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conducting properties, with T_c's of 117 K being increased to 135 K on annealing in flowing O_2 at 300 °C, as shown by ac susceptibility data in Figure 4b. In addition, a volume fraction of > 80 % at 100 K is observed.[11] An in-depth study of the superconducting properties of samples prepared by this route is reported elsewhere.[11]

A vital consideration when preparing mercury-based cuprates in sealed quartz tubes is the possibility of pressure build-up in the tubes, causing explosions, and for this reason quartz tubes have always been encased in steel bombs to contain any such eventuality. In the studies reported here, we have deliberately increased the apparent pressure within the quartz tubes to exceed their estimated tolerance. The pressure tolerance of sealed quartz tubes of the dimensions discussed earlier is approximately 15 atm. A quick calculation for a simple, single-skinned reaction vessel would tell us that for these tubes (of internal volume ~5.5 × 10^{-6} m^3), this maximum pressure would be attained with just 1.08 × 10^{-3} mol of HgO, i.e. just 0.23 g of mercury oxide in the initial starting mixture. Of course, in the cases of the DSRV-type reactions, the internal volume is greatly reduced, thus reducing yet further the apparent maximum quantity of HgO possible to stay within the tolerance limits stated above.

In previous studies, sample mass has generally been kept low in order to give a minimum pressure of mercury, thus minimizing the possibility of explosions. However, in those reports, and others which have calculated the pressures within the reaction vessels, it has been assumed that all of the HgO decomposes at the reaction temperature. Through our steady increase of the ratio of HgO to available space within the reaction vessel, we have shown that not all of the mercury is in the vapor state since if this were the case, explosions would certainly have occurred. Indeed, we have prepared samples of up to 20 g of Hg-1223 (corresponding to 5 g of HgO in the initial mixture) in DSRV-type reactions, without explosions. Thus, this final constraint on sample mass has been lifted, since the actual pressure in the quartz tubes is constant, given that enough HgO is present to saturate the atmosphere. For the case of the quartz tubing used here (with the dimensions stated above), this constant reaction pressure is still below the strength limit of the quartz, and thus any sample mass could, in principle, be used.

In conclusion, we have developed a synthetic methodology towards the bulk-scale preparation of high purity samples of Hg-1223. Importantly, we have found that increasing the sample mass actually increases the phase-purity, and by this route, we have prepared bulk samples (up to 20 g) with exc̶ ̶ ̶ t phase purity, substantial superconducting volume fraction, and T_c values in excess of 130 K. We believe that there is no upper limit to the sample mass which may be prepared by this methodology; there is a clear potential for the production of kilogram-sized batches, or even larger. We have shown that the reaction for formation of Hg-1223 from the binary oxides proceeds primarily via a solid-state route, and thus that applied pressure, which may be gained from increased sample mass, or decreased volume of the reaction vessel, will give enhanced phase-purity by coaxing HgO into the solid state.

[1] J. G. Bednorz, K. A. Müller, Z. Phys. B **1986**, 64, 189.
[2] M. K. Wu, J. R. Ashburn, C. J. Toring, P. H. Hur, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, C. W. Chu, Phys. Rev. Lett. **1987**, 58, 908.
[3] C. N. R. Rao, A. K. Ganguli, Chem. Soc. Rev. **1995**, 24, 1.
[4] S. N. Putilin, E. V. Antipov, O. Chmaissem, M. Marezio, Nature **1993**, 362, 226.
[5] A. Schilling, M. Cantoni, J. D. Guo, H. R. Ott, Nature **1993**, 363, 56.
[6] G. B. Peacock, I. Gameson, M. Slaski, W. Zhou, J. R. Cooper, P. P. Edwards, Adv. Mater. **1995**, 7, 925.
[7] L. Gao, Y. Y. Xue, F. Chen, Q. Xiong, R. L. Meng, D. Ramirez, C. W. Chu, J. H. Eggert, H. K. Mao, Phys. Rev. B **1994**, 50, 4260.
[8] S. M. Loureiro, E. V. Antipov, E. T. Alexandre, E. Kopnin, M. F. Gorius, B. Souletie, M. Perroux, R. Argoud, O. Gheorghe, J. L. Tholence, J. J. Capponi, Physica C **1994**, 235, 905.
[9] B. A. Scott, E. Y. Suard, C. C. Tsuei, D. B. Mitzi, T. R. McGuire, B.-H. Chen, D. Walker, Physica C **1994**, 230, 239.
[10] S. Lee, M.-O. Mun, M.-K. Bae, S.-I. Lee, J. Mater. Chem. **1994**, 4, 991.
[11] C. Panagopoulos, J. R. Cooper, G. B. Peacock, I. Gameson, P. P. Edwards, W. Schmidbauer, J. W. Hodby, Phys. Rev. B **1996**, 536, 2999.

