

# Improving Si Anode Performance by Forming Copper Capped Copper-Silicon Thin Film Anodes for Rechargeable Lithium Ion Batteries



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## ARTICLE INFO

### Article history:

Received 2 March 2015

Received in revised form 10 April 2015

Accepted 23 April 2015

Available online 25 April 2015

### Keywords:

Copper-Silicon film  
electrochemical impedance analysis  
magnetron sputtering  
lithium ion batteries  
anode

## ABSTRACT

In this work, we deposit a bare and a Cu capped CuSi films (that contains 10 at. Cu 3  $\mu\text{m}$  thicknesses) by magnetron sputtering. The samples are galvanostatically tested with C/12 rate: the Cu capped CuSi film delivers 850  $\text{mAhg}^{-1}$  after 30th cycles, and it retains stable up to 100 cycle with 99% coulombic efficiency, whilst the bare CuSi film performs a gradual decrease in capacity over 100 cycles.

To understand the electrochemical process kinetics, influence the cycling performance, the impedance is measured by using impedance spectroscopy in equilibrium conditions at various states of charges. The results show Cu atoms being ductile, form a network to prevent the electronic isolation of Si particles or delamination of the film. Plus, they buffer the mechanical stress generated in the electrode following the volumetric changes during cycling. In the presence of the Cu top layer the surface reactivity of the CuSi electrode, and its interaction with the electrolyte, is also changed leading to a stable passive film formation and longer cycle life. Therefore, the top layer does not only exert remarkable favorable effects on the capacity, but also improves the coulombic efficiency and the rate capability of the electrode.

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## 1. Introduction

Nowadays the need for smaller and lighter portable electronic devices has increased which led the researchers to look for new anode materials of higher specific energy [1]. Among the alternatives to the existing carbonaceous materials, the use of silicon (Si) as anode material in lithium ion batteries (LIB) becomes remarkable because Si being the second most abundant element on earth, has a huge theoretical capacity of about 4200  $\text{mAh g}^{-1}$  when reacts with Li (at high temperature). However, Si anodes face several challenges. First, crystalline Si undergoes a 400% volume expansion during the lithiation process. During this reaction an immense stress as high as 1 GPa is generated [2]. Such high pressure easily causes pulverization, cracks formation and delamination of the film from the current collector, which brings about a failure in early states of cycling test. Second, the electrochemical alloying potential of Si is above the solvent reduction level, leading to the formation of solid electrolyte interface (SEI). While SEI formation has been well studied in

graphite, the formation mechanism of this passive film is not fully understood for Si anodes [1–2].

Recently, different designs have been proposed to overcome the quick failure problem of Si anodes. One approach is to improve the mechanical stability of Si anodes by either forming alloy with other ductile materials to act as a buffer or by using nano-sized materials dispersed uniformly in a buffer matrix. In this sense, Cu is used as an inactive but beneficial additive material in various forms other than substrate or current collector [3–6]. Indeed, in previous studies, it has been suggested that depositing Cu atoms on Si particles significantly improve the electrical contact and the cycle life of the electrode [5–7]. Considering this fact, in 2005 Kim et al. [7] 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 study, to enhance the reversible lithium storage capability, the cycle life and the rate-capability of the Si anode, multilayer structured Cu/CuSi anodes are designed. In the first design (bare) a very thin Cu layer is deposited on the substrate to enhance the adhesion of the film. Then, Cu and Si atoms are co-deposited to form uniformly dispersed copper silicides, which create an electronically conductive network in the film. In the second design (Cu capped), a Cu layer is coated on top of the first

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one to improve the mechanical, physical and surface properties of the Cu/CuSi film. Herein magnetron sputtering is chosen as a production technique because highly energetic sputtered particles (Cu and Si in our case) form well adherent film. And these particles are expected to form intermetallics in the coating, which would lead an improvement in the reversibility of the lithiation reactions.

To discuss the reason of the electrochemical performances of these designs, electrochemical impedance spectroscopy (EIS) is used. This powerful method gives information about electrochemical and physical properties of the electrodes if the time constants are resolvable [8]. In the EIS experiment a small sinusoidal voltage is applied using a fixed frequency approach and the current of the cell is measured accordingly. The analyses of impedance spectra are performed utilizing both Nyquist and Bode plots. Each spectrum is discussed based on the equivalent circuit built in series or parallel combination of resistances and a capacitance. The resistances due to each kinetic step during the electrochemical reactions are explained based on time constants, as previously stated in literature [9–13].

So far, structural changes of copper coated Si thin film [14], and the formation of SEI on Si thin film anodes [10] have been investigated by using EIS method. However, the unique structures of our Cu capped design (Cu/CuSi/Cu) is expected to perform different reaction kinetic than the other Si anodes reported in previous studies. Therefore, in this work, the impedance behaviors of these two designs (Cu/CuSi and Cu/CuSi/Cu) at different states of charges (SOC) during cycling are systematically investigated in order to better understand the electrochemical kinetics and mechanism of capacity fading.

