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Electronic structures of perovskite-type strontium chromium oxyfluoride thin films

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1 Introduction

Perovskite-type chromium oxides exhibit unique physical properties due to the strong Cr 3*d*–O 2*p* interaction. A typical example is $SrCrO_3$ containing Cr^{4+} ($3d^2$), which exhibits antiferromagnetic metallic behaviors because its transport property lies in the crossover region between itinerant and localized carriers [1,2]. The physical properties of perovskite-type chromium oxides can be readily modified through topotactic fluorination because insertion or substitution of F^- ions provides additional holes or electrons to the Cr ions, respectively [3,4]. In this study, we investigated the electronic structures of strontium chromium oxyfluoride thin films by X-ray photoemission (XPS) and absorption spectroscopies (XAS), and discussed them in comparison with those of $SrCrO_{2.8}$ and $SrCrO_3$ thin films.

2 Experiment

Precursor $SrCrO_{2.8}$ thin films were deposited on $LaAlO_3$ (001) substrates by pulsed-laser deposition. The obtained $SrCrO_{2.8}$ thin films were further subjected to fluorination using polyvinylidene fluoride at 250 °C for 12 h in Ar gas flow. Oxidized films were prepared by annealing the $SrCrO_{2.8}$ precursor thin films at 250 °C for 2 h in air. The typical thickness of the films was ~50 nm.

Crystal structures of the films were investigated by X-ray diffraction, and chemical compositions were evaluated by energy dispersive X-ray analysis. Cr 2*p* and valence band XPS spectra were measured at 300 K using a VG-SCIENTA SES-2002 electron-energy analyzer with an energy resolution of 300 meV at a photon energy of 1200 eV. The Fermi level of the samples was set as that of an *in situ* evaporated gold foil which was in electrical contact with the sample. The O *K*-edge XAS spectra were measured at 300 K by the total-electron-yield method.

3 Results and Discussion

In order to examine the changes of the valence numbers of Cr by the oxidation and fluorination of the Sr_2IrO_4 thin films, we performed Cr *L*-edge XAS measurements, as shown in Fig. 1. It is known that the shape of Cr *L*-edge XAS spectrum of Cr^{4+} is very different from that of Cr^{3+} and that the valence number of Cr can be roughly estimated from the linear combination of Cr^{4+} and Cr^{3+} XAS spectra [5]. As seen in Fig. 1, the positions of the highest L_3 and L_2 peaks (578.7 eV and 587 eV) of the oxidized film were almost the same as those of the $SrCrO_3$ reference, indicating that the oxidized film had Cr^{4+}. Thus, we determined the chemical formula of the oxidized film as $SrCrO_3$. Note that the peak at ~582 eV was not observed in the oxidized film, which may be due to a change in Cr-O bond lengths associated with lattice strain and/or degraded crystallinity. On the other hand, the valence numbers of Cr in both precursor and fluorinated films were estimated to be 3.6 ± 0.1 by linearly combining the spectra of the oxidized film (Cr^{4+}) and $LaCrO_3$ reference [6] (Cr^{3+}). Assuming $x + y = 3$ in $SrCrO_xF_y$, the chemical composition of the fluorinated film can be estimated as $SrCrO_{2.6}F_{0.4}$. Note that our fluorinated film had a higher fluorine content than polycrystalline bulk sample, $SrCrO_{2.8}F_{0.2}$ [4], probably reflecting a higher reactivity of thin films than bulk because of larger surface areas and smaller volumes.

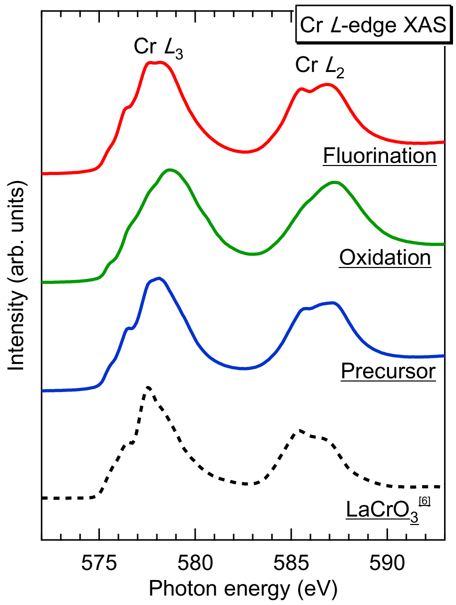

Fig. 1: Cr *L*-edge XAS spectra of the $SrCrO_{2.8}$ precursor film (blue line), the oxidized film annealed at 250 °C in air (green line), and the film fluorinated with PVDF at 250 °C (red line). The reference spectrum of the $LaCrO_3$ (Cr^{3+}) [6] is also shown in the figure.

