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Influence of the metal-induced crystallization on the structural and electrochemical properties of sputtered $LiCoO_2$ thin films

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ABSTRACT

$LiCoO_2$ thin films were fabricated using the metal-induced crystallization (MIC) method. The condition to create the MIC effect was investigated. The location and thickness of the Al coating used to manufacture the $LiCoO_2$ cathode thin film electrodes were varied, and the structural and electrochemical characteristics of the $LiCoO_2$ thin film electrode were investigated by Raman spectroscopy, field emission scanning electron microscopy and charge-discharge tests. The degree of crystallization of $LiCoO_2$ increased in the order of uncoated $LiCoO_2$ (lowest), Al(coating)/$LiCoO_2$/Al foil, and $LiCoO_2$/Al(coating)/Al foil (highest), for identical heat treatment condition (600 °C, 1 h). The crystallization of $LiCoO_2$ occurred more quickly as the Al thickness decreased, and it is considered that crystallization of $LiCoO_2$ is delayed owing to the formation of an alloy between Li-Al when there is more Al.

1. Introduction

The modernization of semiconductors, micro-devices, and subminiature machine components such as micro-electro-mechanical system is accelerating because of the rapid development of processing technologies. However, issues remain with the development of energy sources for devices operation. Therefore, developments of high performance subminiature thin film batteries are essential for implementation for micro systems [1–6]. Moreover most electronic devices are now carried by individuals, and the concept of wearable electronics will become mainstream knowledge. Therefore, devices will become smaller and power consumption will also decrease through continuous development, and the driving energy sources will be microminiaturized. Subminiature thin film batteries are the power sources that best fit these requirements.

Thin film batteries have small energy storage capacities because they have smaller volumes than conventional bulk batteries; however, they have outstanding performance characteristics such as durability, energy density, temperature characteristics, and self-discharge rates. The characteristics of these thin film batteries are mainly influenced by cathode thin film electrodes; $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ are used as active electrodes in common with bulk batteries [7–12]. $LiCoO_2$ is the most commonly used because it provides high voltage, long lifetime, and low self-discharge rate [13,14].

Complete crystallization is required for the cathode active material $LiCoO_2$ to show outstanding characteristics in thin film batteries. $LiCoO_2$ thin films that are deposited by sputtering have an amorphous structure and it is known that a high-temperature heat treatment process over 800 °C is required for crystallization [15]. However, several problems owing to degradation occur during the heat treatment process. Therefore, various studies are being performed to reduce the crystallization heat treatment process temperature [16–24]

We have previously reported that the crystallization heat treatment temperature can be reduced by applying the metal induced crystallization (MIC) effect [25]. If crystallization heat treatment is performed after depositing thin film electrode on amorphous aluminum (Al) coated substrates, then the amorphous Al that has a low crystallization temperature is crystalized first. At this time, Al performs the role of a crystallization seed to reduce the crystallization energy of $LiCoO_2$, and the crystallization temperature can be lowered to 600 °C. It was found that defects such as micro-cracks and blow holes in the thin film surfaces were also reduced.

In order to investigate the conditions to create the MIC effect, the location and thickness of the Al coating used to manufacture the $LiCoO_2$ cathode thin film electrodes were varied, and the structural and electrochemical characteristics of the $LiCoO_2$ thin film electrodes were investigated.

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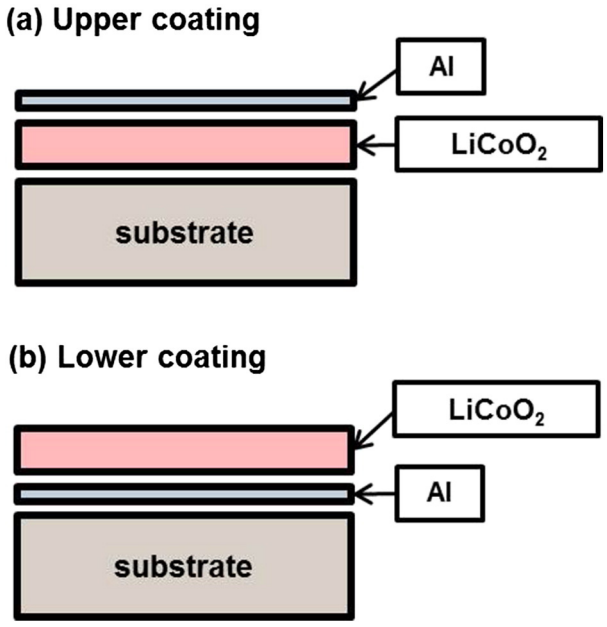

Fig. 1. Schematic diagrams of (a) Al coated on top of the $LiCoO_2$ (upper coating sample) and (b) Al film underneath the $LiCoO_2$ (lower coating sample).

