

EFFECT OF THE DISTANCE BETWEEN CRUCIBLE TOP AND SUBSTRATE ON THE REACTIVELY EVAPORATED Mn OXIDE FILMS

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Manganese (Mn) oxide films for lithium secondary batteries were prepared using reactive evaporation method. The film properties depend on the oxygen flow rate, Mn deposition rate, and substrate temperature. The oxygen flow rate was fixed at 5 sccm through this study. The substrate temperature was not controlled in this study. The Mn vapor is oxidized during the evaporation process as well as on the substrate surface. So, the film composition would depend on the distance between crucible top and substrate. The variation of distance gives rise to the variations of substrate temperature and of deposition rate of oxide films. It was found that Mn_3O_4 films with a Hausmannite structure could be prepared under the condition of Mn deposition rate of 3~10 Å/sec. The hierarchy of the Mn deposition rate was recognized in the parameters governing the film properties. It is most important to maintain the value of the Mn deposition for the range of 3~10 Å/sec.

KEYWORDS: manganese oxide films, Hausmannite structure, reactive evaporation, vacuum deposition, lithium secondary batteries

I. INTRODUCTION

People are willing to purchase small sized and hybrid vehicles in these days. It is due to the revolution of people's mind after suffering big waves of oil crises over the last three decades. The power sources recently focused are lithium secondary batteries, fuel cells and so on.^{1,2} A tight race in the development of power sources has long been continued. A combination of manganese (Mn) oxide and lithium (Li) was focused in this study as the positive and negative electrodes, respectively. Mn oxide with spinel structure is one of the best materials for the positive electrode in the Li secondary batteries.³ Our goal is to prepare Mn spinel (λ - MnO_2) films.⁴⁻⁶ They have generally a high structural stability upon lithiation. Mn is more abundant and less expensive than cobalt (Co), so that the overall cost would be minimized if $LiMn_2O_4$ is used as the positive electrode. Toxicity (if any) or recycling are already well known. The operating voltage of 3~5V could be obtained with this material.

Almost all the oxide materials for positive electrode are prepared by the sintering method.⁴⁻¹⁶ They have inferior of electric conductivity to the metal electrode. So we focused on the thin film technology, so called Hotwall epitaxy, to improve the electric conductivity. Mn oxide films were prepared by using reactive evaporation method.¹⁷⁻²⁷ The Mn_3O_4 films with spinel structure have been successfully prepared on a stainless steel substrate in our early works.^{24,26,27} They are so called Hausmannite. λ - MnO_2 and Hausmannite have fortunately the same spinel structures except the latter has a slightly distorted spinel structure. It means that they would have similar properties through

lithiation. One of the problems is that the Mn evaporant suffers oxidation from oxygen atmosphere during the reactive evaporation process. A separator was introduced in the bottom of the Mn crucible.^{26,27} The oxidation of the Mn evaporant was successfully prevented by this method.

The crystallinity and composition of Mn oxide films are governed by the oxygen (O_2) flow rate, Mn deposition rate, and substrate temperature (T_{sub}). The O_2 flow rate was fixed at 5 sccm through this study. The T_{sub} was not controlled in this study. The Mn vapor is oxidized during the flight to the substrate surface as well as on the substrate surface. So, the oxidation rate would depend on the distance between crucible top and substrate. The variation of distance gives rise to the variations of T_{sub} and of the Mn deposition rate. It was found that the Mn deposition rate has a close correlation with the distance.

The purpose of the present work is to investigate the effect of the distance between crucible top and substrate on the film properties.

II. EXPERIMENT

The deposition apparatus is shown in Fig. 1 (a). Mn was evaporated in the O_2 atmosphere. The O_2 flow rate was controlled by a mass flow controller. The O_2 flow rate was fixed at 5 sccm through this study. Mn oxide film was deposited on a stainless steel substrate by Hotwall epitaxy. The Mn evaporant in the stainless steel crucible was resistively heated. The substrate holder shown in Fig. 1(b) involves a mechanism of varying the distance between crucible top and substrate. Five films can be prepared

