Soft x-ray photoemission study of La$_{1-x}$Sr$_x$TiO$_3$ thin films

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1 Introduction

La$_{1-x}$Sr$_x$TiO$_3$ (LSTO), which has the perovskite-type structure, is a basic material for studying the mechanism of filling-controlled metal-insulator transition [1]. With decreasing x, LSTO changes from a band insulator (SrTiO$_3$, Ti^{4+}, $3d^0$) to a paramagnetic metal, an antiferromagnetic metal, to an antiferromagnetic Mott-Hubbard insulator (LaTiO$_3$, Ti^{3+}, $3d^1$) [2,3]. In previous studies, critical behaviors of the electric structure have been observed in the vicinity of the metal-insulator transition [3,4]. For 0.05 < x < 1.0, LSTO exhibits a Fermi–liquid-like behavior. On the other hand, around x=0.05, LSTO shows a metal–to-insulator transition (MIT) [2]. However, because of the large contribution of surface states to the incoherent part of the photoemission spectra, it has been difficult to quantitatively evaluate the spectral weight transfer from the coherent part to the incoherent part with d-band filling [4]. In this work, we have measured *in-situ* soft x-ray photoemission spectroscopy (SX-PES) spectra of epitaxially grown LSTO thin films (x=0.9, 0.8, 0.7) as a function of composition x.

2 Experiment

LSTO thin films were fabricated eptiaxially on TiO$_2$-terminated SrTiO$_3$ (100) substrates at 950-1000 °C and in an oxygen pressure 1-5 × 10^{-6} Torr by laser molecular beam epitaxy (MBE) method. The LSTO thin films were transferred to a synchrotron radiation photoemission chamber at BL-2C of Photon Factory under ultrahigh vacuum of about 10^{-10} Torr connected directly with a laser MBE chamber [5]. The thickness of the LSTO thin films is 100 monolayer (approximate 39.05 nm) and was examined by reflection high-energy electron-diffraction (RHEED) oscillation. Crystallographic properties examination by atomic force microscope shows a step-and-terrace structure and well-ordered surface. The *in-situ* SX-PES spectra were taken at room temperature with a total energy resolution of 171 meV at a photon energy of 464.8 eV.

3 Results and Discussion

Figure 1 shows the Ti^{3+} concentration (solid line) deduced from the line-shape fitting of the Ti 2p core-level photoemission spectra plotted as a function of nominal La concentration 1-x. With increasing La concentration, the Ti^{3+} concentration increases but is less than that expected as shown by a dashed line. This is contrasted with the case of bulk LSTO, where the estimated Ti^{3+} concentration is in good agreement with the La concentration, indicating that the La substitution changes the valence of Ti from 4+ to 3+. A possible origin of the disagreement for the thin film samples is that the actual La concentration was lower than the nominal the La concentration. Electronic reconstruction and La deficiency is another possible origin of the discrepancy between the La 4d concentration and the Ti^{3+} 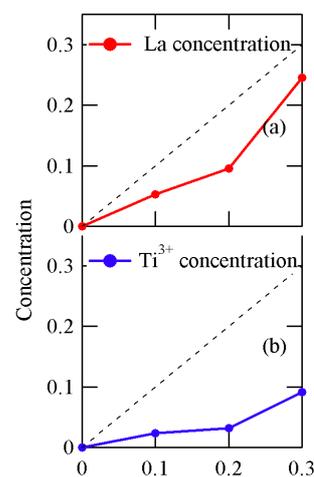concentration (the electron concentration). In the case of La deficiency, three electrons are removed per La deficiency. In the case of electronic reconstruction, half an electron per surface Ti atom is removed.

Fig. 1: Ti^{3+} and La 4d concentrations as a function of the nominal La concentration

Bulk LSTO does not show electronic reconstruction for the following reason. The driving force of the electronic reconstruction is to avoid the divergence of electrostatic potential through charge transfer from the outermost surface . The surface of a scraped bulk crystal is not an atomically flat one and has roughness. In such a type of surfaces, positively and negatively charged regions coexist at the outermost surface on a microscopic scale and the probabilities of the occurrence of those parts are statistically similar. Because of this, the net electrostatic potential produced by the positively and negatively charged parts of the surface is cancelled and does not diverge.

References

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