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Letter

Shape memory effect-induced crack closure in Si thin film deposited on a Ti–50.3Ni (at%) alloy substrate

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ABSTRACT

Cracks developed by tensile loading in the Si thin film deposited on the Ti–50.3Ni (at%) substrate were closed by the shape memory effect of the substrate. The interfacial layer formed after annealing at 873 K between the Si thin film and the substrate was essential for the shape memory effect-induced crack closure. Cracks which formed during lithiation in the Si thin film annealed at 873 K after deposition were closed by delithiation followed by heating up to 373 K.

1. Introduction

Silicon is a good candidate for an anode material of Li ion secondary battery because of high theoretical capacity of 4200 mAh g^{-1} on the basis of $Li_{22}Si_5$ formation, which is 11 times larger than the capacity (∼370 mAh g^{-1}) of the graphitic carbon currently used [1,2]. However, Si electrode shows poor cycle life, which is originated from the large volume change of Si (∼310%) during charge–discharge (lithiation–delithiation) process. Surface cracking and pulverization of Si electrode occur by the repetitive mechanical stress associated with the volume change during charge–discharge, which leads to poor cycle life [3,4]. In order to improve the cycle life, many researches for enhancing the adhesion between Si and a current collector (substrate) have been made since the generation of the stress is restrained by the enhanced adhesion [5–9].

Ti–Ni alloys are deformed by the rearrangement of martensitic variants in martensitic state and the stress-induced martensitic transformation in austenitic state to the extent of strain less than about 7% [10]. Those deformation modes are origin of the shape memory effect and superelasticity which can be used in the field of flexible battery [11,12]. The stress required for the rearrangement of martensitic variants and the stress-induced martensitic transformation of Ti–Ni alloys is 0.1 ∼0.6 GPa which is much smaller than the stress generated during charge–discharge of Si electrode (∼3 GPa)[13]. If Si thin film (as the anode) is deposited on the surface of Ti–Ni alloys (as the current collector) and the stress generated during charge–discharge of Si electrode is transferred well to the Ti–Ni alloys, Ti–Ni alloys would be deformed during charge–discharge through the rearrangement of martensitic variants and/or the stress-induced martensitic transformation and thus some of the stress is expected to be relaxed.

Recently, the present authors reported that the Ti–Ni current collector improved the cycle life of the Si thin film electrode by relaxing some of the stress generated in the Si thin film during charge–discharge through the rearrangement of the B19′ martensitic variants or the stress-induced martensitic transformation [14]. They also reported that a strong adhesion between the Si thin film and the Ti–Ni current collector is essential to relax the stress generated in the Si thin film during charge–discharge. However, mechanical stability of the Si thin film subjected to the shape memory behavior of the Ti–Ni current collector and microstructure of the interface between the Si thin film and the Ti–Ni current collector are not clear yet. In the present study, therefore, changes in morphology of the Si thin film accompanied by the shape memory effect of the Ti–Ni current collector and microstructure of the interface between the Si thin film and the Ti–Ni current collector are investigated.

2. Experimental procedure

A Ti–50.3Ni (at%) alloy ingot was prepared by vacuum induction melting. The alloy ingot was hot rolled into a sheet with a thickness of 0.5 mm. Two kinds of

