

Bonding and electronic states of boron in silicon nanowires characterized by infrared synchrotron radiation beam

Considerable research has been carried out on one-dimensional semiconducting nanowires (NWs). Silicon (Si) NWs have attracted particular attention due to their compatibility with current Si complementary metal-oxide-semiconductor (Si CMOS) integrated circuit technology and their better scalability. These NWs have potential for use in the channel, source and drain regions of MOS field-effect transistors (FETs). Impurity doping will be of increasing importance in realizing high-speed transistor channels using SiNWs. However, to be able to realize them, it is important to clarify the states of impurity atoms, such as their chemical bonding states and electrical activity. First, we applied Raman scattering and electron spin resonance (ESR) [1]. Local vibrational modes of ¹¹B and ¹⁰B in SiNWs were observed by Raman scattering measurements, indicating B doping into the crystalline Si core of SiNWs. Asymmetric broadening due to Fano resonance was also observed in the Si optical phonon peak, showing the electrical activity of B atoms in SiNWs. These techniques also clarified the segregation behaviors of B and P atoms in SiNWs [2]. Fourier transform infrared (FT-IR) techniques also allow the vibrational characterization of impurity atoms in bulk Si. However, it is very difficult to apply FT-IR techniques to characterize impurity atoms in nanostructures due to the difficulty of preparing sufficiently large samples. The use of IR synchrotron radiation (IR-SR) as an IR light source in BL43IR has the advantage of a greater brilliance than conventional IR light sources using thermal radiation. The brilliance of IR-SR is 10² times higher than that of general blackbody light. This allows the optical spectrum, in even microscopic regions, to be measured down to lower frequencies. IR-SR in BL43IR also has a wide range of wavenumbers from the visible to far IR regions, making it possible to characterize nanostructure materials such as SiNWs.

SiNWs were synthesized by laser ablation of a Si target with nickel (Ni) as the metal catalyst. The growth mechanism of SiNWs is VLS (vapor-liquid-solid) growth [3]. Figure 1(a) is a schematic illustration of our laser ablation system for the synthesis of SiNWs. A special collector made of quartz was installed in the quartz tube to effectively collect SiNWs grown in an Ar gas atmosphere. Laser ablation was continued for 3 h to deposit thick layers of SiNWs with the aim of increasing the optical absorption by B atoms. The thickness of the layer of SiNWs reached 10 μ m order (Fig. 1(c)). Typical STEM and high-resolution TEM

images of SiNWs synthesized using $Si_{98}Ni_1B_1$ targets (Fig. 1(b)) are respectively shown in Figs. 1(d) and 1(e). The SiNWs are composed of a crystalline Si core and surface oxide layer. The average core diameter is about 20 nm and the thickness of the surface oxide layer is about 10 nm.

The whole range of the IR-SR absorption spectra observed for B-doped and undoped SiNWs is shown in Fig. 2. Four peaks were observed at 468, 806, 1085, and 1200 cm⁻¹ for both samples, which were assigned to different oxygen-related modes in the surface oxide layer of the SiNWs by comparison with the results for bulk silicon. The first peak at 468 cm⁻¹ is due to the rocking mode of the O atom about the axis through the two Si atoms. The second peak at 806 cm⁻¹ is due to symmetrical stretching of the O atom along the line bisecting the axis formed by the two Si atoms. The third and fourth peaks at 1085 and 1200 cm⁻¹ are due to the asymmetrical stretching motion of the O atoms. In this stretching motion, the O atoms move back and forth along a line parallel to the axis through the two Si atoms. These results show that our IR-SR technique is applicable even for the characterization of Si nanostructures. In addition to these oxygen-related



Fig. 1. (a) Schematic illustration of synthesis of SiNWs by a laser ablation system. Photographs of (b) a target and (c) a sample for IR synchrotron radiation measurements. Typical (d) STEM and (e) high-resolution TEM images of SiNWs synthesized using the $Si_{89}Ni_1B_{10}$ target.



Fig. 2. (a) IR-SR absorption spectra observed for B-doped and undoped SiNWs. (b) IR-SR absorption spectra observed for B-doped and undoped SiNWs.

peaks, a new peak was observed at about 625 cm⁻¹ in B-doped SiNWs [4]. The peak position is similar to those of the ¹¹B (618 cm⁻¹) and ¹⁰B (643 cm⁻¹) local vibrational peaks observed by Raman measurements. The intensity of the IR-SR peak at 625 cm⁻¹ shows a good correlation with that of the Raman result. Based on the peak position and its dependence on the B doping level, the newly observed IR-SR peak at 625 cm⁻¹ is assigned to the B vibrational peak in SiNWs. The positions of the IR-SR absorption peaks are at higher frequencies than those of the Raman peaks. The Raman measurements were performed at room temperature, while the IR-SR measurements were performed at 4.2 K. Hence, the higher frequency shift at lower temperatures can be mainly explained by the temperature effect. The reason why we performed IR-SR measurements at 4.2 K is that the electronic transition peaks explained below become narrow and easily observed.

The electronic transition of B in Si can be observed in the far-infrared region. Two peaks were newly observed at about 278 and 319 cm⁻¹ (Fig. 3) [4]. The high noise in the low-frequency region is due to the sensitivity of our IR-SR measurements. Burstein et al., while performing low-temperature IR measurements of B-doped bulk silicon, were the first to note discrete electronic transitions of bound holes from the ground state of neutral B acceptor atoms to a series of hydrogen-like excited levels lying below the band edge [5]. The most characteristic peaks are observed at about 278 and 320 cm⁻¹ and are respectively assigned to the 1s-2p and 1s-3p transitions of B in Si. The newly observed peak positions for B-doped SiNWs correspond very closely to the 1s - 2p and 1s - 3p transitions. These peaks were not observed for undoped SiNWs, showing that they are related to electronic transitions from the ground state of a neutral B acceptor atom to excited levels. The full width at half maximum data of the 1s - 3p transition of B in SiNWs is plotted in Fig. 3(b) in addition to the previously reported data. The broadening of the absorption peaks is likely to be due to the effect of higher B doping in the SiNWs.

These results clearly demonstrate the potential usefulness of the IR-SR method as a new tool for characterizing nanomaterials.



Fig. 3. (a) IR-SR absorption spectra related to electronic transition of B in SiNWs synthesized using $Si_{98}Ni_1B_1$ targets. (b) Dependence of FWHM on B concentration.

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