

LETTERS

Noble and Coinage Metal Nanowires by Electrochemical Step Edge Decoration

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A general method is described for the electrodeposition of long ($>500 \mu\text{m}$) nanowires composed of noble or coinage metals including nickel, copper, silver, and gold. Nanowires of these metals, with diameters in the range from 60 to 750 nm, were obtained by electrochemical step edge decoration (ESED), the selective electrodeposition of metal at step edges. Nanowire growth by ESED was accomplished on highly oriented pyrolytic graphite surfaces by applying three voltage pulses in succession: An oxidizing "activation" pulse, a large amplitude, reducing "nucleation" pulse, and a small amplitude reducing "growth" pulse. The activation pulse potential was optimized to oxidize step edges on the graphite surface just prior to deposition. The nucleation pulse had an overpotential for metal deposition of between -150 and -500 mV and a duration of 5–100 ms. The growth pulse had a small deposition overpotential of less than -100 mV. Nanowire growth was characterized by a time-independent deposition current, and consequently, the nanowire radius was proportional to the square root of the deposition time in accordance with the expected growth law.

I. Introduction

Metal nanowires that are a few microns in length can be prepared using a variety of methods including template synthesis,^{1–18} solution phase reduction,^{19–21} and physical vapor deposition (PVD) onto carbon nanotubes.²² Nanometer-scale metal lines that are hundreds or thousands of microns in length can be prepared on silicon surfaces using electron beam lithography,^{23,24} or by PVD;^{25–28} however, there are few methods for preparing unsupported metal nanowires that are longer than $10 \mu\text{m}$.

We have recently described a method for preparing molybdenum nanowires that are up to $500 \mu\text{m}$ in length.^{29,30} Our method, called electrochemical step edge decoration, or ESED,³⁰

involves the electrodeposition of MoO_2 selectively at step edges on a graphite surface, and the subsequent reduction of these MoO_2 nanowires to molybdenum metal nanowires at $500\text{--}650$ °C in hydrogen. This two-step method (Scheme 1) is versatile, but it cannot be used to prepare nanowires composed of metals that do not have a stable, electronically conductive oxide, and this includes the noble metals. Of course, noble metals can be electrodeposited directly, but attempts to obtain nanowires by ESED have so far been unsuccessful. The problem is that potentiostatic growth produces discontinuous nanowires because the number density of metal nuclei located along the step edge are too low. In this Letter, we describe a method for preparing long ($>500 \mu\text{m}$) nanowires composed of four different noble and coinage metals.

II. Experimental Methods

II.A. Nanowire Electrodeposition. All electrodeposition experiments were carried out in glass, one-compartment, three-

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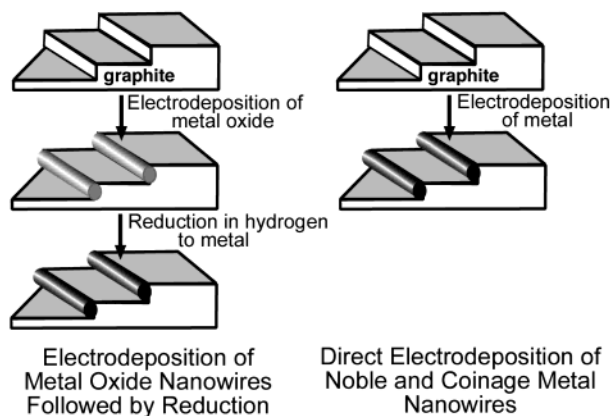
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TABLE 1: Composition of Plating Solutions and the Pulse Parameters Employed for Nanowire Growth

metal	plating solution ^a	E_{ox}, t_{ox} (V _{SCE} , s)	E_{nucl}, t_{nucl} (V _{SCE} , s)	E_{grow} (V _{SCE})
nickel	1.0 mM NiSO ₄ ·6H ₂ O, 0.1 M Na ₂ SO ₄	0.8, 5	-1.0, 0.005	-0.900
copper ^b	2.0 mM CuSO ₄ ·5H ₂ O, 0.1 M Na ₂ SO ₄	0.8 V _{Cu} , 5	-0.8 V _{Cu} , 0.005	-0.005 V _{Cu}
silver ^c	1.0 mM Ag ₂ SO ₄ , 0.04 M Na ₂ SO ₄ ·10H ₂ O, 1.0 mM saccharine, pH = 2.0	1.1 V _{Ag} , 5	-0.8 V _{Ag} , 0.100	-0.180 V _{Ag}
gold	2.0 mM AuCl ₃ , 0.1 M NaCl	0.8, 5	-0.8, 0.010	+0.560
palladium ^d	2.0 mM PdCl ₂ , 0.1 M HCl	0.8, 5	-0.8, 0.010	+0.300

^a All solutions aqueous, all potentials are V_{SCE} except where indicated. ^b V_{Cu} = + 0.019 V_{SCE}. ^c V_{Ag} = + 0.720 V_{SCE}. ^d References 39 and 40.

