

Short communication

Studies of the structure of vacuum deposited silicon films on metal substrates as anode materials for Li-ion batteries

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Available online 24 May 2006

Abstract

Our prepared vacuum deposited silicon films on Ni and Cu substrates show excellent cycle performance opposing to the conventional silicon film having short cycle life. In this paper, the reasons for this long cycle behavior were studied by the measurements of scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electronic microscopy (TEM) and selected area electron diffraction (SAED). At first glance, it seemed that the vacuum deposited silicon films were amorphous from XRD. However, we found that the films consisted of nano-particles with polycrystalline structure. Large surface energy and specific volume of the nano-crystals kept the structure stable against collapsing during the expansion and shrinkage process under lithium insertion and extraction. Consequently, the vacuum deposited silicon films presented good cycling performance.

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Keywords: Li-ion batteries; Anode; Vacuum deposited Si film; Nano-particles; Polycrystalline

1. Introduction

Li-ion battery is the most promising secondary battery as the power source of the most modern portable IT equipment. Li-ion batteries are required to double their capacity. For the purpose to meet this demand, the active materials are better to be replaced by new materials with larger reversible capacity. Silicon is considered to be one of the most promising candidates due to its high theoretical capacity and the satisfactory working voltage. The cycle performance of silicon, however, is quite poor due to the large expansion and shrinkage during Li charging/discharging [1–3].

We succeeded to attain excellent cycle performance by making vacuum deposited thick silicon films [4–6]. However, the reason why the vacuum deposited silicon films can achieve long cycle performance is still unknown. Their X-ray diffraction (XRD) patterns showed no sharp diffraction peaks implying that it would be amorphous. However, it is well known that the amorphous silicon is very difficult to form from pure metallic

silicon. Here we examined the structure of the deposited silicon films in detail by utilizing scanning electron microscopy (SEM), XRD, transmission electronic microscopy (TEM) and selected area electron diffraction (SAED) methods to find the reasons for their excellent cycling.

2. Experimental

Silicon films were vacuum deposited on a 30 μm thick Ni foil or surface modified Cu foil according to our reported process by using phosphor doped n-type semi-conducting Si as the depositing source [5]. About 0.5 g of the Si powder or crushed pieces of the wafer was loaded in a tungsten boat. Then a 30 μm thick 8 cm × 4 cm rectangular metal (Ni or Cu) foil (Nilaco, 99.99% purity) and the Si-loaded tungsten boat were mounted in a vacuum chamber and evacuated under the pressure of 10⁻⁷ Torr for 5 h at room temperature. Electric current was supplied to melt the loaded Si in the tungsten boat. Silicon was evaporated and then deposited to the surface of the metal foil. The deposition rate was about 10 Å s⁻¹. The thickness of the deposited silicon films was controlled by monitoring a quartz vibration micro-balance mounted near the substrate in the vacuum chamber. Prior to the vacuum deposition the surface of the Ni foil substrate was etched

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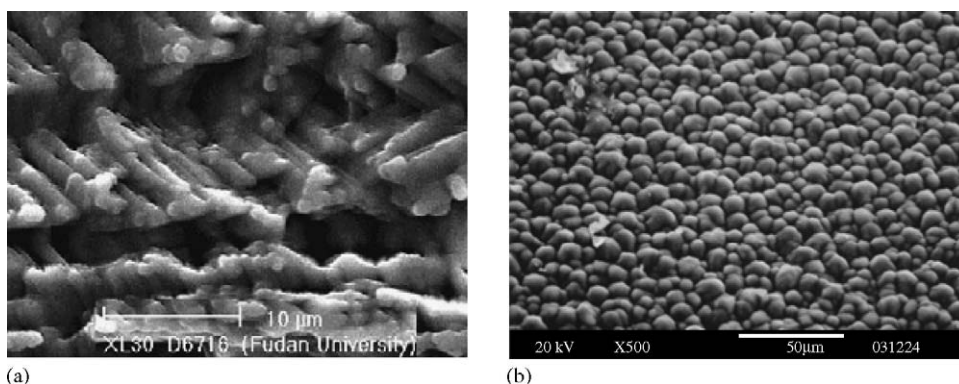


Fig. 1. SEM micrographs of vacuum deposited Si films on (a) the Ni foil etched with FeCl_3 and (b) on the rough Cu foil.

with aqueous solutions of FeCl_3 (1 M for 3 min and then 0.3 M for 3 min at an ambient temperature) for obtaining rough surface, which enabled the silicon film to stick tightly because of the anchor effect.

