

FABRICATION OF HIGH ENERGY DENSITY CAPACITORS WITH MICROMACHINED CARBON NANOFIBER ELECTRODES

Gloria J. Kim^{1*}, Gwan-Ha Kim², and Yong-Kyu “YK” Yoon¹

¹University of Florida, Gainesville, FL, USA

²Samsung Electronics Co., Ki Heung, Republic of Korea

*Presenting Author: gloriakim@ufl.edu

Abstract: A three-step fabrication process has been implemented to generate carbon nanofiber electrodes. The method utilizes electrospinning of negative tone photopatternable epoxy SU-8, lithographical patterning, and carbonization. Taking advantage of their high surface area-to-volume ratio, low resistivity, and chemical stability, the carbon nanofibers have been applied as electrodes to fabricate high energy density capacitors. A capacitance of 1.782 nF/mm² using 45 nm SiO₂ as a dielectric layer has been obtained. Successful device implementation and enhanced performance suggest that these carbon nanofiber electrodes also hold promise in extended applications as microbattery anodes and sensor electrodes.

Keywords: electrospun nanofibers, photopatterning, carbon electrodes, high energy density capacitor

INTRODUCTION

Growing interest in renewable energy has increased the demand for high capacity electrode technology for large electric energy storage devices. Recently, Galle et al. reported a multilayer electroplating process [1], where the implemented multiple thin layers have an increased surface area by a factor of number of layers. Alternatively, conductive nanofibers are expected to provide much greater surface to volume ratio. However, an effective and manufacturable fabrication process has not been well established.

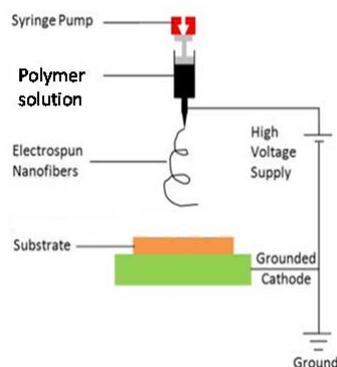
Electrospinning is a simple and cost-effective method for generating nanofibers of various materials including polymers, composites, and ceramics [2]. Yet, high capacity electrode applications based on electrospun nanofibers remain unexplored because of their non-conductive property. Even if electrically conductive nanofibers were obtained to exploit the large surface area, the narrow and long shape would raise electrical resistivity, negatively affecting charging and discharging performance. A process to form a group of conductive nanofibers patterned on a microscopic scale would rectify such slow response [3]. Carbonization of SU-8 has been known to provide outstanding electrical, mechanical, and chemical properties [4, 5].

In this work, to achieve both large surface area conductive nanofiber formation and fast response capability, we have developed a simple three-step fabrication process. The method utilizes electrospinning, lithographical patterning, and carbonization. Also, a multiple intermittent electrospinning scheme has been established to stack the electrospun nanofibers to a desired height, demonstrating the possibility of three-dimensional nanofiber electrodes. Using this process, a high energy density capacitor with improved performance has been implemented.

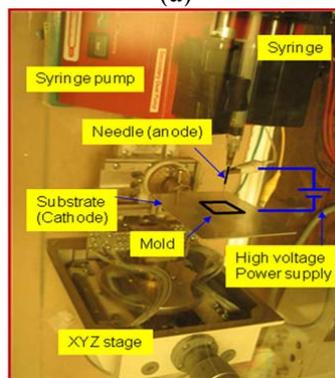
EXPERIMENTAL

Carbon Nanofiber Electrode Fabrication

The electrospinning setup consisted of an adjustable DC power supply (DEL HVPS MOD 603 30KV POS, Spellman High Voltage Electronic Corp.) capable of generating a DC voltage in a range of 0–30 kV, a syringe pump (NE-1000, New Era Pump Systems, Inc.), and a 5 ml syringe connected to a steel needle with an inner diameter of 0.2 mm. The working distance between the needle and the collector ranged



(a)



(b)

Fig. 1: Electrospinning setup: (a) schematic, (b) apparatus

from 7.5 cm to 25 cm. Positive voltages applied to the working solution were between 12.5 kV and 17.5 kV. The solution flow rates were controlled by the syringe pump at a pumping rate of 0.02 ml/min.

