Silicon nitride coated silicon thin film on three dimensions current collector for lithium ion battery anode

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HIGHLIGHTS

- High surface area Cu Micro-cone arrays are used as the current collectors.
- The current collectors can ease the volume-change induced stress.
- Li_3N will be formed during charging and discharging process.
- High ionic conductivity resulting can provide the higher capacity.

ARTICLE INFO

ABSTRACT

Silicon nitride coated silicon (N-Si) has been synthesized by two-step DC sputtering on Cu Micro-cone arrays (CMAs) at ambient temperature. The electrochemical properties of N-Si anodes with various thickness of nitride layer are investigated. From the potential window of 1.2 V–0.05 V, high rate charge-discharge and long cycle test have been executed to investigate the electrochemical performances of various N-Si coated Si-based lithium ion batteries anode materials. Higher specific capacity can be obtained after 200 cycles. The cycling stability is enhanced via thinner nitride layer coating as silicon nitride films are converted to Li_3N with covered Si thin films. These N-Si anodes can be cycled under high rates up to 10 C due to low charge transfer resistance resulted from silicon nitride films. This indicates that the combination of silicon nitride and silicon can effectively endure high current and thus enhance the cycling stability. It is expected that N-Si is a potential candidate for batteries that can work effectively under high power.

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1. Introduction

In this generation, lithium ion batteries (LIBs) are the primary power solution for energy storage of portable electronic devices because of their high energy density [1]. The majority of commercial anodes in LIBs made from graphite enables steady capacitive performance and maintains low cost. Recently, developments in electric vehicles, hybrid electric vehicles, and high power tools in variety have been advanced by continual innovation and improvement in energy storage technologies over the last decade. With a thinner in volume and faster in processing, a trend of increasing demand of batteries with higher specific capacities is ever demanded. Therefore, new materials for high-capacity lithium ion batteries have been the focus of research interest.

Conventional graphite anodes for lithium ion batteries possess a limited capacity around 372 mAhg^{-1}, and many researches have been focused on searching for alternative high capacity anode materials. Alloy-type anode materials, such as Sn, Si or Cu_6Sn_5 etc [2–4], have been intensively studied due to their relatively large specific capacities. Among them, Si has highest theoretical capacity (4200 mAhg^{-1}), which is nearly 10 times more than that of conventional graphite anodes. Si is not only inexpensive but also abundant in earth's crust. However, similar to other alloy-type anode materials, a common issue of Si related electrodes is the volume expansion (>300%) during charge-discharge process by lithium alloying and de-alloying. The large volume expansion leads to severe capacity fading, poor electrical contact, secondary formation of solid electrolyte interface (SEI) and poor cycle stability of the anode materials [5–8]. In order to prevent these drawbacks, doping elements [9–13], nano-sizing particles [8], forming silicon-based composites [14,15] and coating protective layer [16,17] have

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attracted considerable attention in the recent decades.

In literature, Yi et al. group demonstrated the highest energy density, high capacity lithium ion batteries anodes by combination of carbon forming composite anode [18—20].It appears that mitigating the volume expansion and enhancing the electrical conductivity simultaneously by virtue of rational architecture design of conductive networks and buffer space provide an accessible approach to prolong the cycling lifetime of Si-based anodes. In recent years, constructing buffer spaces by morphology control enhances electrochemical performance of silicon [21—23]. Different approaches have been reported, such as core—shell structured [22] chemical vapor deposition (CVD) [24], physical vapor deposition (PVD) [25,26] and electro-deposition [27—30]. These special architectural designs can create buffer spaces for relaxing stress induced by volume expansion. In addition, the cycling lifetime of silicon-based anodes is also improved.

Owing to rapid development of electric vehicles, hybrid electric vehicles and other high power applications have urged lithium ion batteries to exhibit better safety and stability properties. Thin-film electrodes and electrolytes have attracted considerable attention, due to the fact that these thin films can be fabricated and characterized free of binders [31,32]. In this work, silicon nitride thin films were coated on three dimensions Si template by two-step sputter deposition. It is demonstrated that silicon nitride thin film can effectively enhance the high rate stability of Si-based anode.

