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: C, 64.4%; H, 4.7%; N, 1.124%; H, 42.65%. Mo. Calculated: C, 64.4%; H, 4.7%; N, 1.124%; Mo. Electrochemical synthesis of the hybrid Pt/P-MoO2: This was performed by multiple cyclic voltammograms using a Pt foil working electrode, Ag/AgCl reference electrode, and Pt foil as counter-electrode. Thus, 0.91 g of H2MoO4 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 oxidation of pyrrole 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 1.34% H.

Received: July 3, 1996
Final version: October 1, 1996


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 ≤ 100 nm in dimension).[11] 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.[2] 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.[13] The manufacturing of nanostructures, that is, the making of multiple copies reproducibly and at low cost, will require new procedures: methods using organic polymers, for example, imprinting (or embossing) using a rigid master,[4] and polymerization in the nanometer-sized pores of a membrane,[5] 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,[6] compact disks[7] and microtools.[8] 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.[10-11]

Figure 1A shows the procedure schematically. A liquid prepolymer of poly(dimethylsiloxane) (PDMS) is cast...
against an original master whose surface has been patterned with nanometer-sized relief structures, made using advanced lithographic techniques: these features could be SiO₂, Si₃N₄, 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, a 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, 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 ~13 nm, and the heights of the PU lines are ~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 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 ~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 ~50 nm to ~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 ~30 nm. Recently, Chou and co-workers demonstrated a related proce-
of Au on SiO$_2$, fabricated using e-beam writing and with PMMA as the resist film. Before casting of the PDMS replicas, the original Cr master was sputtered with C$_6$F$_5$-C$_2$H$_5$SiCl$_2$ solution in hexane (-2 nm, s.w.) to avoid sticking of PDMS to the surfaces of the SiO$_2$; the Au masters were treated with C$_6$F$_5$-C$_2$H$_5$SiCl$_2$ solution in hexane and C$_6$F$_5$-C$_2$H$_5$SH solution (-3 nm) in ethanol to avoid sticking of PDMS to the surfaces of the SiO$_2$; and Au. AFM images of Figure 5 were obtained using a Topometrix TMX 3010 scanning probe microscope (Mountain View, CA); the images were obtained in the contact mode with a superp is (Model 170-001).

Received: August 14, 1996


[14] Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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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[11] This research was supported by a Grant-in-Aid for Scientific Research on a Priority Area (No. 07253262) from the Ministry of Education, Science, Sports and Culture of the Japanese Government. 

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Experimental

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 a violet-light (Cardio-Hanovia 450 W medium pressure, mercury vapor lamp, ACE Glass) for 20 min, with the lamp positioned at a distance of -2 cm from the sample. The original masters used for Figure 2 consisted of parallel lines of Cr that had been fabricated using laser-focused deposition of Cr atoms on SiO$_2$; [12]. The original masters used for Figure 3 consisted of parallel lines of Au on SiO$_2$, fabricated using e-beam writing and with PMMA as the resist film. Before casting of the PDMS replicas, the original Cr master was sputtered with C$_6$F$_5$-C$_2$H$_5$SiCl$_2$ solution in hexane (-2 nm, s.w.) to avoid sticking of PDMS to the surfaces of the SiO$_2$; the Au masters were treated with C$_6$F$_5$-C$_2$H$_5$SiCl$_2$ solution in hexane and C$_6$F$_5$-C$_2$H$_5$SH solution (-3 nm) in ethanol to avoid sticking of PDMS to the surfaces of the SiO$_2$; and Au. AFM images of Figure 5 were obtained using a Topometrix TMX 3010 scanning probe microscope (Mountain View, CA); the images were obtained in the contact mode with a superp is (Model 170-001).

Received: August 14, 1996


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