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Preparation and electrochemical performance of copper foam-supported amorphous silicon thin films for rechargeable lithium-ion batteries

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ABSTRACT

Amorphous Si thin films, which have been deposited on copper foam by radio-frequency (rf) magnetron sputtering, are employed as anode materials of rechargeable lithium-ion batteries. The morphologies and structures of the as-prepared Si thin films are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). Electrochemical performance of lithium-ion batteries with the as-prepared Si films as the anode materials is investigated by cyclic voltammetry and charge–discharge measurements. The results show that the electrode properties of the prepared amorphous Si films are greatly affected by the deposition temperature. The film electrode deposited at an optimum temperature of 300 °C can deliver a specific capacity of ~2900 mAh/g and a coulombic efficiency above 95% at charge/discharge current density of 0.2*C* after 30 cycles. The Li^+ diffusion coefficiency in copper foam-supported Si thin films is determined to be 2.36×10^{-9} cm^2/s.

1. Introduction

Graphitized carbon has been universally used as the negative electrode material of commercial rechargeable Li-ion batteries [1]. However, the graphitized carbon cannot satisfy the high energy density requirement of batteries for portable electric devices due to its limited theoretical capacity (LiC_6, 372 mAh/g) [2]. Extensive studies have been conducted to seek alternative anode materials [3–5]. Among them, Si-based materials have attracted intensive research interest as Si can give high theoretical specific capacity of nearly 4200 mAh/g ($Li_{22}Si_5$) [6,7]. However, substantial volume changes are associated with the Li alloying and de-alloying process, which causes fast crack and pulverization of Si electrode and results in rapid capacity fade. Many attempts have been made to improve the cycling ability of Si anode such as investigating nanostructured Si [8,9], adding other elements to alleviate the volume change [10,11], and preparing amorphous silicon [12].

Amorphous Si possesses the advantages of smaller volume change and strong adhesion between the active material and current collector. So far, amorphous Si thin film anode has been successfully prepared by chemical vapor deposition (CVD) [13], radio-frequency (rf) magnetron sputtering [14,15], vacuum evaporation [16] and pulsed laser deposition (PLD) [17]. On the other hand, the electrochemical performance of Si thin film depends on the employed substrate. Substrate with rough surface such as three-dimensional (3D) foam structures can enlarge the contact area between the active materials and the current collector. For example, Jiang et al. [18] casted the milled silicon powders into the 3D copper architecture, which exhibited good cycling performance but unsatisfactory specific capacity.

In this study, we report the preparation of amorphous-Si thin film on copper foam substrate by rf magnetron sputtering. Magnetron sputtering is one of the most appropriate processes to fabricate dense Si thin film with strong adhesion to the substrate. The interconnected 3D structure of copper foam favors efficient ionic diffusion and interface contact. Meanwhile, the foam serves as a good conductive current collector and as a rigid matrix that can suppress the volume variation of the active Si material during charge/discharge. Therefore, we investigate the electrochemical properties of Si anode prepared by rf magnetron sputtering on copper foam substrate. Furthermore, we study the effect of deposition temperature on the electrode performance of the amorphous Si thin film and the Li^+ diffusion coefficiency in the film.

2. Experimental

2.1. Electrode preparation

Si thin films were prepared in a JCP-350 multi-target magnetron sputtering system with copper foam as the substrate and N-type monocrystalline Si (99.99%) as the target. The target–substrate distance of the sputtering system was 7 cm. After attaining a base pressure of 1×10^{-3} Pa, high-purity argon (99.999%) was