Negative tone photopatternable epoxy SU-8 2025 (Microchem Inc.) was chosen as the working fluid to fabricate random nanofibers. The epoxy was diluted in cyclopentanone to a solid concentration of 60.87–68.55% by weight. The prepared solution was stored at room temperature. Electrospinning was performed at room temperature under atmospheric conditions (Fig. 1).

SU-8 nanofibers produced under varying conditions had a diameter from 340 nm–3.3 μm , as determined by field emission scanning electron microscopy (FESEM: SU-70, Hitachi Inc., Japan).

A silicon wafer with 200 nm silicon dioxide grown on top was used as a substrate. To maximize uniformity and thickness of the nanofiber layers deposited on the substrate, a multiple intermittent electrospinning scheme consisting of alternating 30-second periods of continuous nanofiber growth and rest was implemented (Fig. 2a).

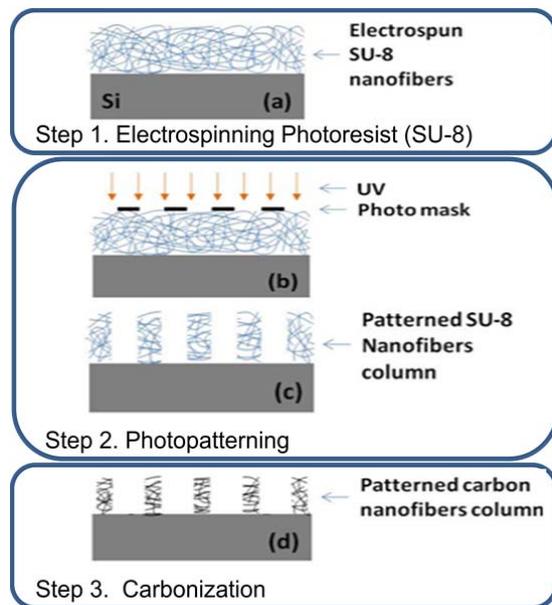


Fig. 2: Fabrication process of the patterned carbon nanofibers

The next step involved lithographical patterning of the stack of electrospun nanofibers. After stacking the SU-8 nanofibers on the silicon substrate, UV exposure (LS30, OAI, Inc., i-line, $\lambda=365\text{nm}$) was applied to the nanofibers, followed by postexposure bake and development to achieve the desired microscopic shape (Fig. 2bc).

The final fabrication step was carbonization of the patterned SU-8 nanofibers in an inert environment. A tube furnace (F79345, Thermolyne Inc.) was supplied with nitrogen gas at a gas flow rate of 1- 10 sccm. Carbonization was performed at 600 $^{\circ}\text{C}$ – 1000 $^{\circ}\text{C}$ (Fig. 2d).

Electrode Characterization

Auger electron microscopy (AES) (Microlab 310-D, Thermo VG Scientific, Inc.) analysis was conducted to verify the conversion of SU-8 to carbon. Resistivities of carbonized SU-8 thin films were measured by using a four-point probe head (C4S, Cascade Microtech, Inc.), a current source (HP 6177C, HP), a current meter (194A, Keithley Instruments Inc.), and a voltage meter (195A, Keithley Instruments Inc.) at room temperature.

High Energy Density Capacitor Assembly

The capacitor consists of two electrodes and a dielectric layer separating the electrodes. Figure 3 shows a capacitor fabrication process. Silicon oxide on a silicon wafer was used as a substrate (Fig. 3a). As a charge collecting electrode, SU-8 with a thickness of 10 μm and an area of 5 mm by 5 mm was spin coated and lithographically patterned (Fig. 3b). SU-8 nanofibers were formed using electrospinning, followed by lithographic alignment and patterning of the SU-8 nanofibers on the SU-8 pad, which would ultimately be converted to a charge collecting electrode after carbonization (Fig. 3c). Both the SU-8 nanofibers and charge collecting pad are pyrolyzed at 900 $^{\circ}\text{C}$ for an hour in nitrogen environment (Fig. 3d). The fabricated carbon nanofibers were coated with dielectric materials alumina and silica. For alumina (Al_2O_3), a 200 nm layer was applied using atomic layer deposition (ALD) by 1,200 cycles of alternating trimethylaluminum ($\text{Al}_2(\text{CH}_3)_6$) and water precursors

