

Block Copolymer Mediated Deposition of Metal Nanoparticles on Germanium Nanowires

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Experimental Details

Pretreatment of wafers. Si(100) wafers (n-type, P doped, 0.0080-0.0200 ohm·cm, 525 μm thickness) purchased from Mitsubishi Silicon America were cleaned in an acetone ultrasonic bath for 10 min. The wafers were then immersed in a hot solution of H₂O₂/H₂SO₄ (1:3) for 20 min to remove organic contamination. After each cleaning step, the wafers were thoroughly rinsed with DI water (18 MΩ, from a Barnstead Nanopure system) and blown dry with a nitrogen stream. The wafer was diced into small pieces for further use.

Block copolymers. Block copolymers were purchased from Polymer Source, Inc. (www.polymersource.com) and were used without purification prior to use. In all cases, the PS-*b*-P2VP or PS-*b*-P4VP was dissolved in toluene at 70°C to make a 0.5 or 1 wt % solution and allowed to cool to room temperature. In order to preload the polymers with HAuCl₄ (Aldrich) or AgNO₃ (Strem), solid HAuCl₄ or AgNO₃ was dissolved in a toluene solution of the block copolymer (0.5 wt %) by stirring for at least for 12 h before use.

Ge nanowire synthesis. Ge nanowires were prepared as described in detail in references 3a and b in the main text.

Ge nanowire (NW) dispersion. Ge NW powders (0.3 mg) were added to 20 g of toluene in a glass vial, followed by vigorous stirring. The dispersion was sealed and stored in the dark. Before each use, the dispersion was agitated in an ultrasonic bath for 20 min.

Removal of the oxide layer on Ge NWs. To a 1.5 mL microcentrifuge tube, 0.5 ml of Ge dispersion was added. The NWs were separated by centrifugation at 3000 rpm for 3 min and dried under a stream of nitrogen gas for 5 min. 0.5 ml of ethanol (95% in water) was then added to the microcentrifuge tube, and the tube was agitated in an ultrasonic bath for 5 min. The dispersion was then centrifuged again to remove the ethanol and residual toluene. This dispersion was exposed to two more cycles of rinsing with ethanol and centrifugation. The NWs were maintained in 0.5 mL of ethanol and agitated in an ultrasonic bath. Next, 0.5 mL of 10% HF (aq) was added into the 0.5 mL Ge nanowire dispersion and held for 1 min before centrifugation at 3000 rpm for 2 min. Immediately, the etched NWs were dried under a flow of nitrogen for 10 min to remove residual water and ethanol. The dried NWs were then re-dispersed in 0.5 mL of toluene and agitated before next step.

Galvanic Displacement on Ge NWs (no polymer; corresponds to Figure 1 in main text). A drop (~ 50 μL) of oxide-terminated (untreated) Ge NWs was placed onto a Si shard and allowed to dry in air. The shard was then immersed in the metal solutions for 1 min, followed by SEM analysis. For TEM analysis, 10 μL of Ge NWs solution was placed onto a copper TEM grid and allowed to dry in air. One drop of metal solution was placed on top of the grid allowed to sit for 1 min. Excess solution was removed with a corner of a tissue and allowed to dry.

Deposition Method 1 (corresponds to Scheme 1 in main text). As described in the main text, in method 1 of Scheme 1, 0.5 mL of a 0.5 wt % solution of PS-*b*-P2VP (MW = 91,500-105,000) or PS-*b*-P4VP (MW = 128000-33500), preloaded with the metal ion precursor (HAuCl₄ or AgNO₃) was mixed with 0.5 mL of a suspension hydride-terminated germanium nanowires (derived from a stock suspension of 0.3 mg of nanowires in 20 mL toluene) in a standard eppendorf, in ambient conditions. The mixture was allowed to react for one minute before centrifugation at 3000 rpm for 2 min to form a visible dark pellet. The toluene was replaced with fresh toluene, the nanowires re-dispersed with brief ultrasonication for 5 min, and the centrifugation process repeated twice to remove as much residual polymer as possible. Transmission electron microscopy (TEM) samples were prepared by placing a droplet of nanowire samples following block copolymer removal, re-suspended in ~1 mL of chloroform, onto carbon-coated 400-mesh copper grids for 25 s and then removing excess liquid using a Kimwipe tip.

Deposition Method 2 (corresponds to Scheme 1 in main text). 10 μ L of the Ge NW suspension, either oxide-terminated (crude) or HF etched, were placed onto a Si substrate and dried under a stream of nitrogen. 10 μ L of metal-loaded polymer solution was then spin coated onto the Si substrate (spin rate = 3000 rpm) for 1 min. The sample was then either heated, in air, in a preheated oven for the desired time, or immersed in Millipore grade water for 1 min.

Electron Microscopy. TEM images were recorded on a JEOL 2010 microscope operating at 200 kV. Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 operating at 5-15 kV.

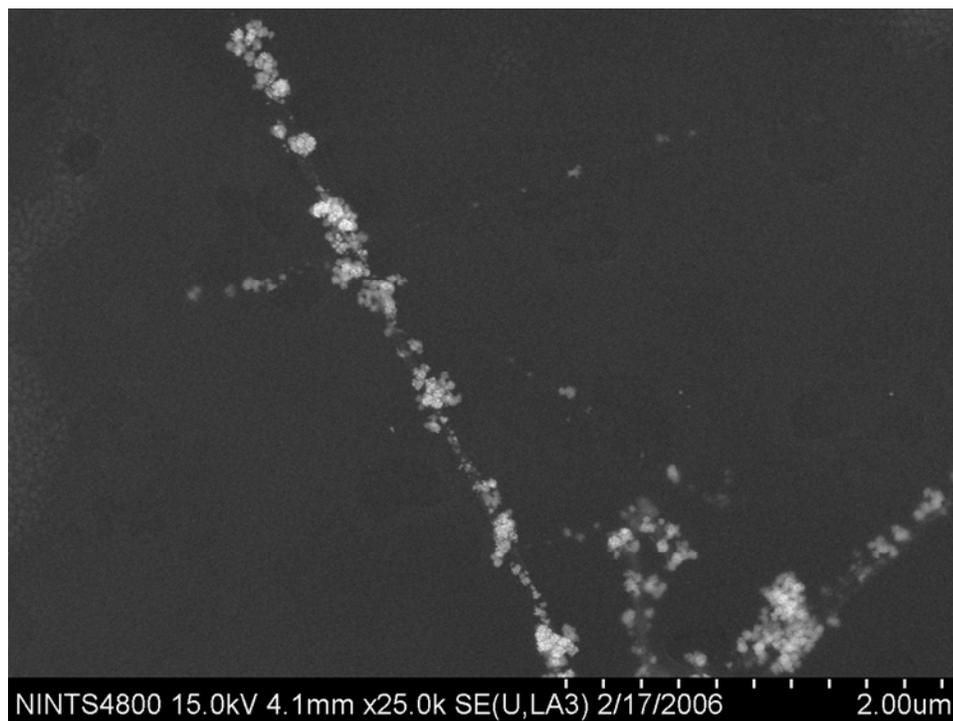
X-ray photoelectron spectroscopy (XPS). XPS (Kratos Analytical, Axis-Ultra) was performed using a monochromatic Al K α with a photon energy of 1486.6eV. Neutralizer was added to compensate the positive charging on the analyzing surface. The instrument was calibrated by the measurement of C 1s. The Ag 3d and Au 4f metallic positions were also calibrated by sputtered Ag and Au films, respectively.

