

Fabrication of glassy carbon microstructures by soft lithography

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

Harvard University, Department of Chemistry and Chemical Biology, 12 Oxford Street, Cambridge, MA 02138, USA

Received 22 April 1998; revised 10 August 1998; accepted 10 August 1998

Abstract

This paper describes fabrication techniques for the fabrication of glassy carbon microstructures. Molding of a resin of poly(furfuryl alcohol) using elastomeric molds yields polymeric microstructures, which are converted to free-standing glassy carbon microstructures by heating ($T \sim 500\text{--}1100^\circ\text{C}$) under argon. This approach allows the preparation of macroscopic structures (several mm^2) with microscopic features ($\sim 2\text{ }\mu\text{m}$). Deformation of the molds during molding of the resin allows preparation of curved microstructures. The paper also presents a method of incorporating these structures on a chip by masking and electroplating. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Glassy carbon; Microfabrication; Soft lithography

1. Introduction

This paper describes the preparation of glassy carbon microstructures by a procedure in which the microstructures of polymeric precursors to carbon are first formed by micromolding, and then converted to glassy carbon by heat treatment ($500\text{--}1100^\circ\text{C}$) under an inert atmosphere. Remarkably, the overall structure of the polymeric shape is largely retained during the carbonization stage, and the process yields structured, glassy carbon microstructures. These microstructures are mechanically stiff and electrically conductive [1,2]. Large-area microstructures ($\sim \text{mm}^2$) with high aspect ratio (5–10:1) and fine surface detail ($\sim \mu\text{m}$) can be prepared by molding in a single-step procedure.

This microfabrication approach is based on molding of a polymer followed by carbonization [3]. This procedure is radically different from the typical microfabrication techniques used in the preparation of micromachined silicon-based sensors and transducers [4,5]. Silicon technology can be divided into two broad classes: additive and subtractive processes [6]. In additive processes, thin films of metals or

dielectrics are deposited and patterned onto the surface; subtractive processes are based on etching. The range of structures that can be generated by etching is constrained by the requirement of some etching procedures for specific crystalline orientation: curved or rounded structures may be particularly difficult to make [4].

We have recently developed a range of microfabrication techniques for the preparation of microstructures in organic polymers [7,8]. We call these techniques, which are based on the use of elastomeric polydimethylsiloxane (PDMS) stamps or molds, soft lithography. Soft lithography includes microcontact printing (μCP) [9–12], micromolding in capillaries (MIMIC) [13,14], microtransfer molding (μTM) [15], and replica molding [16,17]. Many aspects of these techniques have been covered in recent articles and reviews [7,18]. Central to these techniques is the use of PDMS molds. The PDMS molds are prepared by casting PDMS on a bas-relief master patterned in photoresist by photolithography. The most relevant soft lithographic techniques in the work presented here are MIMIC and μTM , in which a pattern of polymer is prepared by molding.

In addition to the familiar allotropic forms of carbon (graphite, diamond, and fullerenes), there are numerous other types of carbon materials, typically prepared by controlled pyrolysis of organic precursors [3,19]. The structural properties—extent of graphitization; size of mi-

* Corresponding author. E-mail: gwhitesides@gmwgroup.harvard.edu

crocrystalline domains; the relative orientation of these domains—of these carbon solids strongly affects their chemical, mechanical, and physical properties [3]. The properties of these carbons depend on the starting organic materials and the processing procedures. Four successive stages have been identified that describe the physico-chemical processes responsible for the conversion of a polymer to carbon solids [3]. Molecules of solvent and unreacted monomer are eliminated during the precarbonization stage ($T < 300^{\circ}\text{C}$). Heteroatoms (oxygen, nitrogen, halogens) are eliminated during the carbonization stage ($300\text{--}500^{\circ}\text{C}$). Rapid mass loss occurs during this stage, and a network of conjugated carbon systems, each electronically isolated from the other, is formed. Hydrogen atoms are eliminated during the carbonization stage ($500\text{--}1200^{\circ}\text{C}$). The aromatic network becomes interconnected; as a result, permeability decreases and density, hardness, modulus, and electrical conductivity increase. Structural defects are gradually eliminated during the annealing step ($T > 1200^{\circ}\text{C}$) [3].

At elevated temperature ($> 2500^{\circ}\text{C}$), some carbon solids graphitize [3]. Carbon materials prepared by pyrolysis have been classified as either graphitizing carbons (soft carbons) or non-graphitizing carbon (hard carbons) [20]. The formation of a liquid mesophase at $\sim 500\text{--}700^{\circ}\text{C}$ enables subsequent graphitization: molecules and aromatic networks are preorganized in liquid-crystal-like aggregates during this stage. Graphitization may then take place within these aggregates since chain stacking is favorable.

Glassy carbon is an example of non-graphitizing carbon: the entangled structure of the crystallites prevents extended crystal growth. It was independently prepared in 1962 by Yamada and Sato from phenolic resins [21], and Davidson from cellulose [22]. Glassy carbon is typically prepared by slow pyrolysis at elevated temperatures of a polymeric precursor (polyvinyl chloride, polyvinylidene chloride, polyacrylonitrile, cellulose, resins of phenol-formaldehyde, or polyfurfuryl alcohol) under inert atmosphere [23]. The structure of glassy carbon consists of long, randomly oriented microfibrils ($15\text{--}50\text{ \AA}$ wide) that bend, twist and interlock to form robust interfibrillar nodes. Glassy carbon, also known as vitreous carbon, derives its name from a fracture behavior that is similar to that of glass. The low density ($1.4\text{--}1.5\text{ g/cm}^3$) of glassy carbon relative to that of graphite (2.27 g/cm^3) and diamond (3.52 g/cm^3) indicates that it is porous. The pores are, however, not connected, as reflected by the fact that glassy carbon is impermeable to liquids and gases [23].

This paper describes a procedure, based on soft lithography, used to prepare glassy carbon microstructures [1,2]. Microstructures with complex, 3D topology are presented as a demonstration of the potential of this fabrication technique. A method to connect these structures to a surface is also described. Potential applications of glassy carbon microstructures in microfabricated devices are then discussed.

2. Experimental procedures

2.1. Materials

The elastomeric molds were prepared from polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning). The furfuryl alcohol-modified phenolic resin was obtained from Q.O. Chemicals (Furcarb LP-520, West Lafayette, IN). Zinc chloride was obtained from Aldrich. The semi-bright nickel electroplating bath was purchased from Technic (Cranston, RI), and used as received. TEM grids were obtained from Polysciences, (Warrington, PA). The positive photoresists (Microposit 1075 and 1110) were obtained from Shipley (Malborough, MA). The SU-8 (50) photoresist was purchased from MicroChem (Newton, MA). The silicon wafers were obtained from Silicon Sense (Nashua, NH). Glassy carbon disks ($\sim 13\text{ mm}$ diameter, 2 mm thick) were obtained from Atomergic Chemetals (Farmingdale, NY).

2.2. Procedures

2.2.1. Fabrication of PDMS molds

The PDMS molds were prepared by casting the PDMS mix (ratio 10:1) on photoresist thin films patterned by photolithography. The photoresist thin films were initially passivated by gas phase reaction with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (Hüls Chemicals) in order to facilitate removal of the PDMS once cured. PDMS was cured for 1 h at 60°C in an oven. The photoresist films were patterned by photolithography to give surface relief structures with thickness $10\text{--}150\text{ }\mu\text{m}$. The contact photomasks used in the photolithographic step were prepared by rapid prototyping: a computer file of the design to be transferred to the photoresist was generated using a drawing software (Freehand 7.0) and printed directly on a transparency using a commercial high resolution printer ($> 3300\text{ dpi}$) [24].¹ This transparency was then used as a contact photomask in the photolithographic step. This technique is rapid and inexpensive for making test and prototype structures: it takes less than 24 h from conception of a design to casting of a PDMS mold using a master generated with that design, and costs less than US\$20 per transparency.

2.2.2. Fabrication of glassy carbon microstructures

The substrates used for the preparation of glassy carbon microstructures consisted of silicon wafers coated with a thin film of chromium (400 \AA) prepared by electron beam evaporation. Curing of the furfuryl alcohol-based resin

¹ Economical mask-making procedures using desktop publishing is also described at <http://mems.isi.edu/archives/tools/PSMASK-MAKER/> by Ash Parameswaran, Simon Fraser University, Burnaby, BC, Canada.

required the addition of $\sim 10\%$ (w/w) of a latent, heat-activated catalyst. We used solutions of 50% ZnCl_2 in water. **Caution:** *The addition of an acid catalyst to a furfuryl alcohol resin induces an exothermic reaction. This reaction is violent if strong acids are used.* The surface relief of the mold was carefully impregnated with the polymer precursor. The excess polymer was removed prior to curing. Thick structures were prepared by degassing the polymer and removing excess solvent by placing the molds in an evacuated desiccator for ~ 8 h. The structures were then placed on the chromium-coated (400 \AA) silicon wafer and cured on a calibrated hot plate or in an oven. The temperature was slowly raised from ~ 60 to $\sim 150^\circ\text{C}$ to

prevent mechanical deformation of the structure. Once cured the PDMS mold was removed and the supported structures were carbonized under a positive pressure of argon up to 1100°C . Carbonization was performed in a tube furnace fitted with a quartz tube. The chamber was deoxygenated by a rapid flow of argon for ~ 20 min prior to carbonization.

