

# Metallic Nanostructures via Static Plowing Lithography

Lon A. Porter, Jr.,<sup>†</sup> Alexander E. Ribbe, and Jillian M. Buriak<sup>\*,‡</sup>

*Department of Chemistry, 1393 Brown Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393*

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## ABSTRACT

A facile route to metallic nano- and microstructures of varying size and geometry is reported. Both nanoparticle formations as well as continuous structures are formed spontaneously on Ge(111) substrates via galvanic displacement from aqueous metal salt solutions. Utilizing an atomic force microscope, patterning is achieved via static plowing lithography through a thin polymeric photoresist. Metal deposition proceeds on exposed portions of the substrate, and the resist is subsequently removed to yield the desired metallic features.

Nanostructured materials continue to be the focus of intense research because of their promise of innumerable practical applications as well as advancing the fundamental understanding of these intriguing materials.<sup>1</sup> In particular, the need for metallic features of increasingly smaller size regimes has imposed increasingly stringent demands upon the preparation of metallic features with reduced dimensions.<sup>2</sup> Metal colloids, quantum dot structures, nanorods, and nanowires have been successfully prepared through a variety of methodologies including hard/soft template-driven syntheses,<sup>3,4</sup> chemical/electrolytic reduction,<sup>5,6</sup> dip-pen nanolithography,<sup>7</sup> micro-contact printing,<sup>8</sup> and evaporation through physical masks,<sup>9</sup> among others. Much work remains, however, in terms of the efficient patterning and utilization of these structures with the goal of preparing higher-order architectures and devices for technologically relevant applications. The successful realization of arrayed nanosensor and nanoelectrode production, molecular electronics, ultra-large-scale integration (ULSI) device fabrication, and nanoelectromechanical systems (NEMS) will require unparalleled precision and control of the metallization geometry, aspect ratio, surface morphology, deposition rate, and substrate adhesion without sacrificing throughput or cost effectiveness. Here we report the utilization of a galvanic displacement-driven deposition protocol of metal salts on a semiconductor<sup>10,11</sup> as a facile approach for the preparation and patterning of metallic nanostructures via static plowing lithography.

Stemming from fundamental scanning probe experiments focused on exploring polymer tribology,<sup>12</sup> static plowing

