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Comparison of models for Raman spectra of Si nanocrystals

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Within the framework of a partial-density approach, the confinement of vibrations in spherical Si nanocrystals is studied and the Raman frequency shifts of Si spheres with different sizes are derived based on the Raman spectra obtained by a bond-polarizability model. The results obtained by the bond-polarizability model are compared with those by the phenomenological model developed by Richter *et al.* [Solid State Commun. **39**, 625 (1981)]. [S0163-1829(97)01312-X]

The recent observation of strong visible photoluminescence at room temperature from low dimensional Si nanostructures has created a different possibility for the applications of Si in optoelectronic devices. These Si nanostructures include porous Si (Refs. 1 and 2) and Si nanometer-size particles.[3,4]

Raman spectroscopy, which is a sensitive probe to the local atomic arrangements and vibrations, has been used to characterize porous Si (Refs. 5–8) and Si nanostructures.[3,9] To characterize and interpret the Raman spectra of semiconductor nanostructures, a phenomenological phonon-confinement model[10,11] has been widely used. This model, originally proposed by Richter, Wang, and Ley[10] (hereafter this model is referred to as the RWL model), has been found to be useful for accounting for the peak-position shift, broadening, and asymmetry of bands observed in nanocrystalline Si,[5–8] Ge[12], and GaAs.[13] The key part of the model is the phonon weighting function. In most cases a Gaussian is used as the weighting function.[5–7] The form of weighting functions has been chosen somewhat arbitrarily, without physical justifications. To our knowledge, there are few microscopic calculations on the vibrational properties in Si nanocrystals. Only recently, Raman spectra of Si nanocrystals were studied by Shen[14] by using a Keating-type potential.[15] The Raman spectra and Raman frequency shifts due to the effect of size for Si spheres and columns were investigated by the present authors based on a partial-density approach.[16]

In the present work, the confinement of vibrations in Si spherical nanocrystals and Raman frequency shifts of Si spheres with different sizes are investigated based on a partial-density approach.[17] The results obtained are compared with those by the RWL model in order to test the validity of the model.

A partial density approach[17] is adopted to calculate the force constants in crystal Si. Within the framework of this approach, the ion-ion interaction contribution is calculated conventionally by the Ewald method, while the electronic related part is obtained by a pseudopotential calculation with the help of linear-response theory. The detailed description of the approach can be found elsewhere.[17] This parameter-free approach could give a good description of the vibrational properties for crystal Si.[17,18]

Since there is a large number of atoms involved in the calculations of Si nanocrystals, in order to reduce the amount of computation, the following assumptions are made. It is not unreasonable to assume that Si atoms are located at their diamond lattice sites and no relaxation exists, since x-ray characterizations have found that the relaxation is rather small.[8] The force constants in Si nanocrystals are taken to be the same as those in the bulk for similar reason. We do not use hydrogen atoms to saturate the dangling bonds, as is usually done in the electronic calculations,[19] in order to reduce the number of atoms involved. This is due to the fact that the very small atomic mass of hydrogen makes the frequency of the Si-H vibrations much higher than that of Si-Si vibrations. If hydrogen atoms are used, they would behave almost like massless atoms, which have very little effect on Si-Si vibrations. The final results are nearly unaffected whether the hydrogen atoms are introduced or not.

We first briefly describe the RWL model. The vibrational wave function of a phonon in an infinite crystal can be written as $\Phi(\mathbf{q}_0,\mathbf{r})$, where $\mathbf{q}_0$ is the wave vector or the momentum of the phonon. In the off-resonant condition, only the optical phonons with $\mathbf{q}_0=\mathbf{0}$ are Raman active in the one phonon scattering process. For nanocrystals the momentum will no longer be a good quantum number owing to the fact that the phonons are localized. This can be described by a weighting function $W(\mathbf{r},L)$ for the phonon amplitude, where L is the size of nanocrystals. The weighting function here is similar to the envelope function in the electronic structures. It can be viewed as a measure of the confinement of vibrations in nanocrystals. The vibrational wave function in a nanocrystal can then be approximated by[10,11]

$$\Psi(\mathbf{q}_0,\mathbf{r})=W(\mathbf{r},L)\Phi(\mathbf{q}_0,\mathbf{r}). \tag{1}$$

