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LETTER

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Electroplate and Lift Lithography for Patterned Micro/Nanowires Using Ultrananocrystalline Diamond (UNCD) as a Reusable Template

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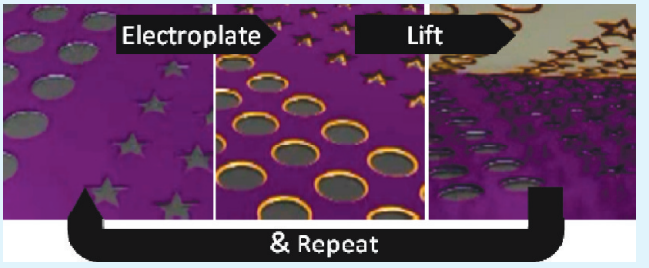
Supporting Information

ABSTRACT: A fast, simple, scalable technique is described for the controlled, solution-based, electrochemical synthesis of patterned metallic and semiconducting nanowires from reusable, nonsacrificial, ultrananocrystalline diamond (UNCD) templates. This enables the repeated fabrication of arrays of complex patterns of nanowires, potentially made of any electrochemically depositable material. Unlike all other methods of patterning nanowires, this benchtop technique quickly mass-produces patterned nanowires whose diameters are not predefined by the template, without requiring intervening vacuum or clean room processing. This technique opens a pathway for studying nanoscale phenomena with minimal equipment, allowing the process-scale development of a new generation of nanowire-based devices.



KEYWORDS: electrode patterning, nontraditional lithography, patterned nanowires, metamaterials, electrochemically deposited semiconductors, UNCD films

INTRODUCTION

Many techniques other than conventional lithography[1−4] exist for making nanowires to study new material properties and new phenomena expected at the 1D nanoscale. Large arrays of free-standing straight nanowires or rods can be made using membrane templates,[5,6] selective crystal growth,[7,8] or solid surface templates.[9] Large arrays of rings can be fabricated by exploiting edge spreading lithography.[10] Additionally, a limited number of nanowires may be synthesized by exploiting differences between the domains of block copolymers.[11] For more complex, nonrepetitive structures, patterned nanowires can be made by the serial methods of electron beam writing[12] or scanning probe lithography.[13] One method that is capable of forming large arrays of complex patterned nanowires is phase shifting photolithography,[14] but the photoresist template must be remade in a multistep process with each batch of patterned nanowires. One generic problem intrinsic to the fabrication of patterned nanowires with all of the previously mentioned lithographic methods, is that the nanoscale templates are sacrificial—all the work of producing the pattern is lost in the fabrication of the nanowires, and the templates and/or patterning steps must be repeated to produce each and every duplicate copy of the nanowires. By contrast, soft lithography transfers a small molecule "ink" that can be used as a nucleation point for deposition[15] or as a resist for a dry etching process.[16] However, soft lithography is not a direct method for producing nanowires or other nanostructures. A special adaptation of the soft lithography method called nanotransfer printing (nTP) utilizes a patterned polymeric stamp coated with a metal film to transfer that film onto a secondary substrate where the metal is released.[17] Arrays of straight nanowires can be formed by the superlattice nanowire pattern transfer technique (SNAP).[18] Although the last two methods are capable of reusing the initial template, deposition is limited to single materials and requires multiple steps for making detailed patterns. Nanowires of gold, palladium, platinum, and bismuth have been fabricated by a technique known as lithographically patterned nanowire electrodeposition (LPNE), utilizing thin films of silver or nickel under corresponding layers of photoresist, via electrodeposition upon the edge of the thin sacrificial silver or nickel layer.[19] This approach is very elegant because it provides control over the patterning of electrodes using simple lithography, and requires only the relatively straightforward control over the thickness of the deposited thin films,