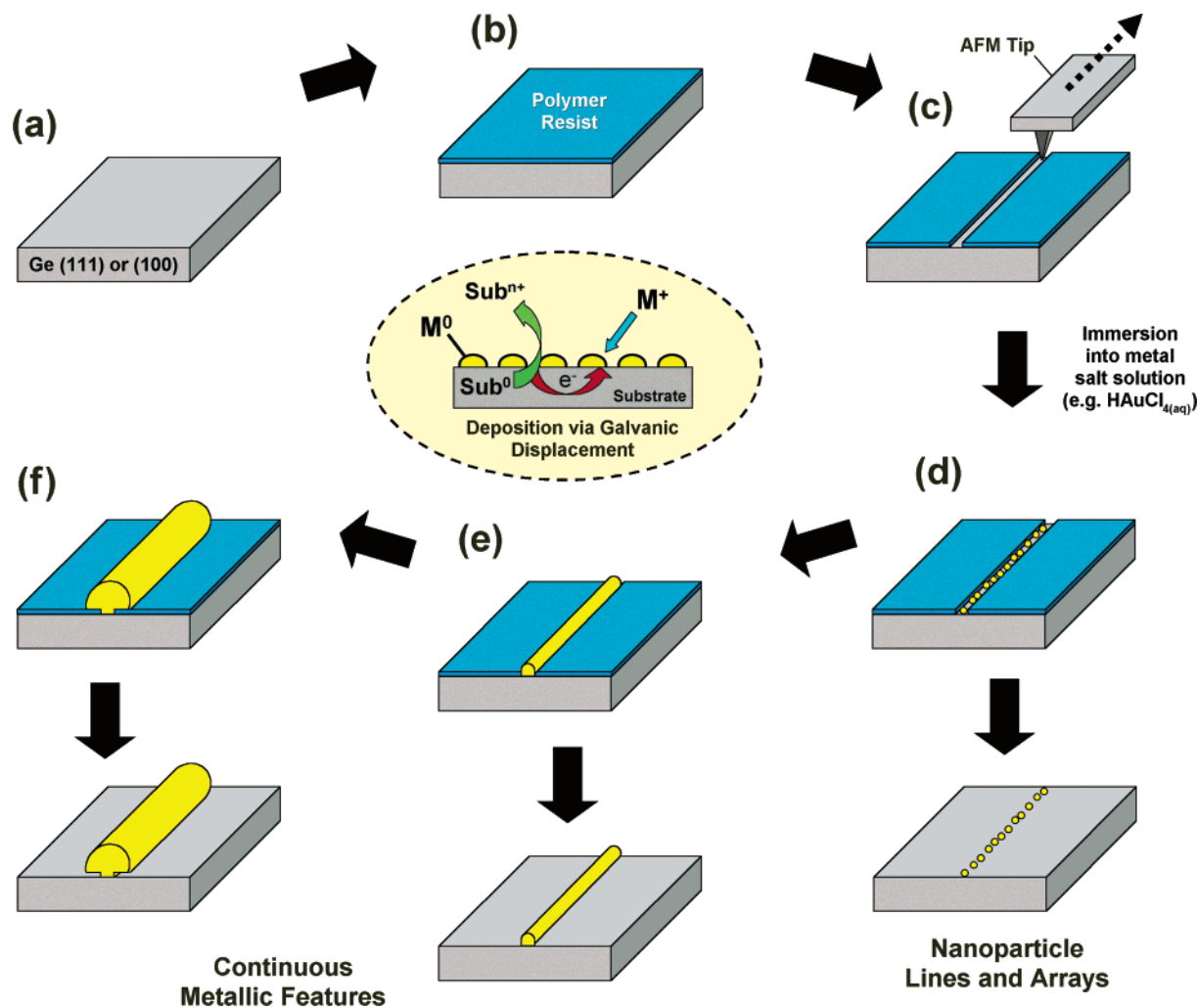
lithography has only recently been utilized as a viable fabrication process.<sup>13</sup> In this facile yet effective method, an atomic force microscope probe is employed to mechanically “plow” away spatially defined regions of a target substrate with extremely high lateral resolution. Utilizing vector scan software, a variety of geometries may be obtained.<sup>14</sup> This technique has been previously utilized to produce etch and evaporation masks for semiconductor device fabrication<sup>12</sup> and has also been used in the direct nanografting of various molecular species and metal clusters into self-assembled monolayer (SAM) systems.<sup>15</sup> In the present study, we propose the use of static plowing lithography to prepare metallic nanostructures of varying geometric configuration with considerable ease and reproducibility. This process is accomplished in four fundamental operations: (1) application of a thin polymer resist onto a Ge(111) substrate (Figure 1b), (2) utilization of an atomic force microscope tip to plow away patterns/domains of the resist, thereby exposing defined regions of the underlying Ge(111) substrate (Figure 1c), (3) immersion of the substrate into a dilute metal salt (such as H<sub>2</sub>AuCl<sub>4</sub>(aq)), where electroless deposition proceeds onto the areas of Ge(111) no longer concealed by the resist (Figure 1d–f), and (4) final removal of all resist via a solvent rinse (Figure 1d–f). The resulting metallic structures were subsequently characterized by utilizing atomic force microscopy (AFM) and scanning electron microscopy (SEM).

An extremely thin layer of a single photoresist (Shipley 1805) was spun onto the surface of a degreased 1 cm<sup>2</sup> Ge(111) wafer fragment (Figure 1b). To obtain a sufficiently thin resist layer, the resist was diluted with propylene glycol monomethyl ether acetate (Shipley Thinner P). Approximately 0.1 mL of the thinned resist (1:15, Shipley 1805/Thinner P) was applied to the substrate and spun on at 2000

\* Corresponding author. E-mail: buriak@purdue.edu.

<sup>†</sup> Present address: Wabash College, Department of Chemistry, Crawfordsville, Indiana 47933.