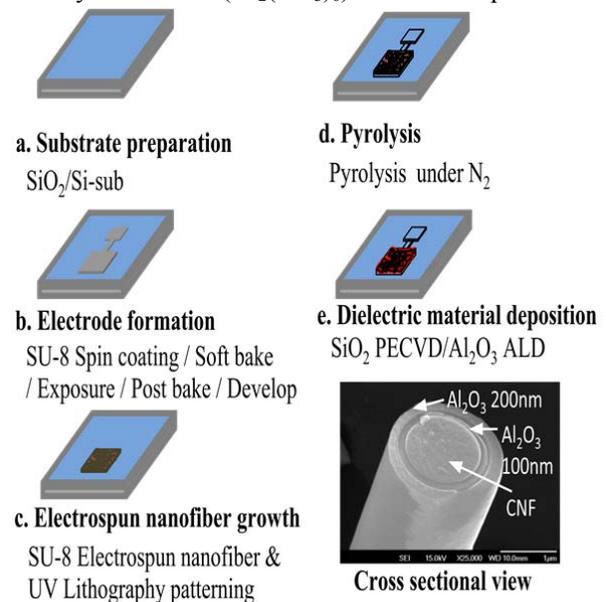


Fig. 3: Fabrication process of a high energy density capacitor

at 250 $^{\circ}\text{C}$. For silica (SiO_2), a 45 nm layer was applied using plasma enhanced chemical vapor deposition (PECVD) (Fig. 3e). A cross-sectional view of a single carbon nanofiber coated with alumina is shown in Fig. 3 as well. Each capacitor was tested in aqueous CuSO_4 solution as a counter electrode.

RESULTS AND DISCUSSION

Characteristics of electrospun SU-8 nanofibers (and thus those of the carbon nanofiber electrodes generated from their pyrolysis) can be fine-tuned by controlling parameters such as working distance between the needle and the collector, applied voltage, and concentration of the material. The average diameter of electrospun SU-8 nanofibers decreases as the travel distance increases due to: (i) solvent evaporation, and (ii) continuous stretching from the electrostatic force [6, 7]. Since electrospinning is driven by charge transport under the applied electric field, a change in applied voltage will alter the mass flow at the needle tip and hence affect the structure and morphology of the fibers [8]. In case of SU-8, higher voltages yielded larger fiber diameters. Increased SU-8 solution concentration increased viscosity, resulting in larger diameter fibers. This is consistent with previous findings that link viscosity and surface tension with the morphology of the electrospun fiber [7, 8, 9].

To realize high uniformity, high density, and high porosity nanofiber electrodes, a simple and efficient electrospinning scheme was devised. As seen in Figure 4, a stacking limit is reached after 60 seconds of continuous nanofiber deposition. This can be attributed to the residual electrostatic charge in the collected SU-8 nanofibers, which repels the subsequently deposited nanofibers of the same charge polarity. By using an intermittent approach, i.e., alternating 30-second periods of electrospinning and rest, the charge repulsion was relieved considerably. After twelve 30-second cycles, a nanofiber stack of up to 80 μm could be obtained.

