

Block copolymer mediated deposition of metal nanoparticles on germanium nanowires†

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Galvanic displacement, mediated by a diblock copolymer, leads to deposition of well dispersed gold and silver nanoparticles on germanium nanowires.

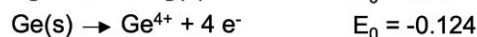
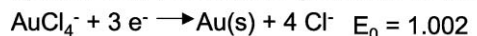
A very efficient approach to semiconductor metallization is galvanic displacement, an electrochemical reaction whereby a sufficiently oxidizing metal ion is reduced to its metallic state, and is accompanied by oxidation of the semiconductor (Scheme 1a).¹ The reactions do not require either an external electron source or a chemical reducing agent. Galvanic displacement reactions of noble metals on flat germanium surfaces are particularly intriguing due

to the apparent formation of an intermetallic metal–germanium interface, leading to a strongly bound metal film, and potentially, an electronically active interface.² While galvanic displacement on flat germanium surfaces has been investigated,² little is known as to whether galvanic displacement reactions on nanostructured germanium surfaces could lead to interesting composite materials, controllably linking metal nanoparticles to this technologically important semiconductor material. Due to the accessibility of germanium nanowires, synthesized in high yield *via* solution processes, as well as by VLS (vapour–liquid–solid) processes, galvanic displacement on germanium nanowires was probed.³

Integration of semiconductor nanowires with extant devices is a critical challenge that requires addressing for many applications.⁴ Because metal nanoparticles interfaced directly to a nanowire provides a means of ‘wiring in’ *via* metallic interconnects and possibly molecules, it is becoming an increasingly relevant approach.⁵ For instance, electroless deposition of metal nanoparticles on carbon nanotubes has been reported, although the oxidation product of the reaction remains obscure.⁶ Galvanic displacement of gold nanoparticles has recently been demonstrated on silicon nanowires (prepared by VLS) in the presence of dilute HF(aq), and the reaction leads to consistent coverage of gold nanoparticles along the length of the Si nanowires.^{5a–b} With germanium nanowires, on the other hand, attempts to carry out galvanic displacement with either gold or silver ionic precursors [HAuCl₄(aq), AgNO₃(aq), respectively], lead to significant corrosion of the nanowire structures; little control of the etching process is possible, and variability is seen from wire-to-wire within the same sample batch. As shown in Figure 1 and the ESI,† the wires are obviously corroded, cleaved, or entirely dissolved, and the metal deposition irregular, even at different metal ion concentrations. The difference between germanium and silicon is related to the oxide coating—germanium oxide is water soluble, whereas the silicon oxide is not.² The rate of oxide etching in the case of silicon is at least partially controlled by the HF concentration; with germanium, however, no such restraint exists in aqueous solution; and undercutting is a severe problem. A new, non-aqueous method to control both metal ion reduction and concomitant germanium oxidation, and germanium oxide dissolution was required. Ideally, the approach should be a simple, solution processable approach permitting large scale functionalization reactions.

Block copolymer micelles that contain polystyrene (PS) and poly(2- or 4-vinylpyridine) (P2VP or P4VP) blocks have been demonstrated to deliver metal ions to semiconductor surfaces for galvanic displacement reactions, leading to deposition of metal nanoparticles.⁷ The micellar cores can be loaded with the metal precursor salt in a quantifiable fashion.⁸ The block copolymer can

a) Half cell potentials (relative to NHE)



b)

Method 1

Metal ion-loaded block copolymer added to solution



Removal of polymer



Method 2

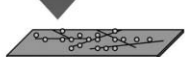
Ge nanowires dispersed on silicon



Spin coating of metal ion-loaded block copolymer



i) Δ, 200°C, 5 min or immersion in H₂O, 1 min
ii) Removal of polymer



Scheme 1 Summary of the two methods described here, utilizing block copolymers to controllably deliver metal ions to the Ge nanowire surface, leading to a galvanic displacement reaction and nanoparticle formation.

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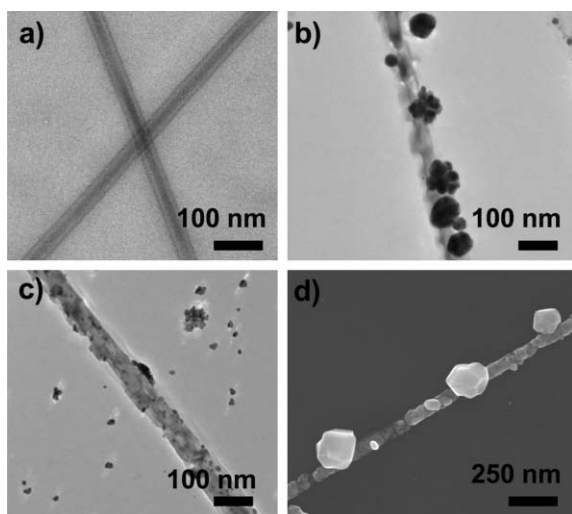


