

NANOFABRICATION

Best of both worlds

Fabricating nanostructures on a substrate often requires a choice between pattern complexity and narrow wire widths. By combining lithographic patterning with electrochemical templating, complex patterns over large areas with critical dimensions well below 100 nm become possible.

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Many techniques have been developed to produce metal nanowires — structures with transverse dimensions much smaller than 100 nm and lengths on the micrometre scale or more. Such nanowires are of interest both as tools for examining electronic conduction at the nanoscale, and as components in next-generation electronic, optical and sensing technologies. Controlled fabrication of complex structures with such large aspect ratios is very challenging. Methods that have been demonstrated so far may be grouped into three categories: lithographic approaches, templated deposition techniques, and direct chemical synthesis. On page 914 of this issue, Menke *et al.* present a new strategy¹ for patterning metal nanowires based on previous work² in the electrochemical community used to create arrays of microelectrodes. Their method, which they term 'lithographically patterned nanowire electrodeposition', combines the complex patterning possibilities of lithography with the precision of templating. The result is a technique that can produce substrate-supported, continuous polycrystalline metal nanowires with widths and thicknesses as small as 20 nm, in complex shapes. The potential utility of this technique is impressive, and opens up many possible applications, including complex interconnect designs, sensor systems, plasmonic waveguides and more complex surface patterning.

Traditional optical lithography techniques, such as those used to produce computer chips, have the advantage that wires in complicated geometries may be patterned in well-defined positions on substrates. However, achieving wires much narrower than readily accessible optical wavelengths often necessitates slow, serial processes such as electron-beam or scanned-probe lithography. The lithographic process generally works by using light or electrons to chemically alter some resist material, conventionally a polymer. The resulting chemical contrast is exploited, in 'positive tone' lithography, to remove the exposed resist with some developer. Both the exposure and development

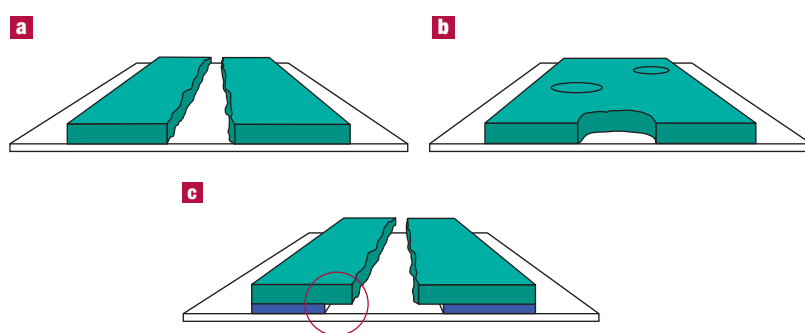


Figure 1 Nanowire fabrication approaches. **a**, Ordinary lithographic fabrication of nanowires involves patterning a resist (green), and the critical linewidth of the eventual nanowire is directly affected by edge roughness of the developed resist. **b**, Templated fabrication of nanowires instead uses a template (such as etched pores) to confine material deposition, but the availability of good templates severely restricts the resulting nanowire geometry. **c**, The lithographically patterned nanowire electrodeposition method uses the controlled etching of a metal underlayer (blue) to form a template (circled in red) for subsequent electrodeposition of the nanowire. The template thickness is set by the metal underlayer's height, and the eventual nanowire width may be controlled by electrodeposition time and conditions. This allows the fabrication of nanowire structures in parallel at very small ($\ll 100$ nm) transverse dimensions, with overall length and geometry dictated by the initial lithography step.

processes can be problematic. The critical wire-width dimension is defined directly by the edges of the exposed and developed resist, as shown in Fig. 1a. Inhomogeneous exposure and development adversely affect wire uniformity directly, with detrimental consequences for applications.