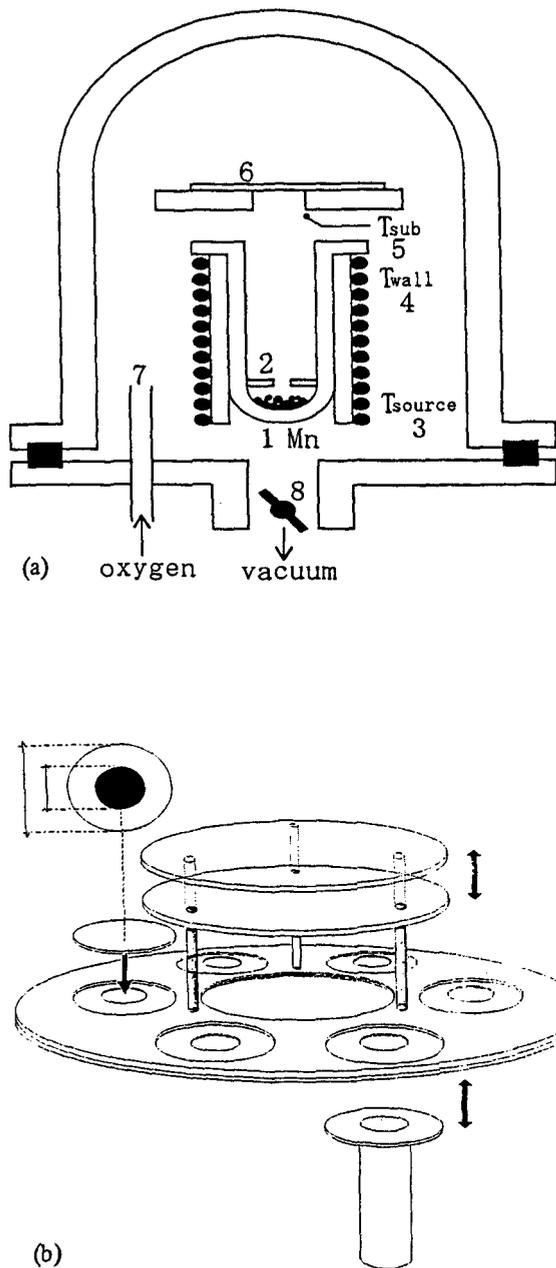


Fig. 1(a). Schematic of the apparatus. 1: Stainless steel crucible for Mn evaporation. 2: A molybdenum (Mo) sheet with a hole is settled in the bottom of the crucible. This sheet is called as a separator in the text. 3: W wire heater for Mn evaporant. The temperature of this area is shown as T_{source} . 4: W wire heater for wall area. The temperature of this area is shown as T_{wall} . 5: Substrate temperature is measured at the substrate surface. It is shown as T_{sub} . 6: Stainless steel substrate. 7: O_2 inlet. 8: Main valve to control the O_2 atmosphere. (b) Schematic of the substrate holder. The distance between crucible top and substrate surface. This distance is called as a height in the following figures.

without breaking a vacuum. The distance will be called as a height in the following figures. Mn crucible has a separator which keeps Mn evaporant off the oxygen atoms.^{26,27} The temperatures of source (T_{source}) and wall areas (T_{wall}) in the crucible were fixed at 950~960 and 900 °C, respectively.

In order to obtain crystallographic information, x-ray diffraction (XRD) measurements for some samples were performed on a RIGAKU Rotaflex 12kW system with a CN2173D6 goniometer. The film thickness was measured by the optical method (interference fringes) and gravimetric method. The micro-interferometer (Olympus) was used.

III. RESULTS AND DISCUSSION

Figure 2 shows the dependence of Mn deposition rate on the deposition run. The T_{source} and T_{wall} of the crucible were kept at 950~960 and 900 °C, respectively. It was shown that Mn deposition rate decreased with increasing the deposition run. The Mn deposition rate increased with decreasing the distance between crucible and substrate. At the first set of runs (from the first to fifth runs), the T_{source} was set at 950 °C. Then, the T_{source} was intentionally increased 10 °C at the second set of runs (after the sixth run). It is due to intend the retrieval of Mn deposition rate of more than 3 Å/sec since it decreases below 3 Å/sec at the fifth deposition run. So, the deposition rate at the seventh run was slightly increased.