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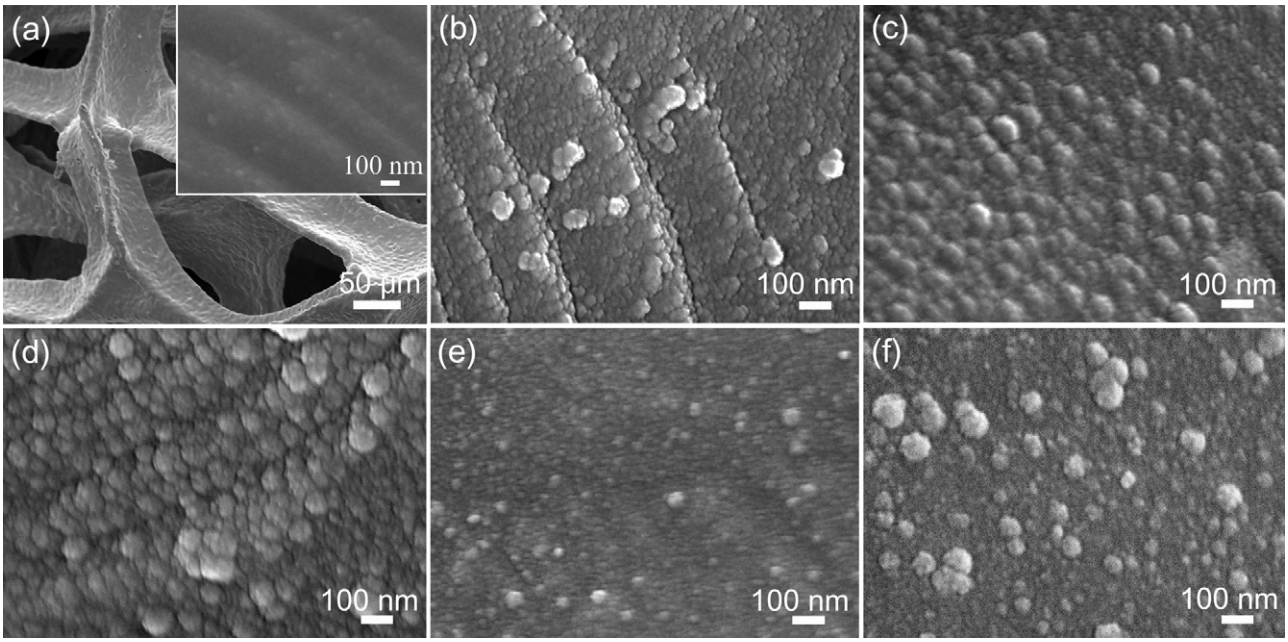

Fig. 1. SEM images of (a) copper foam and Si thin film deposited at (b) room temperature (RT), (c) 100 °C, (d) 200 °C, (e) 300 °C, and (f) 400 °C.

introduced into the stainless-steel chamber. The working pressure was kept at 0.50 Pa. Si thin films were deposited using a constant rf power supply of 50 W. The substrate temperatures were selected as room temperature (RT), 100 °C, 200 °C, 300 °C, and 400 °C, respectively. Before deposition on copper foam substrate, Si target was pre-sputtered for 15 min to remove the contaminants on the surface. Then, the Si thin film was obtained by sputtering for 1 h. The substrate holder was water-cooled through copper tube during the process of experimentation. The amount of the deposited Si on copper foam was measured by electronic balance (BS224S, resolution of 0.1 mg) in combination with inductively coupled plasma (ICP-9000 USA Thermo Jarrell-Ash Corp.) after dissolving the copper substrate by nitric acid. The average loading rate is determined to be 0.52 mg Si per 1 g Cu in 1 h.

2.2. Characterization

The morphologies of Si thin films were characterized by scanning electron microscopy (SEM, FEI Nanosem 430). Phase structures of the as-prepared samples were characterized using D/max-2000 X-ray powder diffraction (XRD) with Cu Kα radiation. Crystallinity of Si thin films was also investigated by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) on a Philips Tecnai-F20 transmission electron microscope. For TEM test, the Si in the thin film was scraped from copper foam and ultrasonically dispersed in ethanol, which was dripped on the copper mesh support.

