

Thin Film Battery Using Micro-Well Patterned Titanium Substrates Prepared by Wet Etching Method

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Abstract: Titanium sheet metal substrates used in thin film batteries were wet etched and their surface area was increased in order to increase the discharge capacity and power density of the batteries. To obtain a homogeneous etching pattern, we used a conventional photolithographic process. Homogeneous hemisphere-shaped wells with a diameter of approximately $40\ \mu\text{m}$ were formed on the surface of the Ti substrate using a photo-etching process with a $20\ \mu\text{m} \times 20\ \mu\text{m}$ square patterned photo mask. All-solid-state thin film cells composed of a Li/Lithium phosphorous oxynitride (Lipon)/LiCoO₂ system were fabricated onto the wet etched substrate using a physical vapor deposition method and their performances were compared with those of the cells on a bare substrate. It was found that the discharge capacity of the cells fabricated on wet etched Ti substrate increased by ca. 25% compared to that of the cell fabricated on bare one. High discharge rate was also able to be obtained through the reduction in the internal resistance. However, the cells fabricated on the wet etched substrate exhibited a higher degradation rate with charge-discharge cycling due to the nonuniform step coverage of the thin films, while the cells on the bare substrate demonstrated a good cycling performance.

Keywords: LiCoO₂, Thin film battery, Wet etching, Photolithography, Surface area.

1. Introduction

There is an increasing demand for power sources to drive small electronic devices consuming low power, such as semi-conductors or MEMS-based technologies, as these technologies develop rapidly. A thin film battery (TFB) is a type of energy storage device that can be fabricated by the consecutive deposition of a current collector, cathode, solid electrolyte, and an anode using vacuum-based technologies such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). The TFB was first introduced by Hitachi of Japan, comprising Li/Li_{3.6}Si_{0.6}P_{0.6}O₄/TiS₂ and fabricated by using a combination of sputtering and CVD, in 1982 and was also developed by NTT (Japan) and Eveready (U.S.A.).¹⁻³⁾ A disadvantage of these TFBs was that the thickness of cathode film was small, and the solid electrolyte exhibited the low ionic conductivity and the poor stability, resulting in a relatively low discharge capacity of a few microamperes. Therefore, they were not widely used and this resulted in a stagnant period for the TFBs. However, Lipon (lithium phosphorous oxynitride) solid electrolyte developed by the Oak Ridge National Laboratory has enabled the expansion of the application area of the TFBs to commercial purposes due to its high ionic conductivity, a wide temperature range, a large stability window, and an especially good stability with air or lithium metal anode.⁴⁻⁶⁾ Nevertheless, there still remains the drawback of their insufficient capacity to drive miniaturized electronic devices. One of the possible methods to increase their capacity is to increase the cathode

thickness through a long deposition time; however it is usually difficult to control the residual stress of the film that causes the peeling-off of transition metal oxide and the underlying films during the post annealing process. Therefore, the cathode film is often not able to be annealed sufficiently, and it can also cause the decrease of rate capabilities. Another possible method is using a parallel or series connection of the stacked cells in a substrate.⁷⁾ Otherwise, it is considered to connect the cells in parallel using each TFBs, but it needs very thin substrate to maintain high energy density.⁸⁾ An additional method is to increase the surface area of the substrate using substrates with three dimensionally (3D) designed structures.⁹⁻¹¹⁾ The TFB system using the 3D structured substrate can considerably increase the capacity as well as power density, but it limits the success of battery fabrication due to the difficulty in conformal deposition of the battery materials, especially when it has a high aspect ratio. Thus, in order to obtain a uniform step coverage, it usually needs high cost equipments such as a CVD system using toxic precursor gases. It is regarded that wet etching is relatively simple and isotropic as compared to dry etching processes using plasma techniques. Although the wet etching process can not give the extremely increased surface area, a relatively smooth trenched surface structure with a low aspect ratio can be formed on the substrate; thus, it is possible to obtain the uniform thin film coverage on the etched surface by simple PVD processes. In this research, an all-solid-state Li/Lipon/LiCoO₂ cell was fabricated using a wet etched Ti sheet metal substrate in order to evaluate the feasibility of PVD method for TFB on 3-D surface and the effect of substrate etching on the TFB performance.