Scanning Auger microscopy (SAM). SAM (JEOL, JAMP-9500F) was carried out with an electron accelerating voltage and emission current of 25 kV and 6 nA, respectively. The Auger peaks of Ge L3M45M45 (1147 eV), Ag M4N45N45 (350 eV), and Au M5N67N67 (2015 eV) were selected for the mapping. The Auger mapping for each element was obtained by plotting $(P - B)/B$, where P and B are peak and background intensities, respectively. The intensities were then scaled using the JEOL processing software for increased contrast.

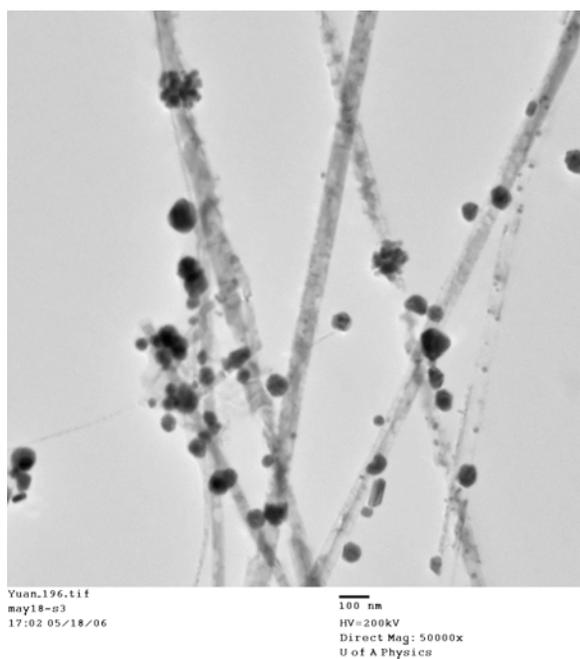
Supplementary Figures

Figure S1. Galvanic displacement on Ge NWs (no block copolymer), at different metal ion concentrations. All reactions carried out for 1 min, ambient temperature, unless stated otherwise.

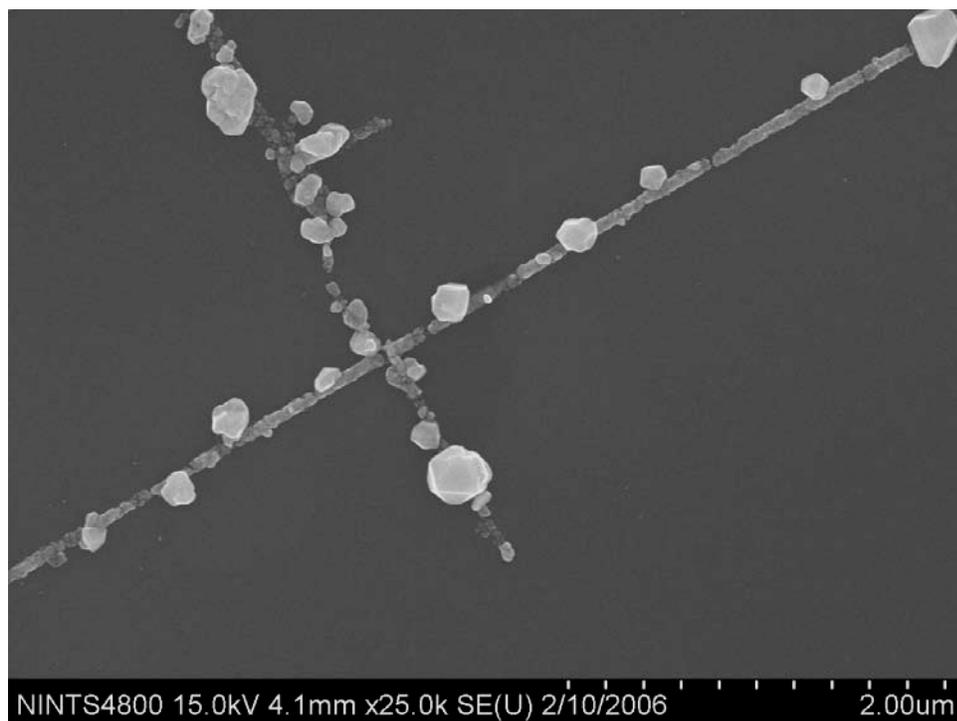
a) SEM image, 1 mM AgNO_3 (aq). The Ge NW has dissolved.



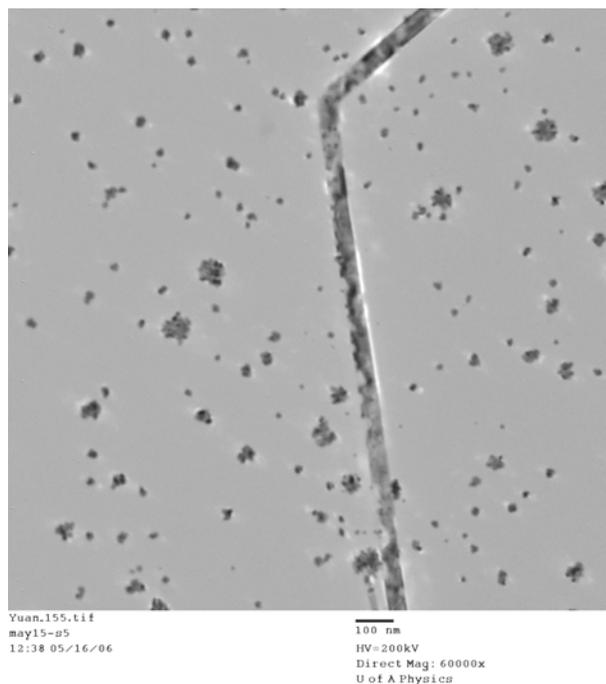
b) TEM image, 0.1 mM AgNO_3 (aq)