A $1\text{ cm} \times 1\text{ cm}$ square foil was cut from the Si-deposited substrate foil and a Ni lead wire was spot-welded at its corner. The square foil was used as the working electrode and mounted in a cylindrical Pyrex glass cell (outer diameter 35 mm, three-electrode system) where Li foils were used as counter and reference electrodes. The used electrolyte was 1 M LiClO_4 solution of propylene carbonate (PC) (Tomiyama Chemicals, the water content less than 20 ppm). The constant current charge/discharge cycle test was conducted with a Hokuto-Denko HA-151 Potentio-galvanostat. The first charging was started at 2.0 V versus with Li/Li^+ toward negative potential direction. All the measurements were performed in a glove box filled with dry argon gas at room temperature.

SEM observation was performed with a scanning electron microscope of Philips XL300. XRD patterns were obtained with $\text{Cu}/\text{K}\alpha$ radiation by a Rigaku RINT-2000 diffractometer. TEM and SAED were performed with a transmission electron microscope of JEOL JEM 2011.

3. Results and discussion

If a metal substrate with a flat surface is used for the vacuum deposition of silicon, the cycle performance of the prepared film

will be very poor. It is necessary to roughen the surface of the substrate to obtain a good cycleability of the deposited silicon film. Etching with aqueous solution of FeCl_3 was effective for Ni foil substrate, and the vacuum deposited Si film adhered tightly to the deep pores and cracks of the etched substrate [5,6]. Its SEM micrograph (Fig. 1(a)) reveals that the Si film appears to present a chocolate-like slick surface. In the case of the substrate of copper foil, after depositing a $3.6\text{ }\mu\text{m}$ thick silicon film, the SEM micrograph of the silicon film was shown in Fig. 1(b). It was covered by snow-like deposit.

The cycling behavior of the deposited silicon films is shown in Fig. 2. In the case of the 670 nm thick silicon film on etched Ni substrate, its capacity could be maintained over 1500 mAh g^{-1} for 400 cycles, and that of the $3.6\text{ }\mu\text{m}$ thick Si film on the Cu foil was over 1250 mAh g^{-1} for 200 cycles. We supposed this good cycle performance should be inherent to the structure of the vacuum deposited Si film.

In order to examine whether the vacuum deposited film is crystalline or amorphous, the XRD pattern was obtained for the vacuum deposited film on a Ni foil. It presents no peak at 28° , typical one for crystal silicon. At first glance, it seemed that the film was amorphous [5]. However, it is well known that the amorphous silicon is very hard to obtain from pure silicon. Therefore, it is necessary to examine in more details whether it is really amorphous or not.

SEM micrographs for the Si films on the Ni and the rough Cu foils are shown in Fig. 3, respectively. Both films consist of

