Carbon-MEMS architectures for 3D microbatteries

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ABSTRACT

Batteries based on three dimensional microstructures are expected to offer significant advantages in comparison to conventional two dimensional batteries. One of the key elements for creating new types of 3D microbatteries is fabricating high-aspect-ratio carbon structures. Our efforts on building positive photoresist structures include: (1) casting photoresist in 3D molds made by DRIE before pyrolysis; (2) multi-exposure and multi-developing processes, and (3) using embedded masks in multi-layer photoresists. Another effort is the fabrication of high-aspect-ratio carbon structures using negative photoresist. We manufactured high-aspect-ratio (~10:1) carbon posts by pyrolysis from negative photoresists in a simple one-step process. Simulation results showed that current density is strongly influenced by the biasing pattern and the geometry of the electrodes themselves. Current density (and therefore power density) is stronger at the edge of electrodes-implying that closer spacing of the electrodes will provide a denser current concentration. Electrochemical tests demonstrate that these C-MEMS electrodes can be charged/discharged with Li. A C-MEMS battery approach has the potential to solve both manufacturing and materials problems simultaneously.

Keywords: microbattery, Li intercalation, C-MEMS, photoresist, pyrolysis, simulation

1. Introduction

As the general tendency of many advanced technologies is towards miniaturization it is evident that the future development of batteries is also aiming for smaller dimensions with larger storage capacity and higher energy densities. Recently there has been a dramatic increase in demand for microbatteries (here, microbatteries are defined as batteries with power output from 20µW to 40mW.) for new miniature portable electronic devices such as cardiac pacemakers, hearing aids, smart cards, personal gas monitors, microelectromechanical systems (MEMS), embedded monitors, and remote sensors with RF capability. Lithium-based batteries exhibit very high energy density values. Highly ordered graphite as well as hard and soft carbons is used extensively as the negative electrodes of commercial Li-ion batteries [1, 2]. The high energy density values reported for these Li batteries are generally based on the performance of larger cells with capacities of up to several ampere-hours. For microbatteries with applications in miniature portable electronic devices, such as cardiac pacemakers, hearing aids, smart cards and remote sensors, the achievable power and energy densities do not scale favorably because packaging and internal battery hardware determine the overall size and mass of the completed battery to a larger extent. Therefore further improvements in advanced microbatteries are intimately linked to the availability of new materials and the development of novel battery designs. One approach to overcome the size and energy density deficiencies of two dimensional (2D) microbatteries, batteries using planar plates as electrodes, is to develop three dimensional (3D) battery architectures based on specially designed arrays composed of high-aspect-ratio three dimensional (3D) electrode elements [3,4]. White and colleagues have calculated that for a micro 3D battery which has electrode arrays with a 50:1 aspect ratio (height/width), the expected capacity may be 3.5 times higher and the surface area 35 times higher than for a conventional 2D battery design [3]. The key challenge in fabricating 3D microbatteries based on carbon negative electrodes is in achieving high-aspect-ratio (>10:1) electrodes to ensure a dramatic improvement in surface-to-volume ratio without a corresponding increase in overall volume. This paper reports the fabrication and lithium intercalation properties of high-aspect-ratio 3D carbon electrode arrays.