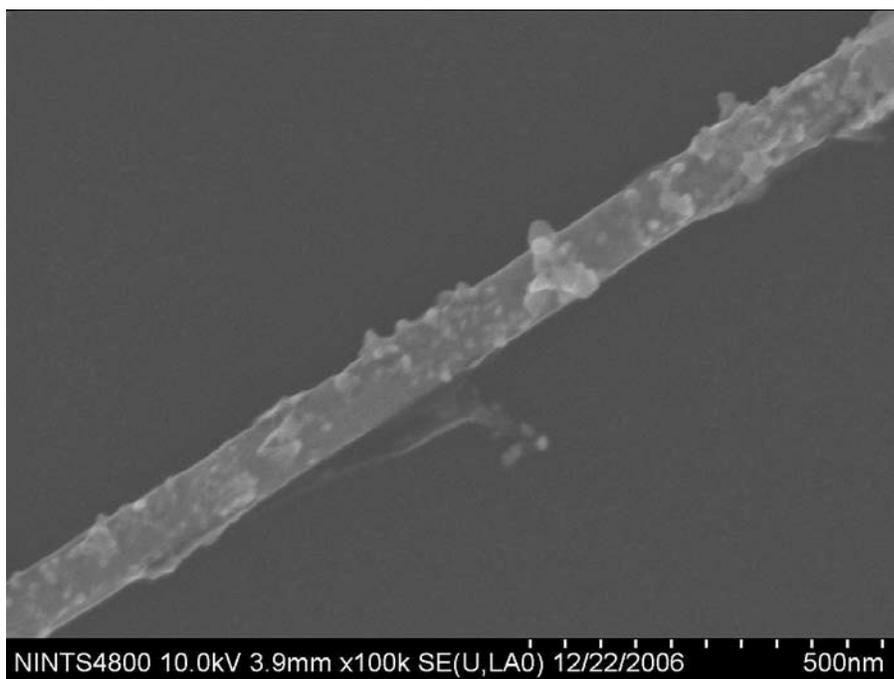
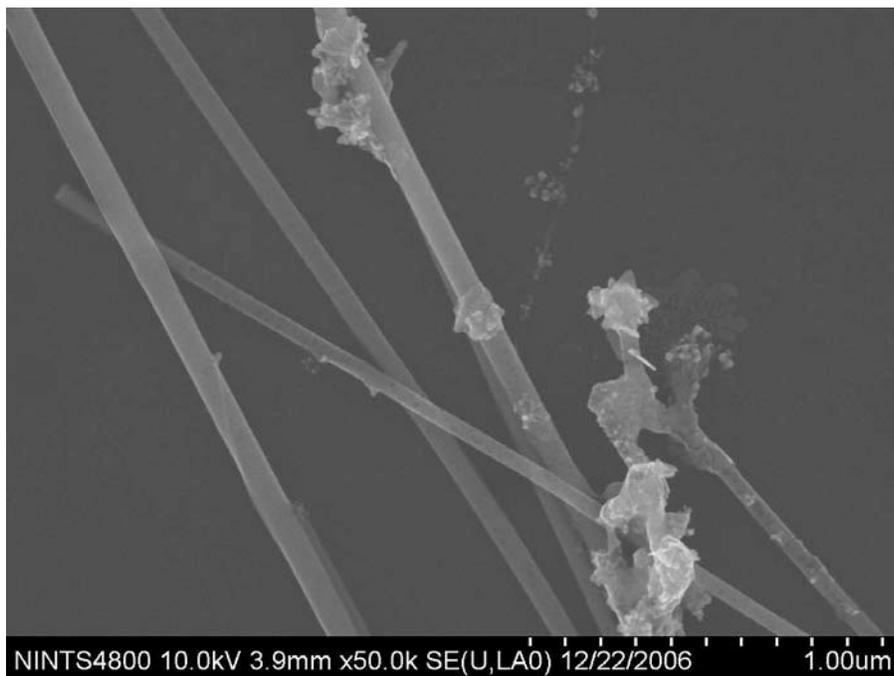
c) SEM image, 1 mM HAuCl_4 (aq). The Ge NW has dissolved. The reduced gold formed along the length of the original Ge NWs.



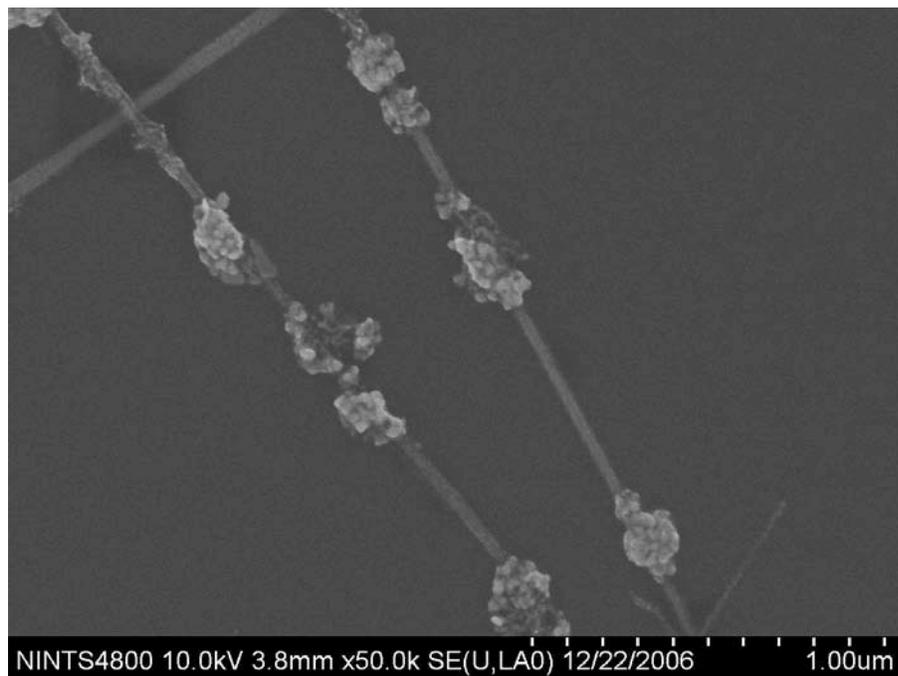
d) SEM image, 0.1 mM HAuCl_4 (aq). Obvious "bite marks" appear down the length of the Ge NW.