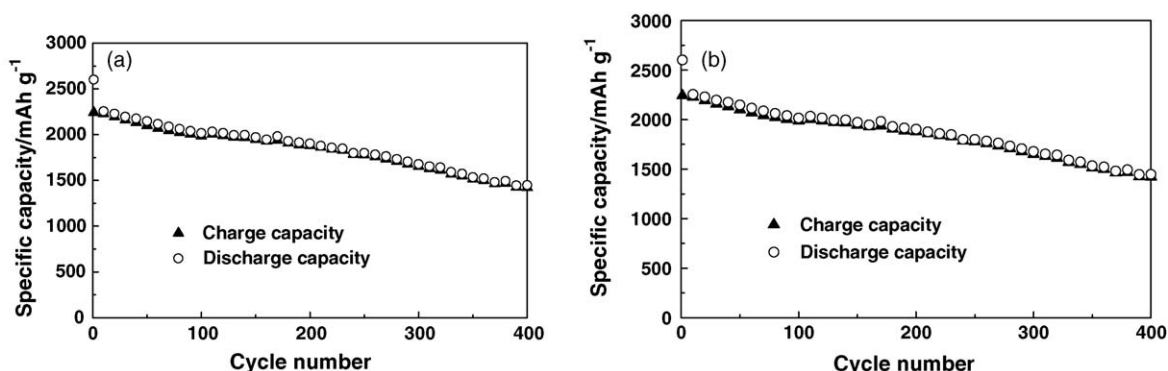


Fig. 2. Cycleability of (a) 670 nm thick Si film on the Ni foil etched with FeCl_3 and (b) $3.6\text{ }\mu\text{m}$ thick Si film on the rough Cu foil.

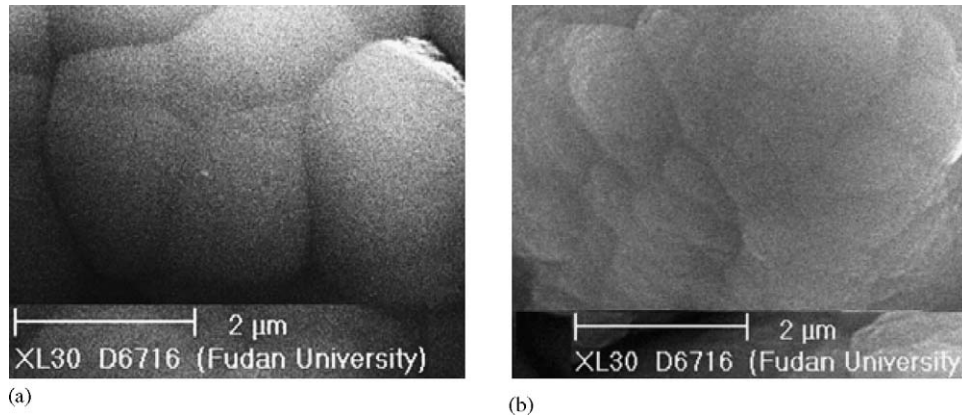


Fig. 3. HREM micrographs of vacuum deposited Si particles on (a) the etched Ni foil and (b) the rough Cu foil.

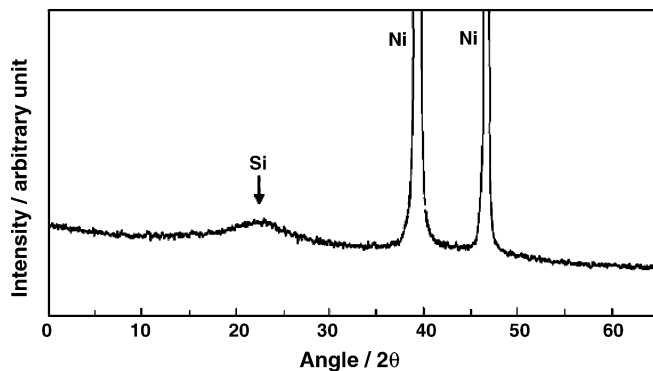


Fig. 4. XRD pattern of the vacuum deposited Si film on a Ni foil obtained by 10 times of repeated scanning.

the aggregation of a number of nano-particles. It is necessary to examine whether the nano-particle is crystal or not.

The XRD patterns were measured again but by the method of repeated data acquisition. A broad peak appeared after over 10 times repetition of data scanning as shown in Fig. 4, which could be supposed to be nano-size crystallines. TEM is a more effective method to detect nano-crystals or crystallines.