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Our work in carbon-microelectromechanical systems (C-MEMS) suggests that C-MEMS might provide a very interesting material and microfabrication solution to the battery miniaturization problem. In C-MEMS, photoresist is patterned by photolithography and subsequently pyrolyzed at high temperatures in an oxygen free environment. By changing the lithography conditions, soft and hard baking time and temperature, pyrolysis time, temperature and environment, C-MEMS permits a wide variety of interesting new MEMS applications that employ structures having a wide variety of shapes, resistivity and mechanical properties. In the current case we use this technique to yield high-aspect-ratio and very high-surface-area carbon electrodes that may be used in microbatteries. The advantages of using photoresists as the starting material for carbon electrodes include the fact that photoresists can be patterned by photolithography techniques resulting in much finer features than possible with the more traditional silkscreening of carbon inks, and, since photoresists are very controlled and reproducible materials, more reproducible carbon electrode behavior can be expected. Hence, complex-shaped, very fine, accurate and reproducible carbon electrodes can be manufactured. In earlier work, we demonstrated that photoresist-derived carbon electrodes show excellent electrochemical kinetics comparable to that of glassy carbon for selected electrochemical reactions in aqueous and nonaqueous electrolytes [5-7]. Each of the C-MEMS battery elements can ultimately be made part of a switchable matrix, e.g., under microprocessor control as illustrated in Fig.1. As an example, we show a high-aspect-ratio C-MEMS battery structure in inset of Fig.1, in which a negative photoresist, SU-8, is used to yield contact fingers and carbon electrode arrays (~ 200 µm high).

In this study, we successfully microfabricated high-aspect-ratio carbon posts (9.4:1) by pyrolyzing SU-8 negative photoresist in a simple, one spin-step process. Electrochemical measurements established that these C-MEMS electrodes can be reversibly intercalated with lithium.

Fig. 1: Smart switchable battery arrays-baxels are addressable just like pixels: in a serial arrangement, voltages add up; in a parallel arrangement, currents add up

2. Experimental

The substrates used were (1) Si, (2) Si₃N₄(2000Å)/Si, (3) SiO₂(5000Å)/Si and (4) Au(3000Å)/Ti(200Å)/SiO₂(5000Å)/Si. Ti and Au layers were deposited by electron beam (EB) evaporation. A negative tone photoresist with different thickness, NANO™ SU-8 100, was spin-coated onto those substrates. Two kinds of mask designs were used to generate SU-8 posts: (1) 180 by 180 arrays of circles with diameter of 50, 40, 30 and 20µm and center to center distance of 100µm, and (2) 90 by 90 arrays of circles with a diameter of 100µm and center to center spacing of 200µm. The photolithography process used for SU-8 photoresist patterning included spin coating, soft bake, near UV exposure, development and post-bake (vide infra). Photoresist-derived C-MEMS architectures were
obtained in a two-step pyrolysis processes using an open-end quartz-tube furnace, in which samples were heated in a nitrogen atmosphere at 300°C for about 40 minutes, then heated in a nitrogen atmosphere with a 2000 sccm flow rate until the temperature reached 900°C. The atmosphere was then changed to forming gas [H₂ (5%)/N₂] flowing at about 2000 sccm. The sample was kept at 900°C for 1 hr, then the heater was turned off and the samples were cooled in a nitrogen atmosphere to room temperature. The heating rate was about 10°C/min.

Two different types of electrodes were studied. One was an unpatterned carbon film, 1.6 µm thick, obtained from AZ 4620 photoresist on SiO₂/Si. This electrode was designed to serve as a reference sample to determine whether pyrolyzed SU-8 exhibited electrochemically reversible intercalation/de-intercalation of lithium. The second sample was a patterned electrode array obtained from SU-8 photoresist, consisting of 180 x 180 posts with a thickness of ~ 150 µm, on unpatterned carbon obtained from AZ 4620. The electrochemical measurements were carried out using a 3-electrode Teflon cell that employed an o-ring seal to define the working electrode to ~ 6.4 cm² (circle of 2.86 cm diameter). In this way, the projected areas for both types of electrodes were identical. The carbon electrodes served as the working electrode while lithium ribbon (99.9% pure, Aldrich) was used as both the counter and reference electrode. The electrolyte was 1 M LiClO₄ in a 1:1 volume mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). All the cells were assembled and tested in an argon filled glove box in which both the oxygen and moisture levels were less than 1 ppm. Galvanostatic and voltammetry experiments were carried out on both types of cells. For the galvanostatic measurements, the current was based on the C/5 rate for graphite (corresponding to 50 µA and 580 µA for unpatterned and patterned films, respectively) and cells were cycled between 10 mV and 1 V vs. Li/Li⁺. The voltammetry experiments were carried out using a sweep rate of 0.1 mV/s over the potential range 10 mV to 2V vs. Li/Li⁺. All the electrochemical measurements were performed with a computer-controlled Arbin multi-channel station. A Hitachi S-4700-2 field-emission scanning electron microscope (FESEM) was used to characterize the C-MEMS structures.

