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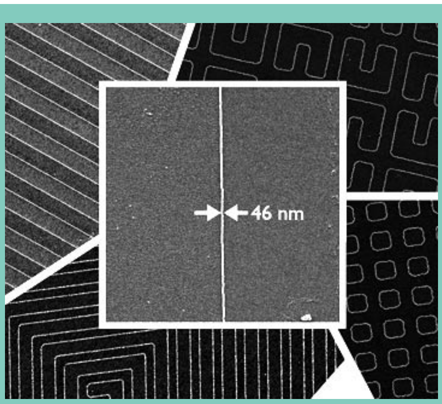
Lithographically Patterned Nanowire Electrodeposition (LPNE) is a new nanofabrication technique in which photolithography is used to define the position of electrodeposited nanowires on the surface of a dielectric such as glass or oxidized silicon. In LPNE, a resist-covered nickel film with a thickness of beween 6 and 100 nm is photopatterned. After development of the resist, the exposed nickel is dissolved in nitric acid under conditions that produce an "undercut" at the resist edges. This undercut functions as a horizontal trench into which metals (e.g., Au, Pt, Pd) can be electrodeposited using the exposed nickel edge present within this trench. As this trench is filled during electrodeposition, a nanowire with a precisely defined height and width is formed along the entire perimeter of the photoresist. LPNE nanowires can have minimum dimensions of 6 nm (h) x 20 nm (w) and lengths of more than 1 cm.



Collage of scanning electron microscope images showing gold, platinum and palladium nanowires prepared using the LPNE method.

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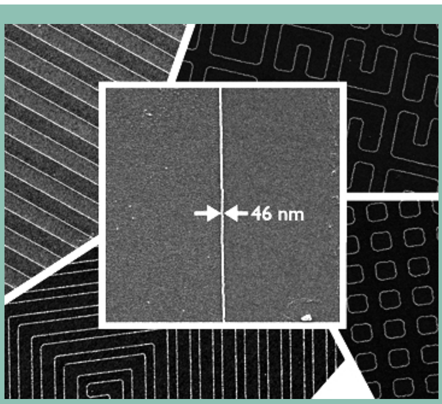

Collage of scanning electron microscope images showing gold, platinum and palladium nanowires prepared using the LPNE method.

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1 Introduction

To pattern metal nanowires on surfaces, electron beam lithography (EBL) is the standard method. EBL permits nanowires with widths as small as 20 nm to be prepared [1, 2]. But EBL is an extremely slow, serial patterning method that, with few exceptions, can not be employed in a production mode to fabricate nanostructures.

We describe here a new parallel patterning method called Lithographically Patterned Nanowire Electrodeposition or LPNE [3]. LPNE produces nanowires with critical dimensions below 30 nm and it exploits photolithography to pattern these nanowires on a glass or oxidized silicon surface. Nanowires are obtained by an electrodeposition process. LPNE combines many of the advantages of EBL and photolithography. We describe this method in greater detail in this paper.

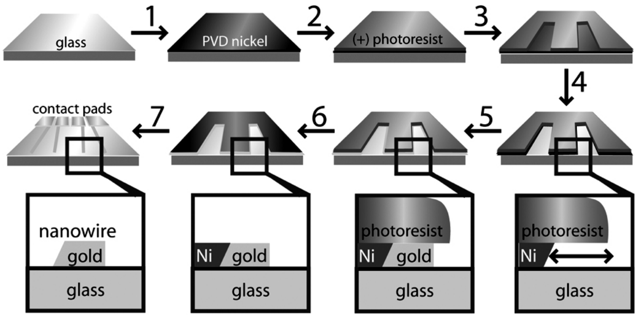

Figure 1 Seven-step process flow for the fabrication by LPNE of gold, platinum or palladium nanowires on glass or oxidized silicon.

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2 Experimental

2.1 LPNE process flow

The LPNE process flow shown in Figure 1 involves the following processing steps:

Step 1) Glass or oxidized silicon was rigorously cleaned in conc. H_2SO_4.

Step 2) A nickel layer with a thickness of 6–100 nm was evaporated. A positive-tone photoresist (Shipley 1808) was spin-coated (2500 rpm for 75s) onto the nickel layer and patterned using a contact mask and 365 nm irradiation at 70 mW/cm^2 for 90 s.

Step 3) This photopatterned surface was developed in 1:4 Shipley MF-351:H_2O for 30 s, and then in pure water for 1 min. The surface was then dried in flowing ultra-high purity N_2.

Step 4) Exposed nickel was dissolved in 0.8 M HNO_3 for 4–6 minutes – depending on the nickel thickness. The horizontal trench (Fig. 1, bottom right) was produced during this dissolution process.

