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formed with this method is limited by the resolution of the microcontact printing (~0.2 μm),[2] by the ability to set the angle and position of the stamp relative to the object to be patterned (~0.01°, and ~2 μm for our apparatus),[8] and by uncertainties in the dimensions of the curved support. The composition of these parts is limited to materials that can be electrodeposited. We believe that our method offers a simple means for fabrication of complex three-dimensional microstructures that will be a valuable complement to other means for microfabrication. Many applications in biotechnology and MEMS should be found.

Received: October 2, 1996
Final version: November 14, 1996

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Fabrication of Glassy Carbon Microstructures by Pyrolysis of Microfabricated Polymeric Precursors**

By *Olivier J. A. Schueller, Scott T. Brittain,* and *George M. Whitesides**

This paper describes a method of fabricating microstructures of glassy carbon and other high-carbon solids. This method uses micromolding of polymers to form precursors to these structures, and pyrolysis of these polymeric microstructures to form the carbon solids. These microstructures are stiff and can be either electrically insulating or conducting, depending on their thermal history. In addition, carbon structures can be very stable thermally, and the surface of carbon is readily functionalized.[1,2] We are developing carbon microstructures as components in microelectromechanical systems (MEMS), microreactors, and other systems in which thermal stability, chemical inertness, engineered surface properties, and electrical conductivity are useful characteristics.

The mechanical, electrical, and chemical properties of high-carbon solids can be controlled over wide ranges by the temperature at which these solids are prepared.[1,2] The range of electrical properties that can be achieved is especially interesting: the conductivity of a phenol-formaldehyde resin can be controlled over a range of ~$10^{19}\Omega^{-1}$ cm^{-1} by pyrolysis. Insulating, semiconducting, and semimetallic behaviors have been observed for pyrolyzed novolac photoresists, depending on the pyrolysis conditions.[4,5]

Glassy carbon is often produced by carbonization of organic polymeric precursors; resins of furfuryl alcohol, phenol-formaldehyde, acetone-furfural, or furfuryl alcohol-phenol copolymers are among those commonly used for this purpose.[2] In this work, copolymers of phenol-formaldehyde or furfuryl alcohol-phenol were formed in patterns on appropriate substrates (silica, Si/SiO_2, glassy carbon) using micro-molding in capillaries (MIMIC)[6–8] and microtransfer molding (μTM).[9] The resulting polymeric structures were carbonized at high temperatures in vacuum (600–1100 °C, 10^{-6}–10^{-7} torr) or in an inert atmosphere (argon), either on the substrate or after being lifted from the surface, to yield high-carbon structures having micron-scale dimensions.

Supported structures of a phenol-formaldehyde resin and of a furfuryl alcohol-modified phenolic resin were prepared by MIMIC, using a patterned poly(dimethylsiloxane)

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[**] This work has been supported in part by the Office of Naval Research and the Defense Advanced Research Projects Agency. It used MRSEC Shared Facilities supported by the National Science Foundation (DMR-9400396). The authors thank Xiao-Mei Zhao for demonstrating microtransfer molding.

  0935-9648/97/0605-0477 $ 17.50+.50/0

(PDMS) master as a mold.[10,11] The PDMS master was placed on a substrate, the pattern in the PDMS forming a network of channels. A drop of polymer was placed at one end of the channels, and the liquid filled the channels by capillary action. Once filled with the liquid prepolymer, the substrate was placed on a hot plate and the polymer slowly cured (from 90 to 150 °C) for 1 h. The PDMS stamp was then removed from the substrate. The structure defined by the surface relief in the PDMS remained on the substrate.

Figure 1A is an electron micrograph of high-carbon wires prepared by carbonization (800 °C) under high vacuum of a phenol-formaldehyde resin, assembled by MIMIC on silica. The inset is a close-up view of a fracture profile of one of these wires. The stamp initially used as a mold consisted of channels that were 50 μm wide and 8 μm deep, separated by 50 μm. The wires, after carbonization, were ~7 mm long, 40 μm wide, 6 μm thick, and were separated by 60 μm. This linear shrinkage of ~20% is that expected for carbonized phenol-formaldehyde resins.[1] During the curing step, the viscosity of the polymer first decreases and then increases with temperature, and the polymeric structure contracts. These changes are responsible for the curvature apparent in the cross-section of the wires.

