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Functionally Graded Si Based Thin Films as Negative Electrodes for Next Generation Lithium Ion Batteries

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ABSTRACT

A functionally graded SiCu film is deposited by magnetron sputtering to overcome the quick failure problem of the Si thick film electrode. As the stress induced by lithium intercalation along the electrode and the embrittlement caused by lithium segregation at the electrode-current collector interface are believed to be the main reasons for capacity fade, depositing a pure Cu layer first, then providing a gradual increase in Si is believed to be a promising solution for future high capacity next generation lithium-ion battery (LIB) anodes. This electrode delivers 2073 mAh g^{-1} with 80% coulombic efficiency in the first cycle and retains 70% of its initial capacity after 100th cycle. We believe that pure Cu layer at the bottom minimizes the segregation of Li due its inactive behavior and increases the adhesion of the coating. Moreover, the gradual decrease of Cu in the first 1.7 micron of the film diverts the stress propagation along the thickness while improving the deformation characteristic during cycling. And, the existence of 10% at. Cu atoms at the top region (around 0.7 micron) along with Si atoms, improves the physical as well as the mechanical properties of the electrode leading to a high electrochemical performance.

1. Introduction

Lithium ion battery (LIB) technology becomes a common subject of both industry and academia due to increasing demands in electrical vehicles and plug-in applications beside portable devices [1,2]. As the current commercial LIB do not have enough energy density to satisfy customers' requirements finding a safe and a high performance electrode is the main focus of researches. In this sense, Silicon (Si) becomes remarkable: (1) Si has the highest gravimetric (4200 mAh g^{-1}) and volumetric capacity (9800 mAh ml^{-1}) when it is fully lithiated ($Li_{22}Si_4$), (2) lithium-rich Si compounds have high melting points, (3) the working potentials vs. lithium (Li) is high enough to eliminate the possibility of metallic-lithium deposition, (4) it is the second-most abundant element in the earth's crust and (5) environmentally benign [3,4].

Although Si has many advantages, it does not represent the ultimate solution for anode material since Si electrodes quickly fail in cycling following extreme volume changes. This leads to a breakup of the electrode and electrical isolation of the active material, eventually. Moreover, the low electrical conductivity of Si and a solid electrolyte interface (SEI) formation following the electrolyte reduction on the Si electrode surface impede its effective use as the negative electrode [5–7].

To enhance the cycle performance, morphological and compositional improvements have been proposed previously. Researches on morphological improvement emphasize the importance of nanotechnology. The production of nano-scale materials decreases the large stresses formed as a result of volume changes promoting better cyclic stability of the nano-structured electrode compared to the bulk Si. This superior mechanical resistance to fracture can be explained by small sized cracks which do not reach their critical sizes for propagation as they do in bulk materials [2]. In 2012, Yang et al. [8] have shown that the nanoscale fracture and deformation mechanisms could be different from those macroscopic ones and they have proved that many materials at nanoscale are more ductile than they are at the normal sizes since the critical sizes for crack propagation have been found to be larger than the dimensions of nanomaterials, in most cases. Moreover, the morphologies of nanoscale Si can shorten the length of the diffusion pathway and improve Li reaction rate with large surface area of Si. Plus, nanosizing makes the material more reactive and reduces energy barriers for alloy formation [9].

So far, different research groups have used Si thin films as electrodes due to the remarkable advantages like being directly connected to the metallic substrate that leads to minimum capacity loss, having 1D structure to allow efficient electron

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charge transport, and easy binderless approach of electrode formation to improve its compatibility for mass production [10,11]. Even though the initial capacity is increased by means of Si film, the first cycles coulombic efficiencies are always low, which prevents its widely used in commercial applications. In this sense, scientists have investigated the lithiation mechanism of Si films and found that the stress induced in the electrode by lithiation reaction is the main reason for their moderate electrochemical performance. Besides that, Pal et al. [12] have stated that the small amount of segregants and impurities may have a major effect on the adhesion and this could embrittle the interface (electrode/current collector) resulting failure.

Previously, it has been shown that the high volumetric changes in the Si thin film electrode cause a vertical cracking which leads small islands formation after the first cycle [13–15]. These islands help the electrode to release the stress while maintaining electronic contact with the current collector. Therefore, the electrode keeps cycling even though the capacity decreases gradually. However, as the Si film thickness increases, after few cycles, the capacity drops precipitously due to high impedance and huge mechanical stress induced in the film, therefore the islands delaminate severely from the current collector resulting in a complete failure.