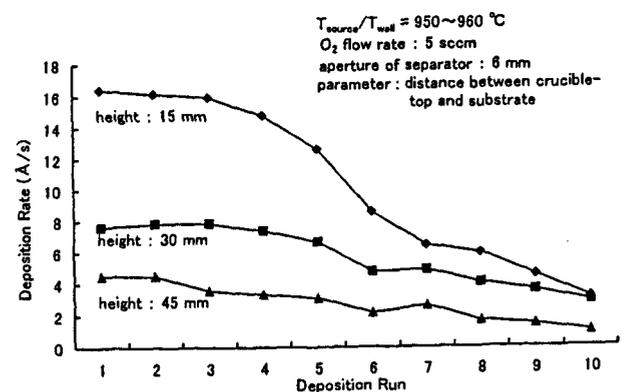


Fig. 2 (a) Dependence of Mn deposition rate on the deposition run.

Figure 3 (a) shows the dependence of relative height of XRD peaks on the deposition run. In this case, the distance between crucible and substrate is 15 mm. The constituent of Mn_3O_4 is evolved (emerged) spontaneously after the eighth deposition run.

Figure 3 (b) shows the dependence of XRD peak height on the deposition run. The distance between crucible and substrate is also 15 mm. The constituent of films is almost

all MnO before the seventh run. It means that the constituent of films varied with increasing the deposition run. At first the constituent of MnO is predominant, after that it is substituted by the Mn₃O₄ structure.

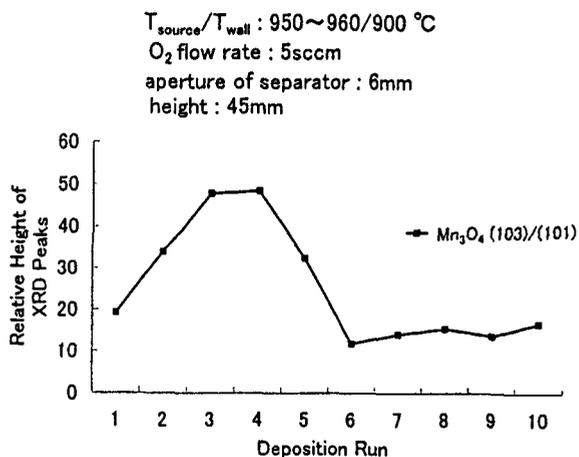
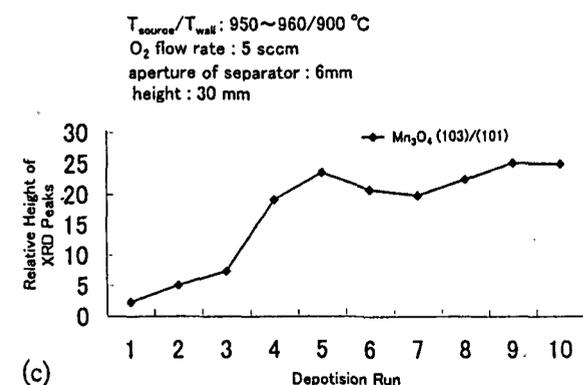
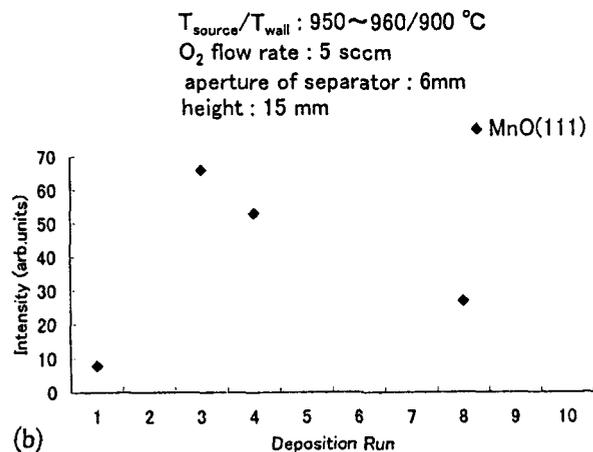
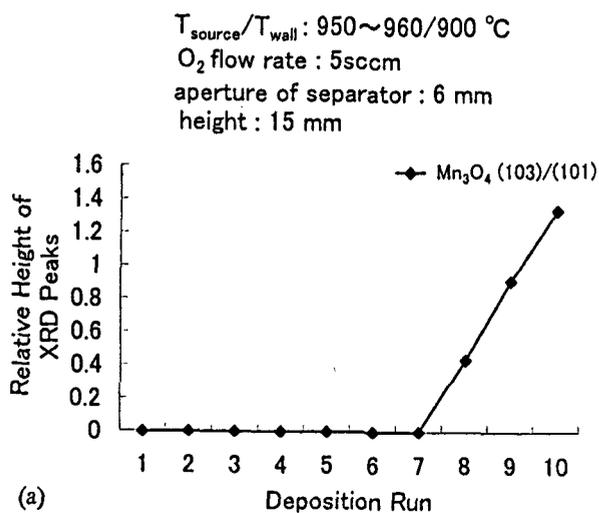