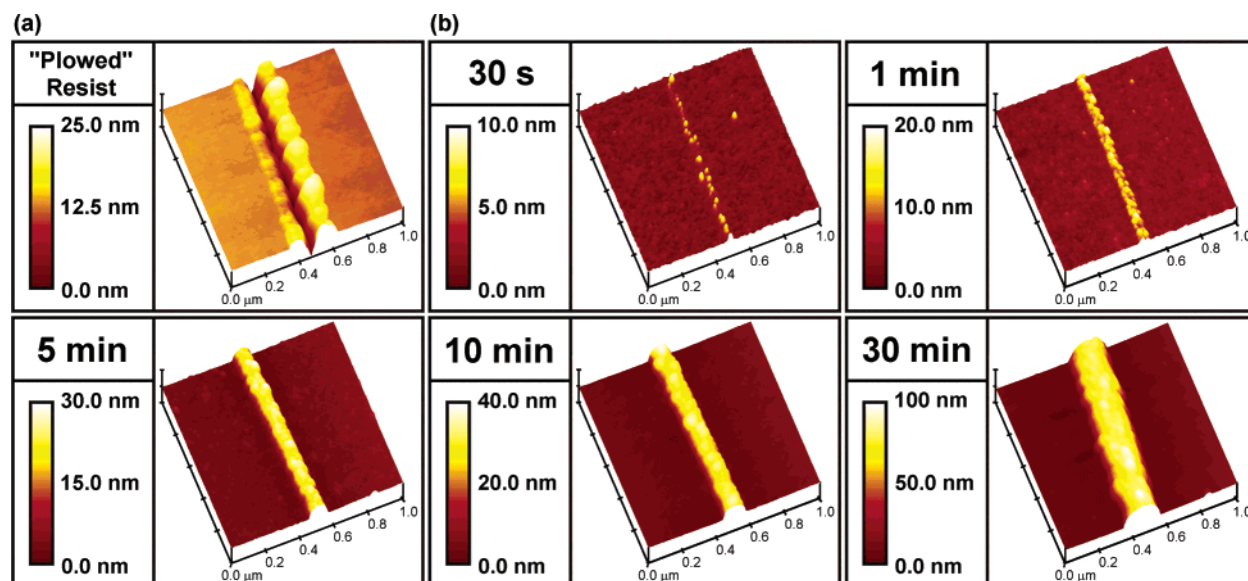
<sup>‡</sup> Present address: National Institute for Nanotechnology (NINT) and the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada.



**Figure 1.** Metallic nanostructures via static plowing lithography: a degreased Ge(111) substrate (a) is coated with a thin polymer resist layer (b), which is subsequently plowed away by utilizing the tip of an atomic force microscope (c). Immersion of the substrate into a dilute, aqueous HAuCl<sub>4</sub> solution for a brief time provides for the deposition of discrete nanoparticles onto the exposed Ge(111) surface via galvanic displacement (d). As deposition proceeds with longer immersion times, grain growth and nanoparticle coalescence eventually yield continuous metallic structures (e), which continue to increase in size with extended periods of electroless plating (f). Once the desired features are realized, the resist is completely removed with a solvent rinse. The inset represents a simplified schematic of the galvanic displacement deposition mechanism.

rpm, followed by a 60 s bake at 95 °C. This resulted in a  $20 \pm 2$  nm resist layer, as determined via ellipsometry and corroborated by atomic force microscopy. The sample was then adhered onto a stainless steel specimen disk (Ted Pella, Inc.) with a small square of carbon tape and secured onto the tube scanner of a Nanoscope III atomic force microscope (Veeco Instruments). An oxide-sharpened (tip radius of curvature  $< 10$  nm) silicon tip (MikroMasch, NSC-15) with a high spring constant (40 N/m) was utilized for both plowing through the thin resist and imaging the resulting furrow. Static plowing was accomplished in contact-mode operation, where the tip was scanned across the sample surface with a constant force (3–5  $\mu$ N). This setpoint proved sufficient to displace the soft polymer resist, thereby exposing the Ge(111) surface as scanning progressed (Figure 1c). Furthermore, this force did not result in any observable damage to the underlying semiconductor substrate. Increasing the force applied to the tip beyond  $\sim 5$   $\mu$ N, however, resulted in 1–2 nm indentations in the germanium surface (Supporting

