論文の内容の要旨

論文題目　Rapid vapor deposition of micrometer-thick silicon-base porous anodes for lithium secondary batteries
（リチウム二次電池に向けたマイクロメータ厚さのシリコン系多孔質負極の急速蒸着技術の開発）

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1. Introduction

Toward efficient use of electric energies including renewable energies, electric energy storage systems are very important. Rechargeable lithium ion batteries have been successfully used with focuses on portable electronic devices and electric vehicles, but further enhancement in capacity/power densities as well as the reduction in cost are in high demand. Silicon (Si) is an anode material with a high theoretical specific capacity, but the high specific capacity accompanies with a four-fold volumetric expansion,[1] resulting in pulverization and delamination of the whole structure of Si. To overcome failure of Si anode, many groups have developed various nanostructures, sometimes via complicated fabrication process.[2] High capacities were reported for such structures, but sometimes the weight of heavy current collectors was neglected for very thin active layers.

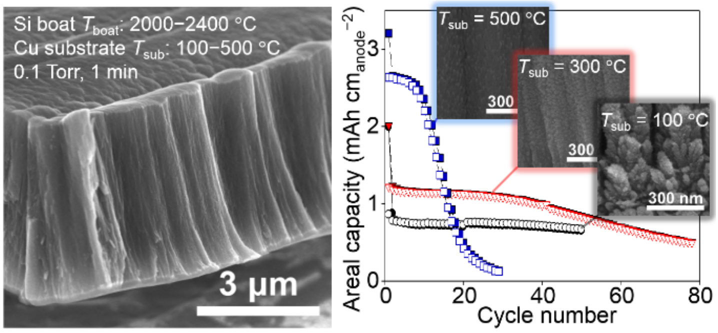
In this research, I rapidly deposited micrometer-thick porous Si-base films in 1 min by rapid vapor deposition (RVD). Control over the amorphous/crystalline structure, film porosity, and surface roughness was realized by the substrate temperature during RVD, and the adhesion at the Si/Cu interface was realized by post-annealing as well as co-deposition of Cu. In particular, control over the roughness of the growing Si films caused by the shadowing effect[3] is important to tailor the film microstructure. The electrochemical performance measurement was performed for the Si films and future prospects toward rapid production of high-capacity Si anodes on Cu collectors using inexpensive, safe Si source are discussed.

2. Micrometer-thick porous Si films by rapid vapor deposition

Physical vapor deposition is an important method to make Si thin films. For semiconductor applications, smooth Si thin films have been made by slowly depositing and thus diffusing Si over the growing film surface. Contrarily, thick and porous Si films are desirable for lithium secondary batteries. I therefore used the RVD process, in which the Si source is heated to 2000−2400 °C in a carbon boat (carbon boat temperature, T_{boat}), well above the melting point of 1414 °C for Si, to increase the Si vapor pressure and thus the deposition rate. Si was deposited on Cu substrates kept at much lower temperature of 100–500 °C (substrate temperature, T_{sub}) under 0.1 Torr Ar atmosphere to induce the rough and porous structure in the deposited Si films.[4]

To achieve a good adhesion of Si to Cu substrates, Cu surface was pretreated by sonication in isopropanol followed by ultraviolet-O_3 exposure to remove the organic contaminants and then by annealing in H_2/Ar flow at 800 °C to reduce the Cu surface. Charge-discharge measurements of the Si films were performed using coin-shaped half cells with Li counter electrode and an electrolyte of 1 M $LiPF_6$ in a 1:1:1 (v/v) mixture of ethylene carbonate (EC), dimethyl carbonate, and ethyl-methyl carbonate in the potential range of 0.005–2.000V vs. Li/Li^+.

Deposition rate changed largely with T_{boat} from 14 μm in 10 s at T_{boat} = 2400 °C to 3–4 μm in 1 min at T_{boat} = 2000 °C. The latter condition proved effective in making porous Si films without any big protrusions (Fig. 1). Porosity of the resulting Si films (p_{film}) changed significantly with T_{sub} from 0.15 at 500 °C to 0.34 at 100 °C while the post-annealing at T_{an} = 600 °C had little effect on the porosity. T_{sub} also affected the crystallinity, changing from a mixed phase of amorphous and microcrystals at T_{sub} = 500 °C to a fully amorphous phase at lower T_{sub}. Post-annealing at $T_{an} \leq 600$ °C did not crystallize the Si films, which is consistent with the known fact that 700 °C is needed to crystallize amorphous Si in 10 min. Composition gradient of Cu in Si films was confirmed by scanning electron microscope with energy dispersive X-ray spectrometer (SEM-EDS) and found largely affected by both T_{sub} and T_{an}. Sub-micrometer-thick Si-Cu intermixed layer was built either at T_{sub} = 500 °C or T_{an} = 600 °C.



