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Short communication

Electrochemical performance of amorphous-silicon thin films for lithium rechargeable batteries

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Abstract

The effect of deposition temperature and film thickness on the electrochemical performance of amorphous-Si thin films deposited on a copper foil is studied. The electrochemical properties show optimum conditions at 200 °C deposition, and thinner films exhibit superior electrochemical performance than thicker ones. A film of 200 nm Si deposited at 200 °C exhibits excellent cycleability with a specific capacity of ∼3000 mAh g^{-1}. This is probably due to optimization between the strong adhesion by Si/Cu interdiffusion and the film stress.
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Keywords: Amorphous silicon; Thin film; Deposition temperature; Interdiffusion

1. Introduction

With the development of portable electronics, many investigations have focused on materials with high specific energy. For anode materials, some of the candidates are silicon, tin, and compounds including these elements [1–4]. Silicon has much higher specific energy (4200 mAh g^{-1} for $Li_{4.4}Si$) than commercially-used graphite (372 mAh g^{-1} for LiC_6). The volume changes (310%) related to Li alloying and de-alloying are however quite substantial and cause fast disintegration by cracking and pulverization of Si. As a result, some of the particles lose electrical contact and this results in capacity loss [5].

Recently, Fujitani et al. [6] developed an amorphous-Si (a-Si) thin-film electrode by sputter deposition as an alternative to the conventional powder electrode. The volumetric energy density of an experimental cell using a Si anode with a $LiCoO_2$ cathode was approximately 1.3 times grater than that with graphite. The cell also exhibited excellent capacity retention. Several other studies have yielded encouraging electrochemical results for sputtered thin films of Si [7–10].

It is known that the origin of the excellent cycleability of Si thin-film anodes is the strong adhesion by the interface silicide and the roughness of the copper-foil substrate [1,6]. Because the Si anode experiences a large Li-induced stress with residual stress during the growth of the thin film, the deposition conditions must be optimized to achieve desirable properties. This paper reports the electrochemical performance of a-Si on copper with respect to deposition temperature and film thickness.

2. Experimental

The Si thin films were deposited using a Si target by RF magnetron sputtering with Ar, with a typical deposition rate of ∼20 nm/min. The substrate was a copper foil for the electrochemical analysis, or a $Cu/SiO_2/Si$ (1 0 0) wafer for the phase analysis. Prior to the deposition of Si, the copper foils were etched with acetic acid (99.7%) to remove copper oxide or any surface impurities, and then pre-annealed at ∼200 °C in the sputtering chamber [11].

The deposition rate was measured using a surface profilometer, and the accurate film thickness was confirmed by cross-sectional transmission electron microscopy (TEM:

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JEM 3000F, JEOL). The phase was analyzed by X-ray diffraction (XRD: M18XHF-SRA, MAC Science) with Cu *Kα* radiation, and scanning electron microscopy (SEM: JSM-6360, JEOL) was used to determine the morphological changes after cycling. Auger electron spectroscopy (AES: Model 660, Perkin-Elmer) with sputtering was performed for the depth-profile analysis.

The electrochemical properties of Si thin films deposited between room temperature and 300 °C were examined with a thickness of 200 and 800 nm. Beaker-type half-cells were used to evaluate the electrochemical properties. The cells were comprised of Li-metal sheets, the Si thin films (1 cm in diameter) as a working electrode, and 1 M. $LiPF_6$ in EC/DEC (1/1 vol. %) (Cheil Industries Inc.) as an electrolyte. The cells were discharged from the initial open-circuit voltage to 0.02 V, and cycled between 0.02 and 1.2 V after the first discharge. All samples were tested at ∼0.5 C current rate (1 C = 4200 mA g^{-1}) up to 200 cycles. The density of silicon (2.33 g cm^{-3}) was used with the measured film thickness to determine the mass of active material.

3. Results and discussion

A cross-sectional TEM of the Si thin film (with a thickness of 200 nm) deposited on a Cu foil at 200 °C is shown in Fig. 1(a). High-resolution TEM with diffraction confirmed the amorphous Si phase. The AES depth profile of the Si thin film deposited on a copper foil is presented in Fig. 1(b). (The depth was calibrated from the sputtering rate of SiO_2.) The TEM and AES results demonstrate that the interfacial oxide and impurities are effectively removed by acid etching. A noticeable change in the interdiffusion length with deposition temperature (up to 300 °C deposition) is not shown within the AES resolution. The XRD patterns in Fig. 2 reveal structural changes in the Si/Cu layer deposited at various temperatures that range from room temperature to 400 °C. The thin films show only Cu peaks, and some Cu_3Si peaks appear at 400 °C [12,13].