2.2.3. Electroplating

Electroplating on glassy carbon disks was performed using a commercial nickel electroplating solution. The bottom side of the disk was protected with a piece of tape. Nickel was deposited on the top surface of the disk by

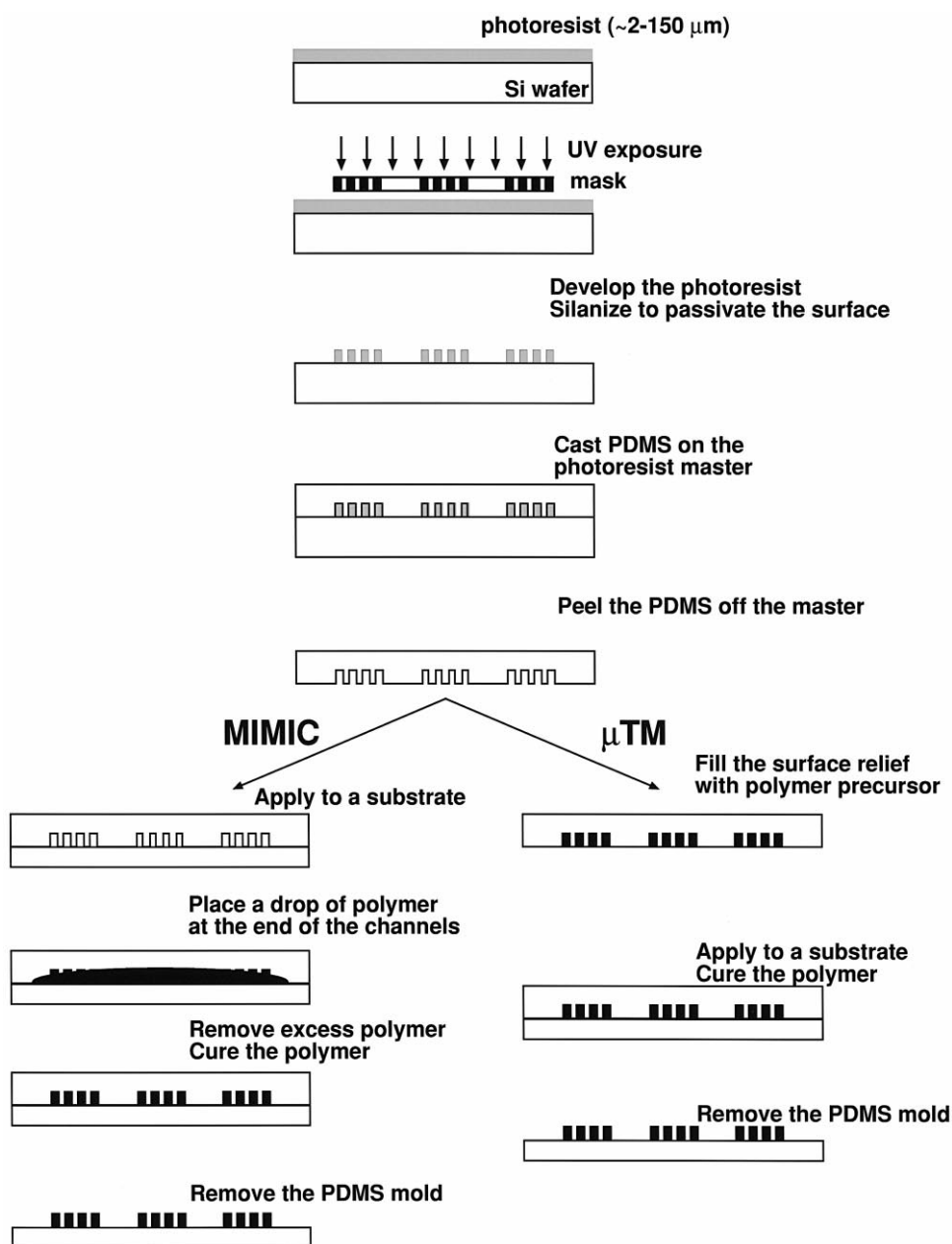


Fig. 1. Schematic description of the preparation of PDMS molds used in MIMIC and μTM , and of their use in molding polymeric microstructures.

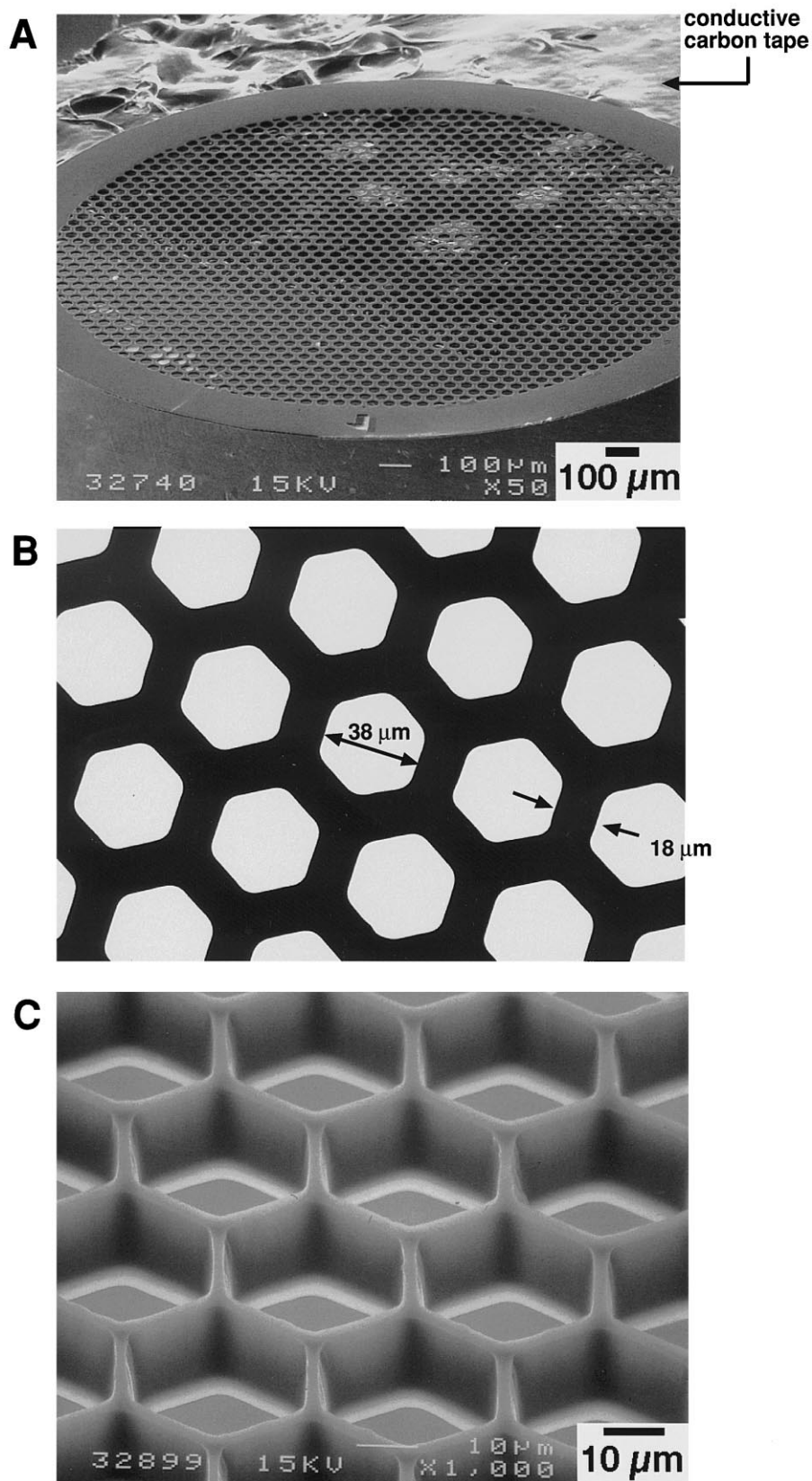


Fig. 2. (A) Scanning electron micrograph of a hexagonal glassy carbon grid (400 mesh). This grid was prepared by μ TM of a polymeric precursor followed by carbonization at 1000°C. A commercial copper TEM grid was used as a mask in the photolithographic patterning of the photoresist to generate the masters on which PDMS molds are cast. (B) Transmission electron micrograph of the glassy carbon grid (400 mesh). (C) Scanning electron micrographs of a high aspect ratio hexagonal glassy carbon grid (600 mesh) prepared by μ TM.

electroplating at a current density of $\sim 15 \text{ mA/cm}^2$ for $\sim 3 \text{ min}$. The photoresist was then dissolved by dipping the disk into acetone and rinsing with ethanol.

2.2.4. Reactive ion etching

The samples were subjected to the O_2 plasma (power = 100 W; pressure of the chamber = 350 mTorr; O_2 flow = 25 sccm) for 10–20 min.

2.3. Instrumentation

Photolithography was performed with a Karl Suss MJB3 UV 400 mask aligner equipped with a mercury lamp (emission peaks at 365, 405, and 436 nm) and operated at 275 W. Scanning electron microscopy was performed on a JEOL JSM-6400 scanning electron microscope operated at 15 keV. The samples were glued on a silicon substrate with either conductive carbon tape or silver paint. Non conductive structures were sputtered with gold using an argon plasma sputter (Hummer II, Technics) for imaging purposes. Reactive ion etching was performed in a Plasma Sciences, RIE-200 W.

3. Results and discussion

3.1. Fabrication procedure and initial characterization of properties

The dimensions of polymeric microstructures fabricated by soft lithography depend on the depth and lateral dimensions of the pattern embossed in PDMS. The lateral dimensions of the microstructures are determined by the resolution of the rapid prototyping technique and photolithographic procedure. Structures with features $> 20 \mu\text{m}$ are routinely fabricated from masks prepared by rapid prototyping. Structures with smaller features are fabricated by using conventional chrome masks with a finer resolution. The thickness of the microstructures is determined by the depth of the pattern in the PDMS mold: that is, the thickness of the patterned photoresist master. We have prepared masters with thicknesses ranging from 2 to 200 μm by photolithography using 350 nm light for exposure. The fabrication procedure is described in Fig. 1. Continuous structures of polymeric precursors to glassy carbon were easily prepared by MIMIC (Fig. 1). In MIMIC, a patterned PDMS mold is placed in contact with a substrate. Conformal contact between the PDMS mold and the substrate results in the formation of microchannels defined by the surface relief structure in the PDMS and the substrate [13,14]. A drop of liquid polymer was then placed at one end of the channels, and the fluid spontaneously filled the channels by capillary action. The polymer was cured by placing the substrate on a hot plate or in a furnace. The temperature of the hot plate or furnace was increased slowly (from ~ 60 to $\sim 150^\circ\text{C}$ over $\sim 1 \text{ h}$) in order to induce the polymer to cross-link [1,2].

