Enhanced direct interband transitions in silicon nanowires studied by electron energy-loss spectroscopy

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We have experimentally observed abnormally enhanced direct interband transitions in silicon nanowires covered with SiO_2 layers by means of electron energy-loss spectroscopy (EELS). Core-diameter dependence of the EELS spectra was systematically studied. It was clarified that both E_1 and E_2 direct interband transitions of Si core are explicitly enhanced, owing to monopolar surface plasmons at a Si/SiO_2 interface whenever core diameter is small. We also discuss the effects of thickness of the oxide layers on the direct interband transitions.

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I. INTRODUCTION

Recently, much attention is focused on surface-plasmon waveguides in nanoscale as other types of photonic devices.[1] Core-shell nanowires, a candidate of the surface-plasmon waveguides, have potential ability to tune plasmonic properties by adjusting substances and thickness of both cores and shells. An important step toward nanowire plasmonics is to understand fundamental properties of valence-electron excitations comprehensively, i.e., core-diameter dependences and shell-thickness dependences of interband transitions, surface plasmons, and volume plasmons. Nevertheless, little is known experimentally about the properties. Electron energy-loss spectroscopy combined with transmission electron microscopy (TEM-EELS) is a powerful method to study valence-electron excitations in individual nanostructures. Peculiar valence-electron excitations have emerged from recent experimental TEM-EELS studies for nanotubes of C, BN, and WS_2,[2–5] Ge nanowires,[6] and Si tips.[7] Reed *et al.* found a strong peak at 5 eV in EELS spectra obtained from Si tips with diameter of 4 nm.[7] According to a dielectric theory,[8] it was explained that direct interband transition is significantly enhanced, owing to monopolar ($m=0$) surface plasmons when the diameter of tips is less than about 10 nm.[7] Although the theory predicted that monopolar surface plasmons exhibit both E_1 and E_2 transition peaks in spectra as shown in Fig. 4 of Ref. 8, there is only a broad 5 eV peak in previous experimental data by Reed *et al.*[7] In this paper, we report high-energy resolution TEM-EELS study on silicon nanowires (SiNWs) covered with SiO_2 layers, which can be regarded as a Si/SiO_2 core-shell nanowires. We clarified that both E_1 and E_2 direct interband transitions of Si core are explicitly enhanced, owing to monopolar surface plasmons whenever core diameter is small. The effect of thickness of the oxide layers (shell) on the direct interband transition is also discussed. This robust experimental result will lead to much interest in a possibility of efficient core-shell nanowire waveguides based on semiconductor materials.

II. EXPERIMENT

SiNWs were synthesized by chemical-vapor deposition using monosilane (SiH_4) as a source gas, gold as catalysts, and templates of a hydrogen-terminated Si (111) surface.[9–11] To prepare specimens for EELS measurements, we grew long SiNWs of 5–30 μm on the templates. As-grown SiNWs are covered by oxide layers, so we refer to them as thick-shell SiNWs. Thick-shell SiNWs were removed from the template in ethanol by ultrasonication. Then, a copper mesh grid with carbon films was dipped into the ethanol where thick-shell SiNWs were dispersed. The long thick-shell SiNWs were easily bridged between carbon films across a hole. Utilizing the bridged SiNWs, we obtained EELS spectra only from SiNWs. We also prepared thin-shell SiNWs to investigate the effect of oxide layers on EELS spectrum. Thick-shell SiNWs were dipped into a 1% HF solution for 5 min to reduce the thickness of oxide layers, converting into thin-shell SiNWs. We have observed the SiNWs by high-resolution TEM (HRTEM) at accelerating voltages of 100–200 kV, and measured the thickness of oxide layers and the diameters of Si core. There were errors of measurement that were caused by uncertainties of boundaries between Si cores and oxide layers: thick-shell SiNWs are usually covered with 1–3.5 nm oxide layers in our growth method and the oxide layers of thin-shell SiNWs are about 0.5–1 nm in thickness.[12] The SiNWs were carefully transferred into a TEM-EELS microscope with high-energy resolution,[13] which was operated at the attainable maximum accelerating voltage of 70 kV. The energy resolution, or the FWHM of the zero-loss peak, was estimated to be 0.15–0.21 eV throughout this study, in which the zero-loss peak was obtained from the carbon films. The size of the illuminated area is about 100 nm in diameter. Using an objected aperture (20 μm ϕ), fast electrons are collected from a specimen area of 60 nm in diameter, where a single SiNW is placed in the center. Fast electrons penetrate the SiNWs nearly normally to the growth axis. Collection semiangle was 5 mrad and typical acquisition times were set at 10–30 s.

