Electron Structure of Nd$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ Thin Film with Oxygen Vacancies Prepared by Soft-X-ray Spectroscopy

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We have studied the electronic structure of the Nd$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ (NSFO) thin film with oxygen vacancies on Al$_2$O$_3$ (0001) substrate by soft-X-ray spectroscopy. The Fe 2$p$ photoemission spectrum exhibits the mixed valence states of Fe$^{2+}$ and Fe$^{3+}$. The electrical conductivity exhibits thermal activation-type behavior and increases with increasing film thickness. The band gap of charge transfer type is in good agreement with the activation energy estimated from the Arrhenius plot. These results indicate the conducting carrier of the NSFO thin film is mainly electron, although the conductivity does not depend on oxygen gas partial pressure.

1 Introduction

La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ (LSFO) bulk ceramic is well known as electron - ion mixed conductor, which is useful for cathode electrode of solid oxide fuel cell (SOFC) operating at intermediate temperature region. The cathode electrode with electron-ion mixed conduction is effective for a high energy transform efficient of SOFC, since the electrode reaction is activated at the three phase interfaces between the electrode surface, the interface of electrode and electrolyte, and electrolyte. However, the prepared thin film exhibited was lower conductivity than the bulk ceramics. Furthermore, the chemical stability has not been also proved thus far.

In this study, we have prepared the Nd$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ (NSFO) thin film by RF magnetron sputtering. If the NSFO thin film exhibits higher mixed conduction or high electron conduction activated by oxygen vacancies, the thin film might be practical as cathode electrode of SOFC with high chemical stability. In this paper, we discuss about the conducting carrier of the NSFO thin film at intermediate temperature region in terms of the electrical conductivity and electronic structure.

2 Experiment

The NSFO thin film was deposited on Al$_2$O$_3$ (0001) substrates by RF magnetron sputtering using a ceramic target. The RF power of the ceramic target was fixed at 50 W. The flow rate of Ar gas, the deposition pressure, and substrate temperature were kept at 0.67sccm, 8.0×10$^{-5}$ Torr and 700˚C, respectively. The film thickness was 42, 66 and 112 nm.

The crystalline quality of the NSFO thin films were characterized by X-ray diffraction with CuK$\alpha$ using Rigaku Miniflex 600. The electrical conductivities were characterized by the AC impedance method using a frequency response analyzer (Solartron 1260) and amplifier (Solartron 1296) in dry atmosphere (Ar/O$_2$ = 4/1) in a temperature region from 700 to 300˚C. In order to probe the conducting carrier, the conductivities were measured by changing the oxygen gas partial pressure ($P_{O_2}$). The measurement frequency region of electrical conductivity was from 32 MHz to 100 mHz.

2.1 Results and Discussion

Figure 1 shows the Fe 2$p$\textsubscript{3/2} core-level PES spectra of the NSFO thin film. The Fe 2$p$\textsubscript{3/2} core-level peak is composed of two structures originating from Fe$^{2+}$ and Fe$^{3+}$ states as shown in the dashed line obtained by Gaussian fitting. The ratio between these mixed valence state is Fe$^{2+}$:Fe$^{3+}$=2:3. The mixed valence states of Fe$^{2+}$ and Fe$^{3+}$ may contribute to the oxygen vacancies. On the other hand, the satellite peak is observed at ~8.0 eV from Fe 2$p$\textsubscript{3/2} main peak. The satellite peak originates from the charge transfer between the O 2$p$ valence band to the unoccupied Fe 3$d$ state, indicating that the valence band consists of the O 2$p$ state hybridized with the Fe 3$d$ state.

The electronic structures were investigated by photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS) measurements at room temperature. These spectroscopic measurements were conducted at the undulator beamline BL-2A MUSASHI of the Photon Factory, KEK. The XAS spectra were recorded in a total electron yield mode. The PES spectra were acquired using VG-Scienta SES-2002 hemispherical analyzer. The resolutions of PES and XAS were set to be approximately 100 and 60 meV, respectively.

Figure 2(a) shows Arrhenius plots of the electrical conductivity of the thin films with 42, 66 and 112 nm thicknesses. Each thin film exhibits thermal activation-
Fig. 2  (a) Arrhenius plots of the electrical conductivity of the thin films with 42 nm, 66 nm, and 112 nm thicknesses. (b) Electrical conductivity of the thin films with 42 nm and 112 nm thicknesses as a function of $P_{O_2}$ at 500°C.

type behavior, which corresponds to the conductivity of semiconducting region. Each activation energy ($\Delta E$) was calculated from the slope of Arrhenius plot. The $\Delta E$ does not much depend on the film thickness, although the electrical conductivity increases with increasing the film thickness.

Figure 2(b) shows the electrical conductivities of the NSFO thin films with 42 and 112 nm thicknesses as a function of $P_{O_2}$ at 500°C. In term of the defect chemical analysis, this result indicates the existence of ionic conduction since the conductivity does not depend on $P_{O_2}$. Therefore, the NSFO thin film has high electron conduction rather than ionic conduction, because the ratio of Fe$^{2+}$ valence state created by oxygen vacancies is $\sim$40% as shown in Fig. 1.

Figure 3 shows the PES and O 1$s$ XAS spectra of the NSFO thin film corresponding to the valence band and conduction band, respectively. From the dipole selection rule, it has been clarified that the O 1$s$-XAS spectrum reflects the unoccupied Fe 3$d$ state hybridized with the O 2$p$ state. The spectral shapes and peak positions are in good agreement with LaFeO$_3$ thin film. Wadati et al. has reported the electronic structure by the LDA+U calculation comparing with the PES and XAS spectra [1]. In this calculation, the CT energy, electron correlation energy and $p$-$d$ transfer integral have been set as $\sim$2.0 eV, 6.0 eV and -1.9 eV, respectively. From the agreements with the calculation and the spectra, Wadati et al. has concluded that the LaFeO$_3$ is a CT type insulator [1].

The energy separation between the top of the valence band and the bottom of the conduction band reflects the value of energy gap ($E_g$). The $E_g$ locates at the bottom of conduction band. The estimated $E_g$ is $\sim$0.5 eV, which corresponds to the $\Delta E$ of the electrical conductivity in Fig. 2(a), indicating the high electron conduction. On the other hand, the LSFO thin film prepared by PLD method has the high metallic conduction without ionic conduction. In fact, the LSFO thin film has no $E_g$ and exhibits the hole-induced state at around $E_F$ below the $t_{2g}$- and $e_g$-subbands of Fe 3$d$ state in the conduction band. However, such a state is not observed in the NSFO thin film. This may contribute to the change in band structure with the oxygen vacancies in NSFO thin film or replacing Nd as La of LSFO. Thus, we would stress that the NSFO thin film has the electron conduction, which is activated by a lot of oxygen vacancies.

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References

Research Achievements

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