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Preparation of $LiMn_2O_4$ films by sputtering method

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Abstract Manganese oxides have been studied as a cathode material in the Li secondary batteries. Preparation of $LiMn_2O_4$thin films were tried with a sputtering method. This material is superior to other materials in the cost performance as well as non-toxicity. The crystal properties were improved after an annealing process. The preparation procedure is introduced through this study.

Keyword Li secondary batteries, Manganese oxide films, Li-Mn-O defect-spinel-structure, Sputtering method, Rapid thermal annealing

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 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, $Li_4Mn_5O_{12}$, 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. [10-23] 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.

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

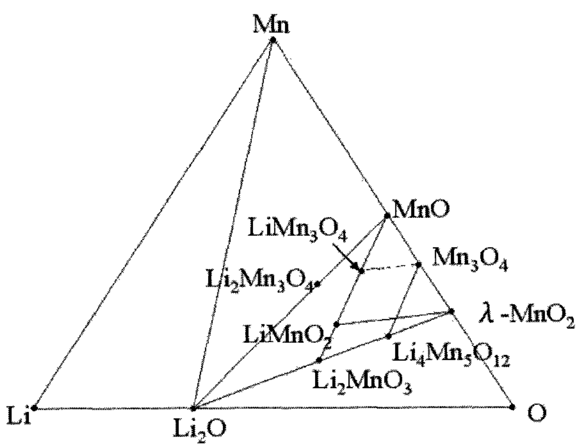

Fig. 1 Li-Mn-O phase diagram

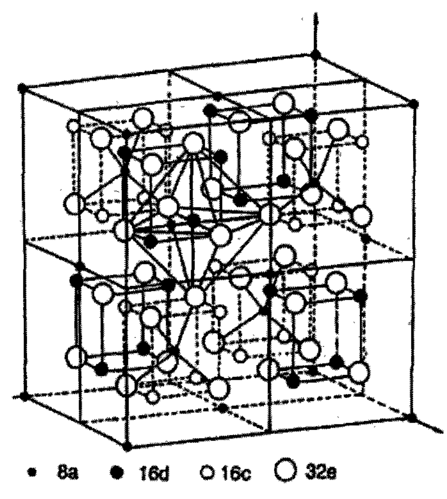

Fig. 2 Spinel structure of $LiMn_2O_4$

2. Experiment

$LiMn_2O_4$ films were prepared on 0.2 mm-thick aluminum (Al) substrates by a magnetron sputtering method. 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 time.

effect on the crystal structure was examined.

Figure 3 shows a 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 an optical method (interference fringes) and gravimetric method.

Table 1 Deposition condition of $LiMn_2O_4$

vacuum pressure [Pa]	4-6
RF power [W]	100
Ar flow rate [sccm]	4
parameter : deposition time [min]	30,60,90
target	$LiMn_2O_4$

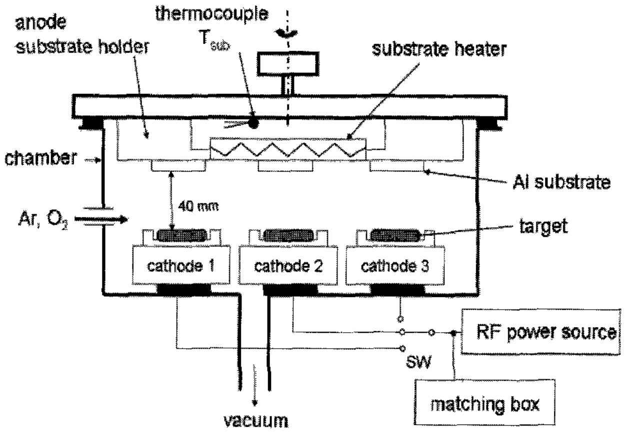

Fig. 3 Magnetron sputtering apparatus

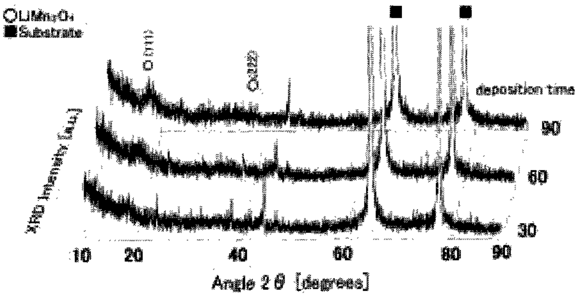

Fig. 4 XRD patterns of deposited films as a function of deposition time

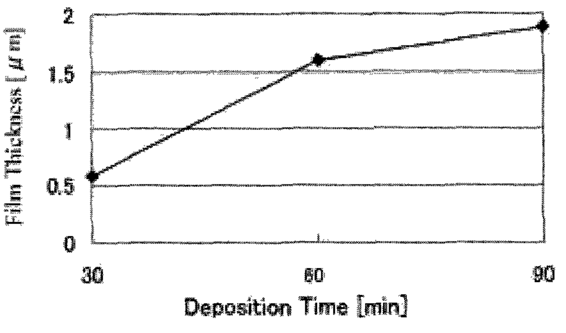

Fig. 5 Dependence of film thickness on deposition time

3. Results and Discussion

Figure 4 shows XRD peaks of the deposited films as a function of deposition time. There are (111) and (222) peaks. They show that these films are constructed with $LiMn_2O_4$.

