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Silver Nano-Inukshuks on Germanium

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ABSTRACT

The integration of metallic nanostructures with semiconductors is important for a variety of technological applications. Through an efficient galvanic displacement reaction on germanium, complex silver nanostructures form spontaneously in aqueous conditions at room temperature. The structures, termed nano-inukshuks, are based on stacks of hexagonal metallic structures that grow, initially, parallel to the surface normal of the germanium. TEM, SEM, XPS, XRD, and EDS indicate that the structures are crystalline silver and, based on open cell potential studies, that their nucleation takes place in the first 100 s, followed by growth of the silver structures, most likely through Volmer–Weber growth.

In the Arctic, the Inuit peoples build stark, beautiful structures called inukshuks out of flat slabs of rock to mark trails and other important places on the flat landscape of the North; one example of these diverse structural forms is shown in Figure 1a. In this paper, we describe a room temperature, aqueous galvanic displacement synthesis of silver nano-inukshuks on germanium surfaces, shown in Figures 1b and 1c; the location, shape, and growth of the nano-inukshuks provide information about the electrochemical landscape of the flat germanium substrate.

There is a great deal of interest in nanostructured metallic architectures due to their unique electrical and optical characteristics. Because the fundamental properties of the metal nanoparticles are highly shape dependent, there has been much focused effort in devising reactions that exhibit a large degree of shape control.¹ For instance, discrete cobalt disks, rods and cubes,² platonic gold nanocrystals³ and other shapes,⁴ silver prisms,⁵ cubes,⁶ rods,⁷ and hexagonal plates⁸

have been synthesized via efficient solution phase reduction methods. The use of simple galvanic displacement reactions,⁹ on the other hand, has just begun to see increasing investigation of the shape, size, and selectivity of the resulting metal deposited on the surface. Films of spherical, oblate, or dendritic metal structures, some of which are crystalline while others undetermined, have been observed on technologically important semiconductors such as silicon and germanium;¹⁰ shape selective syntheses similar to the growing literature on solution phase nanoparticle research have yet to be demonstrated. Here we describe a dip-and-rinse galvanic displacement approach to synthesizing complex, highly regular crystalline silver inukshuk architectures directly on germanium surfaces. Only three ingredients are required: silver nitrate, water, and germanium.

Galvanic displacement reactions are carried out in the absence of an external reducing agent or electric current;⁹ the reducing electrons are derived from the valence band or bonding electrons of the solid and reduce metal ions in solution to metallic particles on the surface. In this case, germanium–germanium bonds in the crystal lattice acted as the reducing agent for the Ag⁺ ions in solution, leading to

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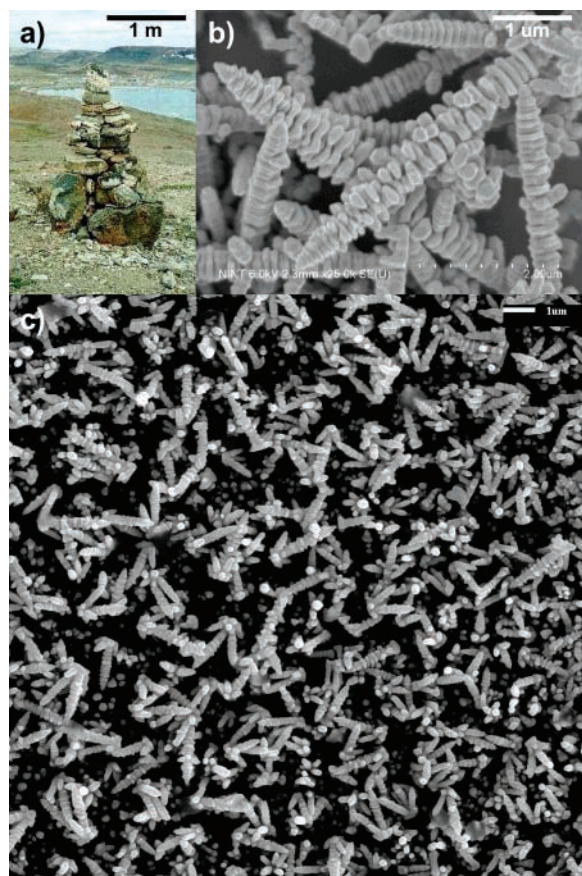
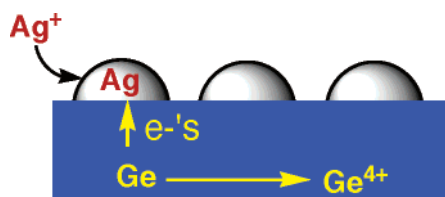


