J MATER SCI 41 (2006) 313–315

Review

Effects of Cu current collector as a substrate on electrochemical properties of Li/Si thin film cells

CHO GYU BONG, LEE BONG KI, SIN WON CHUL, CHO KWON KOO,
AHN HYO JUN, NAM TAE HYUN, KIM KI WON
Information Technology Research Center for Energy Storage and Conversion, Gyeongsang National University, Gazwadong 900, Jinju, Gyeongnam 660-701, Korea

Metallic Si, whose the theoretical capacity reaches to 4200 mAh/g based on the formation of $Li_{4.4}Si$ ($Li_{22}2Si_5$) phase, is a promising anode material for the Li micro-batteries [1]. However, when Si is applied to the Li batteries, the formation of $Li_{4.4}Si$ is accompanied with a large volume expansion of electrode and leads to a rapid capacity fade. Thus, much of the experimental and theoretical effort has been focused on reducing structural change in the Si electrode.

Cu foil has been used as a commercial current collector for Li batteries and applied as a substrate for thin film batteries. Recently, some studies achieved a prolonged lifetime of Li/amorphous Si film cell with high capacity using a mechanically roughened Cu foil substrate [2, 3]. The rough surface of substrate enhanced the adhesive force between an active material and a current collector. Therefore, surface roughness of substrate is an important factor to improve the cycleability of Li/Si film cell.

However, the manufacturing processes of the commercial Cu foil influence strongly on its microstructure as well as surface roughness. Those factors must be significantly treated, when batteries are fabricated at micro scale. Nevertheless, there was no report on clarifying relationship between them. Thus, the investigation of the relationship between microstructure and roughness of substrate as a current collector is important to understand the electrochemical properties of thin film microbatteries.

In this study, a rolling process is applied to roughen the surface of Cu foil and to change its microstructure. It was well known that the formation of shear bands causes peaks and valleys (trenches) in the roughness topography running in the transverse direction [4–6]. The objectives of this study are to examine the structure and the surface feature of differently treated Cu foils and to clarify effects of those factors on the electrochemical properties of Li/Si film cell.

Two kinds of Cu foil substrates with the same thickness were prepared as the current collector of the Li/Si film cell. One is an annealed foil(Cu-2). As-received foil was annealed in a vacuum tube at 773 K for 30 min. The other is a worked foil(Cu-3), which was prepared by a repetition rolling of a Cu sheet, and this process was conducted at Electronics and Telecommunications Research Institute (ETRI).

4 μm thick Si films were fabricated on the Cu substrates by radio-frequency (rf) magnetron sputtering system. The film was grown in the vacuum chamber under pressure of 5×10^{-3} torr at 298 K in Ar atmosphere.

The cell was composed of a metallic Li foil as the reference and counter electrodes, a porous polypropylene separator and a Si film as a working electrode. The electrolyte was 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and dymethyl carbonate (DMC). Charge-discharge measurements were performed with constant current.

The crystalline structures of films were investigated by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM). The surface morphology and the roughness of Cu foils were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Fig. 1 shows the XRD patterns obtained from Cu foil substrates. The differently treated specimens can be obviously distinguished by peak intensity. In as-received foil (Cu-1), the peak intensity of (111) plane is nearly the same with that of (200) plane. When the foil is annealed (Cu-2), a peak of (200) plane appears weakly compared with Cu-1. This is because change in the microstructure of Cu foil occurs during the annealing process. In particular, a strong peak of (200) plane appears in the worked foil (Cu-3) with a very weak peak of (110) plane. This shows a typical texture-like structure formed by a repetition rolling along a certain direction. It can be roughly found that microstructure of Cu substrates are given influences on each pretreatment.

The surface morphologies of the annealed and worked Cu substrates are shown in Fig. 2, where SEM photographs are presented in Figs 2a and b and AFM images are inserted in each figure. The cross sectional profiles

0022-2461
DOI: 10.1007/s10853-005-2656-6

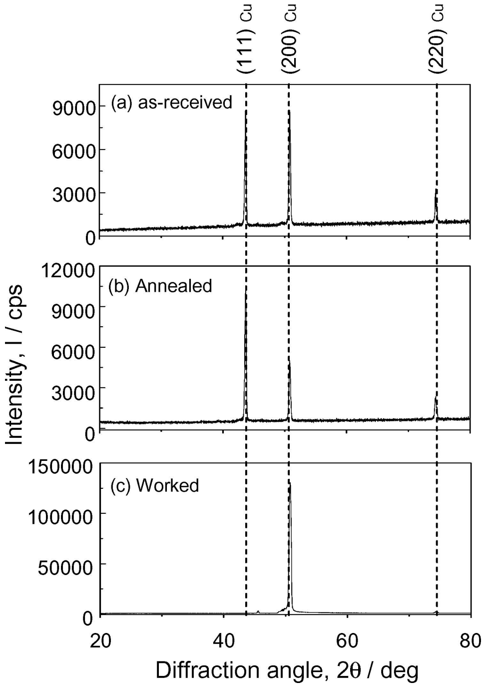

Figure 1 XRD profiles of (a) as-received Cu substrate, (b) annealed substrate and (c) worked substrate.