Discrete structures were more conveniently prepared by μTM [15]. In μTM , the polymeric precursor was applied to the recessed patterns of the PDMS molds (Fig. 1). The excess polymer was carefully removed by wiping it off, while taking care to prevent trapping of air bubbles in the

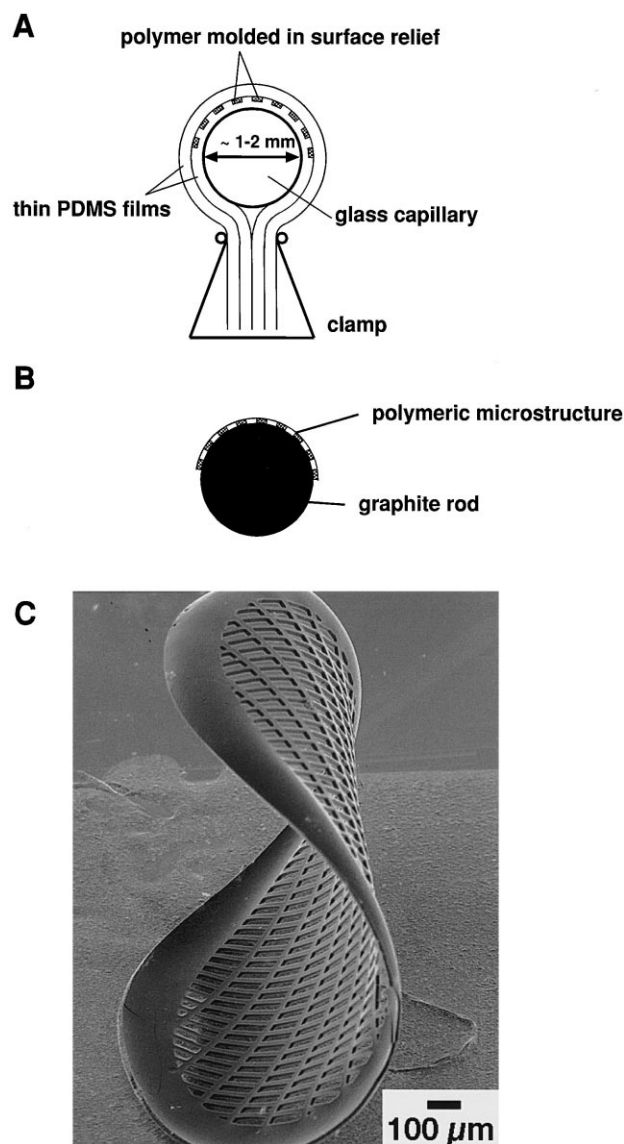


Fig. 3. (A) Schematic diagram illustrating the procedure followed to prepare curved polymeric structures by μTM . A drop of polymer is sandwiched between two thin strips of PDMS deformed against a rounded structure. (B) Once cured, the polymeric structure is carbonized under argon. It is placed on a curved substrate during carbonization to prevent it from collapsing. (C) Scanning electron micrograph of a curved carbon grid prepared by molding a resin of polyfurfuryl alcohol between two thin (~ 0.5 – 1 mm) pieces of PDMS. One of the pieces of PDMS was embossed with the pattern of a grid, while the other piece was smooth. The pieces of PDMS were held together and deformed against a cylinder having a small diameter in order to impart curvature to the mold. The polymer was cross-linked by placing the deformed PDMS mold in a furnace (80 – 150°C). The curved polymeric grid was then gently lifted from the mold and carbonized under argon. The support used during the carbonization process consisted of a graphite cylinder with a radius of curvature similar to that of the polymeric grid.

liquid polymer in the recessed regions of the mold. The mold was placed in contact with the substrate, and the liquid polymer was cured by placing the substrate on a hot plate. In both techniques, the PDMS mold was carefully peeled off of the substrate after completion of the curing step.

The polymeric microstructures prepared by MIMIC or μ TM are subsequently converted to glassy carbon microstructures by thermal treatment in a tube furnace flooded with argon to avoid combustion of the polymeric precursor. We have used a furfuryl alcohol-modified phenolic resin and phenol-formaldehyde resins (Bakelite). It is important to use resins with a high carbon yield (atomic ratio of carbon after/before carbonization ~ 40 – 50%) to limit shrinkage induced by densification and preserve the overall shape of the structure [1–3].

We have previously reported the evolution of the density, weight loss, and linear shrinkage experienced by the solids as a function of heat-treatment temperature [1]. The density increases from 1.29 g/cm^3 for the cured polymer to 1.51 g/cm^3 for a solid generated by pyrolysis at 1000°C . The majority of the weight loss in going from the polymer to glassy carbon ($\sim 45\%$) occurs by $\sim 800^\circ\text{C}$. Shrinkage is steady up to 800°C (up to 20%) and minimal ($< 3\%$) above that temperature. The electrical conductivity

increases sharply at temperatures $> 600^\circ\text{C}$ to reach a plateau (100 S/cm) at $\sim 1000^\circ\text{C}$ [1].

We have also characterized the mechanical properties of some glassy carbon microstructures [2]. We have taken advantage of the electrical conductivity of the glassy carbon solids to actuate cantilevers and suspended microstructures by applying a voltage between these microstructures and a counterelectrode. The measurement of the natural frequency of vibrations (from 1 kHz up to 85 kHz) of cantilevered beams allowed us to determine Young's modulus (10 – 20 GPa) for glassy carbon solids [2], in good agreement with literature values (10 – 40 GPa) [3]. The Q -factor for vibrating glassy carbon cantilevers was estimated to be $Q \sim 10$ – 200 , depending on the thickness of the structures. These low values reflect the contribution of both intrinsic (disordered solid) and extrinsic (air damping) contributions to the dissipation of energy by the vibrating cantilevers.

3.2. Fabrication of microstructures of complex shape or topology

Soft lithographic techniques are amenable to the preparation of micron-sized glassy carbon microstructures, both planar and curved. Diffraction gratings can be incorporated on the surface of glassy carbon either by reactive ion etching or by molding followed by carbonization.

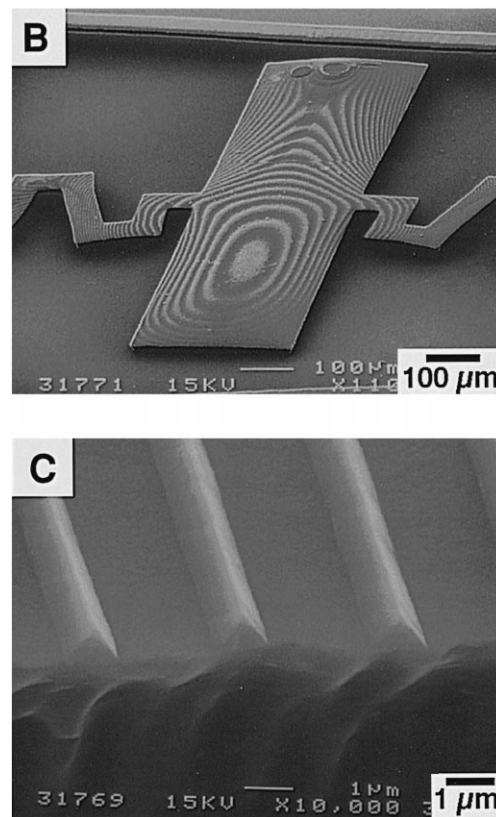
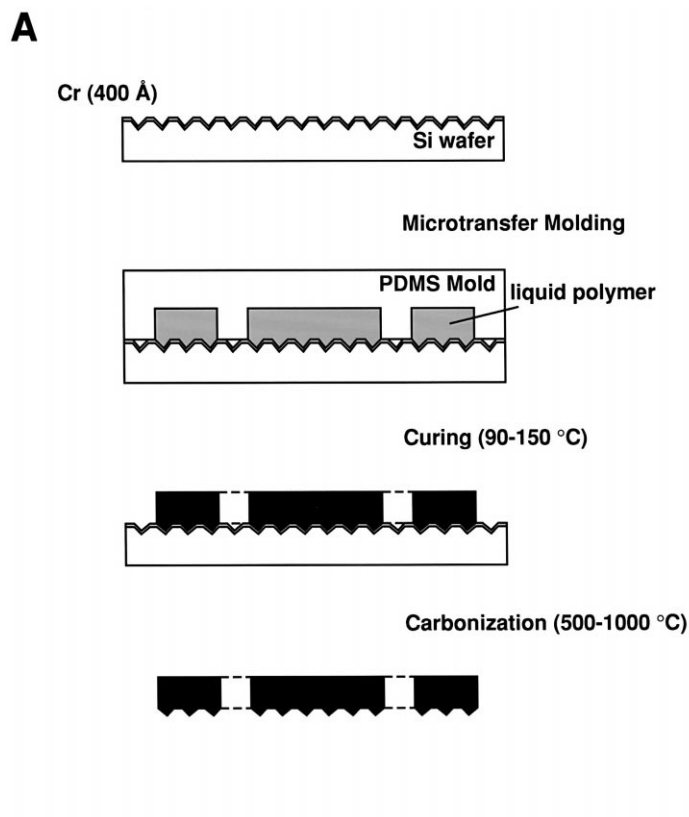


Fig. 4. (A) Schematic describing the preparation of a glassy carbon microstructure with a triangular diffraction grating embossed on its surface. A polymeric precursor was molded by μ TM on a micropatterned silicon substrate. The $2\text{-}\mu\text{m}$ wide troughs in the silicon wafer were generated by anisotropic etching in KOH/water/isopropanol. Chromium was then evaporated on the wafer prior its use as a substrate. (B) Scanning electron micrographs of glassy carbon surfaces with triangular diffraction gratings as surface reliefs. (C) Close-up view of (B).

