Phonon confinement effect of silicon nanowires synthesized by laser ablation

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A gradual downshift and asymmetric broadening of the Si optical phonon peak were observed by Raman scattering measurements of continuously thermally oxidized silicon nanowires (SiNWs) synthesized by laser ablation. This downshift and broadening can be interpreted by the phonon confinement effect. Further thermal oxidation produced a reverse change; namely, an upshift of the optical phonon peak. This is considered to be due to compressive stress since this stress was relieved by removing the oxide layers formed around the SiNW cores, resulting in a downshift of the optical phonon peak. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1931055]

The application of one-dimensional nanostructures such as Si nanowires (SiNWs) to future generations of integrated electronic and optoelectronic devices has been investigated as one of the major subjects of interest in this field.[1–4] As the diameter of SiNWs approaches the de Broglie wavelength of the carrier, the quantum confinement effect increases the band-gap energy and induces visible photoluminescence (PL). Indeed, recent experimental results of scanning tunneling spectroscopy measurements and theoretical calculations have shown an increase in the energy gap of SiNWs.[5,6] Furthermore, PL results have recently indicated a substantial blueshift with decreasing diameter of SiNWs.[7,8]

Another unique feature of low-dimensional structures is the phonon confinement effect. Raman spectroscopy has already been extensively applied to SiNWs to explain the line shape and position of the Si optical phonon peak describing phonon confinement.[9,10] Finite-size effects or disorders partially relax momentum conservation and the selection rule is relaxed. This produces a downshift and asymmetric broadening of the Si optical phonon peak.[11,12] Piscanec *et al.*[9] investigated the dependences of Si optical phonon peaks on probe-laser power and wavelength, and showed the necessity of measuring at very low laser powers to identify the contribution of the phonon confinement effect without the effect of local heating caused by laser excitation during Raman measurements. Bhattacharyya and Samui[10] analyzed Si optical phonons of SiNWs taking into consideration the size distribution of SiNWs. If the diameter of SiNWs is changed by thermal oxidation as reported in Ref 9, a gradual shift of the Si optical phonon peak depending on the step-wise decrease in the diameter of the SiNWs can be expected. Such results, however, have not been yet obtained.

In the present study, in order to observe a gradual downshift and broadening of Si optical phonon peaks due to the phonon confinement effect depending on the diameter of SiNWs, first the diameters of SiNWs were changed by varying the synthesis temperature, and second the core of the SiNWs was controlled by thermal oxidation after synthesis. Furthermore, the effect of strain due to the surface oxidation was also investigated.

SiNWs were synthesized by catalytic laser ablation of Si targets with 1 at. % of nickel (Ni) catalyst, and were deposited on substrates. Each $Si_{0.99}Ni_{0.01}$ targets were placed in quartz tubes and heated to 1000, 1100, or 1200 °C in flowing argon (Ar) gas of 50 sccm and 500 Torr. After a target reached the temperature, a frequency-doubled NdYAG laser with a wavelength of 532 nm was focused on it. In order to avoid continuous irradiation of the same position, the focus point was scanned during laser ablation. In this study, SiNWs were directly deposited on a Si substrate or a SiO_2 substrate for micro-Raman measurements. These substrates and grids were set on a water-cooled Mo holder placed at a downstream position in the quartz tube. The laser power was at about 200 mJ per pulse with a pulse duration of 7 ns at 10 Hz. Some of the SiNW specimens deposited on the substrates were thermally oxidized at temperatures from 700 to 1000 °C for 30 min in O_2 gas with a pressure of 200 Torr. After annealing at 1000 °C, the specimens were treated with 5% HF solution for 30 s to remove surface oxide. SEM (JEOL, JSM-5610, 20 kV) and TEM (JEOL, JEM-4000EX: 400 kV, JEM-2010: 200 kV) measurements were performed to observe the SiNWs and investigate their detailed structures. Micro-Raman scattering measurements were performed at room temperature with a $100\times$ objective and a 532 nm excitation light at a power of 0.02 mW.

