Development of Combinatorial Technique using Electrostatic Spray Deposition Method

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Combinatorial chemistry is the technique in which various compounds are synthesized and evaluated at one time through the combination of the elementary processes in the synthesis process. The combinatorial method is effective in rapid screening of numerous composition of oxides. In recent years, several studies of this technique for thin films have been reported. For instance, Whitacre et al. reported the combinatorial synthesis of $Li_yMn_xNi_{2-x}O_4$ thin film to have a compositional gradient by sputtering [1]. Lippmaa et al. synthesized $La_{1-x}Sr_xMnO_3$ thin film by PLD combinatorially [2]. We expand electrostatic spray deposition (ESD) method to combinatorial chemistry. In ESD method, a charged aerosol of solution precursor is generated and directed to the heated substrate in an electric field to deposit a thin film. Thin oxide films having various composition is easy to prepare by using ESD method without use of expensive apparatus. Especially, we report the study of the combinatorial technique for synthesis and characterization of $LiCo_xMn_{2-x}O_4$ thin film prepared by ESD method. The goal of the present work is to establish of combinatorial synthesis and characterization for thin film using ESD method. Moreover, their electrochemical properties will be able to evaluate combinatorially.

The schematic diagram of set-up for synthesis of combinatorial thin films are shown in Fig.1(a). Using the mobile stage in horizontal direction, the thin film is deposited with moving the substrate. By varying deposition amount on the different areas, the film which has concentration gradients is deposited as shown in Fig.1(b). When other element is deposited similarly on the film possessing concentration gradients, the film which has compositional gradients of some different components is able to be created.

Thin films were deposited on Au or Si substrate using ESD method. To synthesize spinel oxides, a precursor solution of 25mM $LiNO_3$ + 50mM $(Co(NO_3)_2$ + $Mn(NO_3)_2)$ at a molar ratio of 1:x:(2-x) (Li:Co:Mn) in EtOH + 2-(2-butoxyethoxy)ethanol (1:4 v/v) was pumped at 1ml h^{-1} into a stainless nozzle. When a positive high voltage of 5.6kV was applied between the nozzle and the substrate, 2.0cm apart, a fine spray was generated from the nozzle, and a thin film was deposited on the substrate heated at 300℃. Then the thin film was annealed at 700℃ for 5h. Fig.2 shows the SEM image of the cross-section for $LiMn_2O_4$ thin film prepared by ESD method. It had nearly uniform morphology and ca. 0.1 μ m in thickness during deposition in 1h.

The electrochemical property of spinel oxide thin film has been investigated by cyclic voltammetry. The cyclic voltammograms of various spinel oxides $LiCo_xMn_{2-x}O_4$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5) thin films are shown in Fig.3. Two pairs of oxidation and reduction peaks were found around 4.0V and 4.15V for $0 \leqq x \leqq 0.4$. Furthermore, the current of the 4.15V peak decreased with increasing x, and especially the peak disappeared for $LiCo_{0.5}Mn_{1.5}O_4$. The more x increase, the smaller the areas of the peaks tend to be. In cyclic voltammetry, systematic result was obtained with increasing cobalt amount.

The results of the combinatorial synthesis will be presented.

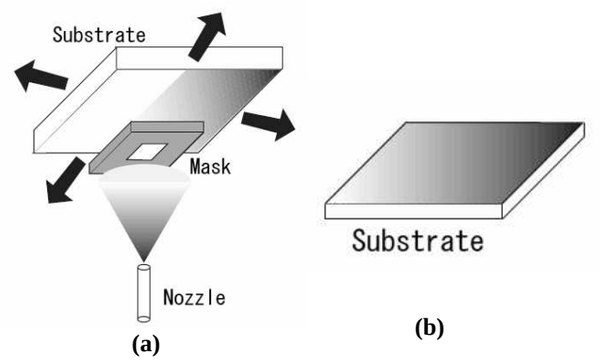

Fig. 1 (a)Schematic diagram of set-up for combinatorial electrostatic spray depositon method, (b)schematic diagram of thin film deposited.

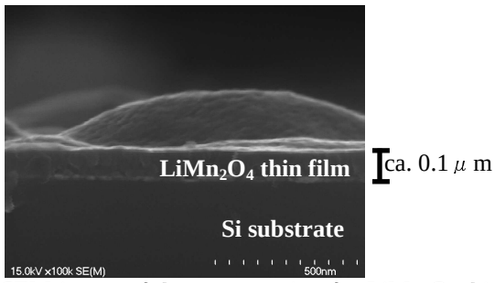

Fig. 2 SEM image of the cross section for $LiMn_2O_4$ thin film on Si substrate prepared by ESD method (15kV, × 100,000).

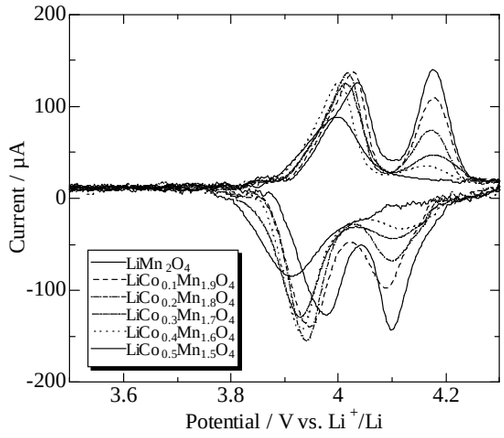

Fig. 3 Cyclic voltammograms of $LiCo_xMn_{2-x}O_4$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5) thin films ($3mVs^{-1}$).

References

[1]J.F.Whitacre et al. *J.Electrochem.Soc.*, **150**,1647(2003)
[2]M.Lippmaa et al. *Appl.Surf.Sci.*, **189**,205(2002)