



Low-density silicon thin films for lithium-ion battery anodes



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ABSTRACT

Density of sputter deposited silicon (Si) thin films was changed by a simple working gas pressure control process, and its effects on the cycling performance of Si films in Li-ion batteries as anodes was investigated. Higher gas pressure results in reduced film densities due to a shadowing effect originating from lower mean free path of sputter atoms, which leads to a wider angular distribution of the incoming flux and formation of a porous film microstructure. Si thin film anodes of different densities ranging from 2.27 g/cm³ (film porosity ~3%) down to 1.64 g/cm³ (~30% porosity) were fabricated by magnetron sputtering at argon pressures varying from 0.2 Pa to 2.6 Pa, respectively. High density Si thin film anodes of 2.27 g/cm³ suffered from an unstable cycling behavior during charging/discharging depicted by a continuous reduction in specific down to ~830 mAh/g at the 100th cycle. Electrochemical properties of lower density films with 1.99 g/cm³ (~15% porosity) and 1.77 g/cm³ (~24% porosity) got worse resulting in only ~100 mAh/g capacity at 100th cycle. On the other hand, as the density of anode was further reduced down to about 1.64 g/cm³ (~30% porosity), cycling stability and capacity retention significantly improved resulting in specific capacity values ~650 mAh/g at 100th cycle with coulombic efficiencies of >98%. Enhancement in our low density Si film anodes are believed to mainly originate from the availability of voids for volumetric expansion during lithiation and resulting compliant behavior that provides superior mechanical and electrochemical stability.

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1. Introduction

Silicon (Si) has been projected as a promising anode material for Li-ion batteries because of its high theoretical capacity (~3580–4200 mAh/g), which is the highest known value among all materials in nature so far. [1] However, Si anode materials suffer from several problems which have prevented its commercial use. The most significant problem with bulk Si is its more than ~400% volume change during the insertion/extraction of lithium ions, which causes mechanical instability, capacity fading and failing in batteries. In order to achieve higher cycling performance without pulverization and delamination, the mechanical failure due to the volume change must be tolerated.

Studies reported in the literature suggested several approaches to overcome the mechanical problems with Si anodes in Li-ion batteries. Nano-sized materials are expected to improve the electrochemical properties of Si anodes due to the high surface to volume ratio and high electrode porosity. [2–4] Among those approaches, C-Si composites [5] such as CNT-Si wires [6,7], Si nanowires [8], Si ribbons [9], SiO_x/Si composites [10,11], Si nanocrystals [12] and Si thin films [13, 14] were promising to improve mechanical stability of conventional

bulk Si anodes. However, these methods were not able to completely solve the major challenges with Si anodes besides the high fabrication cost and impractical methods. Binders between Si nanoparticles were also considered to be a possible solution to the problems caused by high volume change. [2,15] For instance, Si nanotubes covered with a SiO_x layers have provided specific capacity of 1200 mAh/g at the 600th cycle. [16] Theoretical specific capacity values of Si-based anode materials with active or inactive chemical binders typically range from 300 to 1700 mAh/g [17–20], which is much lower than the ~3580 mAh/g capacity of elemental Si. Inactive binders, which can not contribute to the specific capacity, would further decrease the total capacity of the battery cell. Nevertheless, search for Si anodes with good capacity retention and high electrochemical performance is still ongoing.

Besides the methods and Si nano-materials mentioned above, Si thin films have shown extensively high specific capacities. [14,17,21–24] Thin films have important advantages over large size Si structures such as higher surface area and low Li-ion diffusion pathway. However, conventional Si thin films still have the problems that are observed in bulk materials (e. g. volume expansion). In a previous study reported by the authors of this work, a density modulated multilayer Si thin film anode approach has been developed, which can provide a robust high capacity electrode approach for Li-ion batteries. [25] These films were able to provide a high coulombic efficiency up to 99% and

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reversible specific capacity as high as $\sim 1700 \text{ mAh g}^{-1}$ after 50 cycles. [26] Low-density layers are believed to be performing as compliant layers during volume change making the films more durable compared to conventional Si film anodes. However, there has not been any attempt to understand the effect of the density of Si thin films on cycling performance. Therefore, the focus of this paper is to compare the electrochemical characteristics of Si thin film anodes of different densities.

