

CARBON MICROMACHINING (C-MEMS)

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Abstract

Photopatterned resists, heat treated (pyrolyzed) at different temperatures in different ambient gases, are used as a carbonaceous structural material for micro electro mechanical systems (MEMS). This new material permits a variety of new MEMS applications that employ structures having a wide variety of shapes, resistivities and mechanical properties. Moreover, carbon surfaces form better electrochemical electrodes and are easier to derivatize with a wide variety of organic molecules than the conventionally used silicon. We report results on the preparation of the photoresist-derived carbons, the characterization of these carbons, and electrochemical deposition experiments with conductive polymers on photoresist-derived carbon structures to fashion carbon surface-micromachined test structures, actuators ("artificial muscle") and polymeric batteries.

Introduction

Conventional micro electro mechanical systems (MEMS) have been constructed mostly of silicon-based materials. These have performed both mechanical and electrical functions. In this paper, we describe initial work with a different starting material -- carbon produced by heat treating (pyrolyzing) patterned photoresist. We propose the acronym C-MEMS for such devices.

Carbon Film Preparation

Both negative and positive photoresists can be used to form conductive carbon films, but for the current process description we will only consider AZ-4330 and OCG-825, both of which are positive resists. Silicon wafers are dipped in a dilute HF solution before being spin-coated with a thin layer of these resists. The very viscous AZ-4330 is applied manually on a silicon wafer spinning at 3000 rpm for 30 seconds. The less viscous OCG-825 photoresist is automatically dispensed to the spin coater rotating a silicon wafer at

1000 rpm, also for thirty seconds. In both cases, four applications of photoresist are used to produce a final thickness of about 8 microns and 10 microns, respectively. The photoresist is then carbonized by heating for 1 hour at 600°, 700°, 800°, 900°, 1000° or 1100°C. By changing the ambient gas, we can vary the total amount of shrinkage of the film during heating, the film porosity, and the surface characteristics. For example, changing the ambient gas from pure nitrogen to 70% nitrogen and 30% hydrogen (forming gas) produces dramatic differences in total film shrinkage, as illustrated in Table 1. Trace amounts of oxygen in the "pure nitrogen" may result in perceptible oxidation of the photoresist during heat treatment, consequently a thinner carbon film may be obtained. On the other hand, a limited amount of methane may be produced by reaction of the photoresist with the reductive forming gas at high temperatures, but this reaction is only expected to result in a small decrease in the thickness of the carbon film. We anticipate that the carbon surface will be dramatically different in the two cases. Adding impurities to the resist itself further presents opportunities for structural manipulation of the carbon films.

Film Characterization

The carbon films were characterized by a variety of techniques. A four-point probe was used to determine the film sheet resistance (ohm/square). A Scanning Electron Microscope (SEM) was used to determine the surface structure and the thickness of the carbon films. For microstructure analysis, high-resolution transmission electron microscopy (TEM) was used. A small sample of carbon was removed from the carbon film with a diamond pick and placed on a TEM grid. For mechanical characterization of the pyrolyzed photoresist, the curvature of carbon surface-micromachined beams was evaluated. For electrochemical evaluation, cyclic voltammetry was performed on electrodes fashioned from the pyrolyzed photoresist. Electrochemical deposits of conductive polymers on the carbon electrodes were studied with SEM and AFM.

Results and Observations

Sheet Resistance: The results of a set of four-point probe measurements on OCG-825 (~ 10 μm thick) and AZ-4330 (~ 8 μm thick) heat-treated photoresists (in a nitrogen atmosphere) are compared in Table 2. For each data point, three different locations were measured on each wafer and the values averaged. Carbon films pyrolyzed at 600°C yielded unstable resistivity measurements. However, resistance for the film obtained at 700°C was still high but stable measurements were possible. The resistance decreased dramatically for the films produced at 800 °C and above (see also Figure 1). The samples were typically measured after they had been out of the furnace for several hours. To investigate the change in resistivity of the carbon films over time of exposure to room ambient we remeasured the samples treated at 1100 °C after 24 hours in ambient air. No change in resistivity was observed (see Table 2). Since the OCG-825 and AZ-4330 resists have different initial thicknesses, we are not attaching much significance yet to the fact that the OCG-825 resist (the less viscous resist) leads to the more conductive carbon films. (The data for samples treated at 600°C are in doubt.)