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2. Experimental

A Ti metal sheet (50 μm in thickness) was prepared as a substrate for the TFB because it usually allows good adhesion to thin films. For a uniform etching pattern, a photolithographic process was used. As shown in Fig. 1, a photoresist (PR, AZ-1512, Clariant) of approximately 3 microns was spin-coated and soft-baked for 10 min at 115°C. A photo-mask, with 20 μm \times 20 μm square checker patterns was aligned on the substrate. After UV exposure, the PR coated substrate was developed for 5 min and hard-baked for 30 min at 115°C. The titanium substrate was wet etched using a Ti etchant (TFTN, Transene) for 90 s at 80°C. The residual PR coating layer was stripped using acetone for 5 min and the wet-etched substrate was rinsed by DI water. To evaluate the cell performance, an all-solid-state Li/Lipon/LiCoO₂ structured cell was fabricated in situ using vacuum chambers. On the wet etched Ti substrate that was punched to a diameter of approximately 5 mm, Ti (20 nm)/Co (30 nm)/Pt (200 nm) were consecutively deposited in a DC sputtering chamber wherein platinum functions as a current collector, and the Ti and Co thin films function not only as an adhesive layer between the current collector and the substrate but also as a conductive layer. For the deposition of the LiCoO₂

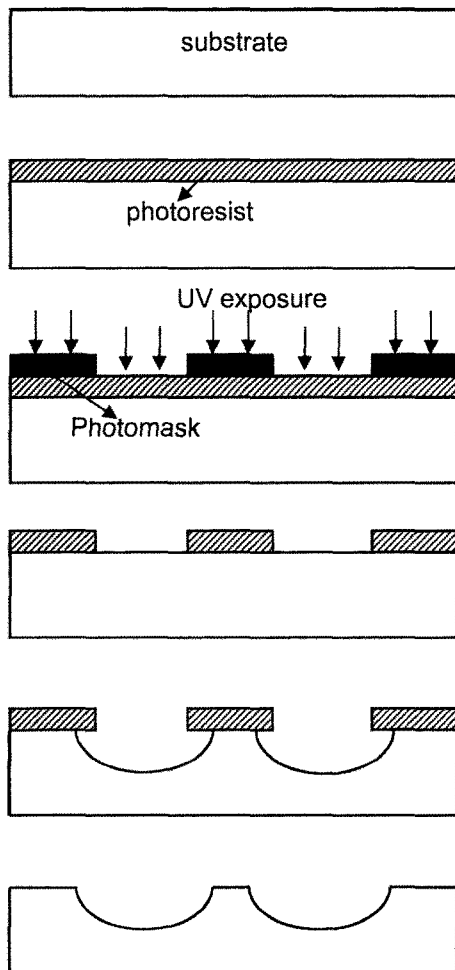


Fig. 1. Preparation of substrate by photolithography and wet etching.

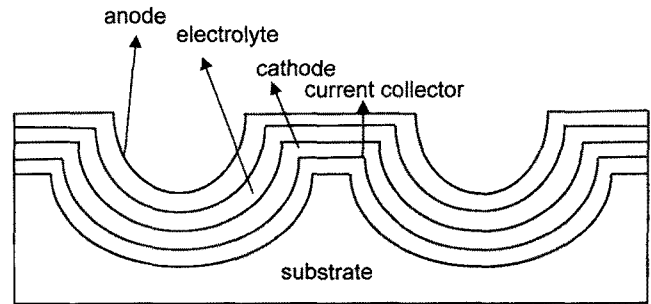


Fig. 2. Schematic cross sectional illustration of TFB using wet etched substrate.

thin film (thickness of 3 μm), a round sintered target of LiCoO₂ was radio frequency (RF) magnetron sputtered with a power density of 3.5 Wcm^{-2} . Prior to the deposition, the vacuum chamber was evacuated to 6.7×10^{-4} Pa. Argon gas (purity 5N) was used as the process gas, and the deposition rate was maintained at 30 nm/min. The resulting LiCoO₂ thin film was heat treated using a rapid thermal annealing (RTA) system installed in a vacuum chamber. Before the heat treatment, a vacuum was initially maintained, and then argon was purged to atmospheric pressure. The temperature was maintained at 650°C for the crystallization of LiCoO₂ during the annealing. The ramping rate of temperature was adjusted in order to restrict the entire process time to within 30 min. On the cathode layer, Lipon (lithium phosphorous oxynitride, thickness: 1.5 μm) and lithium (thickness: 2.0 μm) were employed as the solid electrolyte and the anode, respectively. Lipon was deposited by RF reactive sputtering under pure nitrogen plasma with a Li₃PO₄ sputtering target. For the lithium deposition, a thermal evaporator was utilized in a dry room (dew point: -60°C), and the deposited film had a surface area of 12.56 mm² in a bare substrate. A schematic illustration of the TFB with the wet etched substrate is shown in Fig. 2. The surface characteristics were observed by scanning electron microscopy (SEM, Inspect F, FEI) to observe the effects of wet etching, and the composition depth profile of the LiCoO₂ films was measured by auger electron spectroscopy (AES, PHI-670, Perkin-Elmer). Further, the crystallinity of the LiCoO₂ thin films was analyzed with an X-ray diffractometer (XRD, RINT/DMAS-2500, Rigaku) using Cu K α radiation, and the charge-discharge test was performed by a battery cyler (WBCS3000, Won-A Tech). All the experiments were conducted in a dry room.