3. Results and Discussion

Traditionally, photoresist layers in the 50 to 100 µm and beyond range were challenging to formulate, especially in a positive tone. It proved Very difficult to design a positive tone chemistry to achieve the necessary transparency and to achieve reasonable exposure doses while maintaining steep sidewall angles [8, 9]. Very thick positive Novolak photoresists have the characteristic of popping or forming voids after exposure as a result of the nitrogen generated during exposure. Furthermore, positive photoresists require as many as three coats to achieve a thickness of around 65 µm [8]. The LIGA process in which PMMA resist is exposed with an x-ray source has demonstrated structures on the order of 1mm deep [10]. However, this technique requires an expensive synchrotron source, hence the motivation for a cheaper and easier process based on deep UV resist technology. In this research, we designed three alternative methods to build high-aspect-ratio, thick positive photoresist posts: (1) multi exposure/multi develop, (2) embedded metal masks, and (3) molding. Processing steps and SEM photos for all three processes are shown in Fig. 2. In method (1), 3 layers of AZ 4620 were spin-coated on SiO₂/Si substrates. Between each coating, a 20 minute oven-bake was performed. A 1000 Å thick Au layer was deposited on top of the layered photoresist by sputtering. The gold was subsequently patterned by opening windows in yet another layer of photoresist on top of the gold layer. The gold was then etched, using a commercial Au etchant, to achieve the desired pattern. The resulting Au pattern acted as a contact mask for the underlying stack of photoresist layers. Multi exposure and multi development steps were performed and the optimized condition we established for the multiple exposure/development cycles was 1:20 min for each UV exposure and 2:15 min for each development step. After 7 cycles of exposure/development, the resulting patterns, illustrated in Fig. 2-1(a) and 2-1(b), exhibited severe undercut cuts with crooked sidewalls. Overheating of the bottom layer photoresist and overexposure and overdevelopment of the top layer photoresist resulted in the poor pattern fidelity obtained here. Another attempt to create high-aspect-ratio 3D carbon arrays with a high number of dense carbon microelectrodes involved a process in which two different photoresist layers were alternated with thin gold layers, as shown in Fig. 2-2. In this case the embedded Au masks were intended to overcome the exposure thickness restriction of positive photoresists by making use of a number of repetitive exposure and development steps [20]. Realignment of photomasks is avoided in this process through the use of the multiple embedded photomasks within the resist itself. This method is very time consuming because of the requirement of multiple metal evaporation steps. Moreover, bubbling and peeling were observed in most samples after pyrolysis, as shown in Fig. 2-2(a) and 2-2(b). Making high-aspect-ratio micromolds in Si for templating of C-MEMS electrodes was also attempted. Deep etching in Si was performed to create arrays of pores, as shown in Fig. 2-3 (a) and 3(b). A low viscosity resist such as SP 1827 was spin-coated onto the Si micromold, but it was very difficult for the photoresist to flow into the deep etched pores in the Si because of residual air inside the pores and the viscosity of the resist (see Fig. 2-3(c) and 3(d)). Summarizing, the three described efforts to try to fabricate high-aspect-ratio carbon from positive photoresists all still pose considerable technical challenges to overcome.
One of the most popular deep UV thick photoresists is a chemically amplified, high contrast, epoxy based SU-8 series negative tone photoresist. SU-8 has very high optical transparency, which makes it ideally suited for imaging near vertical sidewalls in very thick films. SU-8 is best suited for permanent applications where it is imaged, cured and left in place since this photoresist is difficult to remove due to its chemical composition. A potential problem with the use of negative photoresists for the fabrication of C-MEMS structures is their oxygen sensitivity. The presence of oxygen inhibits cross-linking [10-12]. We also observed that in the initial attempts to pyrolyze negative photoresists in an oxygen-free environment we often found that the structure tended to burn rather than pyrolyze due to the dissolved oxygen remaining in the negative resist.