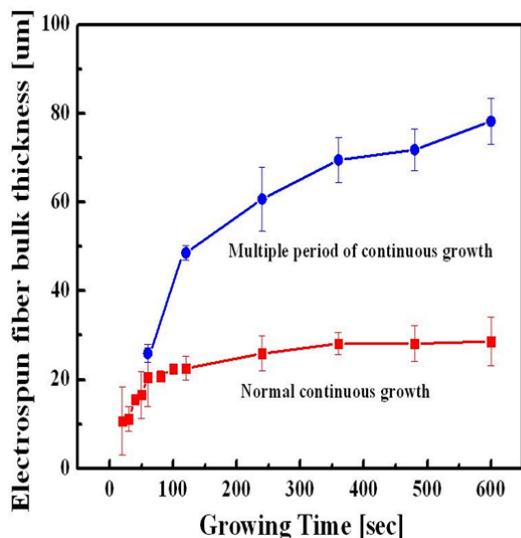


Fig. 4: Effect of multiple periods of continuous growth and normal continuous growth on nano fiber stacking

To circumvent limitations on patternable thickness

and to implement flexibility in pattern design [8], UV lithography was directly applied to the electrospun SU-8 nanofibers. The method obviated the need of additional processes such as post-lithography reactive ion etching or micro molding. Although some rough edges were observed from the nanofibers, overall shape was well defined and the original photo mask pattern was transferred with good fidelity (Fig. 5a).

The patterned nanofibers were pyrolyzed in a nitrogen purged quartz tube furnace (Fig. 5b). The resistivity of the carbon nanofibers is markedly decreased with raised pyrolysis temperature (Fig. 6), in agreement with literature [10] correlating the inverse relationship between pyrolysis temperature and resistivity with the degree of carbonization.

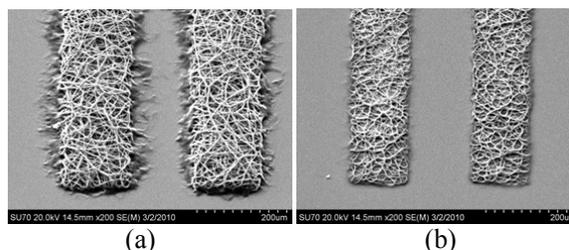


Fig. 5: SEM images of the patterned SU-8 nanofibers: (a) Before pyrolysis, (b) After pyrolysis

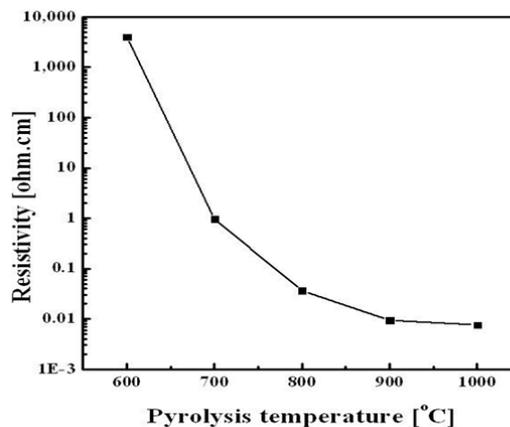


Fig. 6: Resistivity of pyrolyzed SU-8 as a function of pyrolysis temperature

Fig. 7 shows the electrode configuration for I-V curve measurement with the insert showing the magnified view of the fiber lying across a two-terminal pyrolyzed SU-8 electrode pattern. The I-V characteristics of the corresponding single fiber exhibit a linear relationship, indicating that it forms a good ohmic resistor. The calculated resistivity of $\sim 10^{-3}$ ohm \cdot cm represents the intrinsic conductivity of the fiber. Even though resistivity of the pyrolyzed SU-8 nanofiber is higher than that of metal, it has good

conductivity and is chemically stable.

High surface area-to-volume ratio, low resistivity, and chemical stability make these carbon nanofibers an excellent electrode material for energy storage applications. To demonstrate feasibility, high energy density capacitors were assembled using the carbon nanofiber electrodes and different dielectric layers. Capacitance with 45 nm SiO₂ (Fig. 8) and 200 nm Al₂O₃ thin film dielectric layer offered 1.782 nF/mm² and 0.850 nF/mm², respectively.