3. Results and Discussion

It is well known that the wet etching process results in an isotropic and a relatively simple but a low aspect ratio. As shown in the SEM images of Fig. 3, a bare Ti sheet Fig. 3(a) was etched to form hemisphere-shaped wells with a 40 μm diameter and 15 μm depth Fig. 3(b). When a LiCoO₂ film of 3 μm thickness was deposited to on the wet etched substrate and RTA processed at 650°C, the cathode material covered the entire surface of the inner wall and bottom of the well, as shown by Fig. 3(c). A scaled-up image Fig. 3(d) reveals that submicron sized grains composed of LiCoO₂ were well developed on the inner wall of the well following the RTA process. Fig. 4 shows the XRD

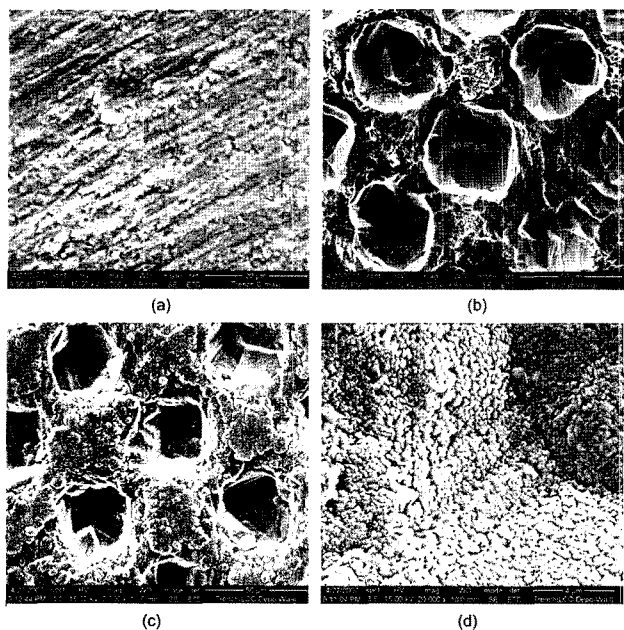


Fig. 3. Scanning electron microscope images of (a) bare titanium surface, (b) wet etched Ti surface, (c) surface after LiCoO₂ deposition, and (d) surface of wall covered by LiCoO₂ after annealing.

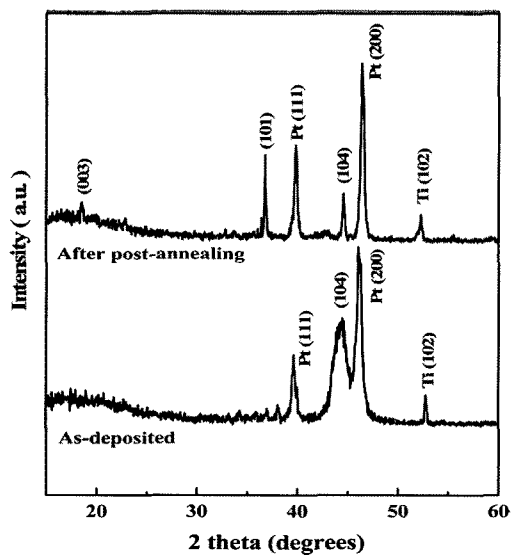


Fig. 4. XRD patterns of LiCoO₂/Pt/Co/Ti on Ti substrate before and after RTA.

