Electrochemical Characteristics of a vertical array of MnO_2 Nanowires Grown on Silicon Substrates for Lithium Ion Rechargeable Microbatteries

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ABSTRACT

We are developing a complementary metal-oxide-semiconductor (CMOS) compatible process for fabricating on-chip microbatteries by growing MnO_2 nanowires as cathodes on silicon dioxide (SiO_2)/silicon (Si) substrates. High aspect-ratio anodized aluminum oxide (AAO) templates integrated on SiO_2/Si substrates can be exploited for fabrication of a vertical array of nanowires having high surface area [1]. These nanowire arrays grown on SiO_2/Si substrates were investigated in terms of electrochemical properties as cathodes. Measurements on the cells assembled with a Li anode and liquid electrolyte resulted in a cathode specific capacity of about 125 mAh/g.

Keywords: Nanowire cathodes, high surface area, microbattery

INTRODUCTION

Conventional rechargeable Li-ion rechargeable batteries have limited capacity and charge/discharge rates. The lack of a small, dependable power source has prevented many small electronic applications from reaching commercialization. The challenge has been to develop smaller, thinner, more reliable rechargeable batteries for applications such as RFID tags, implanted medical devices, surveillance devices, etc. By increasing the surface area of the cathodes, advanced microbatteries can offer significantly higher capacities [2]. West et al, reported investigation of electrochemical properties of electrodeposited *free-standing* MnO_2 nanowires for Li-ion rechargeable batteriesIn. However, this process is not easy to be incorporates into CMOS process. In this study, one-dimensional nanowire shaped manganese oxide on silicon chip has been developed using anodized alumina templates. The advantages of nanowire-based active materials are as follows: 1) 1D geometry of nanowires provides better accommodation of the large volume changes which results in improved cycle performance of the cathode materials, 2) nanowires give a very large electrode surface area and surface to volume ratio to contact with electrolyte which provides conducting pathways for lithium ion and electron which enables efficient charge transport through the electrodes. Thus these advantages can allow fast kinetics, which means improvement of the rate capability. Here we report the preparation and electrochemical properties of MnO_2 nanowires fabricated by electrodeposition which can provide superior performance, while utilizing a low-cost fabrication process.

EXPERIMENTAL RESULTS

The fabrication sequence to grow vertical arrays of MnO_2 nanowires on SiO_2/Si substrates consists of the following steps as shown in Fig 1. (A) First, 1μm thick Aluminum (Al) is sputtered on a SiO_2/Si substrate. (B) Anodization with 0.1M Oxalic acid is performed at a constant voltage of 20V. This process initiates growth of cylindrical pores from surface of Al film. Hexagonal-shaped ordered arrays of alumina nanopore templates with uniform size cylindrical pores can be resulted from this process. Pore dimensions of 10 nm to 200 nm can be controlled by anodizing conditions. (C) Electrodeposition is performed to grow about 1μm long MnO_2 nanowires. MnO_2 nanowires were electrodeposited using a bath prepared by mixing 0.5M H_2SO_4 and 0.5M $MnSO_4$ with galvanostat control at 10mA/cm^2. (D) Finally, wet etching with 1M NaOH is performed to realize exposed vertical arrays of MnO_2 nanowires on a SiO_2/Si substrate. A scanning electron microscope (SEM) image of the vertical array of MnO_2 nanowires grown on a SiO_2/Si substrate obtained after electrodeposition and a subsequent wet etching processes is shown in Fig. 2. It shows the diameter of MnO_2 nanowires is found to be about 80 nm.

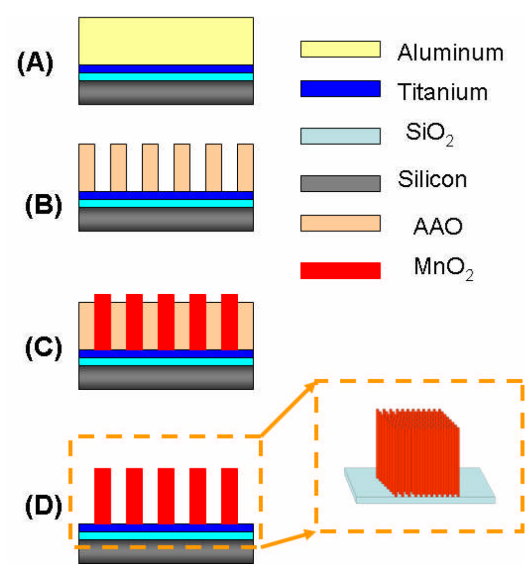

Figure 1: Fabrication of a vertical array of MnO_2 nanowires grown on a SiO_2/Si substrate: (A) Deposition of 1 micron thick Al layer on SiO_2/Si. (B) Anodization to fabricate an AAO consisting of a vertical array of cylindrical pores. (C) Growth of MnO_2 nanowires by electrodeposition. (D) Wet etching to realize the exposed vertical arrays of MnO_2 nanowires.

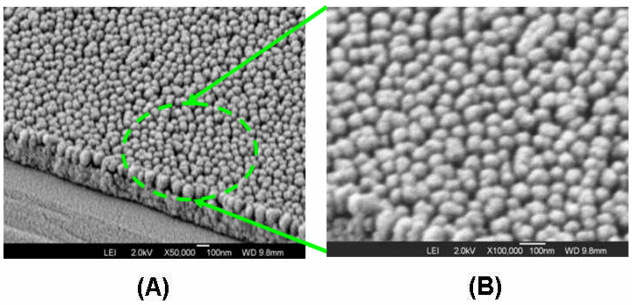

Figure 2: FESEM micrographs of a vertical array of MnO_2 nanowires grown on a SiO_2/Si substrate (A); zoomed image of a circled area in (A). A diameter of nanowires is about 80 nm.

Fig. 3 presents voltage profiles of the vertical array of MnO_2 nanowire grown on SiO_2/Si substrate as cathodes, which was cycled at a constant current of 50 mA/g [3]. The first discharge and charge capacities are approximately 125 and 100 mAh/g, respectively. It is observed that there is no plateau in the voltage profiles, which means the crystal structure of electrodeposited MnO_2 nanowires is amorphous. The electrochemical properties of the MnO_2 electrode can be modified by some methods like heat treatments [4].

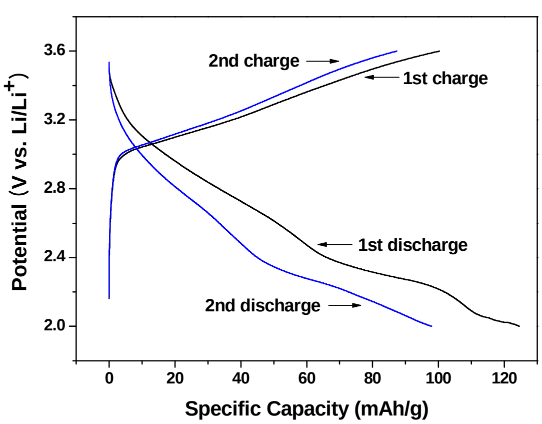

Figure 3: Voltage profiles of the MnO_2 nanowires grown electrode for the first two cycles. The first charge/discharge curves are plotted in black and the second charge/discharge curves are in blue.

CONCLUSIONS

We're developing a novel CMOS compatible process which can realize a fabrication of on-chip microbattery using vertical arrays of MnO_2 nanowires as cathodes. We have investigated electrochemical characteristics of vertical arrays of MnO_2 nanowires. Our novel process has the potential to increase effective cathode surface area by a factor of at least five and has the potential to reduce the cost of cathode fabrication by a factor of at least ten.

ACKNOWLEDGEMENTS

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