Fig. 5(a) is the TEM micrographs of the film formed on the copper substrate. A number of parallel crystal lattice lines with different orientation exist almost over the surface. This verifies that the film is not amorphous but consists of polycrystallines. SAED in Fig. 5(b) proves it clearly. A number of bright spots distributed in an irregular manner in Fig. 5(b) imply that the film consists of a number of randomly oriented small crystallites. In general, amorphous silicon is very difficult to obtain from silicon single crystal even under super rapid cooling. This is attributed to the formation of very stable sp^3 configuration for Si atoms instead of unstable sp^2 or sp ones. Accordingly, the formation of sp^3 crystal is expected to be very rapid during the evaporation process resulting in the aggregation of randomly oriented nano-crystals. It is known that nano-particle has very large specific surface area and very high surface energy. The high surface energy likely stabilizes the particle shape and prevents crystallines against collapsing during the expansion and shrinkage process from lithium insertion and extraction. On the other hand, the specific volume of nano-crystal is larger than that of the normal silicon crystal, and the larger volume can absorb the mechanical stress during lithium insertion. As a result, silicon films of polycrystallines show excellent cycle performance.

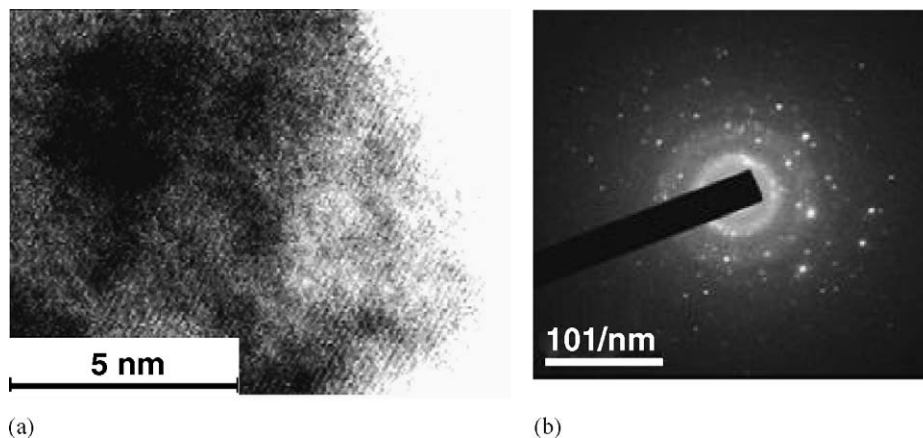


Fig. 5. (a) TEM micrograph and (b) SAED pattern of vacuum deposited Si particle on the rough Cu foil.

4. Conclusion

Vacuum deposited Si films on rough Ni and Cu substrates have been prepared and they show excellent cycle performance. It was found that the vacuum deposited Si films consisted of tiny nano-particles. Apparently XRD pattern indicates that the film is possibly amorphous. However, in fact the films consist of nano-particles with polycrystalline structure from the measurements of TEM and SAED. Large surface energy and specific volume of the nano-particles can keep the structure stable against the expansion and shrinkage during lithium insertion and extraction to ensure good cycling behavior.

Acknowledgements

Financial supports from Shanghai Science & Technology Committee (0452nm064) and China Natural Science Founda-

tion (20474010 and 20333040) are greatly appreciated. The authors' deep appreciation is due to Dr. Mikio Aramata of Shinetsu Chemical Co., Ltd., Japan, for his kind discussion on the film structure and the provision of p-type Si sources.

References

- [1] Y.P. Wu, X.B. Dai, J.Q. Ma, Y.J. Chen, *Lithium Ion Batteries: Applications & Practice*, Chemical Industry Press, Beijing, 2004, pp. 99–101.
- [2] R.A. Huggins, *Solid State Ionics* 113–115 (1998) 57–67.
- [3] H. Li, X. Huang, L. Chen, Z. Wu, Y. Liang, *Electrochem. Solid State Lett.* 2 (1999) 547–551.
- [4] S. Ohara, J. Suzuki, K. Sekine, T. Takamura, *Electrochemistry* 71 (2003) 1126–1132.
- [5] T. Takamura, S. Ohara, M. Uehara, J. Suzuki, K. Sekine, *J. Power Sources* 129 (2004) 96–100.
- [6] M. Uehara, J. Suzuki, K. Tamura, K. Sekine, T. Takamura, *J. Power Sources* 146 (2005) 441–444.