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Magnetic sputtered amorphous Si/C multilayer thin films as anode materials for lithium ion batteries

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HIGHLIGHTS

- The amorphous silicon/carbon multilayer thin films were synthesized by magnetic sputtering.
- The Si/C multilayer films displayed a good cycling performance and structure stability.
- The micro-scale films displayed a good long cycling performance.
- The effects of the amorphous carbon layers to the cycling performance were discussed.

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ABSTRACT

We have successfully synthesized the amorphous silicon/carbon (a-Si/C) multilayer thin films by magnetic sputtering method. The bonding characteristics and phase identification were investigated by X-ray diffraction (XRD) and Raman spectrum. The electrochemical performance of the a-Si/C multilayer thin films as anode materials for lithium ion batteries showed that with various thicknesses of Si layers, the electrodes displayed huge differences on the reversible capacity and cycling stability. The 500 nm a-Si/C multilayer films, with the thickness ratio $d_{Si}:d_C = 5:1$, displayed a high reversible capacity of about 2000 mA h g^{-1} over 200 cycles at 1C rate and a best structure integrity at various charging/discharging rates test. The micro-scale a-Si/C multilayer thin films (1.1 μm) also showed a good cycling performance with a capacity of about 1900 mA h g^{-1} at a current density of 2000 mA g^{-1} over 200 cycles.

1. Introduction

The commercial graphite anode is widely used in lithium ion battery due to its stable cycling performance [1]. But its drawback is also obvious. The relatively low specific capacity (372 mA h g^{-1}) [2] is not suitable for high power and high energy density lithium ion batteries [3]. Among the candidates [4–6], silicon, with its highest theoretical specific capacity (4200 mA h g^{-1}; $Li_{22}Si_5$), is considered as the most potential one to meet the demands of high performance lithium ion batteries (LIB). Despite the high power and high energy density nature, silicon suffers from a huge volume expansion (~310%; $Li_{22}Si_5$) [7] during the intercalation and de-intercalation of Li$^+$, resulting in poor capacity retention, high initial cycle irreversible loss and low columbic efficiency [8]. Hence many efforts have focused on addressing the drawbacks and of all the solutions, to synthesize nanostructure anodes is a feasible approach to minimize the volume expansion effects, and many researches have demonstrated that nano-scale silicon together with the carbon buffer can significantly improve the electrochemical performance of the Si-based electrode, including the carbon coated Si nanowires [9–11], Si nanoparticles [12–14], Si/C nanocomposite [15,16], Si/C nanotubes [17,18], porous Si structure [19–21] and Si/C nanofilms [22,23] electrodes, et al.

As well as the high capacity retention, the better structure stability of Si electrode also plays an important role in the electrochemical performance. In our previous work, the a-Si/C multilayer thin films showed a good electrochemical performance during the test [24]. In this work, we studied the appropriate thickness ratio of Si/C (d_{Si}/d_C) in 30 nm periodic thickness multilayer a-Si/C films that showed best structure stability and high capacity retention during

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the long cycling. Thin film deposition technology provides a good way to accurately control the thickness of the films and allows the study of the nano-size effects on electrochemical performance of the a-Si/C films.

2. Experimental procedure

2.1. Materials preparation

The a-Si/C multilayer films were prepared in a high vacuum chamber equipped with two sources: ratio frequency (RF) magnetic sputtering of a silicon target and direct current (DC) magnetic sputtering of a carbon target. The copper foil and silicon substrates were placed 10 cm away from the Si and C targets. The two sources were driven simultaneously and separately to ensure that they can alternately work during the deposition process. The sputtering powers for Si target and C target were both 300 W. The vacuum chamber was pumped to 2.0×10^{-3} Pa by a molecular pump and the deposition of both Si and C layers was proceeded in pure Ar with a working pressure of 1 Pa. The deposition rates calculated from total film thickness were 5.8 nm min^{-1} for carbon and 18.0 nm min^{-1} for silicon. So the thickness of Si and C layer in one periodic layer and the total thickness of the film could accurately be controlled by the deposition time. Before the deposition of a-Si/C multilayer films, a 50 nm Ti thin film was deposited as the intermediate layer and the C layer of the a-Si/C multilayer films was first deposited on the Ti layer to get a relatively better adhesive strength. At the end, an about 15 nm carbon layer was deposited on the top of the films to avoid the oxidation of Si.

2.2. Characterization and electrochemical measurement

The a-Si/C multilayer films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectrum and X-ray photoelectron spectroscopy (XPS). The a-Si/C multilayer films deposited on copper foils were directly used as the electrode for lithium ion batteries and the lithium metal was used as the counter electrodes. 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) was utilized as the electrolyte, and the EC/DMC = 1:1 in volume. The half-cell was assembled in a glove-box filled with pure Argon (99.99%) in the presence of an oxygen scavenger and a sodium drying agent. Cyclic voltammetric measurements were performed on LAND CR2016 battery test system in the voltage range of 0.01–1.2 V at a scan rate of 0.1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) measurement was conducted on a CHI600E Electrochemical Workstation in the frequency range from 10^{-3} Hz to 10^5 Hz. The alternating amplitude was 5 mV.