Fabrication of Polymeric Microstructures with High Aspect Ratios Using Shrinkable Polystyrene Films**

By Xiao-Mei Zhao, Younan Xia, Dong Qin, and George M. Whitesides*

Microstructures with high aspect ratios are increasingly important in micro-electromechanical systems (MEMS). These structures are often fabricated by screen-printing,[1] and more recently by a modified photolithographic procedure:[2,3] X-ray photolithography (LIGA) is also an important new technique.[4] Fabrication of structures with high aspect ratios challenges conventional photolithography in a number of aspects. Special spin-coaters are necessary to prepare homogeneous films of photoresists thicker than ~20 μm.[2] Multiple exposures to UV light or a single exposure to a synchrotron X-ray radiation[5] is typically needed in order to pattern a film of photoresist thicker than 50 μm. With special optics (large exposure gap optics), it is now possible for UV lithography to pattern layers up to 100 μm thick in a single exposure.[2,3] This procedure, however, re-

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quires a carefully carried out process of multilayer spin coating/baking and specially designed proximity printing equipment which is not available in most research laboratories. Here, we report a simple technique for fabrication of polymeric structures–reactive ion etching (RIE) of a stress-oriented, shrinkable polystyrene film[6] coupled with thermally induced shrinkage and shape-change in this film– for fabrication of polymeric microstructures with with an aspect ratio of ~10, and up to 120 μm in height.

Masks used in RIE can be either commercial products, such as TEM grids and metallic masks fabricated by electroforming, or home-made, free-standing polymeric microstructures fabricated by MIMIC and lift-off.[7,8] Figure 1a shows a scanning electron micrograph (SEM) of a free-standing epoxy web. This custom-designed pattern, which we call an inverted honeycomb, is interesting as a possible negative Poisson ratio material.[9] The polydimethylsiloxane (PDMS) mold used to fabricate this free-standing microstructure was made by a recently developed rapid prototyping technique.[10] This free-standing film was ~9 μm thick, 5 mm wide, and 7 mm long. This polymeric web was coated with ~30 nm of Au to protect it from being etched in the O₂ plasma. The area of the home-made polymeric mask is limited by the fragility of the micron-thick film: the largest mask we have ever made is 1 × 1 cm² in size. Fabrication of the polymeric mask requires careful work because the film is fragile, but an intact mask, when coated with Au, is reusable many times.

The pattern of inverted honeycomb shown in Figure 1a was transferred into a shrinkable polystyrene film by RIE. Figure 1b shows an SEM image of the polystyrene film that has been etched for 30 min in an O₂ plasma. The feature shown in Figure 1b was 2.3 μm deep, measured using a profilometer. This etched polystyrene film was allowed to shrink at 110 °C for ~2 h. The shrunken film is shown in Figure 1c. This polystyrene film shrank by a factor of ~5 in the x direction and by a factor of ~4 in the y direction. The depth (~45 μm) of the patterned features increased by a factor of ~20 (45 μm ≈ 2.3 μm × 20). Figure 1d shows an SEM image of a polyurethane replica of this shrunken film. The protrusive bow-tie-type structures were ~45 μm high.