A representative SEM image of the SiNWs is shown in Fig. 1(a), and representative TEM images are shown in Figs. 1(b) and 1(c). The TEM images show that the SiNW is sheathed by a layer of amorphous SiO_x having a thickness of about 13 nm, with a core of crystalline Si. The diameter of the Si core is about 17 nm. The diameter of the SiNWs was observed to significantly depend on the synthesis parameters, such as the synthesis temperature, as shown in Fig. 1(d). The diameter of the SiNWs decreased with decreasing synthesis temperature.

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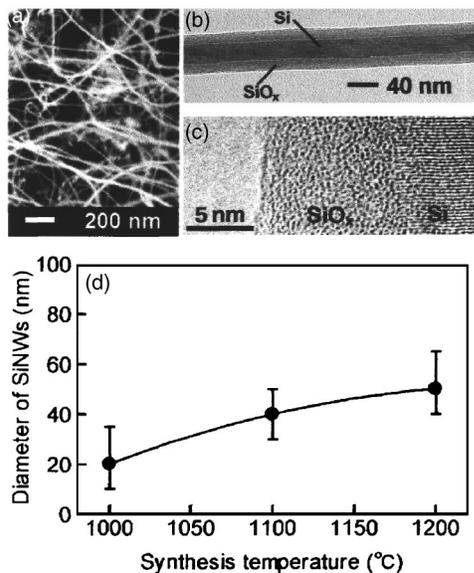
FIG. 1. (a) Representative SEM image, (b) TEM image, and (c) high-resolution TEM image of SiNWs synthesized by using $Si_{0.99}Ni_{0.01}$ targets. (d) Dependence of the diameter of SiNWs on synthesis temperature.
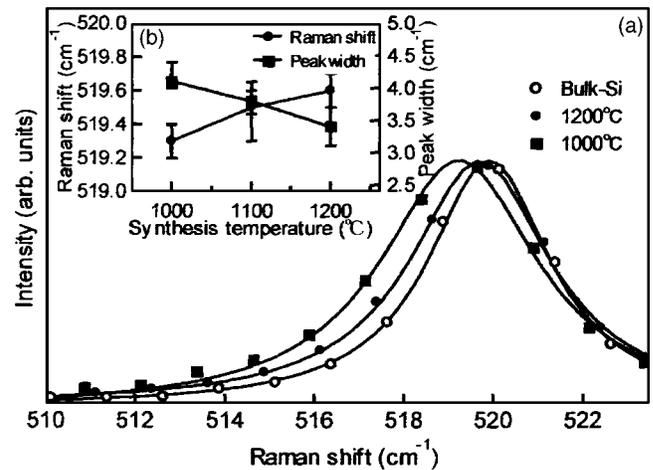

FIG. 2. (a) Optical phonon peaks of SiNWs measured by micro-Raman scattering and (b) the dependence of the Raman shift and peak width of the optical phonon peak on synthesis temperature.

The dependence of the phonon confinement effect on the diameter of the SiNWs was investigated by micro-Raman scattering measurements. In this experiment, SiNWs were collected not on Si wafers but on SiO_2 substrates to avoid Si substrate effects on the Raman signal and to observe only the Si optical phonon from the SiNWs. In addition to this, the use of SiO_2 substrates made continuous oxidation and Raman observation of the same SiNWs possible. The downshift and asymmetric broadening of the Si optical phonon peak were observed in the Raman spectra of the SiNWs as shown in Fig. 2. The optical phonon peak was found to clearly shift toward a lower wave number with decreasing synthesis temperature; namely, decreasing diameter of the SiNWs.

The downshift of the optical phonon peak due to the phonon confinement effect was also investigated by changing the thickness of the surface SiO_2 layer. In order to increase the thickness of the SiO_2 layer and consequently decrease the diameter of the crystalline Si core in the SiNWs, the SiNWs synthesized at 1200 °C were thermally oxidized at temperatures ranging from 700 to 1000 °C for 30 min in O_2 gas. The results are shown in Fig. 3. The width of the optical phonon peak increased with the oxidation temperature. The optical phonon peak once slightly shifted toward a lower wave number and then shifted to a higher wave number again after annealing at above 900 °C. This upshift is probably caused by the increase in compressive stress due to the progress of surface oxidation. The gradual peak shift and broadening due to continuous oxidation are the first experimental results obtained so far for the phonon confinement effect and subsequent compressive stress.

