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N-type doped amorphous Si thin film on a surface of rough current collector as anode for Li-ion batteries

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Abstract

In this study, we report on the preparation of n-type doped ~ 400 nm thick amorphous Si thin film on a surface of 9 μm rough current collector. The electrochemical cycling test of designed anodes revealed that Si thin film on the surface of rougn exhibited stable capacity retention (~ 67 μAh cm^{-2}) for 120 cycles. Rate capability test showed the unaltered performance of prepared electrode after applying a current rates up to 300 μA cm^{-2}.

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Keywords: rough current collector; silicon; thin film; n-type doped; amorphous; magnetron sputtering; lithium ion battery

1. Introduction

Lithium ion batteries (LIBs) are the best technology among secondary battery technologies due to high volumetric and specific energy density. Meanwhile miniaturization of portable electronics, small and microscale devices requires a design of high capacity, lightweight and small size energy sources.

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Commercially successful graphite anode with a theoretical capacity of 372 mAh g^{-1} fades into the background due to another material, silicon (Si), which can provide more energy and power densities thanks to its high theoretical capacity of 4200 mAh g^{-1}. Hence, Si with a mass equal to that of graphite can produce eleven times more electrons [1]. However, Si, having issues of significant volume change during lithium ions insertion, still meets challenges in its way to commercialization. There are several strategies to improve Si anode: using amorphous phase for uniform expansion [2,3]; doping to increase electrical conductivity [4,5] and decreasing size of particles up to nanoscale to prevent material degradation [6].

For small and microscale batteries, thin film electrodes are the most suitable technology. To date, Si thin film with a thickness of 50 nm was reported to show a real promise working for several thousand cycles [5]. In contrast with the Si nanopowders production for conventional LIBs, scale up of nanoscale Si thin film is not a challenge due to many available facile and fast deposition techniques. Use of Si thin film provides an ideal opportunity to design high capacity microscale LIBs (<15 μm). Nonetheless, to achieve a reasonable high energy and power density microbatteries, the thickness of Si should be kept minimal with considerable amount of active material (mass loading). As one of the possible solutions is use a current collector with rouph surface. This provides better adhesion for Si thin film as well as increases surface area. It is expected, that the curvatures will prevent the delamination of Si thin film usually emerging due to stresses between Si nanoparticles at their expansion. Thus, the Si thin deposited on rough surface is able to overcome the volume expansion and following material degradation as well as to achieve high energy and power densities.

Here, we introduce an electrochemical study on a amorphous ~ 400 nm thick Si thin film anode on a surface of 9 μm rough cooper (Cu) current collector, which is the thinnest among all foils were used for deposition of n-type doped a-Si thin film anodes before, to our best knowledge. We believe, that the use a thiner current collectors is more able to satisfy the dimentional requirements of lithium ion microbatteries (LIMBs).

2. Experimental section

2.1. Deposition of Si thin film

N-type doped 400 nm thick a-Si film was deposited on a rough Cu substrate on a magnetron sputtering system (Kurt J. Lesker Company®) using n-doped Si target (99.99%, 5 cm × 0.5 cm, Kurt J. Lesker Company®). The sputtering was performed in a vacuum chamber under pressure of 5 mTorr in an inert atmosphere of Ar (99 %) for 1 h at the power of 80 W. The substrate was rotated at 5 rpm to evenly distribute the Si deposition. The mass of Si thin film was obtained by weighing the substrate on microbalance before and after deposition and constituted around 0.07 mg. A Si thin film was sputteren onto a flat polished Cu foil for the comparison.

2.2. Characterization

The surface morphology of Si thin film electrode was investigated by top-view scanning electron microscopy (SEM) on Crossbeam 540 (ZEISS). The amorphous phase of the Si thin film was identified by Raman LabRAM HR Evolution (HORIBA) at the laser wavelength of 532 nm. In order to check the thickness, Si thin film was sputtered on quartz substrate at the same conditions. The thin film thickness of around 400 nm was determined by AFM on C3M SmartSPM™-1000 (AIST-HT) in tapping mode using a cantilever with Al reflective side, with the length of 125 μm and the resonant frequency of 200-440 kHz (NSG30_SS by TipsNano).

2.3. Battery assembling and electrochemical test

The CR2032 coin cells with the flat and rough Si thin film anodes were assembled inside a glove box filled with high purity argon (Ar, 99.9995% purity). Metallic lithium was employed as both a counter and reference electrodes. The electrolyte was 1M $LiPF_6$ solution in ethylene carbonate, dimethyl carbonate and diethyl carbonate (in 1:1:1 by volumetric ratio). Porous polypropylene membrane (Celgard® 2400) was used as a separator. Cycling voltammetry

tests were conducted on VMP3 galvanostat/potentiostat (BioLogic Science Instruments) between the initial open circuit voltage and 0 V *vs.* Li^+/Li, then between 0 – 3 V after the first cycle. Galvanostatic charge-discharge measurements were conducted within 0.1 – 1.5 V on a battery testing system from Arbin Instruments®. The charge-discharge half-cell tests were performed at ~ 30 μA cm^{-2} (0.2 C) at ambient temperature. Rate capability were measured at the current densities of 15 μA cm^{-2} (0.1 C), 30 μA cm^{-2}(0.2 C), 150 μA cm^{-2}(1 C), 300 μA cm^{-2} (2 C) and again 15 μA cm^{-2} (0.1 C) in a voltage range of 0.1 – 1.5 V. All the potentials given in the paper are referred to the Li^+/Li. In order to avoid an error related to Si thin film mass evaluation, the capacity was given as areal (mAh cm^{-2}).