Si powder → Micrometre-thick porous Si films on Cu in 1 min

Fig. 1 Structure and electrochemical performance of 3−4-μm-thick porous Si films rapidly deposited in 1 min on Cu at different T_{sub} = 100, 300, 500 °C and post-annealed at T_{an} = 600 °C.[4]

The charge-discharge measurement was performed for the Si films with T_{sub} = 100, 300, 500 °C and T_{an} = 600 °C with a similar effective thickness t_{eff} = 3−4 μm (calculated using a value of 2.33 g cm^{-3} for bulk Si crystal). The dense Si film (T_{sub} = 500 °C) exhibited the highest initial charge (lithiation) capacity of 4045 mAh g_{Si}^{-1} (closed to the theoretical capacity of 4200 mAh g_{Si}^{-1}) with a discharge capacity of 3328 mAh g_{Si}^{-1} at a 0.05C charge-discharge rate, however showed a rapid degradation to a 15% capacity retention after 20 cycles. The small porosity (p_{film} = 0.15) was advantageous to realize the good initial capacity by preventing the oxidation of the Si films before making the cell and the formation of excess SEI, however disadvantageous to make a reversible volume change during cycling. The porous Si film (T_{sub} = 100 °C) exhibited the opposite characteristics; the initial charge and discharge capacities were as small as 2759 and

1151 mAh g_{Si}^{-1} at a 0.05C charge-discharge rate, respectively, whereas showed a good capacity retention of 70% after 50 cycles. The large porosity (p_{film} = 0.33) was disadvantageous in preventing the oxidation of the Si films and the excess SEI formation, however advantageous to make a reversible volume change during cycling. For areal capacitance, an attractive value of 0.66 mAh cm_{anode}^{-2} was achieved at a 0.05C rate for the porous Si film (at T_{sub} = 100 °C) at the 50th cycle but further progress is needed to reach 4 mAh cm_{anode}^{-2} for the commercial cells.

3. Rapidly deposited, porous Si-Cu anodes having diffuse interface by metal co-deposition

In the previous chapter, Si-Cu intermixed layer was built with sub-micrometer thickness by the temperature control during RVD and post-annealing. In this chapter, I examined further control over the Cu composition gradient via rapid co-deposition of Si and Cu.[5]

Cu has a lower melting point (1084 °C) and higher vapor pressure than Si and thus Cu will be preferentially vapor deposited at the initial stage if Cu and Si sources are vaporized in the same boat. Si-Cu films were deposited on the pretreated Cu substrates, and electrochemical measurement was performed by using three-electrode beaker cell with 1 M $LiClO_4$ in a 1:1 (v/v) mixture of EC and propylene carbonate as electrolyte. Half-cell measurements were carried out with a Li metal counter electrode in the potential range of 0.005 V–1.200 V vs. Li/Li^+.

According to the Cu composition profiles in the Si-Cu films by SEM-EDS, the pure Si films deposited at T_{sub} of 100–300 °C contained little Cu, while the Si-Cu films deposited at low T_{sub} of 100 °C contained much Cu increasing with the Cu content in the source. Moreover, the Si-Cu films had a gradient profile in Cu content as expected.

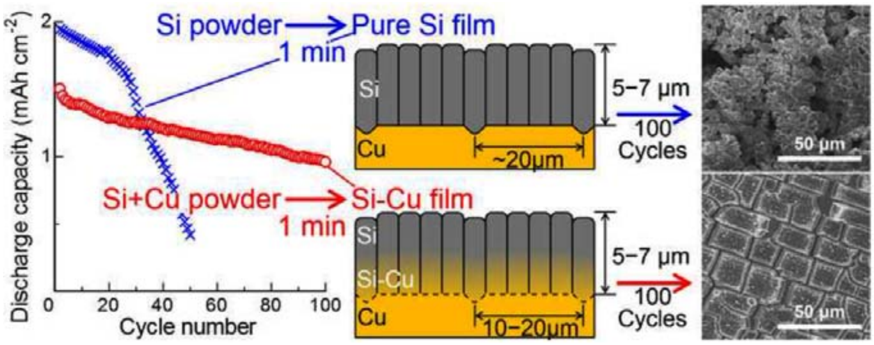


Fig. 2 Electrochemical performance and failure behavior of the porous Si and Si-Cu films (t_{eff} = 3.1–3.5 μm) rapidly deposited in 1 min on Cu at T_{sub} = 100 °C and post-annealed at T_{an} = 600 °C.[5]

