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Preparation of Ni Current Collector and MoS₂ Cathode in Three-Dimensional Li Ion Microbattery Based on Silicon MCP

Tao Liu¹, Li Sun¹, Jia Lai¹, Lianwei Wang¹, Zhonguang Lu², Jonathan C.Y.Chung² and Paul K.Chu²

Abstract—Three-dimensional Li ion microbatteries are known for their high surface area which leads to high current and capacity compared to traditional planar batteries. This paper describes economical approaches to prepare half 3D microbatteries based on silicon microchannel plates (MCP). The high aspect ratio silicon MCP is formed by electrochemical etching and a nickel layer coated on the silicon MCP as a current collector by electroless deposition. A molybdenum sulfide layer is electro-deposited onto the nickel coated silicon MCP as a cathode. The as-deposited molybdenum sulfide film is amorphous whereas the film annealed at a high temperature appears to be highly textured.

Keywords: Microbattery; Microchannel plate; Molybdenum sulfide; Nickel

I. INTRODUCTION

Lithium ion microbatteries, as a typical type of miniature power sources, have been widely used in a variety of applications such as cell phones, microsensors, RFIDs (Radio Frequency Identification), transmitters and miniature medical devices. Since the 1990s, Li ion microbatteries have developed rapidly, matching the growing needs for miniature power sources of smaller sizes and larger capacities. Traditional planar (2D) thin-film lithium ion batteries, usually comprising layers of cathode, electrolyte and anode grown in sequence on different kinds of substrates, have been taking up a large proportion of battery market. However, the main drawbacks associated with the low current and low capacity are holding back further upgrades of these planar cells [1]. Three-dimensional (3D) microbatteries have been proposed to overcome the deficiency of traditional 2D ones. High electrode surface area of the 3D architecture can lead to high power density while maintaining a short ion intercalation/deintercalation length between anode and cathode. Moreover, the adequately exploitation of vertical dimension enables the battery to hold a small footprint area, which can be significant for portable devices. Batteries of different 3D structures have been reported in the last few years. Peled and coworkers developed a perforated silicon structure based 3D microbattery by electrochemical etching and wet etching are utilized to define the electrochemical etching position. The masking pattern is made up of 3*3 μm squares with a spacing of 6 μm between center of each square. Before electrochemical etching of silicon substrate, tetramethyl ammonium hydroxide (TMAH) aqueous solution is used to shape pits on the surface of substrate. High-aspect-ratio silicon MCPs are obtained by electrochemical etching with an etching solution containing hydrofluoric acid and dimethylformamide (DMF) at an appropriate current density, etching bias, illumination intensity and temperature. A cooling system is used to prevent temperature increasing caused by illumination. The etching current density is stabilized by a program based on LabVIEW. Fig. 2 presents the schematic drawing of the etching system. The etching process slows down as etching time increases, and finally the formed silicon MCP separates from the bulk substrate, which is an important consideration for next steps. For uniform deposition of the current collector and cathode layer, the separated silicon MCPs

II. EXPERIMENTAL

The fabrication process of the 3D half cell is succinctly illustrated in Fig. 1.

A. Formation of silicon microchannel plate (MCP)

A 400 μm thick, 4 inches diameter, p-type, <100> silicon wafer is used in this work as the substrate. Silicon oxide used as a masking layer is formed by thermal oxidation, and lithography and wet etching are utilized to define the electrochemical etching position. The masking pattern is made up of 3*3 μm squares with a spacing of 6 μm between center of each square. Before electrochemical etching of silicon substrate, tetramethyl ammonium hydroxide (TMAH) aqueous solution is used to shape pits on the surface of substrate. High-aspect-ratio silicon MCPs are obtained by electrochemical etching with an etching solution containing hydrofluoric acid and dimethylformamide (DMF) at an appropriate current density, etching bias, illumination intensity and temperature. A cooling system is used to prevent temperature increasing caused by illumination. The etching current density is stabilized by a program based on LabVIEW. Fig. 2 presents the schematic drawing of the etching system. The etching process slows down as etching time increases, and finally the formed silicon MCP separates from the bulk substrate, which is an important consideration for next steps. For uniform deposition of the current collector and cathode layer, the separated silicon MCPs

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are segmented into pieces of 1*2 cm by laser cutting machine.