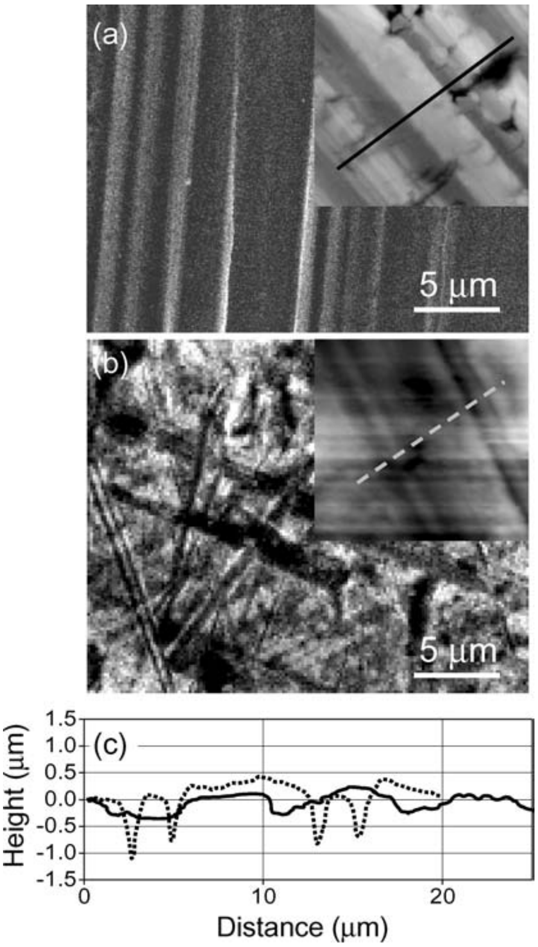

Figure 2 SEM photographs and AFM images of annealed and worked substrates. Cross-sectional profiles correspond to solid lines in the insets of (a) and (b).

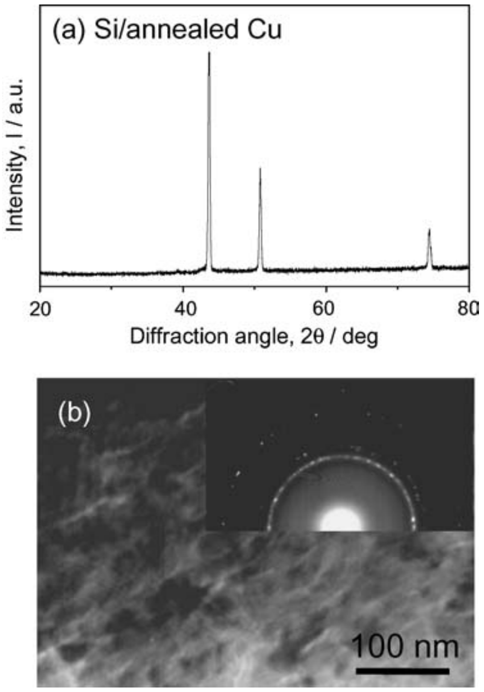

Figure 3 XRD profile and TEM observation of Si film deposited on an annealed Cu substrate.

of solid lines in the insets are represented in Fig. 2c. Trenches, which were formed during the rolling process, are observed on surfaces of the two Cu substrates and are mostly arranged parallel to the rolling direction. In distinction to trenches with one direction in Cu-2, trenches in Cu-3 are formed with various directions. This means that the Cu-3 substrate was more severely worked rather than the Cu-2 substrate.

Root mean square (RMS) roughness, which is measured with five AFM images for each specimen, is 320 nm for Cu-2 and 630 nm for Cu-3, respectively. The surface roughness of Cu-3 is near two times of that of Cu-2. It is found that the rolling forms trenches on the surface of Cu foils and roughens their surfaces. In addition, when a repetition rolling is conducted with the Cu foil, depth of trenches becomes deeper and then surface roughness increases as shown in Fig. 2c.

XRD profile of Si film grown on the annealed Cu foil substrate is shown in Fig. 3a. No peaks associated with Si are found and the peaks are the same with those of the Cu substrate. Such results were also obtained from Si films grown on the rest Cu substrates (not sown here). This means that Si film grown on the Cu substrate has amorphous structure. More detail investigation of Si film is performed by TEM observation. TEM image of the Si film grown on the annealed Cu substrate are shown in Fig. 3b and diffraction pattern are inserted in the inset. Hallow and ring patterns can be seen in the inset. The hallow pattern corresponds to the Si film and the ring patterns corresponds to the Cu substrate. Thus, the film fabricated in our study consists of a polycrystalline Cu substrate and an amorphous Si film. Our results coincide

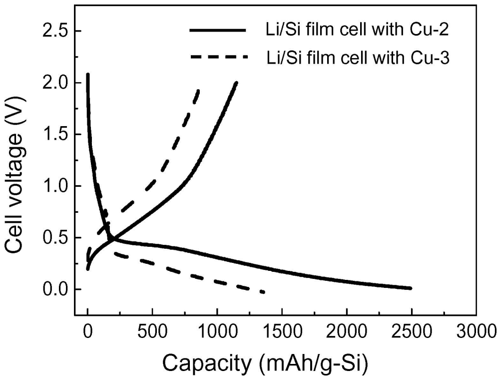

Figure 4 The initial charge-discharge curves of Li/Si film cells with annealed and worked substrates.

