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Design and Characterization of 3D Carbon MEMS for Lithium Ion Microbatteries

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Abstract

Carbon MEMS (C-MEMS) technology enables the fabrication of high aspect ratio carbon electrodes with unprecedented precision. These high aspect ratio electrodes form the basic building blocs for the fabrication of Li ion based carbon MEMS microbatteries. Fabrication and design criteria for a 3D C-MEMS microbattery is described. Methods for increasing the surface area of the resulting carbon are briefly discussed. Electrochemical impedance spectroscopy (EIS) of plasma treated C-MEMS shows a marked improvement in Lithium intercalation kinetics. High aspect ratio C-MEMS microbatteries can provide high capacities per surface area for applications where chip real estate is of paramount importance.

Keywords: Microbattery, Carbon MEMS, C-MEMS, Thin film battery, Lithium ion microbattery

1 - INTRODUCTION

Carbonaceous materials are currently used as anodes in the vast majority of current commercial Lithium ion batteries. The combination of high cyclability, good power density and safety allowed that technology to dominate the arena of portable power. Machining carbon is a very difficult task. It is even more difficult to try using standard machining tools for carbon microfabrication applications. Building microstructures out of polymers is a comparatively trivial task using techniques such as photolithography, stamping, molding, reactive ion etching, etc. Given the right conditions, these polymer microstructures can be transformed through pyrolysis into carbon structure while retaining their general shape. These carbon microstructures can serve as both the anode and the structural building block for C-MEMS based microbatteries as described by Madou et al [1-6].

When a crosslinked polymer, such as exposed SU-8 photoresist, is subjected to high temperatures under vacuum or inert atmosphere, it shrinks and transforms into carbon while keeping its general shape [7]. High aspect ratio carbon microstructures can thus be obtained (see Fig. 1). Battery architectures similar to those proposed by Hart et al. [8] can be fabricated. These microbatteries can inherently pack more active material per unit area than thin film batteries such as those developed at Oakridge National Labs. Thin Film batteries are practically limited to being just tens of microns thick because of the slow evaporation techniques used for depositing the different layers.

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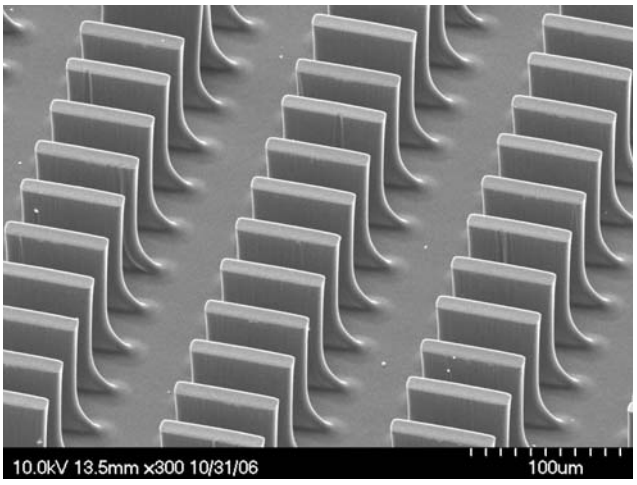

Figure 1 – SEM of 100 μm tall, high aspect ratio carbon anodes. The initial rectangular SU-8 structures were 20 μm x 125 μm with 20 μm spacing between electrodes. The initial height of the walls was almost 150 μm. Signs of shrinkage during pyrolysis are apparent near the base.

On the other hand, hundreds of microns of carbon structures are readily obtainable using the C-MEMS process (see Fig. 1).High aspect ratios carbon microstructures also provide a larger surface area for the intercalation of lithium ion which results directly in microbatteries capable of higher power densities than typical thin film batteries. The total power expected for a thin film battery to be able to support a simple RF transmitter is around 25 mw. Currently, no thin film battery is capable of supporting this power draw without covering a large surface (tens of cm^2).