patterns of these films on the Ti substrates before and after annealing. It can be observed that the LiCoO₂ film exhibiting diffraction peaks similar to the typical diffraction peaks of a hexagonal R-3m structure was well crystallized through the post annealing process, especially exhibiting the (101) preferred orientation, as reported elsewhere.¹²⁾ Considering that the hemisphere-shaped wells were uniformly formed on the Ti sheet with checker pattern, it can be estimated by a simple calculation that its surface area might be increased by 39% as compared to that of the bare substrate. The discharge capacity of the cell on the etched substrate was measured and compared with that of the cell on bare one. As shown in Fig. 5, the discharge capacity of the

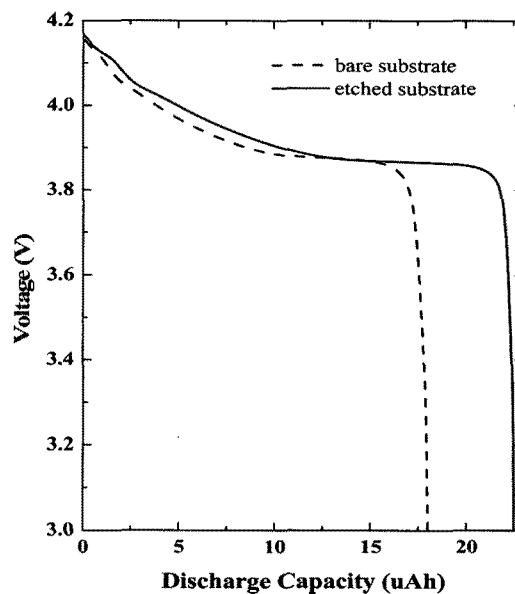


Fig. 5. Discharge capacity of bare substrate and wet etched substrate.

TFB fabricated on the etched substrate was increased to 22.5 μAh , while that of the cell with the bare substrate was 18 μAh , when a constant current of 20 μA was applied within a range of 4.2~3.0 V. Although only about 70% of the theoretical discharge capacity (ca. 69 $\mu\text{Ahcm}^{-2}\mu\text{m}^{-1}$) could be achieved with the cell on the bare substrate, which probably caused by nonstoichiometry deviated from LiCoO₂ or small loss of active materials by the Ti metal diffusion into LiCoO₂ thin film in the interface region during heat treatment as shown in Fig. 6, it was proved that the discharge capacity of the cell

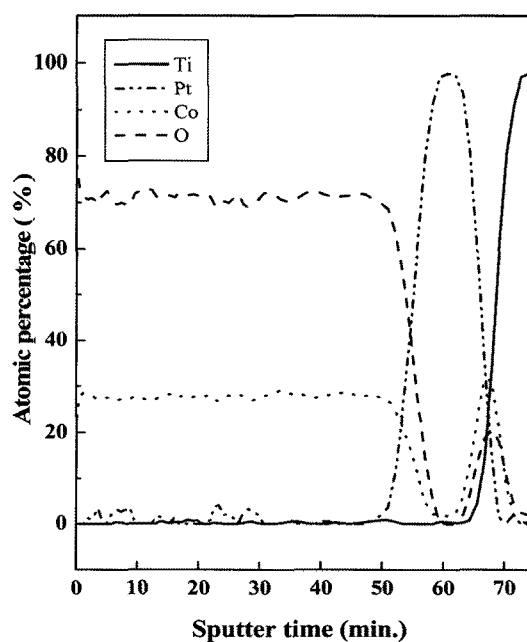


Fig. 6. Depth profile of LiCoO₂/Pt/Co/Ti by Auger electron spectroscopy after RTA process.

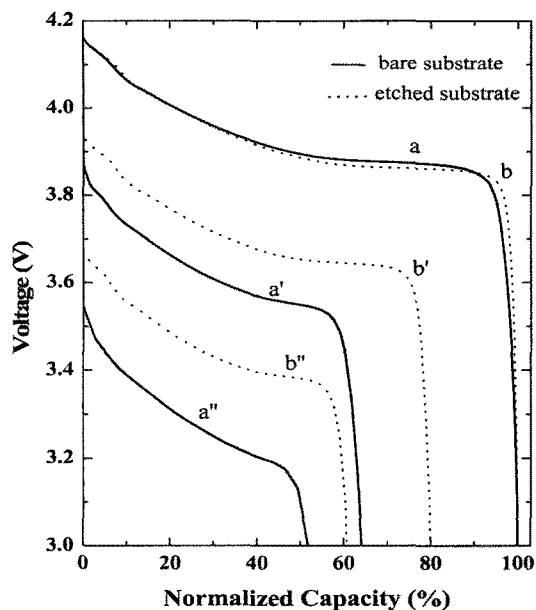


Fig. 7. High rate discharge performances of bare substrate and wet etched substrate.