Templating is one approach to mitigating this difficulty. A suitably designed template can constrain the metal configuration, with a physical boundary of the template providing non-lithographic lateral definition. One popular approach, shown schematically in Fig. 1b, is to use a nanoporous membrane as a template. Such membranes may be prepared in a number of ways, including controlled anodization of aluminium, or chemical etching. Nanowires may be grown by electrodeposition of metal in the pores of these membranes. This technique has been used for some time³ and is highly refined. Recent approaches using etched semiconductor structures have extended templating

down to the sub-10-nm wire-width range^{4–6}. Similar wire widths have been achieved by depositing metal onto suspended carbon nanotubes^{7,8}. However, all of these templating approaches are extremely limited in the types of templates, and therefore wire geometries, that may be produced.

Menke *et al.* take the best of both worlds. They start with a substrate covered with a layer of nickel under a photoresist layer. The thickness of the nickel layer, which can be deposited very precisely, will eventually dictate the nanowire thickness. Photolithography of the resist layer defines the areas where nanowires are required. The nickel exposed in this step is then removed electrochemically by applying an oxidizing potential, and this removal is continued to provide an 'undercut' beneath the photoresist pattern, as shown in Fig. 1c. The undercut sets an upper limit on the final nanowire width, as the now-vertical exposed nickel face acts as an electrode for the deposition of the noble metal of interest. The space between the substrate and overhanging photoresist defines the template for electrochemical deposition of the noble metal nanowire. When nanowire deposition is complete, the photoresist is stripped, and the remaining nickel is etched away with nitric acid. The result is a nanowire with thickness and width that are both controlled at the nanometre scale, and an overall shape that is determined by the initial photolithographic pattern. The authors demonstrate this technique by fabricating nanowires in a variety of complex geometries.

Nanowires made this way are remarkably uniform and continuous. As expected, they exhibit good, metallic conduction down to low temperatures, though the effective resistivity of the nanowire material is significantly enhanced above the bulk resistivity of the wire metal, particularly for small wire cross-sections. This is consistent with expectations based on the elastic mean free path for electrons being limited by boundary scattering.

The fact that the initial patterning step is photolithographic means that comparatively large areas can be covered densely with complex nanowire features, as the fabrication process is performed 'in parallel' — over a whole chip surface at the same time. The semiconductor industry's extensive experience with electrochemical deposition of copper suggests that this type of process should be scalable to wafer-scale substrates and amenable to process optimization. Furthermore, the resulting metal traces do not have to be used directly as wires; the noble metal nanostructures may be used as masks for patterned etching of the underlying substrate. Thus the nanowire pattern may be transferred to raised-surface relief, potentially useful for nano-imprint lithography or other stamping techniques.

The technique should be applicable beyond the combination of metals chosen in this work. With the wide variety of chemically selective etches available, presumably the final wire material is also not limited to the noble metals. Indeed, with relatively recent advances in the electrochemical deposition of various metal oxides⁹ and compound semiconductor materials¹⁰, this technique may allow large-area nanoscale patterning of a wide variety of material systems that are otherwise challenging to structure on these length scales.

REFERENCES

1. Menke, E. J., Thompson, M. A., Xiang, C., Yang, L. C. & Penner, R. M. *Nature Mater.* **5**, 914–919 (2006).
2. Nagale, M. P. & Fritsch, I. *Anal. Chem.* **70**, 2902–2907 (1998).
3. Williams, W. D. & Giordano, N. *Rev. Sci. Instr.* **53**, 410–412 (1980).
4. Natelson, D., Willett, R. L., West, K. W. & Pfeiffer, L. N. *Appl. Phys. Lett.* **77**, 1991–1993 (2000).
5. Altomare, F., Chang, A. M., Melloch, M. R., Hong, Y. & Tu, C. W. *Appl. Phys. Lett.* **88**, 172501 (2005).
6. Melosh, N. A. *et al. Science* **300**, 112–115 (2003).
7. Bezryadin, A., Lau, C. N. & Tinkham, M. *Nature* **404**, 971–974 (2000).
8. Zhang, Y. & Dai, H. *Appl. Phys. Lett.* **77**, 3015–3017 (2000).
9. Therese, G. H. A. & Kamath, P. V. *Chem. Mater.* **12**, 1195–1204 (2000).
10. Xu, D. S. *et al. Chem. Phys. Lett.* **325**, 340–344 (2000).