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Synthesis of Zr doped NiO layers on $NiSi_2$/Si–MCP structures for supercapacitors

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***Abstract*—Three-dimensional supercapacitors consisting of $NiSi_2$/silicon microchannel plates (MCPs) with Zr doped NiO layers have been fabricated. The silicon MCPs produced by electrochemical etching is utilized as a backbone of the 3D structure. Nickle layer was deposited on silicon MCP by electroless chemical deposition. The active Zr doped NiO film and $NiSi_2$ layer are synthesized on the surface of the Si-MCP by annealing the backbone coated by a Zr doped nickel layer under oxygen at 500°C. The multi-layered electrode materials are characterized by field emission scanning electron microscopy (FESEM) and the electrochemical properties are determined by cyclic voltammetry (CV). In addition, the electrochemical properties of the $NiSi_2$/silicon MCP structure with pure NiO layers and the $NiSi_2$/silicon MCP structure with Zr doped NiO layers are compared.**

Keywords- Zr doped NiO; Electrochemical properties; Silicon microchannel plate

I. INTRODUCTION

In recent years, electrochemical capacitors, that possess higher power density than traditional ones, have been exploited extensively to meet the increasing demand of portable electronic devices and electric vehicles [1]. Silicon microchannel plates (Si MCPs), as well as other nanostructured materials, have large specific surface areas and been verified to be a candidate for the application of supercapcitance [2].

Transition metal oxides such as manganese oxide, cobalt oxide, and nickel oxide can be used in electrochemical capacitors [3]. Among the various types of nano-scale materials, nickel oxide (NiO) has attracted much attention for its use in photovoltaic devices, catalysis, fuel cell electrodes, gas sensors, and magnetic devices [4]. The dielectric permittivity of nickel oxide is 11.9 at 25°C [5]. However, the generation of a NiO layer cannot be avoided when the sample is thermally processed in atmosphere containing oxygen after nickel deposition. It has been reported that Li and Zr co-doped ceramic materials exhibit high dielectric permittivity (10^3-$10^{4)}$ in a wide temperature and frequency range [6-8], and also Zr doped NiO possesses high dielectric properties [9,10].

In this work, Si MCPs were made by elecrochemical etching. Deposition of Ni and oxidation to obtain super capacitance has been investigated by our group [2] and NiO is indeed an obstacle hindering further improvement of the performance of the capacitors [11]. In this paper, the silicon MCPs were coated by a Ni layer and a Zr doped Ni layer with electroless plating respectively, then the active Zr doped NiO film and $NiSi_2$ layer, and the NiO/$NiSi_2$ layer are synthesized respectively on the surface of the Si-MCPs by annealing the backbones under oxygen at 500°C. FESEM and cyclic voltammetry were carried out to characterize the samples. The specific capacitance of the sample with Zr doped NiO layer and pure NiO layer was compared to confirm that the performance enhancement of the capacitor was due to Zr doping.

II. EXPERIMENTAL DETAILS

The substrates used in this work were 525 μm thick p-type <100> silicon wafers. A layer of silicon oxide was initially grown by thermal oxidation as a masking layer on the surface of the wafer and then 3 μm × 3 μm squares were patterned on the surface by lithography and wet etching [12]. Then the silicon MCP was formed by electrochemically etching of the silicon in a hydrofluride solution, and finally, the silicon microchannel layer could be peeled from the Si substrate, it was cut into 1 cm × 1 cm squares for further fabrication. The fabrication process of the 3D architecture is succinctly illustrated in Fig. 1.

