Raman characterization of Ge distribution in individual $Si_{1-x}Ge_x$ alloy nanowires

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(Received 30 July 2008; accepted 23 October 2008; published online 17 November 2008)

The distribution of Ge composition in an individual $Si_{1-x}Ge_x$ alloy nanowire (SiGeNW) grown by the vapor liquid solid (VLS) process was studied by micro-Raman spectroscopy by changing the measurement position from the catalyst side to the substrate side. The Si–Si mode in Raman spectra were found to split into two peaks and the intensity ratio as well as the wavenumbers of the two peaks depended on the measurement position. The Raman data revealed that SiGeNWs have a core-shell structure with a low-Ge composition core grown by the VLS process covered with a high-Ge composition shell grown by the conformal deposition. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3028027]

Semiconductor nanowires have attracted considerable attention in recent years because of their unique electronic properties and potential applications as transistors,[1,2] photovoltaic cells,[3–8] and chemical sensors.[9,10] Among various kinds of semiconductor nanowires, group IV semiconductor nanowires such as Si,[3,5–8,11] Ge,[12–15] and $Si_{1-x}Ge_x$ nanowires (SiGeNWs) (Refs. 1, 2, 16, and 17) have most intensively been studied due to their high compatibility with conventional complementary metal-oxide semiconductor technology. In particular, wide controllability of the electronic structure and possibility for the modulation of the band gap within a nanowire make SiGeNWs very fascinating materials.

SiGeNWs are usually grown by the vapor liquid solid (VLS) process by using metal nanoparticles as catalysts.[1,2,16,17] Since the performance of SiGeNW-based devices is strongly affected by the composition, size, shape, etc., detailed studies have been made to realize controlled VLS-growth of SiGeNWs. In particular, the effects of growth temperature and inlet gas composition were investigated in detail to clarify suitable conditions for the growth of SiGeNWs with uniform and controlled alloy composition in both the radial and axial directions.[17] However, because of the complex growth process compared to Si or Ge nanowires, there still remain unknown factors that determine the morphology and composition of SiGeNWs. For example, composition of SiGeNWs is reported to depend not only on growth conditions but also on the diameter when the diameter is below ~ 50 nm.[16]

Raman spectroscopy is a powerful tool to characterize SiGeNWs and is widely used to discuss the growth mechanism.[2,18,19] In a previous work,[19] we studied SiGeNWs by Raman spectroscopy combined with transmission electron microscopy (TEM) and TEM energy-dispersive x-ray spectroscopy (TEM-EDS). Our results suggest that axial VLS growth of SiGeNWs and a conformal growth of $Si_{1-x}Ge_x$ layer on the sidewall of the SiGeNWs core occur simultaneously in a wide growth condition range. We also showed that the Ge composition of the conformally deposited layer (shell) is always higher than that of the $Si_{1-x}Ge_x$ core grown by the VLS process. SiGeNWs have core-shell structures with a low-Ge composition core surrounded by a high-Ge composition shell.

Raman studies of SiGeNWs have been performed for ensembles of SiGeNWs or a whole region of a single SiGeNW.[2,18,19] Therefore, information on microstructures inside SiGeNWs was not obtained from Raman spectroscopy and combination with other characterization techniques was indispensable. In this work, we demonstrate that micro-Raman spectroscopy is a useful tool to characterize inner structures of SiGeNWs and to discuss the growth mechanism when the spectra of small regions are measured from one end of a SiGeNW to the other with a small step. By analyzing Raman data, we show that there is Ge distribution both in the axial and radial directions. The observed data suggests a core-shell structure. Moreover, we show that the compositions of core and shell are not uniform but change gradually along the nanowire axis. The change of the compositions suggests diffusion of Ge from the shell to the core during the growth.

SiGeNWs were synthesized via gold (Au) catalyzed VLS growth using a cold-wall infrared lamp-heated chemical vapor deposition (CVD) apparatus. Details of the growth procedure are found in our previous work.[19] The flow rate of Si_2H_6 and GeH_4 precursors, and H_2 were 200, 200, and 1080 SCCM (SCCM denotes standard cubic centimeters per minute at STP), respectively. The gas pressure and temperature for CVD growth were 0.3 Torr and 450 °C, respectively. The growth duration was 10 min. The diameter and length of SiGeNWs were 80–100 nm and 7–12 μm, respectively.

For Raman measurements of individual SiGeNWs, they were separated from the growth substrates by ultrasonication in ethanol, and the diluted solution was dropped on Au ($\sim$100 nm in thickness) coated Si(100) substrates. The purpose of Au coating was to avoid a Raman signal from a Si substrate. Raman spectra were measured by a confocal mi-

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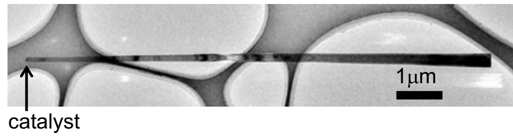

FIG. 1. Typical TEM image of a SiGeNW. The length is 7.5 μm.

croscope (50× objective lens, numerical aperture=0.75) equipped with a single monochromator and a charge-coupled device. Although the diameter of SiGeNWs was smaller than the diffraction limit of the resolution, they were observable from scatter of imaging light through a microscope monitor. From the image on the monitor, an isolated SiGeNW was selected and the catalyst side of the SiGeNW was brought to the center. The catalyst side and the other side (the substrate side) could be distinguished due to slightly conical shape of SiGeNWs, i.e., the substrate side looked darker than the catalyst side. Raman signal from the region of 2 μm in diameter was collected. After the Raman measurement, the stage was moved for 2 μm to bring the next measurement point to the center. The procedure was repeated until reaching the substrate side. The excitation source for Raman measurements was the 632.8 nm light from a He–Ne laser. Rayleigh scattering was removed by a low pass filter (Semrock: LP02–633RU-25).