2. Experimental

Several Si thin films with different densities were fabricated at different deposition pressure values using an RF magnetron sputtering method. Target (i.e. source) to substrate distance was $\sim 15 \text{ cm}$. Base pressure of the system was brought down to about $3 \times 10^{-4} \text{ Pa}$ by a turbomolecular pump back by a mechanical pump. Ultra high purity argon (Ar) was used as the working gas for generating the plasma. As the deposition material source, 99.99% pure p-type Si target (Kurt-Lesker) with a diameter of $\sim 5 \text{ cm}$ was used. RF power was set to 200 W and substrates were rotated at 20 rpm during all depositions. Previous studies have shown that the adhesion strength of the thin films to the substrate is considerably effective on the electrochemical performance of Si thin film anodes. [27,28] Therefore, we sputter deposited a thin chromium layer of $\sim 25 \text{ nm}$ on our substrates (99.99% pure Cr target with diameter: $\sim 5 \text{ cm}$, RF Power: $\sim 150 \text{ W}$, deposition time: $\sim 2 \text{ min}$) before each Si deposition to provide better sticking ability. Targets were cleaned by pre-sputtering for $\sim 3 \text{ min}$. Si thin films were deposited on circular copper (Cu) foil current collectors with the diameter of 1.27 cm and 15–25 μm thickness. Si films deposited on Si wafer pieces were used for imaging and crystal structure analysis purposes. Quartz crystal microbalance method (QCM) was used to measure the mass loading of the deposited films. Quartz substrates were placed on the substrate holder during depositions for this purpose. In this method, difference between the frequencies of QCM crystals before and after the deposition is used to calculate the mass of the films by using the Sauerbrey equation. [29] Details of the weight measurement were explained in our earlier work. [26] Deposition times were adjusted to produce Si films of similar weight $\sim 25\text{--}26 \mu\text{g}$ on Cu foil substrates. Fabrication of each sample and density measurements were repeated about 5 times, and the average density values were taken for each sample of different densities (Table 1).

As described in earlier studies [30–32], by controlling the gas pressure during sputter deposition, it is possible to fabricate high and low density films at low and high pressures, respectively. Therefore, in our study we used this simple and practical approach of changing working gas pressure in order to control the density of our sputter deposited Si film anodes. Deposition pressures for each sample are listed in Table 1. Argon gas flow rate was adjusted between 10 and 15 sccm, and a gate valve was throttled to achieve a desired working pressure within 0.2 Pa–2.6 Pa.

Electrochemical performance of the silicon films was tested by charging/discharging experiments in a two-electrode battery R&D coin cell set-up (Hohsen 2032). Cells were assembled in the argon-filled glovebox with a purity level of $<1 \text{ ppm O}_2$ and H_2O . The lithium foil

was used as the reference and the counter electrode in the coin cell. 1.2 M LiPF₆ in ethylene carbonate/ethyl methyl carbonate with the volume ratio of 3:7 was used as the electrolyte. The batteries were charged and discharged at constant current of 50 μA within a voltage window from 0.1 to 1.5 V (vs. Li/Li⁺) at $\sim 1/8 \text{ C}$ rate.