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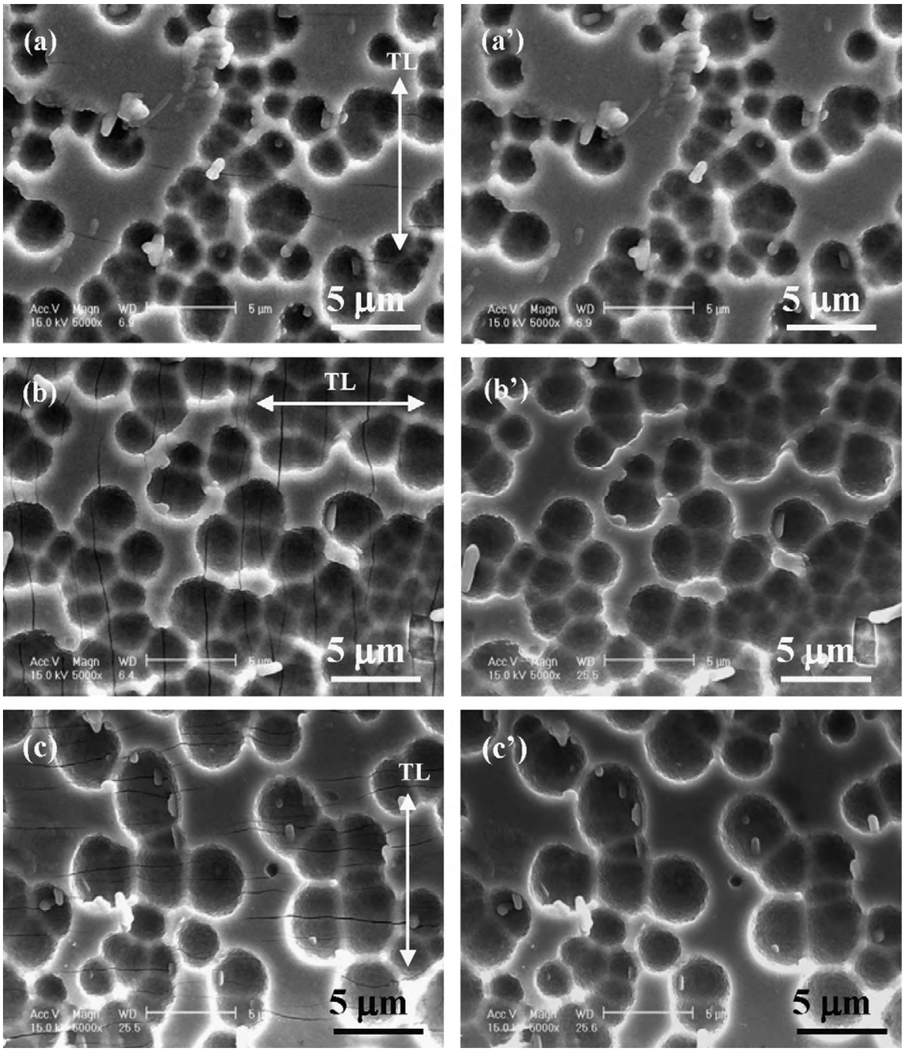

Fig. 1. FE-SEM images of the Si thin film annealed at 873 K after deposited on the Ti–50.3Ni alloy substrate; (a), (b) and (c) were obtained after tensile deformation of 2%, 4% and 7%, respectively; (a′), (b′) and (c′) were obtained after heating (a), (b) and (c) up to 373 K, respectively.

substrates with the sizes of 10 mm × 10 mm and 5 mm × 50 mm were prepared to fabricate Si thin film electrodes and tensile test samples, respectively, and then solution treatment was conducted at 1123 K for 3.6 ks in vacuum.

Prior to Si deposition, one side of the substrates was electrochemically etched in 1 M H_2SO_4 + 2% HF solution to enhance the adhesion with Si film during deposition process. Si thin films were prepared by DC magnetron sputtering under the pressure of $\sim 5 \times 10^{-3}$ Torr in argon (Ar) atmosphere. Thickness of the Si film was 560 nm, measured by an alpha step profiler using Alphastep, KLA Tencor. The Si films deposited on the substrates were annealed at 873 K for 3.6 ks in a vacuum to induce the inter-diffusion between the Si film and Ti–50.3Ni substrates. From differential scanning calorimetry, M_s (the B2-B19′ transformation start temperature), M_f (the B2-B19′ transformation finish temperature), A_s (the B19′-B2 transformation start temperature) and A_f (the B19′-B2 transformation finish temperature) were known to be 283, 268, 298 and 311 K, respectively.

