

## Raman properties of silicon nanoparticles

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Available online 24 January 2006

### Abstract

The Raman spectra of silicon nanoparticles in the size range between  $d = 3.5\text{--}60\text{ nm}$  have been studied experimentally. Scattering processes up to second order are being observed. The experimental results are analyzed in the framework of the phonon confinement model. While this model describes qualitatively the observations for first-order scattering processes, it is not applicable for scattering processes of higher order. From the analysis of second-order scattering, we determine a redshift of the TO phonon at the X and L points. © 2006 Elsevier B.V. All rights reserved.

PACS: 63.22.+m; 78.40.Fy; 63.20.-e

Keywords: Raman; Silicon; Nanoparticles; Phonon confinement

### 1. Introduction

Silicon nanoparticles have gained much attention as potential low-cost emitters for optoelectronics. Especially, the recent demonstration of electrical injection [1] and optical gain [2] makes this material system interesting. As silicon is an indirect semiconductor, the role of phonons for photoluminescence is of significant relevance. However, the vibrational properties of silicon nanoparticles are strongly altered due to the nanoscopic dimensions. This is usually explained in the picture of the phonon confinement effect [3]. While this model seems to be of some value to qualitatively assess the Raman scattering in first-order processes, it is difficult to use for scattering processes of higher order.

In this paper, we have systematically investigated the Raman properties of silicon nanoparticles in the size range of  $d = 3.5\text{--}60\text{ nm}$ . Especially, we have been able to measure higher order scattering processes to gain information on the phonon dispersion off the  $\Gamma$ -point. The observed shifts cannot be fully understood in the phenomenological

phonon confinement picture, but require a more detailed microscopic analysis.

### 2. Experimental details

The silicon nanoparticles have been produced in a low pressure microwave (2.4 GHz) plasma using  $\text{SiH}_4$  as a precursor. The benefit of this technique is its relative simplicity and its scalability which allows it to deliver macroscopic amounts of nanoscopic material. More details on the fabrication can be found elsewhere [4]. Samples with diameters in the range of  $d = 3.5\text{--}60\text{ nm}$  have been fabricated. The particle diameter was determined using the Brunauer–Emmet–Teller (BET) method [5]. A transmission electron micrograph is shown in Fig. 1. It can be seen that the particles are isolated and spherical in shape. For broad size distributions, TEM tends to overestimate the particle diameter, as small particles have much lower contrast than large particles. In the inset, the electron beam diffraction pattern for the sample is shown. An analysis of this pattern reveals that the particles are single crystal, with diamond structure and the same lattice constant as bulk silicon. In infrared transmission spectroscopy [6], we found that these particles are covered by a thin layer of  $\text{SiO}_x$ , with an oxygen mole fraction around  $x = 1.5$ .

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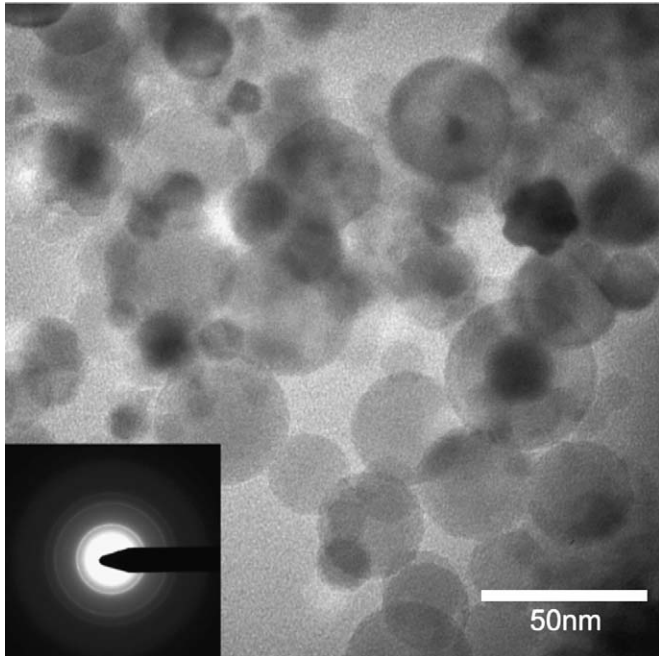


Fig. 1. Transmission electron micrograph of silicon nanoparticles.

