Journal of Power Sources 266 (2014) 353–364

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

The use of well-aligned composite nanorod arrays as anode material for lithium rechargeable batteries

B.D. Polat, O. Keles*

Department of Metallurgical and Materials Engineering, Istanbul Technical University (ITU), Maslak, Istanbul 34469, Turkey

HIGHLIGHTS

- Oblique angle electron beam deposition is used to form well-aligned CuSi nanorods.
- The adhesion of the film is improved by a prior deposition of the non porous film.
- The nanocolumnar morphology improves the electrochemical performance of the anode.
- XPS analyses reveal changes in SEI depending on the thin film's states of charge.
- An electrochemical dilatometer is first used to measure the volumetric changes.

ARTICLE INFO

Article history:
Received 13 January 2014
Received in revised form
26 April 2014
Accepted 3 May 2014
Available online 14 May 2014

Keywords:
Lithium ion battery
Nanorod
Composite thin film
Oblique angle deposition

ABSTRACT

The relations between the morphology and electrochemical performance of the thin film anodes made of copper and silicon are investigated. A well-aligned nanorods containing composite thin film and a composite thin film with no alignment in its structure are fabricated by electron beam deposition. Galvanostatic half-cell measurements show that the well-aligned anode exhibits a longer cycle life with a moderate capacity due the particularities in its composition, structure and morphology: Cu in the films buffers the mechanical stress occurred during lithiation and the existence of amorphous and nano-sized particles enhances cycleability. Moreover, the nanorods formation in the thin film increases the contact area of the anode with Li and decreases the polarization on the electrode surface. Plus, the homogenously distributed nano-sized interspaces among these nanorods enhance the mechanical tolerance of the electrode against volumetric changes.

In this work, the electrodilatometric analysis is also accomplished to measure the volumetric changes occurred upon cycling of the well-aligned nanorods containing thin film anode, and the difference in the electrochemical performances of the composite films resulting from different substrate position versus crucible is evaluated based on the X-ray photoelectron spectroscopy (XPS) analysis on the cycled samples.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

A development on the lithium ion battery (LIB) technology is highly required to improve the use of the effective energy storage devices. Within this concept, there is a great commercial interest in developing advanced electrode material. Knowing that negative electrode is the main contributor to the cell's overall electrochemical performance and silicon (Si) is one of the most abundant elements on earth, this study focuses on improving electrochemical performance of Si based materials used as negative electrode material in LIB. In fact, it is well known that the large volume expansion (400%) encountered during the alloying of Si with Li and the eventual pulverization of anode is the main disadvantage of the Si based anode materials, which restricts their wide usage in LIB.

To enhance the use of such Si based electrodes, researchers investigate the effects of electrode compositions and microstructural morphologies [1]. In literature, to provide a longer cycle life to an electrode, some scientists add a limited amount of copper (Cu) into silicon (Si) anode [2,3]. Cu is particularly chosen, because it has a superior conductivity and good solubility in Si, which in turn improves the electrical conductivity as well as the mechanical flexibility of the deposited film and its binding to Cu current collector [4]. However, deciding the amount of Cu added into the Si anode is

* Corresponding author. Tel.: +90 212 285 3398; fax: +90 212 285 3427.
E-mail addresses: ozgulkeles@itu.edu.tr, b.denizpolat@gmail.com (O. Keles).

http://dx.doi.org/10.1016/j.jpowsour.2014.05.006
0378-7753/© 2014 Elsevier B.V. All rights reserved.

a challenging task. Because, even though Cu increases the cycleability of the Si anode for the above mentioned reason, the theoretical capacity of the anode decreases due to electrochemically inactive behavior of Cu. Therefore, an optimization about the Cu content has been done previously, where the best result has been achieved by forming 90%at.Si–10% at.Cu containing anode material. In addition to this, recently, some researchers work on decreasing the particle size of the electrode [5–7] because it is believed that a nano-sized composite anode will have a higher electrochemical performance. However, during cycling, the nanoparticles merge due to their high surface energy (electrochemical sintering) to form dense blocks which are unable to take part in the electrochemical reaction [8]. Therefore, the particle–particle interaction in the electrode material should be avoided not only compositionally but also geometrically.

The production of Cu–Si nanorods in thin films could prevent "the electrochemical sintering" problem, due to their unique morphology. The interstitial space among these nanostructures (nanorods) is expected to avoid sintering and minimize macroscopic mechanical stresses arising during the insertion and removal of Li^+, so as to preserve electrode integrity. Moreover, these free spaces among the nanorods provide large active sites to accommodate lithium (Li^+) and generate an easy route for the electrolyte to access the entire anode surface, which in turn improves capacity delivered by electrodes [9,10]. In 2011, Ryu et al. prove that the nanostructured electrodes improve the cycle life (nanorod's diameter < 300 nm) because of the fast Li^+ diffusion, which reduces polarization and creates small stresses along the film upon cycling [9].

