EFFECT OF ATMOSPHERE ON CRYSTALLIZATION OF $LiCoO_2$ THIN FILM DEPOSITED BY RF SPUTTERING

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ABSTRACT

Since 1980s, lithium/lithium-ion batteries have emerged as one of the most important power sources for portable electronics due to their high energy density. In order to reduce weight for portable electronics, the demand for lighter and thinner batteries is increasing. To reduce the battery size, using the thin-film rechargeable battery is the best solution. In thin-film batteries, $LiCoO_2$ has been widely used as the cathode material due to the advantages of high energy density and good cycleability. The crystalline $LiCoO_2$ has $R\bar{3}m$ layered structure which provides 2-dimensional accessible path for Li-ion diffusion. Although, the electrochemical properties of thin-film batteries have been investigated recently, the process for the fabrication of thin-film batteries has not been thoroughly studied. Thus, the objective of this work was to study the effect of the atmosphere on the crystallization, morphologies, and electrochemical properties of thin film $LiCoO_2$ cathode deposited by rf sputtering technique.

In this work, $LiCoO_2$ thin films with the thickness of about 2μm were successfully deposited by rf magnetron sputtering method. The $LiCoO_2$ target was fabricated by hot-pressing (700℃for 2h in Ar atmosphere) of $LiCoO_2$ powders which were synthesized from Li_2CO_3 and $CoCO_3$ at 700℃ for 12h. The target was then sputtered in various ratio of Ar and O_2 gas mixture at a total flow rate of 12 sccm under a pressure of 5~50mTorr. The temperature of substrate was kept at 150~350 ℃ during thin film deposition. In order to obtain crystalline $LiCoO_2$, the as-deposited films were annealed at 500~700℃ for 2h in controlled atmosphere.

The crystallization of $LiCoO_2$ was characterized by an X-ray diffractometer using Cu Kα radiation. The resistivity of thin films was measured using a DC four-probe method. The morphology of $LiCoO_2$ thin film was examined by scanning electron microscopy (SEM). The cyclic voltammetry and charge/discharge characteristics of $LiCoO_2$ were also investigated.

From XRD analysis shown in Fig.1, the as-deposited film exhibits an amorphous structure. After annealing at 500℃ for 2h, the amorphous phase started to crystallize. As the annealing temperature increased, the crystallization was also enhanced. Under the flow of pure Ar during deposition, the annealed and crystallized $LiCoO_2$ films exhibited (104) preferred orientation. However, under the flow of 75％ O_2 and 25％ Ar, the intensity of (101) reflection from annealed $LiCoO_2$ film become stronger than that of (104) reflection as shown in Fig.2. As the annealing temperature increased to 700℃, the reflections representing Co_3O_4 were also observed. During deposition and crystallization process, the rearrangement of Li, Co and O ions is strongly dependent upon the content of oxygen. Under oxygen-rich atmosphere, it is believed that $LiCoO_2$ crystallized preferably along oxygen-rich planes. Therefore, (101) reflection became stronger than (104) reflection. After the annealing and crystallization process, finely distributed columnar $LiCoO_2$ crystallites were observed as shown in Fig.3.

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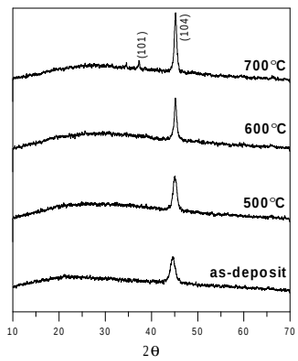

Fig.1 XRD patterns of $LiCoO_2$ thin films (deposited in Ar=12sccm) annealed at various temperatures for 2h

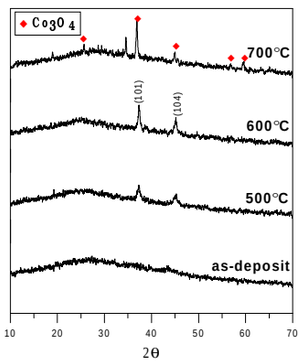

Fig.2 XRD patterns of $LiCoO_2$ thin films (deposited in Ar=3sccm and O_2=9sccm) annealed at various temperatures for 2h

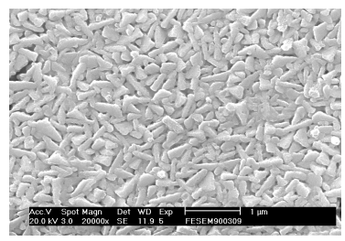

Fig.3 SEM morphology of $LiCoO_2$ thin film (deposited in Ar=12sccm) annealed at 700℃ for 2h