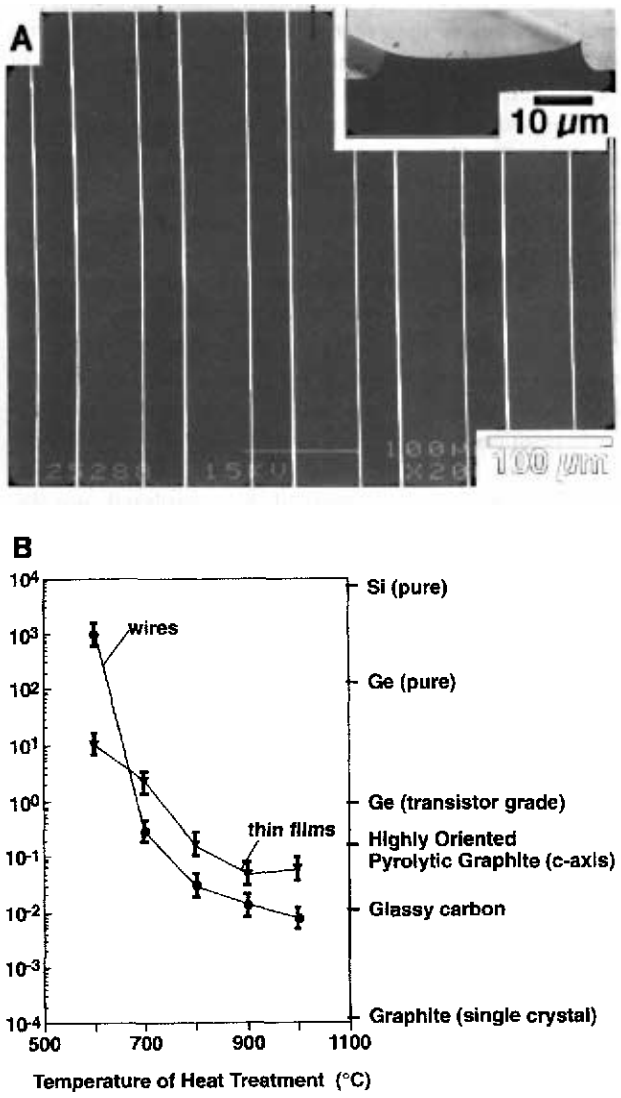

Fig. 1. A) Scanning electron micrographs of 40 μm lines prepared by carbonization of a phenolic resin on silica. The sample was sputtered with gold. The darker features represent the carbon lines prepared at 800 °C (top view). The sharp edges of the wires act as emitters of secondary electrons, which is why the edges appear brighter than the bulk of the lines. The inset is a fracture profile of one of the wires. B) Evolution of the room temperature resistivity as a function of carbonization temperature.[12] Markers on the right axis indicate average resistivity values of known materials. Highly oriented pyrolytic graphite has a resistivity of ~2×10^{-1} Ωcm along the *c*-axis (perpendicular to the graphitic planes), and of ~ 4×10^{-5} Ωcm along the *a*-axis (parallel to the graphitic planes).

The resistivity of wires prepared by carbonization between 600 and 1000 °C was determined by applying patches of silver paint to both ends of an array of 8–12 of the wires shown in Figure 1A and multiplying the overall resistance by the number of wires electrically connected. Figure 1B is a plot of the room temperature resistivity of the carbon solid as a function of the maximum temperature reached during heat-treatment. As expected, the resistivity drops sharply at temperatures >600 °C to reach a plateau at ~1000 °C.[1] Figure 1B also includes the resistivity of thin films (~6 μm) of carbonized phenol-formaldehyde resins measured using a four-point probe. The change in the resistivity of the wires as a function of temperature of carbonization follows the same trend as that exhibited by the thin films. The small discrepancy (< 1 order of magnitude) in the resistivity between thin films and wires may be due to the fact that the dimensions of the wires and thin films were determined by different techniques.[12] It is apparent from this figure that the high-carbon solids we prepared are semiconductors, whose conductivity was controlled by the temperature of carbonization.