B. Preparation of nickel current collector

An electroless approach which could provide conformal and smooth coatings is used to deposit a layer of nickel onto silicon microchannel plate etched by previous method as a current collector of the 3D half cell. The deposition is carried out at 80 °C using a solution prepared by mixing a certain amount of nickel sulfate (NiSO₄), ammonium sulfate ((NH₄)₂SO₄), ammonium fluoride (NH₄F), sodium citrate (C₆H₅Na₃O₇), sodium lauryl sulfate (CH₃(CH₂)₈CH₆OOSO₃Na) and deionized water and by adjusting pH to 8.5 by addition of aqueous ammonia. Catalysis of silicon MCP is not necessary before nickel deposition because of the alkaline environment of the solution, so the preparation process could be simple and economic [5-7]. The mechanism of nickel formation though this method will be discussed below.

C. Preparation of molybdenum sulfide cathode layer

Electro-deposition is carried out to fabricate a layer of molybdenum sulfide cathode on nickel coated silicon MCP. The electrolyte containing tetrathiomolybdate (MoS₄²⁻) anions is freshly prepared by mixing aqueous solutions of Na₂MoO₄ and excess Na₂S and by adjusting the solution pH to 8.0 through addition of hydrochloric acid. A constant negative potential is applied to the nickel coated plate to perform electroreduction of the tetrathiomolybdate anions. The electrolyte is stirred during the deposition process. The deposition time ranges from one to 15 min and the current density is about 1.5 mA/cm².

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Fig. 1. Schematic of process producing the 3D half cell. (a) Electrochemical etching of Si substrate, (b) Electroless deposition of a Ni current collector layer, and (c) Electro-deposition of a MoS₂ cathode layer.

Fig. 2. Schematic of the electrochemical etching device attached to an illumination system and cooling system.

Fig. 3. SEM images of the silicon MCP formed by electrochemical etching: (a) Plain view and (b) Cross-sectional view.
III. RESULTS AND DISCUSSION

Fig. 3 depicts the plain and cross-sectional SEM images of the electrochemical etched silicon MCP with a high aspect ratio of about 25:1. Square holes of about 5 μm side length and 125 μm depth are obtained and the whole silicon MCP has already separated from the substrate, as can be seen from the image. Utilization of such a large vertical surface area for electroactive layers of 3D microbatteries is expected to yield significant increase of the capacity of the battery while maintaining original small substrate footprint.

Several assumptions have been proposed to explain the mechanism of deposition of nickel onto silicon surface by electroless approach [7-9]. We have developed a special solution for nickel deposition and catalysis pretreatment, which would be destructive for samples, can be left out of consideration. We consider that silicon atoms are oxidized by the alkaline solution and hydrogen atoms are produced on the surface of silicon:

\[
\text{Si} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{SiO}_3^{2-} + 4\text{H} \quad (1)
\]

Part of the produced hydrogen atoms combine to form hydrogen while other ones react as reductant of nickel ion:

\[
\text{H} + \text{H} \rightarrow \text{H}_2 \quad (2)
\]

\[
\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni} \quad (3)
\]

\[
\text{H} \rightarrow \text{H}^+ + \text{e}^- \quad (4)
\]

Since the silicon surface is covered by a layer of nickel atoms after a short time of the deposition, hydrogen atoms cannot be obtained by silicon-hydroxyl reaction. However, deposition proceeds and slows down until the process time exceeds 30 minutes. It is probably due to storage of hydrogen atoms among the as-produced nickel atoms. Deposition terminates when hydrogen atoms are totally depleted.