SEM: In the SEM, the carbon films produced from AZ-4330 photoresist at 1100°C in nitrogen appeared smooth and no evidence for pores was observed at the magnification that was used. The thickness of the film obtained from this photoresist heat treated at

1000°C in nitrogen decreased dramatically from its original value (i.e., from 8 down to about 2 microns). On the other hand, resist films treated in forming gas show much less shrinkage (e.g., a 4 micron AZ-4330 film held for 1 hour at 900 °C shrinks only to 3 microns, as shown in Table 1). It is assumed that in a nitrogen atmosphere film oxidation still proceeds, consuming the film rapidly, while in the forming gas only a limited amount of methane is formed and the film consumption remains limited. In further measurements the gases evolving from the heated photoresist will be monitored.

TEM: The high-resolution TEM indicated that graphite-like structures are present in the predominantly amorphous carbon film. The lattice image for the (002) plane was evident in the carbon films, even those obtained by heat treatment at 600°C. The (002) diffraction ring is observed by selected-area electron diffraction, and it is more prominent in the carbon pyrolyzed at 1000°C and at 1100°C. A striking example of some of the graphite-like crystal planes observed in the amorphous carbon matrix is shown in Figure 2. In this case, AZ-4330 was heat treated at 900°C for one hour in forming gas. Studies of carbon films obtained by rf glow discharge (2), low-temperature plasma (3), chemical vapor deposition (4), vacuum-arc (5), electron beam evaporation (6) and sputtering (7) show evidence for the formation of graphite-like regions in a matrix of amorphous carbon. Our observations of the microstructure of the pyrolyzed photoresists are consistent with these findings. The ratio of ordered to amorphous carbon may be of direct relevance to the capacity of the pyrolyzed photoresist to store large amounts of lithium as an electrode in rechargeable lithium batteries (1,8) (see also "Carbon MEMS Structures" below).

Carbon Mechanical Properties: To investigate the mechanical properties of the pyrolyzed photoresists, surface-micromachined clamped-clamped and clamped-free pyrolyzed photoresist were fabricated. An array of those beams is shown in Figure 3. The curvature of these beams is used to determine mechanical properties such as Young's modulus and built-in residual stresses of the photoresist-derived carbons. By studying the mechanical properties of the so-formed carbon beams as a function of heat treatment and gaseous environment, we are able to fine-tune mechanical and electrical properties of C-MEMS according to the application needs.

Carbon Electrochemistry: The electrochemistry and derivatization of carbon is well known (9). Here we report the electropolymerization of conductive polymers on photoresist-derived carbon, and compare the results with deposits on gold electrodes. For the electrochemical experiments described, only photoresists treated at 1100 °C were employed to date. Besides the carbon or gold working electrode, a gold counter electrode and a calomel reference electrode were used in a potentiostat/galvanostat set-up. A typical solution we used to deposit a polypyrrole coat on carbon or gold consists of one part 0.16N HCl and three parts ethanol solution with 3 vol % pyrrole monomer added. The ethanol is added to increase the solubility of the monomer in the solution. An area of approximately 0.2 cm² on the working electrode is defined using Teflon tape, which isolates the remaining part of the electrode from the solution. The solutions are stirred with a mechanical stirrer or by bubbling nitrogen. Cycling the voltage from -1 to +1 V vs SCE, at a voltage scan rate of 100 mV/s, results in a deposition of the polypyrrole on the substrate after 10 to 20 cycles. Following this deposition step, the solution is removed and replaced with blank solution, and further cyclic voltammetry using the same conditions shows the charging and discharging of the polymer film with oxidation and reduction (see Figure 4). The major difference in the cyclic voltammogram observed on a gold electrode in the same solution is that the first sweep towards a negative bias results

in a much larger solvent decomposition onset (most probably hydrogen evolution), subsequent sweeps are identical to those on carbon since both electrodes are basically converted into polypyrrole electrodes after they have been biased anodically. The suppression of the hydrogen reaction on the carbon electrode most likely explains why the deposits on the carbon electrode look smoother and appear more adherent than those on the gold electrode. These observations are being tested further by AFM and tape tests, respectively. Atomic force microscopy was performed on the resultant polypyrrole on the carbon working electrode, and a highly porous, granular deposition of spherical structures was observed with grain sizes ranging from approximately 0.5 to 1 micron in size (see Figure 5).