The phonon wave functions in a nanocrystal can be expressed as a superposition of the eigenfunctions found for the corresponding infinite crystal. Therefore, phonons out of an interval of $\mathbf{q}$ wave vectors centered around $\mathbf{q}_0=\mathbf{0}$ will contribute to the Raman spectra. The first-order Raman spectrum of a nanocrystal, $I(\omega)$, can be calculated by[10,11]

$$I(\omega)\propto\int\frac{|C(\mathbf{q})|^2}{[\omega-\omega(q)]^2+(\Gamma_0/2)^2}\,d\mathbf{q},\tag{2}$$

where $\omega(\mathbf{q})$ is the phonon dispersion curve of the infinite crystal and Γ_0 is the natural linewidth. Equation (2) represents a weighted integration of phonon Lorentzians and $C(\mathbf{q})$ is the Fourier coefficients of the vibrational weighting function expanded in a Fourier integral,

$$W(\mathbf{r},L)=\int C(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{q},\tag{3}$$

$$C(\mathbf{q})=\frac{1}{(2\pi)^3}\int W(\mathbf{r},L)\exp(-i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}.\tag{4}$$

The weighting function will influence the line shape of the phonon Raman peaks via the Fourier coefficients $C(\mathbf{q})$. We use an analytic form of $\omega(q)$, which is expressed as

$$\omega^2(q)=C+D\cos(aq/4),\tag{5}$$

where $C=1.714\times10^5$ cm^{-2} and $D=1.000\times10^5$ cm^{-2}, taken from Ref. 20.

The key part of the model is the phonon weighting function. In most cases a Gaussian is used as the weighting function to characterize the Raman spectra of Si nanostructures,[5–7]

$$W(r,L)=\exp(-\alpha r^2/L^2).\tag{6}$$

The corresponding Fourier coefficients are given by

$$|C(\mathbf{q})|^2=\frac{L^6}{16(2\pi)^2\alpha^3}\exp(-q^2L^2/2\alpha).\tag{7}$$

A sinc function has also been tested[8]

$$W(r,L)=\begin{cases}\dfrac{\sin(2\pi r/L)}{2\pi r/L} & \text{if}\quad r<L/2\\ 0\quad\text{if}\quad r\geqslant L/2,\end{cases}\tag{8}$$

which gives a vibrational amplitude exactly equal to 0 at the boundary. The corresponding Fourier coefficients are given by

$$|C(\mathbf{q})|^2=\frac{4L^4}{(2\pi)^4}\frac{\sin^2(qL/2)}{q^2(4\pi^2-q^2L^2)^2}.\tag{9}$$

It should be noted that the Fourier coefficients of a sinc function given in Ref. 11 are not correct. The choice of a sinc function is based on the assumption that the weighting function may be analogous to the wave function of an electron in a hard sphere potential.

In order to test the validity of the RWL model, a bond-polarizability model[21–23] is used to calculate the Raman spectra of Si spheres from the eigenvalues and eigenfunctions given by the microscopic calculations based on the partial-density approach. The detailed description of the bond-polarizability model can be found elsewhere.[24] In the framework of the bond-polarizability model, the variation of the $\mu\nu$ component of the polarizability tensor due to a phonon mode j with wave vector $\mathbf{q}\sim0$ is a sum of the contributions from each bond in the whole system

$$\Delta\alpha_{\mu\nu}(j\mathbf{q})=\sum_i^{\text{bonds}}\Delta\alpha_{\mu\nu}(i|j\mathbf{q}),\tag{10}$$

where $\Delta\alpha_{\mu\nu}(i|j\mathbf{q})$ is the differential polarizability of the $i$ith bond in the system considered.

