A THREE-DIMENSIONAL MICRO SUPERCAPACITOR OF HIGH SPECIFIC CAPACITANCE USING SU-8 PHOTORESIST AS SEPARATOR

H.X. Xing, X.H. Wang*, C.W. Shen, S.W. Li
Tsinghua National Laboratory for Information Science and Technology
Institute of Microelectronics, Tsinghua University, Beijing, China

Abstract: This paper reports a three-dimensional (3D) micro supercapacitor, featured by SU-8 photoresist as the separator and high-aspect-ratio electrodes. Electrochemical characterization results of the prototype with ionic liquid electrolyte demonstrate that it exhibits both large specific capacitance (311mFcm^{-2}) and high specific energy of 970mJcm^{-2} (270μWhcm^{-2}). Besides, a very robust stability and high charge/discharge efficiency (approaching to 100%) are also observed. As such, the 3D micro supercapacitor can be potentially applied to various energy systems, such as electronic backup power supplies and micro energy storage devices.

Keywords: three-dimensional electrode, micro supercapacitor, SU-8, specific capacitance

INTRODUCTION

Electrochemical capacitors, also known as supercapacitors, are promising energy storage devices that bridge the gap between batteries and conventional capacitors. Supercapactiors can provide higher energy density than conventional capacitors and much higher power density than batteries. Therefore, they exhibit a series of features such as fast rates of charge/discharge, long cycling life and high power density. According to the principles of energy storage, supercapacitors can be divided into two categories: one is the electrochemical double layer capacitor (EDLC), where electrical energy is stored by electrostatic attraction. The electrical charges accumulated by electrostatic force depend on the area of the electrode/electrolyte interface where electrochemical double layers are created [1]. EDLC can provide excellent cycling life due to fast and non-degenerative process between electrode materials and electrolyte. The other type of supercapacitor is the so-called pseudocapacitor, in which electrical energy is stored by fast and reversible redox reactions. Compared with EDLC, it has higher energy density at the cost of power density [2].

The recent development in small and portable electronic devices has increased the demand for power sources that are able to be integrated on a chip with other electronic components potentially. Micro-supercapacitors are expected to be the power sources for miniaturized electronic devices. In micro-scale systems, high performance in limited area is especially required for micro supercapacitors. Notable works have been done on micro supercapacitors and the main goal is to improve their performances in a limited area by using high-capacity active materials and 3D structures. However, the reported micro supercapacitors suffer from either low volume density of the material [3] or insufficient thickness of the electrode [4]. Nowadays, a 3D micro supercapacitor based on self-supporting electrode and deep etching techniques has been designed in our previous work [5], in which a specific capacitance of 90mFcm^{-2} has been achieved due to well-designed structure and nanoporous composite materials. However, the aspect ratio of the electrode is limited by the etching technology on the silicon substrate, the mechanical stability of the electrodes is not robust enough without a supporter.

Here, we designed and fabricated a 3D micro supercapacitor using SU-8 photoresist as the separator which not only further enhance the robustness of the electrode but also increase the thickness of electrode. The proposed method is also conducive to simplify the entire process flow and reduce the cost. The significance of this work lies in the achievement of high-aspect-ratio structure by using more simple fabrication process. Both high specific capacity per unit area and good mechanical stability of the new micro supercapacitor have been achieved.

STRATEGIES AND MATERIALS

In a limited area, the high-aspect-ratio 3D electrodes for micro supercapacitors is a potential solution to miniaturize devices which can make full use of the vertical dimension to improve the performance. Electrodes can store more energy in a fixed area by growing thicker. In the present work, an epoxy-based negative photoresist SU-8 is used as the separator, which is ideally suited for patterning high-aspect-ratio structure with nearly vertical sidewalls in various micromachining and microelectronic applications [6]. Moreover, SU-8 is insulative, chemically stable which can provides considerably strong mechanical support when it is cross-linked [7]. The scheme of the overall 3D micro supercapacitor is shown in Fig. 1. Two interdigital electrodes (black part) are formed on the current collector (yellow part) deposited beforehand and separated by a SU-8 photoresist wall (green part).

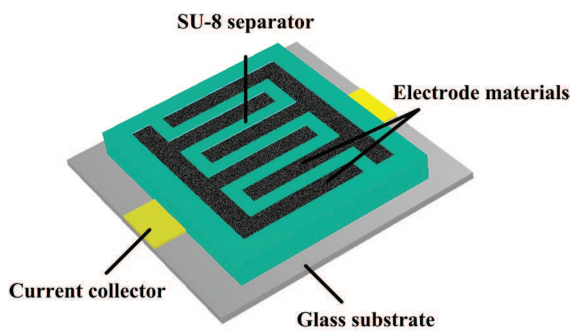

Fig. 1: Schematic of a 3D micro supercapacitor using SU-8 photoresist as the separator.