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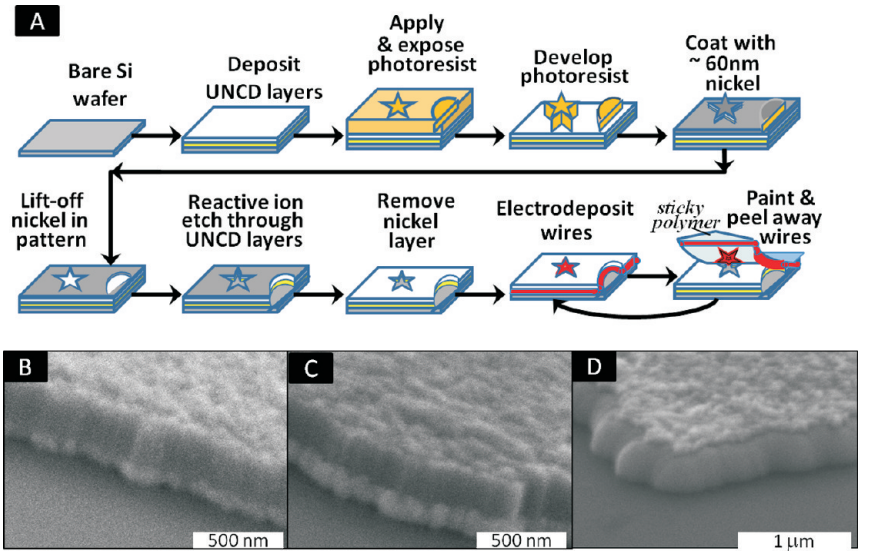

Figure 1. (A) Schematic of the procedure for fabricating the UNCD electrodes and synthesizing multiple copies of the patterned wires. (B–D) Edge views of three UNCD electrodes of identical fabrication, all having 75 nm of N-UNCD layers, showing the ability to grow different thicknesses of wires by varying the duration of electroplating: palladium wire with average thickness of (B) 85, (C) 150, and (D) 430 nm.

rather than the more difficult constraint of the lateral dimensions of the patterns. However, the nobility of the metal films restricts the range of materials that can be deposited using electrodeposition, and the templates are sacrificial. What is lacking among all the known nanowire synthesis methods described above is a single process that can create patterned nanoscale structures of diverse materials, using nonsacrificial templates, without the need for multiple pieces of expensive, specialized equipment.

A new nanowire fabrication technique meeting all of these criteria, referred to as electroplate and lift lithography (E&L), has been jointly developed by a team from the University of Wisconsin–Stevens Point and Argonne National Laboratory, and is described herein. An animated overview of the entire process in .mpg format is available as Supporting Information. E&L is a fast, simple and scalable technique for controlled, solution based, electrochemical synthesis of patterned metallic and semiconducting nano- and microwires on the nanoscale-thin edges of a reusable template. A multilayer ultrananocrystalline diamond (UNCD) template is used as an electrode for wire synthesis in either aqueous or nonaqueous solution. The nonsacrificial UNCD nanoelectrodes allow controlled and repetitive fabrication of nano- and microwire arrays in complex patterns from a variety of functional materials. The material choices are limited only by their ability to be electrochemically deposited. Unlike all other known methods for making patterned wires, this benchtop technique quickly produces large numbers of complex, patterned wires, with diameters controllable in situ without modification of the template, and without intervening vacuum or clean room processes. The technique described here demonstrates a new paradigm shift in the synthesis, processing, and development of a new generation of process-scale, wire-based devices for advanced nanotechnologies, in a highly economical manner.

RESULTS AND DISCUSSION

UNCD is a unique material,[20−24] which is grown by microwave plasma chemical vapor deposition (MPCVD)[20−24] or by the hot filament chemical vapor deposition (HFCVD) process.[25] The latter is commercialized and available on the market through Advanced Diamond Technologies. UNCD grown using the MPCVD technique involves a novel argon-rich methane plasma [Ar (99%)/CH_4 (1%)] that produces diamond films with a 2–5 nm grain size, resulting in films with 4–5 nm rms surface roughness.[26] This is critical for the particular application of growing nanowires with high resolution and low adhesion. The base Ar plasma [Ar (99%)/CH_4 (1%)] produces insulating, undoped UNCD (U-UNCD) films. Alternatively, the addition of N_2 to the gas mixture enables the growth of electrically conductive nitrogen incorporated (N-UNCD) films, with measured n-type conductivity as high as 260 $(\Omega\ \mathrm{cm})^{-1}$.[20,21] Therefore, it is possible to make a thin, highly conductive N-UNCD film, capped by an insulating overlayer of U-UNCD, thereby enabling the development of the novel UNCD-based nanoelectrode templates discussed here. Because of the unique chemistry and growth process, MPCVD deposited UNCD films can be grown at temperatures as low as 400 °C, as confirmed by their CMOS compatibility.[26] Therefore, UNCD can be deposited on glass substrates. In addition, UNCD films exhibit most of the well-known properties of single-crystal diamond, such as high hardness, stiffness, chemical resistance, surface hydrophobicity, wide electrochemical potential window (when conductive) and low-friction (low stiction).