Carbon MEMS Structures

The design and fabrication of two carbon MEMS structures based on the above described pyrolyzed photoresists are now introduced.

A. An electrochemical valve.

In the C-MEMS structure shown in Figure 6, a redox polymer such as polypyrrole coats the sidewalls of 2 to 50 μm diameter holes in the carbon film. Switching the redox polymer in the holes from a charged to a discharged state causes swelling and contraction which enables the opening and closing of the array of holes (artificial muscle or electrochemical valves). Volume changes of these redox gels may also be induced by changing the temperature or pH (10). The first photoresist application in the C-MEMS structure is on top of a sacrificial oxide which is etched away after photoresist exposure to the mask with the hole pattern and before development of the resist but before pyrolysis. After the pyrolysis step, a first thin coat of photoresist on the front surface of the valve seat is exposed from the back, using the holes in the pyrolyzed carbon as the in-situ mask, and developed; the same process is repeated for a thin resist layer on the back of the valve seat. The untreated resist isolates the top and bottom carbon surfaces and enables electropolymerization in the carbon holes only.

B. Carbon-based polymer battery electrode.

We have shown previously (11) that cyclic voltammograms on an electro-active conductive polymer (such as polyaniline and polypyrrole) deposited on small (5 to 15 μm diameter), metal-coated, photopatterned posts of photoresist charge and discharge faster than the same polymer films deposited on a flat substrate. These features are attractive attributes for faster electrochromics, increasing the response of electrochromic devices and improving the charge/discharge rates of rechargeable batteries (11). In the new embodiment of the micromachined battery, the photoresist posts are carbonized and serve directly as the base for the conductive polymer coating on the cathode and as a lithium reservoir on the anode. By increasing the porosity of the carbon posts by heat treating them in different ambient gases and by using additives in the photoresists, a highly porous carbon results. With novolak-type positive tone photoresist, layers of >100 μm in thickness have been patterned by Lockeh et al. (12); therefore it is anticipated that carbon posts of high aspect ratios (height/diameter) of more than 10 should be achievable.

By studying the ratio of amorphous vs ordered carbon we also expect to be able to microfabricate planar batteries with very high specific capacities for lithium incorporation.

Acknowledgment

This research was supported in part by the Berkeley Sensor & Actuator Center (BSAC), A National Science Foundation (NSF)/ Industry/ University Cooperative Research Center, funded by the NSF, and a consortium of industrial corporations and government agencies, and in part by the National Aeronautics and Space Administration. This work was also supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Office of Advanced Automotive Technologies of the US Department of Energy under Contract No. DE-AC03-76SF00098. The idea of the electrochemical valve using artificial muscle was conceived by Dr. Marc Madou and Dr. Rudi Seitz from the University of New Hampshire, Durham, New Hampshire, during private conversations in 1996. The idea of the pyrolyzed photoresist for micromechanical structures was conceived by Dr. Amit Lal.