Some researchers have suggested to improve the mechanical stability of Si thin film anodes by either forming alloy (Fe, Co, Ni, Sn) with other materials to act as a buffer or by using nano-sized materials dispersed uniformly in a buffer matrix [16,17]. Herein, copper (Cu) is used as an inactive but beneficial additive material in various forms other than substrate or current collector. Indeed, in previous studies, Sethuraman et al. [18] have found that Cu appears to act as a glue that binds the electrode together and prevents the electronic isolation of Si particles, consequently decreasing the capacity loss. Furthermore, Murugesan et al. [19] have demonstrated that Cu coating on Si reduces charge transfer resistance, improves the reversibility of the lithiation reaction and promotes the mechanical tolerance to volume expansion. In addition Kim et al. [20] have deposited Cu film by electroless deposition on the composite Si anode. The resulting film performs a remarkable improvement in the cycleability, as expected.

In this work, to control the stress propagation in the film and to promote the integrity of the electrode in cycling we propose to use functionally-graded SiCu film as a negative electrode. The film is designed to have pure Cu, then Cu rich layer close to the electrode/current collector interface and 10%at. Cu-90%at.Si content toward the top of the film (electrode/electrolyte interface). Cu is particularly chosen to be used with Si because it exhibits considerable plastic flow during electrochemical cycling, which is expected to impede the crack propagation. Moreover, its highly electron conductive behavior creates new electron pathway in the film to increases the cycling and rate efficiencies. Plus, its electrochemically inactive behavior vs Li would optimize the volumetric changes in the electrode. And, the existence of Cu atoms at the bottom is believed to increase the adhesion of the film to the Cu current collector [21–23].

The advantages of structured Si thin film electrodes prepared by means of various deposition methods including chemical vapor deposition, sputtering and evaporation have been reported by many bulk and micro-battery research groups [7,24–26]. Among alternatives, magnetron sputtering is preferred because highly energetic sputtered particles (Cu and Si in our case) are expected to form intermetallics in the coating as well as increase the adhesion of the film.

The originality of this work lies on engineering a functionally graded coating to relieve the stresses within the electrode and improve the adhesion of the film to the substrate without sacrifying the capacity delivered by the cell.

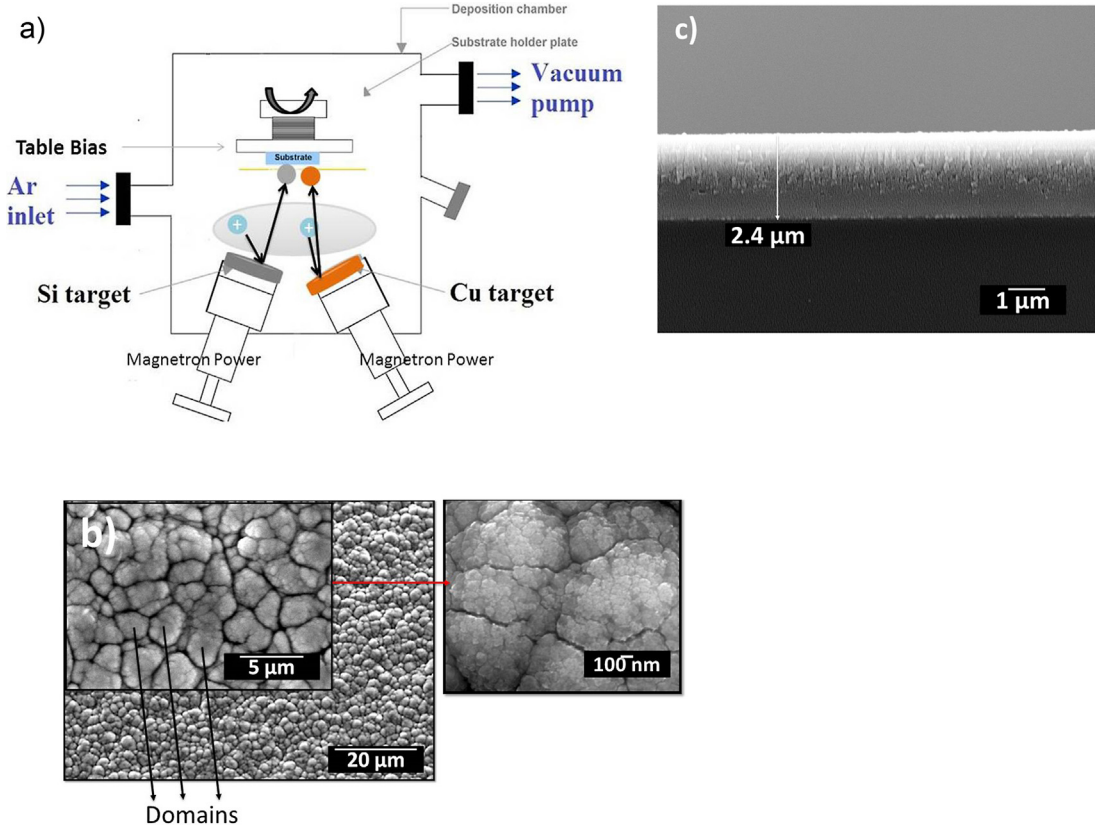

Fig. 1. a) Experimental Setup for magnetron sputtering, b) SEM surface and c) SEM cross sectional views of the functionally graded film.