22].

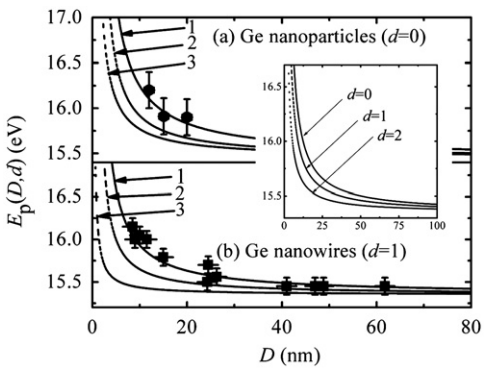

Fig. 1. Comparison of $E_p(D,d)$ between our prediction, using Eq. (7) (labeled as solid line '1') and other experimental and theoretical calculations denoted as dashed lines '2' [9] and dotted lines '3' [16], respectively. (a) For Ge nanoparticles, $D_0=6h=1.47$ nm with $d=0$ and $E_p(\infty)=15.45$ [5]. The symbol ● represents the experimental results from Ref. [14](b) For Ge nanowires, $D_0=6h=0.98$ nm with $d=1$. Other related parameters are listed in Table 1. The symbol ■ represents the experimental results from Ref. [5]. The insertion plot illustrates the trend of $E_p(D,d)$ shift in Ge nanostructures of different dimensions.

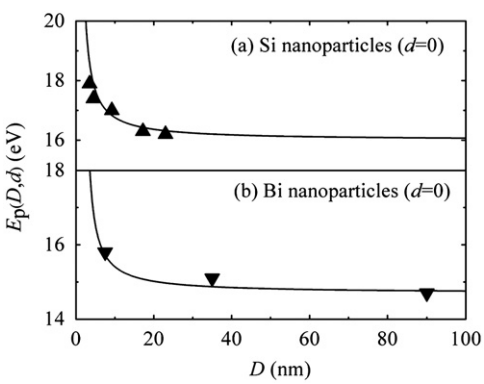

Fig. 2. Comparison between our predicted values using Eq. (7) and available experimental results for $E_p(D,d)$ of Si and Bi nanoparticles. The solid lines denote our predicted values, while the symbols are the corresponding experimental results. $D_0=6$ $h=1.41$ nm and 2.44 nm with $d=0$ for (a) Si and (b) Bi nanoparticles. The symbols ▲ and ▼ denote the experimental results for Si [15] and Bi [8], respectively.

the $E_p(D,d)$ variations are much smaller than that observed in experiments, while our improvised model (cf. Eq. (7)) which now takes both factors into consideration simultaneously, shows a much better agreement, especially for $D>20$ nm. Thus, it is now evident that, from our model predictions, the observed blueshift of $E_p(D,d)$ is caused by both an increase in $E_g(D,d)$ and its correlated lattice contraction effect.

Moreover, to illustrate this variation for Ge nanostructures with the same size but of different dimension, we find that the increase in $E_p(D,d)$ is more dramatic for nanoparticles (with $d=0$) than that of nanowires (with $d=1$). For Ge nanostructures of $D=10$ nm, $E_p(10\text{ nm},0)$ is predicted to be 16.25 eV [14] for nanoparticles while $E_p(10\text{ nm},1)$ is found to be 15.91 eV [5] for nanowires, respectively. These differences could be attributed to the different $A/V=6/D$, $4/D$, $2/D$ for nanoparticles, nanowires and thin nanofilms with $d=0$, 1, 2, respectively. In Fig. 1b, the inserted graph illustrates this shift in the $E_p(D,d)$ variation for nanostructures of Ge with different dimensions. From top down, the three lines represent $E_p(D,d)$ function for nanoparticles ($d=0$), nanowires ($d=1$) and nanofilms ($d=2$), respectively, which very nicely illustrates the dimension effect on $E_p(D,d)$.

To highlight the universality of our improvised model (cf. Eq. (7)), we also show in Fig. 2 the excellent agreement between our predicted values and experimental results for $E_p(D,d)$ of Si and Bi nanoparticles. The consistency seen in both Figs. 1 and 2 clearly demonstrates that our model adequately (and quantitatively) describes the volume plasmon energy, $E_p(D,d)$ as a function of both dimension and size, and now clarifies that the physical origin of the observed blueshift of $E_p(D,d)$ in experiments is an interplay of an increase in $E_g(D,d)$ coupled to a lattice contraction effect.

4. Conclusions

Size and dimension effect on $E_p(D,d)$ is modeled without any adjustable parameter. It predicts that $E_p(D,d)$ increases as D dropping and size effect on $E_p(D,d)$ of wires is weaker than that of nanoparticles and stronger than thin films due to the different A/V. The consistency of model prediction with experimental evidences for $E_p(D,d)$ confirms the origin of the blueshift of $E_p(D,d)$ is the interplay of $E_g(D,d)$ expansion and lattice contraction.

Acknowledgments

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