As for active materials, both good electrochemical properties and sufficient stability are of great importance for designing micro supercapacitors. Therefore, composite electrodes that combine electrochemical active material and polymer binder can meet those requirements well. Nowadays, carbon (active carbon, active carbon fibre and carbon nanotubes), transition metal oxides (R_uO_2, I_rO_2) and conducting polymers (polyaniline, polypyrrole, polythiophenes and their derivatives) have been widely used as material for the electrodes of supercapacitors. Among these, activated carbon (AC) is especially attractive as electrodes for supercapacitors due to its low cost and large specific surface area caused by porous structure. The electrode materials used in our work were prepared as follows: powder of activated carbon ($2000 m^2g^{-1}$, Shanghai Carbosino Co., Ltd.) was first mixed with carbon black to increase the conductivity. A polymer binder, CMC (carboxymethylcellulose sodium), was dissolved in deionized water, and then mixed with the above components to form a suspension. The suspension was injected into the channels and then dried in an electric oven. In this way, active materials were bound together due to the using of CMC. Polymer binder which ensures the stability of the electrode materials is necessary. However, the more amount of polymer binder are added, the more nanopores of AC are blocked by polymer molecules, the more specific surface area is sacrificed as a result. So polymer binders should not occupy a large proportion of the composite. Compared with PVDF, PTFE and other polymer binders, CMC can provide higher viscosity even in a small percent. Considering both specific surface area and stability of the electrode materials, the ratio of each component was 87wt% for AC, 10wt% for carbon black and 3wt% for CMC. The surface area test was taken to show that the designed composite has nanoporous structure with a specific surface area of $1547 m^2g^{-1}$.

The electrolyte used is another factor that affects the performance of micro supercapacitor. Although aqueous solutions have been widely used for EDLC, they suffer from narrow working voltage of no more than 1V, which limits the energy stored. Nowadays, ionic liquids have been attracted a great deal of attention due to their high thermal stability, good conductivity, wide electrochemical window and good recyclability [8-9]. For EDLCs, the size of electrolyte ions should match the pores of electrode materials, which means that the diameter of electrolyte ions should be smaller than that of micro pores in AC. In this work, 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF4]) ionic liquid is chosen as electrolyte for its ions can fit the nanoporous structure of AC well.

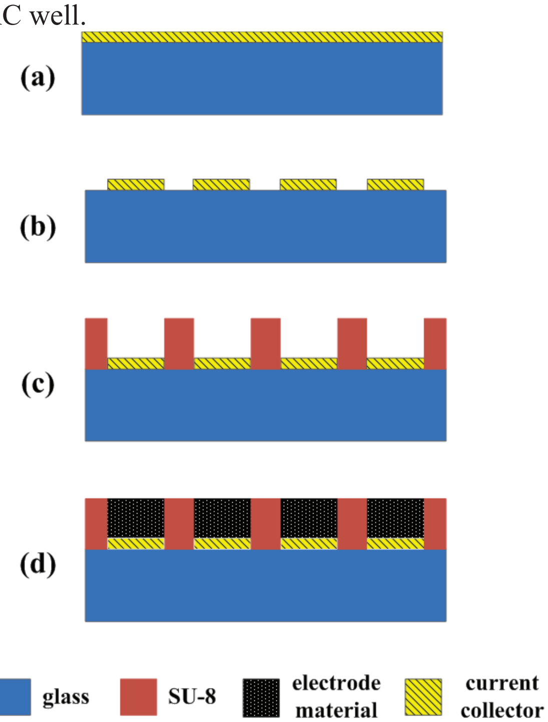

Fig. 2: The fabrication of the micro supercapacitor: (a) deposit a thin golden layer on the glass substrate; (b) form the interdigital current collector patterned by lithography; (c) coat SU-8 photoresist and remove the unnecessary part to achieve the channel by lithography; (d) fill electrode materials into the channel.