2.3. Electrochemical measurement

The 2032 button cells were employed to test the electrochemical performance. High-purity metallic lithium was used as the counter and reference electrode. The copper foam bearing the Si thin film as the working electrode was cut into wafers with 1 cm in diameter. The cell assembly was operated in a glove box (Mikrouna China Universal 2240/750) filled with high-purity argon (99.999%). The electrolyte was 1 mol/L $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with the volume ratio of EC:DEC = 1:1. Cyclic voltammetry measurements were performed using an electrochemical workstation (Potentiostat/Galvanostat Model 263A) between 0.01 and 2.0 V versus Li/Li^+ at various scan rates from 0.20 to 0.50 mV/s. Charge/discharge tests were carried out on a Land battery test system (Land, CT 2001A). The cells were discharged from the initial open-circuit voltage to 0.01 V, and cycled between 0.01 and 2.0 V after the first discharge. All samples were tested at 0.2*C* current rate (1*C* = 4200 mA/g) up to 30 cycles. All the electrochemical tests were carried out at room temperature.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the SEM images of the copper foam substrate and the Si thin films deposited at various temperatures. As seen in Fig. 1a, the copper foam shows 3D interconnected porous structure. Compared with the films deposited at other temperatures, the Si thin film deposited at 300 °C are composed of more compact and smaller grains. Moreover, agglomerated particles can be observed on the surface of the Si thin film deposited at 400 °C. These observations can be understood by the fact that at lower temperature, the inhibited diffusion of Si atom makes the films uneven; while at higher temperature, the increased film critical core radius, sputtering particle energy, and diffusion capacity lead to the formation of large particles.

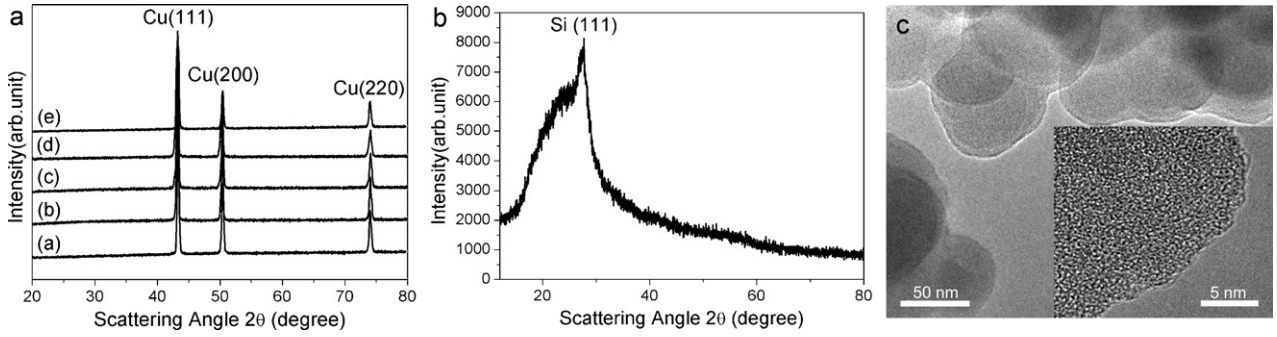

Fig. 2. (a) XRD patterns of Si thin films deposited at various temperatures: curves a, b, c, d, and e correspond to RT, 100 °C, 200 °C, 300 °C, and 400 °C, respectively. (b) XRD pattern of Si powders collected after dissolving the copper substrate. (c) TEM/HRTEM images of Si thin film scraped from copper foam.

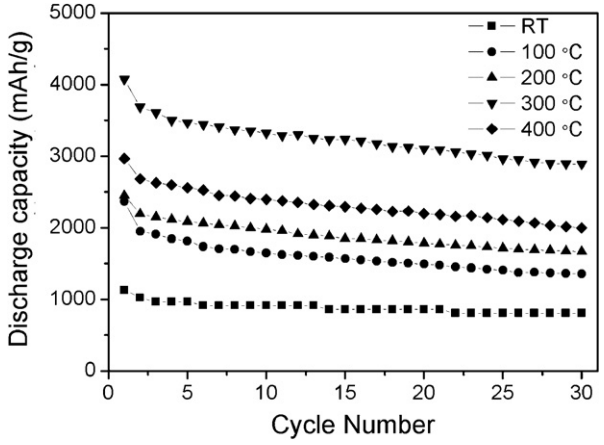

Fig. 3. Cycling performance of Si thin films deposited at various temperatures. The charge/discharge current density is set at 0.2*C* rate (1*C* = 4200 mA/g).