Tensile stress was applied to the specimens (the Si thin film deposited on the Ti–Ni substrate) until reaching to the tensile strain of 2–7%. After unloading, morphology of the Si thin film was observed by field emission scanning electron microscopy (FE-SEM). Then, specimens were heated up to 373 K which is higher than A_f for inducing the shape memory effect. After heating them for 60 s, morphology of the Si thin film was observed again by FE-SEM. Microstructures of the interface between the Si thin film and the Ti–Ni current collector were investigated by transmission electron microscope (TEM) observations using JEOL2010 with an accelerating voltage of 200 kV. Samples for TEM observation were prepared by focused ion beam (FIB) technique.

For electrochemical property measurements, CR2032 coin-type cells were assembled in an argon-filled glove box with a lithium metal anode (Cyprus Foote Mineral, 99.98%, USA) as the count electrode. The electrolyte was 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Lithiation and delithiation were performed by Galvanostatic charge–discharge test at a current density of 50 µA cm^{-2} corresponding to 420 mA g^{-1} (0.1 C). Note that the cell voltage decreases while electrochemical alloying reaction between Si and Li occurs, and finally reaches near 0 V vs. Li/Li^+ after full lithiation (charging). In contrast, the cell voltage increases again during delithiation (discharging, decomposition of Si–Li alloy). Samples for FE-SEM observations were obtained at voltages of 0.01 V (lithiation) and 1.5 V (delithiation) by the control of cut-off voltage.

3. Results and discussion

Fig. 1(a), (c) and (e) is FE-SEM images showing the surface of the Si thin films deposited on the Ti–50.3Ni alloy substrate which have been subjected to tensile deformation of 2%, 4% and 7% at room temperature followed by unloading, respectively. The dimples which were formed by electrochemical etching of the substrates are observed in all figures due to the deposition of thin Si films with 560 nm in thickness. It is found that cracking in all Si films occurs along the direction almost perpendicular to the tensile loading (TL) direction as designated in the figures and the number of cracks increases with increasing tensile strain. The formation of cracks is because the Si film cannot accommodate the tensile deformation of 2–7% without cracking, while the Ti–50.3Ni alloy substrate are deformed by the rearrangement of the B19′ martensitic variants or the stress-induced B2-B19′ martensitic transformation [10]. It is to be noted here that the Si thin films are not detached from the surface of the substrate although many cracks appear.

