Preparation of LiMn_2O_4 Films by RF Magnetron Sputtering MethodMasaaki Isai^{1,2}, Koichi Nakamura², Takayuki Hosokawa², Satoshi Sakai¹,
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Abstract Lithium-manganese oxides have been studied as a cathode material in the Li secondary batteries. Preparation of LiMn_2O_4 thin films was tried with a RF magnetron sputtering method at the substrate temperature (T_{sub}) of R.T.. This material is superior to other materials in the cost performance as well as non-toxicity. The dependence of crystal properties on the Ar flow rate was examined. In the case of 60 min deposition time, the deposition rate was not varied as varying Ar flow rate from 2 to 3.5 sccm.

Keyword Li secondary batteries, Manganese oxide films, Li-Mn-O defect-spinel-structure, RF magnetron sputtering method

1. Introduction

The lithium (Li) secondary batteries have been used for cell phone, video camera, etc. The revolution of energy sources for electric vehicles has been started by using fuel cells and Li secondary batteries. The environmental problems, for example global-warming, have been facilitating the introduction of Li secondary batteries in many applications. These devices require the specific energy density more than 100 Wh/kg and the power density of 40 W/kg. [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 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$, and $\lambda\text{-MnO}_2$ 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 $\lambda\text{-MnO}_2$ or Mn_3O_4 . [5, 6]

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 to 16c 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. [10-23] In our early studies, Mn_3O_4 films have been successfully prepared. [15-23] But, unfortunately, charge-discharge curves could not be measured. It seems that this is due to the deficiency of Li ions moving between positive and negative electrodes during charge and discharge process. This means the deficiency of Li atoms in the positive electrode (Mn_3O_4 films).

In this study, a magnetron sputtering method was introduced to prepare manganese oxide films involving Li atoms. A part of the results are shown in this article.

Fig. 1 Li-Mn-O phase diagram

Fig. 2 Spinel structure of LiMn_2O_4

2. Experiment

LiMn_2O_4 films were prepared on 0.2 mm-thick aluminum (Al) substrates by a RF magnetron sputtering method. The substrate temperature (T_{sub}) was R.T. through this study. The RF power was fixed at 100W with varying the deposition time. The crystal structure of films was identified as LiMn_2O_4 by X-ray diffraction (XRD) method.

The thickness of films was compared as a function of deposition time. The deposition condition is shown in Table 1. The total flow rate ($\text{Ar} + \text{O}_2$) was fixed at 4 sccm through this study.

Figure 3 shows a RF magnetron sputtering apparatus. This apparatus has three targets in the vacuum chamber. So, it is easy to prepare multi-layered-devices without breaking vacuum.

In order to obtain crystallographic characteristics, X-ray diffraction (XRD) measurements were performed with a RIGAKU Rotaflex 12 kW with CN2173D6 goniometer. The film thickness was measured by a gravimetric method.

Table 1 Deposition condition of LiMn_2O_4
The total flow rate ($\text{Ar} + \text{O}_2$) was fixed at 4 sccm.

parameter	values
vacuum (Pa)	5
deposition time (min)	60, 90
Ar (sccm)	1.0, 1.5, 2.0, 2.5, 3.0, 3.5
O_2 (sccm)	3.0, 2.5, 2.0, 1.5, 1.0, 0.5
RF power (W)	100

Fig. 3 Magnetron sputtering apparatus

3. Results and Discussion

Figure 4 shows the XRD peaks of the deposited films as a function of $\text{Ar} : \text{O}_2$ flow ratio. There are (111) and (222) peaks especially in the case of $\text{Ar} : \text{O}_2$ flow ratio of 3.5 : 0.5 sccm. They show that these films are constructed with LiMn_2O_4 .

Figure 5 shows the dependence of deposition rate on the Ar flow rate. The deposition time was fixed at 60 min. It was found that the deposition rate was not varied as varying Ar flow rate from 2 to 3.5 sccm.

