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Citation: Appl. Phys. Lett. 110, 073106 (2017); doi: 10.1063/1.4976027
View online: http://dx.doi.org/10.1063/1.4976027
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Controlled electrochemical growth of ultra-long gold nanoribbons

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(Received 28 July 2016; accepted 28 January 2017; published online 14 February 2017)

This paper describes the electrochemical growth of branchless gold nanoribbons with ~40 nm x ~300 nm cross sections and >100 μm lengths (giving length-to-thickness aspect ratios of >103). These structures are useful for opto-electronic studies and as nanoscale electrodes. The 0.75–1.0 V voltage amplitude range is optimal for branchless ribbon growth. Reduced amplitudes induce no growth, possibly due to reversible redox chemistry of gold at reduced amplitudes, whereas elevated amplitudes, or excess electrical noise, induce significant side-branching. The inter-relatedness of voltage-amplitude, noise, and side-branching in electrochemical nanoribbon growth is demonstrated. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4976027]

Ultra-long nanowires and nanoribbons with aspect ratios >103 are useful samples for learning about fundamental opto-electronic processes, including ballistic and collective charge-transport on ultrafast time-scales.1–3 Such studies will benefit from monolithic wires long enough to allow the excitation to propagate between spatially separated pump- and probe-illumination sites. In the physiology-venue, branchless nanowires are promising neural4 and cellular probes.5 Directed electrochemical nanowire assembly (DENA)6 is a method for fabricating electrode-nanowire assemblies where the nanowire is a single crystal7 of tunable diameter8 and variable composition: In,9 Au,9 Cu,10 Pt,11 and Pd.12 Growth is caused by applying an alternating voltage across working and counter electrodes (CEs) that are immersed in a salt solution, stimulating the dendritic crystallization of the metallic species at the (sharper) working electrode (WE) during the negative half cycles.13 As the term dendritic crystallization suggests, the method tends to produce branched, TV-antenna-shaped structures, and one would like to control the degree to which side-branching occurs during the growth process. Prior applications of DENA have employed voltage-amplitudes of 4–8 V for Au,9,14 Cu,10 Pt, and Pd wires,11,12 and ~16 V for In wires.7 These values are several times larger than the standard reduction potentials of the metals. Here we have employed electro-etched working electrodes having <50 nm tip radii in order to realize growth at considerably lower amplitudes: 0.75–1.5 V. These factors enable the growth of ultra-long gold nanoribbons with length-to-thickness aspect ratios >103. A stability analysis illustrates how small voltages and minimal noise suppress the Mullins-Sekerka instability, rendering side-branching unlikely.

Figure 1(a) depicts the set-up for the DENA-based growth of gold nanoribbons.6,9 This apparatus is mounted on the stage of an inverted microscope (Leica, IRB) under ambient conditions and consists of an electrode pair immersed in aqueous KAuCl₄ solution. To confine the growth to its tip, the working electrode (WE) must be sharper than the counter electrode (CE). Hence, we fabricate the WE by electro-etching 200 μm diameter gold wire (Ted Pella) until its foremost radius is <50 nm.15 The scanning electron micrograph in Figure 1(b) and the inset show a typical WE with a ~25 nm tip radius. The comparatively blunt CE (not shown), made from 500 μm diameter gold wire (Kurt J. Lesker), is electro-etched to a ~2.5 μm radius. The CE is taped to a glass microscope slide that is mounted on the inverted microscope. The WE is mounted in a 3D stage and positioned to have ~1 μm inter-electrode gap relative to the CE. A ~20 μl aliquot of solution composed of aqueous 40.0 mM KAuCl₄ (Sigma) is deposited across the inter-electrode gap. Nanoribbon crystallization is induced by using a function generator (Hewlett Packard, 8116A) to apply a 10–50 MHz square-wave voltage signal to the WE, while grounding the CE. The profile in Figure 1(c) is a representative 37.0 MHz voltage signal. A small (~+35 mV) DC offset is also applied to prevent coating of the ribbon by polycrystalline gold. A component of this study requires the addition of a white-noise signal, supplied by a second function generator (Agilent, 33220A), to the square wave signal. A high bandwidth (4.0 GHz) summing amplifier is used to do so. The average growth velocity (v) of a nanoribbon is determined by collecting movies of its growth and computing the ratio ΔL/Δt, where ΔL is the change in length and Δt the elapsed time. The surface of the microscope slide is made hydrophobic by coating it with poly-dimethyl silane (e.g., Rain-X), causing the solution drop to form a ~90° contact angle that permits the electrode-ribbon assembly to be pulled perpendicularly through the air-water interface—avoiding damaging lateral forces during extraction.