References

1. D.W. Murphy, Insertion Compounds: Relationship of Structure to Electrochemistry, in Solid State Batteries, ed. C.A.C. Sequeira, A. Hooper, Martinus Nijhoff Publishers, The Netherlands, 1985, pp.181-194.
2. G.X. Cheng, S.L. Gu, Y. L. He, Z. H. Wang, H. Xia, W. Zhang and X.K. Zhang, The Microstructural Studies of Hydrogenated Amorphous Carbon Films by Raman Spectra, *Physica Status Solidi A - Applied Research*, **139**, (1993) 459.
3. D. V. Fedoseev, I. G. Varshavskaya, and Y. N. Tolmachev, Synthesis and Properties of Amorphous Films of Hydrogenized Carbon, *Colloid J.*, **58** (1996) 383.
4. A. S. Johansson, and J. O. Carlsson, Crystallinity, Morphology and Microstructure of Chemical-Vapor-Deposited Carbon Films on Different Substrates, *Thin Solid Films*, **52**, (1995) 261.
5. S. Ravi, P. Silva, S. Xu, B.X. Tay, H.S. Tan and W.I. Nanocrystallites in Tetrahedral Amorphous Carbon Films, *Appl. Phys. Lett.*, **69**, (1996) 491.
6. S. Schelz, T. Richmond, P. Kania, P. Oelhafen, and H.J. Guntherodt, Electronic and Atomic Structure of Evaporated Carbon Films, *Surf. Sci.*, **359** (1996) 227.
7. S. Umemura, Y. Andoh, S. Hirono, T. Miyamoto and R. Kaneko, Nanoindentation and Nanowear Tests on Amorphous Carbon Films, *Philosophical Magazine A - Physics of Condensed Matter Structure Defects and Mechanical Properties*, **74**, (1996) 1143.
8. T. Zheng, Q. Zhong, J.R. Dahn, High-Capacity Carbons Prepared from Phenolic Resin for Anodes of Lithium-Ion Batteries, *J. Electrochem. Soc.*, **142**, No.11, November 1995, pp.L211-214.
9. K. Kinoshita, Carbon Electrochemical and Physicochemical Properties, John Wiley & Sons, New York 1988.
10. K. Takada, T. Haseba, T. Tatsuma, and N. Oyama, In Situ Interferometric Microscopy of Temperature- and Potential-Dependent Volume Changes of a Redox Gel, *Anal. Chem.*, **67**, 1995.

11. M. Madou and T. Otagawa, U.S. Patent 5,151,224, U.S. Patent 5,002, 700 and U.S. Patent 4,973, 391.
12. B. Lockeh, A. Maciossek, H. Quenzer and B. Wagner, UV Depth Lithography and Galvanofarming for Micromachining, in *Proceedings of the Second International Symposium on Electrochemical Microfabrication*, M. Datta, K. Sheppard and J. Dukovic, eds., The Electrochemical Society, Inc, Pennington, NJ, 1995, p. 100.

Table 1 Photoresist AZ-4330 shrinkage after heat treatment.

Furnace atmosphere	Thickness before pyrolysis	Thickness after pyrolysis
Nitrogen (Temp. 1000 °C)	8 μm	1.3 μm
70% nitrogen and 30% hydrogen (Temp. 900 °C)	4 μm	3 μm

Table 2 Sheet resistance for OCG-825 and AZ-4330 resists heat treated in nitrogen.

Temperature °C	Sheet Resistance (ohm cm ²)	
	OCG-825	AZ-4330
600	443.67	170.28
700	401.77	438.55
800	50.15	116.01
900	17.39	55.49
1000	10.96	41.13
1100	8.86	32.03
1100*	8.86	32.03

* Measured again after 24 hours in ambient air.

Sheet Resistance (Ohm/square)