FABRICATION

The detailed fabrication process of the device is shown in Fig. 2. Glass substrate was applied in the fabrication instead of silicon with the reason that the micromachining process can be simplified without using additional insulating layer. To form interdigital current collectors, a 20nm/100nm Ti/Au layer was sputtered on the glass wafer as shown in Fig. 2a. Lithography and etching were applied to pattern the golden layer as shown in Fig. 2b. A 200μm-thick SU-8 layer was coated on the Ti/Au layer uniformly, then exposed by UV light and the unexposed SU-8 was removed, the remaining solidified SU-8 were shaped to serve as the separator of the micro supercapacitor in Fig. 2c. Assisted by a microscope, the suspension prepared beforehand was injected into the channels, and then dried under 70℃ in an electric oven. After evaporation of the solvent, the solidified materials and overall channels are shown in Fig. 3a. Each finger of the channels were created to be 300μm wide and 200μm deep, which means one finger of the electrodes was 300μm wide and 200μm thick, and the SU-8 separator between adjacent fingers was 60μm wide. Finally, the prototype was packaged by a PDMS cap using bonding technique, and [BMIM][BF4] electrolyte was injected into the electrode materials. Fig. 3b shows the photo of a sealed prototype, where the black part is the electrode materials with an area of $0.17cm^2$.

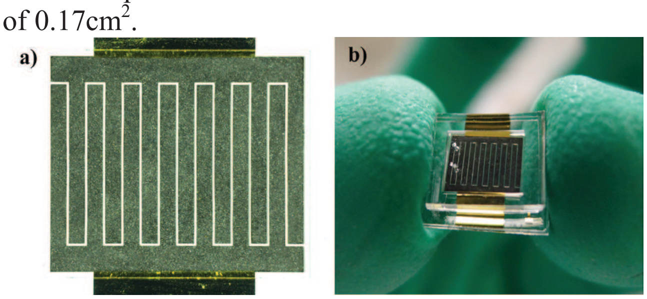

Fig. 3: Optical images of the prototype: (a) inside view of the solidified materials with SU-8. Each finger of is 300μm wide and 200μm deep, the width of SU-8 in between is 60μm; (b) image of the packaged prototype, the black part is the interdigital electrodes, the transparent part on top is a PDMS cap.

.

RESULTS AND DISCUSSION

The electrochemical properties of the prototype were characterized by CHI860D electrochemical workstation. Fig. 4 shows the cyclic voltammetry(CV) curve of the prototype with a scanning rate of 10mV/s. The nearly rectangular shape represents a very good capacitance property. The capacitance of the device C can be estimated by Eq. 1:

$$C = I \cdot (dV / dt)^{-1} \quad (1)$$

where I is the current and dV / dt is the scanning rate. At $10mVs^{-1}$, the capacitance is calculated to be 53mF. As the effective area of the prototype is $0.17cm^2$, and a specific capacitance of $311mFcm^{-2}$ is calculated. The measured capacitance per unit area of the micro supercapacitor is obviously larger than other reported ones [3-5]. The essential reasons are the heavy load of the electrode material per unit area and the large specific capacitance of active materials.

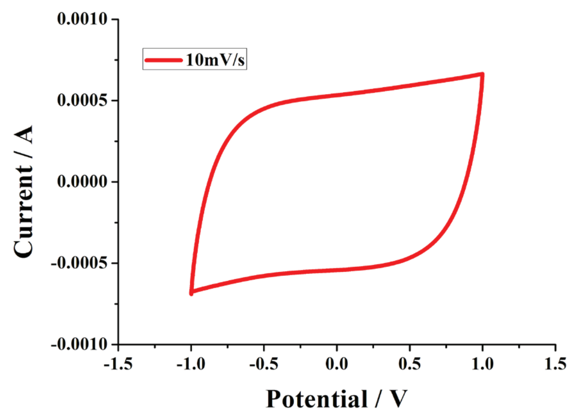

Fig. 4: CV curve of the device at a scanning rate of $10mVs^{-1}$.

Galvanostatic charge/discharge tests were also applied under a current of $1mAcm^{-2}$, shown in Fig. 5. Due to the using of ionic liquid, the working voltage of the device can be expended to more than 2V. Therefore, our device were charged to different potentials, the charging half and discharging half of the curves are both straight lines, which indicates low internal resistance. This charge/discharge efficiency here is approaching to 100%, for the charge time is nearly equal to discharge time, which illustrates the complete reversibility of the charges stored on the double layers. A discharge capacitance can also be deduced from the curve after the IR drop, according to Eq. 2:

$$C = \frac{I \cdot \Delta t}{S \cdot \Delta V} \quad (2)$$

where I is the current, Δt is the discharge time corresponding to the discharge voltage range ΔV and S is the effective area of the prototype. The result is $308mFcm^{-2}$ in this calculation, which is close to the value from CV test. And also, the specific energy of the prototype can be calculated according to Eq. 3:

$$E = \frac{1}{2} CV^2 \quad (3)$$

where E is the stored energy of the device, V is the reached maximal working voltage, and C is the specific capacitance estimated before. A specific energy of 970mJcm^{-2} (270μWhcm^{-2}) is calculated in the galvanostatic charge/discharge tests.