We have made structures with aspect ratios as high as ~10. Figure 2b–d shows epoxy replicas from shrunken poly-
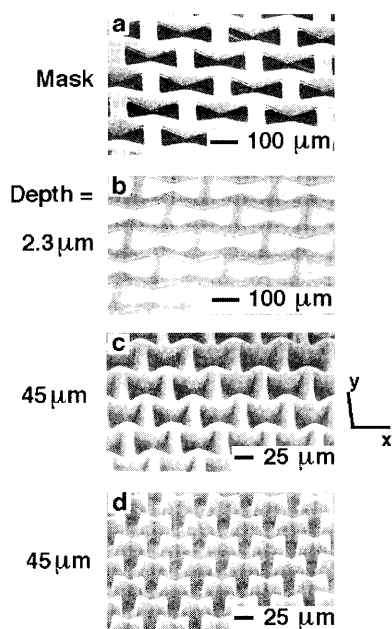
Fig. 1. SEM images of a) a gold-coated free-standing polymeric microstructure used as the mask in RIE; b) a polystyrene film after 30 min of RIE through the mask shown in a); c) the shrunken film b); and d) a polyurethane replica from the sample shown in c). The mask shown in a) was made of heat-curable epoxy and was coated with ~30 nm of gold by sputtering. The features in this free-standing film were a little buckled after being coated with Au. The height of the honeycomb structures was b) ~2.3 μm before shrinking and c) ~45 μm after shrinking. The image in d) was taken at a tilt angle of ~30°.
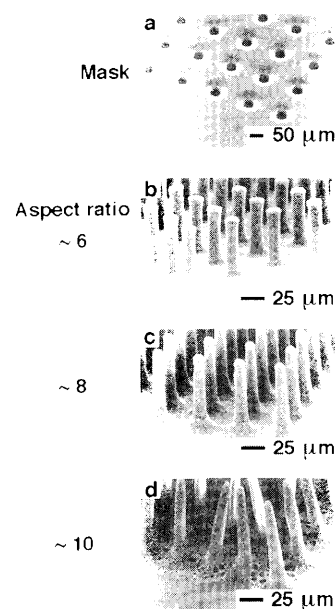
Fig. 2. SEM iamges of a) an Au-coated Si mask and b–d) three epoxy replicas from different shrunken films. The three polystyrene films have been etched in an oxygen plasma through the mask shown in a) for 45, 60, and 75 min, respectively, followed by thermal shrinkage at 110 °C. The diameter of the posts shown in parts b–d was ~12 μm; the height was b) ~71 μm, c) ~96 μm, and d) ~121 μm. Images b–d were taken at a tilt angle of ~50°.

styrene films that have been etched in an O₂ plasma for 45, 60, and 75 min, respectively, followed by thermal shrinkage at 110 °C for 2 h. Due to the softness of the polymers (epoxy and polyurethane) used in replication, and the capillary force[11] acted between these structures, posts with aspect ratios higher than eight tend to collapse and stick with each other (Fig. 2d) after sonication in ether, removal from the solvent, and drying.

We have also fabricated complex 3-dimensional structures using multiple cycles of RIE through a different mask in each cycle. A shrinkable polystyrene film covered with a metallic mask (Fig. 3a) was exposed to an O₂ plasma for 10 min. The mask was then rotated ~90° (Fig. 3b) and reused to further pattern the same film in the second 10 min exposure to the plasma. The etched film was then allowed

to shrink at 110 °C for 2 h. Figure 3c shows a polyurethane replica from this shrunken film. A similar procedure was applied in the fabrication of the second sample (Fig. 3f), except that the mask shown in Figure 3d was used in the first exposure (30 min) to the plasma and the mask shown in Figure 3e in the second (40 min). The mask shown in Figure 3d was a rotary encoder disc having 80 lines/revolution. Since structures in the two masks (Fig. 3d and e) had different spacings, the array of square posts (Fig. 3f) scattered over the region of the rotary disc. The height of individual structures depended on the time of exposure. The top of a post (~62 μm high) sitting right on a line (~48 μm high) was ~110 μm away from the base.

The procedure described here combines RIE, shrinkable polymeric films, and the rapid prototyping technique into a convenient system for rapid fabrication of complex 3-dimensional structures (with aspect ratios up to ~10) with custom-designed patterns at low cost. This system provides a new route in thick-film technology to fabricate microstructures with high aspect ratios without access to sophisticated photolithographic facilities. The types of structures

that we have made so far do not have straight sides and sharp angles between planes, and are unsuitable for some types of applications. They can, however, be made on curved surfaces, and readily yield structures with multiple levels of relief (e.g. Fig. 3c and f).

