Orientation control and ionic conductivity of epitaxial $Li_{0.17}La_{0.61}TiO_3$ film solid electrolyte

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A perovskite-type $Li_{3x}La_{2/3-x}TiO_3$ has been paid much attention to as a solid electrolyte of all solid-state batteries due to its high lithium ion conductivity (~ 10^{-3} S/cm).[1] The structure of $Li_{3x}La_{2/3-x}TiO_3$ has a three-dimensional framework of corner-sharing TiO_6 and alternative ordered La-rich (001) La1-O1 and La-deficient (002) La2-O2 layers along the *c* axis.[2] The conduction mechanism of $Li_{3x}La_{2/3-x}TiO_3$ is intimately related to the crystal structure. Previously, we synthesized $Li_{3x}La_{2/3-x}TiO_3$(111) epitaxial films and evaluated the ionic conductivity.[3] The epitaxial films with a single orientation and a flat surface are suitable for mechanistic studies in the bulk lattice. In the present study, epitaxial $Li_{0.17}La_{0.61}TiO_3$ (LLTO) films with different orientations are prepared and the relationship between orientation and ionic conductivity is clarified.

The $Li_{0.17}La_{0.61}TiO_3$ thin films were deposited on $NdGaO_3$ (NGO) (110), NGO(100), and Al_2O_3(0001) substrates by a pulsed laser deposition method. The orientations of the films were characterized both by the out-of-plane and in-plane X-ray diffraction (XRD) measurements. The thicknesses, densities, and roughnesses of the films were determined by a profilometer and X-ray reflectivity (XRR) technique. The electrical conductivities of the thin films were measured using AC impedance spectroscopy. Comb-type Au electrodes (1 mm wide, 4 mm long) were mounted on the films prior to the measurements. The measurement was conducted in an Ar-filled glove box to prevent reaction of the electrolyte with moisture and carbon dioxide in air that could contribute to the ionic conduction.

The orientations of films synthesized are as follows; LLTO(001) on NGO(110), LLTO(011) on NGO(100), and LLTO(111) on Al_2O_3(0001). The out-of-plane XRD result for the LLTO(001) film showed superlattice reflections attributed to the ordering of La-rich and La-deficient planes. The in-plane XRD results confirmed a four-fold symmetry of superlattice reflections, indicating the 90°-rotated multi-domains on the surface. On the other hand, the superlattice planes in the LLTO(011) and LLTO(111) films existed diagonally across the out-of-plane direction. The thicknesses of LLTO(001), LLTO(011), and LLTO(111) were 78, 78, and 80 nm, respectively. Lithium ion conductivities were measured along the in-plane direction on the epitaxial films; [100] direction on LLTO(001), [01-1] direction on LLTO(011), [100] direction on LLTO(011), and [1-10] direction on LLTO(111). The impedance spectra represent clear semicircles, which can be interpreted as the parallel combination of resistance and capacitance. The capacitances at room temperature were in the order of 10^{-12} F, respectively. Therefore, the resistance components for the epitaxial LLTO films correspond to lithium ion diffusion in the grains and the results confirm that the resistance for lithium diffusion between the grains is negligible due to the close contact between each grain in the epitaxial films. The total ionic conductivities of the [1-10] direction on LLTO(111) and the [100] direction on LLTO(011) were 3.8×10^{-4} and 2.2×10^{-4} S cm^{-1}, respectively, at room temperature, which are comparable to the bulk conductivity of polycrystalline $Li_{0.18}La_{0.61}TiO_3$ (5×10^{-4} S cm^{-1}).[4] In contrast, the conductivities of the [01-1] direction on LLTO(011) and the [100] direction on LLTO(001) exhibited 1.2×10^{-6} and 1.3×10^{-7} S cm^{-1}, respectively. An anisotropic conduction of LLTO was experimentally verified using epitaxial films.

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