Fig. 2a shows the XRD patterns of the Si thin films deposited on copper foam at different temperatures. All the diffraction peaks are attributed to the copper foam and no peak of Si can be detected, especially the typical peak of crystalline Si centered at 2θ degree of 28°. This detection indicates that the prepared Si thin films are amorphous phase. To further confirm this point, the cooper foam was dissolved by dilute nitric acid and the leaving Si powders were collected, thoroughly washed, and dried in vacuum. The phase structure of the obtained Si powders was analyzed using X-ray diffraction, as shown in Fig. 2b. The XRD pattern displays merely a wide diffraction peak, indicative of noncrystalline structure. Furthermore, TEM and HRTEM imaging was used to analyze the microstructure of Si thin film that had been scraped from copper foam. We cannot observe obvious lattice fringes from the HRTEM image (Fig. 2c), giving further evidence to confirm the amorphous nature of the as-prepared Si thin films.

3.2. Electrochemical measurements

Fig. 3 shows the effect of the deposition temperature on the electrochemical performance of the Si thin film. All the samples show good cycle performance, which can be attributed to 3D structures of copper foam that can effectively suppress the volume variation of the active Si [17]. It can be found that the reversible capacity of the film increases with deposition temperature from room temperature to 300 °C and decreases above 300 °C. The room-temperature Si thin film gives a discharge capacity of 800 mAh/g after 30 cycles. In comparison, the sample deposited at 300 °C shows a maintained capacity of ~2900 mAh/g up to 30 cycles. The samples deliver different specific capacities. This is possibly due to the dissimilar adhesion between the films and the substrate, which results in different utilization efficiencies of the active materials. However, at the deposition temperature of 400 °C, poor adhesion is found between the copper foam and the deposited Si thin film, which exhibited inferior performance. It is known that this adhesion problem arises from high-compressive stress, due to the energetic nature of sputtering deposition and the thermal-expansion-coefficient (α) difference between Si ($\alpha = 7.6 \times 10^{-6}\ K^{-1}$) and Cu ($\alpha = 17 \times 10^{-6}\ K^{-1}$) [14]. Additionally, the large agglomerated particles on the surface of the sample heated at 400 °C are easy to peel off from the current collector. Therefore, the electrochemical properties of the Si thin film depend largely on the deposition temperature and 300 °C is found to be optimal in this study.

Fig. 4 shows the first, tenth, and thirtieth charge–discharge curves of the Si thin film deposited at different temperatures between 0.01 and 2.0 V versus Li/Li^+. Apparently, the Si thin film deposited at 300 °C exhibits the best electrochemical performance. The slopping of the charge/discharge profiles can be explained by Li extraction/insertion in amorphous Si without phase transformations. Fig. 5 shows the cycling performance of the Si thin film deposited at 300 °C. The capacity is 4077 mAh/g for the first discharge and 3534 mAh/g for the first charge at 0.2*C* rate. The irreversible capacity is ascribed to the formation of a solid electrolyte interphase (SEI) layer in the first cycle. The reversible capacity retains 71.1% of the first discharge capacity after 30 cycles. Furthermore, the columbic efficiency increases to above 95% at the second cycle and maintains a stable value in the subsequent cycles, indicating high charge and discharge efficiency of the Si thin film. It should be noted that the reversible capacity of the Si thin film deposited on 3D copper foam at 300 °C is higher in comparison with that deposited on copper foil using rf magnetron sputtering