Experimental

Figure 4 summarizes the experimental procedure for fabrication. A metallic (Cu, or Au coated Ni) or metal-coated polymeric mask was clamped with steel clips onto the surface of a polystyrene film. The film was exposed to an O_2 plasma, and the pattern in the mask was transferred into the polystyrene film by etching through slots in the mask. The dimension (r) of the features etched into the polystyrene film was slightly larger than that of the corresponding slot in the mask due to undercut. The patterned film was then transferred into an oven heated at 110 °C and left there for 2 h. It shrank by a factor of ~4–5 in both x and y directions ($r = 4r'$ to $5r'$), while expanding by a factor of ~20 in the z direction ($z' = 20z$; $h' = 20h$); the volume of the film remained roughly unchanged. The aspect ratio ($h'/r' = 100h/r$) of the microstructures increased by a factor of ~100 in this shrinking process. A liquid prepolymer was then used to replicate the structures on the surface of the shrunken film (Figure 4d and e). After curing, the shrunken film was removed by dissolving in ether.

The metallic masks shown in Figures 2 and 3 were obtained as gifts from Dynamics Research Corporation (Wilmington, MA). A mask and a stress-oriented polystyrene film (Kama Corp., Hazelton, PA) was brought into contact and held in place with steel clips on the stage in a home-made reactive ion etcher. The film was exposed to an O_2 plasma (170 mTorr, 44 W, 13 sccm) for 5–120 min. The patterned film was allowed to shrink in an oven heated at 110 °C for 2 h. A thin layer of a liquid prepolymer was applied to the patterned surface of a shrunken film; the whole system was placed in a

Sample 1

— 100 μm — 100 μm

— 50 μm — 25 μm

Sample 2
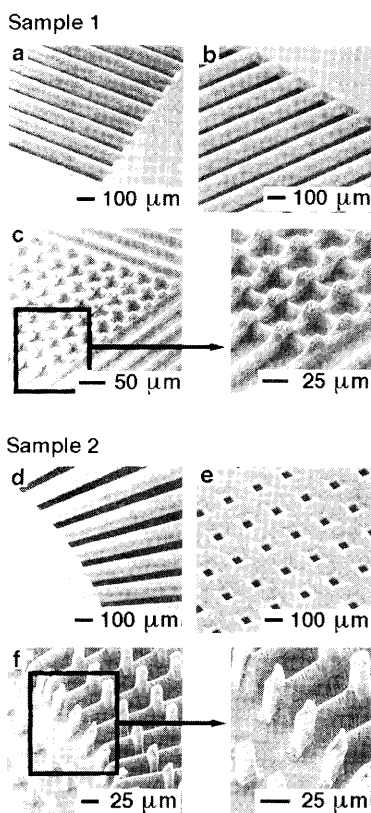
— 100 μm — 100 μm

— 25 μm — 25 μm

Fig. 3. SEM images of different metallic masks (a, b, d, and e) and polyurethane replicas (c and f). The first polystyrene film has been etched twice in a reactive ion etcher for 10 min each duration using the mask shown in a) in the first 10 min of exposure and the mask shown in b) in the second. The second polystyrene film has been exposed to an oxygen plasma for 30 min through the mask shown in d) (a rotary encoder disc) and for 40 min through the mask shown in e) (an array of squares). The two patterned films were allowed to shrink at 110 °C for 2 h. The polyurethane replicas from the two shrunken samples are shown in c) and f). The image in c) was taken at a tilt angle of 45°; image f) at 30°.