The UNCD template is fabricated by depositing alternating layers of N-UNCD and U-UNCD, with the N-UNCD layer in contact with a flat substrate such as silicon with an insulating thermal oxide, and the terminating external layer being U-UNCD. The N-UNCD layer has a high density of electrochemically active sites for nucleation at the exposed edge of the pattern, ensuring favorable conditions for growing uniform, dense, continuous nanowires. The insulating U-UNCD top layer prevents electrodeposition from occurring across the exposed top surface of the U-UNCD/N-UNCD layered structure. Figure 1A shows the schematic for making the U-UNCD/N-UNCD multilayered template electrodes. After fabrication and patterning of the template, the U-UNCD/N-UNCD electrode is immersed in

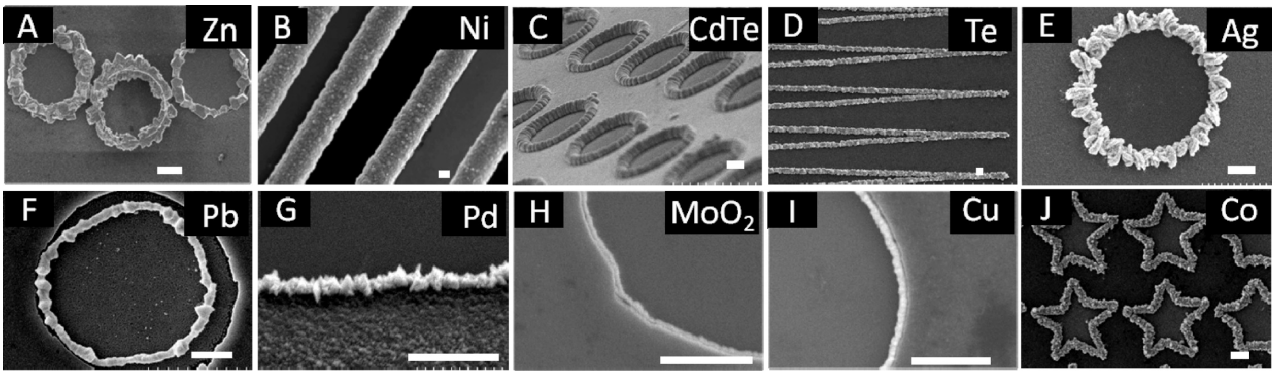

Figure 2. (A–J) SEM images of various materials deposited on the UNCD electrodes. Scale bars are 2 μm.

the electroplating solution, and a potential is applied to the N-UNCD layer to induce the growth of the nanowires on the exposed edges of the N-UNCD layer. The wires are then transferred onto the surface of a polymer layer by depositing a polymer containing solution onto the UNCD template, and lifting away the polymer layer along with the surface adhered wires. The removal of the wires from the template re-exposes the edge of the N-UNCD layer, thus regenerating the bare electrode surface. The nanoelectrode can be used for repeated electroplate and lift cycles to yield duplicate sets of patterned nanowires. The UNCD electrodes described here were reused over 100 times without detrimental effects to the electrodes. The electroplating and lift-off process provides an integrated manufacturing cycle for the serial fabrication of nanowires, using a robust reusable template based on the U-UNCD/N-UNCD layered technology.

Templates for fabricating nanowires of most geometric shapes are produced via lithography, and a dry reactive ion-etching (RIE) step through the U-UNCD/N-UNCD multilayers, protected by a hard mask. The RIE process exposes only the edge of the electrically conductive N-UNCD layer underneath the U-UNCD top layer. The minimum reproducible thickness of the conductive N-UNCD layer, which determines the minimum thickness achievable for the grown nanowire, is currently about 75 nm. Further development of the growth process is presently focused on producing N-UNCD films with thickness <50 nm.

