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Microfabrication of freestanding metal structures using graphite substrate☆

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Abstract

A novel method of fabricating freestanding electroformed metal structures using a rigid porous graphite substrate is reported. Polymethylmethacrylate's adhesion to graphite is much stronger compared with metal-coated silicon or graphite, because of graphite's high porosity and microroughness. Another advantage of graphite is its easy sacrificial removal by abrasion. Results are presented on the fabrication of high-aspect-ratio freestanding copper grids used as collimators in mammography and medical imaging. The method can be used in the production of micromolds for hot embossing and injection mold fabrication of microelectromechanical systems (MEMSs) and for fabrication of arrays of microparts on pick-and-place carriers for assembly into MEMS.
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Keywords: Graphite substrate; LIGA; MEMS; Microstructure release; High-aspect-ratio; Antiscatter grid

1. Introduction

The fabrication of high-aspect-ratio microstructures (HARMSs) using deep X-ray lithography (DXRL) and electroforming requires that the substrate provide good resist adhesion before and after exposure, that the substrate has a conductivity sufficient for the subsequent electroforming process, and that the metal structure can be released from the substrate after electroforming. Metal-coated silicon wafers are conventionally used as a primary substrate. The high conductivity of the metal layer makes the wafer suitable as an electroplating base, but the secondary radiation generated by the metals during the hard X-ray exposure can lead to adhesion failure [1]. Adhesion buffer layers have been used to reduce adhesion failure [2], but they complicate processing and can be difficult to remove especially for HARMS. Incomplete removal of the adhesion layer leads to the formation of voids and other defects in the metal structure during electroforming. Freestanding metal microstructures have traditionally been fabricated using a sacrificial layer, which is then released from the microstructures by chemical etching. Only a few metals are compatible with this sacrificial process, thus limiting the number of metals suitable for electroforming. For example, fabrication of a freestanding copper microstructure is difficult, because the wet etch that removes the release layer may also attack the copper.

Thin conductive carbon films have been used with some success as a plating base [3]. Rigid graphite has been used as a substrate for the fabrication of masks for DXRL [4], although generally with a plating base prepared by precision resurfacing and metal coating.

The properties of graphite, such as rigidity, low cost, and good thermal and electrical conductivity, suggest the uncoated graphite would be a suitable substrate and plating base for fabrication of HARMS using DXRL and electroforming. In this paper, we describe a new fabrication method of freestanding or released metal microstructures based on the use of commercially available rigid graphite sheets as a substrate. Also we discussed the potential application for microelectromechanical systems (MEMSs) of both injection molds and microparts on pick-and-place carriers.

2. Experimental

Commercially available rigid graphite sheets (Goodfellow), ranging in thickness from 0.25 to 1 mm, were used as

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Table 1
Properties of rigid graphite (from Goodfellow)

Average apparent density (g/cm^3)	1.8
Compressive strength (MPa)	151
Flexural strength (MPa)	92
Tensile strength (MPa)	70
Hardness	77
Pore size (μm)	0.8
Grain size (μm)	<4
Electrical resistivity (μΩ m)	1350
Thermal conductivity (W/m K)	120
Coefficient of thermal expansion (K^{-1})	8.4×10^{-6}

the primary substrate and as the plating base for the microfabrication. Properties of rigid graphite as provided by the vendor are presented in Table 1. Polymethylmethacrylate (PMMA) sheets (Goodfellow, CQ-grade) of 1 mm thickness or greater were used as a resist. The graphite substrate was cleaned with acetone and spin coated with a PMMA resist layer ($M_w = 2200$ K, 10% in anizole); after it had dried at room temperature for 2–3 days, it was spin-coated with a second layer of PMMA. After it had dried at room temperature for 3–5 days, a PMMA sheet was solvent-bonded [5] on top using methylmethacrylate (MMA). After drying MMA for a day at room temperature, the substrate could then be exposed.

