Electronic Structure of $LaNiO_3$ Thin Films Studied by Soft X-ray Angle Resolved Photoemission Spectroscopy

Perovskite nickel oxides $RNiO_3$ (R: rare earth) are well known to show interesting behaviors such as metal-insulator transitions, spin and orbital ordering, etc. $LaNiO_3$ (LNO), which is the reference material of the series, exhibits Pauli paramagnetic metal behavior at any temperature (T); however, while the other members (e.g., R = Pr, Nd, Sm) show T-dependent phase transitions [1]. The specific heat and susceptibility data, as well as T^2 dependence of resistivity of LNO suggest that this compound is well described as a strongly correlated system. An enhanced effective mass ($m^* \sim 10m_b$) is also well established. Although growing a single crystal of $RNiO_3$ is very difficult, single crystalline epitaxial thin films have been successfully synthesized for device applications.

Angle-resolved photoemission spectroscopy (ARPES) is one of the most powerful methods to directly investigate the momentum-resolved electronic structures of solids. However, ARPES measurements carried out using vacuum ultraviolet (VUV) photons strongly depends on the surface condition owing to very low photoelectron mean free paths. Recent progress in instrumentation for high-resolution soft X-ray (SX) ARPES has made it possible to perform *in situ* ARPES measurements to reveal the bulk electronic structure of compounds.

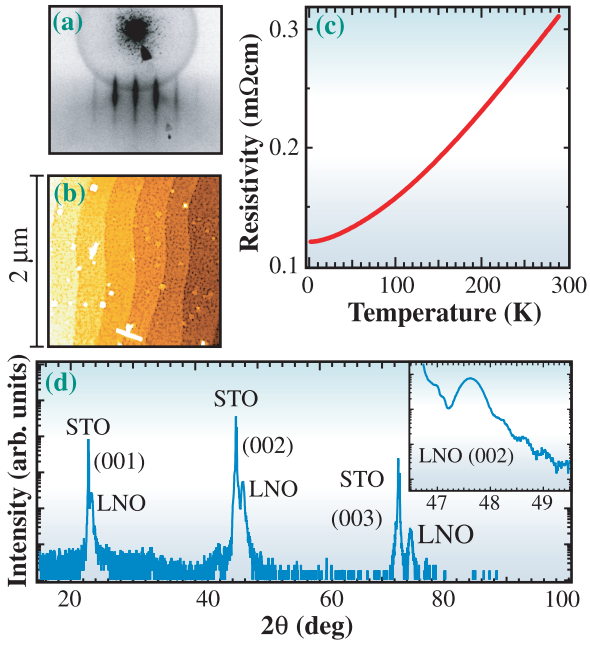

Fig. 1. **(a)** RHEED pattern, **(b)** AFM image, **(c)** temperature dependence of resistivity, and **(d)** XRD pattern (Inset: expansion graph in the vicinity of the (002) Bragg peak) of LNO films grown on STO (001) substrates.

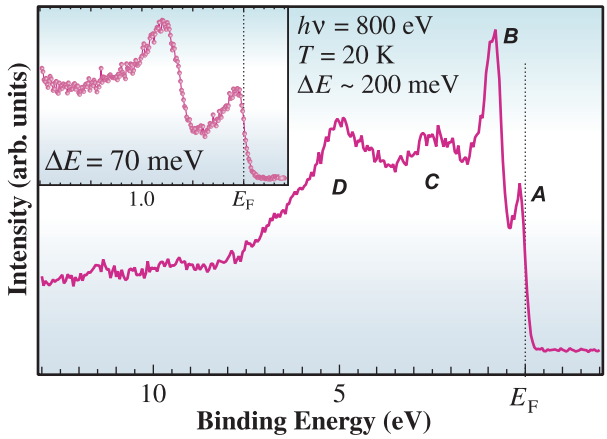

Fig. 2. *In situ* valence band photoemission spectrum of LNO films. The inset shows high-resolution ($\Delta E \sim 70$ meV) photoemission spectrum of near-E_F region.