(a) O_2 RIE

mask
polystyrene film
z = 25 μm

RIE

(b)

Remove the mask

(c) r ≈ 55 μm

h ≈ 4.8 μm

Shrink at 110 °C

(d) r' ≈ 0.22r ≈ 12 μm

z' ≈ 20z
≈ 0.5 mm

h' = 20h
≈ 96 μm

a) Add a drop of prepolymer
b) Cure in situ

(e)

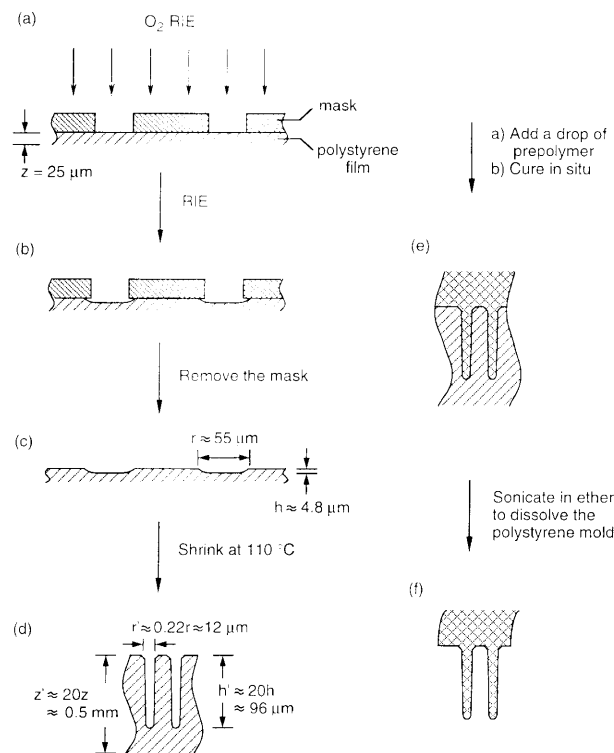Sonicate in ether to dissolve the polystyrene mold

(f)

Fig. 4. Schematic diagram of the fabrication of microstructures with high aspect ratios. The stress-oriented polystyrene film was 25 μm thick. At 110 °C, it shrank by a factor of ~4 in the machine direction and by a factor of ~5 in the transverse direction. It expanded by a factor of ~20 (4 × 5) in the z direction (h and z), leaving the volume of the film unchanged. The aspect ratio of the structures (h/r) in the surface of the polystyrene film increased at least by a factor of ~100 ($h'r/hr'$).

desiccator under vacuum for 20 min to remove air bubbles trapped in the liquid prepolymer. When features on the surface of the shrunken film were deep, many small air bubbles could not escape but settled down at the interface between the liquid prepolymer and the solid shrunken film. The air bubbles were thus replicated into the replica after the prepolymer was solidified (e.g. the surface texture shown in Fig. 2b-d). We used a UV-curable polyurethane (NOA73, Norland Products, New Brunswick, NJ) and a heat-curable epoxy (F114, Tra-Con, Medford, MA) to replicate the surface of shrunken films. The prepolymer of NOA73 was irradiated with a UV light (Type 7825-34, Canrad-Hanovia 450 W medium-pressure Hg vapor lamp, Ace Glass, Inc., Vineland, NJ) for 45 min, with samples placed at a distance of ~1–2 cm from the lamp. The precursor of F114 was cross-linked at 65 °C for 4 h.

[1] H. Moilanen, J. Lappalainen, S. Leppavuori, *Sens. Actuators A* **1994**, *43*, 357.
[2] B. Löchel, A. Maciossek, H. J. Quenzer, B. Wagner, *J. Electrochem. Soc.* **1996**, *143(1)*, 237.
[3] E. Cullmann, B. Löchel, G. Engelmann, C. Reyerse, *Solid State Technol.* **1995**, March, 93.
[4] E. W. Becker, W. Ehrfeld, P. Hagmann, A. Maner, D. Münchmeyer, *Microelectron. Eng.* **1986**, *4*, 35.
[5] V. White, R. Ghodssi, D. Herdey, D. Denton, L. McCaughan, *Appl. Phys. Lett.* **1995**, *66*, 2072.
[6] P. C. Hidber, P. F. Nealey, W. Helbig, G. M. Whitesides, *Langmuir* **1996**, *12*, 5209.
[7] Y. Xia, E. Kim, G. M. Whitesides, *Chem. Mater.* **1996**, *8*, 1558.
[8] E. Kim, Y. Xia, G. M. Whitesides, *Nature* **1995**, *376*, 581.
[9] I. A. Aksay, J. T. Groves, S. M. Gruner, P. C. Y. Lee, R. K. Prud'homme, W.-H. Smith, S. Torquato, G. M. Whitesides, *Proc. SPIE* **1996**, *2716*, 280.
[10] D. Qin, Y. Xia, G. M. Whitesides, *Adv. Mater.* **1996**, *8*, 917.
[11] T. Tanaka, M. Morigami, N. Atoda, *Jpn. J. Appl. Phys.* **1993**, *32*, 6059.