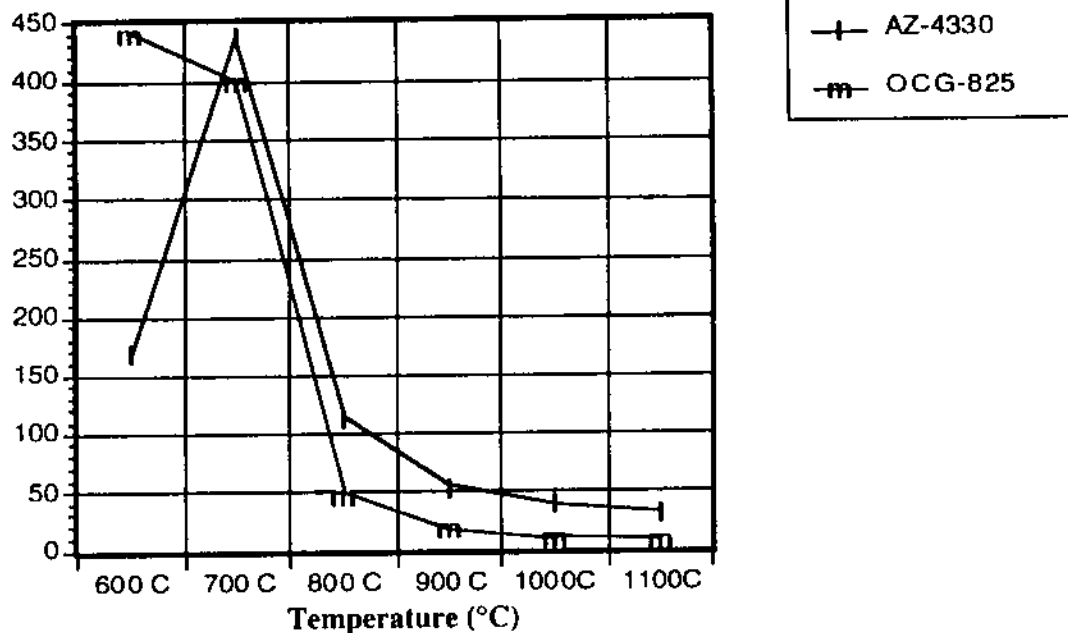


Figure 1. Sheet resistance vs temperature of heat treatment for AZ-4330 and OCG-825 resists.



Figure 2. TEM picture of AZ-4330 pyrolyzed at 900 °C for 1 hour. Graphite-like carbon planes are clearly visible.

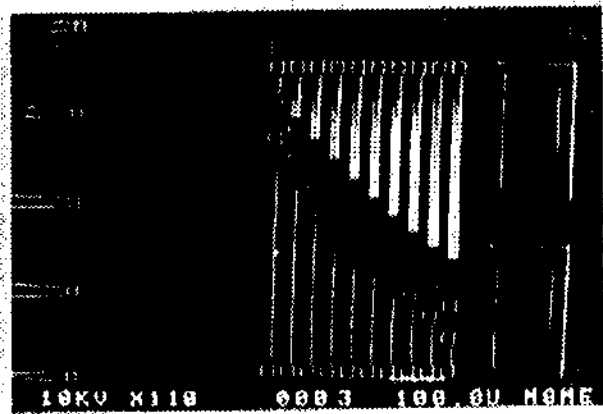


Figure 3. C-MEMS. Clamped/clamped and clamped/free carbon beams. Pyrolyzed AZ-4330 at 900 °C.

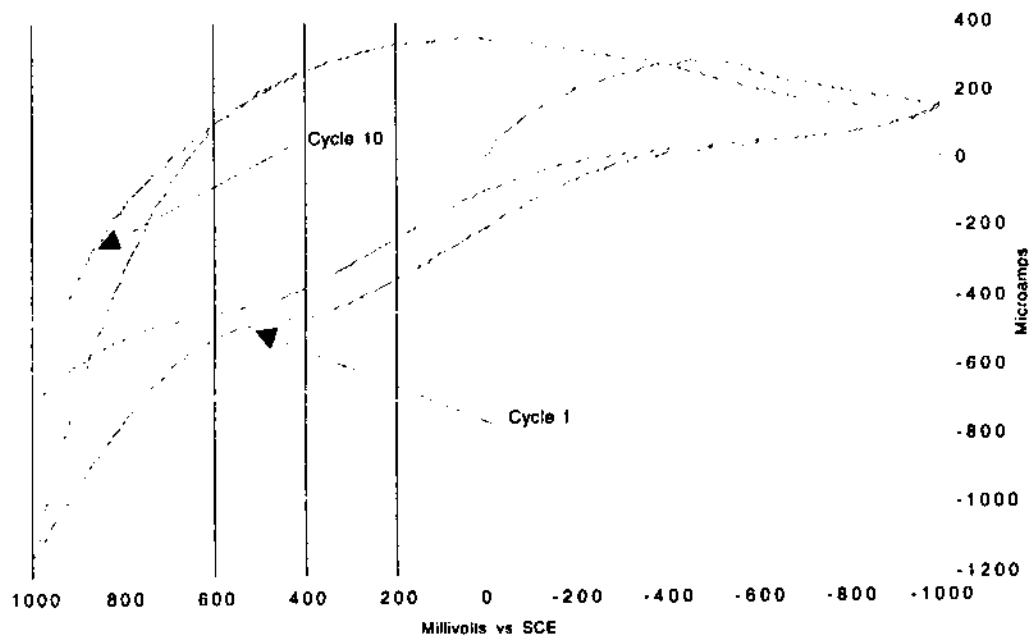


Figure 4. Cyclic voltammetry in blank solution of polypyrrole film on carbon electrode after film deposition.

