

Electrochemical properties of Si thin film electrodes

M.S. Park^{a,b}, G.X. Wang^{a,b}, H.K. Liu^{a,b} and S.X. Dou^a

^a *Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia.*

^b *ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW 2522, Australia.*

1. Introduction

Si thin film has been considered as one of the most promising anode materials for lithium ion micro-batteries because of its large theoretical capacity. However, mechanical pulverization due to the large volume change of Si occurs even in Si thin film electrodes during charge-discharge reactions, which causes the poor electrochemical and structural stability of Si thin film electrodes [1-2]. Recently, density and strong adherence to the substrate of the thin film have been regarded as critical issues because they are directly relevant to the electrochemical performance. Previously, P.N. Kumta et al. [3] reported that Si thin films has been directly deposited on the substrate by radio frequency (RF) magnetron sputtering to avoid any degradation resulting from binders or additives. The result was in the negative for a 1 μm thickness sample because the electrode pulverization which arises from high compressive stress due to the thickness could not be avoided the cycling. On the other hand, the low pressure chemical vapour deposition (LPCVD) technique has been suggested as a promising process by H. Jung et al. [4]. However, electrochemical stability was only founded in the film with a thickness less than 200 nm. In fact, the thickness of the thin film, which is directly related to the volumetric capacity has been limited by the adhesion properties resulting from different fabrication methods. Among the various methods, the pulsed laser deposition (PLD) technique is the most appropriate method to make a denser and thicker thin film which establishes strong adhesion to a substrate in a short time [5-6].

In this paper, we present the preparation and electrochemical characteristics of amorphous PLD-grown Si thin films as a function of thickness. The Si thin films with a thickness over 1 μm show interesting electrochemical performance compared to the previously reported Si thin films [4-5]. The PLD method was suitable for improving the density and adhesion behavior of the films. As a result, Si thin film prepared by PLD appears to be a promising anode material with excellent cycleability for lithium ion micro-batteries.

2. Sample preparation

The Si thin films were directly fabricated on stainless steel substrates, 16 mm in diameter, using the PLD technique. After etching with acetic acid, the stainless steel substrates attached to a heating plate at a distance of 30 mm from the target. The substrate temperature and the beam incident angle were fixed at 500 °C and 45°, respectively. The deposition pressure was 5×10^{-1} Torr of Ar. The Si thin films with different thicknesses were synthesized following the same procedure but with different deposition times, 1 h and 2 h. The microstructure and morphology of the films were characterized by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and atomic force microscopy (AFM). Half cells (CR2032 coin-type) were fabricated for the charge and discharge experiments. The assembly was carried out in an Ar-filled glove box (MBraun, Unilab, Germany) with less than 0.1 ppm each of oxygen and moisture. Li metal foil was used as the counter and reference electrode. 1M LiPF₆ dissolved in a 1 : 1 (by volume, provided by Merck KgaA, Germany) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte, and Celgard membrane as the

separator. The anodic performance of the Si thin films was measured up to the 70th cycle in the range of 0.005 to 1.5 V (vs. Li/Li+).

3. Results

The Si thin films were directly prepared on the stainless steel substrates under optimized conditions using the PLD system. We varied only the deposition time to determine the thickness effects on the electrochemical performance of the films. X-ray diffraction (XRD) results reveal that the Si thin films prepared by the PLD technique can reasonably be considered as amorphous. No strong diffraction peaks of Si was presented except for a single peak near 28° , which has very low intensity and a broad shape, all other reflections can be attributed to the stainless steel substrate.

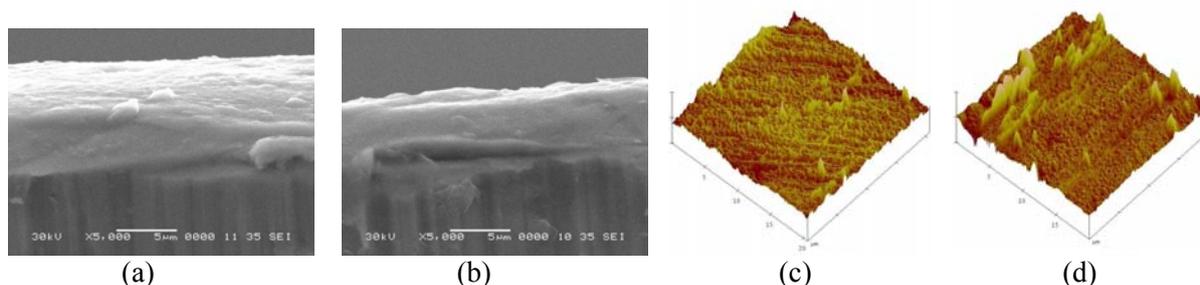


Fig. 1. Cross-sectional SEM image and AFM image of the Si thin films prepared by the PLD technique. (a) and (c) 1 hour deposition time; (b) and (d) 2 hours deposition time.

Cross-sectional SEM images and AFM images of the films are presented in Fig. 1. The thicknesses of the films deposited for 1 h and 2 h are estimated to be about $1.5 \mu\text{m}$ and $3.0 \mu\text{m}$, respectively in Fig. 3 (a) and (b). The thickness increases in proportion to the deposition time and the deposition rate can be calculated as 25 nm/min . The morphology of the films was determined by AFM as shown in Fig. 1 (c) and (d). All samples have a rough surface, which depends on the deposition characteristics of the PLD system and the morphology of the substrate. From the comparison, the thin film deposited for 1 hour has a flatter morphology without irregular pillars and ravines, which might have bad effects on the electrochemical performance because they provide more spaces for dendrite formation and agglomeration.

