

# ADVANCED MATERIALS

Reprint

under vacuum for 3 h. For electrochemical characterization, electrodes were formed by dipping Pt foil in a suspension of the reaction mixture. Chemical analyses. Experimental: 16.44% C, 4.67% N, 1.124% H, 42.65% Mo. Calculated for  $C_4H_3N(PMo_{12}O_{40})_{0.11} \cdot H_2O$ : 16.91% C, 4.92% N, 1.76% H, 44.61% Mo.

**Electrochemical synthesis of the hybrid PPy/PMo12:** This was performed by multiple cyclic voltammograms using a Pt foil working electrode, a Ag/AgCl reference electrode, and Pt coil as counter-electrode. Thus, 0.91 g of  $H_3[Mo_{12}O_{40}] \cdot xH_2O$  ( $x = 17$  as determined by TGA, FW = 2131.5) was dissolved in 50 mL of water and mixed with a solution of 0.70 mL of pyrrole in 50 mL of water. The mixture turned instantaneously from yellow to blue due to the partial oxidation of pyrrole by the phosphomolybdate. The complete oxidative polymerization was carried out by consecutive cyclic potential scans from +0.5 to -0.2 V (vs. Ag/AgCl) at a scanning rate of 1 mV/s. Chemical analyses revealed experimental values of 20.65% C, 6.14% N, and 1.39% H.

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## Replica Molding Using Polymeric Materials: A Practical Step Toward Nanomanufacturing\*\*

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This paper describes a practical procedure—replica molding of organic polymers against masters having nanometer-sized relief features on their surfaces—to fabricate nanostructures (that is, structures with feature sizes  $\leq 100$  nm in dimension).<sup>[1]</sup> Nanostructures are increasingly important as components in new types of electronic, magnetic and optical devices. They are now ordinarily fabricated by advanced lithographic techniques such as e-beam writing, X-ray lithography and proximal-probe lithography.<sup>[2]</sup> These techniques are flexible and capable of providing very small features, but their development into methods for generating large numbers of nanostructures at low cost will require great ingenuity.<sup>[3]</sup> The manufacturing of nanostructures, that is, the making of multiple copies reproducibly, rapidly and at low cost, will require new procedures: methods using organic polymers, for example, imprinting (or embossing) using a rigid master,<sup>[4]</sup> and polymerization in the nanometer-sized pores of a membrane.<sup>[5]</sup> have been demonstrated for this purpose.

The procedure reported here is based on replica molding using organic polymers, a technique that has found widespread applications in the manufacturing of micrometer-sized structures such as diffraction gratings,<sup>[6]</sup> compact disks,<sup>[7]</sup> and microtools.<sup>[8,9]</sup> Here, we extend replica molding to the fabrication of nanometer-sized structures. Replication against elastomeric (rather than rigid) masters enormously increases the ease of separating the master and the replica, protects the fragile structures during separation, and minimizes damage to the master. Moreover, extension of this procedure—replica molding against an elastomeric master while it is bent mechanically—allows the fabrication of nanostructures with a level of control over the form and size of the pattern that is not possible with existing techniques.<sup>[10,11]</sup>

Figure 1A shows the procedure schematically. A liquid prepolymer of poly(dimethylsiloxane) (PDMS) is cast

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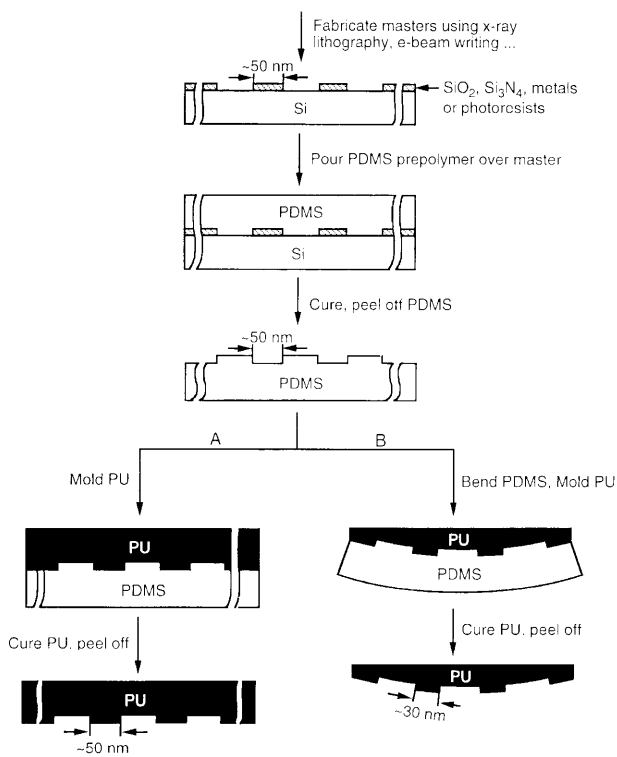