Hard X-ray exposures were performed at bending magnet beamline 2-BM [6] of the Advanced Photon Source at Argonne National Laboratory. The beam size was 100 mm × 5 mm, and the photon energy range was 10–20 keV, after passing through a 1 mm carbon filter and reflecting from a 0.15° grazing-incidence chromium mirror. X-ray masks used for patterning were fabricated by conformal mask technology [7]. The mask consisted of a 250 μm thick silicon wafer with 45–60 μm thick patterned gold absorber layer. The exposed PMMA was developed using the GG developing system [8]. Copper electroforming

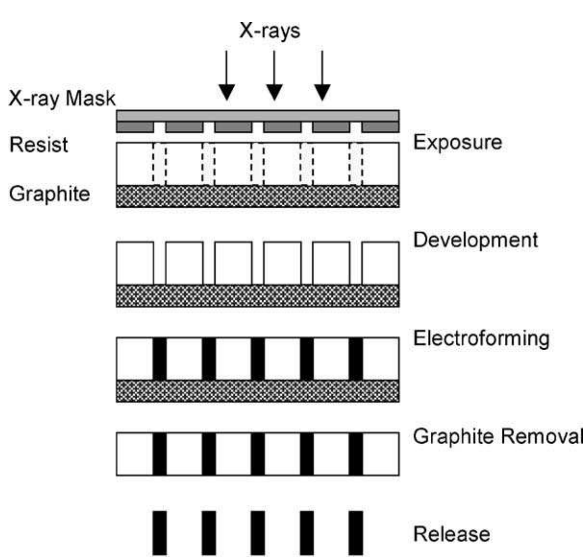

Fig. 1. Process steps for manufacturing freestanding metal microstructures using DXRL and electroforming on graphite.

was performed using a copper sulfate plating bath. After electroforming, the copper microstructures along with the PMMA mold were released from the plating base by abrasive removal of graphite. Both sides of the copper microstructure were polished using aluminum oxide pads. Finally the PMMA mold was dissolved in acetone, resulting in the finished freestanding metal part. The schematic of the fabrication method is shown in Fig. 1.

3. Results and discussion

PMMA adhesion to graphite appeared much stronger compared with metal-coated silicon or graphite, because of graphite's high porosity and microroughness [9]. A graphite substrate may also be preferred over metal-coated silicon wafers because carbon is less dense and has a smaller atomic number than both silicon and metal coatings (Au, Ti, Cu). In the case of a graphite substrate, the adhesion layer is not destroyed by the fluorescence and secondary electron emission generated by the high-Z metals during hard X-ray exposure.

PMMA structures patterned on the graphite substrate remained well attached to the substrate even after development in GG for ∼100 h. Spin coating of graphite with two PMMA layers and drying at room temperature was found to be optimal, while a thinner PMMA layer led to adhesion failure, due to significant penetration of PMMA into the graphite.

Graphite's conductivity was found to be sufficient to perform electroforming directly without a metal base layer. Graphite turns out to be an excellent plating base for copper electroforming using acid sulfate electrolyte and for gold electroforming using sulfite electrolyte. Although copper deposition on the graphite surface usually starts well, for very high-aspect-ratio structures it was necessary to apply electrochemical activation of the carbon surface by reverse current to initiate copper electroplating. We expect graphite will perform well for other electroformed metals such as nickel, lead, and their alloys.

The electroformed metal part must be separated from the plating base to provide a freestanding metallic structure. The advantage of graphite as a substrate is its easy sacrificial removal by abrasion once electroforming is complete. This broadens the range of metals suitable for electroforming and subsequently released. For example, freestanding copper and lead microstructures, which cannot be obtained by using a titanium sacrificial layer, can be easily fabricated using a graphite substrate.