The cyclic voltammogram (CV) in Figure 1(d) illustrates the near-equilibrium redox behavior of gold. This CV plots the electronic current I into the WE versus the overpotential η of the WE. A positive current indicates a positive charge flow into the WE. The overall redox reaction is

\[ \text{Au}^{III} \text{Cl}^- (aq) + 3e^- \leftrightarrow \text{Au}^{(0)} + 4\text{Cl}^- . \]  

The overpotential is defined as \( \eta = V_{\text{App}} - V_{\text{Eq}} \) where \( V_{\text{App}} \) is the applied potential, and \( V_{\text{Eq}} \) is the equilibrium potential at which no current flows. This CV was collected using essentially identical, gold working, reference, and counter-electrodes in 5.0 mM KAuCl₄ (aq) solution. Equation (1)
Some caution is warranted here as a conventional CV may not reflect the non-equilibrium behavior driven by a RF voltage. A scanning electron microscope (FEI Versa 3D Dual Beam) equipped with an energy dispersive X-ray spectrometer was used to characterize the 2.7 × 2.7 μm² sample of a nanoribbon on ITO-coated glass, shown in the inset of Figure 2(a). Weight-percentages of 3.9% Au, 38.6% O, 30.3% Si, 6.2% Na, 10.3% In, and 3.0% Sn were observed, as well as trace quantities of Mg, K, Ca, and Al. The Au and O fluorescence maps [insets, Figure 2(a)] show that the Au signal correlates with the ribbon-location whereas the O signal anti-correlates with the ribbon-location, suggesting that the ribbon is composed of gold. The O, Si, Na, In, and Sn content are attributed to the substrate.

The ribbon-like nature of these nanostructures is evident in the scanning electron micrographs in Figures 2(b)–2(d). The widths of these (and 8 other) samples are between 130 nm and 360 nm. The tip-region shown in Figure 2(e) is narrower, having a lengthwise averaged diameter of 58 ± 3 nm, and the foremost tip width is ~10 nm (inset). The thickness of these ribbon-like wires was characterized by atomic force microscopy (Veeco, di Innovia). Figure 2(f) is a topographical image of a 171 μm gold nanoribbon on a glass coverslip. (This image is a composite 8 overlapping images of the wire). Figure 2(g) compares the topographical profile of the spine of the ribbon to that of the adjacent glass substrate. The dashed line in panel (f) indicates the location of these profiles. The difference between their lengthwise averaged heights is 37 ± 9 nm, a value that is representative of the ribbon-thickness elsewhere along the structure. Hence, the length-to-thickness aspect ratio is 171 μm/37 nm ≈ 4.6 × 10³ for this ribbon. We have topographically examined two other nanoribbons, obtaining the average thicknesses of 44 nm, and 39 nm, demonstrating that the growth of nanoribbons with high length-to-thickness aspect ratios is feasible with this technique.

Figure 3(a) depicts an electron diffraction pattern collected from the nanoribbon shown in panel (f). This study used a 200 kV electron microscope (FEI Tecnai F20 XT) that was set to a 290 mm camera length and a 10 μm diameter area selection aperture. Figure 3(b) shows the simulated

FIG. 1. (a) Side-view of experimental set-up. FG 1 and FG 2 denote the function generators; SA denotes a summing amplifier. (b) Scanning electron micrograph of a gold WE. Scale bar = 1.0 μm. Inset: enlarged view of tip. Scale bar = 200 nm. (c) Square-wave voltage signal used to grow gold nanoribbons. (d) Cyclic voltammogram of aqueous 5 mM KAuCl₄ solution, measured with gold WE, RE, and CE. Dashed lines indicate a typical square-wave period in DENA. Scan rate = 10 mV/s.