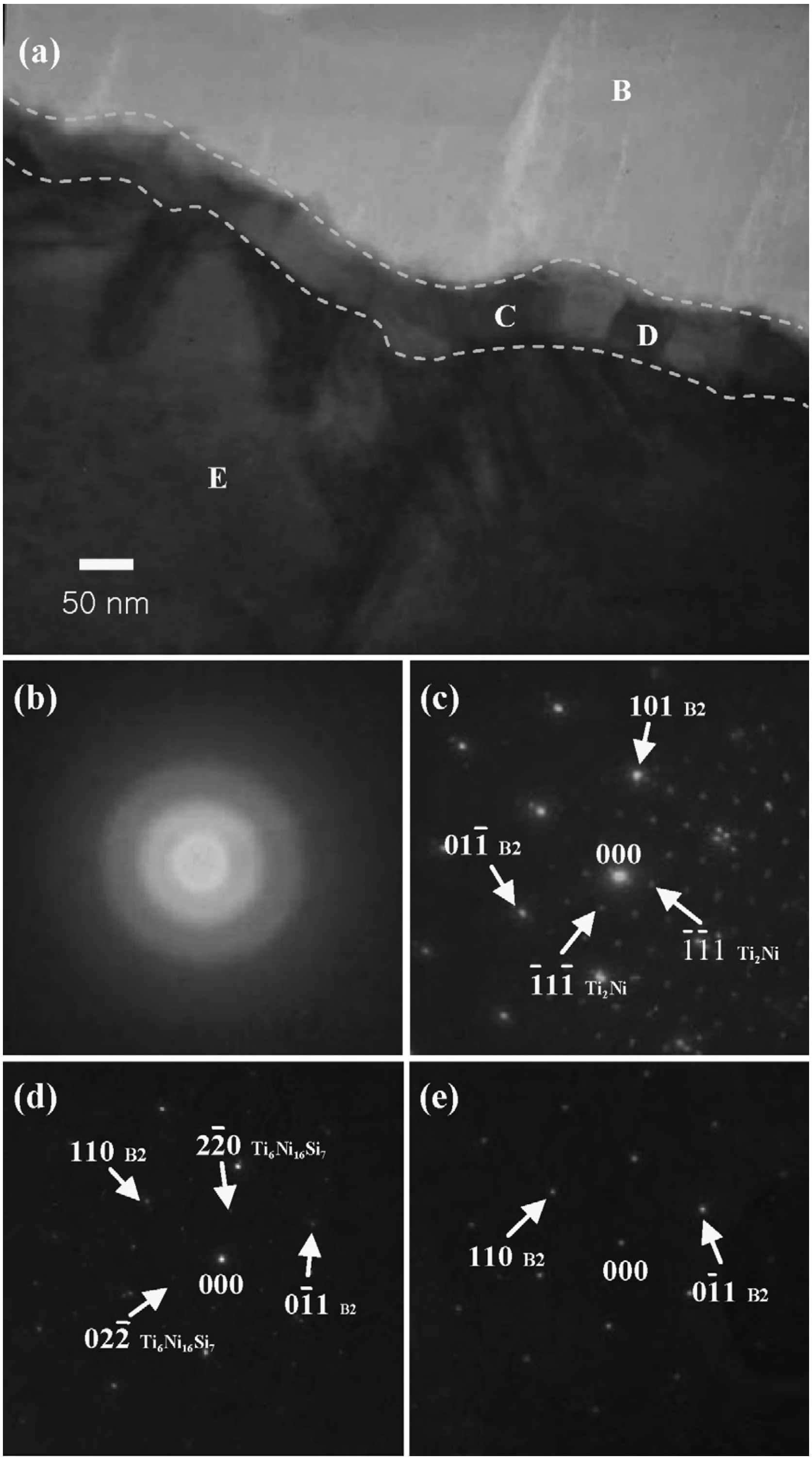

Fig. 2. (a) Bright field image of the Si thin film annealed at 873 K after deposited on the Ti–50.3Ni alloy substrate, (b)–(e) are electron diffraction patterns obtained from B to E in (a), respectively.

After heating up to 373 K, which is much higher than A_f, the surface of Si thin films was observed again by FE-SEM. Fig. 1(a′), (b′) and (c′) is FE-SEM images taken from the same areas as Fig. 1(a), (b) and (c), respectively, after heating up to 373 K after unloading. It is clear that all the cracks which occurred on loading are closed by the heating. The tensile deformation in the Ti–50.3Ni alloy is believed to be recovered by the shape memory effect. Therefore, it is concluded that the crack closure in the Si thin film is due to the shape memory effect of the Ti–50.3Ni alloy substrate. Repeated crack opening and closure in the Si thin film, which occurred several times by repeating the tensile loading and the unloading followed by heating, could be observed at the same place.

In addition to the shape memory effect, a tight bonding between the Si thin film and the substrate is necessary for the crack closure in the Si thin film. If the Si thin film is weakly bonded with the substrate, cracks would not be closed, rather the Si thin film would

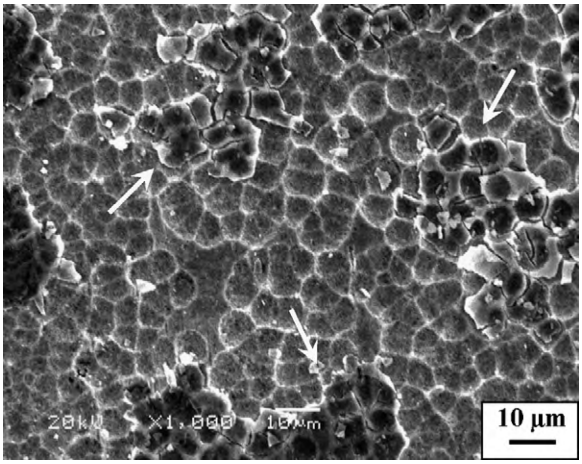

Fig. 3. FE-SEM image taken from the as-deposited Si thin film after lithiation.

be detached from the substrate. From Fig. 1(e), it was found that the Si thin film was not detached from the substrate even after 7% tensile deformation. This means that an interfacial reaction during annealing at 873 K results in the tight bonding between the Si thin film and Ti–50.3Ni alloy substrate.

