Nanocrystals

# Low-Frequency Raman Scattering from Nanocrystals Caused by Coherent Excitation of Phonons\*\*

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Since the first observation of surface acoustic modes from silicon nanocrystals (NCs) embedded in silica by Duval et al.<sup>[1]</sup> low-frequency Raman scattering from NCs has become an important research area in many fields including semiconductor technologies, medical therapeutics, and biophysics.<sup>[2-18]</sup> Recent research has indicated that low-frequency Raman spectroscopy is a feasible non-destructive technique for investigating virus functionalization, for example, introducing viruses on different materials, attaching viruses to quantum dots and carbon nanotubes, and forming multiple superstructures.<sup>[5,6,17]</sup> These superstructures are expected to have important applications in biological science and medicine. However, the current assignment of the low-frequency Raman modes is based on Lamb's theory that mainly focuses on the mode frequencies of an elastic vibration of a free isotropic sphere.<sup>[19]</sup> Many studies have demonstrated that the surface acoustic-mode frequencies observed from free NCs and NCembedded matrix systems are consistent with the theoretical prediction. This is understandable because a large number of frequency values can be selected to match the experimental results. At the same time, other studies have unequivocally

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[\*\*] The authors thank Dong Tang from FEI Company in Eindhoven (The Netherlands) for valuable discussions and technical help with UHRTEM imaging. This work was jointly supported by grants from the Natural Science Foundations (Nos. 60876058, 60976003, 10874071, and BK2008020). Partial support was from the National Basic Research Programs of China (Nos. 2006CB300404 and 2007CB936300) and the National High-Tec Research and Development Program of China (No. 2007AA04Z301). demonstrated that the observed frequencies are lower than the theoretically predicted ones.<sup>[4,12]</sup>

In order to explain the inconsistency, Murray and Saviot<sup>[8]</sup> have presented a complex-frequency model within the framework of Lamb's theory. By considering the effect of an infinite matrix on the NC vibrations they fit the observed frequencies, but the calculated damping (full width at half maximum; FWHM) is evidently larger than the experimental data. A coreshell-matrix model has also been suggested to improve the calculation,<sup>[20]</sup> but the results indicate that the introduction of a thin shell layer with acoustic impedance between the NCs and matrix cannot effectively reduce the damping in the modes.<sup>[15,18]</sup> Further analyses reveal that if a softer interface with acoustic impedance smaller than those of the NCs and matrix exists as a shell layer, as suggested in our previous work,<sup>[18]</sup> the calculated FWHMs are smaller and match the experiment better. Unfortunately, it is rather difficult to probe such a thin interface, thereby hampering better understanding of the origin and narrow FWHMs<sup>[2,3,10,11]</sup> of the low-frequency Raman modes that have been observed from many NCembedded systems such as Ge and GeSi NC-embedded SiO<sub>2</sub>.<sup>[15,18]</sup> In metal-NC-embedded systems, this situation becomes more obvious due to possible interactions between NC surface plasma and acoustic phonons.<sup>[21-23]</sup> In the silver NC-embedded amorphous SiO<sub>2</sub> films, Duval et al.<sup>[24]</sup> have experimentally and theoretically shown that the degree of spatial coherence inside the NCs has a strong effect on the intensity and frequency of the low-frequency Raman vibration mode. Recently, a spatial coherence effect has further been investigated in the supracrystalline arrangement of metallic silver NCs using a classical theory.<sup>[25–27]</sup> It is shown that the coherence effect will also reduce the linewidth of the lowfrequency Raman mode. This implies that Lamb's theory may not be sufficient in explaining the low-frequency Raman spectra. More factors and physical processes must be considered to explain the observed low-frequency Raman spectra acquired from semiconductor NCs randomly embedded in a matrix.

In this work, we investigate this phenomenon in  $Ge_{0.54}Si_{0.46}$ NC-embedded  $SiO_2$ .<sup>[18]</sup> Ultrahigh-resolution transmission electron microscopy (UHRTEM) conducted at the interface between the  $Ge_{0.54}Si_{0.46}$  NCs and  $SiO_2$  does not reveal a disordered or softer interface with acoustic impedance smaller than that of either the NCs or matrix. The anomalous temperature-dependent Raman scattering phenomenon reported here rules out the possibility that the observed phonon modes stems only from elastic continuum vibration.