FIG. 2. (a) Optical image of a gold nanoribbon grown with a voltage amplitude of 0.88 V for 304 s. Scale bar = 50 μm. A video of this event is available online. Inset: SEM micrograph of a nanoribbon (left panel, Scale bar = 1 μm) and X-ray fluorescence maps of same segment showing locations of Au and O (as labeled, Scale bar = 500 nm). (b)–(d) Scanning electron micrographs of curved nanoribbon segments, displaying their ribbon-like shape. Scale bars = 1 μm, 2 μm, and 2 μm, respectively. (e) Scanning electron micrograph of tip region of nanoribbon. Scale bar = 1 μm. Inset: Enlarged view of tip region. Scale bar = 100 nm. (f) Composite topographical image of a ~171 μm long gold nanoribbon. Scale bar = 10 μm. (g) Height profiles collected from the spine of the nanoribbon and the adjacent substrate near the region indicated by the white dashed line in panel (f). (Multimedia view) [URL: http://dx.doi.org/10.1063/1.4976027.1]
crystallization of super-cooled melts. To see if electrical noise induces side-branching, and, consequently, can be used to tailor the morphology. For example, the Y-shaped structure in the inset, of potential interest for studying surface plasmon-propagation through a junction, was grown by applying a ~4 s pulse of noise at the designated point.

Direct measurement of the current during the (13.5 ns) negative half-cycles is challenging as only a few atoms join the crystal during this period. Instead, we have estimated the current density associated with deposition (i.e., the Faradic current density) by observing the nanoribbon growth velocity. Figure 5(a) plots the average growth velocity \( \langle v \rangle \) (unfilled circles) versus the voltage amplitude. Mass conservation implies that growth at velocity \( \langle v \rangle \) requires an average current density of

\[
\langle j \rangle \cong z e \rho_{Au} \langle v \rangle ,
\]

where \( \rho_{Au} = 5.89 \times 10^{28} \text{ m}^{-3} \) is the number density of gold, and \( z e \) (where \( z = 3 \)) is the charge that is transferred during a step of Equation (1). These values (filled circles) are given by the right axis in Figure 5(a). The current density increases

![FIG. 3](image1.png)

![FIG. 4](image2.png)

![FIG. 5](image3.png)
sharply with amplitude beyond a threshold of \(~750\text{mV}\). This plot is essentially a non-equilibrium voltammogram for gold reduction during DENA. To model this process, we assume that the overall deposition process (Equation (1)) is rate-limited by a single-electron step of the form \(O^+ + e^- = R^0\), where \(O^+\) is a gold species in the \(z = 1\) oxidation state, and \(R^0\) is the rate-limited product. The Butler-Volmer equation relates the current density collected by an electrode to the overpotential \(\eta\)^{21}

\[
\jmath = \jmath_0 \frac{c_{O^+}}{c_{O^0}} e_{O^+}^{-\frac{1}{2}} \left( e^{\eta z_{k}\rho_{AB} \Delta z_k} - 1 \right) \left( e^{(1-\eta) z_{k}\rho_{AB} \Delta z_k} - 1 \right),
\]

(3)

where \(\eta\) is defined above. \(\alpha\) is the symmetry factor associated with the energy barrier to reduction, and \(\beta\) is the inverse thermal energy \((k_BT)^{-1}\). \(c_{O^+}/c_{O^0}\) is the interfacial (bulk) concentration of species \(O^+\). The Gibbs-Thomson factor \(\rho_{AB} \gamma_k\) accounts for curvature effects.\(^{22}\) \(\gamma\) is the surface tension of the gold-solution interface, and \(k\) is the local curvature of the interface defined such that a protrusion (depression) has a positive (negative) curvature. The solid line in Figure 5(a) is a best-fit of Equation (3) to the estimated current density data. An exchange current density of \(\jmath_0 \approx 1100\text{A m}^{-2}\) and symmetry factor \(\alpha = 0.145\) are needed to account for the \(~750\text{mV}\) threshold to charge flow. The other fitting parameter values are reported in the caption. The fit quality is reasonably good, indicating that the Butler-Volmer model accurately describes the high frequency (37 MHz) gold reduction that occurs during the DENA process.