Fig. 1. Schematic illustration of the procedure.

against an original master whose surface has been patterned with nanometer-sized relief structures, made using advanced lithographic techniques; these features could be  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ , metals, or photoresists, for example, poly-(methylmethacrylate) (PMMA). After curing, the cross-linked and elastomeric PDMS is carefully peeled from the master; its surface replicates the relief nanostructures on the surface of the original master. The nanostructures present on the PDMS replica are, in turn, re-replicated using a rigid organic polymer, for example, an photochemically-curable polyurethane (PU), to produce polymeric nanostructures very similar to (or indistinguishable from) those on the surface of the original master. Replica molding of PU against a PDMS master could also be carried out while the PDMS master is bent mechanically (see Fig. 1B); this procedure generates PU nanostructures having smaller feature sizes than those on the original master.

Figure 2 shows atomic force microscopy (AFM) images of a Cr master,<sup>[12]</sup> its PDMS and PU replicas made from the PDMS master. The most important feature of this replicated PU nanostructure is its replication of nanometer-scale features. The heights of the Cr lines on the original Cr master are  $\sim 13$  nm, and the heights of the PU lines are  $\sim 8$  nm. These images demonstrate that within our ability to compare similar structures, the nanostructures are faithfully reproduced over a large area.

We also monitored the reduction in quality of the nanostructures on the original master and the PU replicas. Figure 3A shows an AFM image of a gold master before it

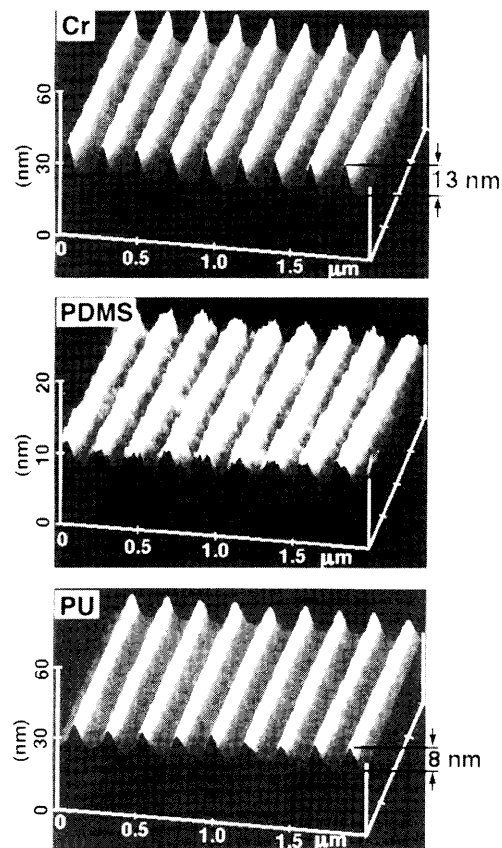


Fig. 2. AFM images of (top) Cr master, middle) its PDMS replica, and bottom) PU replica from the PDMS master. The apparently poor quality for the image of the PDMS master was a characteristic of AFM images of these elastomeric materials, and probably reflects distortion of the surface of the elastomer by the proximity of the probe, rather than the imperfection in the surface.

was used to cast PDMS masters; Figure 3B shows an AFM image of this gold master after it has been used to cast seven PDMS replicas. No observable reduction in quality was found in these gold nanostructures. Figure 3C shows an AFM image of the first PU replica generated from the fourth PDMS master cast from this gold master; Figure 3D is an AFM image of the sixth PU replica cast from the fifth PDMS master. Again, no obvious change in quality was observed for these nanostructures on the PU replicas. This procedure, therefore, has the capability of generating multiple copies of nanostructures starting from a single master. Both the simplicity and low cost of this procedure confirm its potential use in nanomanufacturing.

Figure 3E shows an AFM image of another gold master having features of  $\sim 50$  nm in size; Figure 3F shows an AFM image of a PU replica cast from a PDMS master (cast from this gold master) while it was bent mechanically (see Figure 1B). The dimension of the features was reduced from  $\sim 50$  nm to  $\sim 30$  nm in this process.