Fig. 2 shows TEM observation results obtained from the sample annealed at 873 K for 3.6 ks. Fig. 2(a) is a bright field image and Fig. 2(b), (c), (d) and (e) is electron diffraction patterns obtained from the areas of B, C, D and E in Fig. 2(a), respectively. From the diffraction patterns of Fig. 2(b) and (e), the areas of B and E are found to be the amorphous Si thin film and the substrate with the B2 structure, respectively. It is clear that a reaction layer with a width of 50–70 nm is formed along the interface between the Si thin film and Ti–50.3Ni alloy substrate as delineated by dotted lines. From the diffraction patterns of Fig. 2(c) and (d), the areas of C and D are found to be Ti_2Ni and $Ti_6Ni_{16}Si_7$, respectively. Therefore it is concluded that a reaction layer consisting of Ti_2Ni and $Ti_6Ni_{16}Si_7$ is formed along the interface between the Si thin film and Ti–50.3Ni alloy substrate by annealing at 873 K.

The reaction between Si and Ti–Ni alloys has been studied in the field of Ti–Ni microactuators because they were usually prepared by depositing Ti–Ni alloy thin films on the surface of Si wafer. Ti–Ni alloy thin films were annealed at 773 K for crystallization after deposition since they were generally amorphous, which results in an interfacial reaction between Si wafer and Ti–Ni alloy thin films [15]. Various kinds of silicides such as $TiNiSi_2$, $Ti_4Ni_4Si_7$, Ti_2Ni_3Si, $NiSi_2$ were formed at the interface between Si substrate and Ti–Ni alloy thin films [16–19]. In Ti–Ni–Si alloys where Si is substituted for Ni in an equiatomic Ti–Ni, Ti_5Si_3, $Ti_6Ni_{16}Si_7$ and $Ti_4Ni_4Si_7$ were formed [20]. In the present study, one kind of silicide, $Ti_6Ni_{16}Si_7$ is mainly observed. The discrepancy may come from the difference in fabrication method, annealing condition and alloy composition, although not clear yet.

In order to investigate morphological changes in the Si thin film deposited on the Ti–50.3Ni alloy substrate during charging (lithiation) and discharging (delithiation), samples were taken at the end stages of charging and discharging and then FE-SEM observations were made on the samples. For comparison, the Si thin film/Ti–50.3Ni substrate sample which was not annealed after Si deposition (as-deposited) was investigated also. Fig. 3 is a FE-SEM image showing the Si thin film of the as-deposited sample after lithiation (end stage of charging). From the previous study, any interfacial reactions between the Si thin film and Ti–50.3Ni alloy substrate were not observed in the as-deposited sample [14]. It is found that only small amount of the Si thin film remains after lithiation as designated by arrows. Most of the Si thin film is considered to be detached from the substrate because interfacial bonding between the Si thin film and Ti–50.3Ni alloy substrate is weak.