A linear stability analysis by Haataja and co-workers\(^{21}\) illustrates how electrochemical systems that obey Equation (1) can become unstable and undergo side-branching.\(^{21}\) A microscopically rough interface is sketched in the inset to Figure 5(a). Let this interface represent a profile of the nanoribbon, like that in Figure 2(g). This profile \(x(t)\) may be decomposed into a sum of Fourier modes, each of spatial frequency \(k\) (units: rad/m), a few of which are sketched in the inset. The contribution of a single mode is \(\mp \Delta z_k(x,t) = vt + \delta z_{0,k} e^{ikx} e^{i\omega t}\). \(v\) is the steady-state growth velocity of the interface in the \(z\)-direction, and \(\Delta z_{0,k}\) is the amplitude of the \(k\)th mode. The factor \(e^{i\omega t}\) is the stability factor. If the surface is stable, the amplification rate \(\omega_k\) (for each mode) is equal to zero, but for an unstable surface \(\omega_k\) is non-zero. If \(\omega_k\) is positive (negative), mode \(k\) will experience amplified (retarded) growth. If, for example, all modes other than \(k\) are stable, the nanoribbon-profile will become wave-like (with spatial wavelength \(k = 2\pi/k\)), and the crests of the wave will become side-branches. This effect occurs because a protrusion on a surface steepens the local solute concentration gradient and, thereby, increases the local current density and the growth rate of the protrusion. This feedback mechanism is known as the Mullins-Sekerka instability.\(^{23}\) Time-differentiation of \(\mp \Delta z_k\) gives the growth velocity of the \(k\)th mode: \(v + \dot{\delta} z_k = v + \omega_k \delta z_k\). Growth at velocity \(v\) gives the current density \(j + \dot{\delta} z_k = ne \rho_{AB} (v + \delta z_k)\), where Equation (2) was used. Substituting \(\omega_k \delta z_k\) for \(\delta z_k\) gives the current density fluctuation, which is a measure of the electrical noise level

\[
\delta j_k(x,t) = n e \rho_{AB} \delta z_k.
\]

(4)

Hence, the noise-level \(\delta j_k\) and the amplification rate \(\omega_k\) are proportional to each other, implying that elevated noise levels can amplify the growth rate of the protrusions.

For a roughened but flat electrochemical interface, Haataja and co-worker\(^{21}\) have derived a dispersion relation for \(\omega_k\): (Equation 16 in Ref. 21)

\[
\omega_k \approx \frac{k}{\rho_{AB}} \left[ \frac{1}{(1 + \alpha) - \frac{3}{2} - j} \right] \frac{jk^2}{k},
\]

(5)

where the unitless current density is \(j = \frac{j}{j_0}\) and \(j_0 = \frac{\text{mol Au}}{L_w}\). This function is plotted for five experimentally realized \(j\)-values (near \(4.9 \times 10^{-8} \text{A m}^{-2}\)) in Figure 5(b). To attain these plots, the diffusion coefficient of gold chloride was estimated to be \(D = 1.0 \times 10^{-9} \text{m}^2 \text{s}^{-1}\), and a value of \(L_w = 3.5 \times 10^{-6} \text{m}\) was used for the diffusion length, giving \(j_0 = 3306 \text{A m}^{-2}\). These plots show that \(\omega_k\) is positive for finite ranges of \(k\)-values, denoting the unstable modes. Moreover, the magnitude of \(\omega_k\) across these unstable regions increases with \(j\). Hence, larger voltage amplitudes \(V_{\text{App}}\), which drive larger current densities \(j\) [by Equation (3)], are expected to induce stronger degrees of side-branching. Thus, an upsurge in either the amplitude \(V_{\text{App}}\) or the noise \(\delta j_k\) will inflate the amplification rate \(\omega_k\) and induce side-branching. This picture explains our main observations: that minimal voltage amplitudes are required to suppress side-branching, and that excess noise tends to induce it (Figure 4). A more quantitative analysis will benefit from direct measurement of the deposition current density and a 3D theory that addresses the cylindrical geometry and, possibly, surface tension anisotropy of the crystalline nanoribbon.

In conclusion, we report the methodology for the electrochemical growth of ultra-long, branchless gold nanoribbons. Their fabrication is enabled by the use of sharp, electro-etched working electrodes that permit wire growth with voltage amplitudes in the 0.75–1.0 V range. Reduced amplitudes induce no growth, possibly due to the nearly reversible redox chemistry of gold at low amplitudes, whereas elevated amplitudes, or excess electrical noise, strongly enhance the degree-of side-branching. Collectively, these results illuminate the relationship between voltage amplitude, electrical noise, and side-branch formation during electrochemical dendritic growth and illustrate how side-branching may be controlled. The fabrication of long, branchless nanoribbons is one application. It is also possible to add noise in a controlled manner in order to fabricate nanoribbons with branches at selected points along the main trunk—another structure of optoelectronic interest. Finally, the common effect (side-branch formation) that amplitude and noise cause suggests that shot noise, which scales with amplitude, may be an important factor in the DENA process. This possibility will be examined in the future.

This work was supported by an NSF EPSCoR IRR Track II Nebraska-Kansas Collaborative Research Award (1430519) and the NIH Brain Initiative (1R21EY026392).
We thank Professor Larry Weaver for edifying theoretical insights and Tim Sobering and David Thurmstrom for electronic assistance.