Synthesis of Nickel Nanowires Via Electroless Nanowire Deposition on Micropatterned Substrates

Supporting Information

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Experimental section

Materials and Sample Preparation. Gold and chromium were obtained from Alfa Aesar, Inc. (Ward Hill, MA) and were of 99.995% purity. Nickel (II) sulfate hexahydrate (99%), dimethylamine borane complex (97%), and sodium hydroxide (≥98%, pellets) were obtained from Sigma Aldrich, Inc (St. Louis, MO). Sodium pyrophosphate decahydrate crystal was purchased from Mallinckrodt Baker, Inc (Phillipsburg, NJ). Hexadecanethiol (99+%) (HDT), 16-and hydroxy-1-hexadecanethiol (99+%) (MHL) were obtained from Assemblon, Inc. (Redmond, WA). All reactants were used without further purification.

The preparation of SAMs used in this study has been described in detail previously. Briefly, first Cr (~ 50 Å) and then Au (~1000 Å) were thermally deposited onto Si native oxide wafers, which were etched with piranha solution (3:1 mixture of sulfuric acid and 30% hydrogen peroxide). Well-organized self-assembled monolayers were formed by placing the prepared Au substrates in a 1 mM ethanolic solution of the appropriate alkanethiol molecule (with –CH₃ or –OH terminal functional groups) for 24 h at ambient temperature (21 ± 2 °C). To ensure that the prepared SAMs were well-ordered and free from significant chemical contamination, for each batch, one sample was taken and characterized using single-wavelength ellipsometry (Gaertner Scientific Corp., Skokie, IL) and time-of-flight secondary ion mass spectrometry (ION TOF Inc., Chestnut Hill, NY) prior to electroless deposition.

UV photopatterning of SAMs. UV photo patterning of SAMs was performed using the following procedure. First, a mask (a copper TEM grid, 150 mesh, Electron Microscopy Inc., Hatfield, PA) was placed on top of the SAM to be patterned (MHL, SAM#1). The SAM with mask on top was then placed 50 mm from a 500 W Hg arc lamp equipped with a dichroic mirror and a narrow band-pass UV filter (280 to 400 nm) (Thermal Oriel, Spectra Physics Inc.).
SAM surface was exposed to UV light for 2 h to ensure photooxidation was complete. The UV photopatterned SAM#1 was then immersed in a freshly-made 1 mM ethanolic solution of the second alkanethiol (SAM#2) for 24 h. In the areas exposed to UV light, the photooxidized SAM#1 was displaced by SAM#2. A SAM#1/SAM#2 patterned surface was thus obtained. The patterned surfaces were rinsed copiously with degassed ethanol and dried with nitrogen gas.

**Nickel Electroless Deposition.** The plating solution employed in this study consisted of 0.08 M nickel (II) sulfate hexahydrate (NiSO$_4$$\cdot$6H$_2$O), 0.14 M sodium pyrophosphate decahydrate (Na$_4$P$_2$O$_7$$\cdot$10H$_2$O) (complexing agent), and 0.07 M dimethylamine borane (DMAB, (CH$_3$)$_2$NHBH$_3$) (reducing agent). The solution pH was adjusted to 10 using sodium hydroxide before the addition of DMAB, and used immediately after preparation. Depositions were performed at 45 °C for times ranging from 0.5 to 30 min.

After deposition, samples were rinsed thoroughly with copious amount of deionized water and absolute ethanol, dried with nitrogen gas, and transferred to the TOF SIMS, SEM or XPS instruments for analysis.

**Scanning Electron Microscopy (SEM).** SEM measurements were performed on a dual-beam FIB instrument (Nova 200 Nanolab, FEI Company) with electron beam energy up to 30 keV. This instrument is also equipped with an energy dispersive x-ray (EDX) microanalysis system.

**Atomic Force Microscopy (AFM).** The AFM images were collected using the tapping mode of a Dimension 3100 microscope from Nanoscope. The AFM images were processed with WSxM. $^6$

To determine the widths and heights of the nanowires, ten profiles perpendicular to the nanowire at ~2.5 µm intervals along the wire were obtained. The reported widths are the average of the full width half maxima (FWHM) of the nanowire cross-sections. Since the sample surfaces are relatively rough, the height of the nanowires were obtained in the following way. The highest
point of the nanowire was first measured. Then the average of the substrate height was
determined close to the nanowire. The reported nanowire height is the average of the difference
of these two values:

nanowire height = <(highest point – average substrate height)> nm

For both nanowire and height the reported error is the standard deviation of the measurements.

**Time-of-flight Secondary Ion Mass Spectrometry (TOF SIMS)**

TOF SIMS spectra were acquired using an ION TOF IV spectrometer (ION TOF Inc., Chestnut
Hill, NY) equipped with a Bi liquid metal ion gun. Briefly, the instrument consists of a load lock
for sample introduction, preparation and analysis chambers, separated by gate valves. The
pressures of the preparation and analysis chambers were maintained at <5×10⁻⁹ mbar. The
primary Bi⁺ ions had a kinetic energy of 25 keV and were contained in a ~100 nm diameter
probe beam, which was rastered over a (100 × 100 µm²) area during spectra acquisition and a
(500 × 500 m²) area during image acquisition. All spectra were acquired within the static regime
using a total ion dose less than 10¹⁰ ions cm⁻², which is within the static SIMS regime. The
secondary ions were extracted into a time-of-flight mass spectrometer using a potential of 2000
V and were reaccelerated to 10 keV before reaching the detector. For each experiment, at least
three samples were prepared, and three areas on each sample were examined. The ion intensity
data presented is an average of these measurements and the uncertainty reported is the
corresponding standard deviation.

Optical images of the samples were captured using a video camera (ExwaveHAD, Sony)
mounted in the TOF SIMS analysis chamber.
Figure S1. The variation of nanowire height with width. Nanowire heights and widths were determined from AFM images.
Figure S2. Mass spectrometric images of a nickel nanowire formed on a patterned –CH₃–OH terminated SAM. SIMS images centered at m/z 58 (⁵⁸Ni⁺) and m/z 31 (CH₂OH⁺), which is a characteristic ion of a –OH terminated SAM. Also shown is an overlay of the images with m/z 58 in red and m/z 31 in green. Area of analysis: (500 x 500) µm². Nickel electroless deposition and SIMS analysis conditions are as in Figure 3. Ion intensities are shown using a heat scale, as in Figure 3.
References


