Doping and hydrogen passivation of boron in silicon nanowires synthesized by laser ablation

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Local vibrational modes of boron (B) in silicon nanowires (SiNWs) synthesized by laser ablation were observed at about 618 and 640 cm^{-1} by Raman scattering measurements. Boron doping was performed during the growth of SiNWs. Fano [Phys. Rev. **124**, 1866 (1961)] broadening was also observed in the Si optical phonon peak. These results prove that B atoms were doped in the SiNWs. Hydrogen (H) passivation of B acceptors in the SiNWs was also investigated. A broad peak was observed at around 650–680 cm^{-1} after hydrogenation, demonstrating that B dopants were passivated by the formation of the well-known H–B passivation centers. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2372698]

Silicon nanowires (SiNWs) are very likely to be used as building blocks in nanoscale devices and circuits. For realization of nanoscale silicon devices, it is important to establish doping methods and to control the carrier densities. In general, SiNWs are synthesized by chemical vapor deposition (CVD),[1,2] laser ablation,[3–5] and high temperature annealing.[6,7] In the case of CVD, they were synthesized by metal-assisted vapor-liquid-solid (VLS) growth, which has the advantages of size and site control of SiNWs. Several results for boron (B) doping in SiNWs have been reported.[8–12] Until now, the B-doping effect has been investigated by resistivity and conductance measurements. However, to evaluate the mean electrical properties and control the carrier density of SiNWs, Si/SiO$_2$ interface defects such as P_b centers and other impurities need to be investigated, since there are possibilities for compensation due to interface defects and contamination by metal catalysts. On the other hand, B-doped SiNWs synthesized using oxygen-assisted VLS growth[10] are not contaminated by metal impurities. Not using nanometer-sized metal catalysts, however, makes size control difficult and thus impedes investigation of size-dependent properties. Optical measurements such as Raman scattering measurements can identify information on B dopants as distinct from other impurities. For example, the bonding structures and sites of B in SiNWs can be investigated by Raman scattering measurements. These, however, have not yet been investigated.

It is also important to investigate the effect of hydrogen (H) on the electrical activity of B dopants, especially H passivation of B in SiNWs. This has been extensively studied for B-doped bulk Si.[13–18] When H atoms are introduced into B-doped Si, the H atoms become located at the bond-centered sites between B and neighboring host Si atoms, as a result of which the so-called H–B passivation centers are

formed.[14–18] Hydrogen passivation of B in Si is very efficient because the Coulomb attraction between interstitial H$^+$ and B$^-$ results in a very large capture radius.[13] Thus, almost all B in Si can be passivated by H. However, the H passivation effect has not yet been investigated for B-doped SiNWs.

In the present study, we performed B doping for the formation of *p*-type SiNWs during laser ablation of a Si target with B and Ni atoms as a dopant impurity and a catalyst, respectively. Size control of SiNWs due to laser ablation has been investigated in our previous paper.[19] The state of B in SiNWs was investigated by Raman scattering measurements. As a result, a local vibrational mode of B in the Si crystal core of SiNWs was observed. This mode confirms that B atoms locate in the substitutional sites in crystalline Si core of SiNWs, where they are activated. We also investigated the H passivation effect in B-doped SiNWs and succeeded in observing a peak related to the formation of so-called H–B passivation centers.

B-doped SiNWs were synthesized at 1200 °C in flowing argon (Ar) gas at 50 SCCM (SCCM denotes cubic centimeter per minute at STP) by laser ablation of a Si target with a nickel (Ni) catalyst and boron. Two kinds of targets, namely, Si$_{89}$Ni$_1$B$_{10}$ and Si$_{99}$Ni$_1$, were used. A frequency-doubled Nd doped yttrium aluminum garnet laser (532 nm, 7 ns pulse width, 10 Hz, and 150 mJ/pulse) was used to ablate the targets. In this experiment, SiNWs were directly collected on a SiO$_2$ substrate to avoid Si substrate effects for Raman scattering measurements. Scanning transmission electron microscopy (STEM) (Hitachi, S-5500, 30 kV) and transmission electron microscopy (TEM) (JEOL, JEM4000EX: 400 kV, JEM-2010: 200 kV) were used to observe the SiNWs and to investigate the details of their structures. Micro-Raman scattering measurements were performed at room temperature with a 100× objective. Three kinds of excitation lights with wavelengths of 488, 532, and 633 nm were used. The excitation powers were set to be about 0.02 mW to avoid local heating effects due to the excitation laser.[20] Hydrogen atom treatments (HAT) using remote downstream methods of

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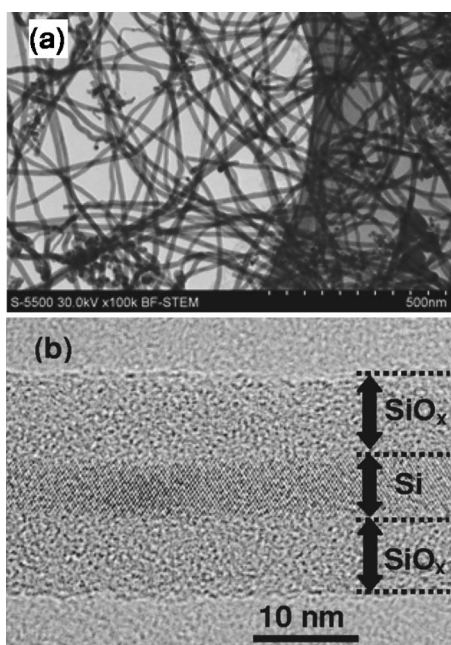b)Also at Special Research Project on Nanoscience, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8573, Japan.