TEM measurements were performed to observe the change of the diameter of the crystalline Si core in SiNWs. Here, the SiNWs used in TEM measurements are not the same SiNWs but synthesized at the same time. The data spread is shown in Fig. 4(g). Hence, the TEM images shown in Fig. 4 are the representative ones before and after thermal oxidation, and Fig. 4(e) shows the SiNWs with the minimum core diameter observed in this study. The diameter of the crystalline Si core in SiNWs gradually decreased with in-

creasing oxidation temperature and showed a drastic decrease after oxidation at 1000 °C.

In order to check the contribution of stress, the specimens were treated with HF solution to remove the surface oxide layer and consequently relieve the stress after thermal oxidation at 1000 °C. Figure 5 shows the optical phonon peak of a specimen before and after 5% HF treatment for 30 s. The position of the optical phonon peak downshifted up to about 519.4 cm^{-1} and the peak width decreased up to about 4.3 cm^{-1} after the HF treatment. This result demonstrates that the upshift is due to an increase in compressive stress toward the center of the SiNW arising from the expansion of the surrounding SiO_2 layer. The position and width are close to those obtained for the specimen after annealing at 700 °C. The lowest position of the optical phonon peak was obtained for the specimen after thermal oxidation at 800 °C, as shown in Fig. 3(b). This result suggests that slight residual stress exists even after 5% HF treatment for 30 s.
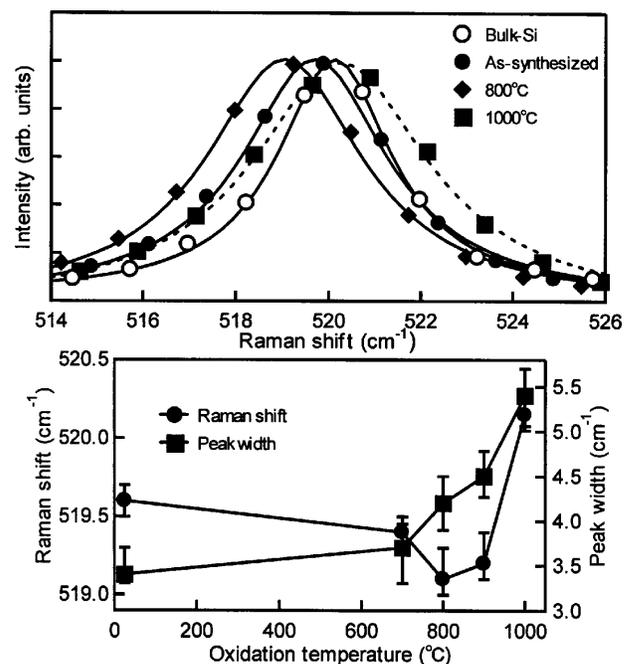

FIG. 3. Dependence of (a) the optical phonon peak of SiNWs and (b) the Raman shift and peak width on oxidation temperature.
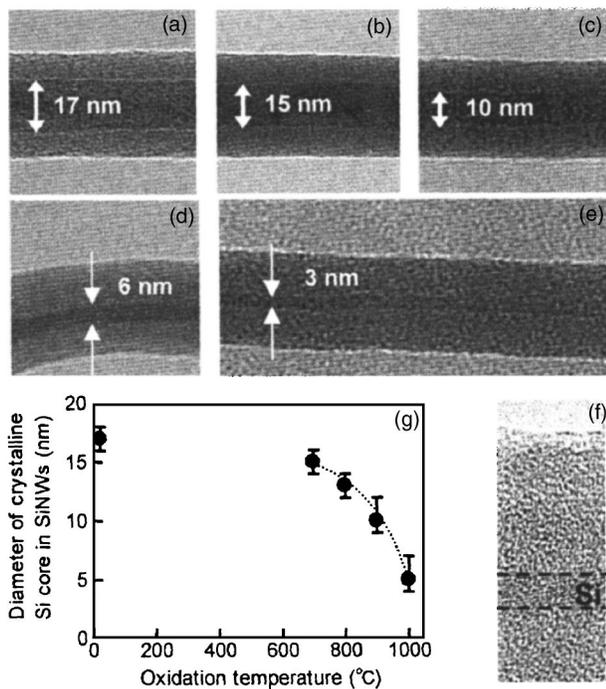
FIG. 4. (a) TEM images of SiNWs synthesized at 1200 °C and the SiNWs thermally oxidized at (b) 700 °C, (c) 900 °C, (d) 1000 °C, (e) 1000 °C, and (f) high-resolution TEM image of SiNWs thermally oxidized at 1000 °C. The images in (e) and (f) show SiNWs with the minimum core diameter of 3 nm. (g) Dependence of the diameter of crystalline Si core in SiNWs on thermal oxidation temperature.
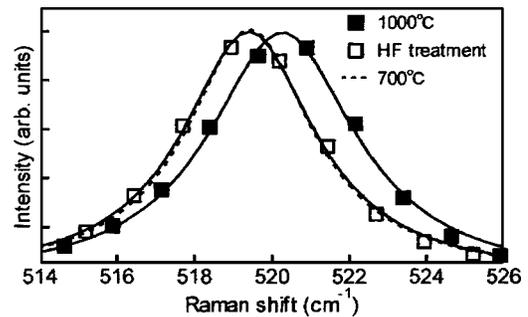