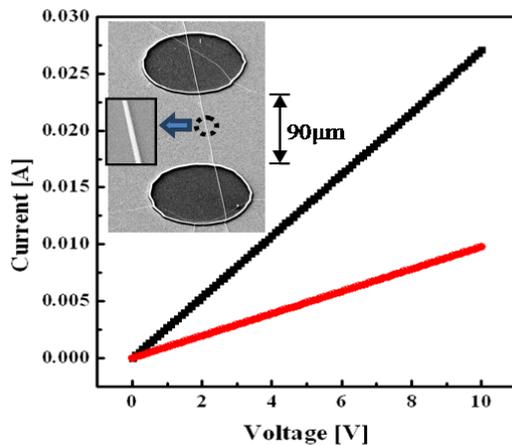


Fig. 7: Characterization of a single carbonized SU-8 nanofiber using four-point measurement

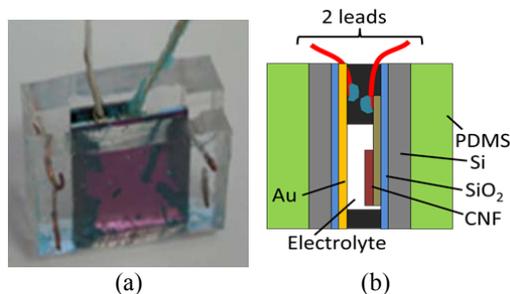


Fig. 8: Fabricated capacitor: (a) Oblique view, (b) Cross-section view

CONCLUSION

A three-step fabrication process has been implemented to generate carbon nanofiber electrodes and their application in high energy density capacitors has been demonstrated, taking advantage of the high surface area-to-volume ratio, low resistivity, and chemical stability. Successful device implementation and enhanced capacitor performance suggest that these carbon nanofiber electrodes also hold promise in extended applications as microbattery anodes and sensor electrodes.

ACKNOWLEDGEMENT

This work is in part supported by the National Science Foundation (CAREER:ECCS 1132413) and the Korea Research Foundation Grant (KRF-2008-

357-D00104). The authors would like to thank Dr. Seong-Hyok Kim and Dr. Mark G. Allen in the Georgia Institute of Technology for valuable discussion and alumina deposition.

REFERENCES

- [1] Galle P, Kim S-H, Shah U, Allen M G 2010 Micromachined capacitors based on automated multilayer electroplating *2010 IEEE International Conference on MEMS* 332-335
- [2] Huang Z-M, Zhang Y-Z, Kotaki M, Ramakrishna S 2003 A review on polymer nanofibers by electrospinning and their applications in nanocomposites *Composites Science and Technology* **63** 2223-2253
- [3] Kim G H, Kim G J, Yoon Y K 2010 Lithographical patterning and carbonization of electrospun SU-8 nanofibers for a high capacity electrode *2010 Hilton Head Workshop 2010: A Solid-State Sensors, Actuators and Microsystems Workshop* 210-213
- [4] Wang C, Jia G, Taherabadi L H, Madou M J 2005 A novel method for the fabrication of high-aspect ratio C-MEMS structures *Journal of Microelectromechanical Systems* **14** 348-358
- [5] Kim G H, Kozarsky E, Jee H S, Kim K T, Kim J, Takeuchi E, Yoon Y K 2009 Carbon nanotube embedded 3-D carbon microelectrodes for rechargeable microbatteries *AVS 56th International Symposium & Exhibition*
- [6] Doshi J, Reneker D H 1995 Electrospinning process and applications of electrospun fibers *Journal of Electrostatics* **35** 151-160
- [7] Demir M M, Yilgor I, Yilgor E, Erman B 2002 Electrospinning of polyurethane fibers *Polymers* **43** 3303-3309
- [8] Shi J, Wang L, Chen Y 2009 Microcontact printing and lithographic patterning of electrospun nanofibers *Langmuir Letter* **25** 6015-6018
- [9] Deitzel J M, Kleinmeyer J, Harris D, Beck Tan N C 2001 The effect of processing Variables on the Morphology of Electrospun Nanofibers and Textiles *Polymer* **42** 261-272
- [10] Singh A, Jayaram J, Madou M J, Akbar S 2002 Pyrolysis of negative photoresists to fabricate carbon structures for microelectromechanical systems and electrochemical applications *Journal of the Electrochemical Society* **149** E78-83