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**Figure 1.** a) TypicalTEM image acquired from a Ge<sub>054</sub>Si<sub>0.46</sub> NC-embedded amorphous SiO<sub>2</sub> film prepared by radio-frequency magnetron co-sputtering at  $T_a = 1100$  °C. b,c) UHRTEM images of NCs 1 and 2 in (a) with sizes of 3.8 and 2.3 nm, respectively. No interface can be observed between the NCs from the two images.

We then propose a theory that uses the collective modes comprising coherent excitation of phonons of a large number of NCs to explain the narrow FWHMs as well as anomalous temperature dependence of the Raman intensity.

Figure 1a depicts a typical UHRTEM image of the  $Ge_{0.54}Si_{0.46}$  NC-embedded SiO<sub>2</sub> film after annealing at  $T_a$  of 1100 °C. The amorphous SiO2 matrix and lattice fringes from the NCs can be clearly observed. Figure 1b and c shows the UHRTEM images of NCs 1 and 2 with sizes of 3.8 and 2.3 nm, respectively. Both NCs have sharp boundaries with the amorphous matrix with the absence of a thin ordered shell layer between the NCs and matrix. In the previous investigation on the interface structure by energy-dispersive X-ray composition microanalysis,<sup>[18]</sup> we have shown that the interface regions of the NCs have no noticeable element deficiencies. The interface layer has compositions between those of the alloy NC and SiO<sub>2</sub> matrix. Similar results have also been observed on the surfaces of Ge NCs embedded in SiO<sub>2</sub> matrix.<sup>[28]</sup> This result in conjunction with our current observation indicates that a disordered interface layer with an acoustic impedance smaller than those of the NCs and matrix does not exist. The above observation unequivocally discloses that the very small damping observed in the low-frequency acoustic mode cannot arise from a softer or disordered interface.<sup>[18]</sup>

To further investigate the low-frequency vibration modes, we examine the temperature-dependent Raman spectra and two typical results obtained from the samples prepared at  $T_a = 1000$  and 1100 °C are displayed in Figure 2a and b, respectively. With increasing measurement temperature from 77 to 300 K, the location and peak shape of the low-frequency Raman mode are relatively unchanged (the peak-position shift is smaller than  $0.5 \text{ cm}^{-1}$ ), but the intensity undergoes an obvious increases. In fact, this phenomenon can be observed from all the samples processed at different  $T_a$ s. The result is compared to the 521 cm<sup>-1</sup> transverse optical (TO) mode of the silicon substrate acquired simultaneously, as shown in Figure 2c. Intensity reduction and simultaneous red-shift



**Figure 2.** Temperature-dependent low-frequency Raman spectra of the Ge<sub>054</sub>Si<sub>0.46</sub> NC-embedded amorphous SiO<sub>2</sub> films produced at different temperatures: a)  $T_a = 1000$  °C and b) 1100 °C. For comparison, the Raman spectra of the Si substrate 521 cm<sup>-1</sup> TO mode acquired simultaneously is displayed (c).

 $(>4 \text{ cm}^{-1})$  can clearly be observed from the 521 cm<sup>-1</sup> mode with increasing measurement temperature. This phenomenon can be attributed to the effects of thermal expansion and anharmonic coupling to other phonons.<sup>[29–31]</sup> The behavior of the low-frequency mode is contrary to that of the 521 cm<sup>-1</sup> Si TO mode. If we consider that the low-frequency mode stems only from the vibration of free elastic spheres, a higher measurement temperature will expand the lattice. This corresponds to larger NCs resulting in a red-shift of the mode frequency according to Lamb's theory. Meanwhile, the intensity should decrease, as in the 521 cm<sup>-1</sup> Si TO mode, and so this anomalous behavior needs to be clarified.

