

Si–Zr alloy thin-film anodes for microbatteries

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Abstract

Zr–Si thin films were deposited on copper substrates by co-sputtering method of two pure targets. The structure and surface morphology of the films have been characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM). The composition was measured by Rutherford backscattering spectroscopy (RBS) and energy-dispersive X-ray spectroscopy (EDS). The electrochemical results showed that alloying with Zr improves the cycling performance, while as a result the reversible capacity decreases. It appears that the electrochemical cycling performance can be further improved by controlling the film deposition conditions such as substrate temperature and bias sputtering. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Currently, there exists a need for thin-film solid state microbatteries as power sources for small electronic devices such as smart cards and micro electromechanical system (MEMS). In general, lithium metal has been used for the anode material in thin-film microbatteries. In view of safety, materials availability, and practical manufacturing, however, it is necessary to replace the lithium metal anode by new material [1–3].

Silicon-containing thin films are promising materials for anode materials of microbatteries because of high capacity. The theoretical capacity for the reaction of silicon and lithium is 4000 mAh/g, corresponding to $\text{Li}_{21}\text{Si}_5$ [4,5]. The major drawback for Li–Si electrode is its poor cyclability caused by mechanical cracking due to the volume change of lithium silicide during charge-discharge process [5,6]. Recently, this problem has been significantly improved by synthesizing metal silicide alloys with active (Si) and inactive metal elements such as Cr–Si [7] and Ni–Si [8] alloys. Therefore, metal silicide alloys can be thought to be suitable as anode materials for thin-film microbatteries. On the other hand, in the NiSi electrode it is assumed that the reaction of NiSi with lithium results in the formation of element Ni and Li_xSi [8]. However, such decomposition reaction may cause the structural instability of silicide alloys and capacity fade.

A strong affinity between components of silicide alloys seems to be essential for good cyclability of silicide electrodes because the strong bonding of metal atoms with Si may limit lithium alloying with Si to form Li_xSi alloys and prevent structural rearrangements of the electrode. The Zr–Si system was chosen here for investigation, because of its large negative heat of mixing of the constituent elements [9].

In this work, we report the preparation and electrochemical evaluation of the Zr–Si alloy thin films.

2. Experimental

Zr–Si thin films were deposited on a Cu substrate (12 mm diameter) by co-sputtering of two separate targets, Si and Zr. The film composition and thickness of the films were controlled by the rf power for the Zr target by deposition time, respectively. A substrate was water-cooled during deposition for an amorphous film formation. For some samples, the substrate was not cooled, or a dc negative bias was applied to the substrate ranging from 0 to –100 V. The base pressure was 2×10^{-6} Torr. The pressure of Argon during deposition was 5×10^{-3} Torr.

For electrochemical measurements, coin type half cells were constructed using the film electrodes in 2016 coin cell hardware. Cells were assembled in an argon-filled glove box. The electrolyte was 1 M LiPF_6 dissolved in a 50:50 (vol.%) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (provided by Cheil Industries, Inc.,

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South Korea), and a lithium foil for the counter and reference electrode. All cells were tested at 30 °C with a constant current of 30 μA between 0 and 1.5 V.

The composition analysis for the Zr–Si thin film was carried out by Rutherford backscattering spectroscopy (RBS), and energy-dispersive X-ray spectroscopy (EDS). The surface morphology was observed by atomic force microscopy (AFM). The structural properties were determined by X-ray diffraction (XRD), and the chemical states of the elements in the films were analyzed by X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-deposited Si–Zr thin films. Two peaks near 44 and 50° are diffracted from the copper substrate. No peak is observed in relation with Si–Zr thin film, hence, it seems that all the films were nearly amorphous or nanocrystalline structure.

Fig. 2 shows the first and second discharge (lithium insertion) – charge (lithium extraction) curves for the Zr–Si thin-film electrodes with different compositions. The alloying of Si with Zr leads to the capacity reduction. It indicates that the Zr–Si bonding is maintained during the Li insertion process.

The discharge plateau regions are observed for films with smaller Zr content, such as $\text{Si}_{0.8}\text{Zr}_{0.2}$ and $\text{Si}_{0.7}\text{Zr}_{0.3}$ but invisible for the $\text{Si}_{0.6}\text{Zr}_{0.4}$ electrode (Fig. 3). This behavior is apparent, which shows the differential capacity for the

