



The effect of copper coating on nanocolumnar silicon anodes for lithium ion batteries



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ABSTRACT

In this work, a very thin (20 nm) copper (Cu) coated silicon (Si) nanocolumns are produced by an oblique angle deposition method. Galvanostatic half-cell measurements show that, the Cu coated Si nanocolumn arrays perform 1700 mAh g^{-1} in the first cycle, then after 10 cycles its performance is stabilized to 500 mAh g^{-1} with 99% coulombic efficiency for 90 cycles. This high performance is related to its particular morphology and physical properties: having homogeneously distributed nano-sized porosities in the Cu coated film increase the mechanical tolerance of the electrode against the volumetric changes occurred during galvanostatic test, plus the ductile behavior of the Cu film holds the electrode together to prevent the electronic isolation, pulverization or delamination of the coating, moreover the formation of $\text{Cu}_{15}\text{Si}_4$ intermetallic increases the mechanical resistances of the coating against the stress generated in the electrode, and the existence of the Cu top coat between the Si nanocolumns and the electrolyte changes the surface reactivity of the electrode, hence its interaction with the electrolyte leading to higher coulombic efficiency once a stable passive forms on the anode.

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1. Introduction

Carbonaceous materials including graphite are currently used as anodes in commercial lithium ion batteries (LIB). However, the low theoretical capacity (372 mAh g^{-1}) of graphite leads researchers to look for alternative materials of higher specific energy [1]. Among the alternatives Si becomes prominent due to its high theoretical capacity (3579 mAh g^{-1} , at room temperature) and high abundance on earth [2]. But, its wide usage has been restricted due to poor conductivity and lack of elasticity, resulting in low capacity retention and short cycle life [1,2]. During cycling, in lithiation, Si expands followed by the alloying reactions with lithium ions (Li^+) and Si atoms impinge on each other, then in delithiation, Si tends to contract due to de-alloying of Li^+ , resulting in detachment from their surroundings. This abrupt change in stress causes a rupture from the current collector and eventually the anode dies. Moreover, an unstable solid electrolyte interface (SEI) formation on the Si anode is another problem causing a rapid decay in capacity [3].

Recently, different assumptions have been made to design Si electrodes [4–6]. One of them is using low dimensional structured Si (such as nanotubes, nanowires, nanocolumns, thin films) to decrease the tendency for crack initiation and propagation. Because the possible interstitial spaces (porosities) among these nanostructures are expected to minimize “the electrochemical sintering” process and to increase the mechanical tolerance against volume changes during cycling.

Moreover, these porosities provide large active sites to accommodate lithium (Li^+), and decrease polarization; resulting in long service life [7,8].

So far, to form Si nanocolumns, laser irradiation of silicon surface [9], chemical vapor deposition of SiH_4 [10,11] and lithography based ion etching methods [12] have been used. Besides, oblique angle deposition (OAD) via electron beam evaporation method has attracted attention since the process avoids the hazardous handling of flammable, explosive or cancerogenic nanoparticles. In addition, OAD enables direct deposition of the well-aligned inclined nanocolumns on the current collector, eliminating the need of binder or conductive additives which ensures the direct transportation of the electrons; hence a fast Li^+ diffusion through their adjustable, small diameters [13].

The mechanism of the nanocolumn formation in the OAD method has been studied previously [13–21]. In OAD method the morphology of the film is controlled mainly by incident flux angle. Therefore, to produce nanocolumns, substrate position should be fixed to receive evaporated particle vapor flux at highly oblique angles ($\theta > 70^\circ$). Under this circumstance, the vapor flux has vertical and lateral components where the first induces film growth and the later brings shadowing effect, giving rise to self-alignment and lateral sculpturing of the nanocolumns.

Indeed, previously Thornton has been mentioned that the film morphology mainly depends on the ratio of T_S/T_M (where T_S is the substrate temperature and T_M is the melting temperature of the material to be deposited) [21]. In his assumption the shadowing effect, ad-atoms surface diffusion and the surface–volume recrystallization processes are found to be dependent on this ratio [21]. When the substrate temperature

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is kept low (around room temperature) during the experiment, shadowing effect becomes one of the dominated mechanisms of OAD method, over “surface diffusion process” [14,15]. In the beginning of the coating, the surface diffusion rate is very slow, thus the impinging atoms randomly form islands on the substrate (when the film growth is governed by Volmer–Weber or Stranski–Krastranov process). Then, as deposition proceeds, the initially nucleated islands act as shadowing centers and they receive more impinging atoms as compared to the ones shadowed. At the end of this deposition process it is possible to grow inclined nanocolumns, where homogeneously distributed porosities are formed among them [22].

Although nanocolumnar films are seem to be promising electrodes for LIB, generally they suffer from poor adhesion to the substrate surface due to the low energies of evaporated particles. To overcome this problem, a group of scientists have used Cu as an inactive but beneficial additive material in various forms, other than substrate or current collector [23–25]. It is believed that the presence of Cu in the electrode improves the adhesion of the film to Cu substrate (because of the possible diffusion between the film with the substrate) and ameliorates the mechanical flexibility as well as the electrical conductivity of the coating (owing to the high solubility of Cu in Si, its ductile and electrical conductive behaviors) [25]. However, deciding the amount of Cu into the Si film is a challenging task since Cu being electrically inactive versus Li decreases the initial discharge capacity of the anode. Thereby, some researchers have co-deposited limited amount of Cu with Si [6] or have changed the composition (the ratio of Cu/Si) along the film thickness to form graded nanostructures with low Cu content [23,24].