Figure 6 also shows the dependence of deposition rate on the Ar flow rate. In this case, the deposition time was fixed at 90 min. It was found that the deposition rate was gradually decreased as increasing the Ar flow rate. The deposition rates were slightly smaller than those of 60 min deposition time.

Figure 7 shows the dependence of deposition rate on the deposition time. These films were sequentially deposited with varying deposition time from, 30 to 90 minutes without breaking vacuum. The $\text{Ar} : \text{O}_2$ flow ratio was fixed at 2.5 : 1.5 sccm. It was found that the deposition rate was gradually decreased as increasing the deposition time. It seems to be due to the degradation of target material (LiMn_2O_4). The color of target surface was changed from black to brownish-colors after deposition process. It was noticed that the target surface has changed in composition just after the first deposition run. It seems that the deviation from stoichiometry is occurred because of the desorption of oxygen contents from the target surface.

Fig. 4 XRD patterns of deposited films as a function of $\text{Ar} : \text{O}_2$ flow ratio. The total flow rate ($\text{Ar} + \text{O}_2$) was fixed at 4 sccm.

Fig. 5 The dependence of deposition rate on the Ar flow rate. The deposition time was fixed at 60 min.

Fig. 6 The dependence of deposition rate on the Ar flow rate. The deposition time was fixed at 90 min.

Fig. 7 The dependence of deposition rate on the deposition time. The Ar : O₂ flow ratio was fixed at 2.5 : 1.5 sccm.

In the case of 60 min deposition time, the deposition rate was not varied as increasing the Ar flow rate from 2 to 3.5 sccm as shown in Fig. 3. In the case of 90 min deposition time, the deposition rate was gradually decreased as increasing Ar flow rate as shown in Fig. 4. It seems that this is due to the degradation of target material. The degradation means the deviation in composition from the stoichiometric ratio of LiMn₂O₄. Some oxygen contents tend to desorb from the target surface. The total flow rate of Ar + O₂ was fixed at 4 sccm through this study. So, the increase of Ar flow rate means the decrease of O₂ flow rate. In this situation, it means that the deviation from stoichiometry is facilitated as increasing the Ar flow rate. There is still some ambiguity to explain the relationship between the deposition rate and Ar flow rate.

For 90 min deposition time, The surface of target material was severely deteriorated as compared with the case of 60 min deposition time. The oxidation of target surface during sputtering process was not so proceeded that the deposition rate was not steeply decreased in the 60 min deposition time.

In this study, LiMn₂O₄ was used as a target material. There are many other manganese oxides, for example LiMnO₂, Li₂MnO₃, LiMnO₄. A possibility of deviation from stoichiometry of target material after deposition runs has to be considered. There is an idea which could overcome such a problem. The composition on the target surface could be maintained by using a reactive sputtering. The stoichiometry of films would be maintained by optimizing the Ar to O₂ flow ratio. The investigation of stoichiometry will be the subject of future study.

4. Conclusion

It was found that the LiMn₂O₄ films were successfully prepared by a magnetron sputtering method at T_{sub} of R.T. These films could be prepared even varying the Ar : O₂ flow ratio with keeping the total flow rate at 4 sccm. In the case Ar : O₂ flow ratio of 3.5:0.5 sccm, these films have (111) and (222) peaks as well as (311).

The dependence of deposition rate on the Ar flow rate was examined. In the case of 60 min deposition time, the deposition rate was not varied as increasing Ar flow rate from 2 to 3.5 sccm.

In the case of 90 min deposition time, the deposition rate was gradually decreased as increasing the Ar flow rate.

The dependence of deposition rate on deposition time was investigated. The Ar flow rate was fixed at 2.5 sccm. It was found that the deposition rate was gradually decreased as increasing the deposition time. The degradation of target material (LiMn₂O₄) seems to be responsible for this phenomenon.

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