3. Results and discussion

Fig. 1 shows the Raman spectrum of Si thin film, which was observed to be identical regardless different surface conditions of a substrate. Raman spectra exhibited the peak around 480 cm^{-1}, indicating an amorphous phase of Si. This provides a key benefit to obtained thin film anode since amorphous structure decreases damage of electrode by evenly distributing residual stresses during volume expansion of Si, in contrast with crystalline structure, which expands in one direction of the lattice, increasing magnitude of stresses on electrode[2].

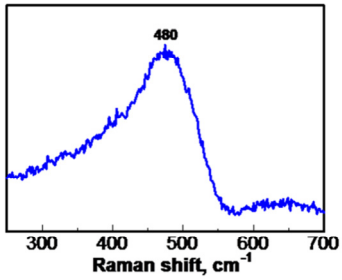

Fig. 1. Raman spectrum of Si thin film.

The materials morphology was investigated by SEM. From Fig. 2, one can observe the top-view images of substrates with different surface conditions without (upper row) and with Si thin film (lower row). The first foil (Fig. 2a) has relatively smooth surface, without corrugations and irregularities. Second foil (Fig. 2b) has rough surface with hill-like formations with approximate dimensions of 3 μm× 3 μm × 1 μm (l×w×h). Figures 2c,d illustrate Si deposited on each type of substrate. It can be seen, that thin film repeats the substrate structure in both case.

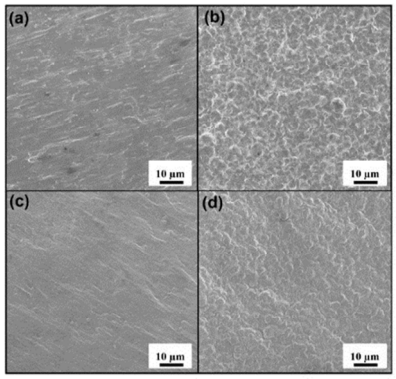

Fig. 2. SEM images of substrates and Si on their surface. (a) flat Cu, (b) rough Cu, (c) Si on flat Cu, (d) Si on rough.

In order to evaluate the electrochemical performance of Si thin film on Cu substrate as an anode material, cycling voltammetry (CV) was carried out at a scan rate of 0.1 mV s^{-1} between 0 and 3 V. Both investigated Si thin film electrodes demonstrated the same peaks' positions of Si lithiation/delithiation reaction on CV regardless of the substrate's surface condition. From Fig. 3a, in the first cathodic scan we can detect the peak at 0.4 V, which is usually ascribed to the formation of SEI layer. In the following cycles, the peak disappears due to irreversible nature of SEI formation reaction, indicating that the formed SEI film is stable[7]. The cathodic peaks at 0.1 V and 0.02 V indicate a reversible lithiation of Si with formation of Li_xSi_y alloy in the first cycle. The anodic peaks at 0.41 V and 0.53 V correspond to a delithiation of Li_xSi_y back to Si. One can notice the polarization of second and third scans at lithiation at 0.18 V, which may be a result of the resistivity increase after SEI layer formation that is known to be a very thick on Si-based materials [8]. Obtained peak positions are in a good agreement with the literature data for Si thin film anodes [9–11].

Fig. 3b-c demonstrates the charge/discharge profiles of the samples recorded at a current density of 30 μAcm^{-2} in the potential range of 0.1 – 1.5 V chosen based on the CV data. All samples demonstrate the plateaus at the same potentials related to lithiation for discharge curve and delithiation for charge curve, and are in a good agreement with the CV plot. Observing the charge-discharge curves for a-Si thin film on flat (see Fig.3b) and rough (see Fig.3c) substrates, we can detect the initial discharge capacities of around 95 and 94 μAh cm^{-2}, respectively. Besides, the SEI formation process causes an irreversible capacity loss in the first cycle. Thus, the irreversible capacity loss constitutes 17 and 25 μAh cm^{-2} for flat and rough Si film anodes, respectively. The large irreversible capacity found in cycle 1 for rough Si thin film is due to its large surface area comparing with the flat anode. One can notice that there is no difference in capacities between both samples in the 50th cycle – around 65 μAh cm^{-2}. However, upon cycling a-Si on rough substrate shows better cycling stability. Thus, the charge capacity loss for flat sample was around 24 μAh cm^{-2} upon cycling whereas a rough Si anode had a loss of only 4 μAh cm^{-2}.