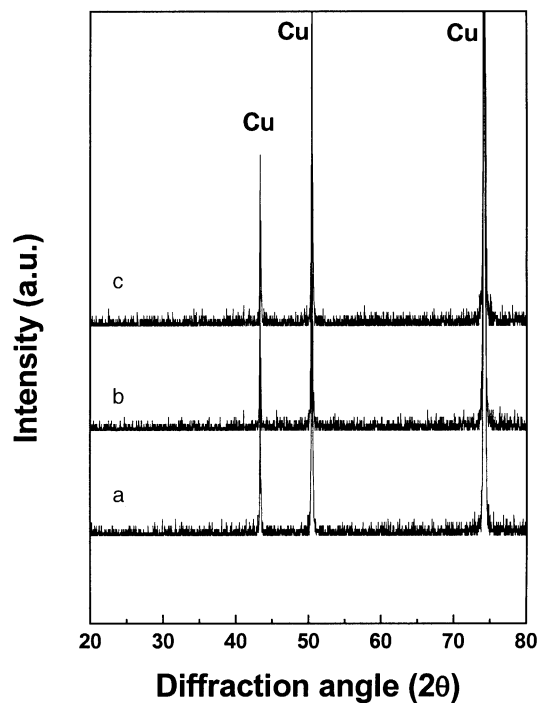


Fig. 1. XRD pattern of the as-deposited $\text{Si}_{0.6}\text{Zr}_{0.4}$ thin film: (a) $\text{Si}_{0.8}\text{Zr}_{0.2}$, (b) $\text{Si}_{0.7}\text{Zr}_{0.3}$, (c) $\text{Si}_{0.6}\text{Zr}_{0.4}$.

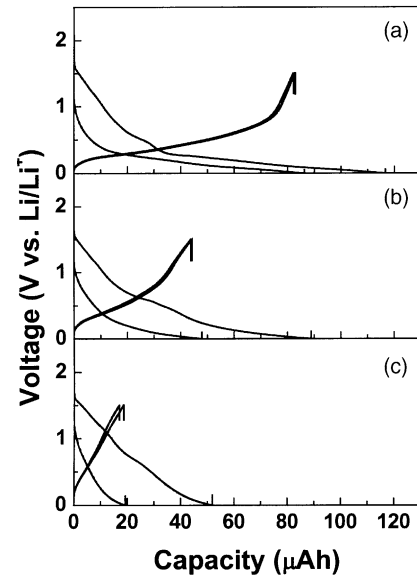


Fig. 2. The discharge–charge curves for the Zr–Si thin-film electrodes with different compositions: (a) $\text{Si}_{0.8}\text{Zr}_{0.2}$, (b) $\text{Si}_{0.7}\text{Zr}_{0.3}$, (c) $\text{Si}_{0.6}\text{Zr}_{0.4}$.

second cycle of the same cells as in Fig. 2. For comparison, the differential capacity of the Si thin film is also shown. The plateaus evident for samples in Fig. 2 appear as sharp peaks in Fig. 3, in which the strong peaks are indicative of the formation of bulk-like Li–Si alloys. The differential capacity curve of $\text{Si}_{0.8}\text{Zr}_{0.2}$ film appears to be similar to that of Si film. For $\text{Si}_{0.7}\text{Zr}_{0.3}$ and $\text{Si}_{0.6}\text{Zr}_{0.4}$, the differential curves become very smooth, which is consistent with the steep slopes of the voltage profiles. This suggests that there are no distinct phase transitions related with the formation Li_xSi alloys.

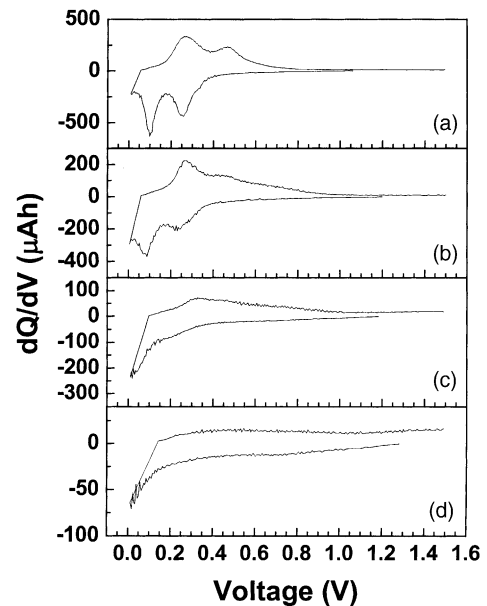


Fig. 3. The differential capacity vs. voltage for the second cycle of the Si and the Zr–Si thin-film electrodes with different compositions: (a) Si, (b) $\text{Si}_{0.8}\text{Zr}_{0.2}$, (c) $\text{Si}_{0.7}\text{Zr}_{0.3}$, (d) $\text{Si}_{0.6}\text{Zr}_{0.4}$.

