論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Synthesis, structure, and electrochemical properties of hetero-epitaxial electrode/solid electrolyte films for all solid-state batteries
著者(和文)	KimSangRyun
Author(English)	SangRyun Kim
出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第9357号, 授与年月日:2013年12月31日, 学位の種別:課程博士, 審査員:菅野　了次,大坂　武男,川路　均,平山　雅章,中村　二朗
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第9357号, Conferred date:2013/12/31, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質電子化学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　理学　）
学籍番号： Student ID Number		指導教員（主）： Academic Advisor(main)	菅野　了次
学生氏名： Student's Name	金　相侖 (Kim Sangryun)	指導教員（副）： Academic Advisor(sub)	平山　雅章

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

All solid-state batteries composed of hetero-epitaxial electrode/solid electrolyte films have potential as new configurations for lithium batteries with high power and high capacity characteristics. This thesis deals with synthesis, structure, and electrochemical properties of hetero-epitaxial electrode/solid electrolyte multi-layer films.

In **Chapter 1 'General introduction'**, background and problems on current lithium batteries were presented. Demands for new battery system with high power and high capacity were explained. As an advanced battery system, the author proposed all solid-state battery composed of hetero-epitaxial electrode/solid electrolyte films. The importance of clarifying properties of epitaxial thin film solid electrolyte and hetero-epitaxial electrode/solid electrolyte interface was described.

In Chapter 2 '**Experimental**', experimental procedures used in this thesis were explained. Methods for synthesis and structural/electrochemical characterizations of epitaxial thin film were described.

In Chapter 3 '**Synthesis and electrochemical properties of epitaxial $Li_7La_3Za_2O_{12}$ thin film solid electrolyte**', the epitaxial $Li_7La_3Za_2O_{12}$ films with (001) and (111) orientations were synthesized on $Gd_3Ga_5O_{12}$ single crystal substrates. Since the epitaxial films included no grain boundaries and hence no grain boundary resistance, the lithium ion conductivities in the grains of the (001) and (111) films were determined to be 2.5×10^{-6} and 1.0×10^{-5} S cm^{-1}, respectively, at room temperature. The epitaxial thin films of $Li_7La_3Za_2O_{12}$ solid electrolyte contained large amounts of Al in the grains and exhibited ionic conductivities in the order of $10^{-6} \sim 10^{-5}$ S cm^{-1}.

In **Chapter 4 'Synthesis and electrochemical properties of epitaxial $Li_{0.17}La_{0.61}TiO_3$ thin film solid electrolyte'**, the effects of synthetic conditions, film thickness, and crystal orientation on properties of epitaxial $Li_{0.17}La_{0.61}TiO_3$ thin film solid electrolyte were examined. The $Li_{0.17}La_{0.61}TiO_3$(111) film grown at the low temperature of 750 °C contained a sufficient amount of lithium in the lattice and exhibited a high total ionic conductivity of 3.8×10^{-4} S cm^{-1} with negligible resistance at the grain boundaries. Both ionic and electronic conductivities of epitaxial $Li_{0.17}La_{0.61}TiO_3$ film increased as film thickness decreased. A nano-sized interface region of $Li_{0.17}La_{0.61}TiO_3$ exhibited different conductive properties with a bulk region. The parallel directions to the *ab* planes in the $Li_{0.17}La_{0.61}TiO_3$ films showed high ionic conductivities of the order of 10^{-4} S cm^{-1}. The formations of parallel *ab* planes along the out-of-plane direction should exhibit superior conductivities in multi-layer configurations.

In **Chapter 5 'Fabrication of electrode/solid electrolyte multi-layer films using $Li_7La_3Z_2O_{12}$'**, the properties of electrode/solid electrolyte multi-layer films using $Li_7La_3Z_2O_{12}$ were investigated. The $Li_7La_3Z_2O_{12}$ depositions caused interfacial reactions with epitaxial thin film electrodes by atomic inter-diffusions, resulting in poor battery performances of the multi-layer films. Although the interfacial reactions were suppressed by the introduction of $LiNbO_3$ buffer layer, the multi-layer films showed no electrochemical activities. The formation of stable and electrochemically-active interfacial layer by other buffer layers is required in order to improve battery performances of all solid-state thin film batteries using $Li_7La_3Z_2O_{12}$ as solid electrolytes.

In **Chapter 6 'Synthesis, structure, and electrochemical properties of hetero-epitaxial electrode/solid electrolyte multi-layer films using $Li_{0.17}La_{0.61}TiO_3$'**, structures and electrochemical properties of hetero-epitaxial electrode/solid electrolyte multi-layer films were characterized. The low deposition temperature of 750 °C was found to inhibit the growth of the interfacial layer formed by the chemical reaction of $LiMn_2O_4$ electrode and $Li_{0.17}La_{0.61}TiO_3$ solid electrolyte. The electrochemical activity of the $Li_{0.17}La_{0.61}TiO_3/LiMn_2O_4$ multi-layer film demonstrated that the $LiMn_2O_4$ and $Li_{0.17}La_{0.61}TiO_3$ function as the electrode and solid electrolyte, respectively. The introduction of $SrRuO_3$ buffer layer between $Li_4Ti_5O_{12}$ electrode and $Li_{0.17}La_{0.61}TiO_3$ solid electrolyte significantly improved structural stabilities of the multi-layer films. Atomic-level observations using scanning transmission electron microscopy clarified that a stable and electrochemically-active interfacial layer generated by inter-diffusions of atoms facilitates battery reactions through hetero-epitaxial interfaces without structural changes in electrode and solid electrolyte.

In **Chapter 7 'Fabrication of $LiMn_2O_4/Li_{0.17}La_{0.61}TiO_3/SrRuO_3/Li_4Ti_5O_{12}$ multi-layer film for all solid-state battery'**, the properties of hetero-epitaxial $LiMn_2O_4/Li_{0.17}La_{0.61}TiO_3/SrRuO_3/Li_4Ti_5O_{12}$ multi-layer films for all solid-state battery were investigated. The electrochemical properties were evaluated along the horizontal and vertical directions of the multi-layer films. However, the multi-layer films exhibited no reaction peaks associated with the $Li_4Ti_5O_{12}$ and $LiMn_2O_4$ electrodes. The scanning transmission electron microscopy results suggested that potentials of $Li_{0.17}La_{0.61}TiO_3$ and $LiMn_2O_4$ in $LiMn_2O_4/Li_{0.17}La_{0.61}TiO_3/SrRuO_3/Li_4Ti_5O_{12}$ multi-layer film were reversed from those in $Li_{0.17}La_{0.61}TiO_3/LiMn_2O_4$ multi-layer film. The analyses on defects structures in multi-layer films indicated that the formations of V_{Li}' in $Li_{0.17}La_{0.61}TiO_3$ and $Li_i^{\bullet}$ in $LiMn_2O_4$ is required.

In **Chapter 8 'General conclusions'**, conclusions obtained in this thesis are summarized. The careful optimization of synthetic conditions for multi-layer stacking and the introduction of the buffer layer between the electrode and solid electrolyte enabled hetero-epitaxial growth of $LiMn_2O_4(111)/Li_{0.17}La_{0.61}TiO_3(111)/SrRuO_3(111)/Li_4Ti_5O_{12}(111)$ multi-layer films on $SrTiO_3(111)$ and $Al_2O_3(0001)$ substrates. These processes were performed from the physical and chemical point of view. However, the interfacial structures in electrode/solid electrolyte multi-layer films changed by differences in potentials. The control of electrochemical potentials in the multi-layer system is key issue to realize the advanced all solid-state battery system with ideal hetero-epitaxial structures.