FIG. 1. Representative (a) STEM and (b) high-resolution TEM images of the SiNWs synthesized using a $Si_{89}Ni_1B_{10}$ target.

FIG. 2. (Color online) (a) Optical phonon peaks of the SiNWs synthesized using a $Si_{89}Ni_1B_{10}$ target (B-doped SiNWs) and a $Si_{99}Ni_1$ target (undoped SiNWs) and that of bulk Si measured by micro-Raman scattering with 532 nm excitation wavelength. (b) Magnification of the Raman peak observed for B-doped SiNWs. (c) Dependence of the line shapes on the excitation wavelength.

high-flux H atoms were performed at 150 and 180 °C for 30 min. In this method, the specimens were placed in a quartz tube 60 cm away from the plasma source and hydrogenated only by H atoms. Thus, damage by H plasma is completely prevented using this remote method. The full details of laser ablation and hydrogenation procedures are reported in Refs. 5 and 21, respectively.

The STEM image of typical SiNWs synthesized using a $Si_{89}Ni_1B_{10}$ target is shown in Fig. 1(a). A large number of SiNWs were synthesized. The high-resolution TEM image is shown in Fig. 1(b). Si lattice fringes are seen inside the SiNW, showing that the SiNW is sheathed with a thick amorphous SiO_x ($x \leqslant 2$) layer and the core is crystalline Si. The formation of such thick amorphous layer has been reported for heavily B-doped SiNWs.[12] The average Si core diameter of SiNWs synthesized using a $Si_{89}Ni_1B_{10}$ target was about 5 nm.

Figure 2(a) shows Raman spectra observed for undoped and B-doped SiNWs synthesized by using $Si_{99}Ni_1$ and $Si_{89}Ni_1B_{10}$ targets, respectively. Raman spectrum observed for bulk Si is also shown for comparison. The intense peak is attributed to the Si optical phonon peak. In the case of SiNWs, this peak comes from their crystalline Si core. The optical phonon peak observed for SiNWs (519.0 cm^{-1}) clearly shows a shift and a broadening toward a lower wave number than that for bulk Si (520.1 cm^{-1}). These are mainly due to the phonon confinement effect.[5,19,20,22–24] The optical phonon peak observed for B-doped SiNWs also showed a broadening toward higher wave number in addition to the asymmetric broadening towards lower wave number due to phonon confinement. This is attributable to the Fano effect.[25] This so-called Fano broadening is due to the coupling between discrete optical phonons and the continuum of interband hole excitations in degenerately doped *p*-type Si.[25] As a result, the presence of free holes in *p*-type Si gives rise to a characteristic change in the Raman line shapes of the optical zone-center phonon. Figure 2(c) shows the dependence of
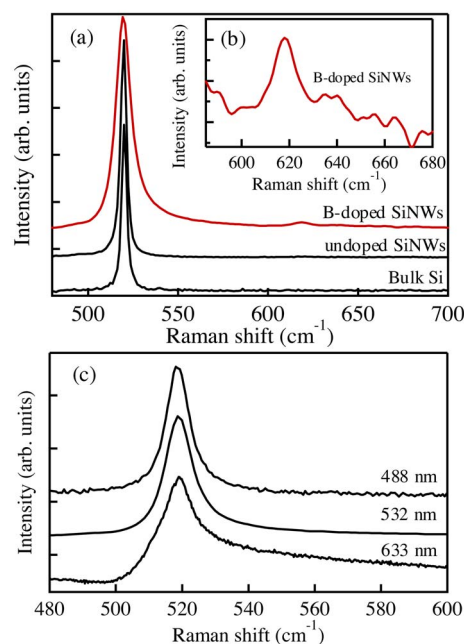
the Raman line shapes on the excitation wavelength. The optical phonon peak showed a large broadening to higher wave number with increasing excitation wavelength. The phonon peak observed at 633 nm excitation clearly showed an antiresonance at low wave number. These line shapes are the characteristics of the Fano effect, indicating heavy B doping in SiNWs.