III. RESULTS

First, we give an overview of structures and EELS spectra of SiNWs. As shown in Fig. 1, it is confirmed that a thick-shell SiNW is covered with an oxide layer of about 1–2 nm in thickness, while a thin-shell SiNW is covered with an

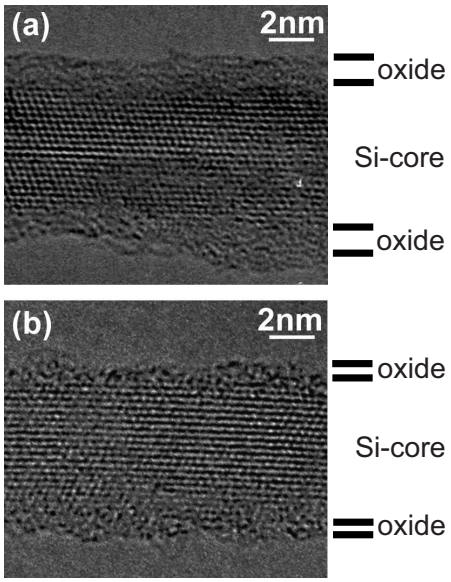

FIG. 1. HRTEM images of (a) a thick-shell SiNW and (b) a thin-shell SiNW.

oxide layer of about 1 nm. Figures 2(b) and 3(b) show a series of EELS spectra obtained from thick-shell and thin-shell SiNWs, respectively. The background spectra due to the tails of the zero-loss peaks were subtracted by Lorentzian fitting.[3] Figures 2(a) and 3(a) show row spectra in the region

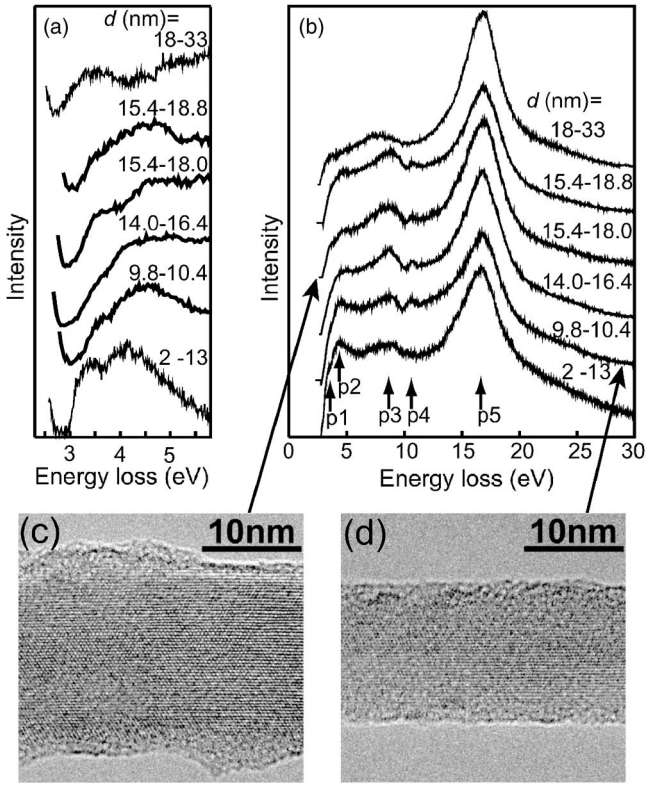

FIG. 2. The dependence of EELS spectra of thick-shell SiNWs on core diameters d (a) before and (b) after the zero-loss tails are subtracted. [(c) and (d)] HRTEM images of SiNWs utilized for the EELS measurements.