Fig. 3(a) Dependence of relative height of XRD peaks on the deposition run. In this case, the distance between crucible and substrate is 15 mm. (b) Dependence of XRD peak height on the deposition run. The distance between crucible and substrate is also 15 mm. (c) Dependence of relative height of XRD peaks on the deposition run. The distance between crucible and substrate is 30 mm. (d) Dependence of relative height of XRD peaks on the deposition run. The distance between crucible and substrate is 45 mm.

Figure 3 (c) shows the dependence of relative height of XRD peaks on the deposition run. The distance between crucible and substrate is 30 mm. The constituent of Mn₃O₄ gradually increases with increasing deposition run.

Figure 3 (d) shows the dependence of relative height of XRD peaks on the deposition run. The distance between crucible and substrate is 45 mm. The constituent of Mn₃O₄ is dominant before the sixth deposition run. But this structure is in evidence after the sixth run though the strength is small.

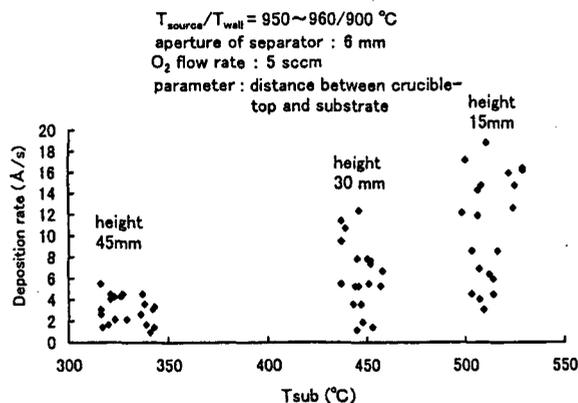


Fig. 4 Deposition rate dependence on the T_{sub} . The parameter is the distance between crucible top and substrate.

Figure 4 shows the deposition rate dependence on the T_{sub} . The parameter is the distance between crucible top and substrate. The T_{sub} varied with varying the distance. The scattering of the deposition rate is due to the oxidation of films.

There are three parameters that govern the film properties, for example, composition and crystallinity. They are O_2 flow rate, Mn deposition rate, and T_{sub} . The O_2 flow rate was fixed at 5 sccm through this study. The deposition rate and T_{sub} vary with varying the distance between crucible top and substrate. The film composition did not vary with varying the T_{sub} from 320 to 560 °C in this study. This temperature variation did not deteriorate film properties. The crucial parameter governing the film composition is the Mn deposition rate providing that under the fixed O_2 flow rate condition. It was found that the Mn_2O_3 films could be prepared providing that the Mn deposition rate was stayed between 3 to 10 Å/s.

IV. CONCLUSION

The Hausmannite (Mn_2O_3) films for Li secondary batteries were prepared by the reactive evaporation method. The effect of the distance between crucible top and substrate on the film properties was investigated.

It was recognized that the Mn deposition rate is a key parameter which governs the film composition. The Mn_2O_3 films can be successfully prepared under the Mn deposition rate between 3 to 10 Å/s provided that the O_2 flow rate, the aperture size of separator, the T_{source} , and the T_{sub} are 5 sccm, 6 mm, 950~960, and 900 °C, respectively.

The T_{sub} varied from 320 to 560 °C with varying the distance between crucible top and substrate. It was found that this temperature variation has no effect on the film properties.

This study helps us understanding the reactive evaporation process of Mn oxide films. This method could also improve the reproducibility of Mn oxide films for Li secondary batteries.

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