Figure 2(b) shows an enlargement of Fig. 2(a) ranging from 550 to 680 cm^{-1} observed for B-doped SiNWs. A peak was observed at about 618 cm^{-1} on the shoulder of the optical phonon peak broadened by the Fano effect. This peak was not observed in undoped SiNWs and bulk Si. Boron acceptors, as substitutional impurities lighter than the host atoms, give rise to local vibrations at frequencies higher than the maximum phonon frequency in the silicon lattice. In the case of substituted B in bulk Si, local vibrational modes of B were observed at about 620 and 643 cm^{-1}.[26] The intensity ratio of the two peaks reflects the natural abundance of the two isotopes of ^{11}B (80.2%) and ^{10}B (19.8%).[26] The position of the former peak is close to that of the peak observed at 618 cm^{-1} for B-doped SiNWs. In addition to the peak at 618 cm^{-1}, a peak can be faintly seen at about 640 cm^{-1}. This peak can be seen also in Fig. 3. The intensity ratio of the two peaks is estimated as being roughly 4:1, which is in good agreement with the value reported for B-doped bulk Si. Based on these results, these peaks are attributed to the local vibrational modes of B in SiNWs. This demonstrates that B atoms had been doped in substitutional sites of crystalline Si core of SiNWs during laser ablation, although B atoms preferentially segregate in SiO_2 rather than Si sites.[27]

To investigate the H effect in SiNWs, we introduced H atoms to B-doped SiNWs. The result is shown in Fig. 3(a). A broad peak was observed at around 650–680 cm^{-1} after HAT treatments at 150 and 180 °C, respectively. H passiva-
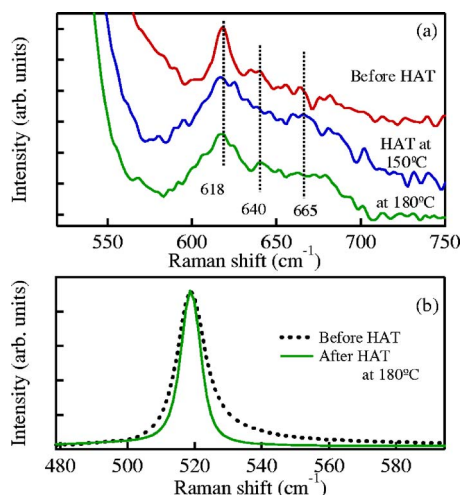
FIG. 3. (Color online) (a) Raman spectra of localized vibrations due to B in SiNWs before and after HAT at 150 and 180 °C, respectively. (b) Changes in the Raman line shapes of the Si optical phonon observed for B-doped SiNWs before and after HAT at 180 °C. The SiNWs were synthesized using a $Si_{89}Ni_1B_{10}$ target. The 532 nm excitation light was used.

tion leads to pronounced changes in the vibrational spectrum of the B atoms due to the formation of so-called H–B passivation centers.[26] The formation of these H–B passivation centers reduces the symmetry of B atoms from the tetrahedral symmetry of substitutional B atoms to axial symmetry with respect to the H–B axis, causing a splitting of the triply degenerate B mode with T_d point group symmetry into a doublet and a singlet with C_{3v} point group symmetry. As a result, two Raman peaks were newly observed at about 652 and 680 cm^{-1} in B-doped bulk Si after hydrogenation. The frequency of the broad peak newly observed after HAT is in good agreement with that of B-doped bulk Si.[26] This proves that B dopants in SiNWs were passivated by the formation of H–B passivation centers, suggesting that the method of hydrogen passivation is a potential technique for controlling the hole carrier concentration in SiNWs.

Figure 3(b) shows the change in the Raman line shapes of the Si optical phonon observed for B-doped SiNWs before and after HAT at 180 °C. After HAT at 180 °C, asymmetric broadening due to the Fano effect decreased, indicating that H passivation of B dopants decreased the density of free holes. Hence, the result also shows the passivation of B dopants in the crystalline Si core of SiNWs by H atoms. Furthermore, the phonon peak again showed a broadening after an annealing at 300 °C. The result indicates the recovery of free holes, resulting in reappearing of the Fano broadening. In the bulk Si case, it is possible to estimate the active B concentration by comparing the line-shape parameters deduced from the Raman spectra to those reported in the literature for different B concentrations.[28] In the case of SiNWs, however, it is difficult to estimate the active B concentration, since asymmetric broadening due to the phonon confinement effect coexists in the optical phonon peak. In the light of observation of Fano broadening and the local vibrational modes of substitutional B in SiNWs, the B concentration in SiNWs is probably in a range exceeding $10^{19}–10^{20}$ cm^{-3}.

In conclusion, we synthesized B-doped SiNWs by laser ablation of Si targets with B and Ni. Boron doping was confirmed by a Raman peak at 618 cm^{-1}, which is attributable to

the local vibrational mode of B in SiNWs. Fano broadening was also observed in the optical phonon peak for B-doped SiNWs, which indicates heavy B doping during laser ablation. A broad peak was observed at around 650–680 cm^{-1} after hydrogenation. This result shows that the H–B passivation centers are formed, resulting in the passivation of B dopants in SiNWs by H atoms.

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