SCHEME 1: Two Methods for Implementing Electrochemical Step Edge Decoration To Produce Metal Nanowires



electrode cells. The composition of the metal plating solutions is provided in Table 1. These solutions were prepared using Nanopure water ($\rho > 18 \text{ M}\Omega$) and were purged with N₂ before each experiment. Nanowire electrodeposition experiments were carried out on the basal plane surface of ZYA or ZYB grade highly oriented pyrolytic graphite (HOPG) crystals obtained from Advanced Ceramics Inc. (Cleveland, OH). The basal plane surface of a HOPG crystal was cleaved using adhesive tape immediately prior to use. The growth of metal nanowires was carried out using the 3-pulse potential program shown in Figure 1. The values for the oxidation potential, E_{ox} , the nucleation potential, E_{nucl} , and the growth potential, E_{grow} , are listed for each of these four metals and palladium in Table 1. Unless otherwise indicated, all potentials are referenced to a saturated calomel reference electrode, V_{SCE}. Potential pulses were applied using an EG&G model 273 or 263 potentiostat/galvanostat. After deposition, the HOPG working electrode was removed from the plating solution, rinsed with water, and air-dried prior to characterization by SEM.

II.B. Microscopy. Freshly rinsed samples were placed in a desiccator and stored overnight prior to examination. Scanning electron microscopy (SEM) was carried out on uncoated samples using a Philips FEG-30XL microscope equipped with an EDAX elemental analyzer.

III. Results and Discussion

The graphite basal plane has an extremely low surface free energy of 35 dyne cm⁻¹.³¹ For this reason, the electrodeposition of virtually any material onto this surface occurs by a Volmer–Weber mechanism. That is, three-dimensional nanostructures are promptly formed at the earliest stages of the deposition process. For some materials including metal oxides such as MoO₂,^{29,30,32} and the conductive polymer polypyrrole,³³ nucleation occurs preferentially at step edges on the graphite surface. The propensity for nucleation at defects, a ubiquitous feature of many different types of deposition processes, is usually explained in terms of an energetic preference of nuclei for sites

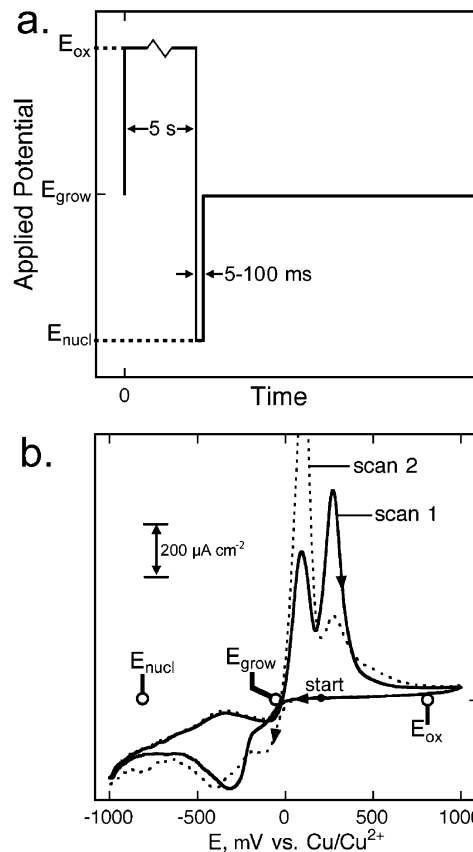
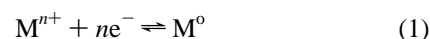


Figure 1. (a) Triple voltage pulse used to prepare metal nanowires in this study. (b) Cyclic voltammograms of a copper plating solution at an HOPG electrode showing the values for E_{ox} , E_{nucl} , and E_{grow} typically used for the preparation of copper nanowires. The solution was aqueous 2.0 mM CuSO₄·5H₂O, 0.1 M Na₂SO₄. Two oxidation waves seen at +100 and +350 mV_{SCE} are assigned to copper stripping (+100 mV_{SCE}) and oxidation of Cu⁰ to CuO (+350 mV_{SCE}).