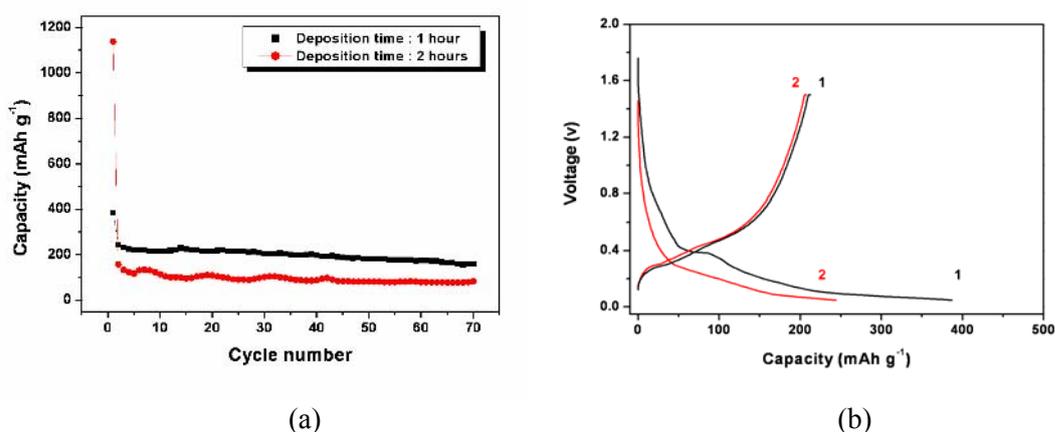


Fig. 2. (a) Cyclic performance of the Si thin films with different deposition times up to the 70th cycle, and (b) Charge-discharge profiles for the first two cycles of the Si thin film deposited for 1 hour.

The thickness of the thin film is one of the most influential factors on the electrochemical properties, as is shown in Fig. 2 (a). The capacity of the $1.5 \mu\text{m}$ thick Si film is superior to that of the $3.0 \mu\text{m}$ film in spite of the smaller amount of active material. The major reason

why the thicker film shows bad results in the cyclic testing is probably that higher compressive stress caused by the larger thickness might obstruct Li ion insertion during the discharge cycle and accelerate mechanical crumbling. Moreover, huge uneven buckles on the surface of the thicker film might provide more opportunity to form a solid electrolyte interphase (SEI) film. In actuality, the thicker Si film shows a larger irreversible capacity loss in the first cycle, which supports this inference. In order to demonstrate the electrochemical reactions of the Si thin film during cycling, charge and discharge curves of the film prepared for 1 h during the initial two cycles are presented in Fig. 2 (b). The 1st discharge capacity and 1st charge capacity are estimated as 96.7 $\mu\text{Ah}/\text{cm}^2$ and 52.6 $\mu\text{Ah}/\text{cm}^2$ respectively. The initial coulombic efficiency (ICE) is only 54.4 %, which is caused by the large irreversible capacity in the 1st cycle. The irreversible capacity is attributed to the formation of the SEI film due to the decomposition of the electrolyte on the surface of the thin film. In evidence, a plateau is observed near 0.4 V, which disappears in the 2nd cycle in Fig. 2 (b).

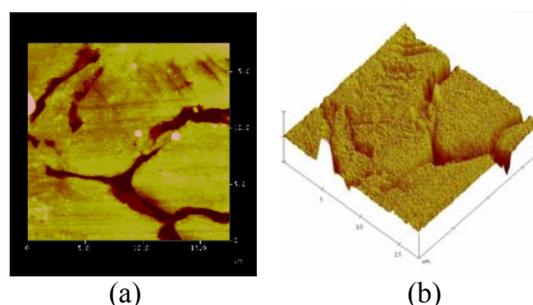


Fig. 3. AFM images after 100 cycles of the Si thin film deposited by the PLD process for 2 hours ; (a) 1-Dimensional image and (b) 3-Dimensional image.

Fig. 3 shows AFM images of the Si thin film electrode with a thickness of 3.0 μm after 100 cycles. Obviously, there are some large cracks on the surface, which were not visible before cycling. These cracks have been formed by mechanical crumbling due to the large volume expansion of Si in the alloying process. Although the PLD process has increased the density and adhesion of the films, the pulverization of electrode unfortunately could not be avoided during cycling. One may argue that higher density causes higher residual stress in the thin film, but it may tend to prevent the loss of the electric contact of Si films. We also note that one possible reason for the good cyclic performance is that the optimized conditions had increased adherence at the interface between the substrate and the amorphous Si thin film.

Acknowledgments

This work was supported by the Australian Research Council through the ARC Discovery Project “Synthesis of nanowires and their application as nanosensors for chemical and biological detection” (DP0559891) and the ARC Centre of Excellence for Electromaterials Science.

References

- [1] M. Winter, J.O. Besenard, *Electrochim. Acta* 41 (1999) 31.
- [2] L.Y. Beaulieu, K.W. Eberman, R.L. Turner, L.J. Krause, J.R. Dahn, *Electrochem. Solid-State Lett.* 4 (2001) A137.
- [3] J.P. Maranchi, A.F. Hepp, P.N. Kumta, *Electrochem. Solid-State Lett.* 6 (2003) A198.
- [4] T.H. Moon, C.J. Kim, B.W. Park, *J. Power Sources* (2005) in press.
- [5] N. Kuwata, J. Kawamura, K. Toribami, T. Hattori, N. Sata, *Electrochem. Commun.* 6 (2004) 417.
- [6] M. Inaba, T. Doi, Y. Iriyama, T. Abe, Z. Ogumi, *J. Power Sources* 81-82 (1999) 554.