Active Control of the Oxidization of a Silicon Cantilever for the Characterization of Silicon-based Semiconductors

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We propose a novel technique of oxidizing silicon cantilever tips to characterize silicon-based semiconductors by tip-enhanced Raman measurements. The technique uses thermal oxidization process under steam atmosphere. It is aimed for the suppression of Raman scattering originating from the silicon tip itself without degrading the tip sharpness. The thickness of the oxidized silicon on the silicon tip is controlled by the thermal oxidization time. We successfully obtained 250-nm thick silicon dioxide in 1100 °C temperature under steam at 10-min oxidization time. Using the oxidized tip, we experimentally verified that silicon Raman vibration was completely suppressed.

Nanoelectromechanical systems (NEMS) provide compact and highly reliable sensors and actuators.[1] Silicon (Si) is a widely used substrate for NEMS devices because the Si-processing technology has great advantages in terms of high reproducibility and the capability of batch fabrication. Device miniaturization by NEMS requires nanometer characterization of Si devices. Finding out lattice defects, impurities, stress state, etc. of Si devices in the nanometer scale are the key issues that need to be studied in order to improve integration with NEMS devices.

Tip-enhanced Raman spectroscopy (TERS) is a promising tool for nondestructive characterization of Si devices in the nanometer scale.[2,3] Raman scattering cross section is inherently very small ($\approx 10^{-30}\,cm^2$). However, tips coated with silver have successfully enhanced the weak Raman signal due to excitation of localized surface plasmon polaritons.[4,5] The spatial resolution is determined not by the excitation wavelength but by the tip diameter which is ≈30 nm.[6]

Commercially available Si cantilever tips are widely used as a base material for TERS tips.[6–8] It is cost effective, and tip-height control by AFM provides a convenient and efficient way to regulate tip-sample interaction in TERS measurement. Si tips are also advantageous in terms of the reproducibility of tip shapes and the variety of available force constants compared with other non-Si tips. However, at room temperature, the Si–Si phonon mode of Si is observed at $520\,cm^{-1}$.[9] When we observe Si samples by TERS using silver-coated Si tip, the Raman signal from the tip overlaps with Raman signals from Si sample at $520\,cm^{-1}$.[2]

In this letter, we thermally oxidized commercially available Si cantilever tips. We devised Si tip to suppress the Si–Si phonon mode of the tip. The processed tip surface is oxidized from Si to amorphous silicon dioxide (SiO_2) without degrading the tip sharpness. The proposed method is quite advantageous compared to SiO_x coated Si tip by deposition, which makes tip apex dull.[10]

Thermally oxidizing Si cantilever at 1100 °C with steam will convert Si surface to SiO_2. Si cantilevers mounted on a quartz boat is inserted into a furnace which is heated up to 1100 °C. Simultaneously, steam generated from boiled pure water is fed into the furnace. Figures 1a and 1b show the transmission electron microscope (TEM) images of the oxidized Si cantilevers (Advanced TEC Cont provided by Nanosensors). Contrast difference between the non-oxidized (Si) part and oxidized (SiO_2) in the tip is observed. The bright areas represent the SiO_2 while the dark areas denote the Si. In Figure 1a, the thickness of 100-nm SiO_2 layer was obtained by 3-min oxidization. The inset

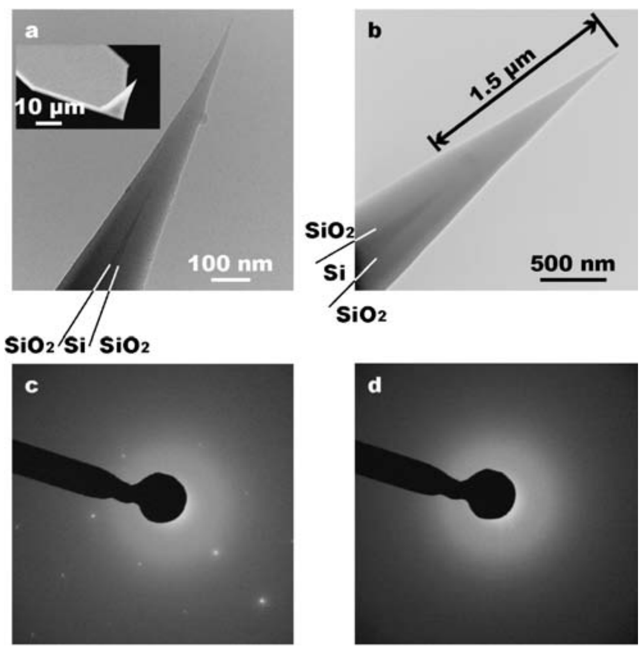

Figure 1. TEM images of the oxidized Si tips at different thermal oxidization time. (a) 100-nm and (b) 250-nm thick SiO_2 layer were obtained at 3-min and 10-min oxidization, respectively. Diffraction patterns of the 250-nm SiO_2 tip were observed at the (c) Si part and the (d) tip apex.

