Improvement of electrochemical performance of Si thin film anode by rare-earth La PIII technique


Abstract

Si thin film is considered a good candidate for rechargeable Li-ion thin film battery anode material because it possesses large lithium adsorption capacity, good thermal and chemical stability. However, the fast capacity decay upon charge–discharge cycling has hindered the application of Si thin films. In this investigation, Si thin films were sputtered on Cu foils and characterized. One of the explanations for the bad cycling characteristics is the poor adhesion between the Si film and the Cu substrate. Some Cu foils were treated by Plasma Immersion Ion Implantation (PIII) method using rare-earth La element to improve the adhesion strength between the Si thin films and the Cu substrate in order to enhance the cycling performance. Electrochemical analysis revealed that La PIII surface treatment on the Cu foil substrate was effective in strengthening the interface adhesion between the Si thin films and the Cu substrates. Subsequently, the electrochemical performance of the Si thin film anodes was improved.

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Keywords: Si thin film anode; Plasma Immersion Ion Implantation (PIII) technique; Rechargeable Li-ion thin film battery

1. Introduction

Rechargeable Li-ion thin film battery is one of the best candidates for the energy storage of future mini-portable electronic devices. Si thin film possesses the highest energy storage capacity (up to 4200 mA h g⁻¹ for Li₂₂Si₅) [1] and can be considered as a good anode materials for the rechargeable Li-ion thin film batteries. Si also has good thermal and chemical stability, acceptable reversibility and suitable charge–discharge voltage. However, practical application of Si film has been hindered by the fast capacity decay upon charging and discharging. The poor cycling property was attributed to the large volume change of the Si anodes (volume expansion ratio: 4.12) [2] during the reversible reaction. Subsequently, detachment of the Si film from the substrate may occur. It was proposed that by enhancing the adhesion strength between the Si thin films and the substrates could improve the cycling performance of Si anodes [3–10]. In this investigation, PIII (Plasma Immersion Ion Implantation) La surface treatment was adopted to enhance the surface properties of the Cu substrate prior to the deposition of the Si thin film in order to improve the electrochemical performance of the Si thin film anode.

2. Experimental procedure

Cu foils with thickness of 300 μm were used as the substrates. The Cu foils were surface treated by La PIII, while some foils without treatment were used as the control for comparison. Si thin films were deposited by RF magnetron sputtering deposition onto the Cu substrates with and without La PIII surface treatment. The thickness of the deposited Si thin film was about 350 nm. Prior to the La PIII surface treatment, the Cu foils were sputtered by Argon ions for 20 min in the PIII vacuum chamber. The La PIII was then performed at a voltage of 20 kV for 1 h at the pressure of 2 × 10⁻³ Pa. Subsequently, Si thin films were deposited on the La PIII surface treated Cu substrate.

The electrochemical performance of the Si thin films was investigated with three electrodes in the form of half-cells, with the Si thin film and the Li foils being the working electrodes and the reference electrodes, respectively. LiPF₆ (1 M) in ethylene carbonate-diethyl carbonate (EC-DEC) solution (volume ratio of...
1:1) was used as the electrolyte. All half cells for testing were assembled in a glove box with pure argon gas with less than 1 ppm H2O and O2. Cyclic voltammetric (CV) measurement was conducted at a sweeping rate of 0.1 mV s\(^{-1}\). The charge–discharge tests were performed at the constant current of 100 μA using a PAR potentiogalvanostat instrument. XRD, SEM, SEM-EDS and XPS techniques were also used to analyze the crystal structure, microstructure and composition of the Si thin film anodes deposited. The samples after charge–discharge cycling were taken out from the package and examined in the SEM immediately.

3. Results and discussions

3.1. Structures, surface morphology and La depth profile of the samples

XPS depth profiling revealed that the PIII implantation depth of La in the Cu foil was within 10 nm, as shown in Fig. 1. The XRD pattern confirmed that the Si thin films on the La PIII treated and untreated Cu substrates were both in the amorphous state. Figs. 2 and 3 show the SEM micrographs of the Si thin films on the treated and untreated Cu foil substrates after the charge–discharge cycling test. Many small cracks could be observed on the surface of the Si thin film deposited on the untreated Cu foil, which should be caused by the large mechanical stress attributed to the volume expansion of Si during the reversible electrochemical reactions. The Si film on the Cu foil with La PIII treatment did not show any crack. Only some small aggregations on the surface were observed. SEM-EDS analysis revealed that these aggregations were Li–Si alloy and residue of the electrolyte.