Figure 5 shows the dependence of film thickness on deposition time. From this result, it is found that the thickness is increased as increasing the deposition time. But, the thickness is gradually saturated after 60-minute deposition time. It seemed due to the degradation of target material ($LiMn_2O_4$). The films were sequentially deposited with varying deposition time from, 30, 60, and 90 minutes without breaking vacuum. The color of target surface was changed from black to brownish-colors after deposition process. It was noticed that the target surface has changed just after the first deposition run.

Annealing Effect

The annealing condition is shown in Table 2. The films for annealing process were deposited at 100W for 60 minutes under Ar atmosphere. The annealing was controlled as a function of annealing time. The annealing time was varied as 1, 2, 5 and 10 minutes. The annealing temperature was fixed at 400℃. It was found that the crystallinity of films was improved after the annealing process.

Table 2 Annealing condition of $LiMn_2O_4$ films

annealing temperature [℃]	400
parameter : annealing time [min]	1,2,5,10

Figure 6 shows the XRD data of annealed films as varying the annealing time. A datum of un-annealed film is also shown for comparison. The strength of (111) peaks for all samples was increased after annealing process. It was recognized that the crystallinity of films was improved after annealing process.

Figure 7 shows the dependence of XRD intensity on the annealing time. The XRD intensity was gradually increased as increasing the annealing time. But, it saturates after 5-minute annealing time.

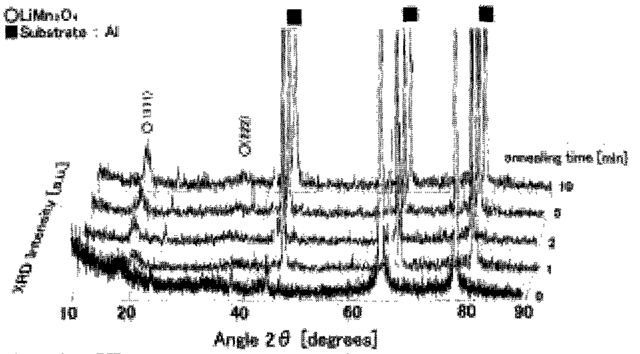

Fig. 6 XRD patterns of annealed films as a function of annealing time

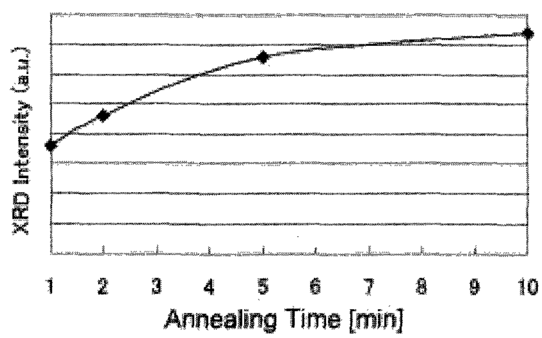

Fig. 7 Dependence of XRD intensity on the annealing time

It seemed that a degradation of films, for example, decreasing of film-thickness after re-evaporation of films and variation of composition were happened during annealing process. It is difficult to conclude whether the annealing time should be long or not. An optimum annealing condition will be studied after investigating the composition of annealed films.

In this study, $LiMn_2O_4$ was used as a target material. There are many other manganese oxide, for example $LiMnO_2$, Li_2MnO_3, $LiMnO_4$. A possibility of deviation from stoichiometry of target material after deposition runs has to be considered. There is some ideas which could overcome such a problem. The composition on the target surface could be maintained by using a reactive sputtering. The stoichiometry of films could be maintained by optimizing the flow rate of Ar to O_2. The investigation of stoichiometry will be the subject of future study.

4. Conclusion

It was found that the $LiMn_2O_4$ films were successfully prepared by a magnetron sputtering method. The dependence of film thickness on deposition time was investigated. It was found that the thickness of films was increased by increasing the deposition time. But, the thickness is gradually saturated after 60-minute deposition time. The degradation of target material ($LiMn_2O_4$) seems to be responsible for the crystallinity of films.

The dependence of annealing effect on annealing time was investigated. It was found that the crystallinity of films was improved after theannealing process. An optimum annealing condition has to be studied after investigating the composition of annealed films.

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