As shown in Fig.3(a) and 3(b), a typical SU-8 array of posts on Au/Ti/SiO₂/Si is uniform with straight walls and good edge profiles. The average height of the posts shown here is around 340 µm and the average thickness in the midsection of the posts (i.e., the rod diameter) is 50 µm. After pyrolysis, the overall structure of the cylindrical posts is largely retained, as shown in Fig.3(c) and 3(d). The height: width ratio (midsection of the posts) of the pyrolyzed material corresponds to an aspect ratio of 9.4:1. The posts have shrunk much less during the pyrolysis process near the base of the structures than at the midsection due to the good adhesion of SU-8 to the substrate. The tops of the SU-8 posts have shrunk a little less than the midsection as well, perhaps due to overexposure. Shrinkage of the posts is dependent on height. For SU-8 samples whose post heights ranged from 100 to 350 µm, after pyrolysis, the indicates the fact that different heights and sizes of SU-8 patterns induce different amounts of shrinkage during pyrolysis. In our previous work on AZ 4330, a positive photoresist, the average vertical shrinkage was around 74% while only minor lateral changes occurred after pyrolysis [5]. The minimal lateral shrinkage in this case is partially due to the fact that the positive photoresist structures we made are much thinner and, even for SU-8, close to the surface. Thus, there was less lateral shrinkage. Compared with positive photoresist, SU-8 gave less vertical shrinkage as well as better adhesion after pyrolysis.

Despite the good adhesion of SU-8, our post patterns peeled from the substrate when using a one step pyrolysis process at 900°C in a vacuum furnace. This problem was finally solved when we switched to the two step
pyrolysis procedure in \( \text{N}_2/\text{forming gas} \) as described above. The better results are most likely due to the following contributions: (I) the post-bake process cross-links the SU-8 better, enhancing adhesion of SU-8 to the substrate and (II) the SU-8 adhesion to the substrate results in tensile stress in the carbon posts near the interface and the two step heating process with its slow heating rate releases this stress more effectively. Another consideration is that slower de-gassing occurs in a forming gas atmosphere. Heat-treatment during crosslinking generates gaseous by-products and subsequent out-gassing may cause the formation of micro-cracks which disintegrate the sample. In vacuum, this out-gassing would tend to be faster and thus more destructive [11].

![Fig. 3.](image)

Fig. 3. (a) and (b): Typical SEM photos of SU-8 photoresist arrays before pyrolysis. (c) and (d): carbon post arrays after pyrolysis