2. Experimental method

The thin film electrodes used in this study were manufactured by DC sputtering, using $LiCoO_2$ sputtering target manufactured by Toshima (Japan). The target was located on the bottom of the chamber and a primary rotary pump and secondary turbo molecular pump were used to maintain an initial pressure of 5.73×10^{-4} Pa. Deposition was conducted in Ar/O_2 of 0.30 Pa introduced by a mass flow controller. Gas flow ratio of Ar/O_2 was 4/1 with a total gas flow amount of 150 sccm. The temperature during deposition was heated to no more than 60 °C and the distance between the substrate and target was 9 cm.

The substrate was Aluminum foil. First, the Al foil was acid cleansed for 5 min at 70 °C in 10% sulfuric acid solution to remove impurities. Preprocessing was performed within a fume hood, and $LiCoO_2$ film was then deposited on the acid cleansed substrate.

Al coating was used for MIC effects. Fig. 1 shows the two types of thin film electrode structures that were manufactured: Al coated on top of the $LiCoO_2$ (upper coating sample) and an Al film underneath the $LiCoO_2$ (lower coating sample). DC sputtering was used to deposit the Al with parameters of 0.08 mV in Ar atmosphere of 200 sccm, with coating times of 10 s, 60 s, and 1200 s. However, accurate measurement of film thickness was impossible because the Al film were too thin after the short coating times of 10s and 60s; thus, approximate values proportional to time were used to calculate the thickness. The calculated Al thicknesses were 3 nm, 20 nm, and 400 nm, and the manufactured Al-coated $LiCoO_2$ films were crystallization heat treated for 1 h in O_2 at 400 °C, 500 °C, 600 °C respectively.

The morphology of the deposited films was studied by field emission scanning electron microscopy (FE-SEM, Jeoul, JSM-6701F) at an accelerating voltage of 30 kV. Raman spectroscopy was conducted with a spectrometer equipped with a triple monochromator (HORIBA, LabRAM, HR800UV). Radiation with a wavelength of 514 nm (100 mW) from an argon ion laser was used as the light source. In order to examine the electrochemical properties of thin film cathodes, coin-type cells were assembled with lithium foils as the counter and reference electrodes and 1 M $LiPF_6$ in ethylene carbonate (EC): diethyl carbonate (DEC) (1:1, vol.%) as the electrolytic solution. The charge–discharge test was carried out with a battery cycler (Won A Tech, WDCS3000s) at a constant current density of 10 $\mu A/cm^2$ in the potential range of 3.0–4.2 V at room temperature.

3. Results and discussion

Fig. 2 shows the Raman experimental results according to the crystallization heat treatment temperature of the upper coating samples. The Al coating thicknesses in Fig. 2(a)–(c) were 400 nm, 20 nm, and 3 nm, respectively. The figure shows that the peak intensities of 488 cm^{-1} and 598 cm^{-1} that correspond to the crystallization of $LiCoO_2$ increased as the heat treatment temperature increased in all samples. However, it can be seen that the crystallization peak of the sample with 3 nm coating thickness is the sharpest. This means that

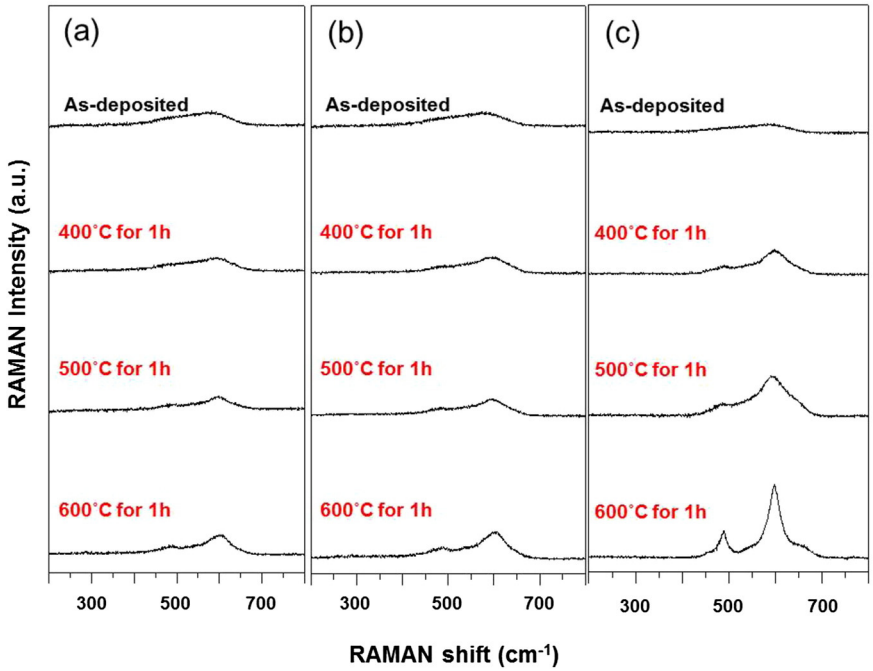

Fig. 2. Raman spectra of (a) Al(400 nm)/$LiCoO_2$/substrate, (b) Al(20 nm)/$LiCoO_2$/substrate and (c) Al(3 nm)/$LiCoO_2$/substrate.

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