Figure 1. (a) A stone inukshuk in Northern Canada. (b) Silver nano-inukshuks formed by immersion of Ge(111) p-type in a 1.0×10^{-3} M silver acetate (aq) for 4 h. (c) Nano-inukshuks prepared by immersion of Ge(111) p-type in 1.0×10^{-3} M silver nitrate (aq) for 4 h.

Ag(s) and concomitant oxidation of Ge(s) to Ge^{4+} in the following spontaneous redox reaction.



In contrast to reactions on silicon, the resulting Ge^{4+} product, germanium oxide, is water soluble and does not form an insulating dielectric which would inhibit further metal deposition in absence of a fluoride source.^{10a,d}

Silver nano-inukshuk formation is observed at concentrations around 10^{-3} M of AgNO_3 (aq) at room temperature on flat or rough, native oxide-capped germanium surfaces as shown in the scanning electron microscope (SEM) images of Figures 1b and c, and Figure 2, at times of 2 h or more, depending upon concentration and silver salt chosen. The nano-inukshuks appear as ~ 300 nm diameter stacked hexagons with facets, and can grow up to 10 or more microns in length, perpendicular to the (111) planes of the silver hexagons. The hexagonal plates themselves are 50–75 nm thick, and in the first 4–6 h of deposition, are approximately parallel to the surface normal of the germanium, leading to

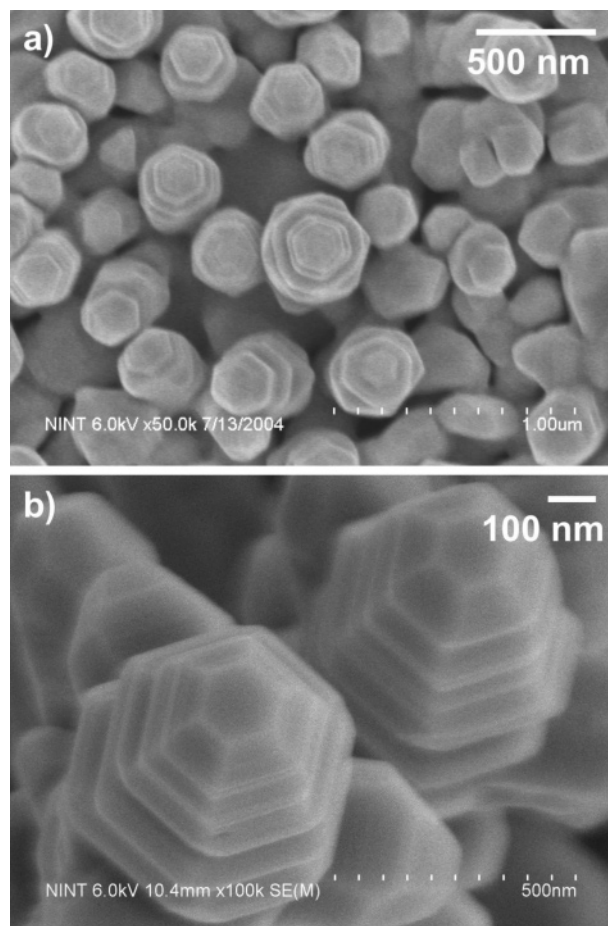


Figure 2. (a) Silver nano-inukshuks prepared by immersing n-type Ge(100) in 1.0×10^{-3} M AgNO_3 (aq) for 4 h. (b) Close-up of facets on the tips of silver metallic nano-inukshuks formed on p-type Ge(111) with 1.0×10^{-3} M AgNO_3 for 24 h.

growth of nano-inukshuks out from the surface (Figures 1c and 2). Over extended periods of time, approaching 24 h, concomitant etching of the germanium undercuts the vertical inukshuks, and thus many are observed scattered on the surface (Figure 1b).