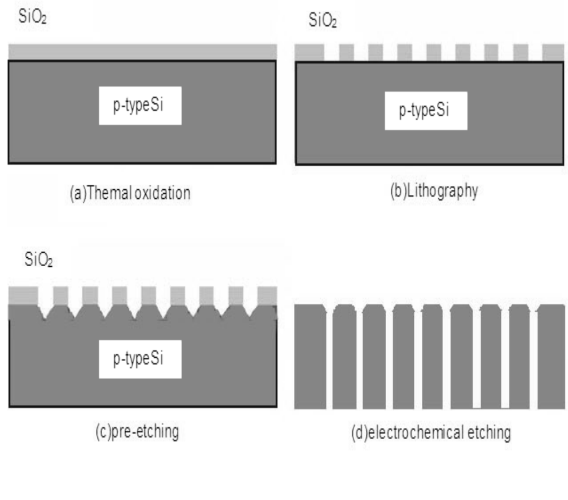

Figure 1. Process of the silicon MCP

The electroless plating solution for the preparation of the nickel coatings contained 50 ml water and materials as shown

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in Table 1. The samples were at first put in a 1:100 Triton X-100 solution for 30 seconds for wetting enhancement. The smooth Zr-doped Ni layer and pure Ni layer were formed in a solution at 80℃ for 30 min to cover all the surface area of the silicon MCP. Afterwards, the samples were rinsed with de-ionized water. In this work, the sample with the pure NiO layer is designated as S_1 and the other sample with Zr doped NiO layer is labeled as S_2.

TABLE I. MATERIALS AND CONDITIONS USED IN THE ELECTROLESS PLATING (* ADDED FOR ZR DOPING).

Chemical name	***Concentration[g]***
$NiSO_4 \cdot 6H_2O$	13.7
* $Zr(SO_4)_2 \cdot 4H_2O$	0.88
Sodium dodecyl sulfate	0.03
NH_4F	12.27
Sodium citrate	3
$(NH_4)_2SO_4$	3.3
Ammonia	x (pH adjusted to 8.0-9.0)

Finally, the $NiO/NiSi_2$/Si-MCP and $NiSi_2$/Si-MCP with Zr doped NiO layer (Fig. 2) electrodes were fabricated by thermal treatment in oxygen at 500℃ for 5 min. The morphology of the samples was examined by FESEM. The electrochemical analysis was performed in an undivided cell comprosing the sample as a working electrode, a platinum counter electrode, and an SCE reference electrode. The electrolytic solution was 2M KOH and the electrochemical properties were determined by cyclic voltammetry (CV).

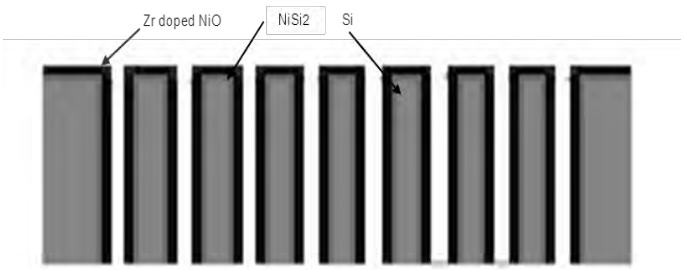

Figure 2. Structure of the Zr doped NiO /$NiSi_2$/Si-MCP electrodes.

III. RESULTS AND DISCUSSION

A. Morphologies

The top-view SEM images of sample S_1 and S_2 after annealing at 500℃ are depicted in Fig. 3. Picture (a) is the cross section of S_1. Thin NiO layers are found on the surface of the channels. In the picture (b), regular square windows can be found apparently, which is 3D ordered Ni/silicon MCP array. The picture (c) is a magnified picture of (b) and small scraggly matters can be found on the surface of the sidewalls, which are active materials. The morphologies of sample S_1 [2] is approximately the same as S_2.