Information). The resulting resist furrows were immediately characterized via atomic force microscopy, employing the same tip, by switching to intermittent contact, or tapping-mode, operation for imaging. Tips were observed to remain sharp following static plowing, foregoing the need to exchange tips, and no residual resist material was observed to adhere to the tip surface. Continuous furrows, flanked by displaced resist (Figure 2a), were reproducibly obtained at scanning speeds of nearly 100  $\mu$ m/s, with lengths of hundreds of micrometers, restricted only by the range of the available AFM scanner. Once the desired resist plowing was completed, electroless deposition served to facilitate pattern transfer. The entire substrate was carefully removed from the AFM specimen disk and immersed into a dilute, aqueous solution of HAuCl<sub>4</sub>. Exposed domains of Ge(111) result in intimate electrical contact between the semiconductor bulk and the metal salt solution, whereas the residual resist concealed the majority of the wafer surface from the aqueous plating solution. Metal deposition onto exposed Ge(111) then



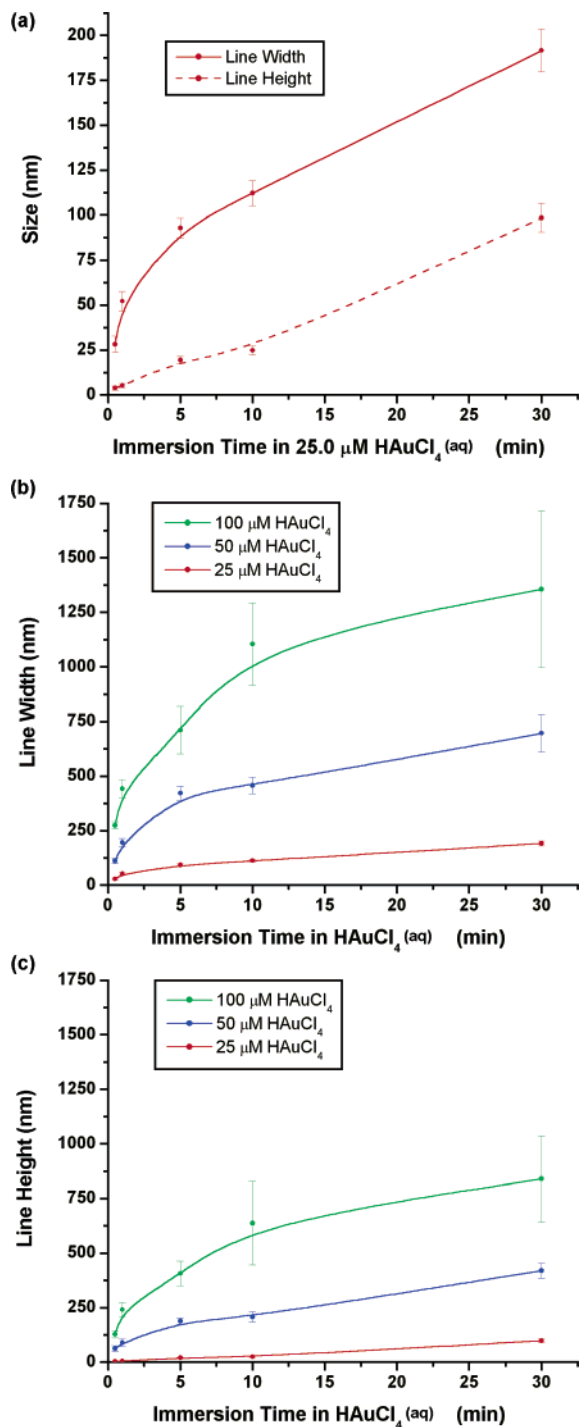
**Figure 2.** Intermittent contact (tapping) mode atomic force micrographs illustrating a resist furrow produced by static plowing (a) and the gold nanostructures (b) on Ge(111) resulting from increasing immersion times in 25  $\mu\text{M}$   $\text{HAuCl}_4(\text{aq})$  at 25  $^\circ\text{C}$  following resist removal.

proceeds via galvanic displacement.<sup>10</sup> Following electroless deposition, the substrate was removed from the plating solution and washed thoroughly with water, ethanol, tetrahydrofuran, and pentane. This removed any residual plating solution and stripped the remaining resist material. The samples were then dried under a steady stream of nitrogen, and the resulting metallic structures were characterized via AFM and SEM.