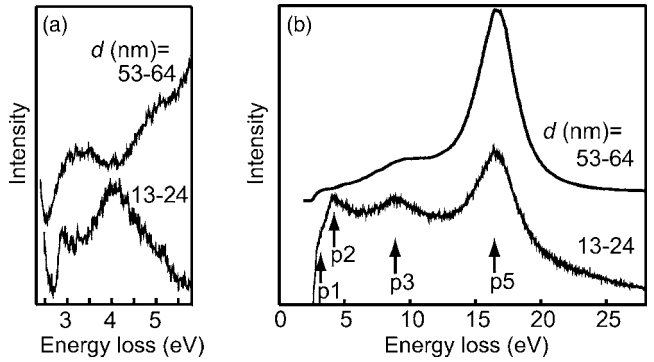

FIG. 3. EELS spectra from thin-shell SiNWs (a) before and (b) after the zero-loss tails are subtracted.

up to 5.8 eV before the background spectra were subtracted. The core diameters d are indicated at the right sides of the spectra. There exist five kinds of peaks indicated by p1, p2, p3, p4, and p5 in Figs. 2(b) and 3(b); the p1 peak is revealed as a shoulder of the p2 peak. Figures 2(a) and 3(a) verify the existence of the p1 peaks. The most remarkable change in spectra as the core diameter decreases is that the spectra exhibit both the p1 and p2 peaks explicitly and their intensities relative to the p3 and p5 intensities increase. This is the experimental data that shows systematic variations of low-loss EELS spectra with the decrease of core diameters of core-shell nanowires.

A. Peak assignment

For essential peaks in this study, the thick-shell SiNWs have the p1 peaks at 3.3–3.6 eV and the p2 peaks at 4.1–4.7 eV, and the thin-shell SiNWs have the p1 peaks at 2.9–3.3 eV and the p2 peaks at 4.1–5.0 eV, although the spectrum features are somewhat different depending on core diameter. Feature of this double peak becomes explicit as core diameter decreases. We can attribute the p1 and p2 peaks at 3–5 eV to two direct interband transitions in crystalline Si known as E_1 at 3.4 eV and E_2 at 4.25 eV,[14] respectively, by the following reasons. The imaginary part of the dielectric function of Si, $\mathrm{Im}[\epsilon_{\mathrm{Si}}]$, which is related to single-electron excitations, has sharp peaks at 3.4 and 4.25 eV.[14] Actually, the interband-transition peak in an EELS spectrum reflects the feature of $\mathrm{Im}[\epsilon]$, although the EELS peak is slightly shifted from the energy of the maximum in $\mathrm{Im}[\epsilon]$.[15,16]

The main peak, p5, in Figs. 2(b) and 3(b) ranges between 16.6 and 16.9 eV. The p5 corresponds to the volume plasmon peak, which is located at 16.7 eV in bulk Si.[15] For Si clusters of 3.5–10 nm in diameters, the peak energy shifts toward higher energy and the spectra are broadened as the cluster sizes decrease.[17] For Ge nanowires, the peak energy increases significantly when the diameters d are less than about 25 nm.[6] It is likely that the blueshifts occur when d is smaller than the Bohr diameters, ~10 nm for Si and ~48 nm for Ge, although the reason is still under discussion.[6,17] Our experimental result agrees with those reports since the peak shift does not occur when $d > 10$ nm.

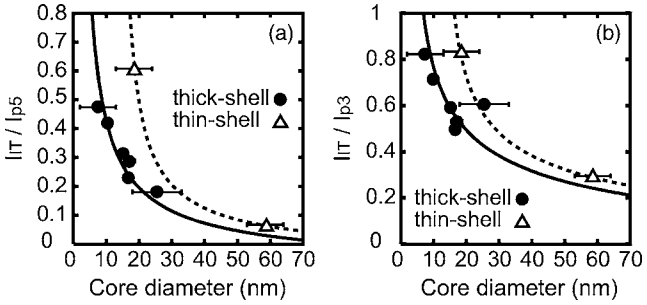

FIG. 4. I_{IT}/I_{p5} and I_{IT}/I_{p3} as a function of core diameter.

The broader p3 peaks, which are seen at 7.0–8.7 eV for thick-shell SiNWs and at 8.7–10 eV for thin-shell SiNWs, are attributed to excitations of plasmons at the Si/SiO_2 interfaces, by the following reasons. The plasmon energy at a planar Si/SiO_2 interface is 7–9 eV,[18–20] which is in good agreement with the p3 peak energies of thick-shell SiNWs. Actually, Fig. 6(b) shows a peak around 7.9 eV. On the other hand, the p3 peaks of thin-shell SiNWs are located at slightly higher energy than those of thick-shell SiNWs. When the thickness of SiO_2 overlayers is extremely decreased, the interface plasmon energy should approach the surface-plasmon energy of bare-Si structure, 11.6 eV.[21] Furthermore, the spectrum from a SiNW with a large diameter should be analogous to that from a silicon foil. Good agreement of p3 peak energies with one at the planar interface is presumably due to the prismatic shape of SiNWs,[9] which probably have long and narrow flat interfaces.