Fig. 1 (a) TEM image of pristine Ge nanowires. (b–d) Ge nanowires subjected to aqueous galvanic displacement for 60 s in ambient: (b) TEM, 0.1 mM AgNO₃ (aq), (c) TEM, 0.1 mM HAuCl₄ (aq), (d) SEM, 1.0 mM HAuCl₄ (aq).

be therefore utilized to provide a point of restriction with respect to the passage of reagents to the semiconductor interface. As previously demonstrated on flat semiconductor surfaces, the size of formed metal nanoparticles can be controlled at the nanoscale, and the obtained structures, arrays of sub 20 nm metal nanoparticles, are vastly different than the much larger, irregular metal deposits observed in absence of block polymer.² The two approaches detailed in this study are summarized in Scheme 1.

Germanium nanowires, prepared from a supercritical fluid liquid–solid (SFLS) synthesis,^{3a–c} were either used as is (oxide-capped) or etched (hydrogen terminated) *via* treatment with dilute HF [10% (aq)], to remove the external oxide coating,^{3d} rendering the nanowires hydrophobic. In method 1 of Scheme 1, 0.5 mL of a 0.5 wt% solution of polystyrene-*block*-poly(2- or 4-vinylpyridine) (PS-*b*-P2VP or PS-*b*-P4VP, respectively), preloaded with 0.2–0.6 molar equivalents of metal ion precursor (HAuCl₄ or AgNO₃) per pyridyl group, was mixed with 0.5 mL of a suspension of 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 to form a visible dark pellet. The toluene was replaced with fresh toluene, the nanowires redispersed with brief ultrasonication, and the centrifugation process repeated twice. As shown in Fig. 2a–d, sparse deposition of gold and silver nanoparticles is observed on the oxide-capped Ge nanowires, using PS-*b*-P2VP (MW = 91 500–105 000), with a ratio of Mⁿ⁺/pyridyl of 0.5. Scanning Auger microscopy (Fig. 2c–d) confirms the elemental identity of gold and silver deposits. Much greater deposition was observed, however, when the Ge nanowires were etched with HF (aq). As shown in Fig. 2e–f for silver using 0.5 wt% PS-*b*-P4VP (MW = 128 000–33 500) in toluene, with a ratio of Ag⁺/pyridyl groups of 0.6, even coatings of metal nanoparticles over the entirety of the nanowire length are observed. XPS verifies that the deposited nanoparticles are indeed Au⁰ or Ag⁰.†

While no control over particle spacing on the nanowires was observed, the choice of block copolymer molecular weight and