One of the important applications for freestanding microformed metal grids is mammography. Mammogram image quality can be significantly improved by using an antiscatter grid transparent for primary radiation and opaque to scattered radiation from all directions. Using graphite as a substrate, we were able to fabricate a freestanding copper antiscatter grid for mammography [10,11]. The images of a

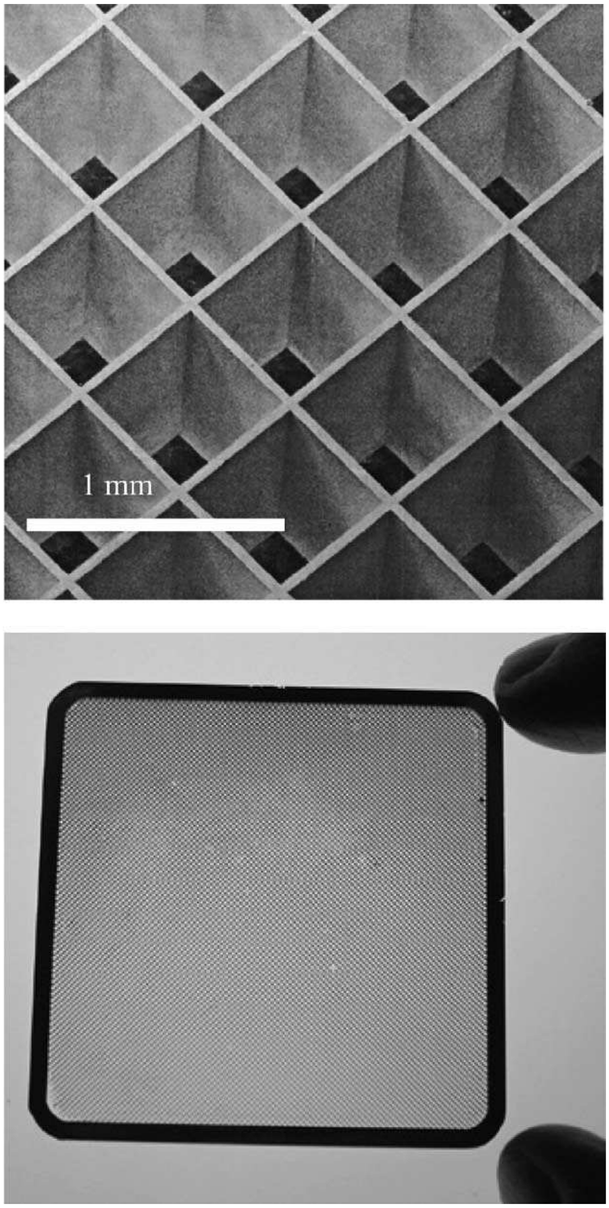

Fig. 2. (a) A scanning electron micrographs and (b) a photograph of low magnification of a 1.5 mm thick freestanding copper grid with 25 μm thick cell walls and a 550 μm period.

1.5 mm thick freestanding copper grid for mammography with an aspect ratio of 60 are shown in Fig. 2.

High-aspect-ratio electroformed metal molds also can be fabricated using a graphite substrate. The electroformed structure is overplated with additional metal to form the base of the mold. Finally the graphite can be easily removed by abrasion. An example of a copper mold for grid fabrication is shown in Fig. 3. This process is potentially applicable to the fabrication of both hot embossing and injection molds used to fabricate components for MEMS. Micromolds can be fabricated by first electroforming in an appropriate metal, such as nickel, and then overplating additional nickel to form the base of the mold (Fig. 4a). After graphite and

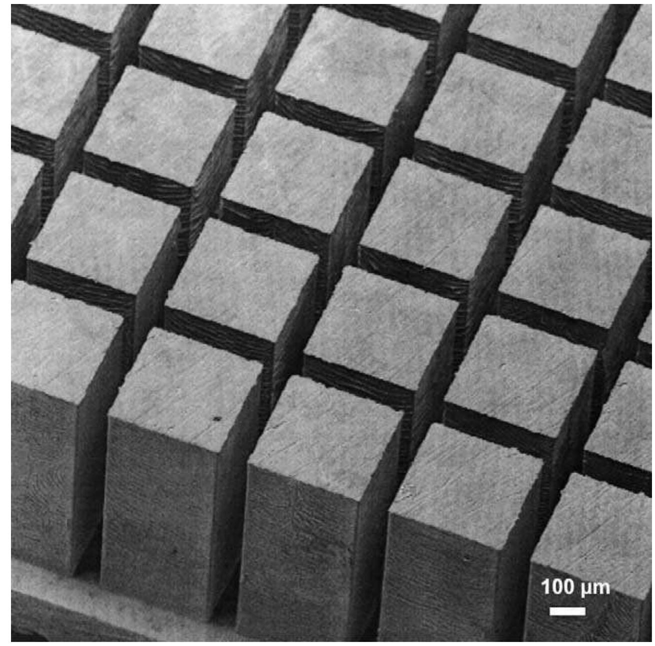

Fig. 3. A scanning electron micrograph of a copper mold for the grid fabrication. Trenches are 100 μm wide and 1 mm tall with a periodicity of 500 μm.

