EFFECT OF SUBSTRATE TEMPERATURE ON THE CRYSTAL PROPERTIES OF $LiMn_2O_4$ FILMS PREPARED BY RF MAGNETRON SPUTTERING

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Abstract:

The $LiMn_2O_4$ films for Li secondary batteries have been prepared by a RF magnetron sputtering method. The $LiMn_2O_4$ powder was used as a target material. The deposition rate, XRD, and surface morphology were investigated as a function of substrate temperature (T_{sub}). It was found that the deposition rate had a peak at around the T_{sub} of 200 °C. This research was also designed for preventing the target material being oxidized during the reactive sputtering process. A quartz tube was inserted between shutter and target. It seems that the quartz tube is effective to prevent oxidation of target material.

Keywords: *$LiMn_2O_4$ thin film, RF magnetron sputtering, Li secondary batteries.*

1. Introduction

The lithium (Li) secondary batteries have been used for cell phones, video cameras, etc. The revolution of energy sources for electric vehicles has been started by using fuel cells and Li secondary batteries. These devices require the specific energy density more than 100 Wh/kg and the power density of 40 W/kg, respectively. [1]

Various materials have been used for the positive electrodes of Li secondary batteries. [1], [2] Recently, various manganese oxides have been investigated as a positive electrode material. Manganese is less-toxic and abundant material as compared with Cobalt. We have been focusing especially on the Li-Mn-O defect-spinel-structure (so called defect-spinel-structure). [3], [4] If this structure is adopted as a positive electrode, the operating voltage and theoretical capacity are 3-4 V and 148-213 mAh/kg, respectively. [3], [4]

The defect-spinel-structure is defined by Mn_3O_4, $Li_4Mn_5O_{12}$, and λ-MnO_2 triangle in the Li-Mn-O phase diagram as shown in Fig. 1. [4] Our goal is to prepare films with this structure. These defect-spinels are considered to have high structural stability upon insertion and desorption of Li ions.

The defect-spinel- structure described above could be obtained through the reaction between Li and λ-MnO_2 or Mn_3O_4. [5], [6], [16]-[23].

Figure 2 shows the manganese-spinel-structure of $LiMn_2O_4$. There are vacancies (16c) near the 8a sites. Li^+ ions can diffuse alternatively, for example, from 8a to16c and then to 8a. [7]

All of the materials for the positive electrodes have been prepared by a sintering method.[3]-[9] These powders have to be mixed with some binders and high electric conductivity materials like carbon black to apply the metal electrode. This process has complex procedures and induces thick films. This is less attractive in the point of energy density than the deposition process proposed in this paper. In order to solve these problems, various deposition methods have been introduced. [10]-[26] In our early studies, Mn_3O_4 films have been successfully prepared with preventing the oxidation of evaporant during the recative evaporation process. [16-22] But, unfortunately, charge-discharge curves could not be measured. It seems that this is due to the deficiency of Li ions move between positive and negative electrodes during charge and discharge processes.

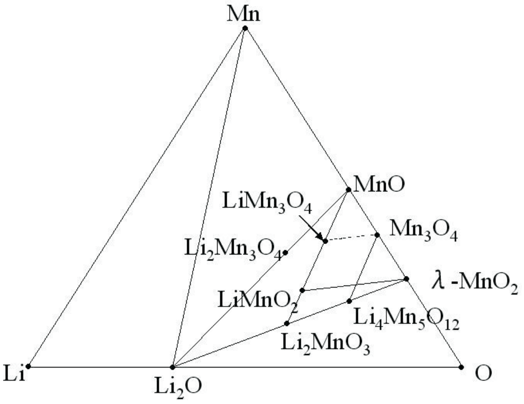

Fig. 1. Li-Mn-O phase diagram.

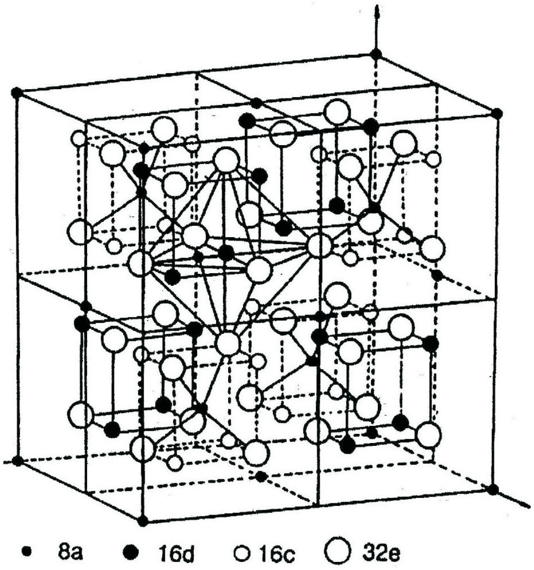

Fig. 2. Spinel structure of $LiMn_2O_4$.