The polarizability of the whole system is calculated as a sum of independent contributions from each bond, based on the calculated eigenvalues and eigenvectors. Then, the Raman intensity in the $\mu\nu$ polarization for the backscattering configuration is given by

$$I_{\mu\nu}(\omega)\propto[n(\omega)+1]\sum_j\delta(\omega-\omega_j(\mathbf{q}))|\Delta\alpha_{\mu\nu}(j\mathbf{q})|^2,\tag{11}$$

where $[n(\omega)+1]$ is the Bose-Einstein population factor. Neither Fröhlich interactions nor electro-optic effects are incorporated in the model.

In the framework of the bond-polarizability model, Raman spectra are obtained from the contributions of each bond in the system considered, based on the calculated eigenvalues and eigenvectors. The microscopic characters are considered in this model.

The eigenfrequencies and eigenvectors can be calculated by a direct diagonalization of the dynamical matrix for Si spheres with the force constants given by the partial-density approach.[17] The Si spheres consisting of up to 657 atoms are studied. Si nanocrystals with other shapes, for example, cubes are also considered. The calculated results are almost identical if the number of atoms involved are the same compared with that of a sphere.

From the calculated eigenvectors, one can get the insight into the confinement of vibrations in Si spheres. Figure 1 shows the calculated vibrational amplitude of a Si sphere for the most Raman active mode. This Si sphere consists of 357 atoms with a diameter of $L=23.5$ Å. The most Raman active mode in the present situation has the highest frequency. Other modes only give minor contributions to the Raman intensity. The amplitude at the center of the sphere is normalized to be 1. It can be seen from the figure that the vibrational amplitude attenuates from the center to the boundary. At the boundary the vibrations with respect to the center are quite small, only 3.6%. The vibrational amplitude can be viewed as the envelope function or weighting function described above. The sinc and Gaussian weighting functions are also plotted for comparison. For the Gaussian weighting function, the coefficient of $\alpha=8\pi^2$ has been widely used in the literature.[5–7] It gives too strong confinement. Only a small amount of atoms in the central part of the sphere can vibrate. This weighting function gives results which are far from those obtained by the microscopic calculations. Other values of α have been tested. It is found that a value of $\alpha=9.67$, obtained by the best fitting, can give a better description. From Fig. 1 it can be seen that a sinc function and a Gaussian function with $\alpha=9.67$ could give relatively good descriptions of the vibrational confinement in Si spheres. By using the bond-polarizability model, Raman spectra of Si nanocrystals can be calculated from the eigenvalues and

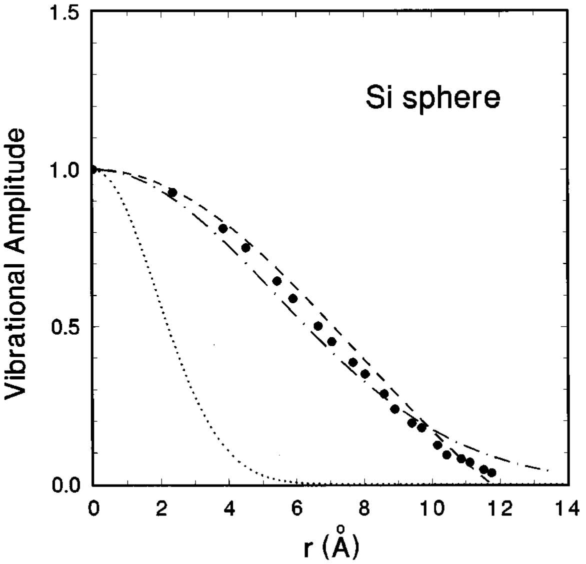

FIG. 1. Calculated vibrational amplitude (solid circles) for the most Raman active mode versus the distance from the center of a Si sphere consisting of 357 atoms. The vibrational amplitude at the center is normalized to be 1. The diameter of the sphere is 23.5 Å. The lines are the results from using a sinc weighting function (dashed line) and a Gaussian weighting function with the coefficient $\alpha=8\pi^2$ (dotted line) and $\alpha=9.67$ (dot-dashed line).