3.2.1. Fabrication of glassy carbon grids

We have fabricated glassy carbon grids by carbonizing polymeric grids assembled by MIMIC and by μ TM. Grids combine light weight with structural integrity. We have also prepared carbon replicas of metallic transmission electron microscopy (TEM) grids. In that case, commercial TEM grids were used as the mask in the photolithographic step. PDMS molds were prepared by casting PDMS on the patterned photoresist. Glassy carbon grids with a high mesh size (up to 600) were prepared by μ TM followed by carbonization under argon at 1000°C of the polymeric microstructures. Whereas carbon TEM grids with a low mesh size (100 or 200 mesh) are commercially available, we are not aware of carbon grids with a higher mesh size. A high mesh size enables a larger fraction of viewing area while providing mechanical support for samples. Since they are electrically conductive, the glassy carbon grids we

prepared by soft lithography could be used as sample holders in TEM, taking advantage of the resistance of carbon to radiation. Furthermore, since glassy carbon is relatively inert, such grids could be used in the preparation of TEM samples in strongly acidic, basic, or otherwise corrosive environments. Fig. 2A shows a carbon grid with an hexagonal pattern (400 mesh). The diameter of such a grid is ~ 3 mm. Fig. 2B is a low resolution transmission electron micrograph of a carbon grid (400 mesh). The black frame corresponds to the conductive glassy carbon mesh. Fig. 2C is a close-up view of a carbon grid (600 mesh) with high aspect ratio ($\sim 5:1$). The width of the frame is ~ 3 μ m.

3.2.2. Fabrication of curved microstructures

Curved glassy carbon microstructures can be prepared by taking advantage of the elastomeric properties of PDMS.

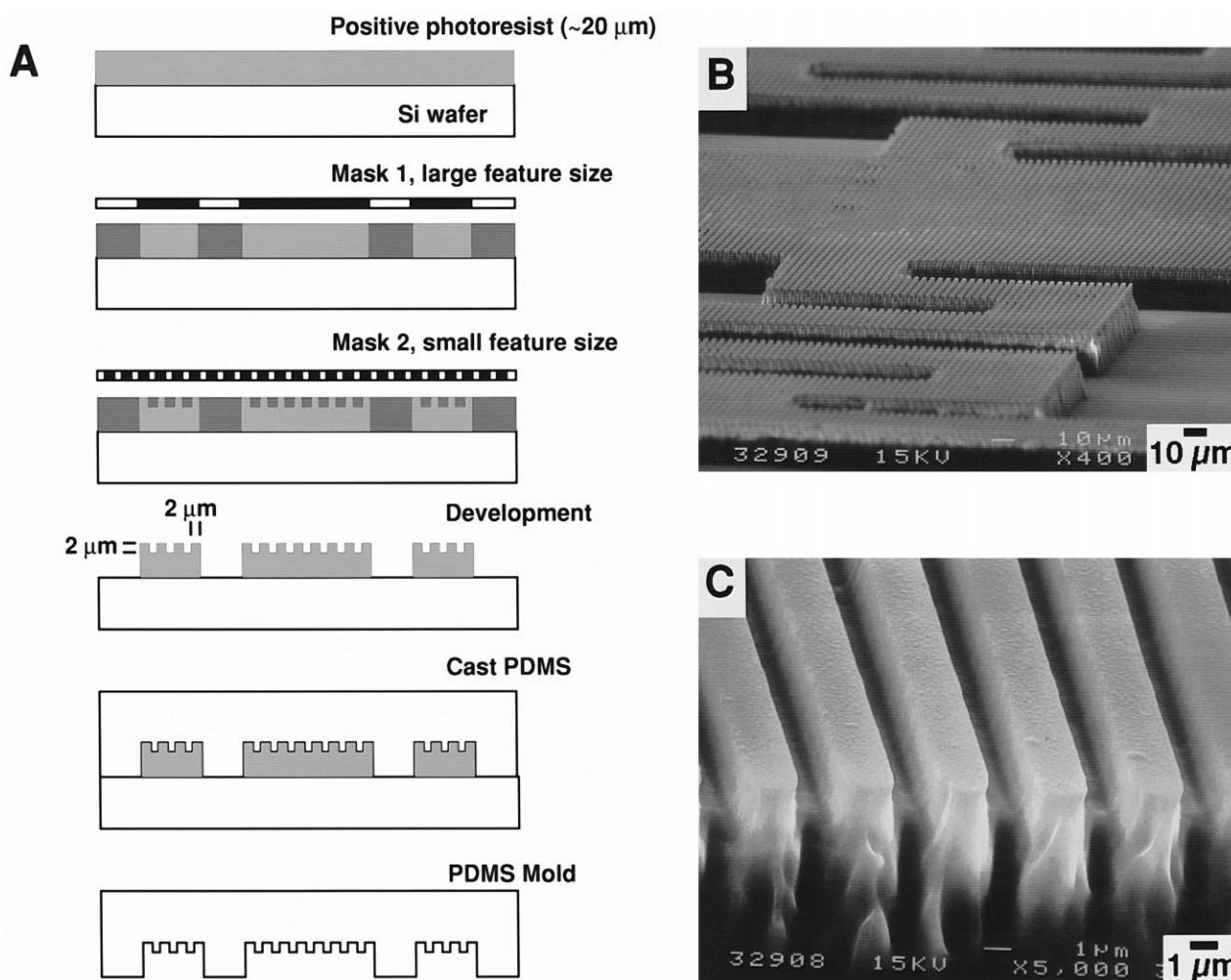


Fig. 5. (A) Schematic diagram describing the preparation of a glassy carbon microstructure with a square diffraction grating surface relief. A 40- μ m thick positive photoresist film was first exposed through a mask to define the outline of the structure. The smallest feature size on that mask was about 50 μ m. A second exposure through a mask with 2- μ m lines was then performed in order to define the grating on top of the photoresist pattern. Development of the exposed film of photoresist yielded a pattern of photoresist with a diffraction grating embossed on its surface. PDMS cast on that pattern of photoresist was used as a mold for the preparation of glassy carbon microstructures. (B) Scanning electron micrograph of a polymeric structure patterned by μ TM using the PDMS molds prepared as described in (A). (C) This close-up view shows the sharp features of the diffraction grating. The polymeric structure was coated with a thin film of gold to prevent charging during imaging.

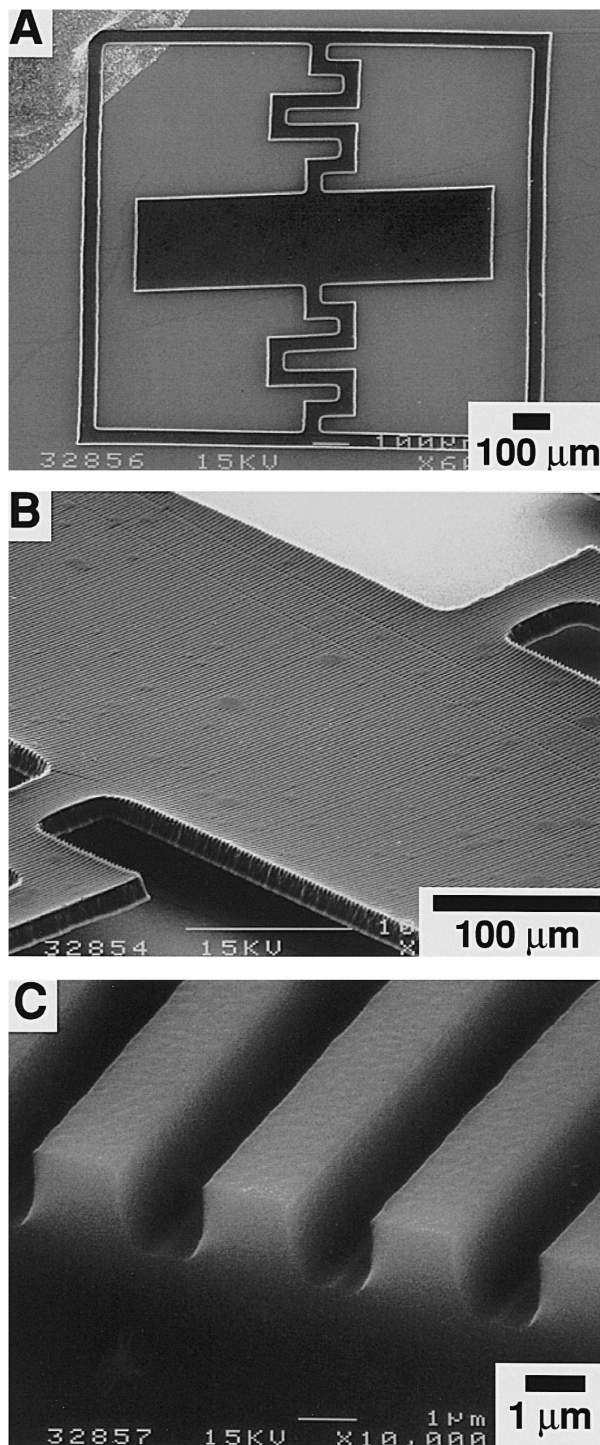


Fig. 6. Scanning electron micrograph of a glassy carbon microstructure prepared by carbonization at 1000°C of the polymeric structure generated by the methodology described in Fig. 5. This micrograph displayed in (A) shows the macroscopic dimensions of the structure, whereas micrographs (B)–(C) obtained at higher magnification show the diffraction grating embossed on the surface of the glassy carbon microstructures.

Fig. 3A–B illustrates the procedure followed to prepare curved microstructures by deformation of a PDMS mold. The deformations imparted by exterior forces on the PDMS mold are apparent on the polymeric structures cross-linked

in the deformed PDMS mold. Subsequent carbonization of these polymeric structures yields curved glassy carbon grids (Fig. 3C). These curved microstructures clearly demonstrate the convenience of the soft lithographic techniques to fabricate non-conventional structures: such structures would be impossible to make out of glassy carbon or silicon using conventional micromachining techniques.

3.2.2.1. Fabrication of diffraction gratings on glassy carbon surfaces. Microstructures incorporating diffraction gratings embossed on their surface can be conveniently prepared using soft lithographic techniques. Polymeric precursors to carbon can be molded against diffraction gratings embossed either in silicon (Fig. 4) or in PDMS (Figs. 5 and 6). Triangular and square gratings can therefore be prepared in one-step procedures. Holographic gratings have also been replicated in glassy carbon using appropriate PDMS molds. Fig. 4A outlines the procedure followed for the preparation of a triangular grating. Anisotropic etching of a silicon wafer yielded a surface with etched troughs.