The deposition–temperature effect on the cycle-life performance in the range from room temperature to 300 °C is presented in Fig. 3. The electrochemical properties reach an optimum condition at 200 °C deposition. In the Si thin films deposited at room temperature, most of the capacity is rapidly lost after 20 cycles, and a discharge capacity of ∼290 mAh g^{-1} (with a retention of ∼10%) is reported

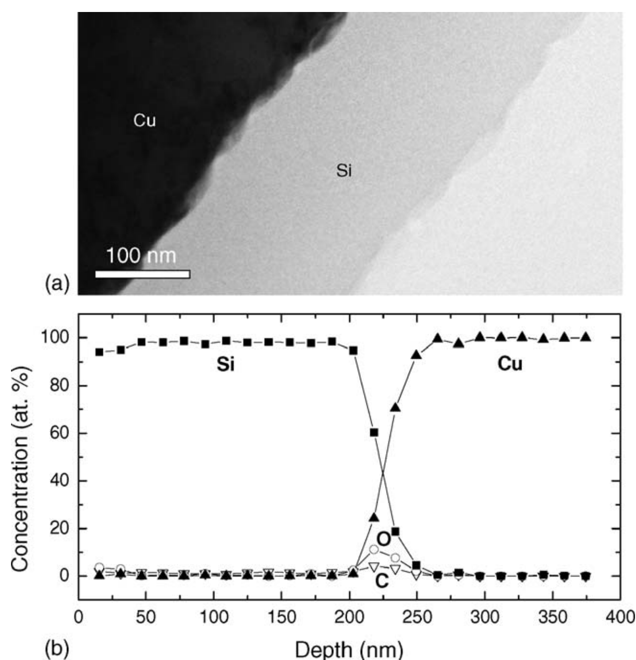

Fig. 1. (a) Cross-sectional TEM image of amorphous Si thin film (with thickness of ∼200 nm) deposited on Cu foil at 200 °C. (b) AES depth profile of Si thin film deposited on Cu foil.

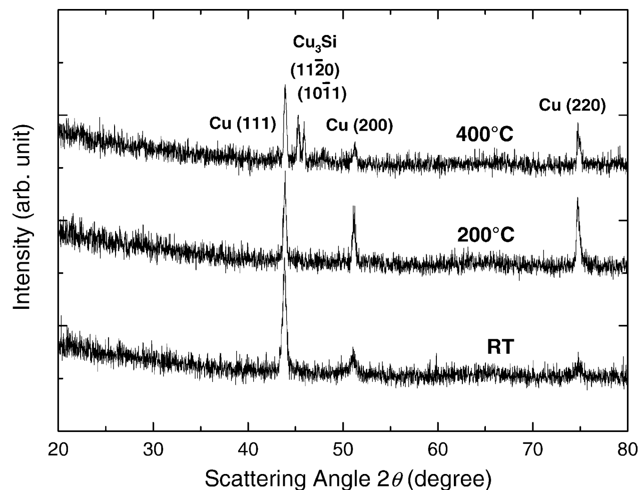

Fig. 2. X-ray diffraction patterns of Si (∼500 nm)/Cu (∼200 nm) layer deposited on SiO_2 (100 nm)/Si (1 0 0) wafer at various temperatures ranging from room temperature (RT) to 400 °C. Samples were tilted by ∼5° for zero-background Si substrate.