3.2. Electrochemical analysis

Si can react with Li to form several alloys by electrochemically driven solid-state amorphization [6]. The CV test results of the Si thin films were shown in Figs. 4 and 5. Two pairs of distinct CV peaks were obtained from the Si thin film deposited on the untreated Cu foil (Fig. 4) in the 0–1.0 V range at the sweeping rate 0.1 mV/s. The first pair of peaks was observed at...
84 mV and 260 mV, while the second pair was found at 206 mV and 480 mV. These two pair of peaks should correspond to the formation and decompounds of two kinds of Li–Si alloys. In contrast, more than two pairs of peaks were recorded in the CV analysis of the Si thin film deposited on Cu foils treated by La PIII in the 0.9 V to −0.05 V range. One pair of CV peak can be found below 0.1 V from Fig. 5. This phenomenon can be attributed to the formation of the Li22Si5 phase as proposed by earlier researchers [11]. High electronic resistance and polarization can also be found from Fig. 7. This might be caused by the assemblage and electric lead contact of the half-cell.

Charge–discharge cycling test at 100 μA constant current were carried out. There existed some difference in the Li capacity between the La PIII treated and the control Si thin film, as shown in Figs. 6 and 7. For the Si thin film on the La PIII treated Cu foil, the energy storage capacity attained 4000 mA h g⁻¹. This can be attributed to the formation of the Li22Si5. It is also noticed that there was no capacity loss in the first charge–discharge cycling test. For the Si film on the untreated Cu foil, the energy storage capacity was only 3300 mA h g⁻¹ and the initial irreversible capacity loss was 14%. Figs. 8 and 9 show that the cycle performance of the Si thin film on the La PIII surface treated Cu foil was much better than that on the untreated Cu foil.

The Si film on La PIII treated surface showed better electrochemical performance. This is attributed to the enhancement of the adhesion between the Si thin films and the Cu foils. We believe that La PIII treatment may have improved the adhesion of the Si film on the Cu substrate by the following means:

(1) Rare-earth La reacted with Cu and Si and strong Si–La–Cu bond was formed at the interface. However, due to the large amount of oxygen on the surface of the Cu substrate, it is suspected that the formation of such Si–La–Cu bonds could be difficult.

(2) La atoms might have reacted with the oxygen on the surface of the Cu substrate forming O–La–O bonds, which in turn has improved the bonding between the Si thin film and the Cu substrate. This viewpoint can also be used to explain the lower initial discharge capacity loss in the Si thin film on the La PIII treated Cu foils. This conforms to Ohara et al.´s suggestion ascribing the initial irreversible capacity of the Si thin film to the existence of the oxidized Si in the original Si thin films [12].

(3) The ion implantation (PIII) might have led to an increase in the defects concentration on the Cu foil surface, which subsequently could facilitate the diffusion and reaction of the Si atoms and Cu atoms. It was reported that defects in the sample could help to release large mechanical stress.
when Si reacts with Li. Rough surface prior to Si deposition was found advantageous to the formation of films with better adhesion [2]. The mechanism of La PIII enhancement of the adhesion between the Si thin film and the Cu substrate should be further studied in greater detail.

4. Conclusions

Si thin films on the La PIII treated Cu foil was found to possess energy storage capacity of 4000 mA h g⁻¹, good reversibility and cycleability. Si thin film anode on La PIII treated Cu foil could attain close to 100% charge–discharge efficiency after 16 cycles at 100 μA constant current. It is concluded that the PIII technique was effective in enhancing the adhesion of the Si thin films on the Cu foil substrates. Subsequently, the electrochemical performance and cycling properties of the Si thin film anode was improved.

Acknowledgement

The work described in this paper was supported by the CERG grant from Research Grants Council of the Hong Kong Special Administrative Region, China (CityU 1316/03E).

References