PMMA are removed, the remaining metal part can be used for embossing or injection molding thermoplastics or slurries to fabricate polymer or ceramic microparts for assembly into MEMS.

For the production of many discrete microparts in electroformed metals for later assembly into MEMS, the batch of microparts must be released, yet temporarily held to be later individually picked from the batch and placed into MEMS. This pick-and-place assembly can be facilitated by attaching a carrier to the array of electroformed parts while still attached to the graphite (Fig. 4b). The carrier may be attached by means of temporary adhesive or magnetic forces in the case of ferrous and ferromagnetic parts, such as nickel and permalloy. After graphite and PMMA are removed, the individual parts may be picked off the carrier and placed into MEMS manually or with automated equipment.

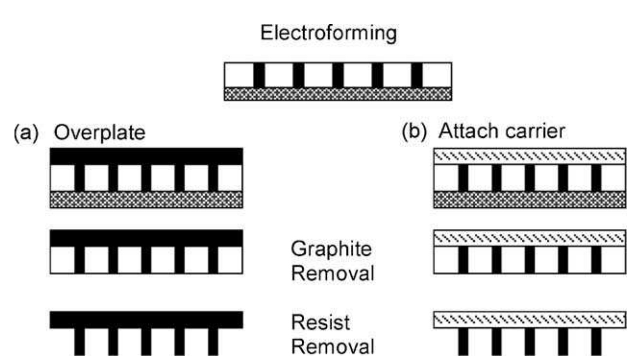

Fig. 4. Process steps (after the metal electroforming in Fig. 1) for the fabrication of (a) an injection mold for MEMS manufacture, and (b) arrays of small MEMS components for subsequent pick-and-place assembly.

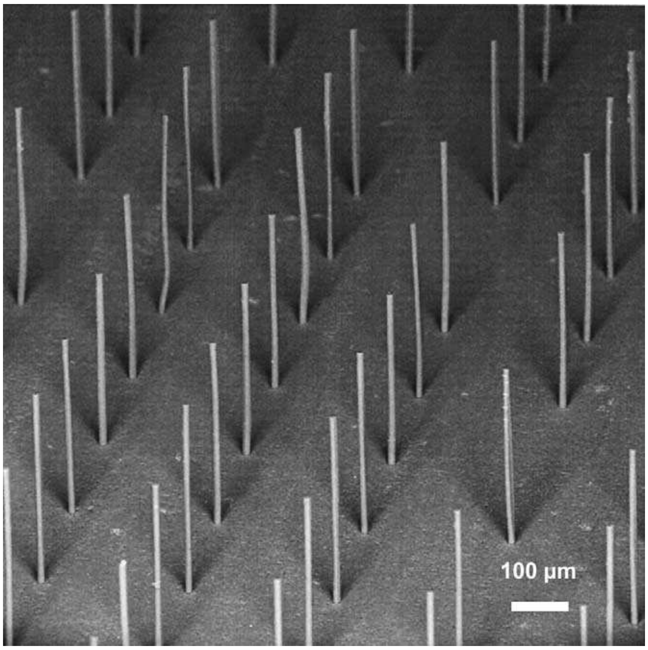

Fig. 5. A scanning electron micrograph of 25 μm in diameter and 860 μm tall SU-8 columns.

