The development of next-generation secondary batteries continues to promote integration and miniaturization. Al-solid-state Li-ion batteries using nonflammable solid electrolyte and thin film electrode materials not only offer significant advantages in terms of improved safety and chemical and thermal stability, increased power and energy densities, and large potential windows, but also can be produced to much smaller dimensions than conventional Li-ion batteries containing liquid electrolytes. As with conventional batteries, the performance of thin-film batteries is influenced strongly by the nature of the embedded interfaces, such as electrode/electrolyte and electrode/current-collector interfaces, as well as the grain and domain boundaries within the electrode and/or electrolyte materials. Detailed knowledge of the interface structures, which provides insights into formation mechanisms of the interfaces and the effects of microstructure on electrochemical properties, is essential for efficient materials and device design. Here based on a systematic study using state-of-the-art scanning transmission electron microscopy (STEM), we report the epitaxial growth mechanism of a typical cathodic LiMn$_2$O$_4$ thin epifilm by exploring the detailed structural and compositional variations in the vicinity of a film/substrate interface, while reveal the structures and composition of the domain boundaries (DBs) and consider their effect on Li-ion mobility and ionic conductivity of La$_{2/3-x}$Li$_x$TiO$_3$ (LLTO) electrolytes. Direct observation of atom columns shows the LiMn$_2$O$_4$ epifilm forms an atomically flat and coherent heterointerface with the Au(111) substrate, but that the crystal lattice is tetragonally distorted with a measurable compositional gradient from the interface to the crystal bulk. The growth mechanism is interpreted in terms of a combination of chemical and physicomechanical effects, namely a complex interplay between the internal Jahn-Teller distortions induced by oxygen non-stoichiometry and the lattice misfit strain. DBs in LLTO are shown to consist essentially of two types: frequently occurring 90° rotation DBs and a much less common antiphase-type boundary. It is found that the 90° DBs are coherent interfaces consisting of interconnected steps that share La sites, with occupancies of La sites higher than in the domain interiors. The DBs suffer different degrees of lattice mismatch strain depending on Li content. The lattice strain and resultant Li and O vacancies and the high La occupancy at DBs are expected to result in lower interdomain Li-ion mobility, which will have a deleterious effect on the overall Li-ion conductivity.\cite{1,2}


Acknowledgement: A part of this research was supported by the Japan Society for the Promotion of Science (JSPS) through its “Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)".