Vibrational states in low-dimensional structures: An application to silicon quantum wires

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Available online 27 August 2007

Abstract

The Raman scattering in Si nanowires is studied by means of the local bond-polarization model based on the displacement–displacement Green's function within the linear response theory. In this study, the Born potential, including central and non-central interatomic forces, and a supercell model are used. The results show a notable shift of the main Raman peak towards lower energies, in comparison with the bulk crystalline Si case. This shift is compared with the experimental data and discussed within the quantum confinement framework.

Keywords: Raman scattering; Silicon nanowires; Phonons

1. Introduction

Low-dimensional semiconductors at nanometer scale have recently triggered remarkable scientific and technological interest, due to their unique physical properties and potential applications. In particular, silicon quantum wires (SiQW) could be used as building blocks for many nanodevices in microelectronics [1]. The phonon behaviors in such nanostructures are expected to be significantly different from that in the bulk materials, due to the quantum confinement. Raman spectroscopy is an accurate and nondestructive technique to study the elementary excitations as well as the details of microstructures. For example, line shapes of Raman spectra may give useful information on crystallinity, amorphicity, and dimensions of nanoscale silicon.

Raman scattering in semiconductor nanomaterials is being intensively investigated, for example, during the last year there were more than 100 scientific papers about such subject [2]. In this article, we report a theoretical study of the Raman response in SiQW by means of a local polarization model of bonds, in which the displacement–displacement Green's function, the Born potential includ-

ing central and not central forces, and a supercell model are used. This model has the advantage of being simple and providing a direct relationship between the microscopic structure and the Raman microscopy.

2. Calculation scheme

Within the linear response theory, the Raman response [$R(\omega)$] can be expressed by using the local polarization model of bonds as [3,4]

$$R(\omega) \propto \omega \mathrm{Im} \sum_{\mu,\mu'} \sum_{i,j} (-1)^{i-j} G_{\mu\mu'}(i,j,\omega), \qquad (1)$$

where i and j are the index of atoms, and $G_{\mu\mu'}(i,j,\omega)$ is the displacement–displacement Green's function determined by the Dyson equation as

$$(M\omega^2 \mathbf{I} - \mathbf{\Phi})\mathbf{G}(\omega) = \mathbf{I}, \qquad (2)$$

where M is the atomic mass of Si, $\mathbf{I}$ stands the identity matrix, and $\mathbf{\Phi}$ is the dynamic matrix, whose elements are given by

$$\Phi_{\mu\mu'}(i,j) = \frac{\partial^2 V_{ij}}{\partial u_\mu(i)\partial u_{\mu'}(j)}, \qquad (3)$$

being μ, $\mu' = x$, y, or z.

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Within the Born model, the interaction potential (V_{ij}) between nearest-neighbor atoms i and j can be written as [5]

$$V_{ij} = \frac{\alpha - \beta}{2} \left\{ [\mathbf{u}(i) - \mathbf{u}(j)]\hat{\mathbf{n}}_{ij} \right\}^2 + \frac{\beta}{2} [\mathbf{u}(i) - \mathbf{u}(j)]^2, \quad (4)$$

where $\mathbf{u}(i)$ is the displacement of atom i with respect to its equilibrium position, α and β are, respectively, central and non-central restoring force constants. The unitary vector $\hat{\mathbf{n}}_{ij}$ indicates the bond direction between atoms i and j.

If axis z is chosen along $\hat{\mathbf{n}}_{ij}$, the Born interaction matrix (ϕ) between nearest-neighbor atoms has a simple form,

$$\phi = - \begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix}. \quad (5)$$

However, ϕ should be expressed in coordinates of the solid, i.e., it is necessary to make proper rotations of ϕ. For tetrahedral structures, the four interaction matrices of ϕ can be written as

$$\phi_1 = -\frac{1}{3} \begin{pmatrix} \alpha + 2\beta & \alpha - \beta & \alpha - \beta \\ \alpha - \beta & \alpha + 2\beta & \alpha - \beta \\ \alpha - \beta & \alpha - \beta & \alpha + 2\beta \end{pmatrix}, \quad (6)$$

$$\phi_2 = -\frac{1}{3} \begin{pmatrix} \alpha + 2\beta & \alpha - \beta & \beta - \alpha \\ \alpha - \beta & \alpha + 2\beta & \beta - \alpha \\ \beta - \alpha & \beta - \alpha & \alpha + 2\beta \end{pmatrix}, \quad (7)$$

