Compositionally-graded silicon–copper helical arrays as anodes for lithium-ion batteries

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HIGHLIGHTS

- Highly adherent SiCu film is deposited by ion assisted glancing angle deposition.
- Compositionally graded SiCu helical arrays is produced and characterized.
- Change in Cu content along the thickness diverts the propagation of stress.
- Cu rich layer at the bottom improves the adherence of the film.
- Helices being like microsprings, improve the mechanical resistance of the anode.

GRAPHICAL ABSTRACT
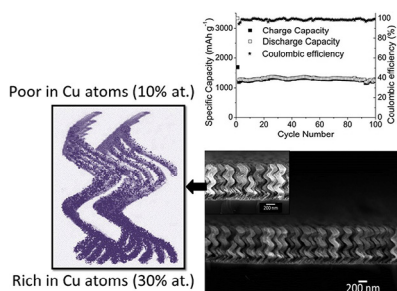
ARTICLE INFO

ABSTRACT

Restrictions in silicon based anodes have been the subject of many researches for years. As an innovative approach, we have adopted ion assisted deposition technique to glancing angle deposition method and have used compositionally-graded structuring. A unique helical shaped gradient film has been produced in which the Cu/Si atomic ratio decreases from the bottom to the top of the coating. With such a unique film (high surface area) more spaces have been created promoting mechanical integrity and reaction between active materials (silicon) with lithium ions. The highly adherent film is formed as a result of ion assisted deposition process and the gradual change in Cu/Si atomic ratio diverts stress through the helices. To compare the performance of the SiCu electrode, a pure Si film is deposited in the same experimental condition. Galvanostatic test results show that although the film with pure Si helices fails after 30th cycles, the compositionally graded anode exhibits a capacity of 1228 mAh g^{-1} at the 100th cycles with 99.5% coulombic efficiencies when cycled at 100 mA g^{-1}, and delivers 815 mAh g^{-1} when cycled with a rate of 400 mA g^{-1}.

Published by Elsevier B.V.

1. Introduction

In response to the needs of modern society and emerging ecological concerns, it is now essential to use low-cost and environmentally friendly energy storage systems. Innovations in energy storage devices result from better material selection and process design.

Among alternative energy storage devices, lithium-ion batteries (LIB) are important in today's world since they are providing electrical power for a wide variety of applications, such as power tools, electrical vehicles, aerospace vehicles, power grids, and small portable electronic devices. So far, various materials (C, Sn, Ge, Al, Sb, and Bi) have been evaluated as anodes in LIB [1–4].

Among them, silicon (Si) is especially attractive due to its high theoretical storage capacity (3579 mAh g^{-1} at room temperature) and high abundance in the Earth's crust. Nonetheless, Si has not yet replaced graphite in commercial applications because >300% volume expansion occurs when the lithium ions (Li$^+$) react with Si during cycling, generating an immense stress (as high as 1 GPa) in the anode. This immense stress causes a break-up of the electrode and the electrical isolation of Si [5]. Moreover, as the electrochemical alloying potential of Si is above the electrolyte solvent reduction level, a passive film forms at the electrode/electrolyte interface. Finally, the high electrical resistivity and the low diffusion coefficient of Li in Si hinder fast electron transfers, resulting in high resistance along the electrode and, hence, failure in the early stages of cycling [5,6].

Despite these challenges, the extraordinarily high energy capacity of Si has motivated researchers to develop techniques to reduce the limitations of Si as a practical anode material. For example, nanoscale morphologies, including thin films, nanowires, and nanotubes, have been designed [4–11]. The free spaces among these nanostructures form large pathways to facilitate electrolyte penetration, increase the accessible surface area of the anode reacting with Li$^+$, and decrease the polarization. Thus, the cycling performance of the electrode improves. In addition to the above, template-directed plating, direct chemical reaction, and nanolithography have all been used by various researchers to produce composite nanostructured Si based thin film electrodes [12–14]. However, long processing time, the restricted aspect ratio of the nanostructures, safety concerns, difficulties in controlling the morphology, low adhesion of the film to the current collector, and limited choices of materials to form composite nanostructures have led investigators to look for alternative production methods [12–14].

In this sense, glancing angle deposition (GLAD) becomes remarkable since it has shown promise for generating thin-film anodes. The advantages of the GLAD method and its film formation mechanism have been explained in detail [12–17]. In this method, process parameters (especially angle of incidence, evaporation rate, and substrate rotation speed) change the morphology of the microstructures from zigzag to helices.

Therefore, in this work we particularly form helices by GLAD method to improve mechanical integrity of the electrode. Therefore, a three-dimensional (3D) helix-containing film is expected to act as "micro-springs" [18] due to its particular morphology, as revealed by Seto et al. [18]. Plus, the separated helical structures enable freedom of ion movement over short distances which would also improve mechanical tolerance of the electrode to the stress induced by volumetric changes in cycling.

