Ru oxidation states in fluorinated Ca$_2$RuO$_4$ 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$_2$RuO$_4$ on LaSrAlO$_4$ (001) substrates via topochemical fluorination of the Ca$_2$RuO$_4$ precursor using polyvinylidene fluoride and characterized the films. We found that the obtained fluorinated thin films had a chemical composition of Ca$_2$RuO$_2$$_{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$_2$RuO$_4$ precursor films were grown on LaSrAlO$_4$ (001) substrates using the pulsed laser deposition and solid-phase epitaxy techniques. The Ca$_2$RuO$_4$ 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 3p and Ca 2p 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 3p and Ca 2s for the Ca$_2$RuO$_4$ and fluorinated films were measured, as shown in Fig. 1. In the spectrum of the Ca$_2$RuO$_4$ film, the Ru spin–orbit split doublet—3p$_{1/2}$ and 3p$_{3/2}$—and the Ca 2s peak were clearly observed at binding energies (E$_b$) of 486.3, 464.2, and 438.2 eV, respectively. Upon fluorination, the Ru 3p 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$_2$RuO$_4$ to Sr$_2$Ru$_4$O$_8$F$_2$, in which no peak shift of Ru 3p was observed [1]. It is speculated that the larger lattice distortion in Ca$_2$RuO$_4$, 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$_2$RuO$_2$$_{2.5}$F$_2$. In contrast to the Ru 3p peaks, the Ca 2s peaks shifted to a 1.2 eV higher binding energy upon fluorination, which suggests a change in the bonding environment around Ca [1-3].
Fig. 1: Ru 3p and Ca 2s XPS spectra of the Ca$_2$RuO$_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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