2 - CARBON MEMS

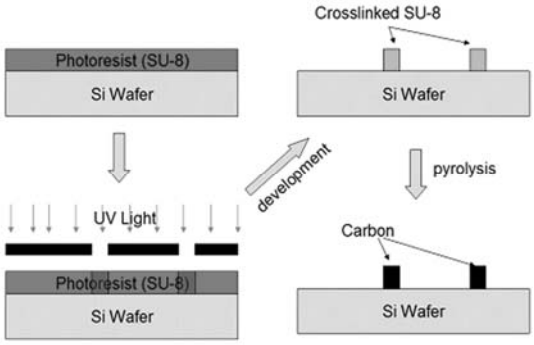

Figure 2 - The basic process flow chart for a typical C-MEMS process using SU-8 negative photoresist.

Carbon MEMS (C-MEMS) is a process that allows the fabrication of carbon structures with feature sizes as small as a few nanometers. The process starts with micropatterning a thin film of polymer using a variety of methods: conventional tool machining, molding, stamping, electrodeposition, photolithography, etc. For the purposes of this paper we will concentrate on C-MEMS that utilize Photolithography as a patterning tool.

The basic process flow is shown in Fig. 2. A photoresist is initially spin coated onto a silicon wafer to a desired thickness. Standard exposure to UV light through a photomask is used to pattern the photoresist. Further processing in an appropriate developer reveals the high aspect ratio photoresist structures. Heating the microstructures to around 900 C^o under an inert or vacuum environment pyrolyzes the photoresist and transforms it to amorphous carbon. The type of carbon obtained depends highly on the type of photoresist used. Pyrolysis of epoxy novolac resins such as SU-8 typically yields a hard carbon structure [9]. The high aspect ratio microstructures (larger than 15 in Fig. 3) achievable with SU-8 make it one of the best candidate starting material.

3 - BATTERY DESIGN AND FABRICATION CONSIDERATIONS

C-MEMS based microbattery devices can surpass the performance of thin film batteries because of their increased surface area and higher storage capacities per chip real estate.
From the analysis described by Hart et al. [8], C-MEMS microbattery architectures can offer 15 times more surface area for the intercalation of Li ion than comparable thin film batteries. A similar analysis can be applied to storage capacities per chip real estate and show that an increase of 350% can be achieved. C-MEMS microbatteries can make better use of a given area on a device than their thin film counterparts. These augmented performance numbers are based on assumptions that dense arrays of high aspect ratio C-MEMS microstructures are easily achievable.

3-1 Array Fabrication Issues

Fabricating SU-8 structures with aspect ratio's larger than 20 have been demonstrated by numerous research groups [10]. Microstructures as high as 350 microns can be obtained without exceeding fabrication time of five hours.
The fabrication of dense arrays of such structures introduces challenges related to during to the development process stage. Propylene glycol monomethyl ether acetate (PGMEA) is capable of dissolving unexposed SU-8. Isopropanol is usually used to rinse away the PGMEA after all the unexposed SU-8 has been removed. The mixture is then blow dried to reveal the high aspect ratio microstructures. At the gas/air/solid interface the liquid exerts surface tension forces on the solid structures. When the PGMEA/Isopropanol mixture is being pushed out of a developed array of high aspect ratio posts, the edge of a drop of PGMEA can encounter a symmetric post at two different heights therefore creating a bending moment on the post. This bending moment is capable of bending the post far enough to touch its neighbor in the array. Once the posts touch, stiction forces come into play and glue the posts together as seen in Fig. 3.

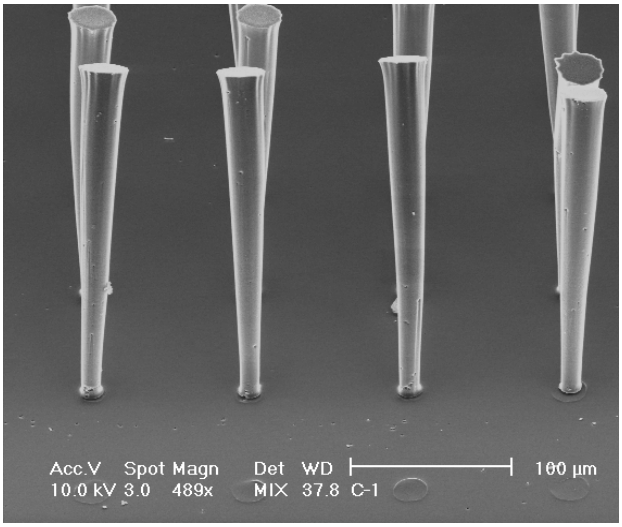

Figure 3 – SEM of 350 µm high carbon posts with an aspect ratio of around 15. The rightmost posts were bent by surface tension and held together by stiction even through the pyrolysis process.