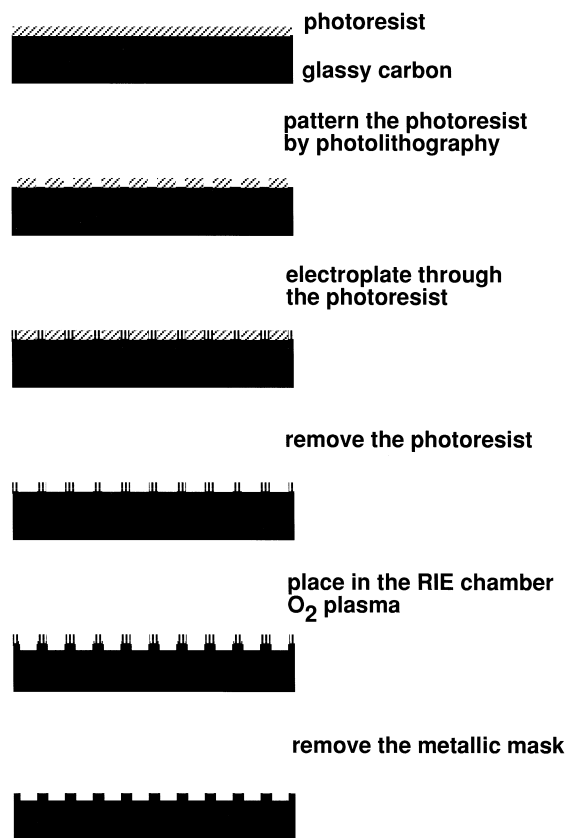


Fig. 7. Schematic diagram describing the procedure used to generate a pattern on a glassy carbon surface by reactive ion etching. A film of photoresist was patterned by photolithography on a glassy carbon surface. Nickel was electroplated through the patterned photoresist, and the photoresist was removed by dissolution in acetone. The nickel pattern defined a metallic mask that protected the underlying surface of glassy carbon during the reactive ion etching procedure. Reactive ion etching was performed with oxygen plasma. The nickel was removed by wet etching in HNO_3 / acetic acid / H_2SO_4 (5/5/2 ml) in water (15 ml).

This surface was coated with a thin film (400 Å) of chromium by electron beam evaporation and used as a substrate for polymeric microstructures prepared by μ TM. Carbonization of these structures yielded glassy carbon

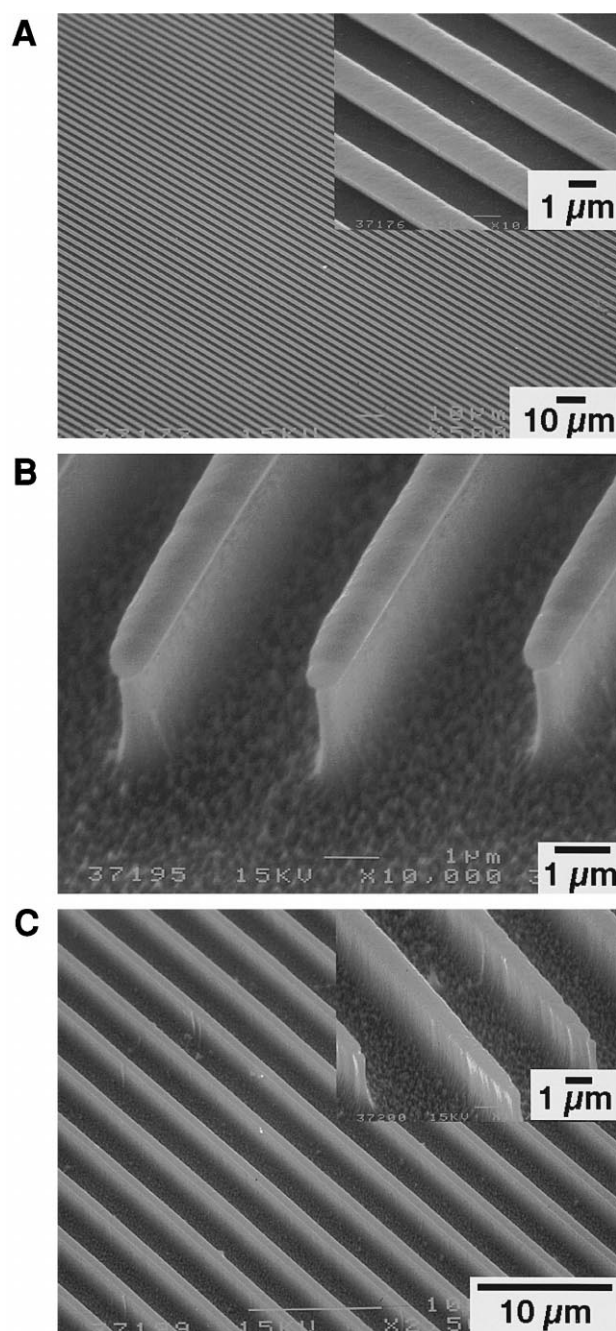


Fig. 8. Scanning electron micrographs of a glassy carbon surface patterned by reactive ion etching. (A) This micrograph shows the pattern of nickel (2- μ m wide lines) used as a mask in the reactive ion etching step. This pattern was electroplated through a photoresist mask; the photoresist was subsequently dissolved in acetone. The inset shows a close-up view of the nickel lines on the surface of glassy carbon. (B) This micrograph shows the glassy carbon surface following etching for 10 min in an O_2 plasma. The top of the lines is still protected by the nickel mask. (C) High aspect ratio walls were prepared by etching the glassy carbon surface for 15 min. The nickel mask was removed by wet etching.

microstructures with triangular diffraction gratings as surface reliefs Fig. 4B–C. Surfaces patterned with square diffraction gratings were prepared according to the procedure outlined in Fig. 5A. The PDMS molds were generated by casting PMDS against photoresist masters embossed with 4- μ m period binary diffraction gratings. The photoresist masters were prepared by successive exposures to UV light of soft-baked photoresist films. A first exposure through a contact photomask prepared by rapid prototyping generated the outline of the structures; a second exposure through a chrome mask patterned in parallel lines generated the micron-sized features on top of the photoresist thin films. The exposed photoresist films were then developed and passivated to yield the masters on which PDMS molds were cast. Fig. 5B–C shows micrographs of cured polymeric structures generated by μ TM of the furfuryl alcohol-based resin using these PDMS molds. Fig. 6 shows the same structure after carbonization at 1000°C. The close-up views demonstrate the resolution of the diffraction gratings, and validate the use of soft lithographic techniques for the fabrication of surfaces patterned with micron-sized features.

3.2.2.2. Patterning by reactive ion etching. More conventional microfabrication techniques can also be applied to glassy carbon surfaces. Fig. 7 outlines the procedure followed to pattern a glassy carbon surface by RIE. A metallic mask was first electroplated on the glassy carbon through a film of photoresist patterned by photolithography (2 μ m lines spaced by 2 μ m). The photoresist was removed by dissolution. The mask protected the underlying carbon surface from oxidation while in the oxygen plasma. The mask could then be easily removed by wet etching in acidic medium. Fig. 8 shows a glassy carbon disk at various stages of the fabrication process. Fig. 8A shows the surface covered with an array of nickel lines. This metallic pattern acts as a mask during etching. Fig. 8B shows the surface after etching for 20 min in O_2 plasma. The nickel mask is still present on top of the lines. Fig. 8C shows the surface after removal of the nickel pattern by wet etching in acidic solution (HNO_3 /acetic acid/ H_2SO_4 (5/5/2 ml) in water (15 ml)). The glassy carbon surface is patterned with thin vertical walls with an aspect ratio of $\sim 2.5:1$. The etching of glassy carbon by O_2 plasma appears to be isotropic: the lateral dimension of the walls diminishes with increasing etching time. This experiment demonstrates that reactive ion etching can be used to create complex patterns with high aspect ratio on the surface of glassy carbon.

3.2.3. Fabrication of high aspect ratio structures and large area structures

We have prepared arrays of interdigitated electrodes or capacitors by μ TM of polymeric precursors to carbon followed by carbonization at 1000°C. Fig. 9 shows SEMs of high aspect ratio structures prepared by μ TM using a

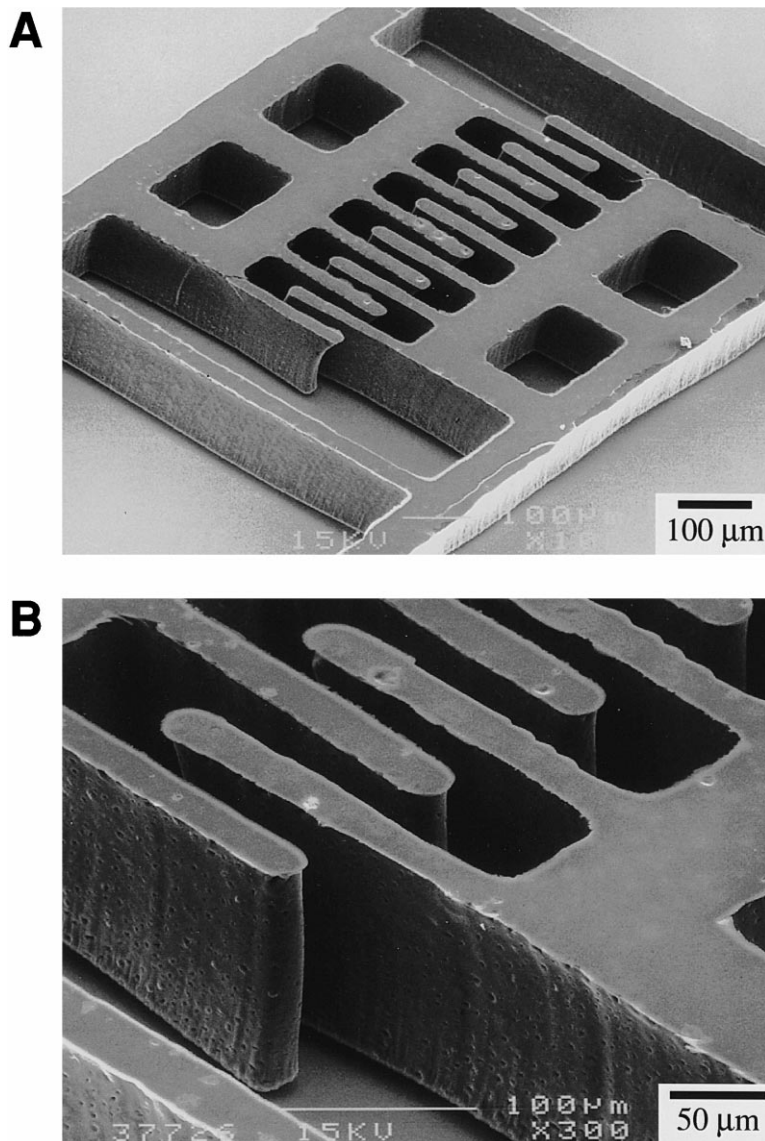


Fig. 9. Scanning electron micrographs of a high aspect ratio glassy carbon microstructure prepared by μ TM. The PDMS molds used in the preparation of these structures had been prepared by casting on ultrathick photoresist. (A) Interdigitated comb structure. (B) Close-up view of (A). The thickness of the structure is $\sim 100 \mu\text{m}$; the width of the beams is $\sim 30 \mu\text{m}$. These micrographs show that the structures tend to shrink slightly during carbonization as a result of densification due to mass loss. Shrinkage induces distortion of the structures, as seen by the slightly bowed walls of the structures.