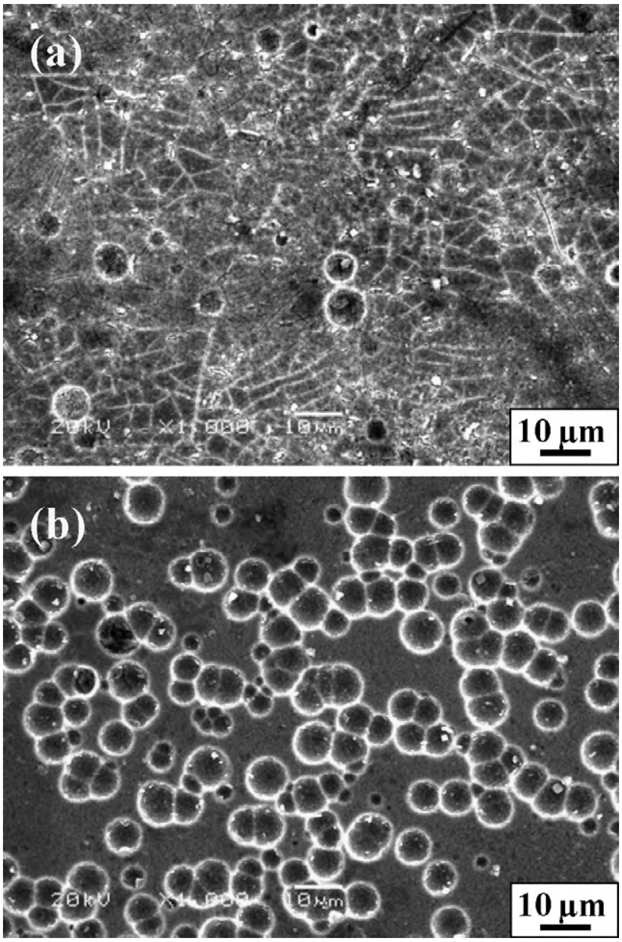

Fig. 4. FE-SEM image taken from the annealed Si thin film after lithiation, (a) and after delithiation followed by heating up to 373 K, (b).

In contrast to the as-deposited sample, the sample annealed at 873 K after Si deposition on the surface of the Ti–50.3Ni substrate (annealed sample) shows results obviously different from Fig. 3. Fig. 4(a) is a FE-SEM image showing the Si thin film of the annealed sample after lithiation. Many cracks are observed in the Si thin film, which is ascribed to large volume expansion by lithiation. It is clear that most of the Si thin film remain unlike the as-deposited sample, although many cracks are developed. A tight bonding between the Si thin film and Ti–50.3Ni alloy substrate in the annealed sample is considered to prevent the Si thin film from being detached. During lithiation, the Ti–50.3Ni substrate is considered to be deformed by the stress transferred from the Si thin film through the tightly bonded interface, which results in the rearrangement of martensitic variants in martensitic state or the stress-induced martensitic transformation because lithiation temperature (286 K) is between M_s (289 K) and M_f (267 K).

Fig. 4(b) shows a FE-SEM image taken from the Si thin film of the annealed sample after delithiation followed by heating up to 373 K for 30 s. The Si thin film remains on the surface of the substrate after delithiation followed by heating, which is confirmed by EDS (energy dispersive spectroscope) analysis. The cracks occurred during lithiation as shown in Fig. 4(a) are not observed no longer after delithiation followed by heating. Since A_s (302 K) of the Ti–50.3Ni substrate is higher than lithiation temperature (286 K), the deformation which occurred during lithiation would remain after delithiation. When the Ti–50.3Ni substrate is heated up to

373 K which is higher than A_f (317 K), the B19′ martensite would be transformed into the B2 parent phase with accompanying the recovery of the deformation. Therefore it is concluded that the crack closure in Fig. 4(b) is attributed to the shape memory effect of the Ti–50.3Ni alloy substrate.

The relaxation of the stress generated in the Si thin film electrode due to the shape memory effect of the Ti–50.3Ni alloy substrate and a tight bonding between the Si thin film and the substrate would play an important role for improving the lithiation–delithiation cycle performance of the Si thin film electrode. In fact, the annealed Si thin film electrode deposited on the Ti–Ni substrate showed superior electrochemical capacity and cycle life to the as-deposited Si thin film [14].

4. Conclusions

In summary, cracks occurred by tensile deformation of 2–7% in the Si thin film deposited on the Ti–50.3Ni (at%) substrate and they were closed by heating up to 373 K after removing tensile load, which was ascribed to the shape memory effect of the substrate. The reaction layer consisting of Ti_2Ni and $Ti_6Ni_{16}Si_7$ which caused tight bonding between the Si thin film and Ti–50.3Ni substrate was necessary for the shape memory effect-induced crack closure. The Si thin films deposited on the Ti–50.3Ni substrate (as-deposited sample) were detached by lithiation, while those annealed at 873 K (annealed sample) were not detached although many cracks occurred. The cracks were closed by delithiation followed by heating up to 373 K.

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