The nano-inukshuks were characterized by SEM, X-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The results indicate that the structures are metallic crystalline silver. Transmission electron microscopy (TEM) of an individual hexagonal plate, isolated by sonication of a sample of nano-inukshuks on germanium in methanol, shows that the flat face of the disk is the Ag(111) face, the most stable crystal plane of silver (Figure 3). The similarity of the faceted tips of the nano-inukshuks as observed by SEM to individual hexagonal Ag plates recently synthesized via a solution phase reverse micelle reduction approach suggests that they may be structurally related.⁸ Open cell potential (OCP) experiments indicate that nucleation of silver on the germanium surface takes place in the first 100 seconds,^{10b} followed by an equilibrium situation of metal nanoparticle growth, most likely via a Volmer–Weber mechanism.^{10d} Dendritic growth of hexagonal silver structures is observed on the wafer edges, pointing to their role as a global cathode, in addition to the

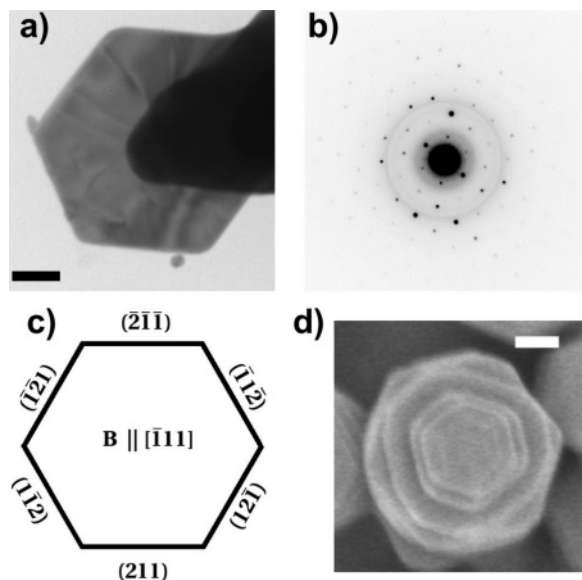


Figure 3. TEM of a silver hexagon isolated by sonication of silver nano-inukshuks in methanol. (a) TEM of a silver metallic hexagon; the black bar is 100 nm. (b) Selected area diffraction (SAED) pattern of the left 1/3 of this figure (omitting dark area). (c) Indexed hexagonal nanocrystal based on the SAED of (b). (d) Close-up of a nano-inukshuk tip for comparison; the white bar is 100 nm.

local cathodic nature of the silver metal deposits;^{10b} OCP experiments indicate that if the edges are not exposed, the surface potential rises by 50–100 mV. Figure 4 shows an optical image of a 1 cm² germanium wafer, with SEM images of different regions. The nano-inukshuks form across most of the face of the wafer, with the exception of the middle spot of the wafer, presumably the global anode as indicated by substantial germanium oxide deposits (by EDS) and little silver deposition, and the dendritic regions near the edges. Figure 5 provides a dramatic representation of the extended growth from the corners of the sample after an extended 24 h immersion of Ge(100) n-type in 1 mM AgNO₃. The dendrites reflect the hexagonal plate parent structure as determined by SEM (figures 5b and c). SEM images of silver-on-Ge samples with no edges appear much less ordered, with few nano-inukshuks and substantial tenacious germanium oxide deposits.

At concentrations below 0.5 mM silver ion, a combination of etching and metal deposition occurs, as represented by Figure 6 and the Supporting Information. At 1×10^{-4} M AgNO₃(aq), triangular and square etch pits with embedded silver nanoparticles are observed on Ge(111) and Ge(100), respectively. At 10^{-5} M AgNO₃(aq), etching of the germanium alone is the predominant process. 10^{-4} M silver ion

