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Impedance study of adsorption phenomena on three-dimensional nano-nickel electrode deposited on silicon microchannel plate

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ABSTRACT

Three-dimensional nano-nickel electrodes fabricated on silicon microchannel plates by electroless deposition are characterized by electrochemical impedance spectroscopy. Compared to the nickel sheet, adsorption of cations and anions is detected due to the larger surface area of the porous nickel structure and three-dimensional architecture of the silicon microchannel plates. Adsorption is sensitive to the frequency and increasing step of the external voltage and different desorption rates of 0.003 and 0.027 A/cm^2 are observed from cations and anions, respectively. The experimental results indicate that adsorption is responsible for the anomalous increase of the impedance in the low frequency region.

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1. Introduction

The adsorption-desorption phenomena constitute the basic and important electrochemical processes at the solid-liquid interface and adsorption of ionic and non-ionic surfactants on the solid/liquid interfaces has been studied experimentally [1–4] and theoretically [5–8]. Adsorption is a complex process and depends on a variety of materials properties such as surface charge, surface free energy, surface roughness, balance between hydrophobic and hydrophilic groups, and specific chemical groups on the surface [2]. Adsorption is widely adopted in industrial applications, for instance, activated charcoal, capturing and using wasted heat to provide cold water in air conditioning (adsorption chillers), synthetic resins, increasing storage capacity of carbide-derived carbon for tunable nanoporous carbon, water purification, and so on [1]. Adsorption involves adhesion of ions from a liquid onto the surface and is a surface-based process whereas desorption is the reverse of adsorption. The surface area of a solid electrode also affects the adsorption efficacy [3].

Owing to the large surface-to-volume ratio, three-dimensional (3D) electrode structures are being used in energy storage devices that require a small footprint but demand high power and energy density [9]. Rechargeable devices such as batteries and supercapacitors can be fabricated as 3D structures by the micro-electromechanical (MEMs) technique and the main objective is to improve the performance in limited space by using high-capacity active materials deposited on large area structures [10–13]. There are different types of 3D electrode structures such as the nanometer or micrometer-size wire arrays [11,12], inter-digital structures [13], and microchannel plates (MCPs) [10,14–22]. The Si MCP is a perforated “through-hole” and free-standing stable substrate formed by photo-assisted electro-chemical etching and delamination from the Si substrate by a modified electrochemical procedure. The MCP has a large area ratio (>70%) and aspect ratio (length/diameter of the hole larger than 40). The surface area gained by the MCP structure can be larger than 100 thus providing the largest surface area increase in the 3D architecture [19,20]. Additionally, the Si MCP structure is stable in most acids and even at high temperature of more than 1000 °C. After deposition of a metal such as nickel, the Si MCP structure is also stable in alkaline media. The Si-MCP can be employed to fabricate 3D Li-ion batteries and supercapacitors with better performance, but the properties of the 3D electrode structure based on the Si MCP have not been evaluated comprehensively [21], especially the adsorption-desorption phenomena induced by the larger surface area. In this work, the 3D nano-nickel electrode based on silicon microchannel plate is studied systemically by electrochemical methods and the adsorption-desorption phenomena are characterized by impedance spectroscopy. Better fundamental understanding of the 3D electrode enables more effective

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development and fabrication of high-performance 3D devices in energy applications.

2. Experimental details

A p-type (100) silicon wafer with a thickness of 525 μm was used and the standard microelectronics fabrication steps were carried out to form the silicon MCP with a high aspect ratio. The steps included thermal oxidation to produce a masking layer and 3 μm x 3 μm squares were patterned by lithography and wet etching. The patterned wafer was pre-etched in a tetramethyl ammonium hydroxide (TMAH) solution (25% at 85 °C) and anodized using a computer-controlled photo-assisted electrochemical system. More details about the process can be found in Refs. 17 and 18. The silicon MCP was cut into 1 cm x 1 cm square pieces for further processing.

Electroless plating was chosen in our experiments because the channels in the silicon MCP could be coated with metal uniformly and the thickness of the metal film could be easily controlled by the bath composition and temperature [17]. The silicon MCP was put in diluted HF for 30 s to remove the native oxide and then soaked in a buffer solution (0.1% Triton X-100 solution) for 30 s to decrease the inner stress and enhance wetting prior to immersion in a plating bath for 20 min. Afterwards, electroless deposition of Ni was carried out in a mixture of 0.3 mol L^{-1} $NiCl_2 \cdot 6H_2O$ (nickel chloride hexahydrate), 0.1 mol L^{-1}NH_4Cl (ammonium chloride), and 0.1 mol L^{-1} $NaH_2PO_2 \cdot H_2O$ (sodium hypophosphite monohydrate) at 85 °C for 15 min. The pH was adjusted to 8.5-9.5 by addition of ammonia. $NiCl_2 \cdot 6H_2O$ was used as the Ni source. NH_4Cl and ammonia were used for pH adjustment and the complexing agents for Ni^{2+} ions and $NaH_2PO_2 \cdot H_2O$ was the reducing agent. The same experimental conditions were adopted to form the nickel-coated Si wafer. For comparison, a high purity nickel sheet (>99.9%) was prepared. The samples were designated as Ni (nickel sheet), Si-Ni (nickel coated Si substrate), and MCP-Ni (nickel coated Si microchannel plate). The electrochemical measurement was performed immediately after electroless deposition to avoid Ni oxidation.