In a system containing a large number of NCs, the collective phonon modes that encompass all the irradiated NCs should have large contributions to the Raman spectra. To see how such collective modes are stimulated, we consider the following Hamiltonian in the secondary-quantization form:

$$H_0 = \sum_i \Omega a_i^{\dagger} a_i + \sum_i X^{\dagger} X(g_i a_i^{\dagger} + g_i^* a_i)$$
<sup>(1)</sup>

where  $a_i$  is the annihilation operator of the phonon in the mode bound to the *i*th NC that is Raman-active to the radiation field expressed by photon operator X,  $\Omega_i$  is the phonon energy of the mode in the *i*th NC, and  $g_i$  is the coupling strength of this mode to the radiation field. For simplicity, we suppose that all the energies of the NC modes are the same, that is,  $\Omega_i = \Omega_0$  for all *i* (the conclusion can be extended to the more general case with random  $\Omega_i$ s). To the first order of Raman scattering strength  $g_i$ , the resultant wavefunction due to Raman scattering in  $H_0$  can be expressed as

$$\Phi_0\rangle = X^{\dagger}|\{n_i\}\rangle + \frac{1}{A}\psi_0^{\dagger}X^{\dagger}|\{n_i\}\rangle$$
<sup>(2)</sup>

where  $|\{n_i\}\rangle$  is the state before Raman scattering in which there are  $n_i$  phonons in the *i*th NC mode for *i* over all the NCs and

$$\psi_0^{\dagger} = A \sum_i g_i \sqrt{n_i + 1} a_i^{\dagger} \tag{3}$$

with

$$A = \left(\sum_{i} g_{i}^{2}(n_{i}+1)\right)^{-\frac{1}{2}}$$
(4)

being the renormalization factor. We note that although the radiation is a plane wave that has different phases at the NCs randomly distributed in space, these phases do not appear in coupling strengths  $g_i$  because of the Raman-active couplings in  $H_0$  that have quadratic factor  $X^{\dagger}X$  for the radiation leading to the cancelation of the random phases in the plane wave. This means that the components stimulated by Raman scattering in wavefunction  $|\Phi_0\rangle$  are in quantum coherence. Hence, Raman scattering produces "collective" modes<sup>[32]</sup> that encompass all the modes bound to the NCs in the radiation area rather than to individual NC modes.

Broadening of the Raman resonance peaks for the NC modes is due to coupling between the bulk phonon modes of the matrix. Owing to the absence of a soft interface between the NCs and matrix, the broadening effect is certainly strong, leading to large linewidth in the spectrum. This situation, however, can be drastically changed if the relevant NC modes are collective ones with coherent components in all the NCs within the irradiated area. The coupling of NC modes to the matrix bulk phonons are linear terms of the displacements as described in the following secondary quantization form:

$$H_1 = \sum_m \omega_m b_m^{\dagger} b_m + \sum_{m,i} \left( \lambda_{m,i} a_i^{\dagger} b_m + \lambda_{m,i}^* b_m^{\dagger} a_i \right)$$
(5)

Where  $b_m$  is the annihilation operator of phonons in the *m*th bulk mode,  $\omega_m$  is its energy, and  $\lambda_{m,i}$  is the coupling strength between the *m*th bulk mode and *i*th NC mode. The bulk modes are also plane waves in the matrix that have phases at the NCs depending on the positions of the NCs. Since the positions of the NCs are random, the phases of a bulk wave *m* at different NCs are also random. These random phases correspond to the phases of coupling strengths  $\lambda_{m,i}$  since coupling just occurs between the plane waves of the bulk phonons and local modes bound to the NCs. In the collective mode  $\psi_0$  stimulated by Raman scattering, the random phases in the coupling with the bulk phonon modes may significantly reduce the effective broadening of the resonance peak due to destructive interference.

The Raman spectrum can be calculated with the phonon Green function.<sup>[33]</sup> For  $\psi_0$ , the imaginary part of the self energy due to coupling with the bulk phonons can be calculated as

$$\Gamma_0(\omega) = \pi A^2 \sum_m \left| \sum_i \lambda_{m,i} g_i \sqrt{n_i + 1} \right|^2 \delta(\omega - \omega_m)$$
(6)

Therefore, the Raman spectrum can be expressed as

$$I(\omega) = \frac{\sum_{m} \left|\sum_{i} g_{i} \sqrt{n_{i} + 1}\right|^{2} \delta(\omega - \omega_{m})}{(\omega - \Omega_{0})^{2} + \pi^{2} A^{4} \left(\sum_{m} \left|\sum_{i} \lambda_{m,i} g_{i} \sqrt{n_{i} + 1}\right|^{2} \delta(\omega - \omega_{m})\right)^{2}}$$
(7)

where  $\omega$  is the Raman shift energy. Here  $n_i$  is the phonon number in the *i*th NC mode and so it is temperature-dependent if  $\Omega_0$  is comparable to the thermal energy  $k_B T$ , where  $k_B$  is Boltzmann's constant and T is the temperature. If we adopt the thermal distribution for the NC modes, we have

$$n_i \equiv n_T = \frac{1}{\exp\left(\frac{\Omega_0}{k_B T}\right) - 1} \tag{8}$$