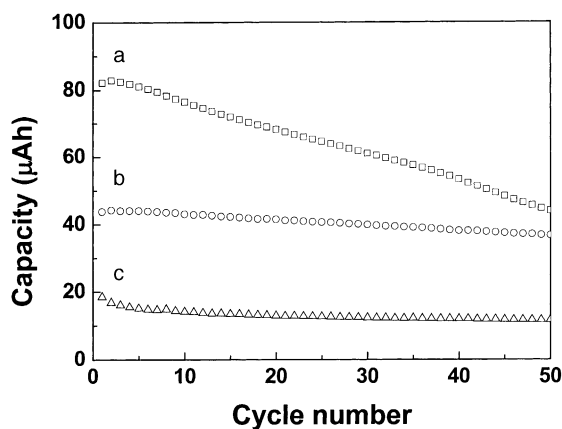


Fig. 4. The capacity vs. cycle number for the Zr–Si thin-film electrodes with different compositions: (a) $\text{Si}_{0.8}\text{Zr}_{0.2}$, (b) $\text{Si}_{0.7}\text{Zr}_{0.3}$, (c) $\text{Si}_{0.6}\text{Zr}_{0.4}$.

Fig. 4 shows the capacity versus cycle number for the Zr–Si thin-film electrodes. The $\text{Si}_{0.7}\text{Zr}_{0.3}$ and $\text{Si}_{0.6}\text{Zr}_{0.4}$ thin-film electrodes show better cycling performance than the $\text{Si}_{0.8}\text{Zr}_{0.2}$ one. It is suggested that the strong bonding of Zr atoms with Si atoms may prevent Si from alloying large amount of Li and remain the microstructure of film stable during cycling. On the other hand, the poor cyclability of the $\text{Si}_{0.8}\text{Zr}_{0.2}$ electrode may be attributed to the cluster of Si in the thin film, as inferred from plateaus in the voltage profile curve or peaks in differential capacity plots as shown in Figs. 2 and 3.

In general, the structure of thin films is dependent on the deposition conditions such as the substrate temperature and substrate bias voltage.

Fig. 5 shows the discharge–charge curve for the $\text{Si}_{0.8}\text{Zr}_{0.2}$ thin films prepared with substrate cooling (curve a), without substrate cooling (curve b), and under substrate bias voltage of -100 V without cooling the substrate (curve c). The plateau-like region around 0.5 V observed in curve (a) decreases when deposited without cooling the substrate and

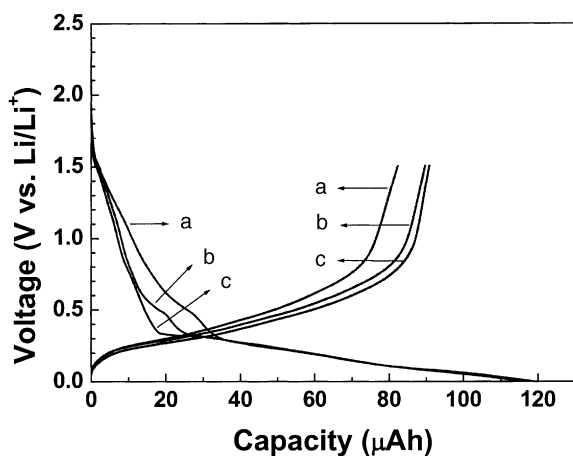


Fig. 5. The discharge–charge curves for the $\text{Si}_{0.8}\text{Zr}_{0.2}$ thin-film electrodes prepared (a) with substrate cooling, (b) without substrate cooling, and (c) under substrate bias voltage of -100 V without cooling the substrate.

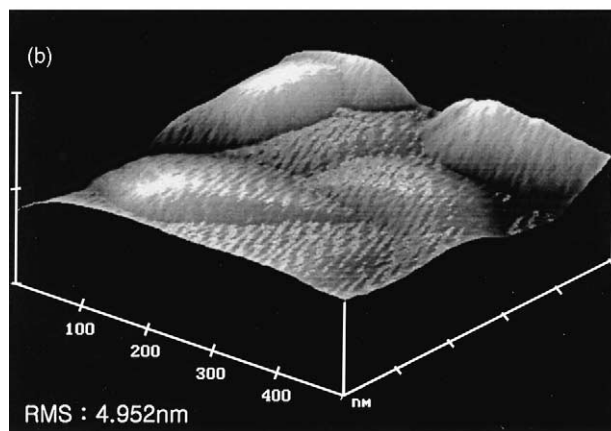
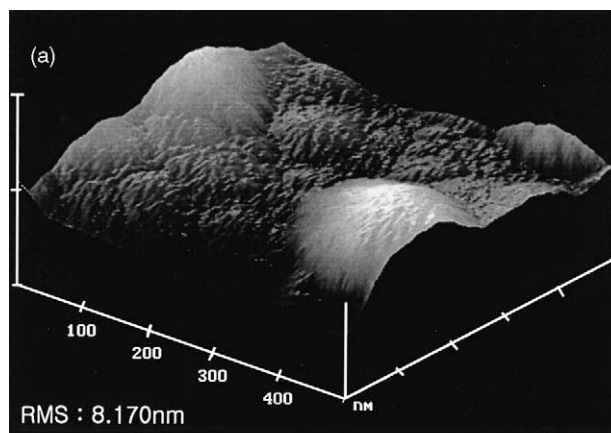


Fig. 6. The AFM images of the $\text{Si}_{0.8}\text{Zr}_{0.2}$ thin films prepared (a) by normal sputtering and (b) sputtering under negative bias voltage.

more significantly when the bias voltage is applied during deposition, which leads to the reduction of the initial irreversible capacity loss.