of high coordination on the surface.³⁴ For the electrodeposition of metal at HOPG surfaces, step edge selectivity is also promoted by the fact that step edges have the ability to catalyze electron transfer to metal ions in solution.^{35–38} Previously, we have electrodeposited metal oxides selectively at step edges on an HOPG surface by applying a deposition overpotential that exceeds the threshold for nucleation at steps but is smaller than the nucleation overpotential required to obtain a significant nucleation rate on terraces.^{29,30,33} When the deposition process is continued long enough for individual particles nucleated along a step edge to coalesce, nanowires with diameters of between 13 and 500 nm and lengths up to 500 μm have been obtained.^{29,30,32}

Although this strategy, called electrochemical step edge decoration or ESED, works well for metal oxides, attempts to obtain nanowires by the direct step edge-selective electrodeposition of metals according to the reaction



have failed. Specifically, in our experiments with copper, silver, nickel, gold, and palladium, it has become clear that no growth potential exists that produces a high linear density of metal nuclei along step edges ($>20 \mu\text{m}^{-1}$), as required for the formation of nanowires, without also producing rapid nucleation of metal on terraces. Thus, metal nanowires cannot be obtained on HOPG surfaces using reaction 1 and the potentiostatic method described previously.^{29,30}

In this Letter, we describe a general method for employing reaction 1 to produce metal nanowires by ESED. Recently, we have used a variant of this method to produce palladium nanowires.^{39,40} Here we discuss this method in greater detail and demonstrate its generality by producing long ($l > 500 \mu\text{m}$) metal nanowires composed of nickel, copper, silver, and gold, with diameters in the range from 60 to 750 nm. The step edge selective growth of metal was obtained by applying three voltage pulses in succession as shown in Figure 1a: An oxidation pulse of 0.8–1.0 V_{SCE} for 5 s, a reducing nucleation pulse of $-1.0 V_{\text{SCE}}$ for 5–100 ms, and a growth pulse with an overpotential of duration of between 20 s and several minutes. This triple-pulse scheme produces a nucleation density along step edges of 20–40 μm^{-1} . With continued growth, this dense linear array of metal nuclei evolves into a continuous nanowire with a diameter of 50 nm or so. If either the oxidation or the nucleation pulses are omitted, the nucleation density along step edges is less than 5 μm^{-1} on average and metal nanowires are not obtained.

Typical values for the three pulse potentials are superimposed on a cyclic voltammogram for copper in Figure 1b. We have found that an oxidation potential close to $+0.8 V_{\text{SCE}}$ is optimal for all of the different metals discussed here. Likewise, there is considerable latitude in the selection of the nucleation pulse potential. In general, any E_{nucl} with an overpotential⁴¹ for metal deposition exceeding -500 mV produces a high density of metal nuclei on the preoxidized step edge. The selection of the growth potential, E_{grow} , is critical and involves a compromise: values of E_{grow} that are too negative cause the nucleation and growth of metal particles on terraces, whereas values of E_{grow} that are too positive can cause the rate of nanowire growth to be depressed to the point where hours are required. The optimization of E_{grow} for each metal, and each metal plating solution, involves trial and error. Values of E_{grow} for the particular plating solutions used to prepare nanowires in this study are listed in Table 1.

Scanning electron micrographs of copper nanowires with diameters ranging from 70 to 340 nm are shown in Figure 2. After the nucleation voltage pulse is applied, nanowire growth at E_{grow} is characterized by a constant current, i_{dep} . The transport of metal ions under these conditions occurs under conditions of mixed diffusion and convection control and a simple growth law can be derived:

$$r(t) = \sqrt{\frac{2i_{\text{dep}}t_{\text{dep}}V_{\text{m}}}{\pi nFl}} \quad (2)$$

In this equation, t_{dep} is the total deposition duration, V_{m} is the molar volume of the electrodeposited metal, and l is the total length of metal nanowires on the graphite surface. Equation 2 assumes hemicylindrical nanowire geometry. The radii of the electrodeposited copper nanowires, measured from SEM data like that of Figure 1, increased in proportion to $t^{1/2}$, as predicted by eq 2. This growth law was also observed for nickel, silver, and gold, and representative SEM images of nanowires of these three metals are shown in Figure 3. For all three of these metals,