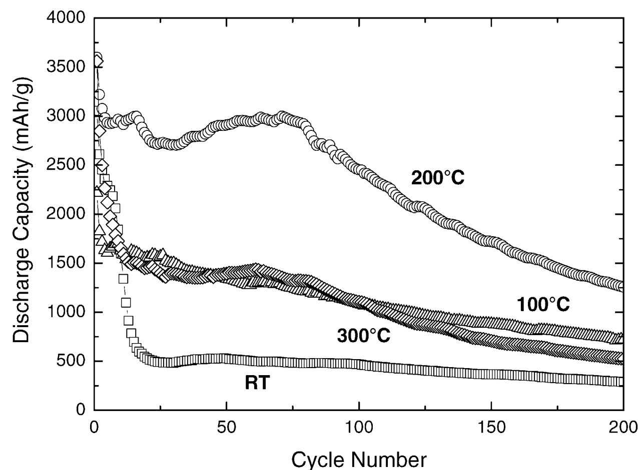

Fig. 3. Cycle-life performance of 200 nm Si thin films deposited between RT and 300 °C, up to 200 cycles at 0.5 C rate (1C = 4200 mA g^{-1}). Quality of Si thin films deposited over 350 °C is not good because of poor adhesion on the Cu foil.

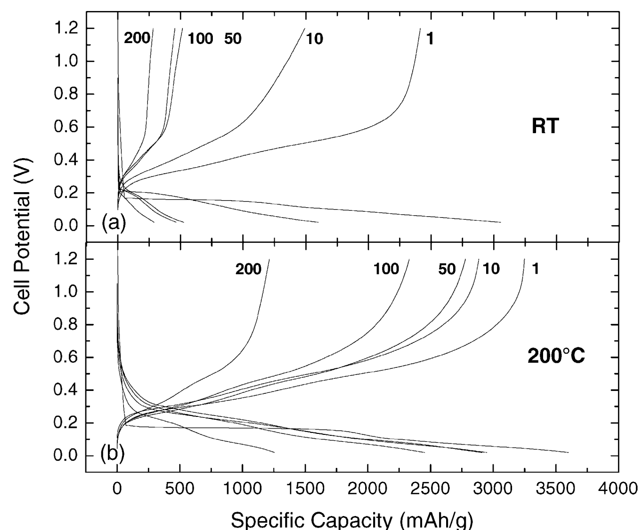

Fig. 4. Voltage profiles of 200 nm Si thin films deposited at (a) RT and (b) 200 °C at 0.5 C rate. Cells discharged from initial open-circuit voltage to 0.02 V, and cycled between 0.02 and 1.2 V after first discharge.

at the 200th cycle. In the 200 °C sample, a capacity of ∼3000 mAh g^{-1} is maintained up to ∼70 cycles, and a discharge capacity of ∼1300 mAhg^{-1} (with a retention of 36%) is obtained at the 200th cycle. Poor adhesion of deposited Si on a copper foil is found at temperatures over 350 °C (unlike samples deposited on an oxidized wafer). It is known that this adhesion problem arises from high-compressive stress, due to the energetic nature of sputter 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}) [14,15].

Silicon thin films deposited at room temperature and 200 °C exhibit a first discharge capacity of ∼3000 and ∼3600 mAh g^{-1}, respectively, and an initial reversible capacity of ∼2400 and ∼3200 mAh g^{-1}, respectively (Fig. 4). Both samples exhibit a good Coulombic efficiency (i.e., charge capacity/discharge capacity) of over 90% after the first cycle. There is a main flat region of ∼0.2 V on the first discharge and a smoothly sloped shape on the followed cycles. The flat region was recently explained by Li insertion in a-Si without phase transformations [16]. The change in voltage profile observed on subsequent cycles is probably due to a change in the kinetics by density, conductivity, chemical diffusivity, etc. [17].

The thickness effect on cycle-life performance is shown in Fig. 5. The as-deposited 800 nm Si is physically bent in a convex form by the residual compressive stress [7]. Thicker films give inferior electrochemical performance to thinner ones. The 800 nm Si films deposited at room temperature fail on the third cycle. By contrast, film deposited at 200 °C yield a first discharge capacity of ∼1500 mAh g^{-1} and superior cycleability of ∼1400 mAh g^{-1} (with ∼91% retention) on the 10th cycle.