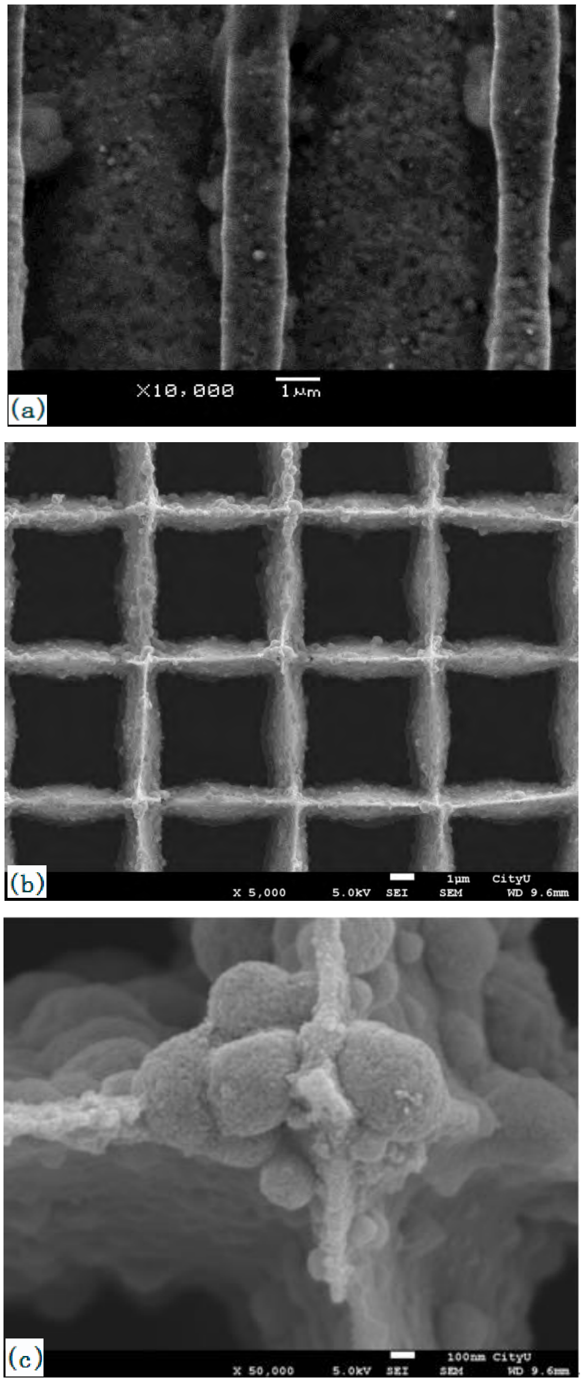

Figure 3. (a)The cross section SEM image of the 3D structure with NiO. (b) Top-view FESEM image of the 3D structure with Zr doped NiO. (c) A magnified picture of (b)

B. Electrochemical properties

Cyclic voltammogram (CV) is frequently used to characterize the electrochemical behavior of electrode materials. Fig. 4 shows that the structure with the pure NiO layers has a smaller current response than the structure with the Zr doped NiO layers and the details of the comparison. The sweeping time is 10 mV/s and the peak potential of these two materials is approximately the same. However, the peak-peak current value of S_2 is twice than that of S_1. The loop curve area of S_2 is 3.2 times of S_1, indicating that Zr doped layers have a better capacitive response according to the difference in the areas.

Fig. 5 shows the CV of sample S_2 after annealing at 500℃ in a 2M KOH solution at different sweeping rates within the potential range from -0.6 V to 0.1 V. Here, the curves show apparent current increase as the sweeping rate gets larger.

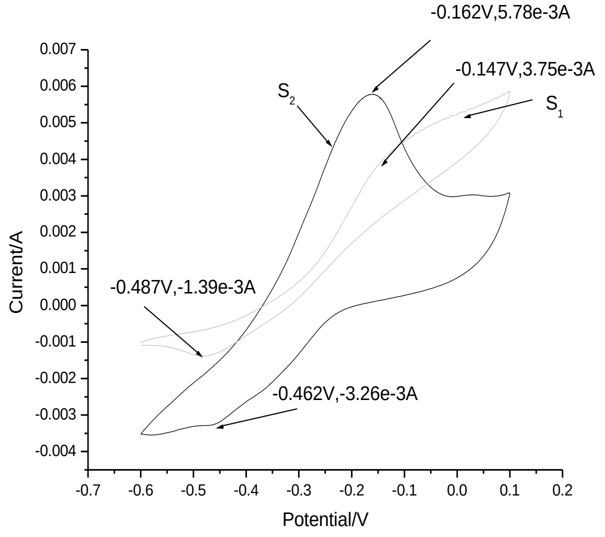

Figure 4. The CV plots of S_1 and S_2.