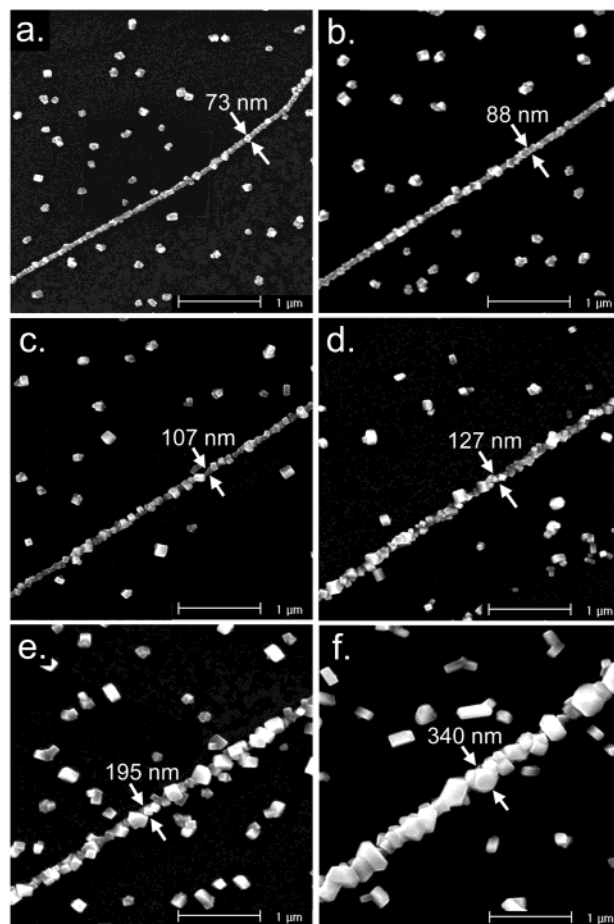


Figure 2. Scanning electron micrographs of copper nanowires. These nanowires were electrodeposited from the solution indicated in Table 1, using $E_{\text{nucl}} = -800 \text{ mV}_{\text{SCE}}$ and $E_{\text{grow}} = -5 \text{ mV}_{\text{SCE}}$. The growth times employed in each experiment were (a) 120 s, (b) 180 s, (c) 300 s, (d) 600 s, (e) 900 s, (f) 2700 s.

nanowires with lengths of more than $100 \mu\text{m}$ were produced in large numbers on the graphite surface.

In contrast to the smooth MoO_2 nanowires prepared on graphite by potentiostatic electrodeposition,^{29,30} individual metal grains (with diameters approximately equal to the diameters of the nanowires) are clearly visible in the SEM images of Figures 2 and 3. Palladium nanowires possess a similar appearance.^{39,40} The metal grains in all of these nanowires are much larger than those seen in MoO_2 nanowires, or in the molybdenum metal nanowire derived from them^{29,30}—the question is, why? We believe that larger grains are formed with the triple-pulse method because nucleation at step edges can occur only during the 5–100 ms nucleation pulse (Figure 4). Subsequently, during the growth pulse, these metal nuclei increase in diameter but the growth potential is too low to permit the formation of new metal nuclei. In contrast, the formation of new metal oxide nuclei appears to continue during the electrodeposition of metal oxide nanowires. Metal particles that have nucleated on terraces can be seen in all of the SEM images shown in Figures 2 and 3 and are also seen on surfaces after the preparation of palladium nanowires.^{39,40} Nucleation at terraces occurs at E_{nucl} albeit with a lower efficiency than nucleation at oxidized step edges. Consequently, we have found that some parallel growth of particles on terraces is inevitable in these experiments.

We have not yet succeeded in our attempts to obtain high-quality, four-point resistance measurements for single nanowires prepared by ESED. However, we know that many nanowires prepared by ESED are electrically continuous over lengths of

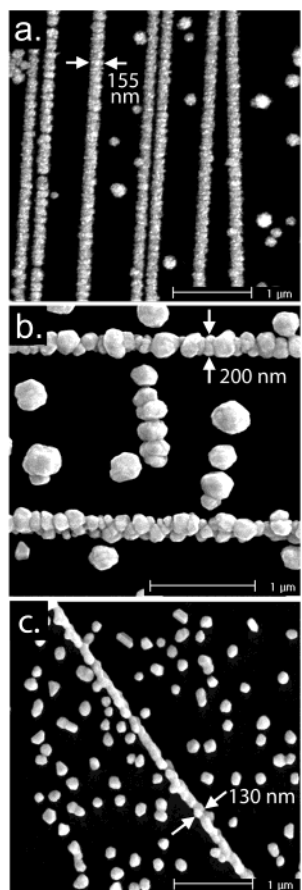


Figure 3. Representative scanning electron micrographs of (a) nickel, (b) silver, and (c) gold nanowires prepared by the potentiostatic double pulse method.

