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Effect of film stress on electrochemical properties of lithium manganese oxide thin films

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Abstract

Using radio frequency magnetron sputtering, we fabricated spinel-phase $LiMn_2O_4$ films with different thicknesses. The stress state of the 200 nm-thick films maintained the compressive stress and that of the 400 nm-thick films changed from compressive to tensile stress during annealing. During the cycle test, the amount of volume change in the 400 nm-thick films was larger than that in the 200 nm-thick films. In the case of the 400 nm-thick, micro-cracks on the surface were generated during the cycle test and this phenomenon caused the stress transition and also a harmful effect on the cycle retention of the cathode thin films.

Keywords: Thin-film stress; $LiMn_2O_4$; Post annealing; Radio frequency magnetron sputter; Microbattery

1. Introduction

The thin-film rechargeable microbattery, serving as an independent power supply in MEMS and a backup source for electronic circuits, has been given much attention [1]. Many types of the microbattery and materials have been proposed [2–4]. During cycling, neither the electrode nor the electrolyte materials should undergo a morphology change that might lead to the formation of chemically unstable, high surface area materials, even at the high rate of cycling desirable in some on-chip microbattery applications. In this work, $LiMn_2O_4$ thin films were deposited using a radio frequency magnetron sputter and the effect of film stress on its microstructure, surface morphology, and electrochemical characteristics was investigated.

2. Experimental

We deposited thin films with different thickness (200 and 400 nm) using radio frequency magnetron sputtering system. A pure and stoichoimetric $LiMn_2O_4$ power was used as a sputtering target. Pt (200 nm)/TiO_2 (20 nm)/SiO_2 (200 nm)/B-doped p-type Si(1 1 1) wafers were used as a substrate. To make the spinel-phase $LiMn_2O_4$, the as-deposited films were annealed by using the furnace at 750 °C for 120 min. The stress of thin film before and after annealing was measured by using thin-film stress measurement (Tencor). The crystal structure and the surface morphology of films were analyzed by using thin-film XRD and FESEM. Galvanostatic charge–discharge half-cell tests were performed with a constant current of 100 μA/cm^2 in the potential range from 3.8 to 4.2 V. After half-cell test, the cycled films were dipped in acetone for 10 min to remove the remaining liquid electrolyte (a solution of 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1 in volume)) and to perform XRD and FESEM measurements for the films.

3. Results and discussion

In the 200 nm-thick films, the state of stress was compressive (bent in concave) before (about −30,000 MPa) and after (about −5000 MPa) annealing. However, when the film thickness was 400 nm, the stress value transformed from the negative (about −15,000 MPa) to the nearly stress-free or the positive (bent in convex) after (about 1000 MPa) annealing. After annealing, both films were the spinel-phase $LiMn_2O_4$, which had preferred orientation of (1 1 1), with

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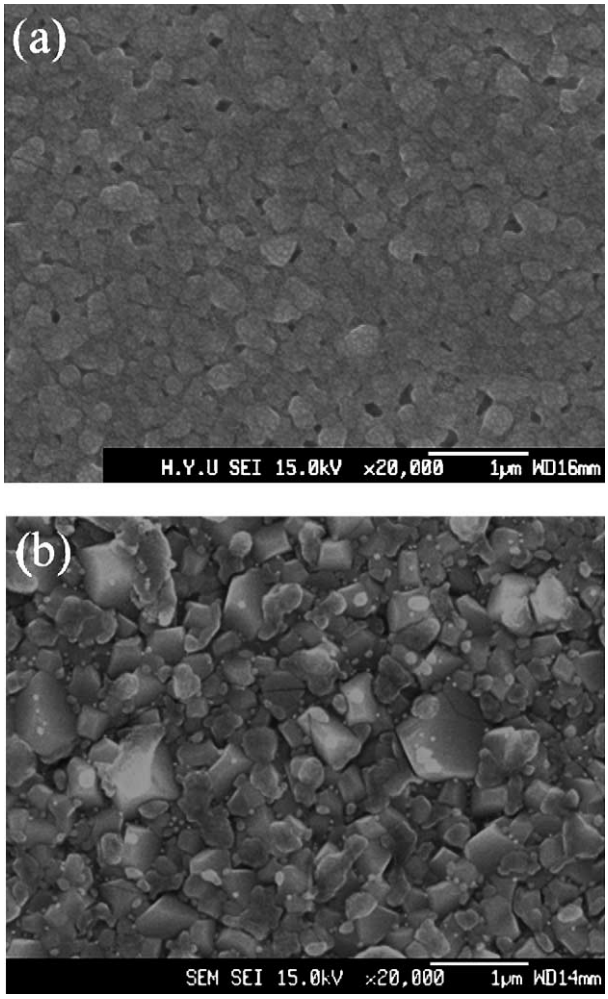

Fig. 1. FESEM images of the annealed films: (a) 200 nm-thick $LiMn_2O_4$ and (b) 400 nm-thick $LiMn_2O_4$.

some impurities such as $LiMn_5O_{12}$, Li_3MnO_4 and Li_2MnO_3. However, in comparison with the $LiMn_2O_4$ powder, the 2θ of (1 1 1) peak was shifted to larger value in the films. In the case of the powder, the 2θ of (1 1 1) peak is about 18.61° (from JCPDS No. 35-0782). The (1 1 1) peak shift of the 200 nm-thick ($2\theta = 18.70°$) film was larger than that of the 400 nm-thick film ($2\theta = 18.65°$). Assuming that the 400 nm-thick film was in nearly stress-free state, this fact implied that lattice of the thinner films was contracted by bending of the film and substrate to become concave. This result agrees with the result of stress measurement.