Figure 2b displays tapping-mode atomic force micrographs of gold nanostructures deposited onto Ge(111) resulting from increasing immersion times in 25  $\mu\text{M}$   $\text{HAuCl}_4(\text{aq})$  at 25  $^\circ\text{C}$  following resist removal. The micrographs presented in Figure 2b display 1  $\mu\text{m}$  segments of 185  $\mu\text{m}$  gold nanostructures produced from linear 185  $\mu\text{m}$ -long resist furrows, a segment of which is shown in Figure 2a. Gold line widths and heights were observed to increase with longer immersion times. Shorter plating times ( $\leq 30$  s) resulted in the formation of discrete gold nanoparticles aligned in a linear formation consistent with the geometry of the resist furrow. The mean nanoparticle diameter and height were determined to be  $28 \pm 4$  nm and  $4 \pm 1$  nm, respectively. More lengthy immersion times ( $>30$  s) led to continuous metallic structures through Volmer–Weber 3D island growth, concluding with nanoparticle agglomeration as a consequence of Ostwald ripening. The resultant continuous gold nanostructures (approximated as semielliptical cylinders) were observed to increase in line width from  $52 \pm 5$  nm for a 1 min immersion to  $192 \pm 12$  nm for 30 min of deposition from 25  $\mu\text{M}$   $\text{HAuCl}_4(\text{aq})$ . Analogously, the line height increased from  $5 \pm 1$  nm to  $99 \pm 8$  nm for the corresponding plating intervals (Figure 3a). The rate of nucleation and gold nano/microstructure growth was markedly accelerated with the utilization of more concentrated  $\text{HAuCl}_4(\text{aq})$  plating solutions (Figure 3b and c). As observed in previous studies, deposition at increased metal ion concentrations resulted in larger microcrystalline grain growth, leading to less uniform line widths as opposed to those for structures deposited from

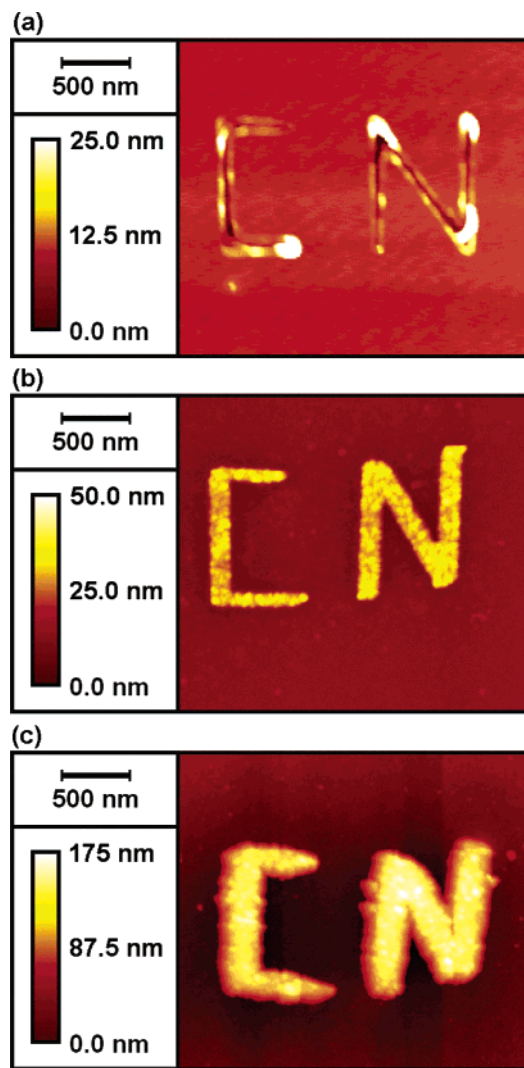
lower concentrations of  $\text{HAuCl}_4$  (Supporting Information).<sup>10</sup> Electrical measurements of a linear gold deposit (105  $\mu\text{m}$  long, 442 nm wide, 241 nm in height) prepared via 1 min immersion into 100  $\mu\text{M}$   $\text{HAuCl}_4(\text{aq})$  indicated that the resistance of the structure was 29  $\Omega$ , in agreement with the value obtained from theoretical calculations (Supporting Information). Metallic copper nanostructures were similarly prepared via immersion into dilute aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$ . We are currently exploring fabrication techniques aimed at producing reliable contacts for nanostructures that we are not able to image with optical methods.