$$\phi_3 = -\frac{1}{3} \begin{pmatrix} \alpha + 2\beta & \beta - \alpha & \alpha - \beta \\ \beta - \alpha & \alpha + 2\beta & \beta - \alpha \\ \alpha - \beta & \beta - \alpha & \alpha + 2\beta \end{pmatrix} \quad (8)$$

and

$$\phi_4 = -\frac{1}{3} \begin{pmatrix} \alpha + 2\beta & \beta - \alpha & \beta - \alpha \\ \beta - \alpha & \alpha + 2\beta & \alpha - \beta \\ \beta - \alpha & \alpha - \beta & \alpha + 2\beta \end{pmatrix}. \quad (9)$$

These four interaction matrices ϕ_1, ϕ_2, ϕ_3, and ϕ_4 are indicated in the inset of Fig. 1(b). Due to the tetrahedral symmetry it is easy to prove that

$$\phi_s = \phi_1 + \phi_2 + \phi_3 + \phi_4 = -\frac{4}{3}(\alpha - \beta)I. \quad (10)$$

3. Results and discussion

The calculations were carried out by using the parameters $\alpha = 120.3\,\mathrm{N\,m^{-1}}$ and $\beta = 23.5\,\mathrm{N\,m^{-1}}$ [4]. In Fig. 1(a), the phonon band structure within the Born model (solid line) is compared with the experimental data (solid circles) [6]. The Raman response of crystalline silicon (c-Si) obtained from Eq. (1) is shown in Fig. 1(b). Notice that the Raman peak of c-Si is located at $\omega_0 = 519.3\,\mathrm{cm^{-1}}$ [7], which corresponds to the highest frequency of optical modes with null phonon wavevector, since the wavevector of the visible light is much smaller than the first Brillouin
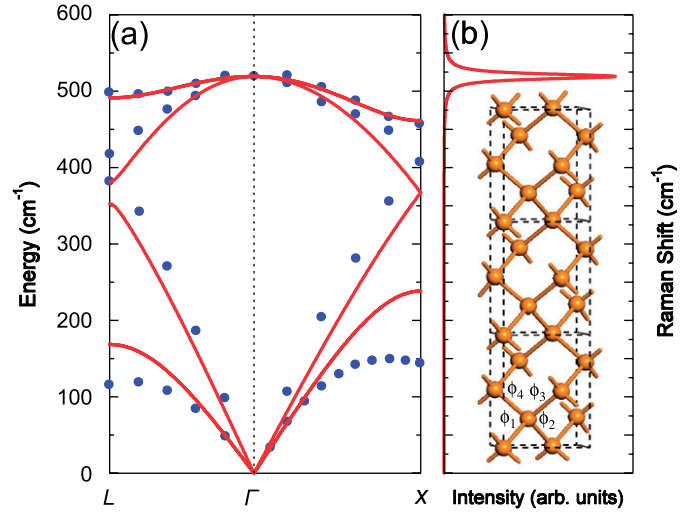

Fig. 1. (a) Calculated phonon band structure (solid line) compared with experimental data (solid circle). (b) Raman response of c-Si. Inset: A segment of the narrowest SiQW used in this article.
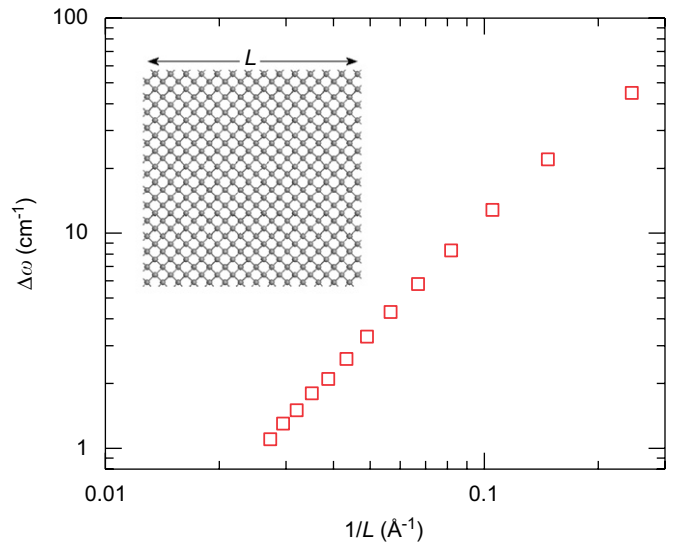

Fig. 2. The shift of the highest-frequency Raman peak ($\Delta\omega$) as a function of the inverse of SiQW width (L). Inset: The cross section of the widest SiQW analyzed in this paper.

zone and then the momentum conservation law only allows the participation of vibrational modes around the Γ point.