PDMS mold cast on thick photoresist. Fig. 10 shows SEMs of a large area glassy carbon structure fabricated by carbonization at 1000°C of a polymeric structure molded in PDMS. We have previously described high aspect ratio carbon microstructures prepared by molding a polymeric precursor against a patterned film of shrinkable polystyrene [25]. Heating induces shrinkage of the polystyrene film and cross-linking of the polymeric precursor.

3.3. Microfabrication issues

We have developed a convenient method for the preparation of complex microstructures of glassy carbon. The physical and chemical properties of glassy carbon, while attractive for specific applications under harsh environ-

ments, also preclude use of conventional microfabrication techniques used in silicon micromachining. Glassy carbon is inert under a wide range of conditions, and cannot be microfabricated by wet etching techniques. Glassy carbon is also very brittle, and cannot be easily micromachined into high aspect ratio microstructures (such as the hexagonal grid shown in Fig. 2C) by mechanical means. Our approach to microfabrication of glassy carbon, based on the availability of PDMS molds, circumvents these problems and allows the fabrication of microstructures of large area and/or high aspect ratio in a few hours. Polymeric microstructures generated by molding using PDMS molds are converted to high carbon solids by carbonization under inert atmosphere. Since this approach is based on the conversion of polymeric structures to carbon structures by

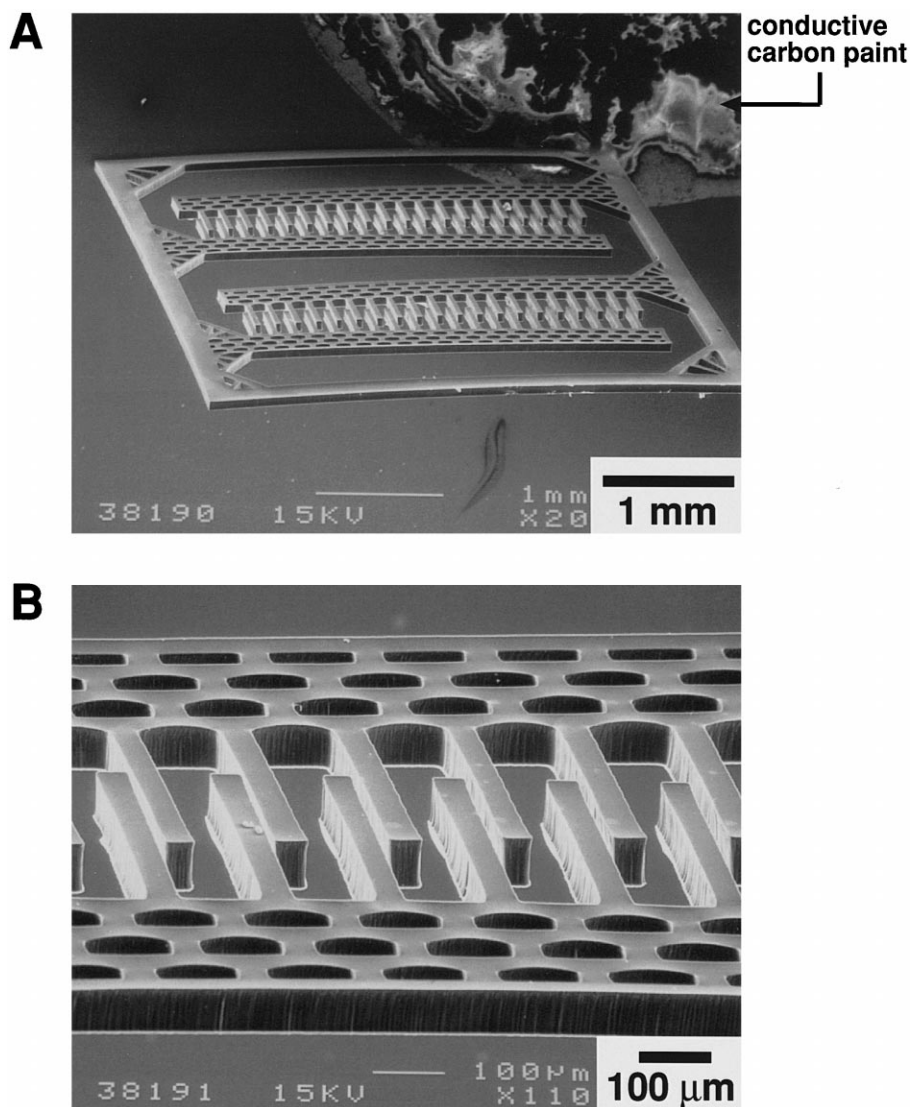


Fig. 10. Scanning electron micrographs of a macroscopic glassy carbon structure with microscopic features prepared by μ TM of a polymeric precursor followed by carbonization at 1000°C. This interdigitated comb electrode was prepared in a single-step procedure without photolithography (beyond that used to prepare the master).

a high temperature process, it is of paramount importance that the shape of the structure be retained during the carbonization step. The elimination of heteroatoms during carbonization induces densification of the structure, which results in shrinkage. Shrinkage combined with residual stress within the polymeric microstructure induce deformation of the microstructures by buckling. Buckling arises as a result of anisotropic shrinkage of the material during carbonization. During curing and in the early stage of carbonization, the polymeric structure is supported on a substrate. Differential shrinkage from the top (unsupported) and the bottom (supported) of the structure results in distortion of the structure.

We have tried to limit the extent of shrinkage and buckling by careful control of the experimental procedures. Polymers with a high carbon content such as furfuryl alcohol-modified phenolic resins and phenol-formaldehyde

resins (Bakelite) are used to minimize shrinkage due to mass loss. Polymers with a high content of carbon (preferably sp^2 or sp hybridized carbon) and a low content of heteroatoms (hydrogen, nitrogen, oxygen, halogens, etc.) are potential candidates for this preparation of microstructures of high-carbon solid. H-resins, with a phenylene diacetylene repeat unit, have a very high carbon yield (> 90%) and could be used as precursors for glassy carbon microstructures if soluble in solvents compatible with PDMS [26].

We use chromium-coated wafers as substrates for the molding of the polymeric resin into microstructures and their subsequent carbonization. Substrates such as Si/SiO₂, glass, quartz, commercial glassy carbon, and films of silver, gold, or nickel induced cracking in the microstructures, whereas chromium-coated wafers yielded intact carbon microstructures. The carbon structures released spon-

taneously from chromium-coated substrates during the carbonization. This observation indicates that the adhesion between the chromium-coated substrates and the polymeric resin (or the developing carbon solid) is weaker than that involving other substrates. Weaker adhesion effectively prevents cracking and limits the extent of buckling.

The polymeric resin, once applied to the PDMS mold, is degassed for several hours (~ 6 – 8 h) prior to transfer to a substrate and cross-linking. This procedure removes excess solvent and increases the concentration of polymers in the mold, thereby limiting shrinkage of the structure due to mass loss. The PDMS mold is then applied to a substrate, and kept at room temperature for 12 h prior curing. We believe that residual stress may decrease with the longer molding procedure. We have used a hot plate or a furnace to induce thermal cross-linking of the resin. On a hot plate, the heat is distributed to the sample from the

bottom, whereas a furnace provides a distributed heat source. We recommend the use of a furnace for the preparation of high aspect ratio microstructures and thick ($> 50 \mu\text{m}$) microstructures: the polymeric resin does not flow out of the mold, and buckling appears to be minimized, when using a furnace. We also recommend slow heating during curing and carbonization in order to minimize the accumulation of stress and cracking.