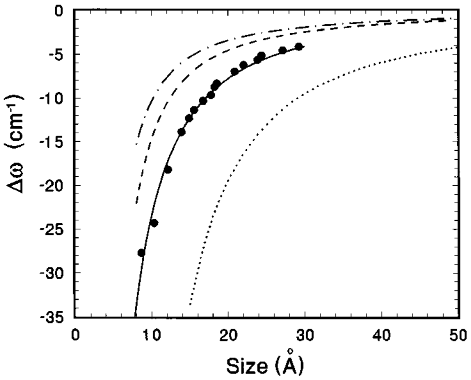

FIG. 2. Relation between the Raman frequency shifts with respect to the bulk LO phonon at the Γ point and the size for spherical Si nanocrystals. The solid circles are the results calculated by the bond-polarizability model and the solid line is the fitted results. The results obtained by using the sinc weighting function (dashed line) and Gaussian weighting function with $\alpha=8\pi^2$ (dotted line) and $\alpha=9.67$ (dot-dashed line) are also plotted for comparison.

eigenvectors obtained from the microscopic calculations based on the force constants given by the partial-density approach.

We define the Raman frequency shift $\Delta\omega$ by

$$\Delta\omega=\omega(L)-\omega_0, \tag{12}$$

where $\omega(L)$ is the Raman frequency of a Si sphere with size L and ω_0 is the LO or TO phonon frequency of the perfect Si crystal at the Γ point. In Fig. 2 the Raman frequency shifts versus size for Si spheres obtained by the bond-polarizability model are given as solid circles. For the convenience of applications, we use an analytic form[16] to describe Raman frequency shifts obtained by the bond-polarizability model,

$$\Delta\omega=-A\left(\frac{a}{L}\right)^{\gamma}, \tag{13}$$

where $A=47.41$ cm^{-1} and $\gamma=1.44$. The fitted results are given in Fig. 2 as a solid line. In Fig. 2 the results obtained by the RWL model with different weighting functions are also given for comparison. It can be seen that the RWL model cannot reproduce satisfactorily the Raman frequency shifts calculated by the partial-density approach and the bond-polarizability model. The model with a sinc weighting function gives relatively better agreement than with a Gaussian function. Especially for small size Si spheres, the Raman frequency shifts obtained by the Gaussian weighting function with $\alpha=8\pi^2$ are too large, while those obtained by the sinc function and by the Gaussian with $\alpha=9.67$ are small although the latter two can give relatively good descriptions of the vibrational confinement. For large size Si spheres, the frequency shifts obtained by the RWL model will be closer to the results obtained by the microscopic calculations. This is due to the fact that for large size spheres the corresponding frequency shifts are very small.

Other forms of weighting functions have been tested. It is found that no weighting functions can give good descriptions of the confinement and Raman frequency shifts at the same time. There are two main reasons why the RWL model cannot reproduce the microscopic calculations. One is due to the fact that the model is too simplified and the microscopic characters are not taken into consideration. The second reason is due to the fact that for small size nanocrystals one cannot use the envelope function or weighting function to describe the phonon wave function in the nanocrystals.

In conclusion, the vibrational properties of Si nanocrystals were investigated in the framework of partial-density approach. It was found that for Si spheres with a small size the RWL model cannot give a satisfactory description of the weighting function and the Raman frequency shift simultaneously. Our results indicate that over the other weighting functions the sinc function can give a good description of the vibrational confinement in Si spheres and a relatively good description of the Raman frequency shifts. Therefore, if the RWL model is used, a sinc weighting function is suggested for Si spheres.

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