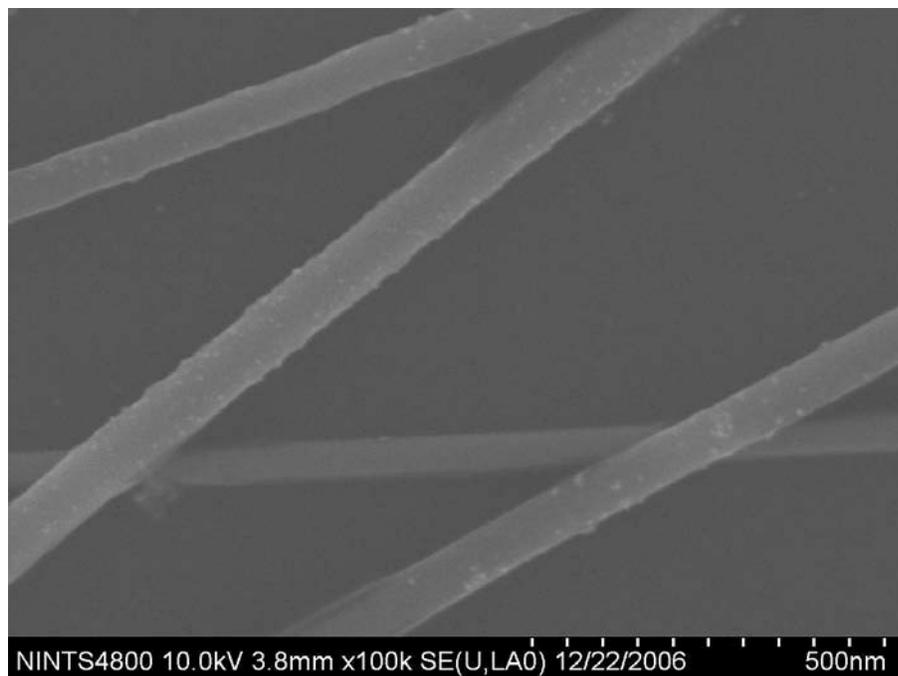
e) SEM images, 10^{-5} M AgNO_3 (aq). The deposition is inconsistent.



f) SEM images, 10^{-5} M AgNO_3 (aq), 10 min.



g) SEM images, 10^{-5} M HAuCl_4 (aq).



h) SEM images, 10^{-5} M HAuCl_4 (aq), 10 min. While some wires appear evenly coated, others have very little or no apparent metal deposition.

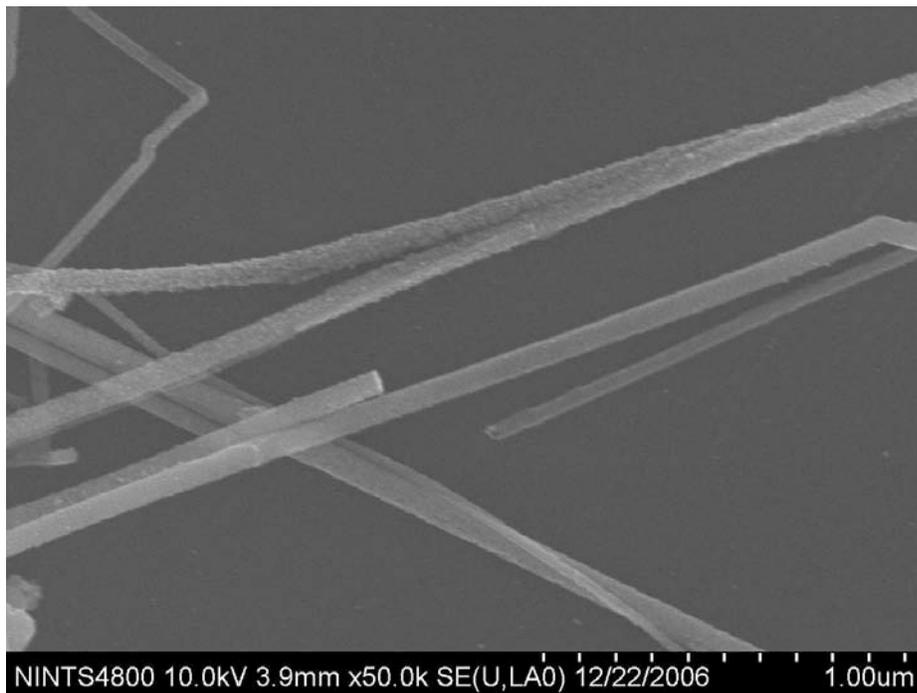
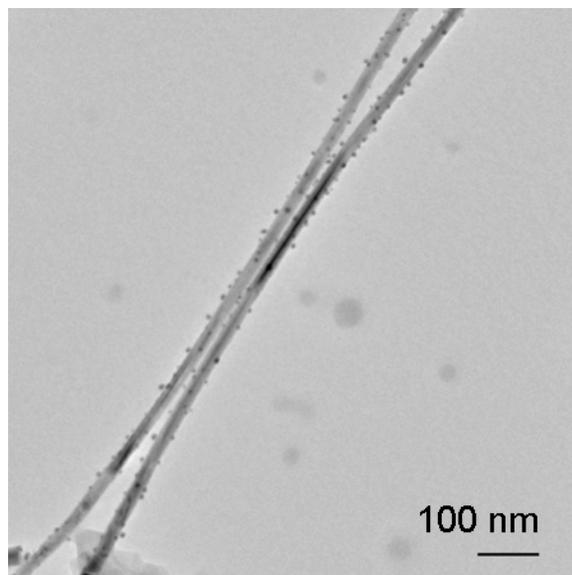
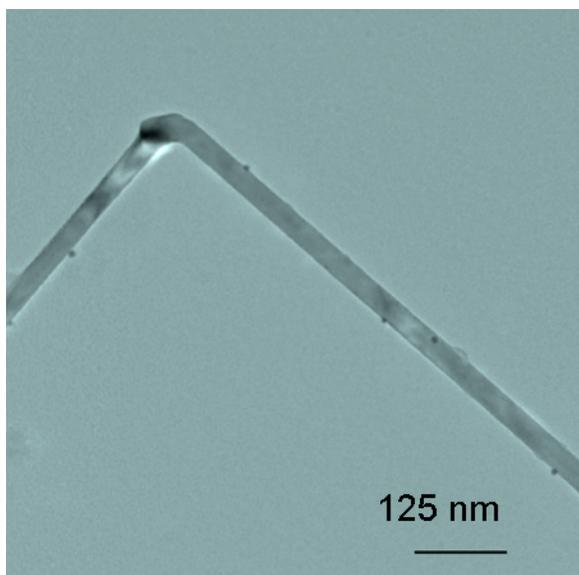


Figure S2. Results of deposition method 1, on oxide-capped (crude) Ge NWs.

a) TEM image, AgNO_3 -loaded PS-*b*-P2VP (MW = 91,500-105,000), at a ratio of 0.2 Ag^+ /pyridyl.



b) TEM image, HAuCl_4 -loaded PS-*b*-P2VP (MW = 91,500-105,000), at a ratio of 0.2 Au^{III} /pyridyl.