Fig. 6 shows the AFM images of the $\text{Si}_{0.8}\text{Zr}_{0.2}$ thin films prepared by normal sputtering (Fig. 6a) and sputtering under negative bias voltage (Fig. 6b). When the negative dc bias is applied to the substrate, Ar ions bombard the surface of the growing film, which leads to a dense film, and smooth surface morphology. The more negative bias applied, the smoother film surface with smaller root mean square roughness value is obtained.

Fig. 7 shows the cycle performance of the $\text{Si}_{0.8}\text{Zr}_{0.2}$ thin-film electrode as a function of the deposition condition. The enhanced cyclability is obtained for the thin-film electrode prepared without cooling the substrate, especially, deposited by bias sputtering.

It is believed that the deposition of Zr–Si film without cooling the substrate and under the substrate bias voltage leads to the homogeneous distribution of Zr and Si atoms and the dense structure of film. This may be responsible for the enhanced cycle performance, but the exact reason is not clear at present. Detailed structural and electrochemical studies are necessary to demonstrate the optimum properties.

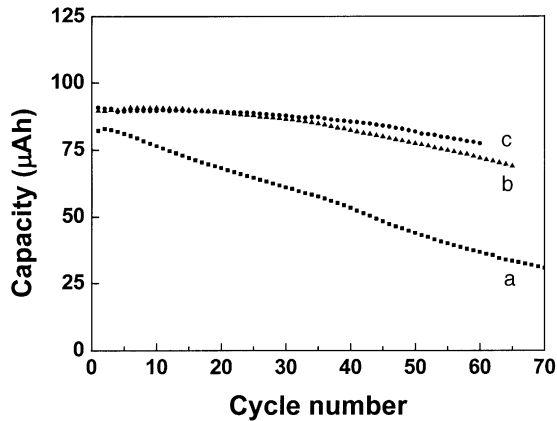


Fig. 7. The capacity vs. cycle number for the $\text{Si}_{0.8}\text{Zr}_{0.2}$ thin-film electrodes prepared (a) with substrate cooling, (b) without substrate cooling, and (c) under substrate bias voltage of -100 V without cooling the substrate.

4. Conclusions

Zr–Si thin-film electrodes are fabricated by co-sputtering from the Zr and the Si target. Electrochemical performance of Zr–Si alloy thin film is dependent on the composition of films and for a given composition of the film, the cyclability can be further improved by controlling the deposition condition such as substrate temperature and bias sputtering. It appears that the uniform distribution of the inactive elements having strong affinity with Si is the important factor for the

enhanced electrochemical cycling performance of the Zr–Si thin-film electrodes. Zr–Si thin film is strong candidate as a negative electrode for rechargeable thin-film batteries although further optimization studies are necessary.

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References

- [1] B.J. Neudecker, R.A. Zuhr, J.B. Bates, *J. Power Sources* 81–82 (1999) 27.
- [2] S.C. Nam, Y.S. Yoon, W.I. Cho, B.W. Cho, H.S. Chun, K.S. Yun, *Electrochem. Commun.* 3 (2001) 6.
- [3] S.-J. Lee, H.-Y. Lee, T.S. Ha, H.-K. Baik, S.-M. Lee, *Electrochem. Solid-State Lett.* 5 (2002) A138.
- [4] R.A. Sharma, R.N. Seefurth, *J. Electrochem. Soc.* 123 (1976) 1763.
- [5] J.O. Besenhard, P. Komenda, A. Paxinos, E. Wudy, M. Josowicz, *Solid State Ionics* 18–19 (1986) 823.
- [6] J.O. Besenhard, M. Hess, P. Komenda, *Solid State Ionics* 40–44 (1990) 525.
- [7] W.J. Weydanz, M. Wohlfahrt-Mehrens, R.A. Huggins, *J. Power Sources* 81–82 (1999) 237.
- [8] G.X. Wang, L. Sun, D.H. Bradhurst, S. Zhong, S.X. Dou, H.K. Liu, *J. Power Sources* 88 (2000) 278.
- [9] A.R. Miedema, *Philips Technol. Rev.* 36 (1976) 217.