The fabrication of LNO thin films and SX-photoemission measurements were carried out using a high-resolution synchrotron radiation PES system combined with a pulse laser deposition chamber at beamline **BL17SU** [2]. The LNO films were grown on $SrTiO_3$ single-crystal substrates. A sintered stoichiometric LNO pellet was used as an ablation target. A Nd YAG laser was used in its frequency-tripled mode (λ = 355 nm) at a repetition rate of 1 Hz. The STO substrates were annealed at 900 °C at an oxygen pressure of 1×10^{-4} Pa before deposition. The substrate temperature was set to 650 °C and the oxygen pressure was 10 Pa during the deposition. The LNO films were subsequently annealed at 400 °C for 30 minutes at the atmospheric pressure of oxygen to remove vacancies. After cooling the sample to below 100 °C and evacuating the growth chamber, the surface morphology and crystallinity of the fabricated LNO films were checked by an *in situ* observation of reflection high-energy electron diffraction (RHEED) patterns. The sharp streak pattern shown in Fig. 1(a) indicates a high-quality and smooth film. After PES measurements, the samples were characterized *ex-situ* in terms of surface morphology by atomic force microscopy (AFM), electrical resistivity by 4-probe method, and crystal structure by X-ray diffraction (XRD) analysis [Fig. 1(b,c,d)] [3].

The *in situ* angle-integrated PES spectra of the fabricated LNO thin films are shown in Fig 2. The features labeled A and B are Ni 3*d* e_g and t_{2g} states,

respectively, which were not resolved clearly in previous PES spectra of polycrystalline LNO. The higher binding energy features labeled C and D are attributed to the O 2*p* dominant states [3].

We also performed photon-energy dependent SX-ARPES measurements of the LNO films to probe the 3-dimensional Fermi surfaces (FSs) of LNO. The FSs obtained from a band structure calculation [4] and the region probed in the Brillouin zone (BZ) are shown in Fig. 3(a), respectively. Figure 3(b) (top panel) shows FS mapping in the k_x-k_z plane obtained by changing the photon energies from $h\nu$ = 570 to 700 eV. We can clearly observe the electron FS located around the Γ-point, as predicted by the band structure calculation. After thus determining the k_z dispersions and the center of the electron FS surface accurately, we then measured tilt angle dependence using a photon energy of 630 eV. As shown in Fig. 3(b) (bottom panel), in addition to the electron FS, the edge of the hole like FS located around the R-point in the BZ was observed. Figure 3(c) shows band maps for two cuts marked in Fig. 3(b). In cut1, the experimentally determined band dispersion results in the formation of the electron FS, while in cut2, the bands forming the hole like FS are unambiguously identified. These bands and FSs are responsible for the strongly correlated properties of LNO.

The successful mapping of 3-dimensional FSs using *in situ* SX-ARPES measurements of LNO thin films thus opens up exciting possibilities for studying the momentum-resolved electronic structure of 3-dimensional highly correlated materials undergoing phase transitions.

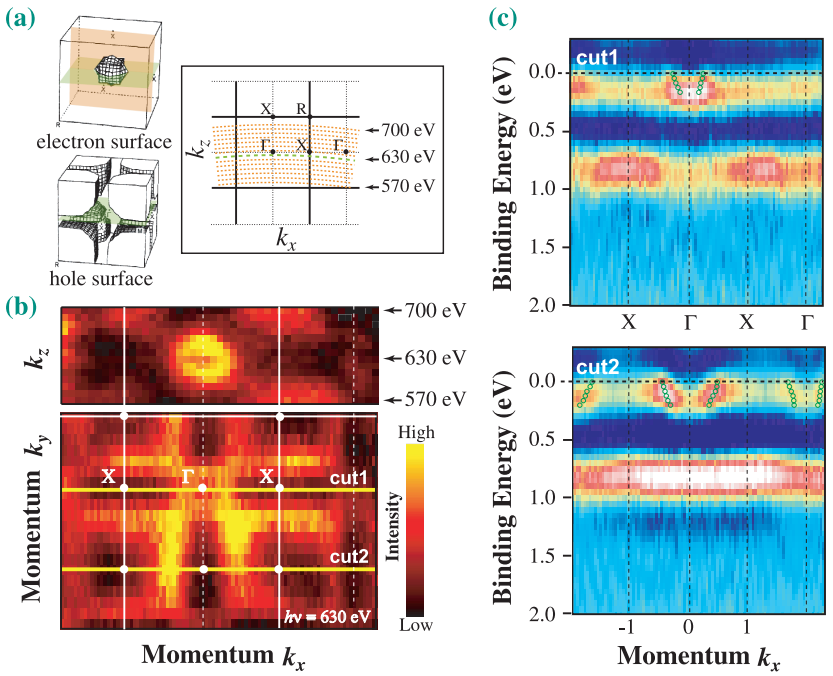

Fig. 3 **(a)** Fermi surface (cubic notation) of LNO obtained from a band structure calculation [4] and the momentum region probed by SX-ARPES of this study. **(b)** Fermi surface mapping obtained by SX-ARPES. **(c)** Second-derivative intensity maps for two cuts marked in **(b)**.

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References

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