We have also demonstrated the fabrication of metallic nanostructures utilizing static plowing lithography operating in vector scan mode. Vector scan operation allows for the AFM tip to be driven along paths of arbitrary length scales at predefined angles while also providing for control over  $z$ -axis displacement and applied force. Utilizing the NanoScript software (Veeco Instruments), a general programming script provided access to a myriad of customized scan profiles. Figure 4a illustrates one such profile utilized to prepare a series of resist furrows forming the letters “CN” employing static plowing lithography. The realization of this pattern demonstrates the ability of this technique to cope with scan directions other than the major scan axis successfully. The torsion forces placed upon the tip throughout portions of its path at times result in the asymmetrical displacement of the resist, as seen in Figure 4a. Panels b and c of Figure 4, however, provide evidence that this failed to inhibit pattern transfer via electroless deposition from 25  $\mu\text{M}$   $\text{HAuCl}_4(\text{aq})$ . Although some drift was observed as a consequence of an open-loop instrument, the structures appeared to be clearly defined and free of any significant defects. As before, the structural dimensions were shown to increase with more lengthy plating times. Whereas vector scan operation provided an effective route to lines, letters, and various “hollow” designs, raster scan mode did provide an effective route to “solid” shapes and patterns. Solid features were generated

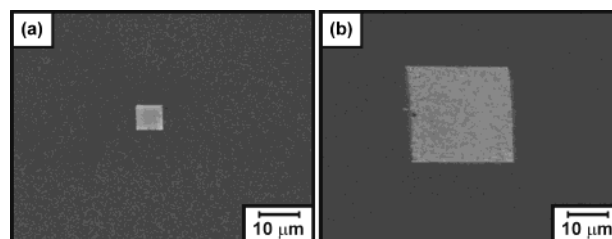


**Figure 3.** Effect of immersion time on gold nanostructure line width (solid red line) and height (broken red line) patterned via static plowing lithography on Ge(111) from a 25  $\mu\text{M}$  HAuCl<sub>4</sub> at 25 °C (a). Width (b) and height (c) data for gold nano/microstructures prepared from 25  $\mu\text{M}$  (red), 50  $\mu\text{M}$  (blue), and 100  $\mu\text{M}$  (green) solutions of HAuCl<sub>4</sub> at 25 °C.

by plowing away large domains of resist material through the use of multiple, closely spaced scan lines. To ensure the complete removal of the resist, typically 2 to 3 passes over the entire region of interest (512 scans, 10–100  $\mu\text{m/s}$  scan rate) were performed. Figure 5 illustrates successful pattern transfer with scanning electron micrographs of 5  $\times$  5  $\mu\text{m}$  and 20  $\times$  20  $\mu\text{m}$  gold contact pads fabricated by static



**Figure 4.** Intermittent contact (tapping) mode atomic force micrographs illustrating a series of resist furrows produced by static plowing (a) and the gold nanostructures on Ge(111) resulting from 5 min (b) and 30 min (c) of immersion in 25  $\mu\text{M}$  HAuCl<sub>4</sub>(aq) at 25 °C following resist removal.



**Figure 5.** Scanning electron micrographs of 5  $\times$  5  $\mu\text{m}$  (a) and 20  $\times$  20  $\mu\text{m}$  (b) gold contact pads fabricated by static plowing lithography on Ge(111) resulting from a 30 min immersion in 25  $\mu\text{M}$  HAuCl<sub>4</sub>(aq) at 25 °C following resist removal.

plowing lithography on Ge(111) resulting from a 30 min immersion in 25  $\mu\text{M}$  HAuCl<sub>4</sub>(aq) following resist removal. Once again, some drift was observed in the pattern, yet the resulting contact pads exhibited clean edges and were largely free of defects.

In conclusion, we have reported a facile yet effective route for the rapid fabrication of metallic nano- and microstructures

of varying size and geometry via static plowing lithography. Both nanoparticle formations as well as continuous metal structures are obtained via galvanic displacement from aqueous metal salt solutions. This approach is compatible with photoresist coating processes that are ubiquitous in industrial and academic fabrication environments. Future endeavors are currently focused upon applying this efficient technique to more technologically important substrates such as silicon and compound semiconductors as well as on developing facile new routes to novel device applications such as molecular electronics, microelectronic sensor elements, and microfluidics, among others.

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**Supporting Information Available:** Detailed experimental procedures for wafer treatment, resist application, static plowing lithography, and metal deposition along with additional micrographs. This material is available free of charge via the Internet at <http://www.pubs.acs.org>.

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