Step 5) The metal nanowire was electrodeposited from an aqueous plating solution. Palladium was electroplated from aqueous 2 mM $PdCl_2$, 0.1 M. KCl. Platinum was deposited from 1 mM K_2PtCl_6 in 0.1 M KCl, and gold was deposited from a commercial gold plating solution (Clean Earth Solutions, Carlstadt, NJ – a 6 mM solution). The deposition time is discussed in greater detail below. A saturated calomel reference electrode (SCE) and a 2 cm^2 platinum foil counter electrode were also employed to carry out this electrochemistry. Potential control was provided by a EG&G 273A potentiaostat.

Step 6) The photoresist layer was removed by extracting sequentially with electronic grade acetone, methanol, and finally ultrapure water.

Step 7) Nickel was removed by exposure to 0.8 M HNO_3 for 30 min.

2.2 Nanowire characterization

Scanning electron microscopy (SEM) images were obtained using a Phillips Model XL-30FEG operating at between 10–20 keV. Prior to imaging, all nanowire samples were gold-coated using a plasma coater to eliminate charging. Atomic force microscopy (AFM) images were obtained using a Park Scientific Instruments CP using Mikromasch AFM tips. Raw AFM images were processed by subtraction of the sloping baseline, estimated by least squares fitting, line-by-line, using a second order polynomial.

3 Results and discussion

In the LPNE process flow shown in Fig. 1, steps 1–3 involve standard microfabrication procedures and we do not discuss these in greater detail here. It is important to know, however, that the thickness of the evaporated nickel film defines the height of the incipient metal nanowire that will be obtained at the end of the LPNE process. This thickness can be adjusted from 5 nm to 60–80 nm.

Step 4, involving removal of the nickel from lithographically patterned surface is a critical step because the horizontal trench at the edges of the photoresist is also produced during this process. The duration of exposure to the nitric acid etching solution is determined by preparing a calibration plot of undercut depth versus exposure time for a fixed nitric acid concentration. This calibration plot (Fig. 2a) is obtained by over-depositing metal into the trench in Step 5, causing excess metal to “spill out” of the trench. The photoresist is then removed as usual in Step 5 and nickel and nanowire are both imaged using SEM. The depth of the trench can be determined directly from these images. The nickel layer can also be removed electrochemically by anodizing this layer in NaCl solution [3] but the vertical orientation of the HNO_3-etched edge (seen in Fig. 2b) is not obtained by electrochemical etching. Instead, the edge is angled from vertical by ≈60°. This produces a wedge-shaped nanowire instead of the rectangular cross-section that is obtained using the vertical nickel edge of Fig. 2b.

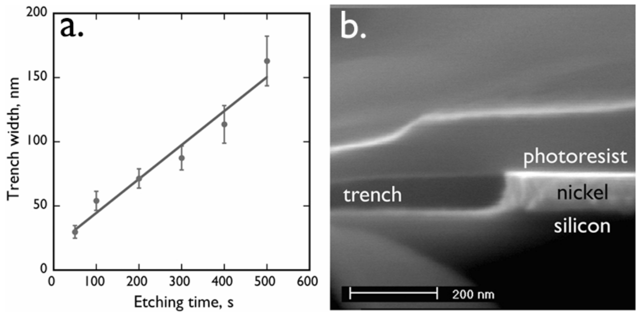

Figure 2 a) Plot of trench depth versus etching time in HNO_3 (0.8 M). The optimum trench depth was in the 300 nm range. b) Cross-sectional SEM image of the horizontal trench showing the vertical orientation of the nickel edge. This edge is used as an electrode to electrodeposit a nanowire within the confines of the trench.

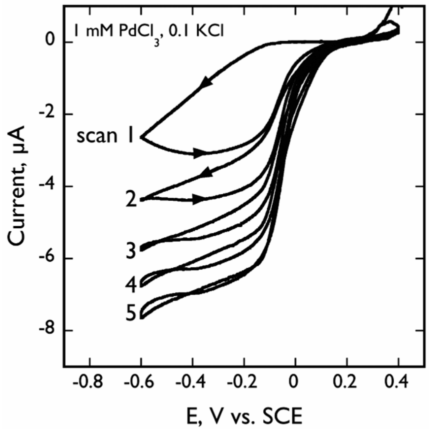

Figure 3 Cyclic voltammogram (20 mV/s) of palladium electrodeposition at a nickel edge in Step 5 of the LPNE process.