3. Results and discussion

In this work, the carbon layer deposited in all the samples was 5 nm in thickness. The relatively thin C layer can significantly improve the stability of the electrode without high capacity reduction. And the effect of the various thickness of the Si layer on the electrochemical performance as the anode for lithium ion battery (LIB) was investigated. As has been illustrated in Table 1, Sample A, B and C corresponded to films with different silicon and carbon thickness ratios (d_{Si}/d_C) but with the same total film thickness (t_T). Sample A, D and E contained the same d_{Si}/d_C but different t_T. Sample F and G was the pure Si film with a film thickness of 500 nm and 350 nm, respectively. 350 nm equaled to the content of Si in the multilayer Sample A.

Fig. 1(a) and (b) was the planar and the cross-section SEM of the multilayer sample, respectively. The boundaries between the Si and C layers could be clearly observed. Fig. 1(c) was the low-angle X-ray diffraction patterns (LAXRD). From the LAXRD, the modulate period of the multilayer film was calculated with the modified Bragg formulas:

Table 1
Sample A–F with different thickness ratios (d_{Si}/d_C) and different film thicknesses (t_T). Sample A, B and C have different d_{Si}/d_C but the same t_T. Sample A, D and E have the same d_{Si}/d_C but different t_T. F and G were the pure Si film with the thickness of 500 nm and 350 nm, respectively.

Sample	A	B	C	D	E	F	G
d_{Si}/d_C	5:1	6:1	7:1	5:1	5:1	Pure silicon	Pure silicon
t_T	500 nm	500 nm	500 nm	1100 nm	1300 nm	500 nm	350 nm

$$d = \lambda_{Cu}/2\sqrt{\left[(n+1)^2 - n^2\right]/(\sin^2\theta_{n+1} - \sin^2\theta_n)}$$

The wavelength of the incident X-ray $\lambda_{cu} = 0.154$ nm, with the number of the LAXRD peaks (n) and angle (θ), the modulate period was calculated to be about 25 nm, which was consistent with the pre-determined modulation period.

The periodic structure was further confirmed by the XPS depth profile in Fig. 1(d). Because of the different sputter rate for Si and C (silicon is relatively easier removed by sputtering than carbon), the XPS sputtering time didn't exactly correspond to the thickness ratio of Si and C from XPS spectrum. Fig. 1(e) showed the Raman spectrum of the a-Si/C multilayer thin films. The transverse acoustic (TA) at 155 cm^{-1}, longitudinal optic (LA) at 310 cm^{-1}, transverse optic (TO) at 375 cm^{-1} and longitudinal optic (LO) at 485 cm^{-1} are the typical feature of amorphous Si vibration modes [22,25], the typical D (1360 cm^{-1}) and G (1580 cm^{-1}) [26] peaks of amorphous C were also detected. The results confirmed the multilayer thin films possess disordered amorphous phase but no significant amounts of crystalline Si or C. Analogous structure information can also be observed in XRD pattern in Fig. 1(f), the peaks that were identified corresponded to Cu diffraction from the copper substrate, no significant peaks corresponding to Si and C were observed, indicating the amorphous structure of Si and C.

Fig. 2(a) showed the cycling performance of the a-Si/C multilayer thin films at a current density of 2000 mA g^{-1} (1C for Sample A, F and G, 0.9C for Sample B and C, 0.5C for Sample D and E). Sample A with a $d_{Si}/d_C = 5{:}1$, gained a best cycling stability during the charge/discharge process. The specific capacity was about 2000 mA h g^{-1} after 200 cycles. As the d_{Si}/d_C increased, Sample B reached a capacity of about 3000 mA h g^{-1} at 130th cycle and then showed a slightly capacity decrease with the cycle numbers, which indicted that Sample B had higher capacity but lower stability than Sample A. Compared with Fig. 1(a), the SEM image after 200 cycles (Fig. 2(b)) showed the structural fracture and pulverization of the films. A dramatically capacity fading could be seen in Sample C, which predicted that under the high d_{Si}/d_C, the buffer effect of the C layer weakened by the large expansion of Si layers. Sample G (350 nm pure silicon sample) displayed a capacity failure after only 40 cycles, which indirectly confirmed the buffer effect of carbon in the multilayer samples. But due to the high ion conductivity induced by carbon additive, the insertion and extraction of Li^+ in Sample C was easier than that in the pure Si Sample F, thus deep Si layers of Sample C suffered the structural expansion at early cycles, leading to the fast structural breakdown during the charge/discharge process, which may explain the even poorer electrochemical performance of Sample C than the pure silicon Sample F. Sample A, D and E had the same d_{Si}/d_C ratio but different film thicknesses, and they all displayed high capacity retention and high coulombic efficiency of 1950 mA h g^{-1}, 99.7% for D and