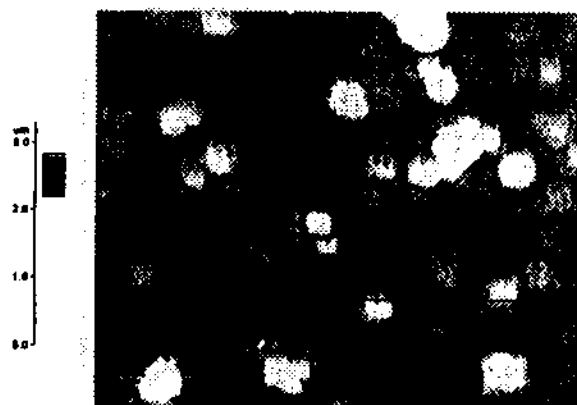


Figure 5. AFM picture of Polypyrrole on carbon.

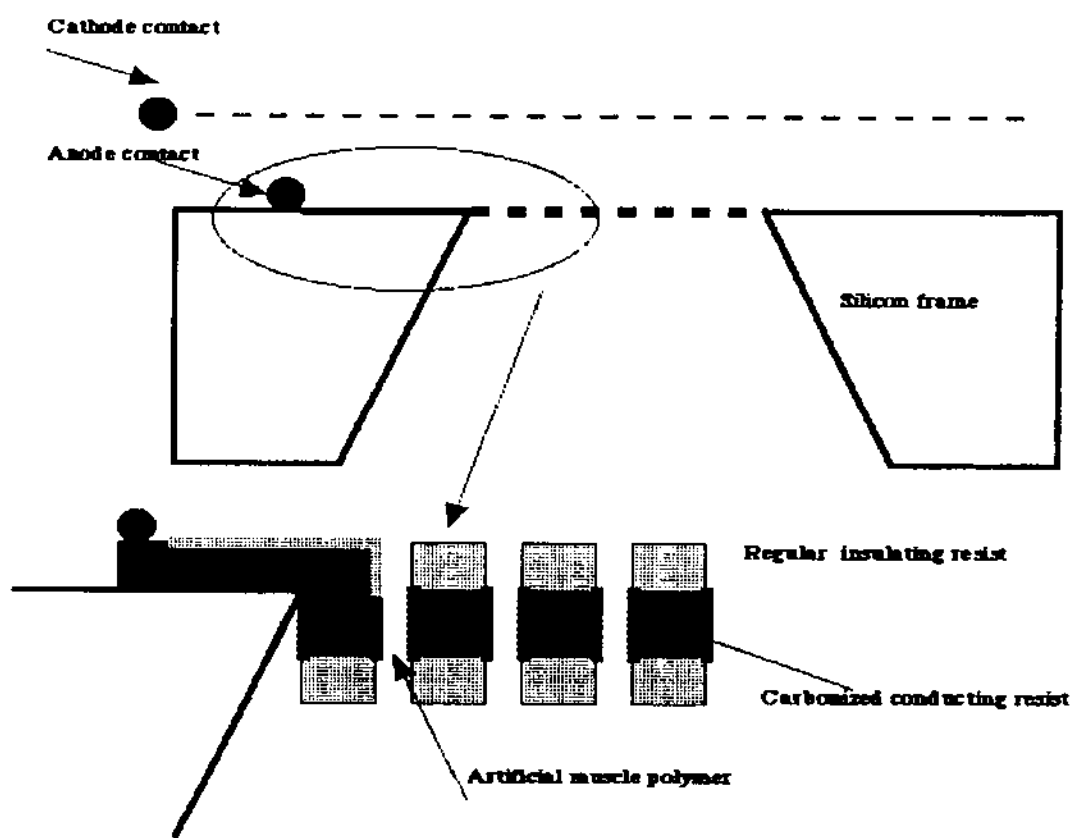


Figure 6. C-MEMS support structure for artificial muscle.