Even though the cycle life of the anode is improved as a result of the helical morphology (improved electrode design), the service life of nanostructured thin films is still limited owing to the low electrical conductivity of Si and the high ohmic contact resistance between the thin film and its substrate [19]. Thus, to promote electron transfer along the nanostructures, to improve the adhesion of the film to the substrate, to alleviate the influence of expansion and to divert the stress formed along the helice additional Cu was incorporated into the structured film (improved material selection) [20–24]. Previous studies had suggested that depositing Cu atoms on/with Si particles would significantly improve the electrical contact, the coulombic efficiency, and the cycle life of the electrode [22,23]. However, deciding the optimum amount of Cu to add into the Si thin film is a challenging task. Although Cu increases the cycleability of the Si thin film, the theoretical capacity of the film decreases because Cu is electrochemically inactive versus Li. Therefore, optimization of Cu/Si ratios along the nanostructured thin film is highly desired.

One approach to handling this problem is to engineer a Cu–Si nanostructure with high surface area, where the Cu/Si ratio gradually changes from the substrate to the top of the nanostructure.

In this work, first in literature we have adopted ion assisted deposition technique to glancing angle deposition method and have used compositionally graded structuring to produce a thin film having compositionally-graded SiCu helices. During the film growth, the ratio between Cu and Si was precisely controlled and dynamically tuned. For comparison, a pure Si helices containing thin film is also produced in the same experimental conditions. A lithiation mechanism for anodes with the compositionally graded helices is proposed on the basis of electrochemical impedance spectroscopy at different states of charge and cyclic voltammetry for different cycles.

2. Experimental

The experimental setup used in this study is given in Fig. 1a. During the GLAD evaporation stage, two quartz-crystal microbalances (QCMs) were used independently to monitor the deposition rates and thicknesses of Cu and Si, separately.

Four kinds of substrates were used: a Si wafer for cross-sectional scanning electron microscopy (SEM), a stainless steel disc (15.5-mm diameter and 1.5-mm thickness) for compositional analysis, a glass disc (Tedpella) for structural analysis, and a mirror-like surface-finished copper disc (15.5-mm diameter and 1.5-mm thickness) for electrochemical experiments.

The pure Si and Cu pellet source materials were placed in separate graphite crucibles, and the chamber was pumped to a base pressure of about 3×10^{-6} Pa. Prior to deposition, the samples were initially sputtered for 8 min using 900 eVAr$^+$ ions from a Kaufman ion source at a gas feeding rate of 8 sccm. The incident angle of Ar$^+$ ions to the substrate's normal orientation was about 35°, and the pressure in the chamber was 0.01 Pa. Then, the shutters inserted for each source were opened, and the deposition was started. The deposition time was 15 min.

To form helices, the substrate was rotated by a stepper motor with an azimuthal rotational speed of 0.2 rpm, when the crucible surface has 85° with substrate surface normal. To obtain gradual compositional variation along the helices, the evaporation rates of the Si and Cu sources were separately controlled. The evaporation rate of Si was 1 nm s^{-1} during the entire process, but that of Cu changed from 0.3 nm s^{-1} in the first 2 min, then to 0.18 nm s^{-1} in the following 5 min, and finally to 0.09 nm s^{-1} for the last 8 min, as read by the QCM.

After cleaning (sputtering), immediately at the start of deposition, the ion energy was reduced to 250 eV, and Ar$^+$ ion-assisted deposition was conducted at 250 V and 23 mA for 5 min to establish a dense, adherent thin film. After that, the Ar flow and ion gun were turned off, but evaporation still continued. The ion source parameters used in the experiments were as follows: 30 mA beam, 40 V discharge, 100 V accelerator. For comparison, in the same experimental conditions a pure Si film with helices is deposited on the substrates.

The surface morphology and the thickness of the "pristine" (i.e., no charging or discharging) Si and SiCu thin films were determined with field-emission SEM (JEOL JSM 7000F and JEOL 5410). The phases present in the pristine SiCu thin film were determined by x-ray diffraction (XRD) analysis (Philips PW3710 System) with a 2θ range of 10–90° in steps of 0.05° (with CuKα at 40 kV and 30 mA). The amount of Cu/Si atoms along the thin film thickness was monitored by glow discharge optical emission spectroscopy (GDOES) analysis (JobinYcon Horiba), where the RF excitation mode is used with 50 W power and 900 Pa pressure.

The composition of the film was determined by energy dispersive x-ray (EDS) analysis (Oxford). The weights of the films were