Figure 1 shows a typical TEM image of a SiGeNW. The length is 7.5 μm. We can see that the SiGeNW is slightly conical. The catalyst side is thinner than the substrate side. The formation of conical SiGeNWs suggests that in addition to axial VLS growth, conformal deposition of a $Si_{1-x}Ge_x$ layer proceeds. It should be noted here that in the case of Si nanowires (SiNWs) grown in the same condition, the diameter was almost the same from the catalyst side to the substrate side. Therefore, the addition of Ge precursors (GeH_4 gas) is considered to initiate the conformal deposition.[19]

Figure 2(a) shows a typical Raman spectrum of a single undoped SiGeNW. The signal from the whole region of a SiGeNW is collected. Three major peaks can be seen at 500–520, 400–410, and 280–290 cm^{-1}, which are assigned to optical phonons caused by the motions of adjacent Si–Si, Si–Ge, and Ge–Ge pairs, respectively.[20] The peak around 420 cm^{-1} is a local vibration mode of the Si–Si pairs modulated by the adjacent Ge atoms.[21] Figure 2(b) shows an expansion of the Si–Si mode. We can see a small shoulder at the high-wavenumber side of the peak. In a previous work,[19] we showed that the composition of as-grown SiGeNWs can be estimated with a reasonable accuracy from the shift of the Si–Si peak. The Ge composition estimated from Fig. 2(b) is about $x=0.28$.

Figure 2(c) shows the micro-Raman spectra of a SiGeNW measured at the positions A–F indicated in the illustration. Signals from the region of 2 μm in diameter are detected in each measurement. Note that the Raman intensity changes depending on the measurement position. The intensity is smaller at the catalyst side than at the substrate side. This is mainly due to different volumes caused by slightly conical shape of SiGeNWs and to different compositions discussed later. To make the comparison of the spectral shape easier, the spectra are normalized at the position of the Si–Si mode. We see that the relative intensity of the Ge–Ge and Si–Ge modes increases only slightly by changing the measurement position from A to F. On the other hand, the shape

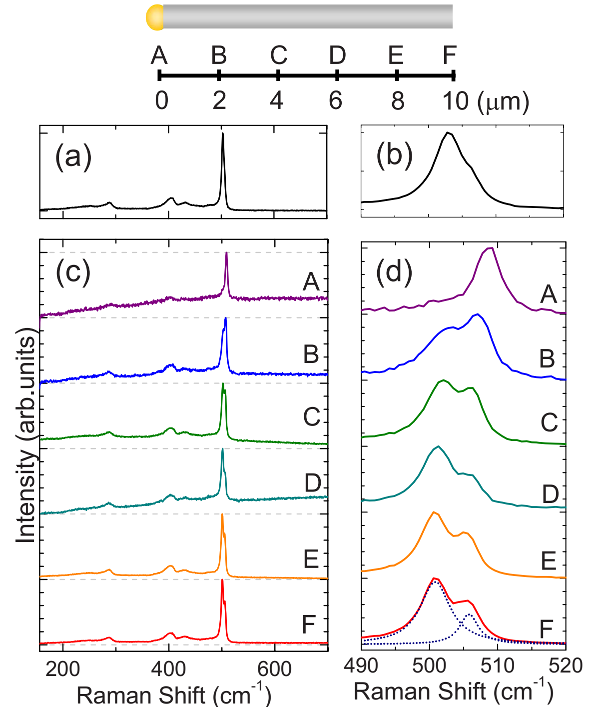

FIG. 2. (Color online) (a) Typical Raman spectrum obtained from a whole region of a single SiGeNW. (b) Expansion of the region of the Si–Si vibration mode of (a). (c) Typical Raman spectra of a SiGeNW measured at the point indicated by bars in the illustration. Distance between the measurement points is 2 μm. Signals from the region of 2 μm in diameter are detected in each measurement. (d) Expansion of the region of the Si–Si vibration mode. The dotted curves in F are the results of the fitting by two Lorentzians.

of the Si–Si mode changes drastically. Figure 2(d) shows the expansion of the Si–Si mode. We can clearly see that the Si-Si mode splits into two peaks. This implies that SiGeNWs are not uniform. The intensity ratio of the two peaks depends on the measurement position. To discuss the change of the intensity and the wavenumbers of the two peaks more in detail, we deconvolute the peak by two Lorentzian functions. Dotted curves in F are the results of the fitting. All the data could be well-fitted by two Lorentzian functions.