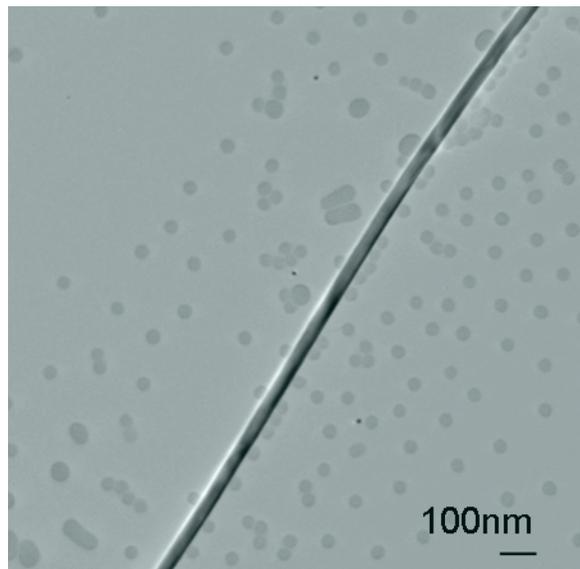
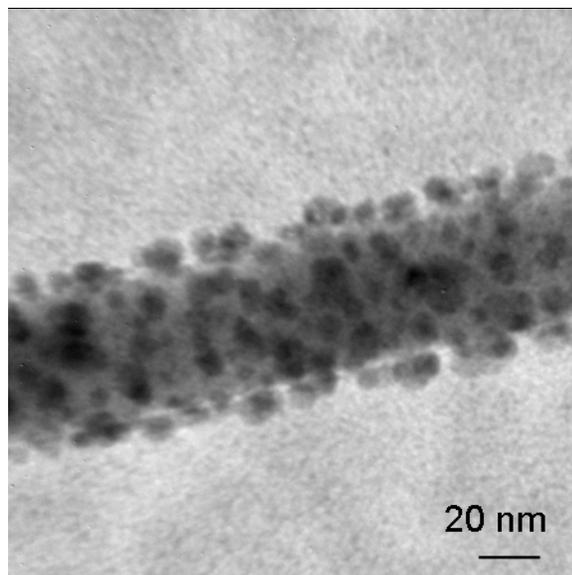
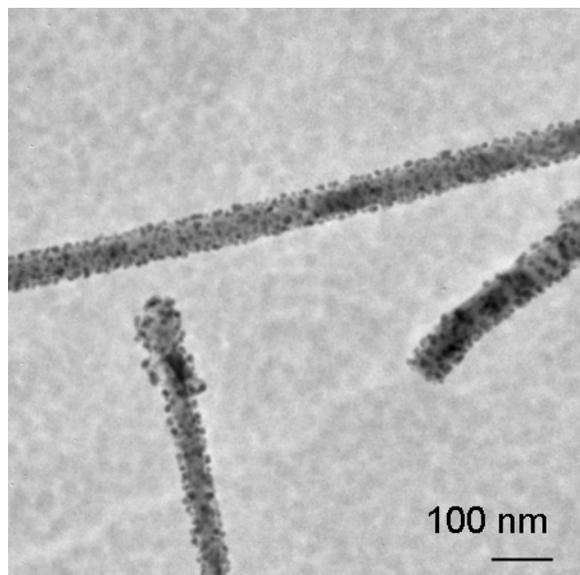
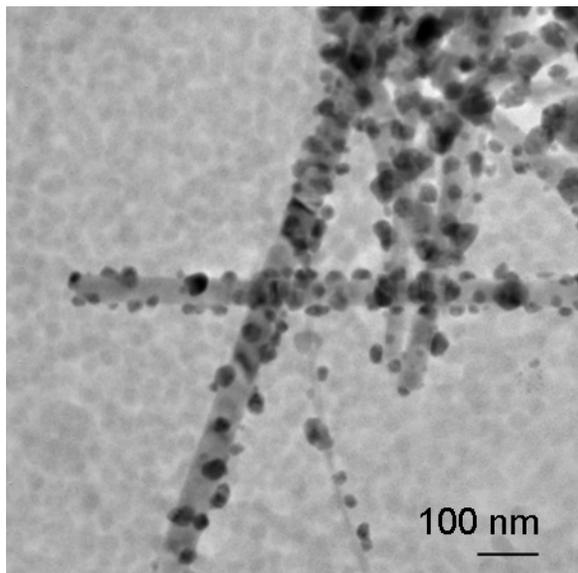


Figure S3. Results of deposition method 1, on hydrogen terminated (etched) Ge NWs.

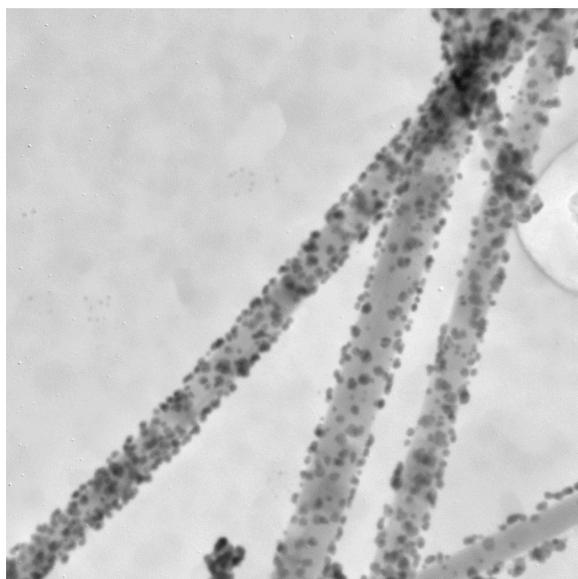
a) TEM, AgNO_3 -loaded PS-*b*-P2VP (MW = 91,500-105,000), Ag^+ /pyridyl = 0.2, 0.5 wt % polymer in toluene.



b) TEM, AgNO₃-loaded PS-*b*-P2VP (MW = 91,500-105,000), Ag⁺/pyridyl = 0.5, 0.5 wt % polymer in toluene.



c) TEM, HAuCl₄-loaded PS-*b*-P2VP (MW = 91,500-105,000), HAuCl₄/pyridyl = 0.2, 0.5 wt % polymer in toluene.



