Electrical Double Layer Catalyzed Wet-Etching of Silicon Dioxide

Supporting Information

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Growth of Carbon Nanotubes (CNTs)

Si substrate with 300 nm thermal oxide was cleaned with piranha solution (WARNING: Piranha solution reacts violently with many organic materials and should be handled with extreme care. All work should be performed in a fume hood.). Aqueous solution of FeCl₃ (0.01 M, filtered through 0.2 µm filter) was applied onto one end of the wafer with a cotton swab. The substrate was calcined at 900 °C in air for 1 hr in a quartz tube that was heated in a tube furnace. The CNT growth was initiated by flowing a mixture of Ar (250 sccm) and H₂ (25 sccm) through the quartz tube at 900 °C. The gas mixture was saturated with EtOH vapor by flowing through a bubbler that was filled with ice-cold absolute EtOH before it enters the quartz tube. The growth time was 1 hour. After the growth, the tube furnace was allowed to cool to r.t. under flowing Ar/H₂. The diameter of the as synthesized CNT was measured with a Nanoscope III AFM using the tapping mode. Figure S1 shows the diameter distribution of the CNTs.

Patterning Mark

E-beam lithography: The substrate with CNTs was spin coated with a layer of PMMA (3k rpm, 1 min, 950K PMMA C5, MicroChem) and baked on a hot plate at 180 °C for 2 min. E-beam lithography was carried out using an FEI field emission SEM equipped with an NPGS system.

The pattern was developed in 1/3 MIBK/IPA developer (MicroChem) for 1 min. A layer of Au (50 nm) with a Cr or Ti adhesion layer (5 nm) was evaporated onto the substrate using a thermal or e-beam evaporator. Lift-off was achieved by soaking the substrate in CH₂Cl₂ overnight. An SEM image of the mark along with a CNT is shown in Figure S1.

Shadow masking: The substrate with CNTs was evaporated a layer of Au (50 nm) with Cr or Ti adhesion layer (5 nm) using an index TEM grid (SPI, 200 mesh) as a shadow mask. An e-beam evaporator with a long throw distance (> 50 cm) was used. The shadow masked evaporation produce arrays of Au squares that are about 100 μ m in size and separated by about 20 μ m from each other.

Etching

The substrate with the mark was imaged with SEM (Hitachi S-4700) to locate the CNTs relative to the mark. The substrate was then placed in a glass vial that was filled with 0.26 M of TMAH (MF CD-26 developer, Microposit) or 0.26 M of NaOH. The solution was heated in an oil bath at 50 °C for 2 – 12 hours. After the reaction, the substrate was rinsed with deionized water and dried with a stream of N2. The area where the CNT was known to exist was imaged with tapping mode AFM.

Electrical Measurement

Source and drain electrodes (50 nm Au with 5nm Cr adhesion layer) were patterned onto the trench with e-beam lithography as described above. The source and drain electrodes were contacted with a probe station and the electrical properties were measured with a semiconductor analyzer. The Si substrate was used as the back gate.

Raman Spectroscopy

We used a home build micro-Raman setup that consists of an inverted microscope fitted with a 40 x objective (NA: 0.60), a holographic notch filter, and a single stage 0.27-m spectrograph fitted with a liquid N₂ cooled CCD camera. A He-Ne laser (633 nm, laser power before entering the microscope: 4 mW) was used as the light source. The sample with SiO₂ trench was placed on a translational stage. The trench is invisible under the optical microscope; its approximate location was located relative to the Au/Cr marks. The polarization of the laser was parallel to the trench. Several to several tens of Raman spectra were collected by scanning the laser beam across the trench. This ensures that at least one of the spectra was collected while the laser was focused on the trench. No Raman peak of CNT was observed from the trenches.

Etching Rate of Bulk SiO₂

A clean Si substrate (300 nm of thermal oxide) was cleaved into two pieces. One piece was immersed in a vial that was filled with 0.26 M of TMAH and the other was immersed in a vial

that was filled with deionized water. Both vials were tightly capped and heated in an oil bath at 50 °C for 143 hours. The two substrates were rinsed with deionized water and dried with a stream of nitrogen. The thickness of the oxide layers were measured with an ellipsometer (Rudolph EL III, three measurements each) to be 302.47 ± 0.12 nm and 275.53 ± 0.16 nm for the wafers in water and in TMAH, respectively. The average etching rate of SiO₂ by TMAH was calculated to be 0.188 ± 0.002 nm per hour.

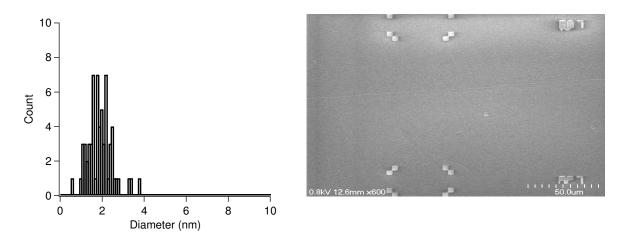


Figure S1. (Left) Diameter distribution of the as synthesized CNTs. (Right) An ultra-long CNT near a set of marks.

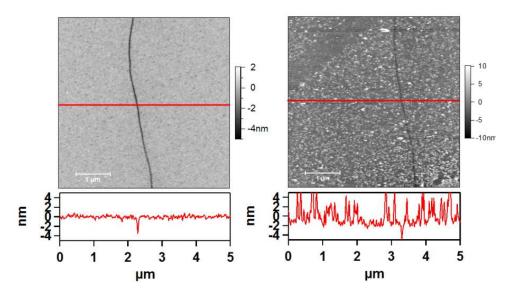


Figure S2. AFM images and line profiles of SiO₂ trench produced by etching with 0.26 M of TMAH (Left) and 0.26 M of NaOH (Right).

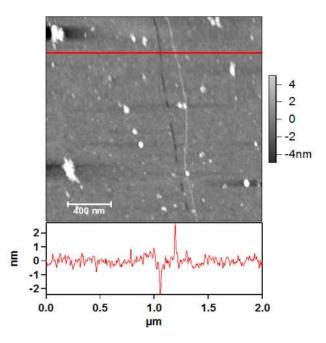


Figure S3. (Up) Tapping mode AFM image of a carbon nanotube on the side of a trench. (Bottom) A line profile of the image.