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Fabrication of a symmetric micro supercapacitor based on tubular ruthenium oxide on silicon 3D microstructures

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HIGHLIGHTS

- We have fabricated a micro supercapacitor with 3D microelectrode processed through ICP technique.
- Hydrous ruthenium oxide with tubular morphology is successfully synthesized by means of the cathodic deposition technique.
- "Grassy micro prominence" on surface of Si arrays is believed to be micro template for cathodic electrodeposition process.
- Specific geometric capacitance and gravimetric capacitance of microelectrode reach 99.3 mF cm^{-2} and 70 F g^{-1}, respectively.
- Specific geometric capacitance of micro supercapacitor reach 23 mF cm^{-2}.

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ABSTRACT

A micro-supercapacitor with a three-dimensional configuration has been fabricated using an ICP etching technique. Hydrous ruthenium oxide with a tubular morphology is successfully synthesized using a cathodic deposition technique with a Si micro prominence as a template. The desired tubular $RuO_2 \cdot xH_2O$ architecture facilitates electrolyte penetration and proton exchange/diffusion. A single MEMS electrode is studied using cyclic voltammetry, and a specific capacitance of 99.3 mF cm^{-2} and 70 F g^{-1} is presented at 5 mV s^{-1} in neutral Na_2SO_4 solution. The accelerated cycle life is tested at 80 mV s^{-1}, and satisfactory cyclability is observed. When placed on a chip, the symmetric cell exhibits good supercapacitor properties, and a specific capacitance as high as 23 mF cm^{-2} is achieved at 10 mA cm^{-2}. Therefore, 3D MEMS microelectrode arrays with electrochemically deposited ruthenium oxide films are promising candidates for on-chip electrochemical micro-capacitor applications.

1. Introduction

The rapid development of micro-electro-mechanical systems (MEMS) and microelectronics enables the miniaturization of systems. Microsystems with integrated sensors, actuators and control circuits have been used in various areas, such as the automotive and microelectronics industries, as well as space exploration, biomedical research and healthcare [1]. In these applications, micro-batteries [2] are the leading potential power sources, while other candidates [3] continue to emerge, such as miniaturized solar [4] and mechanical vibration energy harvesters [5]. However, the limited life span of micro-batteries is a major problem when these batteries must be integrated into inaccessible systems where maintenance and replacement are impossible. In addition, micro-batteries are ineffective during low temperature or high power applications, such as wireless transmission. Micro-supercapacitors can be paired with either micro-batteries to enhance their peak power and cycle lifetime or energy harvesting devices to store the generated energy. Moreover, micro-supercapacitors with a high energy density can work as stand-alone and maintenance-free power sources during numerous applications.

Recent efforts in the micro-supercapacitor field have focused on increasing the energy and power densities by improving the material properties and architecture of the devices [6–11]. Most of the reported micro-supercapacitors have a shared platform of inter-digital electrodes. Activated carbon powder was ink jet-printed on inter-digital gold current collectors by Pech et al. [12], producing micro-supercapacitors with a 27 mF cm^{-2} geometric capacitance. Jiang fabricated a double layer supercapacitor utilizing vertically aligned 80-μm-high carbon nanotube forests on silicon

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wafers, generating a capacitance density of 428 μF cm^{-2} and a power density of 0.28 mW cm^{-2} [13]. Xue fabricated solid-state electrochemical micro-supercapacitors using photolithography, electrochemical polymerization and solution casting techniques [14]. Sun reported the electrochemical fabrication of three-dimensional (3D) polypyrrole (PPy) electrode architectures for micro-capacitors with a geometric capacitance and a specific power of 29 mF cm^{-2} and 2.2 mW cm^{-2}, respectively [15].

Three-dimensional (3-D) architectures offer new approaches for miniaturized power sources. These micro devices are designed to have a small footprint while providing power and energy density sufficient for operating autonomous MEMS devices and microelectronic circuits. Beidaghi developed activated C-MEMS structures for micro-supercapacitor applications [16]. These micro-capacitors presented specific capacitances up to 75 mF cm^{-2} at 5 mV s^{-1} after electrochemical activation. The energy density of this micro-capacitor was further improved by conformally coating PPy on the C-MEMS structures [17]. The electrochemical characterizations revealed that these micro-capacitors could deliver a specific capacitance of approximately 162.07 mF cm^{-2} at 20 mV s^{-1}. The recent advances in the design and fabrication of on-chip micro-supercapacitors were comprehensively reviewed by Beidaghi and Wang [18].