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d) TEM, H_{AuCl}₄-loaded PS-*b*-P2VP (MW = 91,500-105,000), H_{AuCl}₄/pyridyl = 0.5, 0.5 wt % polymer in toluene.

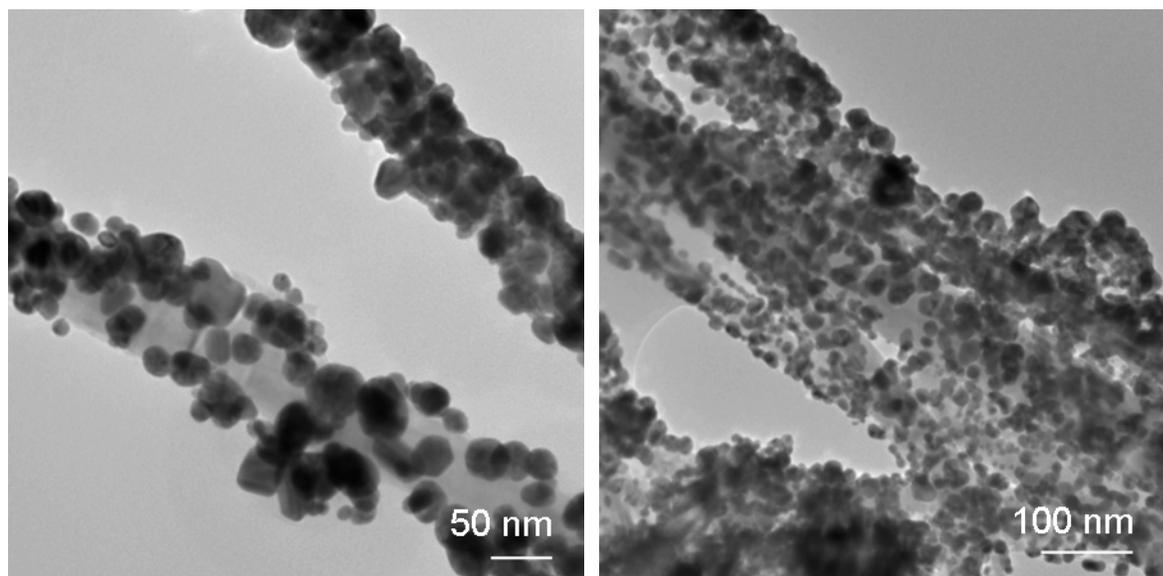


Figure S4. TEM, Deposition method 1, HF etched Ge NWs, using PS-*b*-P2VP (MW = 25,500-23,500), H_{AuCl}₄/pyridyl = 0.5, 0.5 wt % polymer in toluene.

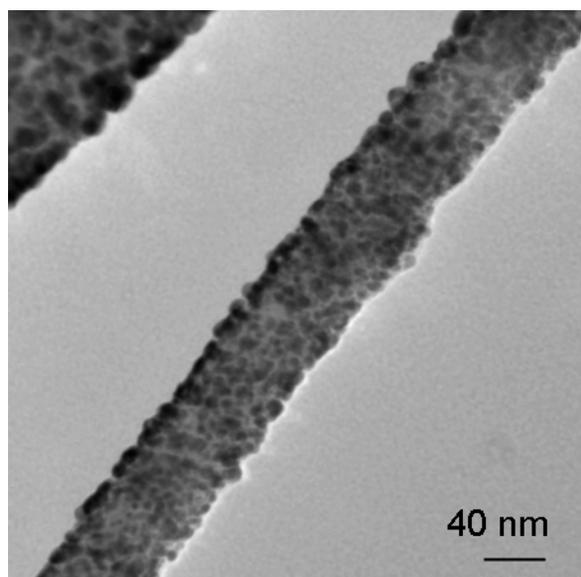


Figure S5. TEM, Deposition method 1, HF etched Ge NWs, using PS-*b*-P2VP (MW = 91,500-105,000), H_{AuCl₄}/pyridyl = 0.5, 1.0 wt % polymer in toluene.

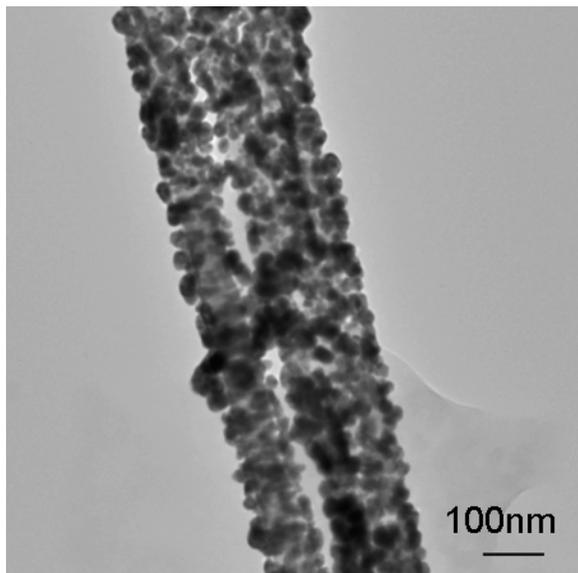
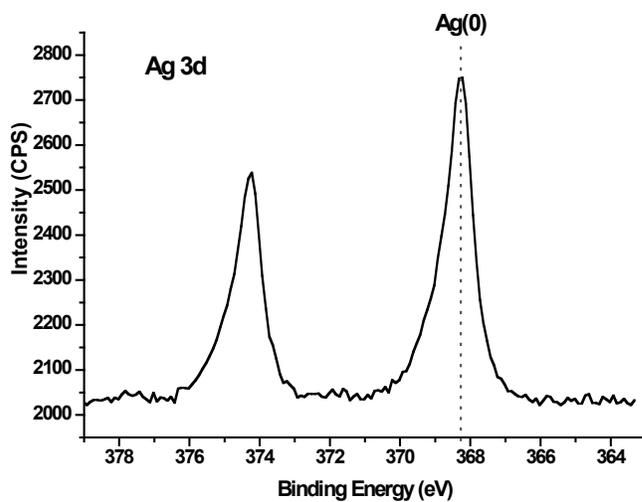


Figure S6. XPS, Deposition method 1, HF etched Ge NWs, using PS-*b*-P2VP (MW = 91,500-105,000), 0.5 wt % polymer in toluene.