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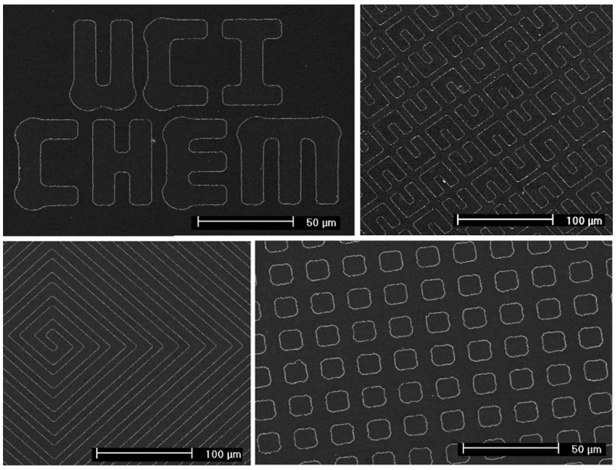

Figure 4 SEM images of patterned gold nanowires prepared using LPNE on glass.

In step 5 of the LPNE process, the metal nanowires are electrodeposited *potentiostatically* but cyclic voltammetry can tell provide some important qualitative information aoub this process. Cyclic voltammograms for the electrodeposition of palladium (Fig. 3) show that for scan 1, the voltammogram shows slow palladium deposition kinetics, but the kinetic facility for Pd deposition improves dramatically with continued scanning. This effect, which is also seen for gold and platinum, is expected as the nickel edge electrode surface is replaced by freshly deposited Pt, Pd, and Au creating a superior noble metal electrode surface.

A defining feature of the LPNE method is the capability to pattern nanowires over large areas of a surface (e.g. 1×1 cm^2). Figure 4 shows several different patterns that we've obtained for gold nanowires. The nanowires shown here are 20–40 nm in thickness and 50–100 nm in width.

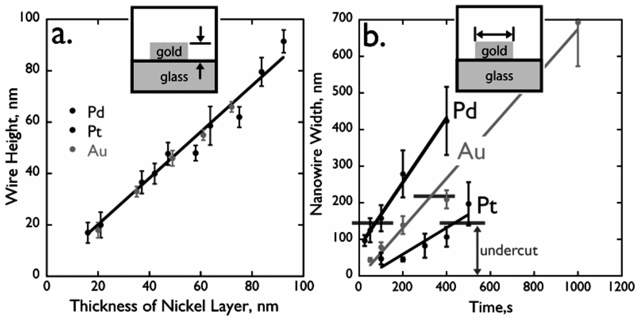

Figure 5 a) Plot of nanowire height versus the thickness of the evaporated nickel layer. This plot had a slope of 1.0 for all three metals, gold, platinum, and palladium. b) Nanowire width versus deposition time for the same three metals. Deposition conditions for each are as specified in Section 2.

The main constraint on patterning is the interwire distance or "pitch" which is constrained by the diffraction limit of the light used for the photolithography process. In practice, we have found it difficult to produce a pitch of less than 1 µm whereas EBL is capable of 40 nm pitch under ideal conditions. The inability of LPNE to pattern nanowires in closer proximity to one another constitutes its main disadvantage relative to EBL

Wire height (perpendicular to the surface) and width (in the plane of the surface) can be independently specified using LPNE. As already indicated, the nanowire height is equal to the thickness of the nickel layer evaporated in Step 2 of the process (Fig 5a). The width is determined by the electrodeposition time, applied potential, and the composition of the metal plating solution (Fig 5b). The minimum dimensions that we have obtained for gold nanowires are 6 nm (height) x 20 nm (width) for nanowires that are continuous for lengths of at least 100 µm.

4 Conclusion

LPNE is a nanowire fabrication technique in its infancy. At its present state of development, LPNE provides a means for patterning gold, platinum, and palladium nanowires with minimum dimensions down to 6 nm x 20 nm on glass and oxidized silicon. The length of these nanowires can be > 1 mm. But LPNE has tremendous potential that derives from the fact that it exploits electrochemistry to form nanowires. This means that nanowires having a wide range of compositions ranging from II-VI semiconductors such as CdSe and ZnO to thermoelectric materials such as Bi_2Te_3 and PbTe will eventually be obtainable using variants of the LPNE method.

These method variations must overcome a purely practical problem with the basic LPNE method described here: materials such as CdSe and Bi_2Te_3 cannot be obtained using the nickel edge employed for noble metals because these materials are incompatible with the HNO_3 required for nickel dissolution in Step 6. Thus, a major thrust in our laboratory at present is the development of new LPNE protocols for materials like these that exploit sacrificial films composed of metals other than nickel.

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