Elucidating Si—Si Dimmer Vibration from the Size-Dependent Raman Shift of Nanosolid Si

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It has been surprising that with the solid size reduction, the transverse optical (TO) Raman mode shifts to lower frequency and new low-frequency Raman (LFR) acoustic modes are generated and shift to higher frequency upon nanosolid Si formation. Understanding the mechanism behind the TO red shift and the LFR creation and blue shift has long been a challenge. On the basis of the BOLS correlation [Sun et al. J. Phys. Chem. B 2002, 106, 10701], here we show that the TO red shift arises from the cohesive bond weakening of the lower coordinated atoms near the surface region of the nanograins, and the LFR arises from intergrain interaction. Strikingly, simulating the TO peak shift confirms the assumption, originated by Shi and Jiang, that the magnitude of surface atomic vibration is always higher than the bulk value and remains constant at particle size greater than 1 nm. Practice also provides a way for elucidating information of an isolated Si—Si dimer vibration.

Vibration of atoms at a Si surface is of increasing interest because the behavior of phonons has direct influence on the electrical and optical properties in semiconductor nanosolids, such as electron—phonon coupling, photoabsorption, and photomission.1 The frequency of transverse optical (TO) phonon undergoes a red shift2 whereas the low-frequency Raman (LFR) data. For the TO red shift (corresponding to wavelength of \( \lambda \))

\[ \omega(R) = \omega(\infty) + A(a/R)^{\kappa} \]  

(1)

where \( A \) and \( \kappa \) are adjustable parameters used to fit the measured data. For the TO red shift, \( A < 0 \) and \( \omega(\infty) = 520 \text{ cm}^{-1} \) (corresponding to wavelength of \( 2 \times 10^4 \text{ nm} \)). The \( \kappa \) varies from 1.08 to 1.44 and 2.0.14 The \( a \) is the lattice parameter that contracts with the solid dimension.15 For LFR blue shift, \( A > 0 \), \( \kappa = 1 \), and \( \omega(\infty) = 0 \). Therefore, the LFR results from nanosolid formation. The currently available models for the TO red shift are based on assumptions that the materials are homogeneous and isotropic, which is valid only in the long-wavelength limit. When the size of the nanosolid is in the range of a few nanometers, the continuum dielectric models are intrinsically limited. Therefore, the existing models could hardly reproduce satisfactorily the Raman frequency shifts near the lower end of the size limit though they contribute to the understanding from various perspective. Therefore, deeper insight into the physical origin of the blue and red shift is desirable.

Raman scattering is known to arise from the radiating dipole moment induced in a system by the electric field of incident electromagnetic radiation. The laws of momentum and energy conservation govern the interaction between a phonon and a photon. The total energy \( E \) due to the lattice vibration consists of the component of short-range interactions \( E_S \) and the component of long-range Coulomb interaction \( E_C \).

\[ E = E_S + E_C \]  

(2)

The short-range interaction corresponds to the TO mode, which describes the covalent bonding and thus is correlated to bond energy \( E_b \), bond length \( d \), and the coordination number (CN, or \( z \)). The long-range part corresponds to the LFR mode and represents the weak interaction between nanosolids.

Figure 1 shows the least-squares fitting of the size dependent LFR frequency for the nanosolid silicon. The LFR frequency depends linearly on the inverse \( R \). The zero intercept at the vertical axis indicates that when \( R \) increases toward infinity, the LFR peaks disappear, which implies that not only the blue shift in the LFR peaks but also the origin for the LFR peaks are purely intergrain vibrations that produce acoustic phonons. The slope values are 97.77, 45.57, and 33.78 for the \( 3404, 3406, \) and \( 3408 \) crystal plane, respectively.

For the Raman TO mode, the energy due to short-range interaction of a single pairwise bond can be expressed in a
Taylor’s series

\[ E_S = \sum_{n=0}^{\infty} \left( \frac{d^n u(r)}{n! dr^n} \right) (r - d)^n \]

When the atom is in the equilibrium position, the bond energy is \( u(d) = E_b \). The third term is the vibration energy of a single bond due to the short-range interaction, in which the force constant \( k = \frac{d^2 u(r) dr^2}{dr^2} \) and the vibration amplitude \( x = r - d \). For a single bond, the \( k \) is strengthened but for a single lower coordinated atom, the resultant \( k \) could be lower. Because the short-range interaction on each atom results from its neighboring coordinating atoms, the atomic vibrating displacement is the contribution from all the surrounding coordinates, \( z \). Considering the vibration amplitude \( x \ll d \), it is reasonable to take the mean contribution from each coordinate as a first-order approximation, i.e., \( k_1 = k_2 = \ldots = k_i = \mu_S(c\omega)^2 \), and \( x_1 = x_2 = \ldots = x_i = (r - d)/z_i \). Therefore, the energy due to short-range interaction of a certain atom with \( z \) coordinates follows:

\[ E_S = \sum_{i} \left[ -E_b + \frac{1}{2} \mu_S c^2 z_i \omega^2 \left( \frac{r - d}{z} \right)^2 + \ldots \right] \]

\[ = -zE_b + \frac{1}{2} \mu_S c^2 z_i \omega^2 (r - d)^2 + \ldots \]  

where \( \mu_S = m_S/2 = 2.34 \times 10^{-26} \text{ kg} \) is the reduced mass of a Si–Si dimer and \( c \) is the speed of light. Equilibrating (4) to (3) times \( z \), we have the phonon frequency (wavenumber, \( \omega \)) as follows:

\[ \omega = \frac{1}{c} \left[ \frac{z}{\mu_S} \frac{d^2 u(r)}{dr^2} \right]^{1/2} = \frac{z(E_b)}{d} \]  