The pure Si film showed poor cycling performance with a discharge capacity of ~500 mAh g_{film}^{-1} at 0.1C at the 50th cycle, while Cu addition at even the smallest content (5 wt% Cu source) enhanced the film performance remarkably to 1518 and 1250 mAh g_{film}^{-1} at the 50th and 100th cycles, respectively. The Cu composition gradient in the film and the diffuse interface between the film and the Cu substrate possibly yielded the gradient volume expansion and the stress defocusing at the interface. The film had a 10–20-μm-sized square domain structure after cycling, which showed no pulverization and suppressed the delamination from the substrate.

4. Carbon nanotube (CNTs) and Si hybrid films for anode in LiBs

The porous Si-Cu films rapidly deposited on Cu substrates showed improved cycle performances due to gradient Cu content, but failure of Si anode still existed. I examined the use of flexible CNTs to support the Si active layer. Using Cu substrates with CNT arrays prepared by my collaborator Mr. Na, a standing-wall structure was prepared by densifying the arrays via wetting-drying treatment with ethanol, and Si was deposited on it by RVD. The CNT-Si films had a wall-shape core-shell structure, providing enough spaces for the volume expansion (Fig. 3a,b). The CNT–Si hybrid film by Fe catalyst for CNT growth suffered from the corrosion of Fe during electrochemical reaction, resulting in poor cycle performance, while the CNT–Si hybrid film by Co catalyst for CNT growth were more stable with an areal capacity of 1.33 mAh cm_{anode}^{-2} at the 80th cycle (Fig. 3c).

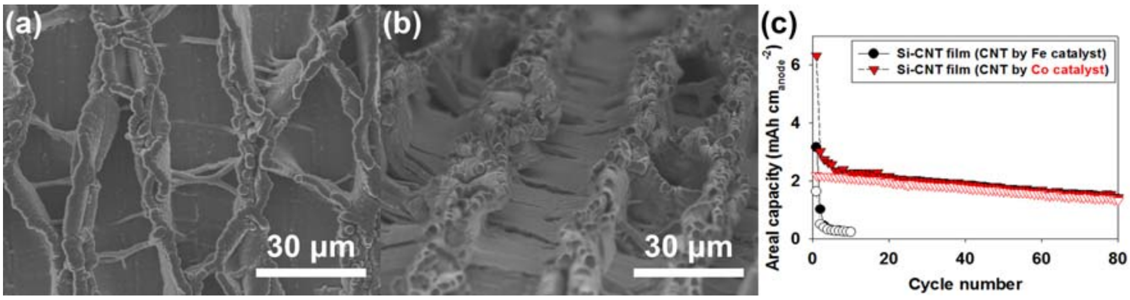


Fig. 3 (a) Top-view and (b) tilted-view SEM images of the CNT-Si hybrid films. (c) Electrochemical performance of the CNT–Si film with CNT arrays grown by different catalysts (Fe and Co).

5. Conclusions

I realized rapid fabrication of micrometer-thick porous Si films in 1 min directly on Cu collectors by RVD. Their porous structure was tailored by the substrate temperature during and post deposition. The adhesion of the films to Cu substrates was improved by surface treatment of Cu plate as well as post-annealing. Co-deposition of Si with Cu yielded a diffuse interface between the films and substrates, resulting in enhanced cycle performance of 1250 mAh g_{film}^{-1} and 0.95 mAh cm_{anode}^{-2} at the 100th cycle. In addition, when the RVD method is applied to the capillary force-assisted self-organized CNT arrays, RVD yielded wall-structured CNT-Si hybrid films with an areal capacity of 1.33 mAh cm_{anode}^{-2} at the 80th cycle, which suggests an alternative method for making practically thick 3-dimensional Si-base films. Although further improvement is needed, the RVD method, yielding micrometer-thick films rapidly from an inexpensive and safe Si source, is a promising route to fabricate Si anodes for lithium secondary batteries.

References:

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