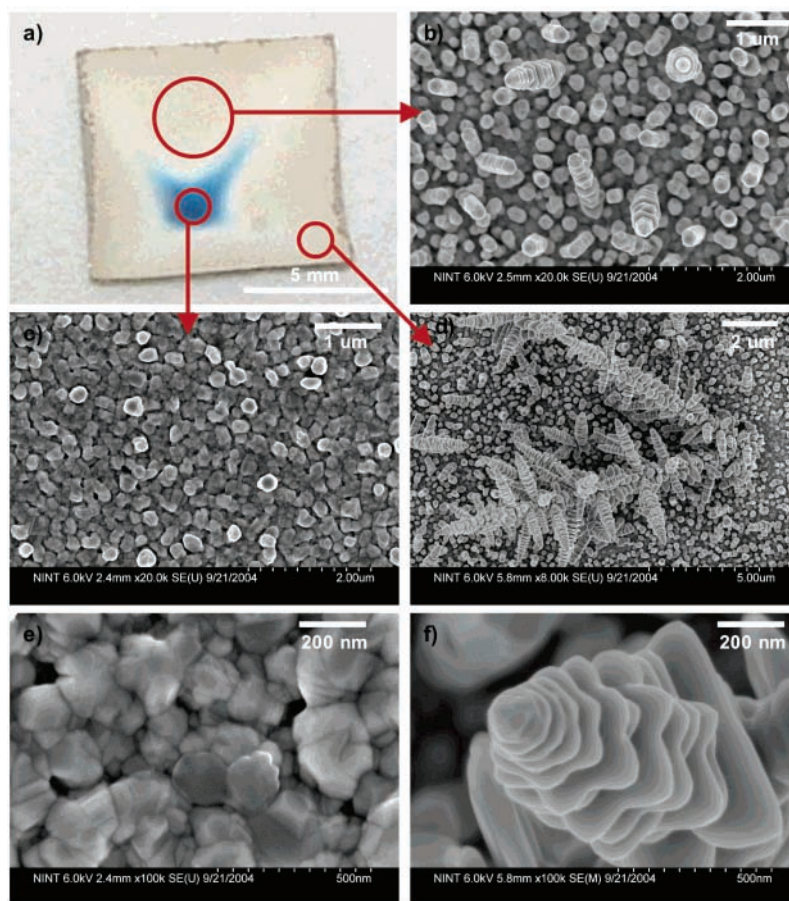


Figure 4. Demonstration of different regions of silver deposition across the face of a Ge(100) n-type wafer after 4 h, with 1.0×10^{-3} M AgNO₃. (a) Optical photograph of a 1 cm diameter wafer, showing the X-shape and areas of silver deposition (light colored areas). (b) The aligned nano-inukshuks form predominately on the flat planes across the front of the wafer, as shown in this SEM. (c,e) SEM images of the center of the X-shape; EDS indicates that this central area is made up of germanium oxide and some silver. (d,f) Toward the corners, dendritic structures are observed (SEM images).