3.4. Prototyping components

In order to make devices, the free-standing glassy carbon microstructures need to be affixed in a reproducible fashion to a surface, and electrically connected. Fig. 11A outlines the strategy used to integrate a carbon microstructure to the surface of a silver-coated silicon wafer. A thin film of positive photoresist acted as glue to immobilize a

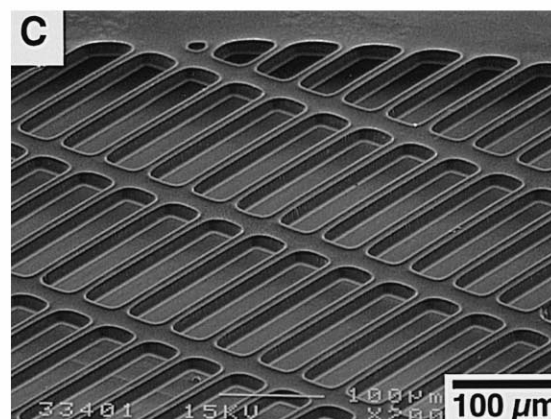
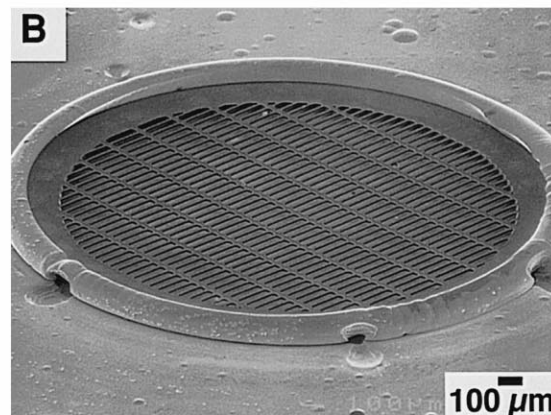
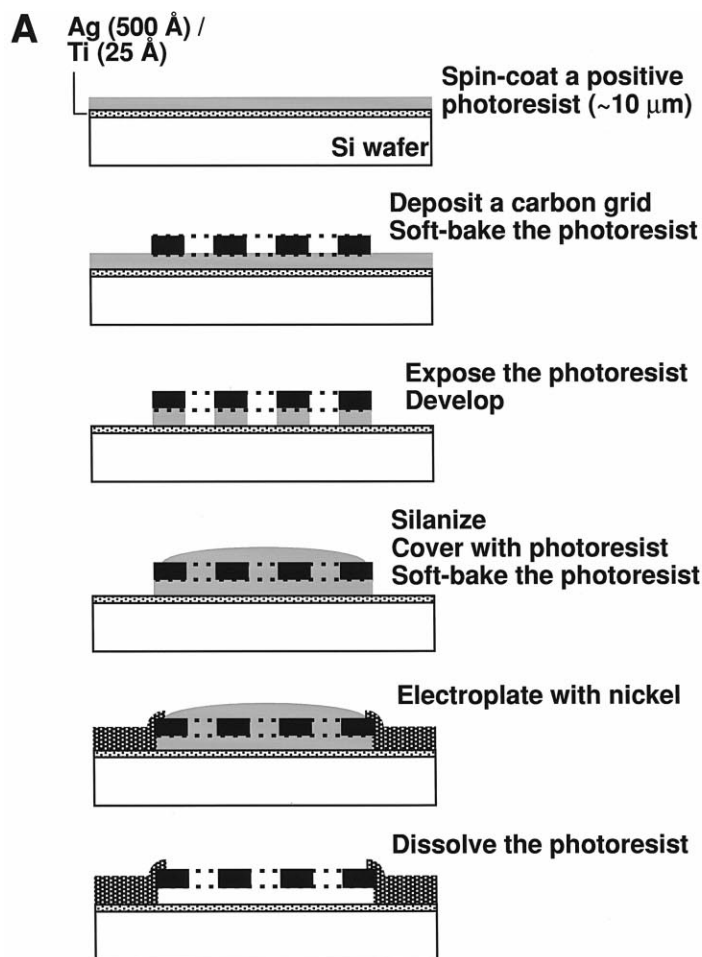


Fig. 11. (A) Schematic diagram describing the integration of a carbon grid to a substrate. A silver-coated silicon was used as the substrate. A $\sim 10\text{-}\mu\text{m}$ thick film of positive photoresist was spin-coated on the wafer. A glassy carbon grid was placed on the photoresist film which was subsequently soft-baked on a hot plate. The soft-baked photoresist acted as a glue and the grid was stuck to the surface of the wafer. Exposure of the photoresist followed by development removed most of the photoresist, with the glassy carbon grid acting as a mask. The underlying silver film now exposed could be used as the (anode/cathode) in the electroplating of nickel. The grid was covered with a drop of photoresist in order to prevent it from plating during the electrodeposition step. Plating generated an even thin film of nickel that engulfed the carbon grid once it reached it. The photoresist was dissolved in acetone to give a suspended glassy carbon grid $\sim 10 \mu\text{m}$ apart from the substrate. (B) Scanning electron micrograph of a carbon grid integrated onto a surface using the methodology described in (A). (C) Close-up view of (B). The underlying wafer is visible through the carbon grid.

glassy carbon grid to the wafer. The grid acted as a mask in the photolithographic step, and the exposed positive photoresist (not shielded by the grid) was removed following exposure and development. After development, the glassy carbon grid was simply supported by a thin layer of patterned photoresist. The grid was then irreversibly affixed to the surface by electrochemical deposition of a film of nickel. Since glassy carbon is conductive, the grid has to be electrically isolated from the underlying (cathode) in order to prevent deposition of the metal on the grid itself: once the thickness of the nickel film is comparable to that of the supporting photoresist layer, contact between the nickel film and the grid will induce plating of the grid. The shielding of the grid was accomplished by covering it with a drop of photoresist. After completion of the electroplating step, the photoresist was dissolved in acetone. The micrographs in Fig. 11B–C show that the grid is rigidly held by a nickel film. The edges of the nickel deposit around the grid have outgrown the grid to form a circular ‘lip’. The grid is not in contact with the underlying surface of the wafer. This strategy should prove useful in the integration of glassy carbon microstructures on surfaces, and interconnection of these structures with external electrical circuitry.

Other strategies can potentially enable the integration of glassy carbon microstructures to devices. Glassy carbon microelectrodes have been fabricated by embedding glassy carbon fibers in glass capillaries [27]. The development of composites based on carbon fibers has required tailoring of the surface properties of the carbon fibers for enhanced adhesion with the binder [28–31]. The adhesion between carbon solids and polymers, glasses, ceramics, or metals may provide a route toward integration of glassy carbon microstructures to functional devices [32]. A better approach would be one that limits the manipulation of the glassy carbon microstructure: heat-treatment of the microstructure ‘on-site’, in the early stages of microfabrication of a device, would facilitate integration of glassy carbon microstructures to devices and potentially enable the development of glassy carbon MEMS based on existing processes.

3.5. Potential applications of glassy carbon in microfabrication

Carbon solids are used in applications taking advantage of their extremely high thermal resistance and good thermal conductivity [33]. Carbon solids have been used in applications requiring stability to high operating temperatures and rapid temperature changes such as friction-induced heating (e.g., nose cones and leading edges of glider-type reentry vehicles or ballistic devices, linings of blast tubes). Other applications of carbon solids include nuclear moderators, heat exchangers, electrodes in electric arc furnaces used in the production of steel, alloys, and ceramics, and as refractory linings in metallurgical furnaces [33].

The chemical inertness of glassy carbon has prompted its use in analytical chemistry. Vessels fabricated out of glassy carbon are used as crucibles in the decomposition of ores under acidic or caustic environments. Glassy carbon containers are also used in the epitaxial growth of silicon crystals [33]. Carbon solids have been widely used as an electrode material for analytical and electrochemical applications [34–42]. Glassy carbon is inert over a wide range of electrical potentials [32,43]. Tailoring of the interfacial properties (electron transfer rate, surface energy, selectivity) of glassy carbon electrodes is achieved by surface chemistry [43]. Chemisorption and physisorption of enzymes, recognition elements, polymers, or metallic clusters can be accomplished by procedures including electrochemical pretreatment, polishing, or laser activation [44]. Examples of electrochemical biosensors derived from glassy carbon include glucose and lactate biosensors [23]. Electrochemical sensing of biologically important compounds has also been performed in vivo using modified carbon electrodes [23,45].

The properties of glassy carbon are complementary to those of silicon. Since glassy carbon is structurally isotropic, its physical properties do not depend on crystalline orientation. It is electrically conductive (1–100 S/cm) and does not require extraneous doping procedures. Its conductivity can be controlled over this range by the conditions of preparation. Glassy carbon has a lower mass density (1.4–1.5 g/cm³) than silicon (2.33 g/cm³), although the atom densities (C: 7.5×10^{22} atom/cm³; Si: 5×10^{22} atom/cm³) are similar.² Carbon and silicon also have different reactivities. Carbon is obviously less stable than silicon towards oxidation by gaseous oxygen. However, carbon is stable in strong bases, unlike silicon. The thermal stability of glassy carbon depends on its temperature of preparation: glassy carbon prepared at 3000°C is stable in air at temperatures as high as 500°C. Carbon is stable in a non-oxidizing environment at temperatures as high as its temperature of preparation. Carbon has no defined melting point ($T_{\text{mp}} > 3500^\circ\text{C}$) while that of silicon is comparatively low ($T_{\text{mp}} = 1410^\circ\text{C}$). The lower Young’s modulus of glassy carbon (10–40 GPa) compared to that of silicon (190 GPa for monocrystalline silicon, 40–170 GPa for polysilicon) can be an advantage in applications where the stiffness of silicon is a limiting factor: electrostatically driven glassy carbon structures will require lower voltage to induce deflection than counterparts in silicon.

The physical and chemical properties of carbon solids in general and glassy carbon in particular suggest that glassy carbon is a potential candidate as a structural solid for functional components of sensors or actuators operated under extreme conditions such as elevated temperatures and corrosive environments.

² The atom densities were calculated from the densities and atomic weights of silicon and glassy carbon.

4. Conclusions

We have demonstrated a new approach for the fabrication of glassy carbon microstructures. This approach is fundamentally different from the conventional microfabrication techniques developed for the elaboration of silicon microstructures. Complex surface topologies such as diffraction gratings or curved structures can be prepared in a single step molding procedure followed by carbonization. The conductivity of glassy carbon allows further elaboration of microstructures by electroplating followed reactive ion etching. The chemical, physical, and biological properties of glassy carbon make it a potential candidate for use of these microstructures in applications where resistance to high temperatures, corrosive environments, or biocompatibility are needed. Protection of glassy carbon against oxidation would increase the range of conditions under which devices fabricated out of glassy carbon can be used [46–48].

Tailoring of the surface properties of glassy carbon may enable the development of specific sensors and biosensors for microanalytical applications. The surface properties of glassy carbon can be modified by a wide range of techniques, including conventional organic chemistry, electrochemical pretreatments, mechanical polishing, or irradiation. The microfabrication of glassy carbon will allow the development of devices taking full advantage of its chemical, physical, and electrical properties.

Acknowledgements

This work was supported in part by the Office of Naval Research and the Defense Advanced Research Project Agency. It used MRSEC Shared Facilities supported by the National Science Foundation (DMR-9400396).