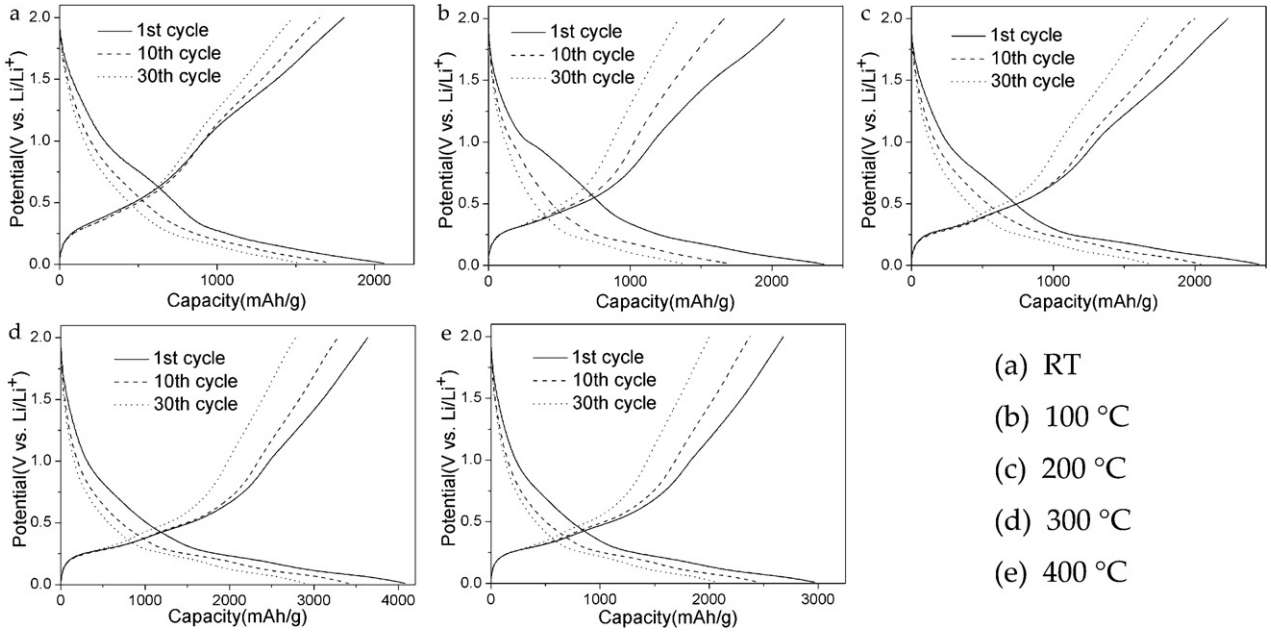

Fig. 4. Charge–discharge curves of Si thin film deposited at various temperatures at the rate of 0.2*C* (1*C* = 4200 mA/g).

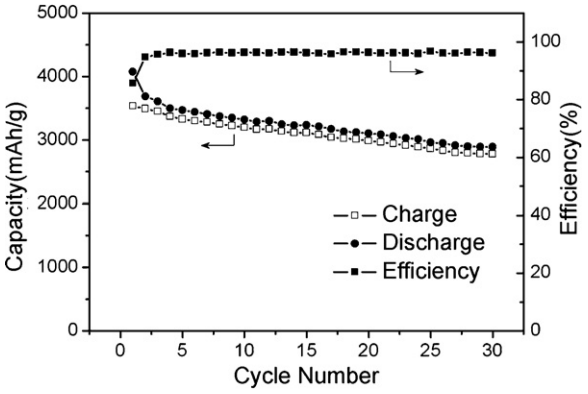

Fig. 5. Charge–discharge capacity and columbic efficiency as a function of cycle number for the Si thin film deposited at 300 °C.

[15]. Thus, the combination of rf magnetron sputtering and copper foam proves to be the efficient strategy to improve the electrode performance of Si film.

3.3. Diffusion coefficiency of Li^+

Cyclic voltammetry is applied to determine the diffusion coefficiency of Li^+ in the prepared amorphous Si thin film. Fig. 6 shows the cyclic voltammetry curves measured between 0.01 and 2.0 V versus Li/Li^+ at potential scan rates from 0.20 to 0.50 mV/s. The activated cells assembled under the same conditions were tested three cycles at various scan rates, and the second cycles were chosen to plot CV curves. The peak currents of both cathodic and anodic peaks increase with increasing potential scan rate and the anodic peaks shift to higher potentials. From low to high scan rate, the rate-determining steps of the electrochemical reaction may change from surface reaction to lithium diffusion in the film. A method to distinguish these different cases is the dependence of the peak current on the potential scan rate [19]. For the surface reaction, the peak current is proportional to the scan rate (ν). When the scan rate increases to above 30 μV/s, the peak current becomes proportional to the square root of the scan rate ($\nu^{1/2}$) due to the semi-infinite diffusion-controlled process. The peak current I_p can be expressed by the classical Randles–Sevchik equation [20]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_0^{1/2} \nu^{1/2} C_0$$

where n is the number of electrons involved in the electrode reaction (1 for transfer of Li to Li^+), A is the contact area between Si and electrode, D_0 is the diffusion coefficient of Li^+ in the electrode and

