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Spectroscopic Changes of Silicon Nanowires Induced by Femtosecond Laser Pulses

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When HF-treated silicon nanowires (SiNWs) were irradiated by femtosecond laser pulses, three new energy transitions appeared in the UV region, which might be attributed to defect-related deep levels, especially oxygen and silicon vacancies rather than their morphology and structure changes.

Silicon nanowires (SiNWs) have attracted much attention in recent years due to their entranced electrical/optical properties and potential applications. In order to tune the band gap and induce a useful level of optical gain of SiNWs, which may provide an excellent platform for novel optoelectronic devices in energy harvesting and conversion and biosensing, many methods have been developed, including surface nanoporous treatment,[1] surface modification with metal nanoparticles,[2] and morphology control.[3] However, limitations exist for these methods, such as complex processes and introduced impurities. Ultrashort pulsed lasers such as femtosecond lasers are considered powerful tools for inducing nonlinear optical effects or microscopic modifications inside solid materials because of their high power density of more than 10 TW cm^{-2} and their ultrashort pulse width.[4] It was reported that the structure and surface properties of materials could be modified by irradiating their surfaces with femtosecond lasers.[5] In this study, femtosecond laser treatments were applied on SiNWs, and the effects of femtosecond laser pulses on the optical properties of SiNWs were investigated. To the best of our knowledge, such study has not yet been reported.

SiNWs were prepared by a slightly modified thermal evaporation method, and the as-prepared SiNWs were etched with aqueous HF to remove their surface oxide layer (see Supporting Information).[6] Typical transmission electron microscopy (TEM) images of the as-prepared and HF-treated SiNWs are shown in Figures 1a and 1b. Clearly, the as-prepared SiNWs had an average diameter of 20 nm, a silica shell of 2/5 outer diameter and a length of several micrometers. After treatment with aqueous HF, the SiNWs were uniform in diameter, and their average diameter decreased to 12 nm. Figure 1c shows a Raman scattering spectrum of the HF-treated SiNWs. The peaks at 514 and 952 cm^{-1} are attributed to SiNWs.[7] They are symmetric and narrow, indicating that the SiNWs were uniform in diameter, in good agreement with the TEM results. Further more, the peak at 514 cm^{-1} is probably due to the downshift of the peak at 520 cm^{-1} of standard Si,[8] and it was claimed that this downshift is due to phonon confinement. The X-ray diffraction (XRD) pattern of HF-treated SiNWs is shown in Figure 1d. Two peaks were observed at $2\theta = 28.54$ and 47.46° and could be assigned to the (111) and (220) planes of silicon (JCPDS 73-2534). Silica ($2\theta = 21.37°$) could also be detected and attributed mainly to quartz substrate, which was used to support SiNWs.

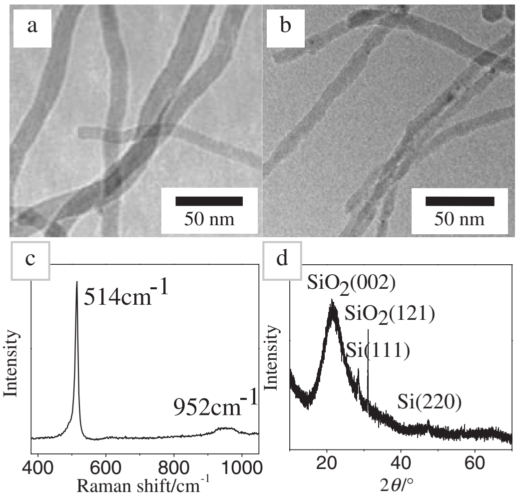

Figure 1. TEM images of as-prepared (a) and HF-treated (b) SiNWs, Raman spectrum (c) and XRD pattern (d) of HF-treated SiNWs.

The femtosecond laser beam used was produced by a regenerative amplified mode-locked Ti:sapphire laser (pulse width: 200 fs and repetition rate: 10 Hz) operating at a wavelength of 800 nm. The beam diameter and pulse energy were estimated to be 8 mm and 0.7 mJ. The laser beam was focused on the center of defined positions for varied periods of irradiation time (9, 13, 17, and 21 s) at room temperature (Figure S1).