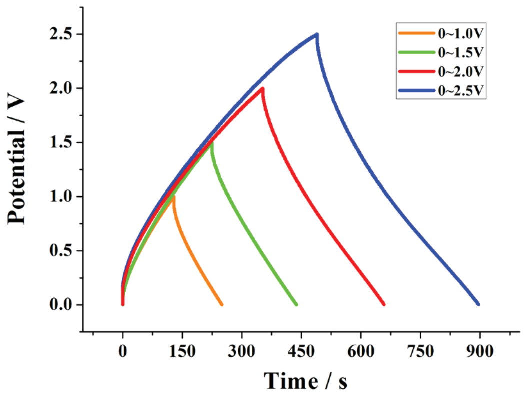

Fig. 5: Galvanostatic charge/discharge curves of the device under a constant current of 1mAcm^{-2}.

The device presented in this paper shows highly competitive specific capacitance and stored energy compared to previous ones, Asisted by SU-8 photoresist, electrodes with the thickness of 200μm are achieved. Besides, the measured capacitance per unit area of this micro supercapacitor even triple that of our previous work (90mFcm^{-2}). [BMIM][BF4] is chosen as the electrolyte to expend the working voltage from 1V to 2.5V, which leads to a much higher specific energy density of 970mJcm^{-2} compared to 45.4mJcm^{-2} calculated before[5]. In general, the newly designed micro supercapacitor has additional advantages including simplified fabrication process, improved mechanical stability and overall good performance.

CONCLUSIONS

A 3D micro supercapacitor of high specific capacitance has been designed, fabricated and characterized. SU-8, the epoxy-based negative photoresist, which serves as the separator for interdigital electrodes is applied to achieve a high-aspect-ratio structure. A large specific capacitance of 311mFcm^{-2} has been achieved in this paper, which is attributed to the combination of the well designed 3D structure and the composite porous active materials. The energy density of the device is significantly promoted, which reaches as high as 970mJcm^{-2} due to both high specific capacitance and the expanded working voltage range by using ionic liquid as electrolyte. We believe this micro supercapacitor built by compatible fabrication method will be applicable to some micro systems such as electronic backup power supplies and micro energy storage devices.

ACKNOWLEGEMENTS

This work is supported by the National Natural Science Foundation of China (No. 60936003), 973 program (No. 2009CB320304), and 863 program (No. 2009AA04Z319) of China. We also wish to acknowledge the technical support of Beijing CapitalBio Co., Ltd. In particular, the authors would like to thank the other members of Prof. Xiaohong Wang's group in Institute of Microelectronics, Tsinghua University, for the helpful discussions.

REFERENCES

[1] B. E. Conway 1999 *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications* (Kluwer Academic/Plenum Publishers).

[2] Elzbieta F., Francois B., 2001 Carbon materials for the electrochemical storage of energy in capacitors *Carbon* **39** 937–950.

[3] Y. Q. Jiang 2009 Planar MEMS supercapacitor using carbon nanotube forests *MEMS2009* (*Sorrento, Italy, January 25-29*) 587-590.

[4] C.W. Shen, X.H. Wang, 2011 A Novel Three-Dimensional Micro Supercapacitor Using Self-support Nano Composite Materials *MEMS2011 (Cancun, MEXICO, January 23-27)* 1285-1288.

[5] C.W. Shen, 2011 A high-performance three-dimensional micro supercapacitor based on self-supporting composite materials J*ournal of Power Sources* **196** 10465-10471.

[6] Dey P.K., Pramanick B., 2010 Microstructuring of SU-8 resist for MEMS and bio-applications *International Journal on Smart Sensing and Intelligent Systems* **3** 118-129.

[7] Bettiol Andrew A, Yan Yuanjun 2012 Radio frequency plasma pre-treatment for selective electroless Ag coating of three dimensional SU-8 microstructures, *Conference on Advanced Fabrication Technologies for Micro/Nano Optics and Photonics* (*January 24-25*).

[8] Anderson J. L. 2002 Characterizing ionic liquids on the basis of multiple solvation interactions *Journal of the American Chemical* **124** 14247-14254.

[9] Wang S. F., Chen T 2007 Effects of hydrophilic room-temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate on direct electrochemistry and bioelectrocatalysis of heme proteins entrapped in agarose hydrogel films *Electrochemistry Communications* **9** 1709-1714.