This work demonstrates a practical protocol based on replica molding for the fabrication of structures in organic polymers with lateral dimensions as small as  $\sim 30$  nm. Recently, Chou and co-workers demonstrated a related proce-

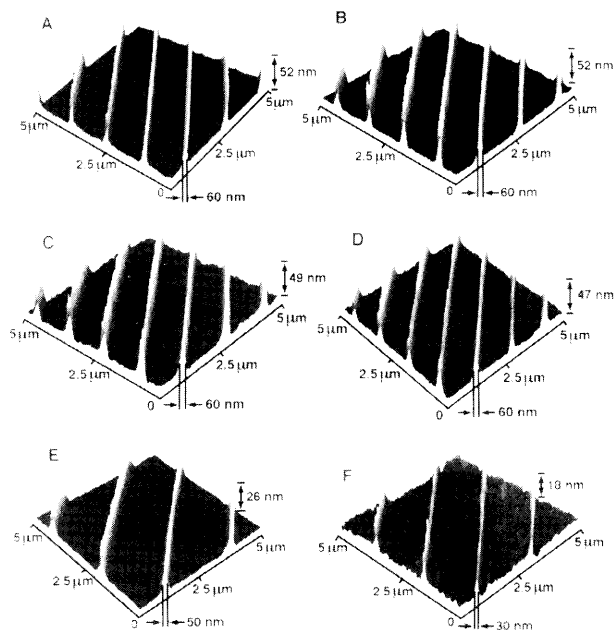


Fig. 3. AFM images of A) Au master before it was used to cast PDMS replicas; B) Au master after it has been used to cast seven PDMS replicas; C) the first PU replica produced from the fourth PDMS master cast from the Au master; D) the sixth PU replica cast from the fifth PDMS master cast from this Au master; E) another Au master before it was used to cast PDMS replicas; and F) the PU replica generated from a PDMS master (cast from this Au master) while this elastomeric master was mechanically deformed by bending.

ture—embossing in organic polymers—that generates polymeric features with dimensions of  $\sim 25$  nm.<sup>[11]</sup> These demonstrations make it clear that the fabrication of multiple copies of nanostructured organic polymers is a practical reality. These types of replication procedures provide a conceptual route to nanomanufacturing: conventional high-resolution lithographic techniques would be used to make masters, and these structures would then be replicated into organic polymers. The ability to make both positive and negative replicas, and to modify the dimensions and shapes of features present on elastomeric masters by mechanical deformation, adds further flexibility to this methodology. Using nanostructures to generate electronically, optically, and magnetically functional components and systems will require a development of new technologies; the present limiting step, i.e. the mass production of nanostructures, finds a range of potential solutions in this work.

### Experimental<sup>[13]</sup>

Poly(dimethylsiloxane) (Sylgard 184) was obtained from Dow Corning. Ultraviolet-curable polyurethanes (NOA 71 and 73) were obtained from Norland Products (New Brunswick, NJ). Elastomeric PDMS masters were fabricated from PDMS (A:B = 1:10) using the procedures described previously [10,11]. Ultraviolet-curable polymers were cured with an ultraviolet light (Canrad-Hanovia 450 W medium pressure, mercury vapor lamp, ACE Glass) for  $\sim 20$  min, with the lamp positioned at a distance of  $\sim 2$  cm from the sample. The original master used for Figure 2 consisted of parallel lines of Cr that had been fabricated using laser-focused deposition of Cr atoms on SiO<sub>2</sub> [12]. The original masters used for Figure 3 consisted of parallel lines

of Au on Si/SiO<sub>2</sub>, fabricated using e-beam writing and with PMMA as the resist films. Before casting of the PDMS replicas, the original Cr master was silanized with C<sub>6</sub>F<sub>13</sub>C<sub>2</sub>H<sub>4</sub>SiCl<sub>3</sub> solution in hexane ( $\sim 2\%$ , w/w) to avoid sticking of PDMS to the surfaces of the Si/SiO<sub>2</sub>; the Au masters were treated with C<sub>6</sub>F<sub>13</sub>C<sub>2</sub>H<sub>4</sub>SiCl<sub>3</sub> solution in hexane and C<sub>6</sub>F<sub>13</sub>C<sub>2</sub>H<sub>4</sub>SH solution ( $\sim 2$  mM) in ethanol to avoid sticking of PDMS to the surfaces of the Si/SiO<sub>2</sub> and Au. AFM images of Figure 3 were obtained using a Topometrix TMX 2010 scanning probe microscope (Mountain View, CA); the images were obtained in the contact mode with a supertip (Model # 1700-00).

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## A New Method for Chemical Modification of Conductive Polypyrroles Without Destroying Their Conductivity\*\*

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Electronically conducting aromatic polymers have been the object of a great amount of research in recent years.

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