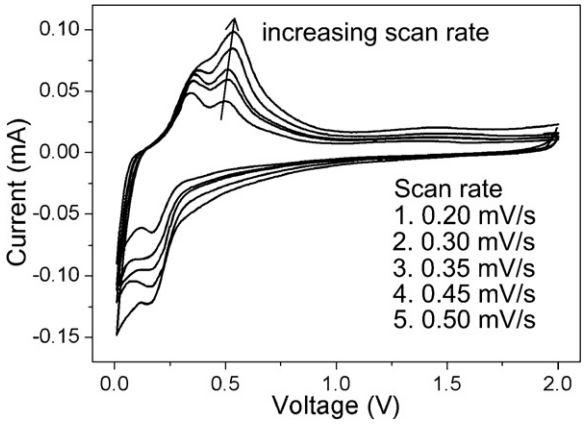

Fig. 6. Cyclic voltammograms at different potential scan rates for the Si thin film deposited at 300 °C.

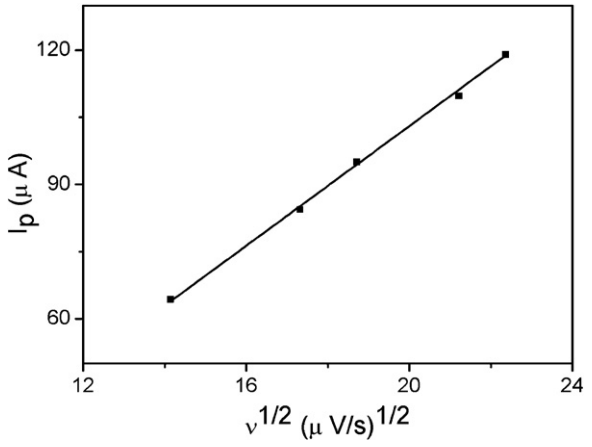

Fig. 7. Dependence of peak current (I_p) on square root of potential scan rate ($\nu^{1/2}$) for the cathodic peak.

C_0 is the bulk concentration of Li^+. The dependence of peak current on the square root of the potential scan rate for the cathodic peak at ~0.20 V at different scan rates is presented in Fig. 7. C_0 can be calculated according to the formula: $C_0 = (x/M) \times \rho$, where x is the number of embedded lithium atoms in each silicon atom which can be calculated according to the discharge–charge electric quantity of CV curves, M is the atomic weight of silicon, ρ is the density of silicon (2.33 g/cm^3). The diffusion coefficiency calculated from the slope of I_p versus $\nu^{1/2}$ is 2.36×10^{-9} cm^2/s, which is larger than that of vacuum-deposited Si thin film (10^{-13} to 10^{-10} cm^2/s) reported by Yoshimura et al. [21]. Therefore, the combination of rf magnetron sputtering and copper foam substrate can obtain dense Si thin film with strong adhesion to the substrate and efficient interface contact. These factors contribute to the higher lithium ion diffusion coefficient.

4. Conclusions

In conclusion, amorphous silicon thin films have been deposited on copper foam by rf magnetron sputtering and investigated as anode materials of rechargeable Li-ion batteries. The electrochemical properties of the films depend on the deposition temperature. The film deposited at 300 °C shows the optimal performance, maintaining reversible capacity of ~2900 mAh/g at 0.2C rate after 30 cycles. The diffusion coefficient of Li^+ in the amorphous Si thin film is determined to be 2.36×10^{-9} cm^2/s. The present results indicate that the combination of rf magnetron sputtering and cooper foam substrate is an efficient route to prepare amorphous Si films with high capacity and cyclability.

Acknowledgments

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