on the etched substrate was increased by 25% under identical deposition and heat treatment conditions. The lack of the discharge capacity compared with the expected value for the increased surface area seems to be due to the non-uniform thickness of LiCoO_2 thin film on the position of the substrate, top, bottom and wall of wells, respectively and the imperfect coverage of Lipon on the whole surface of LiCoO_2 as well. High rate discharge performances of the cell on the etched substrate were also evaluated and compared with those of the cells on the bare substrate. The ratio of the discharge capacity of the cells with different discharge currents to the discharge capacity of the cells at a constant current of $20 \mu\text{A}$ suggests that the cell on the etched

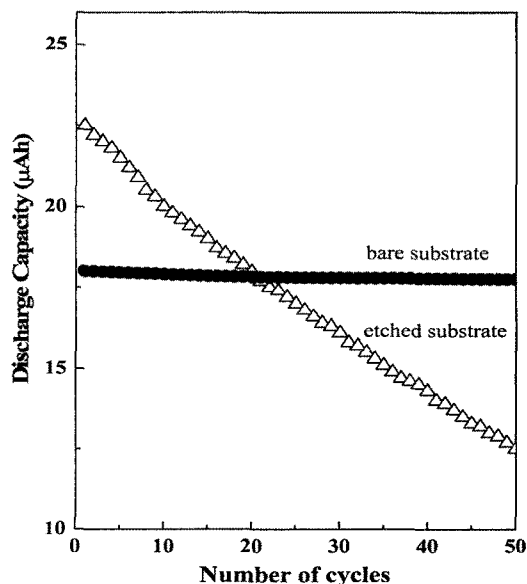


Fig. 8. Cycling behaviors of cells with bare substrate and wet etched substrate.

substrate demonstrated 80% of the initial discharge capacity at a discharge current of $200 \mu\text{A}$ and more than 60% of the initial discharge capacity even with a discharge current of $400 \mu\text{A}$, as shown in Fig. 7 (b-b'-b''). However, only 64% and 52% of the initial discharge capacity could be achieved in the cell on the bare substrate under identical discharge conditions Fig. 7 (a-a'-a''). When the internal resistance of the cells was calculated using Ohm's law ($R = \Delta V / \Delta I$), it was observed that the resistance decreased from 1,670 ohm for the cell on the bare substrate to 1,253 ohm for the cell on the etched substrate, corresponding to a 25% reduction, and this appears to agree well with the result shown in Fig. 5. Therefore, it can be concluded that the increased surface area is advantageous for the high rate discharge capabilities. Fig. 8 compares the charge-discharge cycling behavior of the cells prepared with different substrates in the cut-off range of 4.2 to 3.0 V when a constant current of $20 \mu\text{A}$ was applied. Although the initial discharge capacity of the cell on the etched substrate was higher than that of the cell on bare one, it demonstrated larger capacity decay during cycling. The discharge capacity of the cell on the etched substrate decreased continuously to $12.5 \mu\text{Ah}$ in 50 cycles, while the cell on the bare substrate demonstrated a stable cycling performance. It is estimated that the poor cycling performance was caused by microcracks during charge/discharge, the uneven surface of the substrate or a poor surface coverage of Lipon inside the wells. However, it may be possible to improve the performance by changing the substrate or controlling the surface roughness, etching conditions, deposition conditions, and pattern designs etc. The swing motion of the substrate placed on a stage can also be effective in the uniform step coverage of the thin films.

4. Conclusions

An all-solid-state TFB was successfully fabricated onto a wet etched Ti substrate using conventional PVD techniques. As the substrate was patterned by a photo-etching process, hemisphere-shaped wells with $40 \mu\text{m}$ diameter were uniformly formed on the Ti metal sheet. As the surface area increased, the discharge capacity of the etched substrate increased by 25% of that of the cell on bare one, when a constant current was applied in a range of 4.2~3.0 V; the internal resistance of the cell also decreased to the same value, resulting in a high rate discharge capability. However, the discharge capacity of the cell on the wet etched substrate decreased continuously, while the cell on the bare substrate exhibited a stable cycling performance. It is needed to find out the thin film morphology and uniformity inside the etched wells and control them for further improvement of the stability.

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