The p4 peaks at 10.2–10.8 eV are seen only in four thick-shell SiNWs in Fig. 2(b). The p4 peak is presumably attributed to the interband transitions in SiO_2 overlayers, since previous study reported that EELS spectrum from thin amorphous SiO_2 has one of the interband-transition peaks at lowest energy of 10.6 eV.[16] However, it is unusual that the peak intensity is stronger than volume plasmon peaks of SiO_2 to be located at 22.4 eV (Ref. 15) in Fig. 2(b). Although primary clarification of the EELS spectra was accomplished, further discussion is required to interpret the origin of the p4 peak.

B. Core-diameter and shell-thickness dependences of the direct interband transitions

Figure 4(a) plots integral intensity of the direct interband transition I_{IT} relative to integral intensity of the p5 peak I_{p5} as a function of core diameter, where I_{IT} and I_{p5} are defined as integral intensities in the regions 2.8–5.2 and 15.5–17.9 eV, respectively, for thick-shell SiNWs. Figure 4(b) plots I_{IT} relative to integral intensity of the p3 peak I_{p3} as a function of core diameter, where I_{p3} was integrated between 7.4 and 9.8 eV for thick-shell SiNWs. For thin-shell SiNWs, I_{IT}, I_5, and I_3 are defined as integral intensities in the regions 2.6–5.0, 15.4–17.8, and 7.9–10.3 eV, respectively, in Fig. 4. Clearly, it was found out that both I_{IT}/I_{p5} and I_{IT}/I_{p3} give steep increase with decrease in core diameter for both thick-shell and thin-shell SiNWs. The unusual increases cannot be explained by simple pictures: both I_{p5} and I_{IT} are proportional to the volume of core Si, and I_{p3} is proportional to surface area. We clarify this behavior in Sec. IV.

Figure 4 also shows that both I_{IT}/I_{p5} and I_{IT}/I_{p3} of the thin-shell SiNW are stronger than those of the thick-shell SiNW for a given core diameter. In other words, the direct interband transitions in Si core are enhanced as the shell thickness decreases. This result suggests that we can tune behavior of interband transitions in core-shell nanowires, changing the shell thickness and replacing SiO_2 shell with other reasonable materials.

IV. DISCUSSION

We discuss why both I_{IT}/I_{p5} and I_{IT}/I_{p3} increase as core diameter decreases. In our experiment, it is considered that there are two compound contributions to the increase: peculiar excitation both at the surface and in the bulk. Using a model of cylindrical bare-Si nanowire embedded in a vacuum, Reed *et al.* and Zabala *et al.* showed theoretical characteristics of two kinds of surface plasmons, i.e., monopolar ($m=0$) and multipolar ($m \geqslant 1$) modes.[7,8] The smaller the transferred momentum is, the larger the monopolar contribution is, with respect to other multipolar modes since the multipolar surface-response function is of order m scales as d^{2m}.[22] Simultaneously, the monopolar surface-response function approaches to $\mathrm{Im}[\epsilon_{\mathrm{Si}}]$ as the transferred momentum is small. If only surface contributions are considered, we can say that the smaller the diameter, the closer to $\mathrm{Im}[\epsilon_{\mathrm{Si}}]$ the whole surface response is, and thus the higher the interband transition is. Actually, previous studies showed only the surface contribution using a fine electron probe placed aloof from a nanowire.[6] For the bulk contribution, the interband transitions also appear in the Si core as a usual bulk contribution, although they are in a much less intense fashion than the volume plasmon or than the interband transitions in the surface contribution. It should be noted that the begrenzung effect decreases both interband transitions and volume plasmons in the bulk contribution.[23] This effect can become prominent in nanostructures owing to a small volume and/or surface area ratio. Consequently, a reduction in diameter causes following variation: (i) increase in the contribution of monopolar mode; (ii) approach of the monopolar response function to $\mathrm{Im}[\epsilon_{\mathrm{Si}}]$; (iii) decrease in the bulk contribution with respect to the surface contribution. This leads to the apparent enhancement of the interband transitions.