In this study, a RF magnetron sputtering method was used to prepare manganese oxide films which involve Li atoms. [25]-[26] The effect of quartz tube on preventing oxidation of target material was examined. This research was also designed for preventing the target material being oxidized during the reactive sputtering process. A quartz tube was inserted between shutter and target. It was intended that a quartz tube could act to prevent the oxidation of target material during sputtering process.

The purpose of this work is to investigate the effect substrate temperature (T_{sub}) of the crystal properties of $LiMn_2O_4$ films. The effect of quartz tube on preventing the oxidation of target material was also investigated.

2. Experiment

$LiMn_2O_4$ films were prepared on 0.2 mm-thick aluminum (Al) substrates by a magnetron sputtering apparatus as shown in Fig. 3. The RF powers of 100 and 200W were used in this study. This apparatus has three targets in the vacuum chamber. So, it is easy to prepare multi-layered-devices without breaking vacuum.

The deposition condition is shown in Table 1. The deposition time and Ar flow rate were fixed at 60 min and 4sccm, respectively. The substrate temperature (T_{sub}) was varied from 150 to 300 °C.

In order to obtain crystallographic characteristics, X-ray diffraction (XRD) measurements were performed with a RIGAKU RINT Ultima II. The film thickness was measured by a gravimetric method.

3. Results and Discussion

The crystal structure of films was identified as $LiMn_2O_4$ by X-ray diffraction (XRD) method.

Figure 4 (a) an (b) show the dependence of deposition rate on the Tsub at the RF power of 100 and 200 W, respectively. At the RF power of 100 W, the deposition rate is increased as increasing the T_{sub} as shown Fig. 4(a). The deposition rate is decreased at the Tsub higher than 250°C.

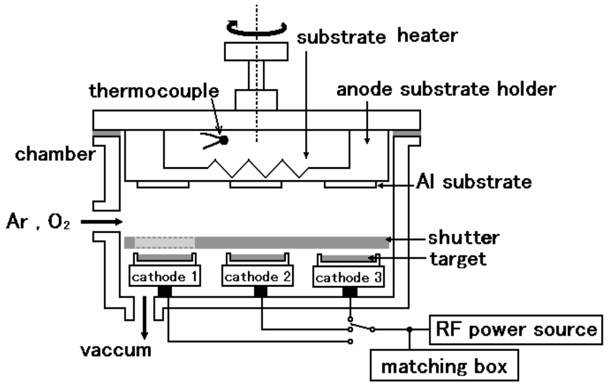

Fig. 3. Magnetron sputtering apparatus.

Table 1. Deposition condition of $LiMn_2O_4$.

vacuum [Pa]	5
deposition time [min]	60
Ar flow rate [sccm]	4
parameter: RF power [W]	100,200
parameter: T_{sub} [°C]	RT,150,200,250,300
target	$LiMn_2O_4$

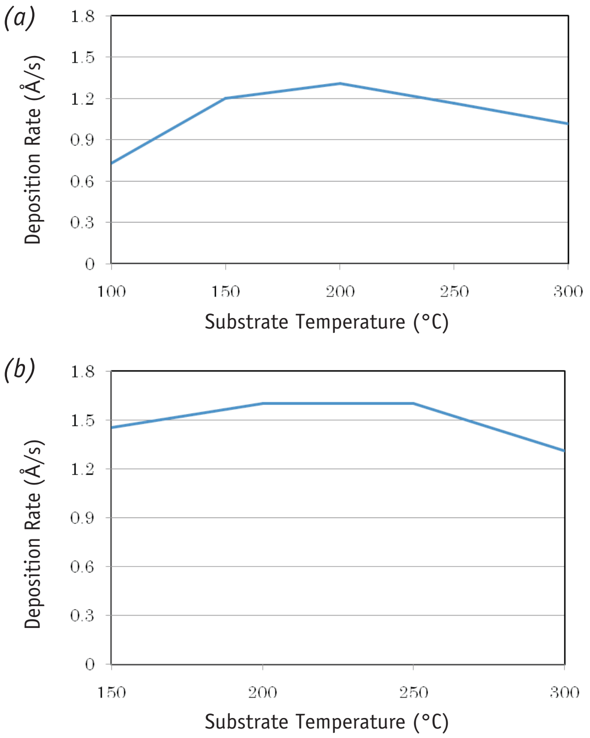

Fig. 4(a) and 4(b). Dependence of deposition rate on the substrate temperature (T_{sub}). The Ar flow rate was fixed at 4sccm.