If we assume that surface tension acts as a constant bending moment (M_y) on a post of length L with a square cross section of side (C), The maximum deflection of the beam is given by:

$$U_{z\max} = \frac{4M_y L^2}{EC^4} \qquad (1)$$

As derived from the simplified Euler-Bernoulli equations [11], this maximum deflection of a post shows a fourth order dependence on 1/C (the width of the beam) and a second order dependence on the Length L.
When considering a battery construction that incorporates a really thin electrolyte such polyphenylene oxide (PPO), increasing the surface area between cathode and anode does not lead to a big decrease in volumetric capacity. Decreasing the post size C, decreasing the distance between posts, and increasing the length L of these posts is desirable in order to maximize surface area available for Lithium intercalation.
While the practical intercalation depth of Lithium inside an as prepared C-MEMS structure is still under investigation, it can be assumed to be around 5 microns. This indicates that a smaller C is also required for better utilization of the active material. The development problem thus becomes an optimization problem that can be solved given the feature size from lithography and the intercalation depth from electrochemical experiments.
Leaving the samples to dry on their own after development does not help mitigate the problem. Sublimation drying and supercritical CO_2 [12] release methods can provide a solution to this issues but they further complicate the processing steps.

4 - SURFACE AREA ENHANCEMENTS

In an effort to fabricate anodes that can support higher current densities, an increased surface area across which the charge transfer reaction can occur is essential.
Several methods have been used in order to increase the surface area of C-MEMS Microbatteries. These methods aim towards an overall goal of creating multilevel fractal electrodes that enhance both the charge transfer through a high exchange surface area but also the current collection through a low resistance path towards metal current collectors.

4.1 - Fast Pyrolysis

During the pyrolysis step, the photoresist transforms into carbon by replacing the carbon chemical bonds with nitrogen, oxygen, and hydrogen with mostly carbon carbon bonds. During the process reactive hydrocarbon gasses are formed. It is thought that if the temperature ramp rate of the pyrolysis is made quick enough, the flow rate of the inert gases is insufficient to remove the reactive gas. These reactive gases linger close to the microstructures and react to form other gases that leave behind micropores as seen in Fig. 4. Ramp rates of around $15C^o$/min to reach $900C^o$ can produces satisfactory results Fig 4a. This microporosity can be enhanced by using even faster rates ($90C^0$/min) resulting in l0 to 15 micron pores shown in Fig. 4b.

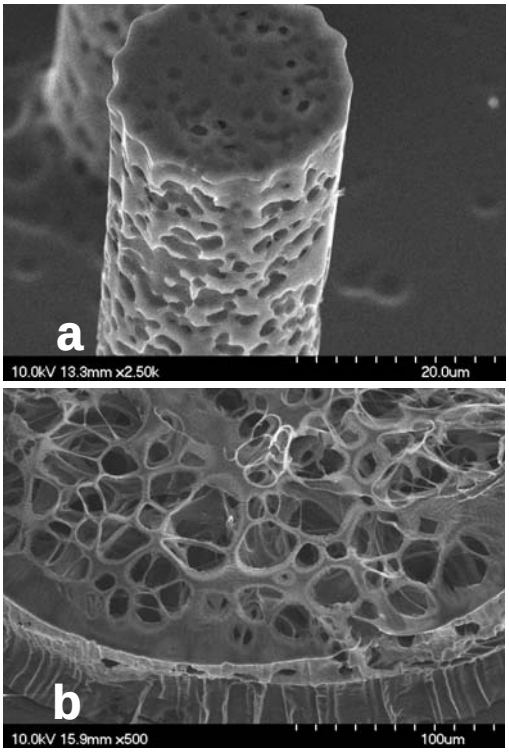

Figure 4 – SEM of Microporous C-MEMS obtained using fast pyrolysis at different ramp rates: a) $15C^o$/min and b) $90C^o$/min from room temperature to $900C^o$

4.2 - Plasma Treatment

While fast pyrolysis can make microporous high aspect ratio C-MEMS structures, treatment with oxygen plasma can increase the surface area on the submicron scale. Surface roughening was done by subjecting the pyrolysed samples to an oxygen plasma environment. Using a moderate power of 300 Watts, under 200 mT of oxygen, for 4 minutes was enough to dramatically change the texture of the C-MEMS microstructures. Two types of indentations were observed as a result of the plasma treatment: larger indentations around 2 microns in size and smaller ridges around 200 nm in width (see Fig. 5).