Here, we elucidate the characteristic of monopolar- and multipolar-surface plasmons at more realistic interface, i.e., the Si/SiO_2 interface, utilizing a simple model: we assume a cylindrical nanowire of bare-Si buried in an *infinite* SiO_2 medium as an extreme case of a thick-shell SiNWs to simplify a problem. The cylindrical surface-response function γ_m is given by[8]

$$\gamma_m(x,\omega) = \frac{x^{-1}}{\epsilon_1(\omega) I_m'(x) K_m(x) - \epsilon_2(\omega) I_m(x) K_m'(x)}, \quad (1)$$

where $x=qd/2$, $\epsilon_1=\epsilon_{\mathrm{Si}}$ and $\epsilon_2=\epsilon_{\mathrm{SiO_2}}$ are the dielectric functions of Si and SiO_2, respectively, ω and q are the energy and

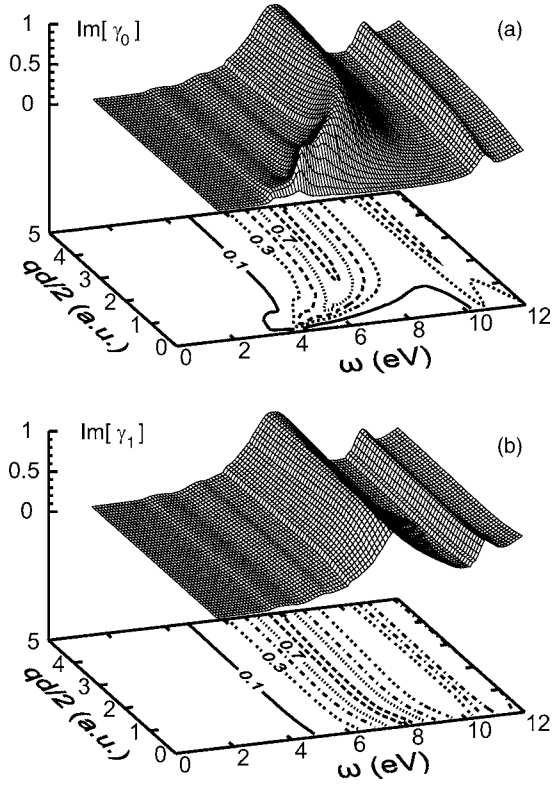

FIG. 5. Plots of surface-response functions of a model SiNW surrounded by an *infinite* SiO_2 medium for (a) monopolar mode ($m=0$) and (b) one of multipolar mode ($m=1$).

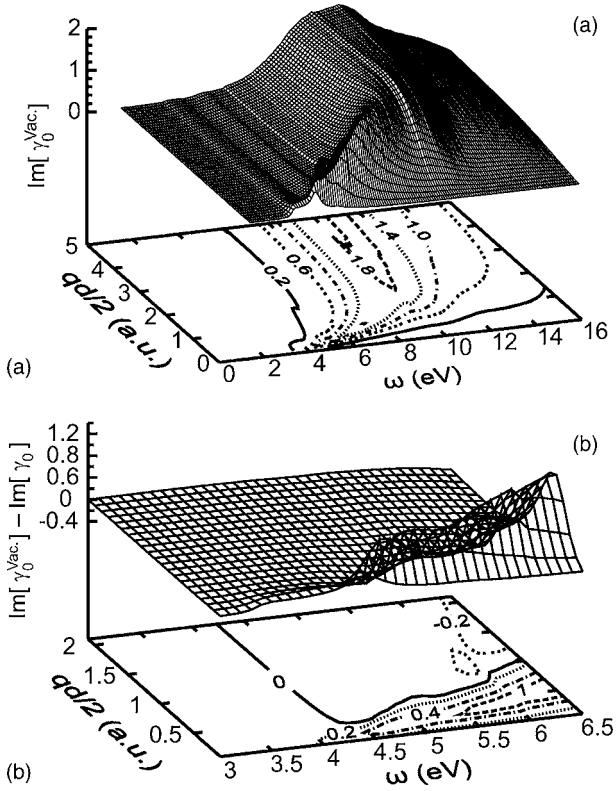

FIG. 6. Plots of (a) surface-response function of a model SiNW embedded in a vacuum for monopolar mode ($m=0$) (Ref. 8) and (b) $\zeta=\mathrm{Im}[\gamma_0^{\mathrm{vac}}]-\mathrm{Im}[\gamma_0]$.