As shown in Fig. 1, the 200 nm-thick film had almost the same size of particles about 0.2 μm. On the contrary, the particle size of the 400 nm-thick film was larger and irregular. As the crystallinity and the particle size increased during annealing, the lattice of the deposited films expanded and the volume of films increased. In the 200 nm-thick films, this effect was not sufficient in comparison with the 400 nm-thick film, so the films still were bent in concave and had compressive stress.

The 200 nm-thick film, more compressive-stressed film, showed good cycle retention (Fig. 2). In the case of the 400 nm-thick film that might be a nearly stress-free film, that film maintained good cycleability until 30th cycle. However, over 30th cycle, the discharge capacity was reduced rapidly. When the half-cell test was over, we tried to measure the stress of the cycled films. However, the $LiMn_2O_4$ films, especially the 400 nm-thick film, were partially removed. These problems caused poor adhesion between the deposited film and substrate. So, we could not be convinced by the results of the stress measuring. Instead of the stress analysis, we analyzed the change of the film crystallity and the surface morphology of the cycled films.

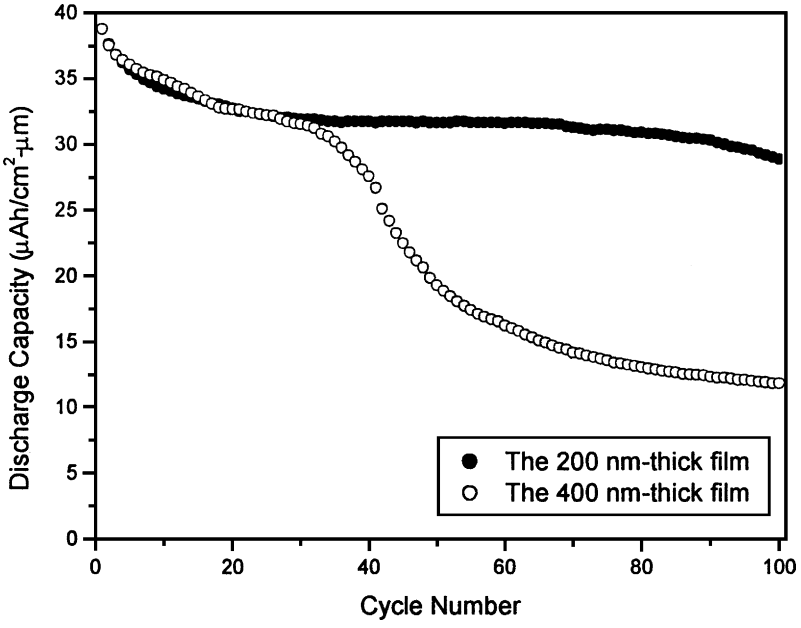

Fig. 2. Discharge capacities of the annealed films (3.8–4.2 V, 100 μA/cm^2).

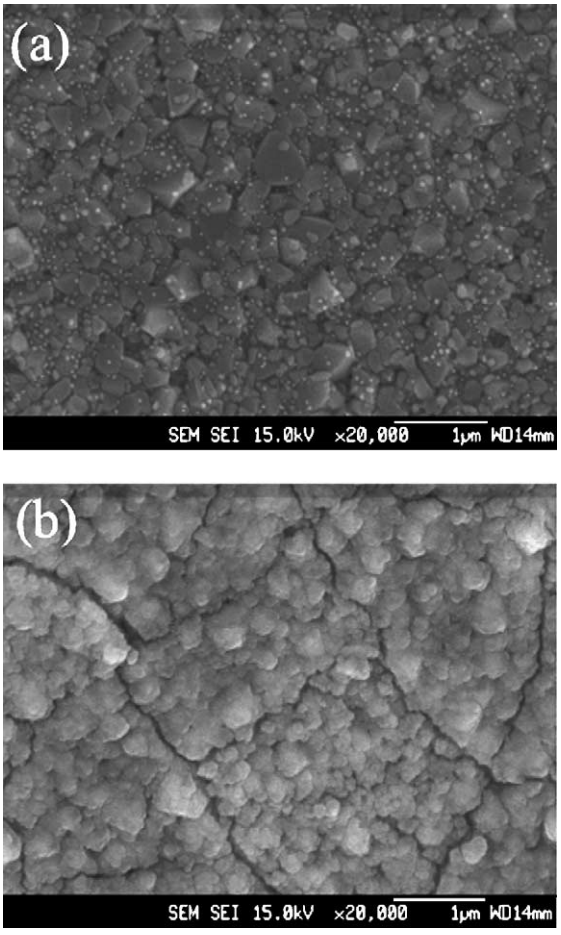

Fig. 3. FESEM images of the cycled films (100 cycles): (a) 200 nm-thick $LiMn_2O_4$ and (b) 400 nm-thick $LiMn_2O_4$.

In the case of the 400 nm-thick film, the value of 2θ of (1 1 1) peak changed from 18.65 to 18.75°. This implied that the stress of the 400 nm-thick film changed to compressive state during the half-cell test. As shown in Fig. 3, the surface morphology of the cycled 200 nm-thick film kept the morphology of uncycled state. However, micro-cracks occurred in the surfaces of the cycled 400 nm-thick films. That micro-crack caused the rapid reduction of the capacity by the harmful effect on the electrical contact with the substrate and particles.

4. Conclusion

In the thinner film, the stress state was the compressive stress before and after the annealing process. However, the stress of the thicker film changed from compressive to tensile during the annealing process. During the cycle test, a volume variation of the deposited film occurred. This phenomenon caused the stress variation of the deposited films. When the film was thicker, the amount of the volume expansion/compression was lager. Therefore, the stress-state transition occurred during the cycle test of the thicker film.

Acknowledgements

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