The Synthesis of Micrometer- and Submicrometer-Size Spheres of Ordered Mesoporous Oxide MCM-41**

By *Michael Grün, Iris Lauer,* and *Klaus K. Unger**

Since its discovery in 1992, MCM-41 has become the most popular member of the M41S family of silicate and aluminosilicate mesoporous materials.[1,2] MCM-41 exhibits a regular pore system which consists of an array of unidimensional, hexagonally shaped pores with a narrow pore size distribution. The pore walls are composed of amorphous silica, as indicated by X-ray diffraction (XRD) measurements.[1] Transmission electron microscopy suggests that the pore walls have an approximate thickness of about 1 nm.[3] The pore size can be adjusted to between 2 and 8 nm during the synthesis by use of surfactants of different chain length or by adding organic auxiliaries such as 1,3,5-trimethylbenzene. High specific surface areas of up to 1500 m²/g have been achieved. Due to its regular pore

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structure and narrow pore size distribution, MCM-41 has been used as a model system for sorption isotherms of various gases[4] as well as a packing material in size exclusion chromatography[5] and normal phase chromatography.[6] Several articles have been published dealing with the synthesis and characterization, formation mechanisms, structure, and catalytic activity of MCM-41 and related materials.[3,7] The incorporation of various metals, e.g. aluminum and titanium into the MCM-41 framework to adjust its catalytic properties has also attracted considerable attention.[8,9]

The synthesis of MCM-41 can be accomplished by several routes, which differ mainly in the pH of the reaction mixture and the source of silica. Amphiphilic templating agents, e.g. alkyltrimethylammonium halogenides, are used together with silica precursors such as tetraalkoxysilanes or colloidal silica. After the reaction the template is removed by calcination. MCM-41 offers unique properties as an adsorbent in separation science and technology. The material obtained by the classical procedure of Beck et al.,[2] however, yields loose agglomerates consisting of a wide particle size distribution. The agglomerates are composed of primary particles of about 50–100 nm.[5] Thus, grinding and sizing to defined narrow cuts yields a large amount of fines[6] and the control of the particle morphology of MCM-41, i.e. the synthesis of beads of defined size could open up new possibilities for the application of MCM-41 as a packing material in chromatography or as an easy-to-handle form of MCM-41 for catalytic purposes. So far, only hexagonal prisms of MCM-41 have been reported in the literature.[2,10] This communication describes the first synthesis of spherical silica particles featuring an MCM-41 structure. All samples were characterized by XRD, nitrogen sorption at 77 K, and scanning electron microscopy (SEM).

The synthesis procedure itself is a modification of Stöber's well-known synthesis of monodisperse silica spheres,[11] which involves the hydrolysis of tetraalkoxysilane in a mixture of a low-boiling alcohol and aqueous ammonia. We modified this procedure by adding a cationic surfactant to the reaction mixture, thus providing a source of micelles which play a crucial role during the formation of MCM-41.[12] In this study, n-hexadecyltrimethylammonium bromide (Sample 1) and n-hexadecylpyridinium chloride (Sample 2) were used as cationic surfactants, while ethanol was chosen as the solvent and tetraethoxysilane served as the silica source. Aqueous ammonia was used as a catalyst. After the reaction, the surfactant was removed by calcination at 823 K.

The XRD patterns show several Bragg peaks at low reflection angles between 2.5 and 7.0° 2θ which are typical of MCM-41 materials. They reflect the quasi regular arrangement of the mesopores in the bulk material. The Bragg peaks can be indexed assuming a hexagonal symmetry. As no order is present along the *l*-axis only (*hkl*) peaks with $l = 0$ are observed. The repeat distance a_0 between two pore centers can be calculated from $a_0 = (2/\sqrt{3}) \cdot d_{100}$. The pore diameter can be calculated by subtraction of