Raman spectra have been recorded at room temperature using a triple-stage Raman spectrometer with a focal length of  $f = 550$  mm in subtractive mode. The data were collected using a CCD camera. As an excitation source, the  $5145 \text{ \AA}$  line of an  $\text{Ar}^+$ -ion laser was used.

### 3. Results and discussion

#### 3.1. First-order scattering

In a bulk crystal, the first-order Raman scattering probes the optical phonon frequency at the  $\Gamma$ -point in the Brillouin-zone due to the  $\Delta k = 0$  selection rule. As the geometrical extension of the crystal is reduced, this selection rule is lifted, and the frequency distribution of the scattered light is composed from a broader interval in  $k$ -space around  $\Gamma$ . The resulting Raman signal is determined by a weighted integral over  $k$  in the first Brillouin zone. Thus, the frequencies near the  $\Gamma$ -point will have the strongest contribution. This is the usual interpretation of the phonon confinement effect [3]. Therefore, it can be said, that with decreasing particle size, the first-order Raman scattering probes the optical phonon dispersion for increasing  $k$ -values. The results for first-order Raman scattering are shown in Fig. 2. For the largest investigated particles with a BET diameter of 60 nm, we find a position for the TO phonon of  $522 \text{ cm}^{-1}$ , close to the value observed for bulk silicon. With decreasing particle diameter, the center frequency of the peak shifts towards smaller energies. To analyze the data, we have plotted in Fig. 3, along with the experimentally determined peak positions, the scattering frequencies expected from the phonon

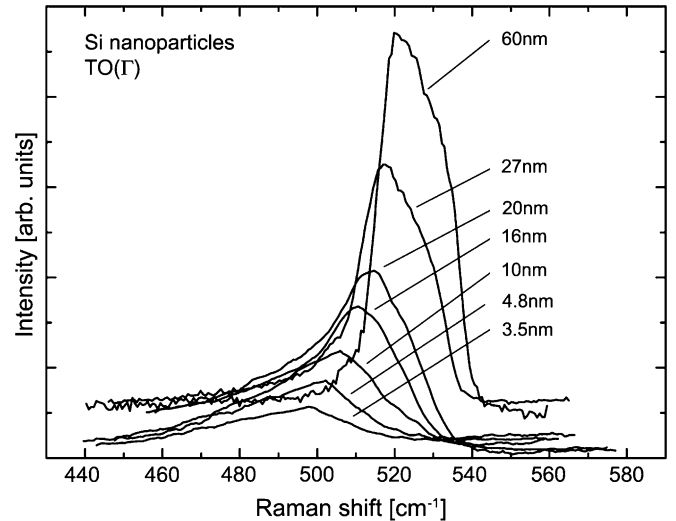


Fig. 2. First-order Raman spectra for silicon nanoparticles with BET diameters between 3.5 and 60 nm.

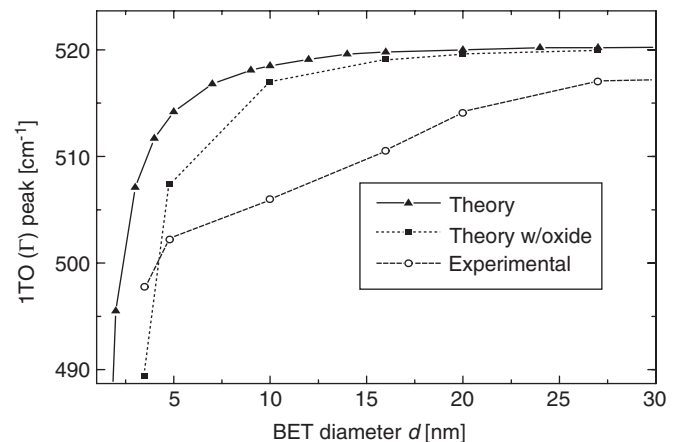


Fig. 3. Theoretical expected peak shift from the phonon confinement model for particles without (solid) and with oxide (short dash), together with the experimentally obtained values.

confinement model, assuming a Lorentz-like oscillator, the dispersion  $\omega(q)$  of the TO phonon in bulk silicon and a Gaussian envelope function. We obtain the scattering intensity from

$$I(\omega) = \int_0^1 \frac{\exp(-q^2 d^2 / 4a^2)}{[(\omega - \omega(q))^2 + (\Gamma_0 / 2)^2]} d^3 q. \quad (1)$$