a) Ag⁺/pyridyl = 0.5



b) $\text{HAuCl}_4/\text{pyridyl} = 0.5$

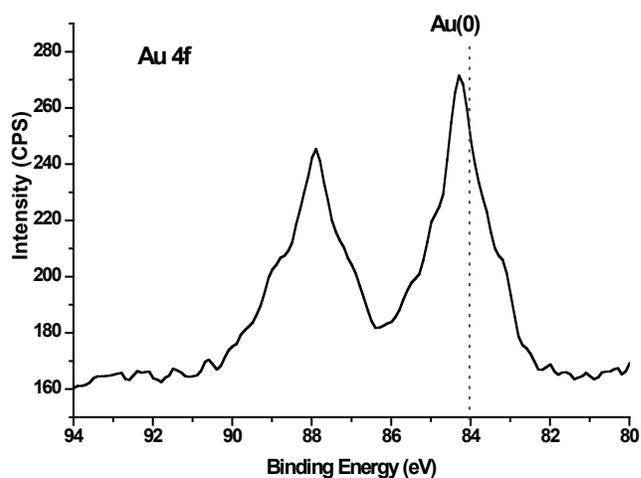
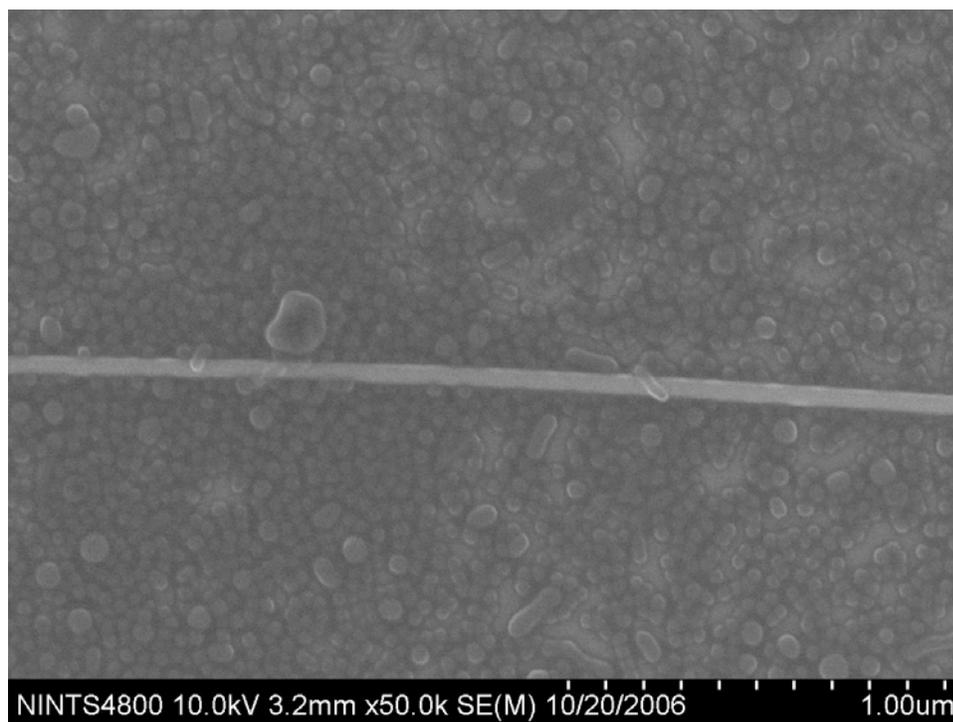
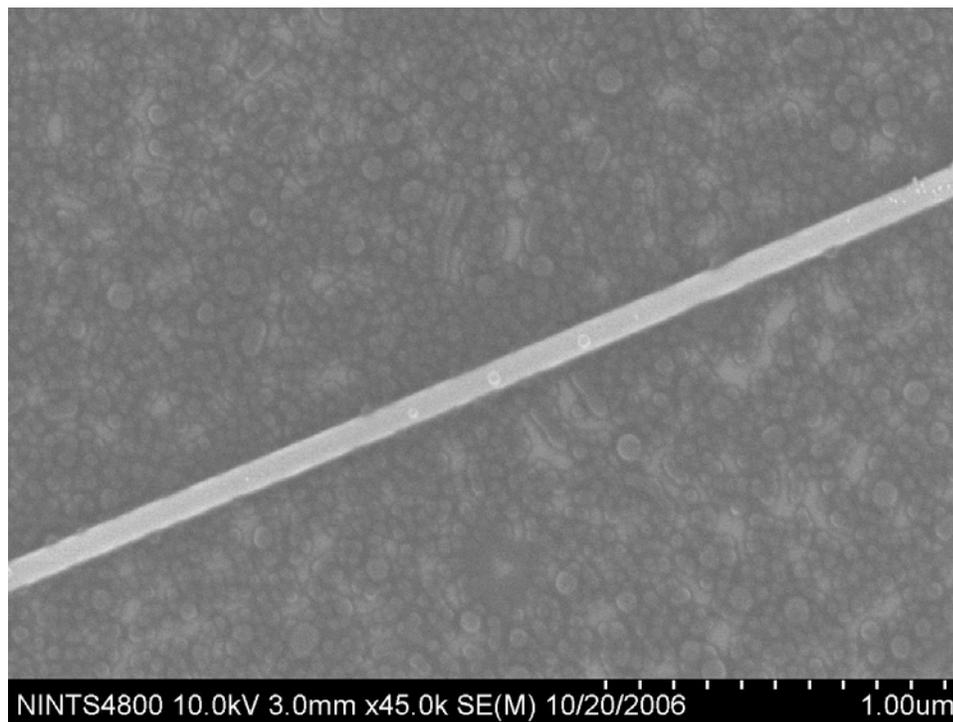


Figure S7. Results of deposition method 2 (thermal treatment) on oxide-capped (crude) Ge NWs, using PS-*b*-P2VP (MW = 91,500-105,000), 0.5 wt % polymer in toluene.