FIG. 5. Optical phonon peak of SiNWs observed for the specimen before and after 5% HF treatment for 30 s. The specimen was oxidized at 1000 °C for 30 min before HF treatment.

Some parts of the peak shift and asymmetric broadening shown in Figs. 2 and 3 can be attributed to the phonon confinement effect in SiNWs. According to theoretical calculations based on the phonon confinement model of Richter *et al.*[11] and Campbell and Fauchet,[12] the Raman intensity is given by

$$I(\omega) = \int \frac{|C(0,q)|^2}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2} d^3q, \tag{1}$$

where $C(0,q)$ is a Fourier coefficient of the confinement function, $\omega(q)$ is the Si phonon dispersion, and Γ_0 is the full width at half maximum of the reference Si. Here, we used the following relations: $|C(0,q)|^2 = \exp(-q^2d^2/16\pi^2)$ and $\omega(q) = [A + B\cos(q\pi/2)]^{0.5} + D$, with $A = 1.714 \times 10^{15}$ cm^{-2} and $B = 10^5$ cm^{-2}.[9] D is an adjusting parameter for the bulk reference Si measured in this study. The value of d corresponds to the diameter of the SiNW. The diameters of the SiNWs are calculated to be about 15, 12, and 9 nm for the specimens synthesized at 1200, 1100, and 1000 °C, respectively, by fitting the observed Raman spectra with Eq. (1). Furthermore, the diameters of the SiNWs after thermal oxidation at 700 and 800 °C were also calculated to be about 13 and 10 nm, respectively. These values correspond to the mean diameters of SiNWs without surface oxide. The calculated values for the SiNWs synthesized at 1200 °C and thermally oxidized at 700 and 800 °C are in good agreement with the values obtained by TEM observation in Fig. 4.

The SiNWs thermally oxidized at 1000 °C have a diameter in the range of 3–6 nm. The width of the optical phonon peak is estimated to be about 15–20 cm^{-1} for the SiNWs with the diameter of 3 nm from the phonon confinement model shown in Ref. 9. However, our Raman results showed the peak width of about 5–6 cm^{-1} after thermal oxidation at 1000 °C. On the other hand, the peak width is estimated to be about 7 cm^{-1} in the case of 6 nm from the phonon confinement model.[9] Therefore, the result of Raman measurements after thermal oxidation at 1000 °C is mainly due to the SiNWs with the diameter of about 6 nm.

In conclusion, the phonon confinement effect on the Si optical phonon of SiNWs synthesized by laser ablation was investigated. The optical phonon peak of SiNWs showed a downshift and asymmetric broadening due to the phonon confinement effect with decreasing synthesis temperature, corresponding to the decrease in diameter of the SiNWs. Thermal oxidation of the SiNWs clearly showed a gradual shift and broadening of the Si optical phonon peak depending on the stepwise decrease in the diameter of the SiNWs. On the other hand, further thermal oxidation produced a reverse change from the phonon confinement effect; namely, an upshift of the optical phonon peak due to compressive stress. This stress was relieved by removing the oxide layer formed around the crystalline Si core in the SiNWs.

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