## 2. Experimental

Bare and Cu capped CuSi films are produced by using a Cemecon CC800/9 magnetron-sputter system. High purity (99.99%) Si and Cu targets ( $500 \times 88 \text{ mm}^2$ ) are used in the experiment. The schematic representation of both films is given in Fig. 1.

The substrates are not stationary but rotating on a planetary holder system to increase the interaction of the Cu and Si atoms along the CuSi composite film. Prior to deposition, the substrates are cleaned with acetone and isopropyl alcohol before being placed

in the coating chamber. The chamber is pumped down to a pressure less than  $10^{-7}$  Torr. To enhance the adhesion of the films, Ar etching is applied to the substrate at 550 V bipolar pulsed with 250 kHz frequency and 1600 ns reverse time. After cleaning, first a Cu layer is deposited for 5 minutes on the substrates with -150 V bias, then for the deposition of the CuSi layer, 350 W and 2200 W are applied to Cu and Si targets for 120 min at -100 V bias. For the Cu capped film, after performing the first design procedure, the power used for Si targets is ceased and the deposition of Cu is continued for an additional 1 min, resulting in a Cu layer on top of the Cu/CuSi film (Fig. 1).

The films are deposited on four different substrates: Glass discs (Thermascal) for X-ray diffraction (XRD) analysis, Si wafers for cross sectional view, stainless steel discs (15.5-mm diameter and 1.5-mm thickness) for compositional analysis, and mechanically polished (1200, 800, 600, 320,  $3 \mu\text{m}$ ,  $1 \mu\text{m}$ ,  $0.5 \mu\text{m}$ ) Cu discs (15.5-mm diameter and 1.5-mm thickness) for electrochemical experiments.

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). The distribution of Cu and Si atoms along the coating (where SS is used as substrate) is displayed by means of glow discharge optic emission spectroscopy (GDOES) analysis (JobinY-con Horiba). During analysis, the RF excitation mode is used with 50 W power and 900 Pa pressure. The phases present in the coatings are determined using Philips PW3710 System with a  $2\theta$  range of  $10\text{--}100^\circ$  in steps of  $0.05^\circ$  (with  $\text{CuK}\alpha$  at 40 kV and 30 mA).

Electrochemical performances of the bare and the Cu capped CuSi electrodes are measured using a 2032 button coin cells, which are prepared in an argon filled glove box (MBRAUN, Labmaster) based on the following sequence: i) a working electrode; ii) a 1 M  $\text{LiPF}_6$  in the ethylene carbonate-dimethyl carbonate, EC:DMC 1:1 (Merck Battery Grade) electrolyte solution iii) a separator (Celgrad 2400) and iv) a lithium metal foil as the counter electrode. Once the cell is assembled in the right order, it is sealed by a pressure crimper inside a glove box. The galvanostatic tests are made at room temperature in between 0.2–1.2 V (vs  $\text{Li/Li}^+$ ) with C/12 rate for the bare and the Cu capped electrodes. To observe the change in surface morphologies of the electrodes in cycling, the cells are

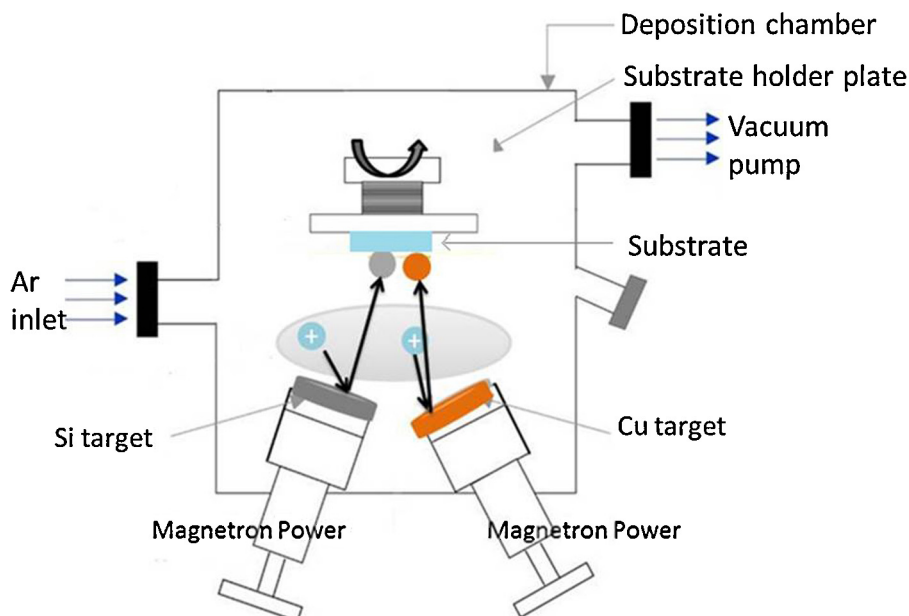


Fig. 1. Schematic representation of the bare CuSi, and the Cu capped CuSi thin film formation.

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