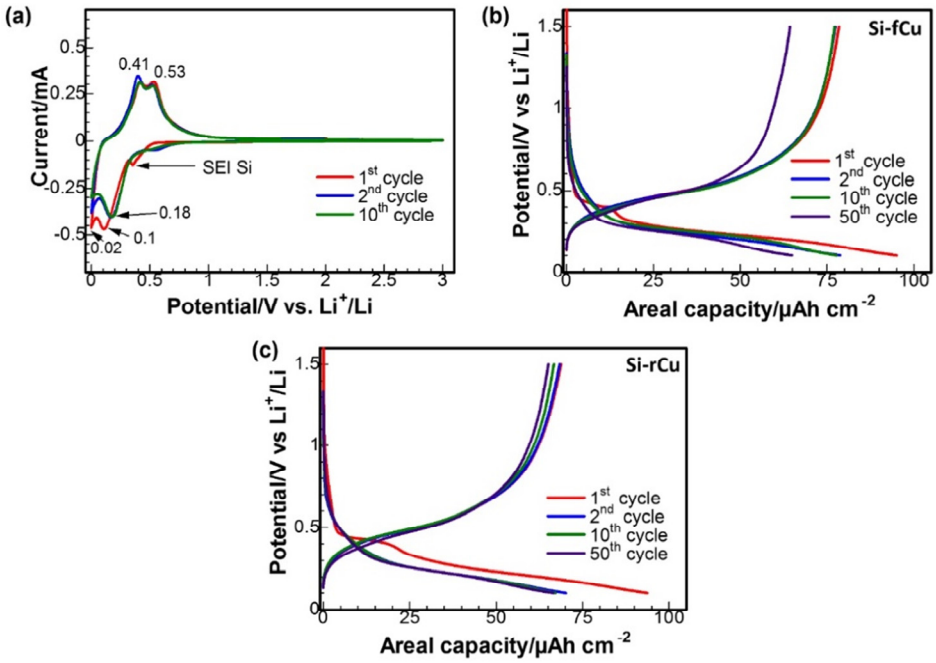

Fig. 3. Electrochemical test results (a) CVs for Si thin film. Charge/discharge profile of Si thin film anode on (b) flat and (c) rough Cu foil.

Rate capability of both current collectors are illustrated in Fig. 4. As shown in Fig. 4a, Si thin film on a flat Cu current collector exhibits similar areal capacities to Si on a rough Cu current collector (Fig.4b) at all current densities applied upon initial 20 cycles. However, the difference in capacity can easily be observed after 20th cycle. We can detect that a flat Si thin film anode can only achieve 48 μAh cm^{-2} in 120th cycle cycling at 15 μA cm^{-2}

(0.1 C). In comparison, a capacity of 67 μAh cm^{-2} can be obtained for the rough Si thin film, about 28% higher than that of the flat one. In contrast to the obvious capacity fading of the latter, the capacity of the rough Si thin film was stable for 100 cycles at 15 μA cm^{-2}(0.1 C). A salient point is that higher cycling rates (up to 300 μA cm^{-2} (2 C)) do not deteriorate the performance of the Si thin film on a rough Cu current collector and its available charge capacity recorded in 1st cycle.

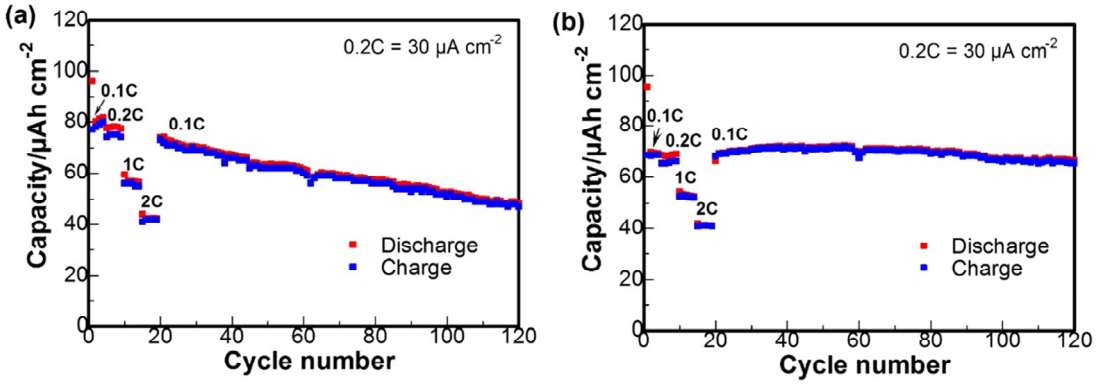

Fig. 4. Rate capability of Si thin film anode on (a) flat, (c) rough Cu foil.

4. Conclusion

In this study, we prepared a n-type doped completely amorphous Si thin film on 9 μm thick rough Cu current collector. The designed electrode exhibited a remarkably improved electrochemical performance in contrast with the flat Si anodes: excellent cyclability with the areal charge capacity of around 67 μAh cm^{-2} over 120 cycles with no noticeable signs of deterioration in performance after applying a current rates up to 300 μA cm^{-2}..

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