The electroplating experiments were conducted at the University of Wisconsin-Stevens Point, in an undergraduate-only environment, using an ordinary laboratory benchtop and no clean room facilities. This demonstrates the simplicity of the nanowire fabrication process. After electroplating, the electrodes were examined with optical and scanning electron microscopy, and it was verified that nanowire growth originated in areas with exposed conductive N-UNCD edges. Figure 1B–-D show a series of three palladium wires grown from a single set of electrodes having an N-UNCD layer with a 75 nm thickness. The minimum wire thickness observed corresponded to the thickness of the conductive N-UNCD layer. Electrodeposition for 2–10 min produced wires with diameters greater than 10 μm. Unlike most other simple template methods for nanowire growth, the wire diameter is not determined from the start of the experiment, and can be adjusted to the desired diameter by varying the growth time. This provides a significant advantage over many other templated growth methods because the characterization at the micrometer scale is considerably easier than at the nanoscale. This simplifies the selection of parameters, because the initial screening of deposition parameters may be performed using a relatively low-resolution optical microscope. Once conditions yielding optically visible wire growth have been identified, smaller diameter wires can be synthesized by reducing the duration of plating. Given a single plating solution, wire diameter, and plating pulse duration, the conditions required to produce other diameters may be predicted, since the wire diameter is proportional to the square root of the plating time. A fully developed predictive model for electrodeposited wire diameters has been developed for molybdenum dioxide nanowires.[27]

The electrochemical technique described here to grow the nanowires is simple enough, such that nanowires can be fabricated from any material that can be electroplated, as shown in Figure 2A–J. Some materials, such as the amorphous MoO_2, grow with a smooth surface morphology, whereas some crystalline metals, such as gold and silver, create more beaded structures, depending on the surface energy and wetting characteristics of each material. The morphology of many materials can be adjusted by fine-tuning the growth parameters such as applied potential, precursor concentrations, and plating bath additives.

The electrochemical technique discussed here for growing nanowires is not limited to aqueous solutions. Ionic liquids can also be used as the electrolyte, further broadening the field of materials that can be used to grow nanowires.[28,29] The wide electrochemical window of ionic liquids as electrolytes and the wide electrochemical window of the UNCD nanoelectrode as a substrate, greatly increase the number and variety of materials that can be used to grow micro- and nanowires electrochemically. Figure 2J shows cobalt wires grown from 1-hexyl-3-methylimidazolium chloride as the solvent. The cobalt wire growth was similar to the growth of wires from aqueous-based materials; continuous metal nucleation occurred specifically on the conductive N-UNCD layer. Given the robust nature of UNCD and ionic liquids, we believe that almost any solid material that can be electrodeposited can now be formed into patterned micro and nanowires.

The electroplated wires were subsequently lifted off the surface of the UNCD template, regenerating the pristine N-UNCD nanoelectrode edge. The polymer used for removing the wires was First Contact Polymer Solution (Photonic Cleaning Technologies, LLC) with embedded carbon nanotubes for increased electrical conductivity of the polymer. The higher conductivity facilitates scanning electron microscope (SEM) imaging, by reducing sample charging under the electron beam. This polymer is normally used for cleaning optics, so it has been formulated specifically to mechanically adhere to most contaminants, yet release from delicate optical surfaces. The polymer solution was