For modelling SiQW, we use a cubic supercell with side $a = 5.431\,\text{Å}$, containing eight Si atoms, and take the periodic boundary condition only along z-direction, i.e., free boundary conditions are applied in x and y directions, as shown in the inset of Fig. 1(b). For SiQW with bigger cross sections, Si atoms are added on $(1\,0\,0)$ and $(0\,1\,0)$ planes to obtain nanowires with larger width (L), conserving their square shapes. We have performed the calculation of the Raman response of supercells containing from 8 to 392 Si atoms. In Fig. 2, the shift of the main Raman response, $\Delta\omega \equiv \omega_0 - \omega_R(L)$, is plotted as a function of $1/L$, where $\omega_R(L)$ is the frequency of the main Raman peak
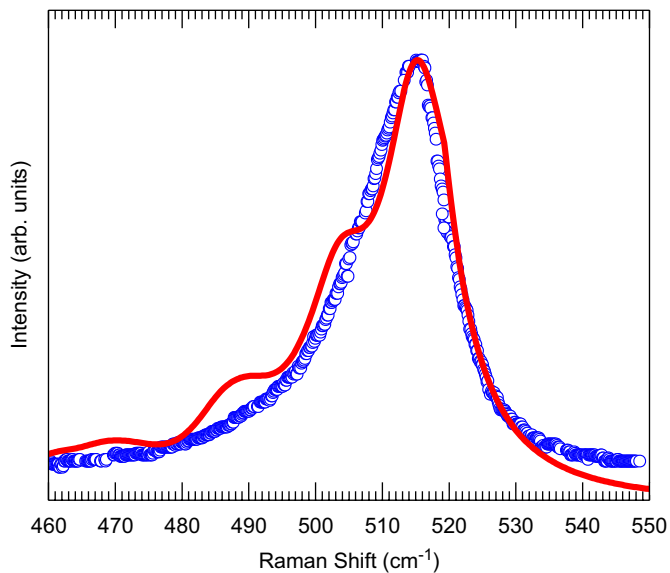
Fig. 3. Raman response of a SiQW with $L = 1.76$ nm (solid line) compared with experimental data (open circles) from Ref. [8].

obtained from a SiQW of width L. Observe that $\Delta\omega \sim L^{-v}$ with v being from 1.4 to 2.0, when $L \to \infty$. This result is in agreement with the effective mass theory, i.e., $2L$ is the longest wavelength in x and y directions accessible for a SiQW of width L, and then the highest phonon frequency of the system can be approximately determined by evaluating the frequency of optical mode at π/L.

In Fig. 3, the calculated Raman response spectrum of a SiQW with $L = 1.76$ nm is compared with the experimental one [8]. The theoretical results include an imaginary part of energy $\eta = 6\,\text{cm}^{-1}$ and an weight function of exp$(-|\omega - \omega_0|/20)$. The inclusion of this weight function is to preserve basic ideas of the momentum selection rule, since in principle only Γ-point or infinite-wavelength optical modes are active during the Raman scattering and for a SiQW there are only finite-wavelength modes in x and y directions. In other words, if the Raman selection rule is visualized as a δ-function at Γ-point, it should be broadened for finite-size systems due to the Heisenberg uncertainty principle, i.e., optical modes with a longer wavelength should have a larger participation in the Raman response.

4. Summary

We have presented a microscopic theory to model the Raman scattering in SiQW. This theory has the advantage of providing a direct relationship between the microscopic structures and the measurable physical quantities. The results show a clear quantum confinement effect on the highest-frequency Raman peaks and $\Delta\omega$ is quantitatively in good agreement with the effective mass theory. Regarding the broadening of Raman peaks, an imaginary part of energy $\eta = 6\,\text{cm}^{-1}$ was chosen to include inhomogenous diameters of SiQW, as well as laser heating effects [9]. The obtained average width $L = 1.76$ nm is smaller than $D = 4.5$ nm estimated in Ref. [8]. This difference could be due to the square form of SiQW considered, as well as the possible oxide layer at the surface of SiQW. This study can be extended to other low-dimensional semiconductors, such as nanotubes and porous materials.

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