A recent bond-order-length-strength (BOLS) correlation mechanism\(^{16-18}\) indicates that the CN imperfection causes the remaining bonds of the lower-coordinated atoms to contract spontaneously \((d_i = c_d)\) associated with bond strength enhancement \((E_j = c_i - E_b)\). Such an event and its consequence modify not only the atomic cohesive energy (atomic CN multiplies the single bond energy) but also the binding energy density in the relaxed region. The former contributes to the Gibbs free energy that dictates all the thermodynamic behavior of the considered solid such as critical temperature for phase transition, liquidization, and evaporation\(^{18}\), the latter, to the Hamiltonian that dictates the entire energy band structures such as the band gap,\(^{17}\) core-level shift,\(^{16,19}\) and the mechanical strength\(^{20}\) of the system. A physically detectable quantity for a nanosolid can be expressed as \( Q(R) \), and as \( Q(\infty) = Nq_0 \) for a bulk solid. The relation between \( Q(R) \) and \( Q(\infty) \) and the relative change of \( Q \) can be expressed in a shell structure:

\[ \frac{Q(R)}{Q(\infty)} = \frac{Nq_0 + N_2(q - q_0)}{q_0 - 1} \]  

where \( q_0 \) and \( q_\infty \) correspond to the \( Q \) value per atomic volume inside the bulk and in the surface region, respectively, \( N_2 = \Sigma N_i \) is the number of atoms in the surface atomic shells. Combining eqs 5 and 6 give the size-dependent TO red shift:

\[ \frac{\omega(R) - \omega(\infty)}{\omega(\infty) - \omega(1)} = \sum_{i=3}^{\infty} \gamma_i \left( \frac{q_i}{q_0} - 1 \right) = \delta_p < 0 \]  

where\(^{15}\)

\[ \gamma_i = \frac{N_i}{N} = \frac{V_i}{V} \approx \frac{c_i}{K} \]

\[ c_i = 2(1 + \exp[(12 - z_3)/8z_3]) \]

\[ z_3 = 4(1 - 0.75/K) \]

\[ m = 4.88, \ z_2 = 6, \ \text{and} \ z_3 = 12 \]  

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Hence, the frequency shift from the dimer bond vibration to the bulk value, \( \omega(\infty) - \omega(1) \), is a constant as \( \delta_p \propto R^{-1} \). Excitingly, this allows us to determine the vibrational frequency of a Si–Si dimer bond \( \omega(1) = 502.3 \text{ cm}^{-1} \) and the bulk shift of 17.7 cm\(^{-1}\), which is beyond the scope of currently available approaches. Figure 2 shows the match between the BOLS predictions with the theoretically calculated and the experimentally measured TO red shift of nanosolid silicon.
In summary, the BOLS correlation has enabled us to correlate the size-created and the size-induced blue shift in the LFR phonon frequency to the intergrain interaction and the red shift in the TO phonon frequency to the atomic CN imperfection reduced atomic cohesive energy. Decoding the Raman red shift leads to quantitative information about the vibration frequency of a Si–Si dimer bond (502.3 cm$^{-1}$) at room temperature and the confirmation of surface atomic dislocation.

References and Notes


According to Einstein’s relation: $z\mu_{b}(\omega_{b})^{2}/2 = k_{B}T$ ($k_{B}$ is the Boltzmann constant and $T$ is the temperature), the vibrational amplitude of an atom is $x \propto z^{1/2}\omega^{-1}$. The reduced magnitude and frequency of an atom in the surface at room temperature are

$$\frac{x_{1}}{x_{b}} = \frac{(z_{b}/z_{1})^{1/2} \omega_{b}/\omega_{1} = (z_{b}/z_{1})^{1/2} c_{1}^{(m2)+1}}{\sqrt{3} \times 0.88^{3.44} = 1.09 \ (Si, m = 4.88)}$$

$$\frac{(z_{b}/z_{1})^{1/2} \omega_{b}/\omega_{1} = (z_{b}/z_{1})^{1/2} c_{1}^{(m2)+1}}{\sqrt{3} \times 0.88^{1.5} = 1.43 \ (metal, m = 1)} \ (10)$$

As the $z_{1}$ change slightly with the curvature of the surface, see eq 8, the vibrational amplitude of an atom at the surface stays almost constant at $K > 3$. This confirms for the first time the assumption originated by Shi21 and Jiang et al.22 that the vibrational amplitude of a surface atom is higher than the bulk value and keeps constant at all particle sizes. It can also be estimated that the frequency of a Si surface atom (with $z = 4$) is around 511 cm$^{-1}$, which is between that of the dimmer (502.3 cm$^{-1}$) and the bulk (520.0 cm$^{-1}$).