3. Results and discussion

Fig. 1 shows the top and cross-sectional Scanning Electron Microscope (SEM) images of the Si films deposited at 0.2 and 2.0 Pa Ar pressures. SEM characterization was done by JOEL 7000f Instrument with 15 kV acceleration voltage. All the films produced did not show any X-ray diffraction peaks (not shown), indicating an amorphous structure. As the pressure is increased films get rougher and a columnar microstructure start to form, which is consistent with the well-known structure zone model (SZM). [33–35] At higher working gas pressures, sputtered atoms go through an increased number of gas phase collisions that reduces their mean free path and increases the angular distribution of the incident flux on the substrate. For example, at the lowest and highest Ar gas pressures of 0.2 Pa and 2.6 Pa used in this study, mean free path of Si atoms as they pass through the Ar gas environment before they reach to the substrate are expected to be about $\sim 4 \text{ cm}$ and $\sim 3 \text{ mm}$, respectively. [36,37] Therefore, given that the target-to-substrate distance in our experiments was about $\sim 15 \text{ cm}$, Si atoms can make a few or tens of collisions before they arrive at the substrate if the pressure is low or high, respectively. At high pressures, due to the wider angular distribution of the incident flux, atoms approaching at oblique angles lead to the “shadowing” effect that results in the formation of more columnar and porous films. [25,26,35] In other words, by simply controlling the working gas pressure during sputtering, a variety of microstructures can be obtained ranging from smooth and dense films to rougher more porous coatings. In addition, Si films of similar weight loading gets thicker as the Ar pressure is increased (Fig. 1), which indicates the reduction in films density. To confirm this, we calculated the film density as a function of Ar gas pressure using QCM mass loading and film thickness values (Table 1), which are plotted in Fig. 2. As can be seen in Fig. 2, film density at the lowest Ar pressure of 0.2 Pa is about 2.27 g/cm^3 , which is close to the theoretical density of 2.33 g/cm^3 for amorphous Si films. [13] As the pressure is increased up to 0.8 Pa, density of Si films drops down to about 1.99 g/cm^3 following a linear behavior, which corresponds to a film porosity of $\sim 15\%$. At higher Ar pressures (Fig. 2), density of Si films further decreases down to $\sim 1.64 \text{ g/cm}^3$ that corresponds to a $\sim 30\%$ porosity, as the pressure reaches 2.6 Pa. As the cross-sectional SEM images of lower density films (Fig. 1) do not show any nano-pores, we believe that most of the porosity originates from atomic scale voids that result from the shadowing effect of higher working gas pressures.

Charging performance and coulombic efficiencies of Si films of different density in Li-ion battery tests are presented in Fig. 3. At initial cycles, all the samples show high specific capacity values ranging $\sim 1500\text{--}2300 \text{ mAh/g}$ (Fig. 3a). High density Si film (i.e. Ar pressure 0.2 Pa) shows the highest specific capacity values starting from $\sim 2320 \text{ mAh/g}$ at the first cycle. However, its capacity value steadily decreases during the cycling tests down to $\sim 830 \text{ mAh/g}$ at 100th cycle, and it appears that it would continue to decrease beyond that. This behavior is consistent with earlier reports [3,17,26,38] that attributes the poor cycling stability of conventional Si films mainly to its extremely high volumetric expansion/contraction approaching $\sim 300\text{--}400\%$ during lithiation/delithiation, which is followed by pulverization and detachment of Si fragments from the current collector. For Si films produced at relatively higher Ar pressures (0.8 Pa and 1.4 Pa), cycling performance gets worse that is depicted by an abrupt decrease in specific capacity at initial cycles and stabilizing at a low capacity of about 100 mAh/g at 100th cycle (Fig. 3b). These films have porosity of about $\sim 15\%$ and $\sim 24\%$ at 0.8 Pa and 1.4 Pa, respectively, as measured from QCM density values (Fig. 2). Poor cycling performance of these films

Table 1

Thickness, density, porosity, and weight loading values of sputter deposited Si thin film samples produced at different Ar gas pressures. Standard deviation in the data listed is $\sim 5\%$.

Sample #	Ar Gas pressure (Pa)	Thickness (nm)	Density (g/cm^3)	Porosity (%)	Weight on Cu foils (μg)
1	0.2	90	2.27	2.6	26.6
2	0.8	97	1.99	14.6	25.3
3	1.4	122	1.77	24.0	26.3
4	2.0	124	1.67	28.3	26.3
5	2.6	128	1.64	29.6	23.3

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