References

- [1] O.J.A. Schueller, S.T. Brittain, G.M. Whitesides, Fabrication of glassy carbon microstructures by pyrolysis of microfabricated polymeric precursors, *Adv. Mater.* 9 (1997) 477–480.
- [2] O.J.A. Schueller, S.T. Brittain, C. Marzolin, G.M. Whitesides, Fabrication and characterization of glassy carbon MEMS, *Chem. Mater.* 9 (1997) 1399–1406.
- [3] G.M. Jenkins, K. Kawamura, Polymeric carbons—carbon fibre, glass and char, Cambridge Univ. Press, Cambridge, 1976.
- [4] G.T.A. Kovacs, *Micromachined Transducers Sourcebook*, WCB/McGraw-Hill, New York, 1998.
- [5] M. Madou, *Fundamentals of Microfabrication*, CRC Press, Boca Raton, FL, 1997.
- [6] G.T.A. Kovacs, K. Petersen, M. Albin, Silicon micromachining, Sensors to systems, *Anal. Chem.* (1996) 407A.
- [7] Y. Xia, G.M. Whitesides, Soft lithography, *Annu. Rev. Mater. Sci.* (1998) in press.
- [8] X.-M. Zhao, X. Younan, G.M. Whitesides, Soft lithographic methods for nanofabrication, *J. Mater. Chem.* 7 (1997) 1069–1074.
- [9] A. Kumar, H.A. Biebuyck, G.M. Whitesides, Patterning self-assembled monolayers: applications in material science, *Langmuir* 10 (1994) 1498–1511.
- [10] Y. Xia, M. Mrksich, E. Kim, G.M. Whitesides, Microcontact printing of octadecylsiloxane on the surface of silicon dioxide, and its application in microfabrication, *J. Am. Chem. Soc.* 117 (1995) 9576–9577.
- [11] Y. Xia, E. Kim, M. Mrksich, G.M. Whitesides, Microcontact printing of alkanethiols on copper and its application in microfabrication, *Chem. Mater.* 8 (1996) 601–603.
- [12] Y. Xia, G.M. Whitesides, Extending microcontact printing as a microlithographic technique, *Langmuir* 13 (1997) 2059–2067.
- [13] E. Kim, Y. Xia, G.M. Whitesides, Micromolding in capillaries: applications in materials science, *J. Am. Chem. Soc.* 118 (1996) 5722–5731.
- [14] E. Kim, Y. Xia, G.M. Whitesides, Polymer microstructures formed by moulding in capillaries, *Nature* 376 (1995) 581–584.
- [15] X.-M. Zhao, Y. Xia, G.M. Whitesides, Fabrication of three-dimensional micro-structures: microtransfer molding, *Adv. Mater.* 8 (1996) 837–840.
- [16] Y. Xia, J.J. McClelland, R. Gupta, D. Qin, X.-M. Zhao, L.L. Sohn, R.J. Celotta, G.M. Whitesides, Replica molding using polymeric materials: a practical step toward nanomanufacturing, *Adv. Mater.* 9 (1997) 147–149.
- [17] Y. Xia, E. Kim, X.-M. Zhao, J.A. Rogers, M. Prentiss, G.M. Whitesides, Complex optical surfaces by replica molding against elastomeric masters, *Science* 273 (1996) 344–350.
- [18] D. Qin, Y. Xia, J.A. Rogers, R.J. Jackman, X.-M. Zhao, G.M. Whitesides, Microfabrication, microstructures and microsystems, in: A. Manz, H. Becker (Eds.), *Topics in Current Chemistry: Microsystem Technology in Chemistry and Life Sciences*, Vol. 194, Springer-Verlag, Berlin, 1998, pp. 1–20.
- [19] E. Fitzer, K. Mueller, W. Schaefer, The chemistry of the pyrolytic conversion of organic compounds to carbon, in: P.L. Walker Jr. (Ed.), *Chemistry and Physics of Carbon*, Vol. 7, Marcel Dekker, New York, 1971, pp. 237.
- [20] I.L. Spain, Electronic transport properties of graphite, carbons, and related materials, in: P.L. Walker Jr., P.A. Thrower (Eds.), *Chemistry and Physics of Carbon*, Chap. 2, Vol. 16, Marcel Dekker, New York, 1981, pp. 119–304.
- [21] S. Yamada, H. Sato, Some physical properties of glassy carbon, *Nature* 193 (1962) 261–262.
- [22] H.W. Davidson, *Brit. Pat.* 860,342, 1962.
- [23] K. Kinoshita, *Carbon, Electrochemical and Physicochemical Properties*, Wiley-Interscience, New York, 1988.
- [24] D. Qin, Y. Xia, G.M. Whitesides, Rapid prototyping of complex structures with feature sizes larger than 20 μm , *Adv. Mater.* 8 (1996) 917–919.
- [25] X.-M. Zhao, Y. Xia, O. Schueller, D. Qin, G.M. Whitesides, Fabrication of microstructures using shrinkable polystyrene films, *Sensors and Actuators A: Physical* 65 (1998) 209–217.
- [26] T.X. Neenan, G.M. Whitesides, The synthesis of high carbon materials from acetylenic precursors. Preparation of aromatic monomers bearing multiple ethynyl groups, *J. Org. Chem.* 53 (1988) 2489–2496.
- [27] A. Schulte, R.H. Chow, Cylindrically etched carbon-fiber microelectrodes for low-noise amperometric recording of cellular secretion, *Anal. Chem.* 70 (1998) 985–990.
- [28] H.T. Oyama, J.P. Wightman, Surface characterization of PVP-sized and oxygen plasma-treated carbon fibers, *Surface and Interface Analysis* 26 (1998) 39–55.
- [29] C.U. Pittman, W. Jiang, G.R. He, S.D. Gardner, Oxygen plasma and isobutylene plasma treatments of carbon fibers—determination of surface functionality and effects on composite properties, *Carbon* 36 (1998) 25–37.
- [30] H. Zhuang, J. Wightman, The influence of surface properties on carbon fiber/epoxy matrix interfacial adhesion, *Journal of Adhesion* 62 (1997) 213–245.

- [31] E. Hage, S.F. Costa, L.A. Pessan, Modification of the carbon fiber surface with a copper coating for composite materials with epoxy, *Journal of Adhesion Science and Technology* 11 (1997) 1491–1499.
- [32] W.E. Van der Linden, J.W. Dieker, Glassy carbon as electrode material in electroanalytical chemistry, *Anal. Chim. Acta* 119 (1980) 1–24.
- [33] J.I. Kroschwitz, M. Howe-Grant (Eds.), *Kirk–Othmer Encyclopedia of Chemical Technology*, Wiley, New York, 1991.
- [34] O. Ikeda, M. Ohtani, T. Yamaguchi, A. Komura, Direct electrochemistry of cytochrome C at a glassy carbon electrode covered with a microporous alumina membrane, *Electrochim. Acta* 43 (1998) 833–839.
- [35] T. Mafatle, T. Nyokong, Use of cobalt(II) phthalocyanine to improve the sensitivity and stability of glassy carbon electrodes for the detection of cresols, chlorophenols and phenol, *Anal. Chim. Acta* 354 (1997) 307–314.
- [36] X. Chu, K. Kinoshita, Surface modification of carbons for enhanced electrochemical activity, *Materials Science and Engineering B: Solid State Materials for Advanced Technology* 49 (1997) 53–60.
- [37] D.C. Coomber, D.J. Tucker, A.M. Bond, Electrochemical reduction of pyrethroid insecticides based on esters of alpha-cyano-3-phenoxybenzyl alcohol at glassy carbon and mercury electrodes in acetonitrile, *J. of Electroanal. Chem.* 430 (1997) 215–225.
- [38] I.G. Casella, M.R. Guascito, Electrocatalysis of ascorbic acid ion the glassy carbon electrode chemically modified with polyaniline films, *Electroanalysis* 9 (1997) 1381–1386.
- [39] A.M.O. Brett, S.H.P. Serrano, I. Gutz, M.A. Lascalea, M.L. Cruz, Voltammetric behavior of nitroimidazoles at a DNA-biosensor, *Electroanalysis* 9 (1997) 1132–1137.
- [40] I.C. Popescu, S. Cosnier, P. Labbe, Peroxidase-glucose oxidase-poly(amphiphilic pyrrole) bioelectrode for selectively mediated amperometric detection of glucose, *Electroanalysis* 9 (1997) 998–1004.
- [41] Z. Senturk, S.A. Ozkan, Y. Ozkan, Electroanalytical study of nifedipine using activated glassy carbon electrode, *J. Pharm. Biomed. Anal.* 16 (1998) 801–807.
- [42] S. Tombelli, M. Mascini, Electrochemical biosensors for biogenic amines—a comparison between different approaches, *Anal. Chim. Acta* 358 (1998) 277–284.
- [43] R.L. McCreery, Carbon electrodes: structural effects on electron transfer kinetics, in: A.J. Bard (Ed.), *Electroanalytical Chemistry*, Vol. 17, Marcel Dekker, New York, 1991, pp. 221.
- [44] N.L. Pocard, D.C. Alsmeyer, R.L. McCreery, T.X. Neenan, M.R. Callstrom, Doped glassy carbon: a new material for electrocatalysis, *J. Mater. Chem.* 2 (1992) 771–784.
- [45] A. Dittmar, S. Mangin, C. Ruban, W.H. Newman, H.F. Bowman, V. Dupuis, G. Delhomme, N.F. Shram, R. Cespuaglio, N. Jaffrezicre-nault, P. Roussel, D. Barbier, C. Martelet, In vivo and in vitro evaluation of specially designed gold and carbon fiber oxygen microelectrodes for living tissues, *Sensors and Actuators B: Chemical* 44 (1997) 316–320.
- [46] J.M. Criscione, H.F. Volk, A.W. Smith, Protection of graphite from oxidation at 2100°C, *AIAA Journal* 4 (1966) 1791–1797.
- [47] D. Cho, B.I. Yoon, H.S. Ha, L. Y.S., Microscopic behavior on the protection of polyacrylonitrile-based carbon fibers from thermal oxidation, *Polym. J.* 29 (1997) 959–963.
- [48] T. Durkic, A. Peric, M. Lausevic, A. Dekanski, O. Neskovic, M. Veljkovic, Z. Lausevic, Boron and phosphorus doped glassy carbon: I. Surface properties, *Carbon* 35 (1997) 1567–1572.