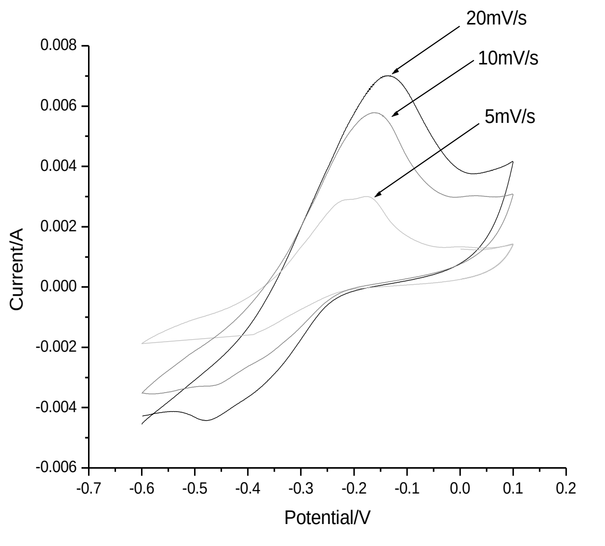

Figure 5. CV plots of sample S_2 at different sweeping rates.

The Ni^{3+} to Ni^{2+} reaction occurs during the CV test in alkaline solution according to Eq. (1).

$$NiO + OH^- \leftrightarrow NiOOH + e^- . \quad (1)$$

These capacitive characteristics are very different from the double layer capacitance, in which case it is normally close to an ideal rectangular shape. Therefore, the capacitance of the $NiO/NiSi_2/Si$-MCP (including materials with pure NiO layers and Zr doped NiO layers) electrode is mainly attributed to the Faraday quasi-reversible redox reaction. Fig. 6 shows the CV plots of 10 cycles chosen from 1000 CV cycles for the materials. There are respectively the 100^{th}, 200^{th}, …, to 1000^{th} cycles. The anodic oxidization and cathode reduction peak currents are almost equal, and so are the loop curve areas. Hence, the stability and repeatability of the materials are demonstrated.

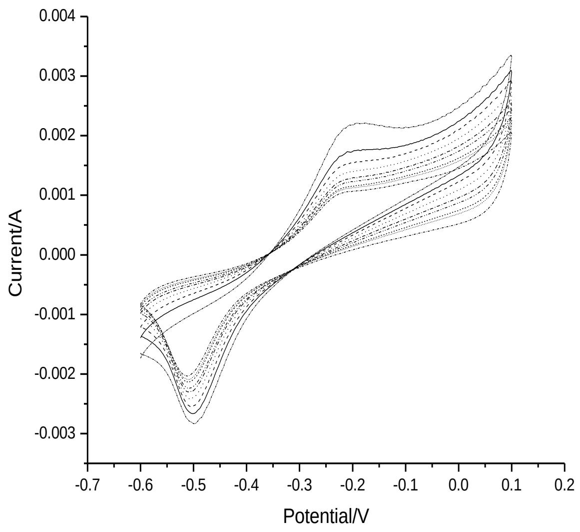

Figure 6. 100^{th}, 200^{th} ... to 1000^{th} CV cycles of sample S_2.

IV. CONCLUSION

Three-dimensional supercapacitors consisting of $NiSi_2$/silicon microchannel plates (MCP) with Zr doped NiO layers have been successfully fabricated. The Zr doped layers show a better capacitive response than the NiO layers, which can store 3.2 times more electric charge than that without Zr. The materials have good repeatability electrochemical capability, although repeatability error cannot be avoided. The Zr doped $NiO/NiSi_2/Si$ MCP also has a more sensitive redox reaction than that without zirconium, and the peak to peak current is twice than that of the $NiO/NiSi_2/Si$ MCP electrode. Further work will focus on adding lithium to achieve better capacitive response.

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