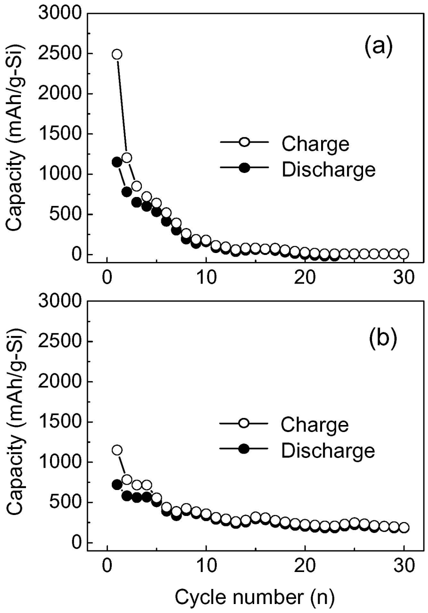

Figure 5 Cycle performance of Li/Si film cell with annealed and worked substrates.

with those of Raman spectroscopy [2] and XRD analysis [7].

The initial charge-discharge curves of Li/Si film cells with different Cu current collectors are shown in Fig. 4. Typical charge curves with two flat regions appear in the two cells. It has been known that two reaction regions are resulted from formations of Li_2Si and $Li_{4.4}Si$ phases [1]. The Li/Si film cell with Cu-2 shows a large amount of charge capacity compared to the Li/Si film cell with Cu-3. Despite of applying the same current density to the cells, for the cell with Cu-3, the plateau related to the formation of Li_2Si phase appears at lower voltage. This means that the internal resistance of Li/Si film cell with Cu-3 is higher than that of the cell with Cu-2. Such difference in the resistance is attributed to the interface between Si and Cu, because the rougher Cu substrate forms wide surface area of the interface. Moreover, the rolling process induces the increase of dislocation density in the substrate and leads to the increase of resistance during charge-discharge reaction. On the other hand, the microstructures of the annealed substrate are stabilized in crystallographic compared to the worked substrate. When considering the XRD analysis of the annealed Cu substrate, (111) plane which has the lowest surface energy in an fcc crystal exists dominantly [8]. The stabilized structure improves electric conductivity of the substrate as well as cell performance in the Li/Si film cell.

Fig. 5 shows the cycle performances of the Li/Si film cells with different Cu current collectors. In the Li/Si film cell with Cu-2, the steep decrease of charge-discharge capacity occurs at lower cycle number, while capacity of the cell with Cu-3 slowly decreases with cycle number. This is considered that the rough surface improves adhesive force with Si film and prevents from crumbling and falling-off of the active material during the charge-discharge reaction. From our electrochemical results, it is concluded that initial capacity depends on the microstructures of substrate and the cycle performance does on surface roughness.

In this study, it is emphasized that the electrochemical performance of Li/Si film cell are not simply improved with roughened Cu foil and the structural properties of substrates must be sufficiently considered prior to the utilization as a current collector.

Acknowledgment

This work was supported by University IT Research Center Project from Ministry of Information and Communication Republic of Korea.

Reference

1. C. J. WEN and R. A. HUGGINS, *J. Solid State Chem.* **37** (1981) 271.
2. K. L. LEE, J. Y. JUNG, S. W. LEE, H. S. MOON and J. W. PARK, *J. Power Sources* **129** (2004) 270.
3. H. IKEDA, M. FIJOIMOTO, S. FUJITANI, Y. DOMOTO, Y. YAGI, H. TARUI, N. TAMURA, R. OHSHITA, N. KAMINO and I. YONEZU, in Proceedings of the Presentation at the 42nd Battery Symposium, Japan, 2001, p. 282.
4. K. MATSUI, *Kobelco Tech. Rev.* **12** (1991) 60.
5. H. KIMURA, Discussion on Pinhole Formation in Pack Rolling of Aluminium Foils, in Proceedings of 70th Spring Meeting Japan Institute of Light Metals, JILM, Tokyo, 1986, p. 65.
6. R. AKERET, *Aluminium* **68** (1992) 318.
7. S. J. LEE, J. K. LEE, S. H. CHUNG, H. Y. LEE, S. M. LEE and H. K. BAIK, *J. Power Sources* **97/98** (2001) 191.
8. D. A. PORTER and K. E. EASTERLING, in "Phase Transformations in Metals and Alloys" (Chapman & Hall, London, 1992) p. 115.

Received 21 February
and accepted 31 May 2005