More complex and/or free-standing structures were also prepared by MIMIC. Figure 2A is a micrograph of a free-standing grid carbonized at 1000 °C under an inert atmosphere. The PDMS stamp used in this case consisted of 50 μm pillars spaced by 50 μm. The film was separated from the substrate (silicon wafer) with a razor blade following the curing step. It was then sandwiched between two Si wafers and carbonized under argon. Figures 2B–D are electron micrographs of grids prepared by carbonization of free-standing structures fabricated by MIMIC in networks of channels formed between two PDMS stamps in conformal contact.[6] The stamps were oriented so that the channels forming the patterns were perpendicular. Once the liquid resin had filled the interconnected channels, it was cured on a hot plate at T~90–150 °C. The stamps were then gently separated. The solidified grid was lifted with tweezers, and subsequently carbonized under argon at T~1000 °C. High aspect ratio structures were also successfully prepared as well (Fig. 2D).

We were also able to fabricate complex structures using the rapid prototyping methods we have recently developed (Figs. 3 and 4).[9,13] Heat-treatment of the solidified resin resulted in the formation of free-standing carbonized mi-

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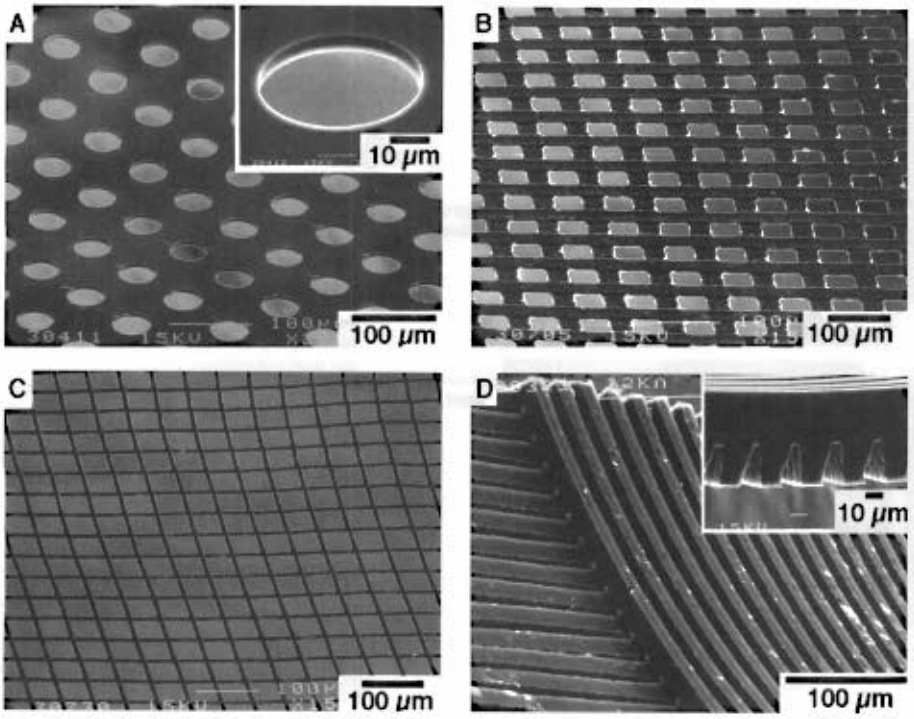

Fig. 2. Scanning electron micrographs of grids prepared by MIMIC and carbonized at 800 or 1000 °C. A) Free-standing grid prepared by carbonization at 800 °C of a cured film of a phenol-furfuryl alcohol copolymer. The thickness of the film (~6 μm) can be estimated from the inset (tilt angle 60°). B–D) These three bilayer grids were prepared by MIMIC of the same polymer between two PDMS stamps with their patterns perpendicular and subsequently carbonized at 1000 °C. The PDMS stamps consisted of B) 50 μm channels and C) 13 μm channels. The lighter background can clearly be seen through both grids. D) The PDMS stamp used in this case was molded on a photoresist surface relief with a higher aspect ratio (~1.5:1) than in A–C; the grid is ~40 μm thick (see inset).