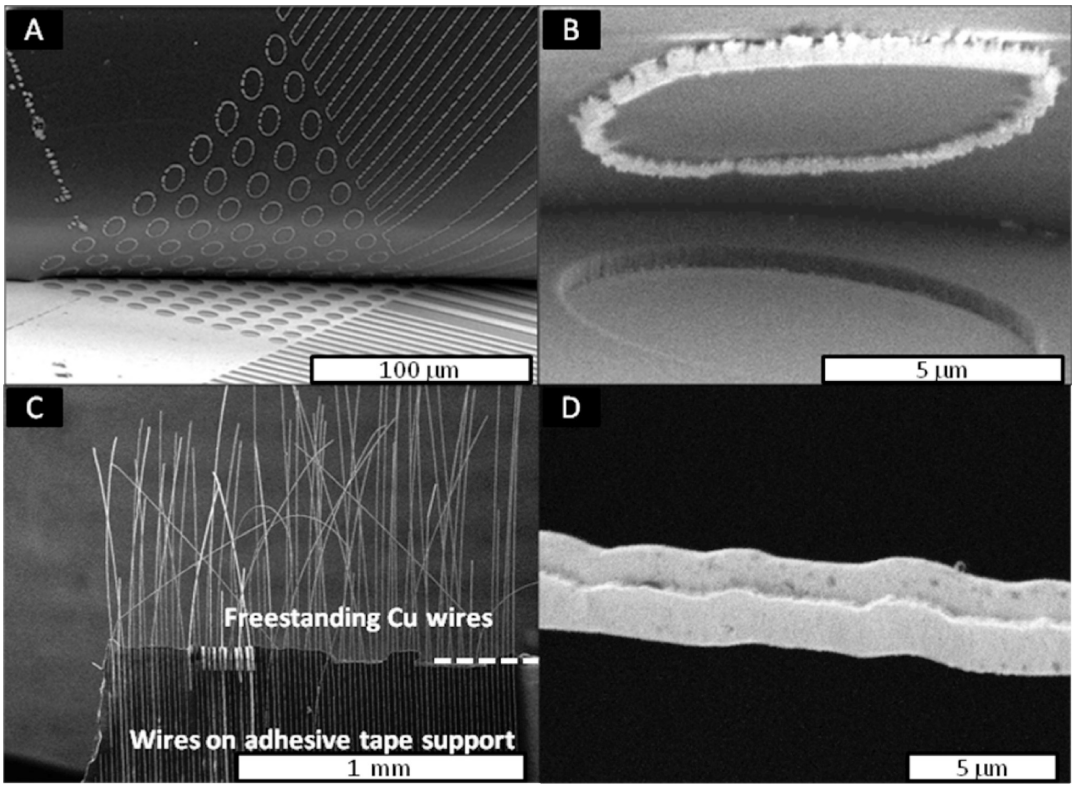

Figure 3. (A, B) Platinum wires being lifted away from the surface of the UNCD electrode. The fractures of the wires are likely a result of the extreme curvature and stretching of the polymer film required to show the peeling interface for the SEM image. (C, D) Copper wires lifted away from the UNCD template: (C) wires held by the adhesive tape at one end, and protruding unsupported off the edge of the tape, (D) the underside of a single freestanding 8.5 mm long wire. The line down the center shows the position of the edge of the template.

simply brushed over the surface of the electrode and allowed to cure by solvent evaporation. The polymer film and the wires adhered more firmly to each other than either did to the UNCD substrate, thus enabling the wires to be lifted off. Because the UNCD surface is known to be highly hydrophobic and mostly H-terminated, without dangling bonds and with a very low work of adhesion,[30] low adhesion of the polymer to the UNCD surface is expected. Images A and B in Figure 3 are SEM micrographs of an array of platinum microwires that have been lifted away from the UNCD template surface, thereby regenerating a pristine electrode edge. Figure 3C shows low adhesion of the wires to the diamond as well as their cohesive strength. Freestanding wires of up to several millimeters in length have been lifted away from the template solely by adhesive tape which held the wires by one end. Figure 3D demonstrates how wires that grow larger than the thickness of the diamond layers mushroom over the edge, to yield wires with a hemicylindrical cross section.

Even in instances of incomplete liftoff, soaking the template in concentrated nitric acid for 10 min generally sufficed to dissolve any residual metal, making the electrode ready for the subsequent growth of new nanowires. If desired, these wires could be made from a different material, or using the same material grown to a different diameter. In any case, following the initial overhead of approximately 2−3 days to fabricate the reusable template, the marginal cost in time required to produce each subsequent batch of nanowires was less than 5 min, if no cleaning of the template was required and adhesive office tape was used for removal of the wires. Thus, after even a few reuses, the time investment per nanowire batch averaged to much less than the many hours or days required to create each new single-use template using electron beam or other traditional lithography methods. Several templates, which have already produced 100+ batches of nanowires, currently remain in use. Even with the slow initial production of these diamond templates, the large number of reuses per electrode suggests that the average production time per batch will approach the marginal production time. The production time could be further reduced by designing an automated system to deposit and lift the wires away in a continuous deposition process, rather than a batch deposition process as practiced now. Finally, it cannot be overemphasized, that this process does not require a clean room once the initial template has been manufactured, thus enabling nanomanufacturing in an industrial setting without a clean room. In an undergraduate environment, the most common failure of the electrodes is delamination of the diamond when using adhesive tape for wire removal, primarily when inexperienced students apply excessive force. The other major mode of failure, also most common during the training of new students, is shattering of the electrodes from the flexing of the silicon wafer substrate. Development of an engineered process rather than an adhesive tape in hand method for removal would minimize this mode of failure.