In this work, to benefit from the advantages of Cu while using it in a very limited amount, a very thin (around 20 nm) Cu layer on Si nanocolumn array is deposited by OAD method. Electrochemical performance of this Cu coated Si nanocolumn arrays is evaluated by comparing its results with those of the bare Si nanocolumn arrays.

2. Experimental details

Experimental setup for OAD in a vacuum chamber is shown in Fig. 1a–b. The custom-made chamber has a cryopump, a Gemini electron beam evaporator and a Themescal controller power supply. Two separately controlled electron-beam evaporation sources, containing Si and Cu pellets are located separately in graphite crucibles, below

the center of the substrate holder unit. As the distance between the source and the substrate is fairly large, the vapor flux can be treated as collimated vapor beams. Additionally, two quartz-crystal microbalances (QCM) are present in the vacuum chamber to monitor and control the deposition rates as well as the thickness of the Cu and Si films independently during the coating process. A shield is used for the source to assure accurate measurements of coatings.

The depositions of the bare and the Cu coated Si nanocolumn arrays are made on three different substrates: Si wafer for cross sectional views and X-Ray Diffraction (XRD) analysis, a stainless steel disk (15.5-mm diameter and 1.5-mm thickness) for compositional, and mechanically polished (1200, 800, 600, 320, 3 μm , 1 μm , 0.5 μm) Cu disks (15.5-mm diameter and 1.5-mm thickness) for surface views and electrochemical analyses. Before the evaporation, all substrates are attached to the substrate holder and the source materials are placed in two graphite crucibles to subsequently evaporate Si and Cu. Then, the chamber is pumped to a base pressure of about 7×10^{-5} Pa. In the mean time, before opening the shutters and starting the deposition, all samples are initially cleaned by pre-sputtering them for 5 min with Argon ions (Ar^+) ions. For this cleaning, an 8-cm Kaufman ion source is used to produce a beam of Ar^+ ions. The source parameters are 1 kV at 30 mA, 40 V discharge, 100 V accelerator and 8 sccm Ar gas. The incident angle of the Ar beam to the substrate's normal is about 35° , and the pressures in the chamber during pre-sputtering and deposition are 1 and 10^{-3} Pa, respectively.

To see the effect of the Cu layer on the electrochemical performance of the Si anodes, 500 nm thick, bare and Cu coated Si nanocolumn arrays are prepared. During production, after cleaning the substrate surfaces under vacuum atmosphere with high energy Ar^+ , first the Si nanocolumn arrays then a very thin Cu film are deposited subsequently on the substrates. The evaporation rate is constant (4 \AA s^{-1}) and the incident flux angle is fixed to 80° for both Si and Cu films.

The surface morphology of the films before and after the cycle tests as well as the film thicknesses are investigated by field-emission scanning electron microscopy (FEG-SEM, JEOL JSM 7000F, with 5 kV and 10 mm working distance). The distribution of Cu atoms along the Si nanocolumn arrays is displayed by Energy Dispersive Spectroscopy (EDS) mapping analysis (Oxford, at 15 kV for 785 s). The phases present in the coatings are determined using Philips PW3710 System with a 2θ range of $20\text{--}100^\circ$ in steps of 0.05° (with $\text{CuK}\alpha$ at 40 kV and 30 mA).

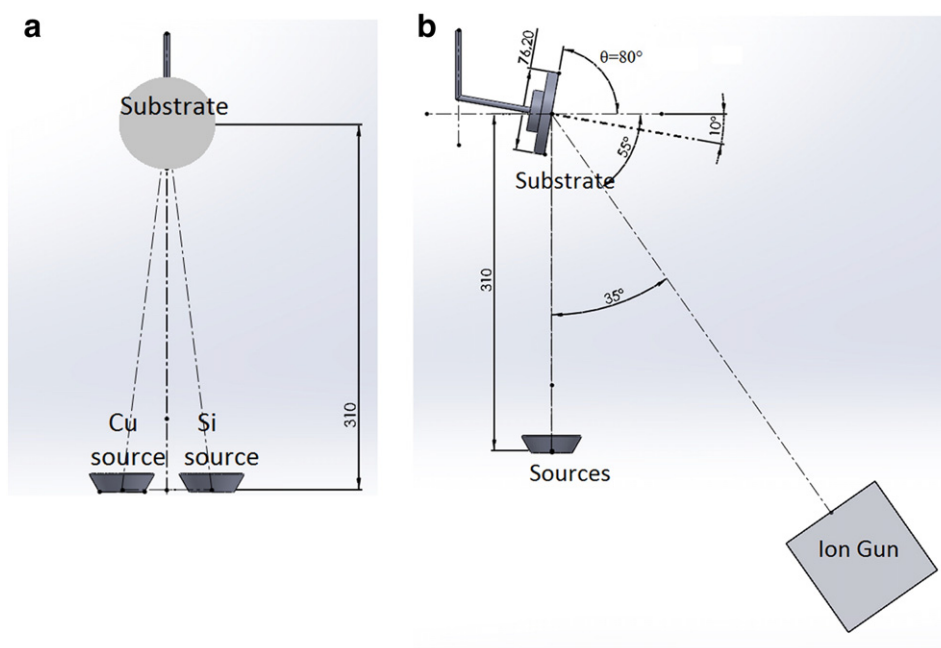


Fig. 1. Illustration of experimental setup for OAD method a) the front view, b) the side view.

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