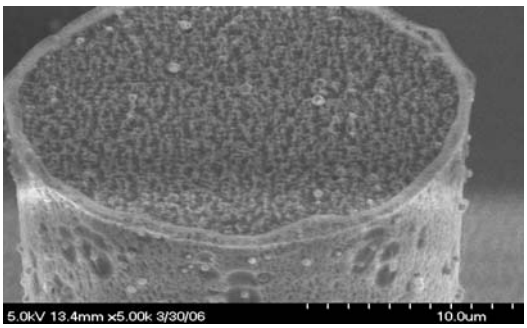

Figure 5 –SEM of C-MEMS surface after plasma treatment.

5 - ELECTROCHMICAL TESTING

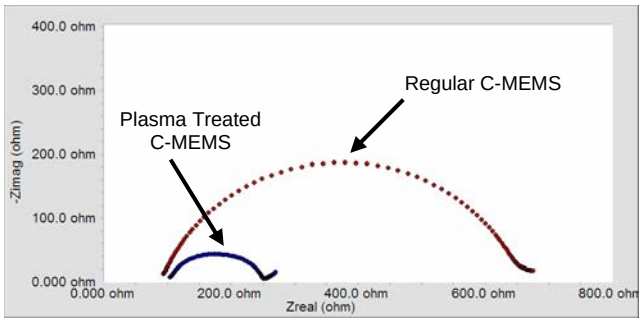

Figure 6 - Nyquist plots of EIS performed on plasma treated and untreated sample.

Electrochemical testing was conducted inside a argon glove box. The lithium intercalation was confirmed through multiple cycles in and out of C-MEMS anodes and results were previously reported in [6]

Electrochemical impedance spectroscopy (EIS) was used to evaluate the effective increase in surface area that can be obtained using oxygen plasma as an example. The tested samples were 2.7 microns thick and 1 cm in diameter. One was treated with oxygen plasma as previously described. The other control sample was left untreated. The C-MEMS surfaces were then placed in a teflon electrochemical cell as working electrodes. The counter and reference electrodes consisted of a lithium metal foil. The electrolyte used was a 1M lithium perchlorate in a 1:1 Ethylene Carbonate/Dimethyl Carbonate mixture.

EIS was performed using a 10mV rms amplitude, from 100Khz to 1Hz. A simple Randles model was used to fit the data and the resulting parameters were extracted from Fig. 6.

	Regular C-MEMS	Plasma treated C-MEMS
R_{ohmic} (ohm)	90	102
R_{ct} (ohm)	550	148
I_o ($\mu A/cm^2$)	57	216

Table 1 – Electrochemical parameters extracted from the analysis of Nyquist EIS plots.

The exchange current density, I_o, was multiplied by almost 4 which can somehow reflect an effective increase in surface area by a factor of 4 (see Table 1). This conclusion assumes that the increase in kinetics of intercalation was solely due to increase in surface area. The chemical nature of the surface as well as the bulk of the material has been probably affected and a conclusive remark is hard to make. Still Plasma treatment allows faster intercalation of lithium into carbon anodes fabricated using the C-MEMS process

6 - CONCLUSION

Fabrication considerations of high aspect ratio C-MEMS electrodes for lithium ion batteries were described. The need for different development techniques in order to achieve dense arrays of high aspect ratio has been identified. Dense arrays of high aspect ratio posts can allow C-MEMS microbatteries to outperform thin film batteries.

Fabrication of higher surface area C-MEMS structures has been demonstrated. Oxygen plasma treatment of C-MEMS has lead to a more facile lithium ion charge transfer therefore enabling higher power density microbatteries.

Acknowledgements

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