2. Experimental

The Cu Micro-cone Arrays (CMAs) were prepared by electroless plating [33]. Firstly, copper cones were electroless plated on the Cu foils after substrate pretreatment. The plated electrolyte was composed of analytical pure $CuSO_4 \cdot 5H_2O$ (0.03 mol/L), $NiSO_4 \cdot 6H_2O$ (0.0024 mol/L), $NaH_2PO_2 \cdot H_2O$ (0.24 mol/L), $Na_3C_6H_5O_7 \cdot 2H_2O$ (0.05 mol/L) and H_3BO_3 (0.50 mol/L) as well as crystallization modifier polyethylene glycol (5 ppm). Above mentioned formula was properly mixed and dissolved in deionized water for 20 min at pH 8.5—9.5 (adjusted by NaOH solution) and solution temperature of 70 °C. After electroless plating, the as-deposited copper cones were transferred to a sputter chamber, and thin films were prepared by two-step sputtering in a DC sputter system. The working pressure was maintained at 3.0×10^{-4} torr for all deposition processes. The working gas (Argon) was set to a flow rate of 30 sccm during sputtering, and Si thin films were deposited using DC supply of 80 W for 1hr. Subsequently, to deposit SiN_x thin films, working gas was changed to a mixture of 28 sccm and 2 sccm of Argon and Nitrogen, respectively. The SiN_x thin films were deposited on the Si/CMAs electrode during the sputtering process with various deposition time. The N-Si composite with different deposition time was denoted as N1-Si, N3-Si and N5-Si, corresponding to 1, 3 and 5 min, respectively. In this study, the mass of active material was weighed by OHAUS microbalance (OHAUS, EX125D) with an accuracy of 0.01 mg. The weight of active material was measured by subtracting Cu as well as CMAs mass from the total mass after sputtering. SiN_x was deposited on coated platinum silicon wafer. First, SiN_x was weighed by OHAUS microbalance. The weighted amount of SiN_x was deposited on silicon wafer for 1 h, with SiN_x estimated around 0.1 mg. It should be noted that the weight of N1-Si, N3-Si and N5-Si was rather similar, which would not affect the electrochemical performance. Furthermore, the SiN_x thickness was estimated by the layer deposition on the silicon wafer within a certain time (460 nm/60 min), and the deposition rate was approximately 7.7 nm/min for SiN_x coatings. Therefore, the thickness of N1, N3 and N5 is estimated about 7.7 nm, 15.4 nm and 23.1 nm, respectively. The SiN_x cross-section image is shown in Fig. S1. The surface morphology was observed by a field-emission scanning electron microscope

((FE-SEM, JEOL 7600F, Japan), and cross section image was obtained by high-resolution transmission electron microscopy (HR-TEM, JEOL Cs Corrected Field Emission TEM, Japan) and Dual-beam Focused Ion Beam system (FEI Helios Nanolab 600i System, USA). Electrochemical properties were characterized by coin cell method (type 2032) with N-Si/CMAs electrodes as working electrodes. Li foil was used as counter electrode and reference electrode. The electrolyte used was 1 M Lithium hexafluorophosphate (LiPF6) in ethylene carbonate and ethyl methyl carbonate mixed solution (volume ratio 1:1). All cells were assembled in an Ar-filled glove box (H_2O < 0.1 ppm, O_2 < 0.1 ppm) to avoid water contamination. The cells were analyzed using charge-discharge process (Arbin-BT2000) in the potential window of 0.05—1.2 V, and the cycling test was analyzed under 0.2C in the same potential window for 200 cycles. The CV tests were performed on an electrochemical workstation (Ametek 263A, USA) at a scan rate of 0.2 mV^{-1} between 0.05 and 1.2 V. The electrochemical impedance spectra (EIS) were analyzed using an impedance spectroscope over the frequency range from 0.1 MHz to 0.1 Hz with 10 mV amplitude at 0.2 V. The X-ray photoelectron spectroscopy (XPS, Ulvac-PHI PHI 1600) was used to derive the surface composition and chemical bonding with an Al Ka X-ray source (1486.6 eV).

3. Result and discussion

The SEM images of CMAs, Si/CMAs, N1-Si/CMAs, N3-Si/CMAs and N5-Si/CMAs electrodes are shown in Fig. 1. Fig. 1(a) presents a typical CMAs current collector fabricated by electroless plating method. The mean diameter is estimated around 1 μm. After the deposition of Si, as shown in Fig. 1(b), pure Si covered directly on CMAs with much larger diameters around 1—2 μm with rough morphology. The CMAs were completely covered, which could act as three-dimensional current collectors to provide more surface active sites for electrochemical reactions. In Fig. 1(c)—(e), the morphology of N-Si/CMAs based electrode was not changed significantly. Furthermore, high-resolution TEM image is provided in Fig. 1(f) to show the overall features of N1-Si/CMAs electrode, which can easily reveal thickness of thin films. The detailed composition is shown in Fig. S2. TEM figure is provided along with STEM mapping. The dark region belongs to Cu signal, while the white region is Si signal. The difference between there two phases is distinct. The results show that three dimensional Si/CMAs and N-Si/CMAs based electrodes can be easily fabricated by sputtering process.

For thicker Si films, a more severe capacity fading was recorded. As shown in Fig. 2(a), the pure Si anode exhibits poor cycling stability. The capacity drops dramatically within 10 cycles. After 10 cycles, the remaining capacity is as low as 525 mAhg^{-1}. It can be attributed to the severe volume expansion of Si during charge — discharge cycles, which damages Si and the broken flacks of Si lose electric contacts, leading to the capacity fading. In contrast, CMAs based electrodes show a rather stable capacity, due to the three dimensional CMAs underneath which plays a crucial role in capacity retention of Si anodes. Furthermore, the coulombic efficiency of the initial process was around 80%, which was higher than that of previous studies of Si anodes as all the process were carried in high vacuum [3]. N1-Si/CMAs, N3-Si/CMAs and N5-Si/CMAs exhibited much stable capacity retention. In particular, sample N1-Si/CMAs was relatively stable during the charge-discharge cycles, as compared with N3-Si/CMAs and N5-Si/CMAs. At 10th cycle, N1-Si/CMAs still possessed a capacity of ~2789 mAhg^{-1}, which was 5 times and 1.6 times higher than that of pure Si and both N3-Si/CMAs and N5-Si/CMAs, respectively. For further comparison in Si/CMAs and N1-Si/CMAs, as referred to Fig. 2(b), the N1-Si/CMAs exhibited initial capacity of 2789 mAhg^{-1} and still had good