At the RF power of 200 W, the deposition rate is increased as increasing the T_{sub} as shown Fig. 4(b). The deposition rate is decreased at the T_{sub} higher than 300°C.

Fig. 5(a) and 5(b) show the XRD data of the $LiMn_2O_4$ films prepared at the RF power of 100 and 200W, respectively.

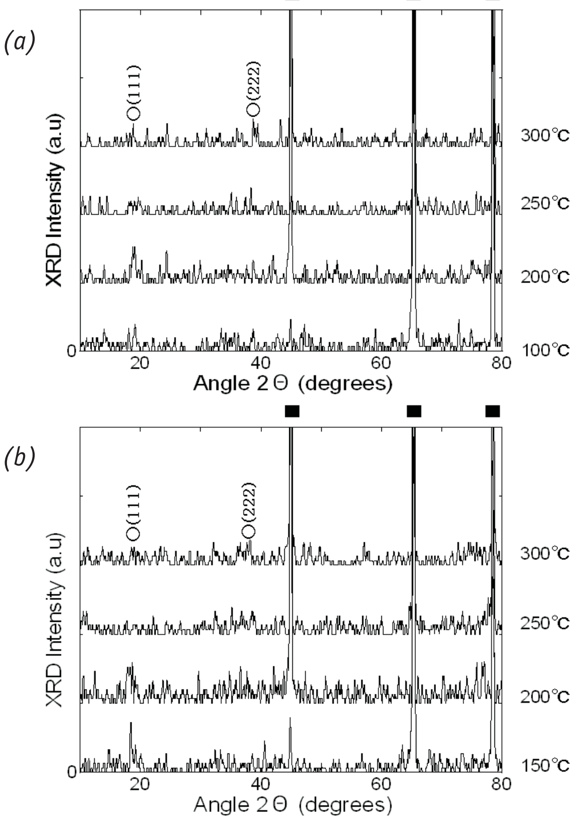

Fig. 5(a) and 5(b). The XRD data of the $LiMn_2O_4$ films prepared at the RF power of 100 and 200W, respectively The parameter is T_{sub}.

The Fig. 5(a) and (b) show that the (111) peaks were disappeared at the T_{sub} higher than 250°C. It seemed that the XRD peaks were disappeared due to the deliquescence of $LiMn_2O_4$ species during keeping films in air after deposition. They must be kept in vacuum until XRD measurements.

This research was also designed for preventing the target material being oxidized during the reactive sputtering process. [25] A quartz tube was inserted between shutter and target. Figure 6 shows the effect of the quartz tube on the deposition rate. In this case, the oxygen gas was introduced. The Ar to O_2 flow ratio was 3:1. The total flow rate was fixed at 4 sccm. The RF power was 100 W and the deposition time was varied from 30 to 90 min. The deposition rate was increased as increasing the deposition time in the case of installing the quartz tube.

It seems that the quartz tube is effective to prevent oxidation of target material. A detailed study are now in progress.

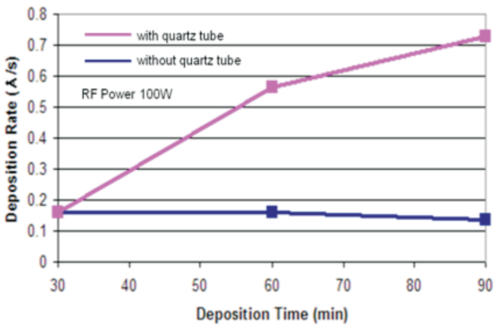

Fig. 6. The effect of the quartz tube on the deposition rate. In this case, the oxygen gas was introduced.

4. Conclusion

The $LiMn_2O_4$ films were successfully prepared by a magnetron sputtering method. A quartz tube was introduced to prevent the oxidation of target material. It was found that the deposition rate was decreased at the T_{sub} of 300°C. A quartz tube was inserted between shutter and target. It seems that the quartz tube is effective to prevent oxidation of target material.

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