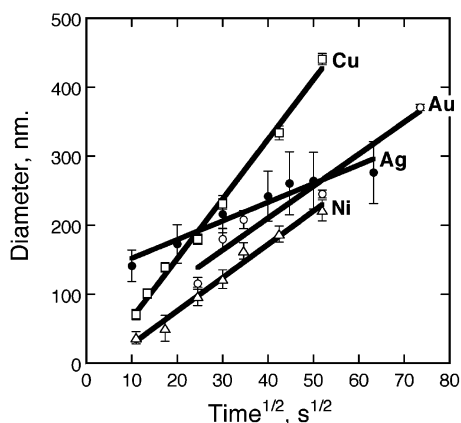
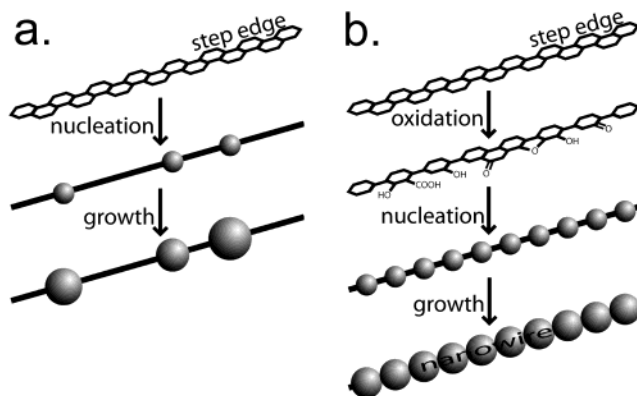


Figure 4. Nanowire diameter versus (deposition time)^{1/2} for the growth of nanowires composed of four metals as indicated. Each series of experiments for a particular metal were performed using a single graphite crystal to limit the variation in the step edge density from experiment to experiment (see eq 2). This crystal was cleaved before each experiment to expose a fresh, clean graphite surface. Error bars for each data point are twice the standard deviation for the mean particle diameter as measured from SEM images.

300 μm or more. This conclusion follows from the observation that nanowire arrays, prepared from noble or coinage metal nanowires using a previously described method,³⁹ are invariably highly conductive. Typical resistances for an array of 300 μm length nanowires are in the range from 0.001 to 10^{-5} Ω , for example. This conclusion is equally valid for ESED-synthesized nanowires composed of copper, nickel, silver, gold, and palladium.

SCHEME 2: Effect of Oxidation of the HOPG Surface on the Nucleation Density of Metal along Step Edges



The electrochemical oxidation of the graphite surface is essential for nanowire growth, but we do not know how the chemistry of the HOPG surface is altered by this oxidation. On the basis of the prior work of McCreery and co-workers,^{35–38} the oxidation conditions employed here are too mild to oxidize sp^2 carbons on terraces, thereby producing step edges on the HOPG surface. Instead, as shown in Scheme 2, we speculate that oxidation of the surface at +0.8 V_{SCE} produces carbonyls, ethers, hydroxyls, and other oxygen-containing functionalities preferentially at steps, thereby increasing the affinity of metal adatoms for steps, reducing the nucleation overpotential, and increasing the nucleation density along step edges.

Summary

Nanowires composed of copper, nickel, silver, gold, and palladium can be directly electrodeposited with size selectivity using the potentiostatic triple-pulse method described here. Nanowires are obtained when metal nanoparticles are forced to nucleate with a high linear density at step edges on the HOPG basal plane. Subsequent growth of these particles causes them to coalesce into continuous metal wires that exceed 100 μm in length and are organized into parallel arrays. Unlike the molybdenum nanowires that we have described earlier,^{29,30} nanowires prepared by direct metal deposition at steps are granular because nucleation is not permitted to occur progressively during growth. Nevertheless, the nanowires prepared using electrochemical step edge decoration are narrowly dispersed in diameter, on average, and can have a mean diameter of between 60 and 750 nm. These structures are likely to be useful both for the investigation of the fundamental physics and chemistry of these nanostructures and for the construction of devices that exploit the unique properties of metal nanowires.

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- (41) The overpotential is the difference between the applied deposition potential and the reversible potential for the metal of interest.