Another benefit we obtain from electrochemical etched silicon MCP is that the deposited nickel layer can adhere well to the top and side-wall area of silicon MCP with a coarse surface, which makes it facile for the preparation of current collector layer for 3D microbattery. Fig. 4 shows the SEM images of nickel coated silicon MCP (The deposition is carried out for 10 min). As can be seen, a smooth nickel layer of about 250 nm thick is deposited onto the top surface and the side-wall area. Fig. 5 depicts the XRD pattern of the deposited nickel.
layer. The most intense peak corresponds to the (400) plane of the substrate silicon. Other peaks match well the standard peak positions of nickel, indicating electroless deposition produces a layer of nickel on the substrate.

The main techniques nowadays for fabricating traditional 2D thin-film cathodes, including chemical vapor deposition, sputtering, evaporation and spray pyrolysis, which require expensive equipments and high temperature environments, are not suitable for preparing cathode layer on surface of high-aspect-ratio silicon MCP. Using electrodeposition can yield layers of cathode material covering all the available surfaces of the 3D structure of nickel coated silicon MCP [10]. The electrolytic reduction of tetrathiomolybdate (MoS\(_2\)) anions proceeds as follows:

\[
\text{MoS}_2^{2-} + 2e + 2H_2O \rightarrow \text{MoS}_2 + 2SH^- + 2OH^- \tag{5}
\]

Tetrathiomolybdate anions are formed by reaction between molybdate and hydrogen sulphide:

\[
\text{S}_2^{2-} + \text{H}_2\text{O} \rightarrow \text{HS}^- + \text{OH}^- \tag{6}
\]

\[
\text{HS}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2\text{S} \uparrow \tag{7}
\]

\[
\text{MoO}_4^{2-} + 4\text{H}_2\text{S} \rightarrow \text{MoS}_2^{2-} + 4\text{H}_2\text{O} \tag{8}
\]

The morphology of the as-deposited cathode layer depends strongly on the concentration of the electrolyte, the rate of deposition, stirring and temperature. The SEM images of the molybdenum sulfide layer on the nickel coated silicon MCP are presented in Fig. 6. Fig. 6a shows a cathode layer of 0.5μm thick deposited for 10 min at 1.5 mA/cm\(^2\) and 20 °C. It can be seen that the layer is relatively smooth and compact. A cathode deposited for 20 min at 10 mA/cm\(^2\) and 20 °C, of a thickness exceed 1μm is shown in Fig. 6b. Strong eternal stress generated during deposition results in a serious fracture of the 3D architecture and cracks of about 0.1 to 0.2 μm thick in the side-wall area. Polymer additives such as PEGDME and PEO have been reported to be doped into deposition electrolyte for producing compact and highly adhesive cathode films [3]. Addition of polymer additives is expected to produce cathodes of fine and close textures in our next work.

The XRD pattern shows no apparent peaks of the as-deposited MoS\(_2\) cathode, indicating that the film is amorphous. After annealing the film at 550 °C in Ar for 1 h, major changes are observed from the XRD pattern, as shown in Fig. 7. The most intense peak corresponds to the (111) plane of NiSi\(_2\) formed by Ni-Si combination during annealing, and other peaks corresponding to the (002), (004), (006) planes of MoS\(_2\), indicate that a highly textured MoS\(_2\) film has been produced on the nickel coated substrate.

IV. CONCLUSION

A three-dimensional half lithium ion cell with a sandwiched structure has been successfully fabricated. The high-aspect-ratio silicon microchannel plate is formed by electrochemical etching. The nickel current collector and molybdenum sulfide cathode are deposited on all available surfaces by electroless and electro-deposition. The annealed molybdenum sulfide presents crystalline, highly textured. These approaches make it possible to produce 3D lithium ion microbatteries at low costs. Further research such as measurements of electrical characteristics of the half cell is under progress.

REFERENCES