Transport and magnetic properties of $Pr_{0.6}Sr_{0.4}MnO_xF_y$ thin films fabricated by topotactic fluorination

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Introduction: Hole-doped perovskite manganite oxides, $R_{1-x}A_xMnO_3$, where R is a rare earth ion and A is a divalent ion, have attracted considerable attention because of their rich magnetic and electrical properties [1]. Among these manganites, $Pr_{0.6}Sr_{0.4}MnO_3$ (PSMO) undergoes a transition from high-temperature paramagnetic insulating to low-temperature ferromagnetic metallic phases with Curie temperature (T_C) near room temperature, which is the highest among the $Pr_{1-x}Sr_xMnO_3$ series [2]. Recently, in ferromagnetic $La_{0.74}Sr_{0.26}MnO_{3-\delta}$ epitaxial thin films, remarkable suppression of T_C and saturation magnetization accompanied with an increase in magnetic coercivity was found by topotactic insertion of fluoride ions into the crystalline lattice [3]. In this study, we introduced fluoride ions into PSMO epitaxial thin films by topotactic fluorination and investigated their electrical transport and magnetic properties.

Experimental methods: 40-nm-thick PSMO epitaxial thin films as precursors were deposited on $SrTiO_3$ (STO) (001) substrates by pulsed laser deposition under the following condition: substrate temperature of 800 °C, oxygen partial pressure of 100 mTorr, laser (KrF excimer, 248 nm wavelength) fluence of 0.6 J/cm^2 and repetition rate of 5 Hz. The obtained PSMO thin films were subsequently annealed at 550 °C for 60 min in the atmospheric pressure of oxygen. Fluorine was introduced into the precursor films by topotactic fluorination using polyvinylidene fluoride at 270 °C for 18 h under an Ar gas flow. Crystal structures were characterized by X-ray diffraction (XRD) measurements. In-plane resistivity (ρ) was evaluated by using four-probe methods with Au electrodes. Magnetization (M) of the films was measured with a superconducting quantum interference device magnetometer.

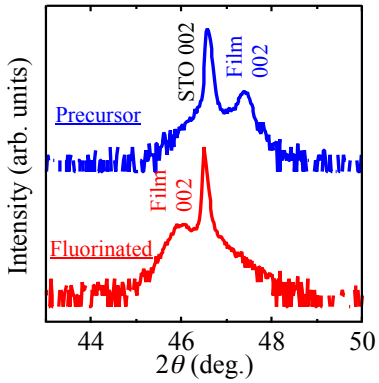

Fig. 1. Out-of-plane 2θ–θ XRD patterns of the precursor and the fluorinated PSMO films.

Results and discussion: Figure 1 shows out-of-plane 2θ–θ XRD patterns of the precursor and the fluorinated PSMO films. The precursor film showed 002 diffraction from perovskite structure at 47.4°, from which the out-of-plane lattice constant was calculated to be 3.83 Å. After the fluorination, the peak shifted toward lower angle of 46.1°, indicating the elongation of c-axis length to 3.93 Å. These results suggest that fluorine was substituted for oxygen. Figure 2 displays ρ and M versus temperature (ρ–T, M–T) curves of the precursor and the fluorinated PSMO films. As shown in Fig. 2(a), the ρ value was increased, and the metal-insulator transition temperature was decreased from 208 K to 196.5 K by the fluorination. Moreover, the M value and T_C were decreased from ~1.2 μ_B/f.u. to ~0.5 μ_B/f.u. and from ~250 K to ~220 K, respectively, with the fluorination. These behaviors were probably caused by electron doping via F^- substitution for O^{2-} and/or suppression of double-exchange interaction due to the coexistence of Mn-O-Mn and Mn-F-Mn chains.

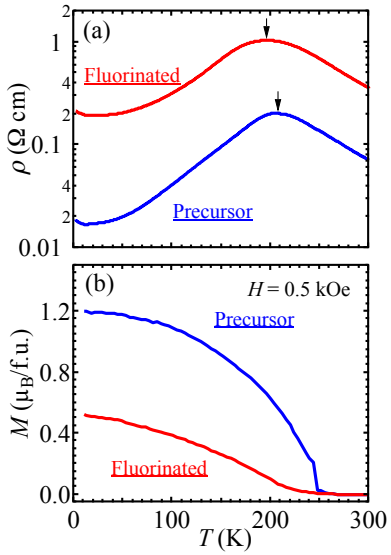

Fig. 2. (a) ρ–T and (b) M–T curves of the precursor and the fluorinated PSMO films.

References: [1] M. Imada *et al.*, Rev. Mod. Phys. **70**, 1039 (1998). [2] C. Martin *et al.*, Phys. Rev. B **60**, 12191 (1999). [3] P.A. Sukkurji *et al.*, Materials **11**, 1204 (2018).

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