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Ru oxidation states in fluorinated Ca_2RuO_4 thin films revealed by X-ray photoemission spectroscopy

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1 Introduction

Layered ruthenium oxyfluorides have various crystal structures and Ru oxidation states and exhibit unique physical properties. While various layered ruthenates have reportedly been topochemically fluorinated with Sr as *A* sites, the fluorination of layered ruthenates containing smaller Ca ions has not been investigated. In this study, we fabricated phase-pure and single-crystalline thin films of fluorinated Ca_2RuO_4 on $LaSrAlO_4$ (001) substrates *via* topochemical fluorination of the Ca_2RuO_4 precursor using polyvinylidene fluoride and characterized the films. We found that the obtained fluorinated thin films had a chemical composition of $Ca_2RuO_{2.5}F_2$ and a Ru^{3+} state, as determined by energy-dispersive X-ray spectroscopy (EDS) and X-ray photoemission spectroscopy (XPS).

2 Experiment

Layered perovskite Ca_2RuO_4 precursor films were grown on $LaSrAlO_4$ (001) substrates using the pulsed laser deposition and solid-phase epitaxy techniques. The Ca_2RuO_4 precursor films were subsequently fluorinated by heating with PVDF under Ar gas flow at 220 °C for 12 h.

The crystal structures of the films were characterized by X-ray diffraction analysis conducted using Cu-*Kα* radiation. The chemical compositions were determined through EDS in conjunction with a scanning electron microscope. Ru 3*p* and Ca 2*p* 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 that was in electrical contact with the sample.

3 Results and Discussion

To investigate the valence of Ru, core-level XPS spectra of Ru 3*p* and Ca 2*s* for the Ca_2RuO_4 and fluorinated films were measured, as shown in Fig. 1. In the spectrum of the Ca_2RuO_4 film, the Ru spin–orbit split doublet—$3p_{1/2}$ and $3p_{3/2}$—and the Ca 2*s* peak were clearly observed at binding energies (E_b) of 486.3, 464.2, and 438.2 eV, respectively. Upon fluorination, the Ru 3*p* peaks shifted to a 0.5 eV lower binding energy, suggesting that the valence of Ru in the fluorinated film is 3+, which is consistent with the chemical composition determined by EDS. This XPS result is in contrast to the fluorination of $Sr_2Ru^{4+}O_4$ to $Sr_2Ru^{4+}O_3F_2$, in which no peak shift of Ru 3*p* was observed [1]. It is speculated that the larger lattice distortion in Ca_2RuO_4, which originates from the smaller ionic radius of Ca, leads to the easier release of oxygen from the RuO_6 octahedra. Considering the EDS and XPS (Fig. 1) results, we determined the chemical composition of the fluorinated thin film as $Ca_2RuO_{2.5}F_2$. In contrast to the Ru 3*p* peaks, the Ca 2*s* peak shifted to a 1.2 eV higher binding energy upon fluorination, which suggests a change in the bonding environment around Ca [1-3].

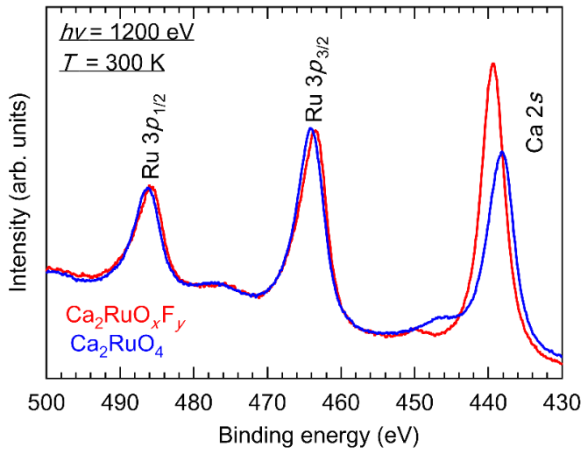

Fig. 1: Ru 3*p* and Ca 2*s* XPS spectra of the Ca_2RuO_4 precursor and the fluorinated films. The spectra were normalized by the peak height corresponding to Ru $3p_{3/2}$.

References

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