We also note that graphite substrates can be used with SU-8 negative resist. The resist showed excellent adhesion for HARMS (Fig. 5), and the structures have successfully copper electroformed. Abrasive removal of the substrate can simplify the difficult process of SU-8 removal after electroforming. The microstructure is open from both sides, and the SU-8, which significantly shrinks at the curing temperature, is dislodged from the structure. Since SU-8 can be effectively used for HARMS microfabrication using UV lithography, we expect the use of graphite substrates will have wider application for MEMS beyond its use in X-ray lithography.

4. Conclusion

We have been successful in the development of a process that uses a graphite substrate to fabricate freestanding metal microstructures and micromolds. The method can be used with both PMMA and SU-8 resists. By using rigid graphite as a substrate, we were able to fabricate a high-aspect-ratio freestanding copper antiscatter grid for mammography. The method has potential in the production of micromolds for injection mold fabrication of MEMS and for fabrication of arrays of microparts on pick-and-place carriers for assembly into MEMS.

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Biographies

Olga V. Makarova received her MS (1979) and PhD (1995) in chemistry from Novosibirask State University and from Boreskov Institute of Catalysis (BIC) of Russian Academy of Sciences, Novosibirsk, Russia, repectively. She was working in the fields of heterogenous catalysis at BIC (1979–1995) and nanoparticle technology at University of Chicago and Argonne National Laboratory (1996–2000). Since 2000, she is a Research Scientist at Creatv Micro Tech, Inc. Her research interests include DXRL and microfabrication.

Derrick C. Mancini is a Staff Physicist at the Advanced Photon Source of Argonne National Laboratory. He has 22 years experience working with synchrotron radiation X-rays, with 80 publications in the field. He obtained his BS in engineering physics and BA in history from Cornell University, MS in physics and MS in materials science from University of Wisconsin-Madison, and PhD in physics from Uppsala University, Sweden. His research interests include the application of synchrotron radiation to technological problems and the development of advanced lithographic techniques and X-ray instrumentation.

Nicolaie Moldovan received his PhD in physics from the University of Bucharest. He joined Argonne National Laboratory in 1998, after leading for several years a microfabrication laboratory in the Romanian Institute of Microtechnology. His field of interest is in developing micromachining technologies (LIGA, bulk and surface micromachining), their characterization, and modelling and simulation of processes.

Ralu Divan received her MS (1977) and PhD (1999) in chemistry from the Department of Chemistry, University of Bucharest, Romania. Between 1977 and 1995 she was with ICCE (Research Institute for Electronic Components), Bucharest and after 1995 she was with the Romanian National Institute of Microtechnology (IMT). Since October 1999 she is with Argonne National Laboratory. Her major areas of expertise are MOS technological processes, development of advanced optical resist processes, and microfabrication technologies. Her actual duties in Argonne National Laboratory are related to the development of soft X-ray lithography for high-aspect-ratio zone plates and hard X-ray lithography for LIGA application.

Cha-Mei Tang is the founder and president of Creatv Micro Tech, Inc. She manages the company as well as directs some of the research. Her current research areas are anti-scatter grids and collimators, biosensors, three-dimensional microscopy and cold field-emission cathodes. She received her BS (1971), MS and EE (1973) and DSc (1977) from Electrical Engineering and Computer Science Department of Massachusetts Institute of Technology at Cambridge, MA. From 1993 to 1996, she was a Guest Scientist at National Institute of Standards and Technology. From 1985 to 1993, she was a Section Head of the Accelerator and Beam Physics Section, Beam Physics Branch, Plasma Physics Division, at Naval Research Laboratory (NRL). Other positions include research physics at NRL, Jacor and Applied Physics Laboratory/Johns Hopkins University. She is a Senior Member of the IEEE, the recipient of 1992 WISE Award for Science as being the most outstanding woman scientist in the Federal Government and a Fellow of the American Physical Society.

David G. Ryding received his BS (1973) and MS (1979) in engineering physics and metallurgical engineering, respectively, from the University of Illinois, Urbana, IL. His research interests include single crystal growth, micro-electronics fabrication, electroplating.

Richard H. Lee has recently retired as a Senior Technician from Argonne National Laboratory with 30 years of experience in electron microscopy. Currently he is working for Mc Crone Associates as a Microscopy Consultant.