The pyrolyzed SU-8 exhibits reversible intercalation/de-intercalation of lithium. In non-patterned films, the electrochemical behavior is similar to that of coke electrodes with no evidence of staging plateaus and a sloping profile [13,14]. The voltammetric sweep (not shown) is analogous to that reported by Ma et. al. with some evidence of electrolyte decomposition near 0.8 V, most of the \( \text{Li}^+ \) intercalation occurring below 0.5 V and a broad de-intercalation peak centered at 0.3 V.[15] For the galvanostatic measurements, the current was based on the C/5 rate for graphite (corresponding to 50 \( \mu \text{A} \) and 580 \( \mu \text{A} \) for unpatterned and patterned films, respectively) and cell voltages varied between 10 mV and 1 V vs. \text{Li/Li}^+. Battery performance measurements on those samples show a large irreversible capacity on the first discharge followed by good subsequent cycling behavior, which is consistent with the behavior of coke materials used as lithium electrode materials. Galvanostatic charge/discharge cycling behavior and a cyclic voltammogram of a patterned carbon array are shown in Fig.4(a) and 4(b). For a fully dense carbon film without any pattern, the capacity we obtained was 0.070 mAh cm\(^{-2}\) (~ 220 mAh g\(^{-1}\)), which is within the range of reversible capacities reported for coke [16] for the second and subsequent cycles. Furthermore, the normalized discharge capacity of a C-MEMS electrode array (180 x 180 posts with a thickness of ~ 150 \( \mu \text{m} \)) was 0.125 mA cm\(^{-2}\) for the second and subsequent cycles, exhibiting a nearly 80% higher capacity than that of the unpatterned carbon film [17]. Therefore, C-MEMS provides a promising material and microfabrication solution to the current battery miniaturization problem.
The study of transport phenomena inside a battery has attracted much attention [3]. The simulation of the current and potential distribution within the battery can provide important insights into future directions for 3D battery designs. In general, non-uniform currents result in poor utilization of the electrode materials, and are thus associated with lower cell efficiencies, reduced electrode stability due to non-uniform stresses and non uniform heat dissipation [3]. Finite element based modeling which takes into account the primary current distribution sheds some light on these issues. It is shown in Fig.5 that electric field, and therefore the corresponding current density (assuming uniform electrolyte resistance), is strongly influenced by the biasing pattern and the geometry of the electrodes themselves. The electric field distribution for a 3x3 electrode array with an alternating anode/cathode configuration is shown in Fig.5(a). The electric field gradient (and therefore power density) is larger at the edge of electrodes. The top view (Fig.5(b)) shows a colored contour of electric field with a maximum around the edges of the electrodes (on the surface) and minimum in the well-areas (in between electrodes). One of the obvious advantages of a 3D electrode is the availability of more surface area per unit volume resulting in greater overall current. As shown in Fig.5(c), the e-field is uniform along the z-axis in the case of infinite electrode boundary conditions. In the case of more realistic electrode boundary conditions where the electrode height is finite and smaller than the cell height, the depth-wise distribution is not uniform along the z-axis as seen in Fig. 5(d) and 5(e). When the depth of cell = 50 microns and the depth of electrodes = 20 microns, Fig.5(d) shows that the electric field varies through the depth with a maximum at the top of electrode and minimum at the bottom of the cell where the electrode meets the insulated bottom surface. In Fig. 5(d), the electric field magnitude is plotted on the vertical axis and the distance from the top of the electrode is plotted on the horizontal axis. The reasons for these variations are edge and boundary condition effects. The edge effects are shown in Fig. 5(e) here by taking a section (vertical plane, either zx or zy) through the middle of 3 electrodes. This electric field distribution is currently being closely studied to determine an optimum configuration for 3 dimensional electrode arrays.
Fig. 5. Modeling results of electric field distribution and current distribution for 3D carbon electrodes of microbatteries. Checkered board biasing is used. (See details in text.)

4. Conclusions

In summary, we have achieved high-aspect-ratio carbon posts (~10:1) by pyrolyzing SU-8 negative photoresist in a simple, one spin-step process. These C-MEMS array electrodes exhibit reversible intercalation/de- intercalation of lithium. Simulation results showed that the electric field distribution is strongly influenced by the biasing pattern and the geometry of the electrodes themselves. We suggest that C-MEMS constitutes a powerful approach to building 3D carbon microelectrode arrays for microbattery applications. Such arrays may be connected with C-MEMS leads and enable switching to high voltage or high current depending on the application at hand.

5. Acknowledgments

The authors appreciate Mr. Yuting Yeh and Prof. Bruce Dunn, Department of Materials Science and Engineering, University of California, Los Angeles, for experimental assistance of Li intercalation into C-MEMS.

References