Electroplate and lift lithography (E&L) is a promising technique that enables the fabrication of arrays of patterned nanowires. Nanowires of virtually any material that can be electroplated are achievable, including (to date) Au, Ni, Pt, Pd, Cu, Zn, MoO_2, Pb, CdTe, Te, Co, Sn, and Ag. The E&L process separates the specialized clean room techniques required to fabricate the template, from the simple benchtop techniques

that can be performed without expensive equipment as the template is put to use. Because the templates on which the micro- and nanowires are grown are permanent, they can be reused multiple times without damaging the UNCD electrode surface. This provides a pathway for precision micro- and nanomanufacturing operations to be performed by small companies unable to afford the trained staff and facilities necessary for traditional clean rooms. The use of electroplating in aqueous and ionic liquids provides a cost-effective means of creating a great variety of nanowire materials that is much less equipment- and energy-intensive than existing vacuum deposition techniques. The new UNCD template demonstrated here can also be used as a test-bed structure for depositing a variety of nanowires, and then transferring them to other substrates for studies of their fundamental materials properties and phenomena such electrical and thermal transport. This opens new pathways for advances in the fundamental and applied science of nanowires, and for applications to diverse nanotechnologies.

EXPERIMENTAL SECTION

UNCD Deposition. The UNCD electrodes were fabricated at Argonne National Laboratory's Center for Nanoscale Materials. Si substrates were seeded using functionalized nanodiamond suspension Ultra Dispersed Diamond in dimethyl sulphoxide (from International Technology Center, Raleigh, NC) to provide a high initial nucleation density that enables growth of ultrathin UNCD films. The conductive N-UNCD layer was grown on top of the Si substrate at ~750 °C to thicknesses from 75 to 400 nm. The insulating U-UNCD layer was grown on top of the conductive N-UNCD layer at 400 °C with similar thicknesses as that of the N-UNCD layer. A photoresist was spin-coated on top of the U-UNCD layer. The photoresist was patterned using a laser pattern generator, standard optical or electron beam lithography. A nickel layer (or alternatively titanium) was deposited as a hard mask for the subsequent reactive ion etching step (RIE) to define the UNCD patterned template. The unexposed photoresist regions were lifted off, leaving the patterned Ni hard mask. Reactive ion etching with oxygen plasma was performed on the UNCD to etch away diamond outside the areas protected by the Ni.

Electroplating Experiments. Details specific to each individual metal (such as plating bath composition and growth potential) are provided in the Supporting Information. For all metals, aqueous plating solutions were mixed using metal salts as precursors, with concentrations ranging from 1 to 100 mM. The electrical connection to the N-UNCD layer was made by disrupting the insulating U-UNCD layer with a diamond tipped scribe in a remote corner of the electrode, and mechanically pressing a small piece of indium metal into that scratch. A metal clip contacted the indium above the solution's surface, while the patterned area of the electrode was held below the surface. The experiments were conducted at room temperature without stirring. Cyclic voltammograms were acquired before each material was plated, in order to determine the optimum electroplating potential versus the reference electrode. A constant potential pulse ranging from 2 s to 10 min was applied to the N-UNCD layer to induce the growth of wires along the thin conductive edge of the N-UNCD.

ASSOCIATED CONTENT

Supporting Information. (1) A video animation of the fabrication process of both the template and the nanowires; (2) additional experimental details of UNCD substrate fabrication; (3) additional experimental details of electrochemical deposition, including a supporting figure; (4) several representative cyclic voltammograms, from a variety of deposited materials; (5) optical micrographs showing nickel deposited using different conditions; (6) statistical analyses of the uniformity of nickel and copper wires under optimal deposition conditions; (7) results from several methods used to clean the electrodes in the advent of contamination to restore functionality to the electrodes; and (8) data relating to the adhesion properties of wires to the template, with further discussion of liftoff methods and statistical analysis of liftoff (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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