momentum of collective electron oscillation along the axis of the cylinder, respectively, K_m and I_m are the modified Bessel functions,[24] and the prime stands for the derivative with respect to the argument x. We use a.u. The surface loss function is proportional to a weighted sum on m of the imaginary part of γ_m, $\Sigma_m(\alpha_m \cdot \mathrm{Im}[\gamma_m])$, where α_m is weighting coefficient.[8] Figure 6(a) plots $\mathrm{Im}[\gamma_m]$ for monopolar mode ($m=0$), $\mathrm{Im}[\gamma_0]$ and Fig. 6(b) plots $\mathrm{Im}[\gamma_m]$ for one of multipolar modes ($m=1$), $\mathrm{Im}[\gamma_1]$ (Ref. 25) using $\boldsymbol{\epsilon}_{\mathrm{Si}}$ and $\boldsymbol{\epsilon}_{\mathrm{SiO_2}}$ from Refs. 14 and 26–28. Monopolar and multipolar modes have different energy dependences on qd: other multipolar modes ($m=2,3,4,\ldots$) have similar behaviors (not shown here) with the $m=1$ mode.[29] Multipolar modes are associated with collective electron oscillations at a cylindrical interface almost independently on qd.[7] Actually, in Fig. 6(b), a multipolar mode has an energy around 7.9 eV, which corresponds to the plasmon energy at a planar Si/SiO_2 interface, 7–9 eV.[18–20] It is considered that this peak at 7.9 eV in Fig. 6(a) contributes to the origin of the p3 peak in Fig. 2. On the other hand, in Fig. 6(a), the energy of monopolar mode strongly depends on qd. When qd is large, the monopolar mode degenerates with the multipolar mode. Remarkably, $\mathrm{Im}[\gamma_0]$ has two peaks at $\omega=3.5$ and 4.4–4.8 eV, reflecting $\mathrm{Im}[\boldsymbol{\epsilon}_{\mathrm{Si}}]$ only when qd is small. These two peaks are very similar to the p1 and p2 peaks in the EELS spectra. As d decreases in our experiment, it seems that $qd/2$ approaches roughly around 0.3 a.u. in which region the two peaks in $\mathrm{Im}[\gamma_0]$ clearly exist. Consequently, we can consider that the two peaks in $\mathrm{Im}[\gamma_0]$ contribute to the increase in the probability of both E_1 and E_2 transitions when core diameter is small, resulting in the steep increase in both I_{IT}/I_{p5} and I_{IT}/I_{p3}.

We briefly discuss shell-thickness dependences of the direct interband transitions. As shown in Fig. 4, both I_{IT}/I_{p5} and I_{IT}/I_{p3} of the thin-shell SiNW are stronger than those of the thick-shell SiNW for a given core diameter. Analogous to the plots in Fig. 5, we have calculated the surface-response function of a bare-SiNW embedded in a vacuum, defined as $\mathrm{Im}[\gamma_m^{\mathrm{vac}}]$ using Eq. (1) and plotted in Fig. 6(a): this calculation was carried out by Zabala *et al.*[8] $\mathrm{Im}[\gamma_0^{\mathrm{vac}}]$ has two peaks at $\omega=3.6$ eV and 4.4–4.8 eV when qd is small. To compare intensities of the interband transitions induced by the monopolar surface modes, we plotted the difference between their surface-response functions, $\zeta=\mathrm{Im}[\gamma_0^{\mathrm{vac}}]-\mathrm{Im}[\gamma_0]$, as shown in Fig. 6(b). It is appropriate to discuss the qualitative difference using Fig. 6(b) since the weighting coefficient α_0 is common to both responses under the same experimental condition.[8] In Fig. 6(b), we can focus on the region of $\omega=3$–5 eV and $qd/2=0.1$–0.3, where the feature of $\mathrm{Im}[\boldsymbol{\epsilon}_{\mathrm{Si}}]$ clearly appeared in both $\mathrm{Im}[\gamma_0^{\mathrm{vac}}]$ and $\mathrm{Im}[\gamma_0]$. In this region, ζ ranges from 0.01 to 0.95. It can be said that the interband transitions induced by the monopolar surface response at the Si/vacuum interface are higher than those at the Si/SiO_2. In other words, decrease in the SiO_2 shell thickness can lead to the increase in the probability of the direct interband transitions.

V. CONCLUSION

In conclusion, we have measured systematic variation of EELS spectra of SiNWs covered with SiO_2 layers. It was clarified that both E_1 and E_2 direct interband transitions of Si core are enhanced owing to monopolar surface plasmons at a Si/SiO_2 interface whenever the core diameter is small. Furthermore, it was found that the transitions are enhanced as the shell thickness decreases.

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