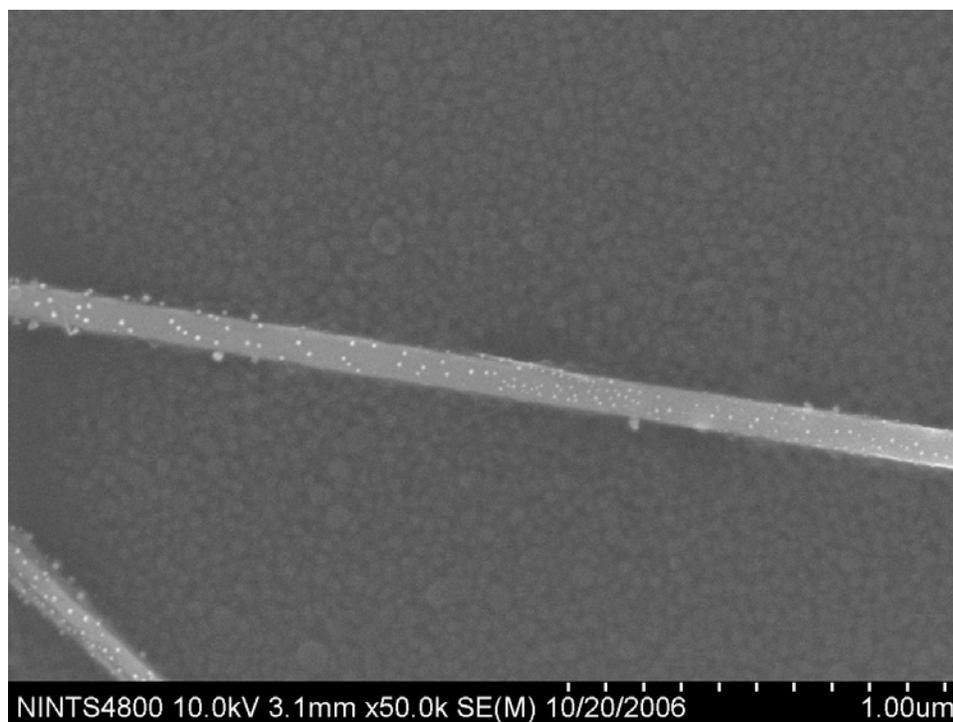
a) SEM, Method 2, 180°C, polymer left on.



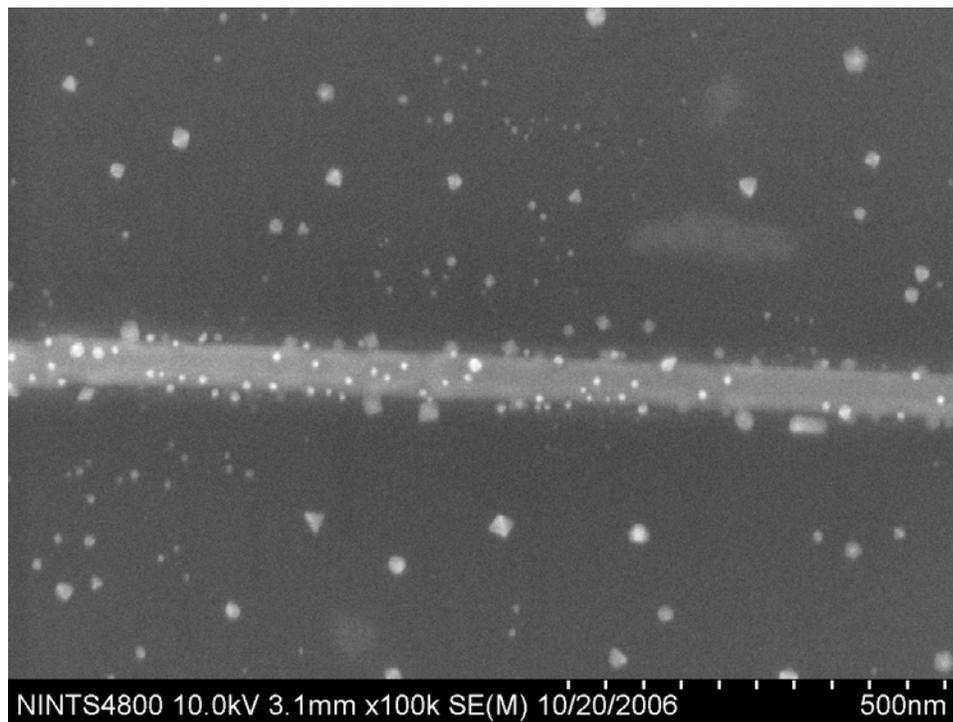
b) SEM, Method 2, 190°C, polymer left on.



c) SEM, Method 2, 200°C, polymer left on.



d) SEM, Method 2, 210°C, polymer left on.



e) SEM, Method 2, 220°C, polymer left on.

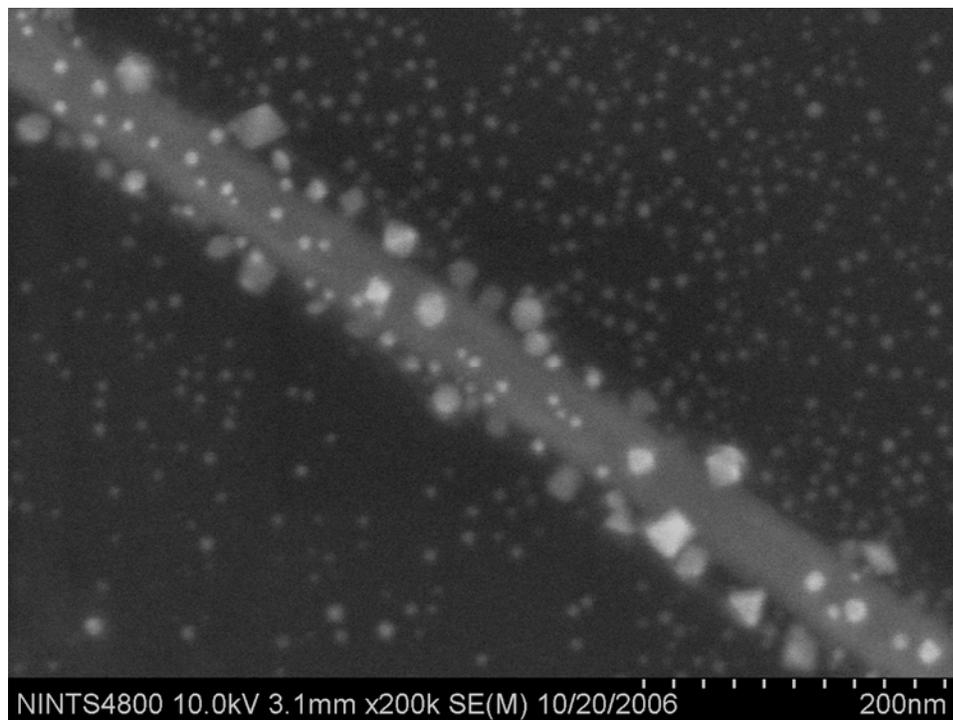


Figure S8. Results of deposition method 2 (water treatment for 1 min), on oxide-capped (crude) Ge NWs, using PS-*b*-P2VP (MW = 91,500-105,000), 0.5 wt % polymer in toluene.

