

## Synthesis and electronic states of $\text{NdNiO}_{3-x}\text{F}_x$ thin films prepared by soft-chemistry method

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### 1 Introduction

Soft chemistry or low-temperature synthesis is a practical synthetic approach toward novel complex oxides [1]. Among them, topotactic reactions which exploit higher mobility of particular elements over others enable easier access to metastable compounds due to its kinetic nature. A large number of mixed anion materials such as oxide hydrides and oxide fluorides have been synthesized so far in a topotactic manner. Though this method has mainly been applied to powder samples, it was recently found that use of topotactic approach for fabricating thin films can reduce the reaction temperature owing to the enhanced reactivity originating from enlarged surface-to-volume ratios in thin samples [2]. However, previous topotactic studies on thin films are limiting to fabricate for well-known compounds rather than discovering novel complex oxides. In this study, we topotactically introduced fluorine ( $\text{F}^-$ ) into perovskite-type  $\text{NdNiO}_3$ , a correlated material with metal-insulator transition at 200 K. As a result, it was found that fluorine ions were partially substituted for oxygen ions to form a mixed perovskite  $\text{NdNi}(\text{O},\text{F})_3$ . Furthermore, spectroscopic measurements revealed that valence states of nickel ions changed from +3 to +2, confirming electron incorporation.

### 2 Experiment

The 80-nm-thick epitaxial  $\text{NdNiO}_3$  thin films as precursors were deposited on  $\text{SrTiO}_3$  (STO) (001) substrates by pulsed laser deposition. Fluorine was introduced into the precursor samples by low-temperature reaction with polyvinylidene fluoride (PVDF). The fluorination was performed under flowing Ar at 350 °C. To investigate the crystal structures and chemical compositions of the samples, we performed X-ray diffraction (XRD) measurements and Al  $K\alpha$  X-ray photoemission spectroscopy (XPS), respectively. Electronic states of the obtained thin films were studied by X-ray absorption spectroscopy (XAS) at the BL-2A of the Photon Factory, KEK, using the total electron-yield method at 300 K.

### 3 Results and Discussion

Figure 1 shows out-of-plane XRD patterns of the precursor and fluorinated  $\text{NdNiO}_3$  films for different reaction times ( $t_F$ ). The precursor film showed 002 diffraction at 48.05°, from which its lattice constant was

calculated to be 3.78 Å. After the reaction with PVDF, the peak shifted toward lower angle, indicating the elongation of lattice dimensions (3.78, 3.95, 3.98, 4.05, and 4.04 Å for the precursor and films with  $t_F = 1, 3, 12$  and 24 h, respectively). These results suggest that fluorine was substituted for oxygen ( $\text{O}^{2-} \rightarrow \text{F}^- + \text{e}^-$ ), which would change the valence of Ni from 3+ to mixed 2+/3+. Depth-resolved composition analysis by sputter-assisted X-ray photoemission spectroscopy revealed that fluorine distribution was almost homogeneous inside the films except the surface having the large amount of fluorine precursor. Assuming the ideal (F+O)/Ni ratio of 3, the compositions of the films were deduced to be  $\text{NdNiO}_{2.5}\text{F}_{0.5}$  for  $t_F = 3$  h and  $\text{NdNiO}_{2.1}\text{F}_{0.9}$  for  $t_F = 12$  h, i.e. the amount of fluorine could be controlled by  $t_F$ .

To examine chemical valence states of nickel atoms, we performed XAS measurements. Figure 1(b) shows Ni  $L$ -edge XAS spectra of identical samples. The spectral shape of both Ni  $L_3$  and  $L_2$  edges changed dramatically after fluorine doping. The observed spectra demonstrate that fluorinated samples mainly contained  $\text{Ni}^{2+}$  ions in contrast to oxide samples which showed  $\text{Ni}^{3+}$ -like peak shapes. These results indicate that the electronic states of nickel oxide thin films can be certainly altered by partial anion substitution.

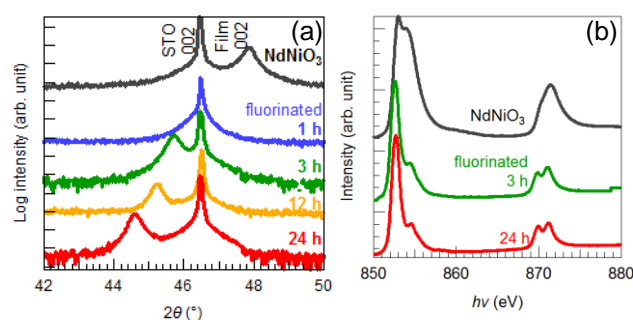


Fig. 1. (a) XRD  $2\theta$ - $\theta$  patterns of the  $\text{NdNiO}_{3-x}\text{F}_x$  thin films depending on reaction times. (b) Ni  $L$ -edge XAS spectra of the films.

### References

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