This leads to the temperature-dependence of the intensity but has almost no effect on the linewidth. Furthermore, we note that if the arguments of  $\lambda_{m,i}$  are randomly distributed over a range of  $[-\alpha,\alpha]$  according to a uniform probability and  $\alpha$ approaching  $\pi$ , the linewidth will be greatly reduced by the destructive interference effect. We suppose that if  $|\lambda_{m,i}| = \lambda_0$ ,  $g_i = g_0$ , and the bulk modes are uniformly distributed in the investigated range with a constant mode density  $\rho_0$ , the spectrum can be calculated as

$$I(\omega) = \frac{M^2 g_0^2 \rho_0(n_T + 1)}{(\omega - \Omega_0)^2 + \pi^2 \rho_0^2 \lambda_0^4 M^2 \left(\frac{\sin \alpha}{\alpha}\right)^4}$$
(9)

Here, *M* is the number of NC modes in the collective modes. If the average wavelength of the bulk modes is *l*, one has  $\alpha \approx \pi D/l$  with *D* being the size of the area involved. In Figure 3a, we plot



**Figure 3.** a) Calculated intensity as a function of shift energy for different values of  $\alpha$ . M = 500,  $\rho_0 = 1000 \text{ eV}^{-1}$ ,  $k_{\text{B}} T = 15 \text{ meV}$ ,  $g_0 = 1 \text{ meV}$ ,  $\Omega_0 = 3 \text{ meV}$ , and  $\lambda_0 = 0.5 \text{ meV}$ . b) Calculated intensity as a function of shift energy for different values of  $k_{\text{B}} T$ .  $\alpha = 40$ . Other parameters are the same as those in (a).

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the calculated spectra for different values of  $\alpha$ . By increasing  $\alpha$ , that is, increasing the area of the collective modes, the linewidth rapidly decreases due to destructive interference. In fact, the radiation spot in the experiment includes many wavelengths of bulk vibrations, and so the peak narrowing can be naturally explained. As shown in the calculated spectra at different temperatures in Figure 3b, the increase in the intensity with temperature agrees well with experimental data.

In conclusion, by carefully examining the interface structure between the representative  $Ge_xSi_{1-x}$  NCs and  $SiO_2$  matrix and the temperature-dependent low-frequency Raman scattering, we have experimentally verified that Lamb's theory cannot adequately explain the low-frequency Raman spectra obtained from the NC-embedded matrix systems. We propose a new mechanism based on the destructive interference effect and the theoretical results are in good agreement with experimental ones. Our results provide the important theoretical basis to expedite the applications of NC materials in many fields including nanotechnology, biomedical engineering, and medicine.

#### **Experimental Section**

Ge<sub>x</sub>Si<sub>1-x</sub> alloy NCs were embedded in amorphous SiO<sub>2</sub> films deposited on Si (100) substrates. The details of the experimental conditions can be found elsewhere.<sup>[18]</sup> To identify the interface structure, UHRTEM images were obtained in a spherical aberration-corrected TEM (FEI Titan 80-300 TEM), which is capable of imaging structures with sub-Angstrom resolution ( $\leq$ 0.08 nm) at an accelerating voltage of 300 kV. The temperature-dependent Raman spectra without polarization were acquired in the temperature range of 77 to 300 K on a T64000 triple Raman system with a back-scattering geometry using the 514.5 nm line of an Ar<sup>+</sup> laser as the excitation source. The diameter of the beam spot is  $\approx$ 1  $\mu$ m. During the measurements the samples were kept in vacuum to avoid excessive sample degradation due to laser irradiation. All the spectra were corrected for the response of the measurement system.

### Keywords:

coherent excitation  $\cdot$  nanocrystals  $\cdot$  raman spectroscopy  $\cdot$  surface vibrations

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