Here,  $a$  is the lattice constant of bulk Si and  $\Gamma_0 = 4 \text{ cm}^{-1}$  bulk the Si Raman line FWHM. Comparing experiment and theory, we note the following: We observe a significant frequency shift already for particles with a BET diameter of  $d = 27$  nm, although in the model the expected shift for this size is negligible. For smaller particle sizes, the discrepancy between experimental and theoretical data increases down to a particle size of 7–10 nm, then decreases again. As we know from infrared and Auger experiments, the particles are covered by an oxide layer [6]. Therefore, we have

reduced the effective particle diameter by a finite thickness (thicknesses taken from [6]) and repeated the calculation. The results are also shown in Fig. 3 (short dashes). Obviously, the introduction of an oxide layer alone is not sufficient to explain the deviation between the experimental and theoretical data. As can be seen in Fig. 1, the particles do not have a narrow size distribution, due to the statistical nature of the fabrication process. From an analysis of the TEM images we find that the particles follow a log-normal size distribution [8], with a standard deviation of approximately  $\sigma = 1.5$ . Therefore, a large fraction of the particles is significantly smaller than the mean particle diameter that is determined using the BET method. To assess the influence of this size distribution we have computed the expected peak shift for particles with a log-normal distribution  $f(d)$  with  $\sigma = 1.5$  using the phonon confinement model used above. The scattered intensity is computed using

$$I(\omega) = \int_0^\infty f(d) \delta d \int_0^1 \frac{\exp(q^2 d^2 / 4a^2)}{[(\omega - \omega(q))^2 + (\Gamma_0/2)^2]} d^3 q. \quad (2)$$

The results of this calculation are not shown here, as there is no significant difference for particles with a broad size distribution (up to  $\sigma = 1.5$ ) and the results for a single particle size. However, it is an important general conclusion that even a broad size distribution will not affect the expected peak shift due to phonon confinement.

As all the structural analysis on the particles investigated here do not show a significant difference to particles studied elsewhere [3], we can only conclude that the particle diameter measured by BET does not reflect the length scale relevant for phonon confinement. Indeed, the BET measurement is probing a different property (specific surface via adsorption) than the Raman scattering experiment. However, the BET diameter is still directly related to the particle size and therefore useful for sample characterization. In the following, we will continue to use the BET diameter to plot our results for clarity reasons.

### 3.2. Second-order scattering

For second-order scattering, the two phonons involved must have equal but opposite wavevector in order to fulfill momentum conservation. Therefore, the strongest scattered signal is due to phonon states where the density of states (DOS) is highest [9]. The intensity of the second-order Raman signal strongly depends on the scattering geometry due to symmetry reasons. The nanoparticles investigated here are randomly oriented, so that all crystalline orientations are present. Therefore the observation of two-phonon processes is always possible independent of the scattering geometry. Our results for second-order Raman scattering are displayed in Fig. 4. For the largest particles we find a prominent peak around  $980 \text{ cm}^{-1}$ . With decreasing particle size, this peak shifts towards lower frequencies. For the smallest particles

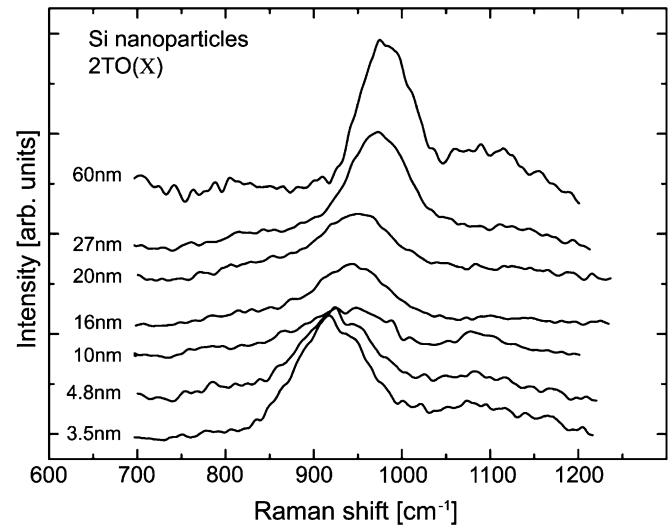


Fig. 4. Second-order Raman spectra for silicon nanoparticles with diameters in the range of  $d = 3.5$  and  $60 \text{ nm}$ .

