Scaling relation for the size dependence of acoustic, dielectric and photoelectronic behaviour of nanosolid silicon

C. Q. Sun,* L. K. Pan and C. M. Li

School of Electrical and Electronic Engineering, Nanyang Technological University Singapore 639798

ABSTRACT

Structural miniaturization provides us with a new freedom that is indeed fascinating. The new freedom of size not only allows us to tune the physical and chemical properties of a specimen by simply adjusting the shape and size but also enables us to gain information that is beyond the scope of conventional approaches. Here we show that a recent bond order-length-strength (BOLS) correlation could reconcile the size effect on nanosolid silicon with elucidation of information such as the single energy level of an isolated Si atom, the frequency of Si-Si dimer vibration, the upper limit of photoabsorption/emission, and dielectric suppression.

Keywords: Photoemission, photoabsorption, porous silicon, dielectrics, acoustic phonons and optical phonons

1 INTRODUCTION

Considerable efforts have been made in recent years to the understanding of the size effect on the acoustic, dielectric, and photoelectronic properties of nanosolid silicon because of the significance of nanosemiconductors in nanoelectronic devices. Among numerous theories that have been developed to explain the size effect such as the size induced blue shift in photoluminescence (PL) and photoabsorption (PA) as well as the phonon softening and phonon hardening, the “quantum confinement” theory is elegantly accepted [1]. However, without triggering the dominating factors in quantum confinement theory, electron-phonon (e-p) interaction or electron-hole (e-h) production, scanning tunneling spectroscopy/microscopy measurement revealed that the band gap expands from 1.1 to 3.5 eV when the Si nanorod diameter reduces from 7.0 to 1.3 nm associated with Si-Si bond length contraction of 10% [2]. This finding challenges the validity of the quantum confinement. Furthermore, all the size induced property changes arise from the same origin, therefore a model that unifies all the available data and provides consistent insight into the effect of size is desirable. Recently, we developed a bond order-length-strength (BOLS) correlation mechanism that is able to fulfill this task.

2 PRINCIPLE

The BOLS correlation indicates that the coordination (CN) imperfection of an atom at site surrounding a defect or near the surface edge causes the remaining bonds of the lower-coordinated atom to contract spontaneously. The spontaneous bond contraction is associated with bond-strength gain or atomic potential well deepening, which localize electrons and enhance the density of charge, mass, and energy in the relaxed region. The enhancement of energy density in the relaxed region perturbs the Hamiltonian and the associated properties such as the band gap width [3], core-level energy [4], Stokes shift (electron-phonon interaction), and dielectric susceptibility [5]. On the other hand, bond-order loss lowers generally the cohesive energy of the lower-coordinated atom from the value of an atom with full CN, which dictates the thermodynamic process such as self-assembly growth, atomic vibration, thermal stability, and activation energies for atomic dislocation and diffusion [6].

Generally, the mean relative change of a measurable quantity of a nanosolid containing \( N_j \) atoms, with the dimensionless form of size \( K_j \), being the number of atoms lined along the radius of a sphere or cross a thin plate, can be expressed as \( \frac{Q(K_j)}{Q(f)} \), for the same solid without CN-imperfection contribution. The \( Q(K_j) \) relates to \( Q(f) = Nq_0 \) as follows:

\[
Q(K_j) = (N_j - N_s)q_0 + N_s q_s = N_j q_0 + N_s (q_s - q_0)
\]

(1)

The \( q_0 \) and \( q_s \) correspond to the local density of \( Q \) inside the bulk and in the surface region, respectively. \( N_s = \sum N_i \) is the number of atoms in the surface atomic shells. Eq (1) leads to the immediate scaling relation:

\[
\frac{\Delta Q(K_j)}{Q(\infty)} = \frac{Q(K_j) - Q(\infty)}{Q(\infty)} = \frac{N_s}{N_j} \left( \frac{q_s}{q_0} - 1 \right)
\]

\[
= \sum_{i < 3} \gamma_i \left( \Delta q_i / q_0 \right) = \Delta q_j
\]

(2)
The weighting factor, \( \gamma \), represents the geometrical contributions from the size and dimensionality of the solid, which determines the magnitude of change. The quantity \( \Delta q/q_0 \) originates the change. The \( \Delta q_i/j \) drops in a \( K_j^{-1} \) fashion from unity to infinitely small when the solid dimension grows from atomic level to infinitely large. For a spherical dot at the lower end of the size limit, \( \gamma_1 = 1, \gamma_2 = \gamma_3 = 0, \) and \( z_1 = 2. \)

It is interesting to note that measurement of size dependence often follows a scaling law:

\[
Q(K_j) = \begin{cases} 
 bK_j^{-1} & \text{(measured)} \\
 Q(\infty) \times \Delta q_j & \text{(theory)}
\end{cases}
\]

Given a functional dependence of the known quantities on bond length, bond strength, and bond nature, it is possible to predict the size dependence of the quantities.

### 3 EXPERIMENT

We prepared the p-Si samples and measured the size dependence of the PL, PA and \( E_{2p} \) peak energies. The particle size was controlled by varying the current density and estimated by matching the measured \( E_{PL} \) to the theory curve that has matched numerous sets of PL data of p-Si, CdS and CdSe nanosolids. XPS, impedance, and Raman measurements were conducted at room temperature.

### 4 RESULTS AND DISCUSSIONS

Calculations were performed with the following relations [7,8]:

\[
\begin{align*}
\frac{\Delta E_{PL}(K_j)}{E_{PL}(\infty)} &= \frac{\Delta E_{G}(K_j) \mp \Delta W(K_j)}{E_{G}(\infty) \mp W(\infty)} \\
\frac{\Delta E_{PA}(K_j)}{E_{PA}(\infty)} &= \sum_{i,j} \gamma_i \left( c_i^{-m} - 1 \right) \mp B(c_i^{-2} - 1)
\end{align*}
\]

\[
\begin{align*}
B &= \frac{A}{E_{G}(\infty)\bar{r}^2}; \quad W(\infty) \approx 0.007, \quad E_{G}(\infty) \approx 1.12, \quad \approx 0 \\
\Delta_H &= \sum_{i,j} \gamma_i \left( c_i^{-m} - 1 \right) \\
\Delta_{e-p} &= \sum_{i,j} \gamma_i \left( c_i^{-2} - 1 \right)
\end{align*}
\]

where \( \Delta_H, \Delta_{e-p}, \) and \( \Delta_{ph} \) correspond to the perturbation of Hamiltonain, electron-phonon coupling and phonon frequency due to the BOLS correlation.

![Figure 1 Agreement between BOLS predictions and observation on (a) acoustic phonon hardening, (b) optical phonon softening of nanosolid Si.](image_url)

Figs 1-3 compare the BOLS predictions with the currently measured data and literature resourced data.
Agreement has been reached for the considered properties, indicating that the size induced property change arise from the lower-coordinated atoms in the surface skin.

![Figure 2](image)

**Figure 2** Agreement between BOLS predictions and observation on the size dependence of (a) blue shift in photoluminescence and photoabsorption, (b) band gap expansion of nano-Si.

![Figure 3](image)

**Figure 3** Agreement between BOLS predictions and observation on (a) 2p core-level shift and, (b) dielectric suppression of nanosolid silicon. The index m = 4.88 represents the covalent nature of Si-Si bond.

## 5 CONCLUSION

Consistency between predictions and observations evidences the enormous impact of atomic CN imperfection to the low-dimensional systems and the validity, universality, and essentiality of the original BOLS correlation.

## REFERENCES