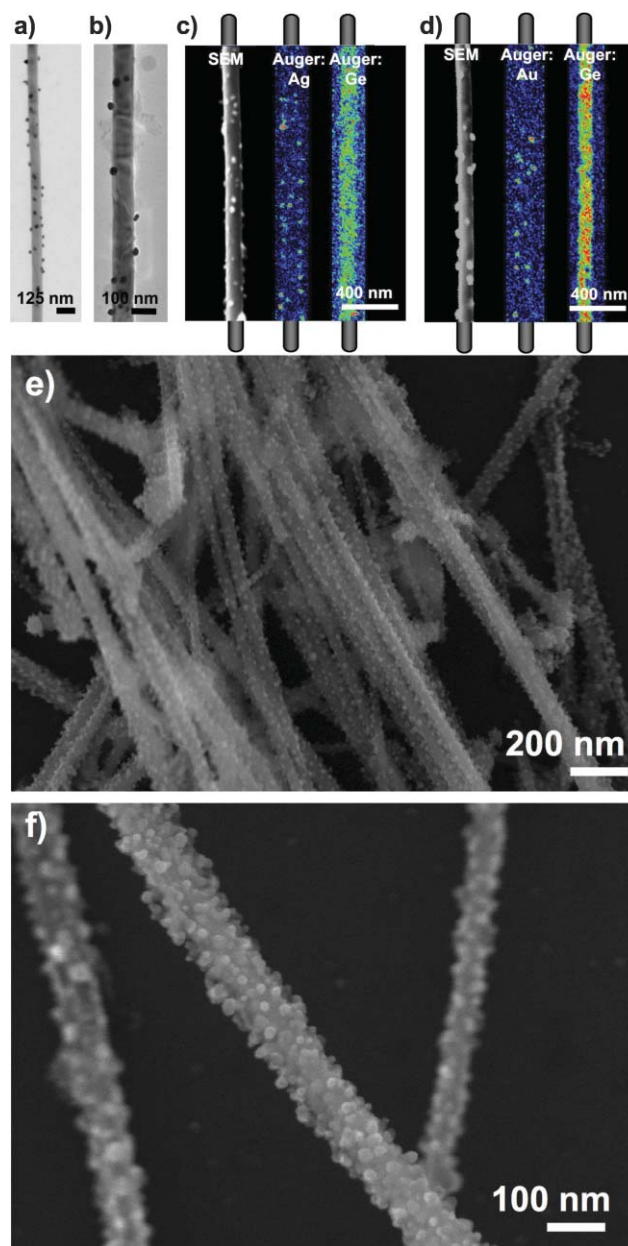


Fig. 2 (a–b) TEM images of oxide-capped Ge nanowires, prepared *via* method 1, with 0.5 wt% PS-P2VP (MW = 91 500–105 000) in toluene, loaded with AgNO₃ and HAuCl₄, respectively; ratio Mⁿ⁺/pyridyl group = 0.5. (c–d) Scanning Auger microscopy of Ge nanowires prepared in the same manner as (a–b). (e–f) SEM images of silver nanoparticles on HF-etched Ge nanowires, formed *via* Method 1, using AgNO₃ and PS-*b*-P4VP (MW = 128 000–33 500, 0.5 wt% toluene, Ag⁺/pyridyl = 0.6).

other experimental parameters influenced the metal deposition outcome. For instance, as demonstrated with PS-*b*-P2VP (MW = 91 500–105 000, 0.5 wt% in toluene), increasing the HAuCl₄/pyridyl ratios from 0.2 to 0.5 resulted in an increase in particle size from ~10 nm to ~20–40 nm.† Increasing the wt% in toluene of PS-*b*-P2VP, keeping the metal loading constant, also predictably led to an increase in particle size. Smaller molecular weights for PS-*b*-P2VP resulted in smaller particles, keeping all other parameters constant. It is clear that modulation of these experimental conditions can afford some degree of control over

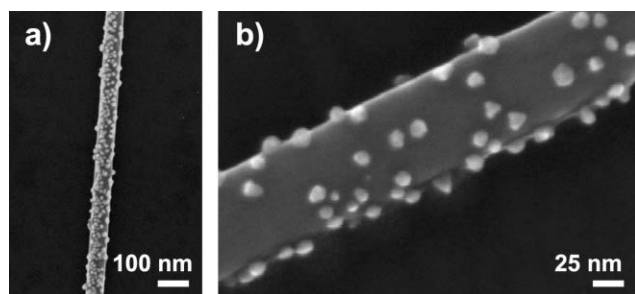


Fig. 3 SEM images of gold nanoparticles on crude Ge nanowires, prepared *via* method 2 with thermal treatment at 200 °C for 5 min. Block copolymer is PS-*b*-P2VP (MW = 91 500–105 000, 0.5 wt%), ratio of HAuCl₄/pyridyl = 0.5.

nanoparticle uniformity when deposited on the germanium nanowires.

In order to provide an alternative to the solution method (Method 1), a second approach was developed that utilizes the propensity of the nanowires to physisorb on a native-oxide capped silicon wafer. Method 2 as outlined in Scheme 1, involves dispersal of hydride- or oxide-terminated Ge nanowires on flat, native oxide-capped Si, followed by spin coating of a monolayer of HAuCl₄-loaded PS-*b*-P2VP block copolymer micelles over the entire surface (MW = 91 500–105 000, 0.5 wt% in toluene, HAuCl₄/pyridyl = 0.5). At room temperature in air, little deposition of gold is noted. Deposition is initiated, however, with brief heating to 200 °C in air (5 min), followed by polymer removal with warm toluene—the results are shown in Fig. 3. Little difference is noted between hydride- or oxide-termination, most likely due to *in situ* oxidation of the Ge–H_x interface under these conditions. The temperature to which the Ge nanowires are heated is critical: 180 °C and 190 °C lead to little metal deposition, and 210 °C and above result in HAuCl₄ decomposition throughout the block copolymer micelles on the silicon surface.^{†9} It remains to be determined if the Au^{III} to Au⁰ conversion is in fact due to galvanic displacement or thermal decomposition of HAuCl₄, or both. A

second variation that leads to metal deposition involves immersion of the same polymer-coated nanowires on silicon in water at room temperature (1 min). The galvanic displacement reaction occurs quickly but with a much higher degree of uncontrolled, random metal growth;[†] the role of the water is presumably to dissolve the formed germanium oxides, allowing the galvanic displacement reaction to continue. The thermal method is preferable if a tighter range of nanoparticle sizes is desired.

To summarize, metal ion delivery, mediated by block copolymers, is an effective method of producing metal nanoparticles on germanium nanowires, thereby avoiding problems of uncontrolled wire etching and undercutting in standard aqueous solution-based galvanic displacement chemistry.

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