There are a few reports in the literature regarding micro-supercapacitors containing ruthenium oxide pseudo-capacitive materials. Liu revealed micro-supercapacitors with hydrous RuO_2 interdigital electrodes that exhibited a specific capacitance of 10.5 mF cm^{-2} at 50 mV s^{-1} [19]. However, the capacitance in the studies mentioned above dropped quickly at higher scan rates. The high internal resistance and limited surface area of the planar electrode caused this behavior. Arnold employed laser direct write and micromachining to fabricate high capacity hydrous ruthenium oxide micro ultracapacitors [20]. The specific capacitance of the laser-deposited materials was comparable to reported values of 720 F g^{-1}. Sugimotoa synthesized the RuO_x electrodes by electrodeposition using a lyotropic liquid crystal template method [21]. The ordered mesoporous RuO_x on an inter-digitated array electrode afforded specific capacitance of 400 F g^{-1}. Pt@RuO_2 core shell nanotube arrays were prepared by electrodepositing RuO_2 on Pt nanotubes and evaluated as micro-supercapacitor electrodes by Ponrouch [22]. The specific geometric capacitance for the RuO_2 core shell nanotube electrodes was 320 mF cm^{-2} at 2 mV s^{-1} and 256 mF cm^{-2} at 500 mV s^{-1}, thus demonstrating the high utilization factor of RuO_2 due to the facilitated proton and electron transport. Hydrous RuO_2 nanotubular array electrodes were synthesized using an anodic deposition technique by Hu [23]. The specific power and energy density of the annealed $RuO_2 \cdot H_2O$ nanotubes were 4320 kW kg^{-1} and 7.5 Wh kg^{-1}, respectively, revealing the characteristics of next-generation micro-supercapacitors.

This study introduces a different approach toward improving the energy and power density of micro-capacitors by combining a Si MEMS current collector with a high surface area and a pseudo-capacitive ruthenium oxide film with a high capacitance. The inductively coupled plasma (ICP) etching and focused-ion-beam method (FIB) techniques were used to fabricate 3D current collectors for micro-supercapacitors. The ruthenium oxide was electrochemically deposited on the pre-etched MEMS arrays to generate a pseudo-capacitive micro cell. This research employed the "grassy prominence" phenomenon for the first time; this distinctive behavior arises during the ICP etching of Si MEMS used as the template for growing the pseudo-capacitive film. A ruthenium oxide film with a unique tubular appearance was electrodeposited on the above-mentioned structure and studied in detail for the first time. Cyclic voltammetry and galvanostatic charge–discharge experiments were conducted to evaluate the electrochemical performance of both a single microelectrode and entire symmetric cells. Utilizing a microstructure in the 3D current collector improved the charge storage properties and the cycle life of ruthenium oxide-based micro-supercapacitors.

2. Experimental

2.1. Design of the micro-supercapacitor

Fig. 1 provides the schematic and processing flow of an MEMS supercapacitor with a 3D structure. It contains a Si structure with a 3D configuration, a layer of SiO_2, a conformal Au layer for the current collector and a continuous layer of electro-active ruthenium oxide. The total footprint area of a typical 3D electrode is 2 × 2 mm and contains 832 pillars that are 50 μm in diameter. The distance between the centers of adjacent pillars is 75 μm, and the pillars are 80 μm high. Structuring and fabricating the electrodes in a 3D configuration generates a higher effective surface area in the device footprint compared to thin film or 2D interdigital electrodes. The fabrication process can be summarized as follows: Step 1 involves etching the silicon substrate with integrated 3D structures using ICP. Step 2 involves applying Au on the surface of the Si substrate via conformal radio-frequency (RF) sputtering. Step 3 involves etching a deep electrical isolation trench using FIB. Step 4 involves conformally electrodepositing ruthenium oxide on the surface of the metallic layer.

2.2. Fabrication of 3D MEMS structures

This experiment applied the BOSCH ICP process. The detailed procedure for fabricating 3D structures was as follows: first, a 200-nm-thick Al layer was deposited on a cleaned Si substrate using RF sputtering under a 100% Ar atmosphere at room temperature. Afterward, the Al layer was structured in a side-by-side pattern using photolithography and wet etching for use as an ICP protection mask. Furthermore, the high-aspect-ratio ICP process was carried out with an STS LPXICP ASE - SR (Britain) to form the 3D structure, while using SF_6 as the etching gas and C_4F_8 as the passivation gas. After removing the Al mask, the conformal SiO_2 layer was formed as an insulator using thermal oxidation. Next, traditional RF sputtering was used to deposit the conformal Au current collectors on the surface with an FHR MS 100X6-L (German). Finally, FIB was carried out with a ZESS FIB/SEM AURIGA (German) in a mediate position to avoid contact (short circuit) between the two microelectrodes.

2.3. Preparation of ruthenium oxide films

Electrodeposition was used to add the ruthenium oxide film to the 3D MEMS Si/Au samples. The two electrodes in each device were connected, and the device was used as the working electrode in an electrochemical cell. Platinum wires served as the reference and counter electrodes. Ruthenium oxide was deposited on the MEMS current collectors using an electrolyte solution containing 5 mmol L^{-1} $RuCl_3$ and 200 mmol L^{-1} $NaNO_3$ at 500 mA cm^{-2} for 500–2000 s. The film prepared was rinsed and dried at 100 °C for approximately 30 min. To remove the effect of leakage current on calculation for capacitance of single electrode, all samples were subjected to cyclic voltammetric charge/discharge with a scan rate 80 mV s^{-1} for more than 200 cycles prior to other experimental investigations. The mechanism for the formation of RuO_2 from the $RuCl_3 \cdot nH_2O$ precursor is very complicated. The hydrated ruthenium chloride is a heterogeneous ionic material with an average ruthenium oxidation state between 3 and 4 [24,25]. Cathodic