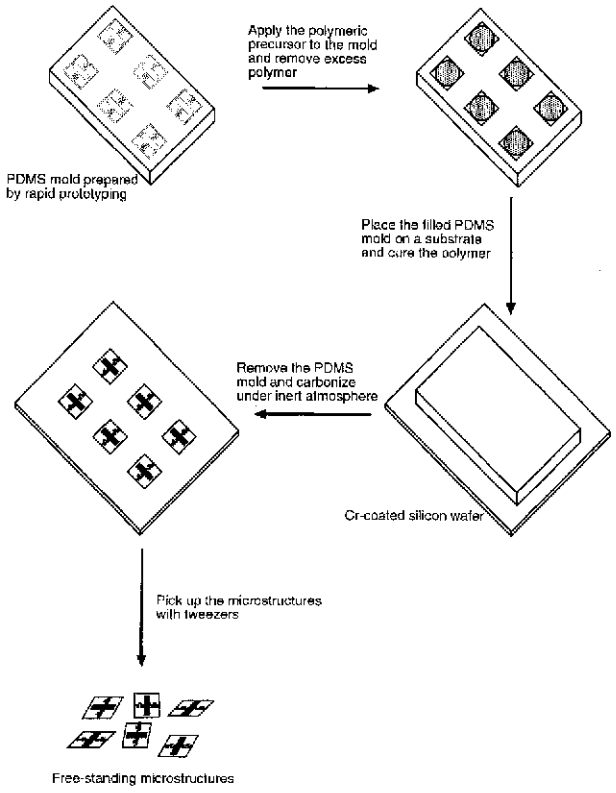

Fig. 3. Schematic diagram outlining the preparation of carbon microstructures by μTM. A liquid phenol-furfuryl alcohol copolymer was applied to the surface of a PDMS mold. The excess polymer was removed, and the PDMS mold was placed on a planar substrate. Once the polymer was cured, the PDMS mold was removed. The supported polymeric structures were carbonized under argon to give free-standing high-carbon microstructures. Thin films of chromium (400 Å) deposited on silicon wafers were used as substrates: the chromium acted as an efficient release agent for the carbon structures. Other substrates that were tested (Si, Ag on Si, Ni on Si) did not perform as well.

crostructures;[14] these structures spontaneously released from the chromium surface as they shrank. Figures 4A–D are electron micrographs of some of the carbonized polymeric structures that we prepared by rapid prototyping and μTM.

The density of carbon solids fabricated by this route was measured by the flotation technique. As expected, it was found that the density increases from 1.20 to 1.51 g/cm^3 in the range of temperature investigated (400–1000 °C).[1] The density of a pyrolyzed phenol-formaldehyde resin reaches a minimum (ρ~1.1–1.2 g/cm^3) at ~400–500 °C, then increases to ~1.5 g/cm^3 at 1200 °C;[1] for comparison, the density of graphite is 2.25 g/cm^3, and that of diamond 3.51 g/cm^3.[15] Shrinkage of the polymeric precursors during carbonization is due to mass loss (elimination of heteroatoms) combined with densification of the solids. Even though we cannot control the amount of shrinkage per se, it will be possible to take this effect into account when designing a target structure, as linear shrinkage never exceeded 20 %.

This work demonstrates that microstructured, high-carbon solids can be prepared by MIMIC and μTM from appropriate polymeric precursors. These fabrication techniques enable the preparation of numerous microstructures in a parallel process, and are easier to use than serial techniques such as stereo laser machining or laser-assisted chemical vapor deposition.[16–19] These structures can be either electrically insulating or conducting, and either supported or free-standing.[20] Their electrical properties can be easily controlled by the temperature of carbonization. Carbon solids exhibit a much wider range in properties than silicon; the ability to tailor the properties of carbon solids through organic synthetic modification of their precur-