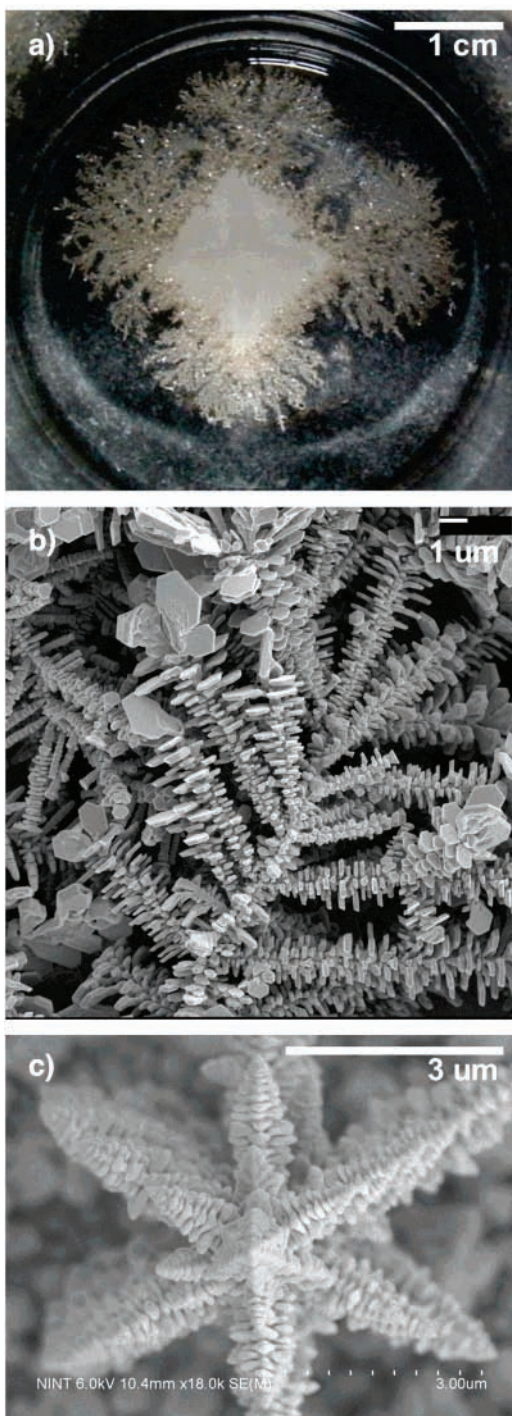


Figure 5. Long-term (24 h) deposition of silver nitrate leads to a large amount of dendritic deposition from the edges and corners of the Ge wafer. (a) Optical micrograph of Ge(100) n-type immersed in 1.0×10^{-3} M silver nitrate. (b,c) SEM images of some of the different dendritic structures observed on the edges of the germanium wafer; all reflect the parent hexagonal inukshuk shape.

appears to be the minimum concentration at which silver deposition on the surface competes effectively with etching. At higher concentrations of 10^{-2} M silver ion, rapid silver deposition occurs, leading to growth in ~ 1 h of somewhat faceted silver dendritic structures on the surface.

The effects of the germanium wafer orientation, doping, choice of counteranion, additives, temperature, light, and stirring, were investigated and found to have small effects

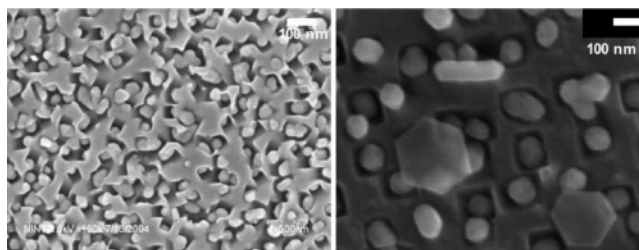


Figure 6. 1.0×10^{-4} M silver nitrate deposition conditions, demonstrating local etching of the germanium substrate induced by silver nanoparticle formation on the surface. (a) p-Type Ge(111) after 1 h deposition. (b) p-Type Ge(100) following 5 h of deposition.

on the galvanic displacement reaction. Wafer orientation is relatively unimportant for nano-inukshuk formation as they were observed on Ge(111) and Ge(100) faces, and even on the rough edges of germanium. Doping, n- or p-type, of the wafers does, however, affect the rate of deposition; optical images in the Supporting Information show that n-type wafers lead to faster overall deposition than p-type. Different Ag(I) salts also yield nano-inukshuks, including AgClO_4 and $\text{Ag}(\text{CH}_3\text{CO}_2)$, although with the former, deposition was more rapid than with AgNO_3 . AgSO_4 , on the other hand, consistently produced more flat dendritic structures. Consequently, few generalizations concerning anion effects can be made at this point. Addition of an equivalent of sodium nitrate to the 1.0 mM AgNO_3 reactions did little to change the outcome, although there appeared to be more etching of the germanium. Since germanium oxides are produced via the galvanic displacement, it could be postulated that germanium oxide acts as a directing agent. The presence, however, of an excess of GeO_2 , purchased commercially, had only a minor influence on a 1.0 mM AgNO_3 deposition except to render the surfaces more difficult to analyze due to residual germanium oxides coating the nanostructures. Higher temperatures (40°C) not surprisingly increase the deposition rate, but the silver is dendritic and more unstructured; lower temperatures (4°C) favor formation of flat plates. Illumination of the reactions with white light irradiation results in continuous metal deposition across the face of the wafer with substantial concomitant oxidation, but nano-inukshuks were clearly visible in most regions of the germanium wafer face. Stirring the solution has a subtle effect on silver deposition; vertical inukshuks are observed on the flat germanium face toward the edges, with the dendritic structures growing off the edge, but the X-pattern of the global anode becomes less obvious visually. These results point to a fine balance between diffusion and silver surface energetics that determines the shape of the resulting structures.

To conclude, galvanic displacement of silver(I) ions leads to complex crystalline, metallic silver nanostructures on native oxide-coated germanium surfaces. Detailed electrochemical studies of the electrodeposition process on germanium and other semiconductors are presently under investigation to correlate structure, potential, and greater degrees of selectivity.

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Supporting Information Available: Detailed experimental procedures and characterization of the nano-inukshuks (XPS, XRD, EDS, SEM), SEM images of other conditions mentioned here not shown, and open cell potential (OCP) profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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