The 200 nm Si film deposited at room temperature is mostly peeled off after 20 cycles and the size of the remaining islands is non-uniform (Fig. 6). After the 20 cycles, the

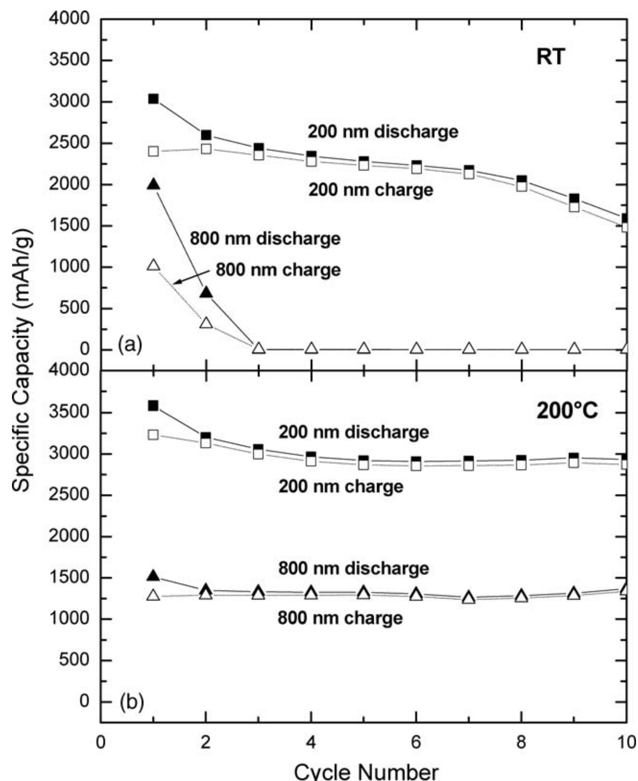

Fig. 5. Cycle-life performance of 200 and 800 nm Si thin films deposited at (a) RT and (b) 200 °C at 0.5 C rate.

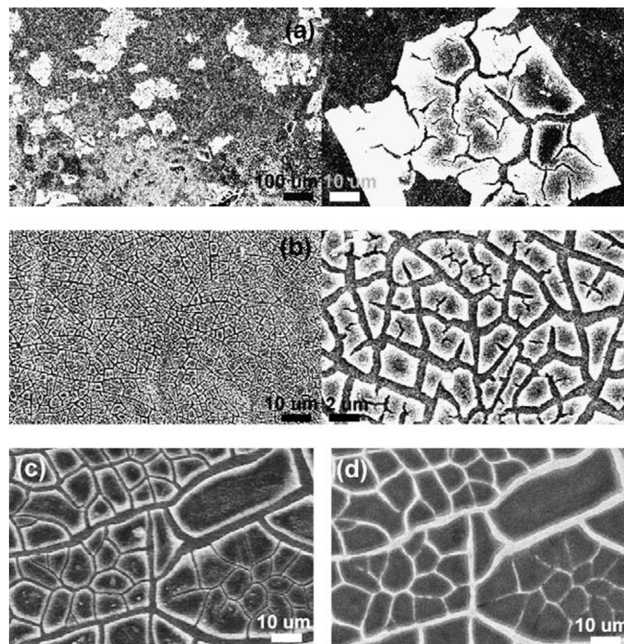

Fig. 6. SEM images of 200 nm Si (with different magnifications), deposited at (a) RT and (b) 200 °C, after 20 cycles, (c) 800 nm Si deposited at 200 °C, after first cycle, and (d) BEI image (composition mode: the heavier, the brighter) of (c).

200 nm Si film deposited at 200 °C consists of islands with a uniform size of ∼2 μm over all of the copper surface. The amount of Si remaining coincides qualitatively with the cycling properties. As the cracking continues, each island keeps dividing into smaller islands. The backscattered electron image (BEI) of Fig. 6(d) reveals the exposure of copper foil.

It has been reported that the island structure of Si reduces the stress that arises from volume expansion/contraction during cycling [1,2]. In addition, moderate heat treatment is crucial to form and maintain the island structure, as confirmed in Fig. 6. The thermal stress that arises with the deposition temperature is superimposed on the growth stress. Therefore it is concluded that the origin of the excellent performance at 200 °C is due to optimization between the strong adhesion by Si/Cu interdiffusion and the film stress.

4. Conclusions

The electrochemical performance of a-Si thin films deposited on a copper foil was studied to investigate the effect of deposition temperature and film thickness. The electrochemical properties indicate an optimum condition at 200 °C deposition, and thinner films exhibit superior electrochemical performance to thicker ones. The morphology after cycling consists of a cracked and island shape, and the amount of residual Si shown by the SEM images coincides qualitatively with the cycling properties. The excellent cycleability with a capacity of ∼3000 mAh g^{-1} probably arises from proper Si/Cu interdiffusion and minimal film stress.

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