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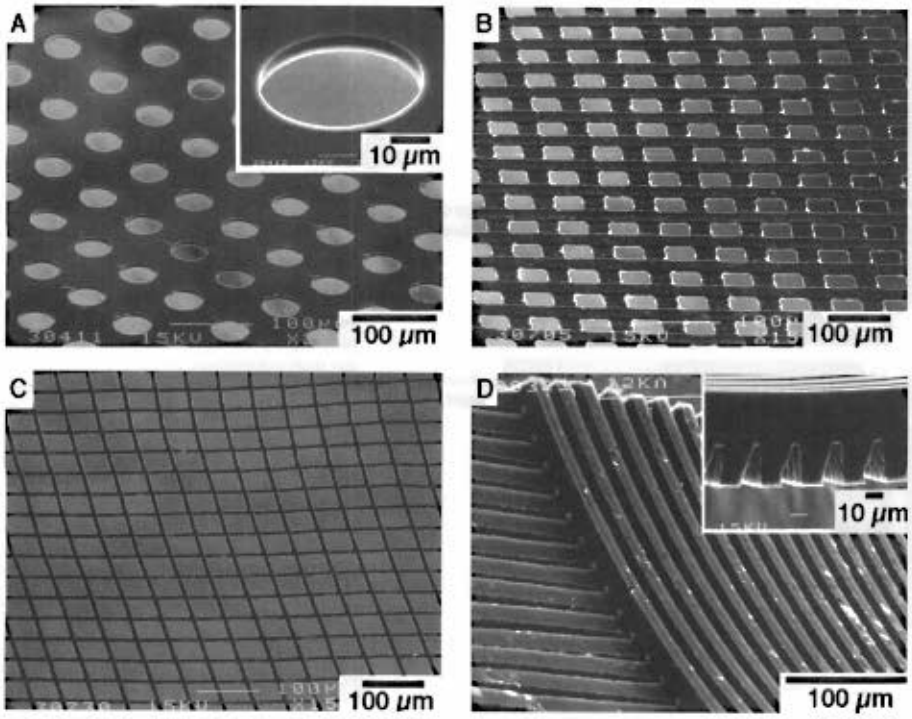

Fig. 4. Scanning electron micrographs of carbon microstructures prepared by rapid prototyping and μTM, and carbonized under inert atmosphere at 1000 °C. The microstructures were mounted with conductive carbon tape or silver paint. A) Concentric circles. B) This structure is similar to that used in some accelerometers. The radial springs allow movement of the central square in and out of the plane of the frame. C) Interdigitated capacitor. D) The initial carbonization step at 1000 °C (in a tube furnace) was followed by heat treatment under Ar up to 1800 °C (in an induction furnace). This structure is an optical deflector: the center plate can be actuated electrostatically.

sors, and by the choice of conditions used in their processing, may make them an attractive alternative to silicon for the preparation of certain types of MEMS. We are currently testing the properties of high-carbon MEMS fabricated by these techniques.

Experimental

Fabrication of the PDMS stamps and molds was conducted according to procedures previously reported [10,11]. The stamps were prepared by casting PDMS (Sylgard 184, Dow Corning) on masters generated by photolithography. Substrates used for the preparation of carbonaceous structures include silicon wafers and silica slides. The phenol-formaldehyde resin was obtained from Georgia Pacific (Bakelite BLS-2700). Viscosity was adjusted by addition of ethanol. The furfuryl alcohol-modified phenolic resin was obtained from QO Chemicals (Furcarb LP-520). Curing of the latter resin required the addition of a latent, heat-activated catalyst such as a 50 % aqueous solution of $ZnCl_2$. The amount of catalyst never exceeded 10 % (w/w) of the resin in order to prevent a too rapid cure and potential deformation of the microstructures. CAUTION: Mixing an acid catalyst with furfuryl alcohol-based resins induces an exothermic reaction. Resistance measurements were performed with a hand-held voltmeter. Resistivity measurements of thin films were performed with a four-point probe manufactured by Alessi, Inc. CA, and a potentiostat/galvanostat from EG&G, Princeton Applied Research (Model 273). SEM was performed on a JEOL JSM-6400 scanning electron microscope operating at 15 keV. Profilometry was performed on a Tencor Alpha-Step 200.

Received: November 14, 1996

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