Figure 2 shows UV–vis spectra of SiNWs recorded before and after varied periods of laser irradiation time. The spectrum profiles for four locations before irradiation were generally identical. However, slightly different absorption intensities were noted, which was probably due to different thicknesses at the four locations of the SiNWs film. The long absorption tail (400–800 nm) was attributed to the indirect band gap of silicon. In the UV region, one absorption peak appeared at ca. 355 nm, which was due to the direct transition at the Γ point [$\Gamma_{25} \rightarrow \Gamma_{15}$]. The second absorption peak at ca. 282 nm was associated with another direct transition, most likely the $\Gamma_{25} \rightarrow \Gamma_{2'}$ transition or possibly at X. The third absorption peak at ca. 225 nm was probably attributed to the direct transition at X or L.[9]

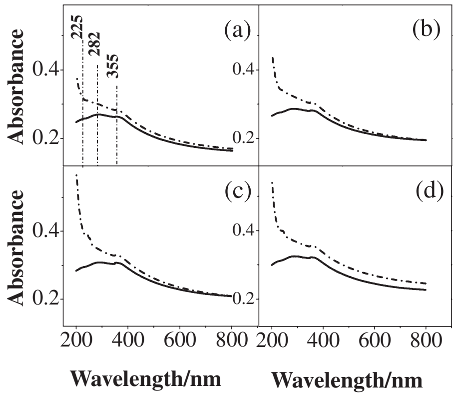

Figure 2. UV–vis spectra of HF-treated SiNWs on quartz plate before (——) and after (–•–•) femtosecond laser irradiation for 9 (a), 13 (b), 17 (c), and 21 s (d), respectively.

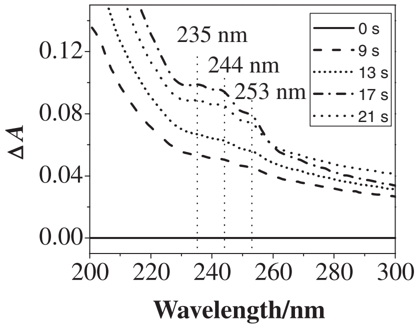

Figure 3. Difference UV–vis spectra of HF-treated SiNWs on quartz plate irradiated with femtosecond laser for 9 (a), 13 (b), 17 (c), and 21 s (d), respectively. The difference spectra were obtained by subtracting the spectrum before laser irradiation from that after laser irradiation.

After femtosecond laser irradiation, the optical absorption increased in the whole range of 200–800 nm. The absorbance increases with decrease of wavelength, and the characteristic peak at ca. 282 nm became insignificant. Thus, femtosecond laser irradiation increased the optical absorption of SiNWs, especially in the UV region. These absorption properties may hold great promise for future applications in ultraviolet optoelectronics technologies such as external modulation and data coding in secure nonline-of-sight communication systems.[10] It is very interesting that after irradiation, three new absorption peaks appeared at 235, 244, and 253 nm between the absorption peaks at 225 and 282 nm, as shown in Figure 3. Clearly, the absorption peaks at 235, 244, and 253 nm increased gradually with increase of irradiation time from 9 to 17 s and then decreased slightly when irradiation time further increased to 21 s. The change in the optical properties of SiNWs points to the significant effects of femtosecond laser irradiation, which may have induced the change of SiNW surface structure.

In order to study the structural evolution of SiNWs under laser irradiation, TEM and selected area electron diffraction (SAED) were used to follow the structural change before and after laser irradiation. As shown in Figure S2,[6] neither the morphology and diameter of SiNWs nor the SAED patterns of SiNWs had significant change before and after laser pulse irradiation, indicating that the femtosecond laser pulses did not change the morphology and internal crystal structure of SiNWs.

It was reported that defects might lead to new energy transitions with intense absorption peaks.[11] Considering that the experiments were carried out under ambient conditions, the laser irradiation should not have introduced any impurities other than crystal silicon and amorphous silica. However, defects such as oxygen and silicon vacancies might have appeared under the laser irradiation. Thus, the appearance of three new absorption peaks was probably attributed to defect-related deep levels, especially oxygen and silicon vacancies. The structural defects most likely produced bands of defects and impurity states in the band gap and thus led to several new energy transitions. As a result, the optical absorption was enhanced, especially in the UV region.

In summary, HF-treated SiNWs showed remarkable optical absorption enhancement by femtosecond laser irradiation. New absorption peaks appeared at 235, 244, and 253 nm, probably due to the formation of surface defects. The new optical absorption properties may endow these SiNW materials with great application potentials in solar cells and other optoelectronics devices to enhance their optoelectronics efficiency and sensitivity.

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