The morphology of the silicon MCP and nickel electrode layer was examined by scanning electron microscopy (SEM). In the electrochemical analysis, the samples were exposed to a 2 M KOH aqueous solution at room temperature (25 °C) and served as the working electrode. A platinum electrode was used as the counter electrode and a mercury oxide electrode (Hg-HgO) served as the reference electrode. The electrochemical tests were performed on a CHI660D electrochemical workstation. The current and impedance data were normalized by the footprint area.

3. Results and Discussion

The overall cross-sectional view of the Si-MCP is shown in the SEM images in Fig. 1(a). The microchannels have a depth of around 200 μm and size of 5 × 5 μm giving an aspect ratio of the microchannels of about 40. The surface area gain (surface area ratio of the 3D structure compared to a similar planar electrode) is as large as 50. The cross-section of the Si-MCP is cut and tilted to show the inner walls of the microchannels. After electroless nickel plating, nickel nano-grains several to hundreds of nanometers in size can be found on the inner walls, as shown in Fig. 1(b). Even though the nano-particles appear on the surface, the Ni film on the surface can still protect the Si due to the thick Ni film (almost 500 nm). Owing to the different size of the nickel grains deposited on the outer and inner surfaces of the Si-MCP, the surface area of the 3D electrode nickel layer increases by almost 100 times due to the 3D architecture of MCP and porous structure of the Ni electrode [22].

The cyclic voltammograms (CV) of the Ni, Si-Ni, and MCP-Ni samples in the potential range of -1.5-0.6 V Hg-HgO acquired at a scanning rate of 10 mV/s are shown in Fig. 2a-c. The same electrochemical behavior is observed from this potential region of the three samples. They are typical oxidation-reduction reaction curves of Ni in a KOH solution [23,24]. During the first increasing sweep, the passive layer which consists of a NiO layer is formed, as indicated by the current peak A_0. On account of the porous MCP-Ni structure, oxidation proceeds quickly and shows a smaller current density peak compared to the Ni sample. With increasing potential, the layer which consists of an α-$Ni(OH)_2$ amorphous layer is formed, as indicated by the current peak A_1. When the potential sweep is reversed at -0.35 V versus Hg-HgO, a reduction process which transforms from α-$Ni(OH)_2$ to NiO is observed corresponding to the cathodic peak C_1. In the potential domain of the plateau (B), the amount of nickel oxide increases and there is simultaneous transformation of α-$Ni(OH)_2$ into less hydrated and crystallized β-$Ni(OH)_2$. At a potential larger than the oxidation peak A_2, β-$Ni(OH)_2$ is oxidized into β-NiOOH and the transformation is complete when the water oxidation current is observed. During the decreasing potential sweep, the reverse reduction reaction from β-NiOOH to β-$Ni(OH)_2$ is observed and it corresponds to the cathodic peak C_2. The similar cyclic voltammogram and same oxidation-reduction process indicate that nickel is deposited on the Si substrate and MCP structures and it is also confirmed by the XRD data in Ref. [15]. However, for the Si-Ni and MCP-Ni samples, the similar current densities of the anodic and cathodic peaks and larger potential

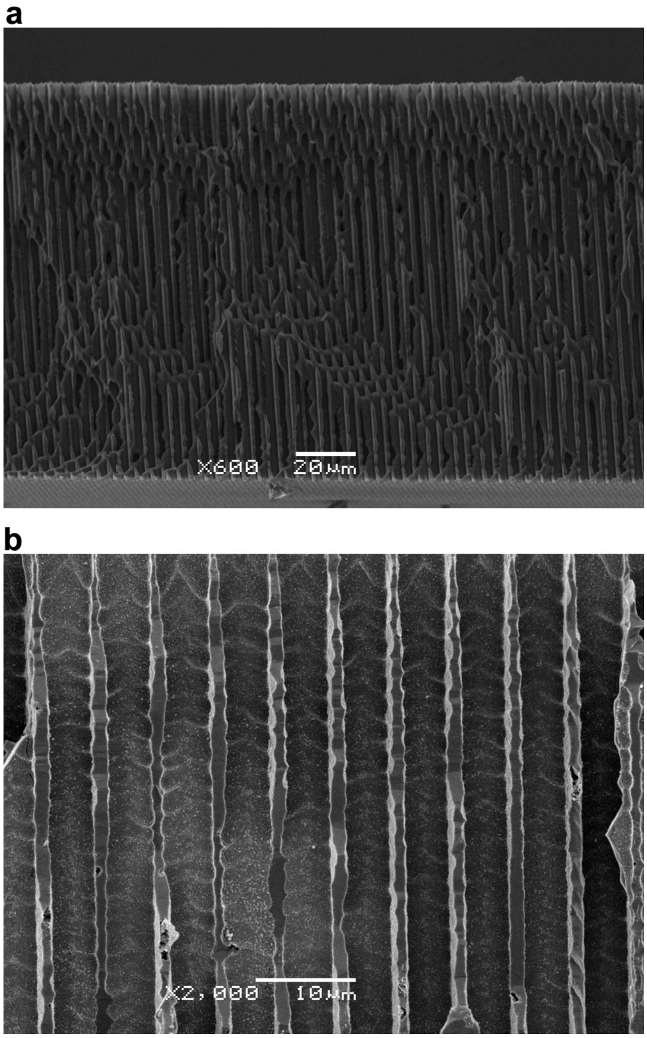

Fig. 1. (a) Cross-section overall view of the Si-MCP formed by electrochemical etching; (b) Morphology of the side wall of the nickel coated Si-MCP.

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