The electronic structures of the valence and conduction bands were probed by synchrotron XPS and O *K*-edge XAS measurements. Fig. 2(a) shows the valence-band XPS spectra of the $SrCrO_{2.8}$, $SrCrO_3$, and $SrCrO_{2.6}F_{0.4}$ films. The valence-band spectrum of the $SrCrO_{2.8}$ film mainly consists of three structures, labeled as *B*, *C*, and *D*. According to previous density functional theory (DFT) calculations and XPS measurements [2], the structures *B*, *C*, and *D* can be assigned as incoherent parts of the Cr 3*d* t_{2g}, O 2*p* non-bonding, and O 2*p* bonding bands, respectively. In the $SrCrO_3$ film, the structures *C* and *D* are rigidly shifted to lower binding energies by 0.25 eV, thereby representing the chemical-potential shift associated with electron doping. Near the Fermi level (E_F), as shown in the inset of Fig. 2(a), the structure *B* was suppressed and a coherent part of Cr 3*d* t_{2g} (structure *A*) evolved owing to the strong electron correlation effects, similar to other strongly correlated metallic transition metal oxides, such as $SrVO_3$, $La_{1-x}Sr_xMnO_3$, and $Ca_{1-x}Sr_xRuO_3$ [7-9]. On the other hand, in the $SrCrO_{2.6}F_{0.4}$ film, a gap opened at E_F and the structure *B* was enhanced, which was consistent with the insulating behavior of the $SrCrO_{2.6}F_{0.4}$ film. The positions of the structures *C* and *D* were the same as those of the $SrCrO_{2.8}$ film, which was consistent with the XAS results, showing that $SrCrO_{2.8}$ and $SrCrO_{2.6}F_{0.4}$ films had the same Cr valence numbers. In addition, a new spectral structure *E* appeared around the binding energy of 7−10 eV. Considering higher electronegativity of fluorine than oxygen, the structure *E* is assignable to the F 2*p* bonding states.

Fig. 2(b) shows the O *K*-edge XAS spectra of the $SrCrO_{2.8}$, $SrCrO_3$, and $SrCrO_{2.6}F_{0.4}$ films measured using linearly polarized light, where the angle between the incident beam and the surface normal (θ_{inc}) was set at 60°. The O *K*-edge XAS spectra correspond to transitions into unoccupied O 2*p* states hybridized with Cr 3*d* and Sr 4*d*. As seen in Fig. 2(b), the peaks at 527–534 eV and those at 534–540 eV can be assigned to the Cr 3*d*-derived states (structures *F*, *G*, *H*, and *I*) and Sr 4*d*-derived states, respectively, by comparing the O *K*-edge XAS spectrum of the $SrCrO_3$ film [6]. Referring to the reported DFT theory calculations of $SrCrO_3$ and CrO_2 [2,10], we assigned the structure *F* to excitations of the unoccupied $t_{2g}\uparrow$ band, the structures *G* and *H* to the combination of unoccupied $e_g\uparrow$ and $t_{2g}\downarrow$, and the structure *I* to the unoccupied $e_g\downarrow$ band. The structure *F* of the $SrCrO_{2.6}F_{0.4}$ film is located at 528.3 eV, which is 0.3 eV higher than that of the $SrCrO_3$ film. This suggests spectral weight transfer from the coherent part to the incoherent part with fluorination due to strong electron correlation effects. Moreover, the peak intensity of the structure *F* of the $SrCrO_{2.6}F_{0.4}$ film was smaller than that of the $SrCrO_3$ film. This is mainly due to the decrease in Cr valence number, as seen in the case of $La_{1-x}Sr_xCrO_3$ thin films [6]. On the other hand, the $SrCrO_{2.6}F_{0.4}$ film showed a larger intensity than the $SrCrO_{2.8}$ film, although the Cr valence numbers were the same. This may be due to local distortion of Cr-O bonds, because XAS using linearly polarized light is sensitive to the angle between the incident beam and the axes of O 2*p* orbitals due to the dipole selection rule [11].

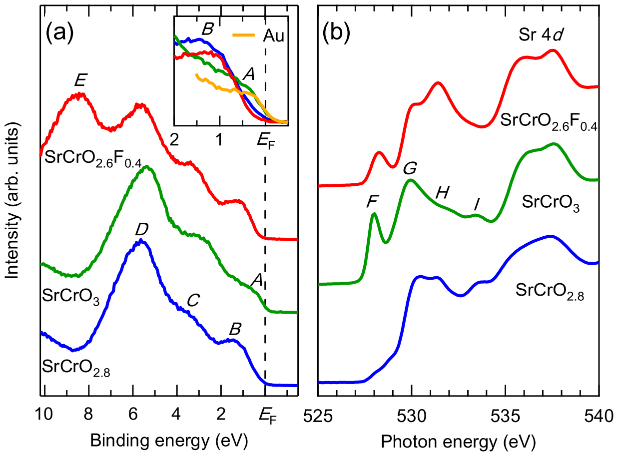

Fig. 2: (a) Valence-band XPS spectra of the $SrCrO_{2.8}$ (blue line), $SrCrO_3$ (green line), and $SrCrO_{2.6}F_{0.4}$ films (red line). The inset of (a) shows the valence-band spectra close to E_F, along with the spectrum from Au foil for energy calibration purposes (gold line). (b) O *K*-edge XAS spectra of the $SrCrO_{2.8}$ (blue line), $SrCrO_3$ (green line), and $SrCrO_{2.6}F_{0.4}$ films (red line) measured at $\theta_{\mathrm{inc}} = 60°$.

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