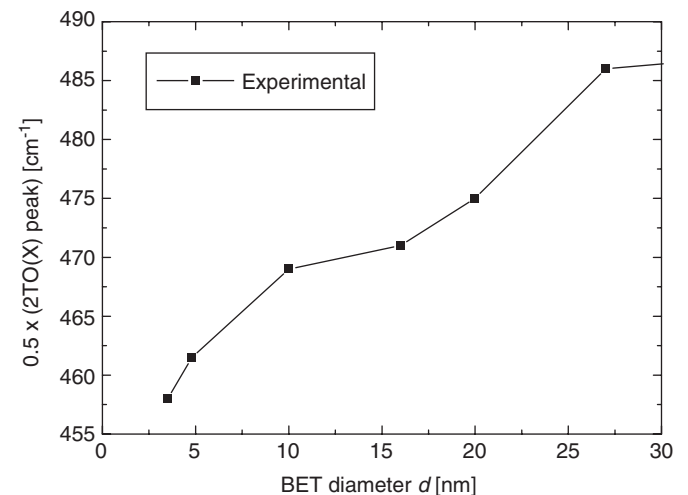


Fig. 5. Observed peak shift for the 2TO(X) Raman peak. The observed frequencies are divided by 2 for easier comparison with the Si phonon dispersion.

( $d = 3.5 \text{ nm}$ ), the peak is found at  $916 \text{ cm}^{-1}$ . Also, a weak side band can be seen at the high-energy side of the peak, but the intensity is too weak to determine its frequencies with reasonable accuracy. As discussed above, the scattering in second order reflects the phonon DOS. For bulk silicon, the DOS features two strong singularities due to the TO phonon at the X-point ( $\sim 458 \text{ cm}^{-1}$ ) and the L-point ( $\sim 481 \text{ cm}^{-1}$ ) [10]. For the degenerate optical phonon at the  $\Gamma$ -point, the DOS approaches zero. Therefore, the scattering in second order delivers complementary information to the scattering in first order. From [10], we can safely assign the low-frequency peak at  $\sim 980 \text{ cm}^{-1}$  in our spectra to the TO-phonon at the X-point. In Fig. 5, we have plotted the spectral shift of the 2TO(X) peak position over the BET diameter. We observe a behavior very similar to the peak shift observed in first order. Especially, the strong redshift

already in the size range of 20–30 nm is resembled. This further supports our statement made above that BET and phonon confinement probe different length scales. The observed redshift of the 2TO(X) peak with decreasing particle size is surprising. The usual argument to explain the redshift for the 1TO( $\Gamma$ ) peak is that the TO dispersion relation in Si only has negative branches in all directions starting from  $\Gamma$  [3]. However, this argument is not valid for TO(X), as this symmetry point reflects the lowest frequency in the TO dispersion [10]. Indeed, if we would just apply the wavevector mixing argument to phonons at the X-point, we would expect a blueshift for the 2TO(X) peak. It is not straightforward to apply the formalism for first-order scattering to second-order, as in the simple phonon confinement model the first Brillouin-zone is approximated by a sphere around  $\Gamma$ . This is a valid approach for first order, as the integral is mostly determined by contributions close to  $\Gamma$ . However, this formalism cannot be used for other symmetry points. Instead, our results do suggest that the atom–atom interaction in silicon nanoparticles are more complicated than the simple phonon confinement model suggests. We conclude from our data that the phonon frequencies at the X- and L-points shift to lower frequencies for nanosized particles. We want to stress that this conclusion is independent from the uncertainty in size determination as we only make a qualitative argument here.

#### 4. Conclusions

We have observed Raman scattering up to second-order for silicon nanoparticles in the size range between 3.5 and 60 nm, fabricated in a RF plasma from SiH<sub>4</sub> decomposi-

tion. We observe a redshift for the TO( $\Gamma$ ) phonon as predicted by the phenomenological phonon confinement picture. For second-order scattering, we find that the TO phonon frequencies at the X and L points are also shifted to lower frequencies, in spite of the fact that these points mimic minima in the phonon dispersion relation. We therefore conclude that for nanoparticles a change in atom–atom-interaction leads to a softening of the optical phonon also for large wavevectors.

#### Acknowledgments

Funded by the DFG via grant SFB 445 ‘Nanoparticles from the gas phase’.

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