So far, in order to have Si nanorods, laser irradiation of silicon surface [11], chemical vapor deposition of SiH_4 [12,13] and lithography based ion etching methods [14] were used. Oblique angle deposition (OAD) via electron beam evaporation method has also taken attention. Because in such an evaporation method, it is possible to avoid the hazardous flammable handling, explosive or cancerogenous metal nanoparticles. In addition, OAD enables direct deposition of the well-aligned inclined nanorods on a current collector, eliminating the need of binder or conductive additives to get homogeneously distributed porosities in thin films, which ensures the direct transportation of electrons; hence a fast Li^+ diffusion through their controllable, small diameters [15].

The mechanism of the nanorods formation during the OAD method has been studied previously. The results show that it is possible to control the orientation of the nanorods growth by changing the incident flux angle because the electron beam deposition is a line-of sight process. Therefore, to have nanorods in OAD method, the substrate position should be fixed to receive the evaporated particle flux under a highly oblique angle (Θ) of the substrate's surface normal ($\Theta > 70^\circ$). The vapor flux ($\vec{F}$) hits the substrate from both vertical ($\vec{F}_I = \vec{F}\cdot\cos\theta$) and lateral ($\vec{F}_{//} = \vec{F}\cdot\sin\theta$) directions: the vertical component ($\vec{F}_I$) induces film growth and the lateral component ($\vec{F}_{//}$) contributes to the shadowing effect [15].

Karabacak et al. [16,17] highlight the importance of this "shadowing effect" and define it as one of the dominated mechanism that controls the oblique angle deposition, competing with "surface diffusion process". At room temperature deposition, since the surface diffusion rate is very slow, the impinging atoms randomly form islands on the substrate, when such growth is governed by Volmer–Weber or Stranski–Krastanov process. As deposition proceeds, the initially nucleated islands act as shadowing centers and all large islands receive more impinging atoms as compared to small ones, leading to inclined nanocolumnar film growth, where homogeneously distributed porosities are formed among the inclined nanorods. Thereby, a decrease in the incident flux angle (Θ) deteriorates the columnar growth, and generates a non-aligned (flat) film when the Θ is 0°. Thus, to control the porosity or interspaces the incident flux angle (Θ) should be close to 90°.

Table 1
EDS analyses of the non-aligned and the well-aligned nanorods containing Cu–Si composite thin films.

Non-aligned Cu–Si thin film				Nanorods containing well-aligned Cu–Si thin film			
Cu		Si		Cu		Si	
at%	wt%	at%	wt%	at%	wt%	at%	wt%
11.46	22.67	88.53	77.33	8.81	17.94	91.19	82.06

Besides the incident flux angle (Θ), substrate surface roughness and evaporation source composition have significant impacts on the composition and the morphology of thin films, which in turn affect their electrochemical performances, when used as anodes in LIB [15–17].

Cracking, pulverization and peeling of the Si based thin film from the underlying current collector during cycling test are major problems encountered when Si based films used as anodes. In literature, different methodologies have been proposed to resolve these problems: one is to engineer a nanostructured compliant layer below or above thin films to reduce the stress [17], another is to engineer a graded composition through the films [18].

In this study, the oblique angle electron beam co-evaporation method is used to produce well-aligned Cu–Si nanorods containing thin film. In order to enhance the electronic contact of the thin film with the substrate and to delay aggregation in the thin film during cycling, first a layer of Ref. [16] a non-aligned (flat) Cu–Si layer is deposited before the well-aligned nanorods as it has been done in our previous work [19]. Furthermore, to compare the electrochemical performances, a thin film with no alignment in its structure is also produced. XPS analyses of both anodes at different states of charges (pristine, 1st discharge and 1st charged states) are also done to discuss the changes in the electrode/electrolyte interfaces of the films, depending on their morphologies. Finally, an in-situ electrochemical dilatometer is used to measure the volumetric change occurred in the first cycles of the well-aligned nanorods containing composite thin film. Among alternative measuring techniques (in-situ neutron images taken during cycling [20], in-situ strain gauge [21], in-situ X-ray [22] measurements and atomic force microscopy [23]) we particularly choose this method because it gives accurate information about non-periodic strain similar to that in amorphous phases or on the surface of the material.

2. Experimental

The non-aligned and the well-aligned Cu–Si nanorods containing thin films were deposited on copper discs (with 15.5 mm diameter and 1.5 mm thickness) using electron beam co-deposition technique. In addition to copper (Cu) discs, a pure silicon (Si) wafer (20×10 mm^2) and a stainless steel (SS) disc (15.6 mm diameter and 1 mm thickness) were also coated during the experiments, to measure the coating thickness, and the composition of the thin films accurately. It should be emphasized that the Cu and Si pellets were put together in a graphite crucible prior to the co-evaporation deposition process, where their ratio (Cu/Si weight ratio) was 1:9, for each sample.

During the experiment, first a non-aligned thin film was deposited on a Cu substrate with an incident flux angle of 0°. Then, the well-aligned composite nanorods were formed when the deposition flux hit onto the substrate surface's normal with an angle of 80° at room temperature.

Download English Version:

https://daneshyari.com/en/article/1286758

Download Persian Version:

https://daneshyari.com/article/1286758

Daneshyari.com