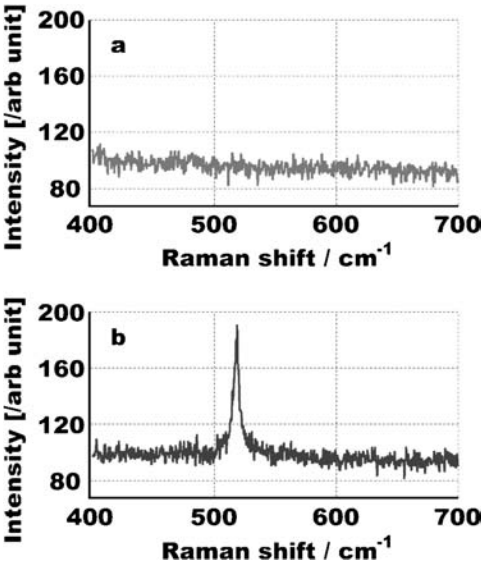

Figure 2. Raman spectra of (a) oxidized Si tip and (b) bare Si tip.

in Figure 1a shows the entire image of cantilever tip observed by scanning electron microscope (SEM). The original sharpness of tip is preserved even after the thermal oxidization. Figure 1b shows the result of 10-min thermal oxidization. In this case, 250-nm thick SiO_2 layer was obtained on the tip surface. The sharpness was still kept.

In order to suppress the Raman scattering of Si tip itself, the volume of SiO_2 has to be larger than the focal volume of excitation laser spot. Thermal oxidization method provides a thick SiO_2 layer with the micrometer length from the tip end just for several minutes, such as $\approx$1.5 µm shown in Figure 1b. The micrometer length of SiO_2 is long enough to suppress Raman signal of Si in the use of both transmission[5,6] and reflection[2,3] mode TERS system. This is because in case of transmission mode,[5,6] the decay length of evanescent field produced by a high N. A. (=1.4) objective lens is $\approx$100 nm. In the case of reflection mode,[2,3] the diffraction limited focused spot by a long working distance objective lens is comparable to micrometer order for visible wavelength excitation.

Figures 1c and 1d show the electron diffraction patterns obtained at the Si part of the tip and the tip apex, respectively. We see a diffraction pattern of diamond-like structure at the Si part, while no diffraction pattern was observed at the tip apex. This fact confirms that the tip apex consists of amorphous SiO_2.

We also spectrally verified the material transformation of the tip from Si to amorphous of SiO_2 by comparing Raman spectra of oxidized Si tip and bare Si tip. In this experiment, an expanded and collimated light from frequency-doubled CW YVO_4 laser (532 nm) was directed to an inverted microscope, and light was focused onto the glass substrate from the bottom side using objective lens (N. A. = 1.4; oil). An annular mask was placed on the collimated light path to make evanescent field illumination on the glass substrate.[5,6] The oxidized tip was positioned inside the focal spot. Raman scattering signal from the oxidized tip apex was collected and guided to a spectrometer (ACTON SpectraPro 2300i, 2400 grooves/mm, slit: 100 µm) and detected by liquid-nitrogen-cooled charge-coupled device (CCD) camera.

Raman spectrum shown in Figure 2a was obtained from the tip oxidized for 10 min. Compared with Raman spectrum of Si tip shown in Figure 2b, Si–Si phonon mode from the tip at 520 cm^{-1} has been completely suppressed. This observation also supports the fact that the original Si material at tip apex was completely oxidized.

Note that thermal oxidization method of Si cantilevers also changes the refractive index of the tip. Because SiO_2 has the lower refractive index compared to Si, plasmon resonance frequency of silver which is coated on oxidized Si tip would be shifted to shorter wavelength.[8,10] Since the thickness of SiO_2 is controllable in the order of nanometer scale by changing the oxidization time, it is expected that effective plasmon resonance frequency can also be manipulated. This is analogous to the mechanism of metallic nanoshell.[11]

In conclusion, SiO_2 tip was obtained by the simple method of thermal oxidization. The sharpness of the tip was kept as the same as before oxidization. Thermal oxidization for fabrication of SiO_2 tips is a new approach to attain ultrasharpened SiO_2 tips with 10 nm in diameter. From measured Raman spectra, we demonstrated there is no Si–Si phonon mode signal from the oxidized tip. It is expected that oxidized Si cantilever tips would be applied to the nanosensing and the characterization for NEMS devices, semiconductors, and so on.

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