Figure 3(a) shows the intensity ratio of the low- to high-wavenumber peaks of the Si–Si mode as a function of the distance from the catalyst. The low-wavenumber peak arises from a high-Ge concentration region, while the high-wavenumber one from a low-Ge concentration region because the Si–Si mode shifts to lower wavenumber with increasing Ge concentration.[20] The relative intensity increases with increasing the distance from the catalyst. The Raman intensity is roughly proportional to the volume contributing to the mode. Therefore, Fig. 3(a) suggests that the volume of the high-Ge concentration region with respect to that of the low-Ge concentration region increases from the catalyst side to the substrate side. This result combined with slightly conical shape of SiGeNWs strongly suggests that the low-Ge concentration region is a SiGeNW core grown by the VLS process and the high-Ge concentration region is the shell made by the conformal deposition. This conclusion is consistent with our previous work by TEM-EDS.[19] Note that we performed the same measurements for more than ten single SiGeNWs and obtained almost the same results for all of them.

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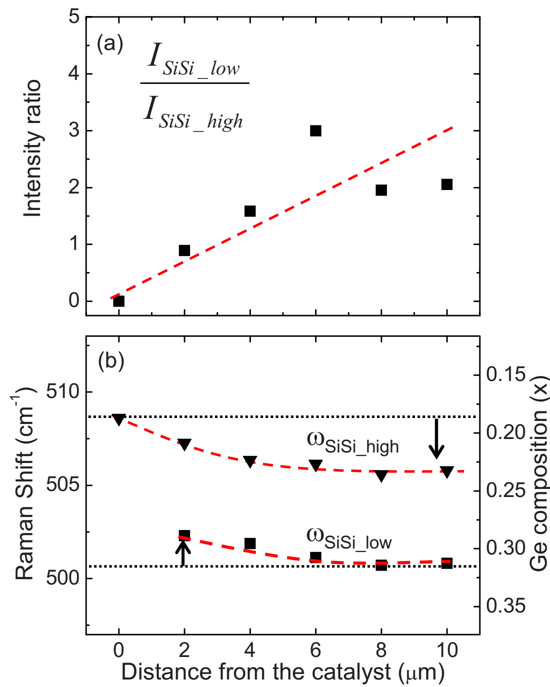

FIG. 3. (Color online) (a) Intensity ratio of low- to high-wavenumber Si–Si modes as a function of the distance from the catalyst. The dashed line is a guide to the eyes. (b) Raman shift of high- and low-wavenumber Si–Si modes as a function of distance from the catalyst. The dashed curves are guides to the eyes. The horizontal dotted lines represent the wavenumber of the low-wavenumber mode at the catalyst side and that of the high-wavenumber mode at 10 μm.

The analysis of Raman data provides more detailed information on the core-shell structure. In Fig. 3(b), Raman shifts of the two Si–Si peaks are plotted as a function of the distance from the catalyst (left axis). Corresponding Ge compositions obtained from the relation between the Si–Si mode wavenumber and the Ge composition at a stress-free condition, i.e., $\omega_{SS}=520.2-62x$, where ω_{SS} is the frequency of the Si–Si mode and x is the Ge composition, are shown on the right axis.[20] We note that the peak wavenumbers are not constant but both peaks shift to lower wavenumber from the catalyst side to the substrate side. At distance zero, i.e., the position at the catalyst, where the conformal deposition is very small, the Ge composition is about 0.19. The value is considered to be a Ge composition of the core grown by the VLS process. The Ge composition of the core increases with increasing the distance and saturates around 0.23. The increase of the Ge composition suggests diffusion of Ge from the higher Ge concentration shell to the core during the growth. Ge diffusion from the shell to the core decreases Ge composition of the shell. This effect is significant in the region where the shell is thin, i.e., when the distance from the catalyst is small. In fact, in Fig. 3(b), at 2 μm the Ge composition is about 0.29. It increases with the distance and saturates around 0.31 at about 8 μm. This saturated value is thought to be the Ge composition of the shell grown by the conformal deposition. The present results suggest that the Ge composition distribution depends not only on growth parameters such as inlet gas composition, temperature, etc., but also on the length. Therefore, growth duration is also an important parameter to control the energy band structure of SiGeNWs.

In conclusion, distribution of Ge composition in single SiGeNWs were studied by micro-Raman spectroscopy. We demonstrated that despite poor spatial resolution, micro-Raman spectroscopy is a powerful tool to characterize the inner structure of SiGeNWs when small regions of a single SiGeNW were analyzed systematically. The Raman results demonstrated that SiGeNWs have a core-shell structure with a low-Ge composition core grown by the VLS process covered with a high-Ge composition shell grown by the conformal deposition. Furthermore, detailed analysis of the Raman data revealed that Ge compositions in the core and the shell are not uniform but gradually change along the axis, i.e., there is Ge composition distribution both in the radial and axial directions. This implies that VLS-grown SiGeNWs have complicated energy band structures and they should be taken into account to design SiGeNW-based devices.

This work is supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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