

Electronic states of perovskite-type bismuth iron oxyfluoride thin films

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1 Introduction

Multiferroic materials such as BiFeO₃ have attracted attention because of the unique property of having both ferroelectricity and magnetic ordering. Recently, polycrystalline forms of bismuth iron oxyfluoride (Bi_{1-x}Ba_xFeO_{3-x/2}F_x; $x = 0.2, 0.3$), in which fluorine replaces some of the oxygen in Ba-doped bismuth iron oxide Bi_{1-x}Ba_xFeO_{3-x/2}, have been synthesized and exhibit a G-type antiferromagnetic ordering with Néel temperature above 770 K [1]. First-principles calculations also predicted that Bi_{0.75}Ba_{0.25}FeO_{2.75}F_{0.25} exhibits multiferroic properties [2]. In this study, we fabricated epitaxial thin films of Bi_{1-x}Ba_xFeO_{3-x/2}F_x ($x = 0, 0.1, 0.2, 0.3$) and Bi_{0.6}Ba_{0.4}FeO_{3-y}F₂ on SrTiO₃ (001) substrates *via* topochemical fluorination of the Bi_{1-x}Ba_xFeO_{3-x/2} precursor and subsequently measured their electronic states by X-ray photoemission spectroscopy (XPS).

2 Experiment

Precursor Bi_{1-x}Ba_xFeO_{3-x/2} ($x = 0, 0.1, 0.2, 0.3, 0.4$) epitaxial thin films were deposited on SrTiO₃(100) substrates doped with 0.5 wt% Nb by pulsed-laser deposition. The obtained Bi_{1-x}Ba_xFeO_{3-x/2} thin films were further subjected to fluorination using polyvinylidene difluoride at 200 °C for 12 h in Ar gas flow. The typical thickness of the films was set to ~130 nm.

Crystal structures of the films were investigated by X-ray diffraction, and chemical compositions were evaluated by energy dispersive X-ray analysis. F 1s, Fe 2p, and valence band XPS spectra were measured at 300 K using a VG-SCIENITA SES-2002 electron-energy analyzer with an energy resolution of 300 meV at a photon energy of 1200 eV. The Fermi level was calibrated against the C 1s signal.

3 Results and Discussion

In order to investigate whether F has been introduced into the fluorinated films, the core-level XPS spectra of F 1s and Bi 4p_{3/2} were obtained for the Bi_{1-x}Ba_xFeO_{3-x/2} ($x = 0, 0.1, 0.2, 0.3, 0.4$) precursor and fluorinated films. Figure 1 shows the F 1s and Bi 4p_{3/2} core-level XPS spectra of the fluorinated Bi_{1-x}Ba_xFeO_{3-x/2} ($x = 0, 0.2$) films. The F 1s

peak was clearly observed in the $x = 0.2$ film, confirming the presence of F in the film. The F 1s peaks were also observed in the XPS spectra of the other Bi_{1-x}Ba_xFeO_{3-x/2} ($x = 0.1, 0.3, 0.4$) fluorinated films. On the other hand, as shown in Fig. 1, no F 1s peak was observed in the spectrum of BiFeO₃. These results suggest that oxygen vacancies in the precursor films play an important role in the introduction of fluorine.

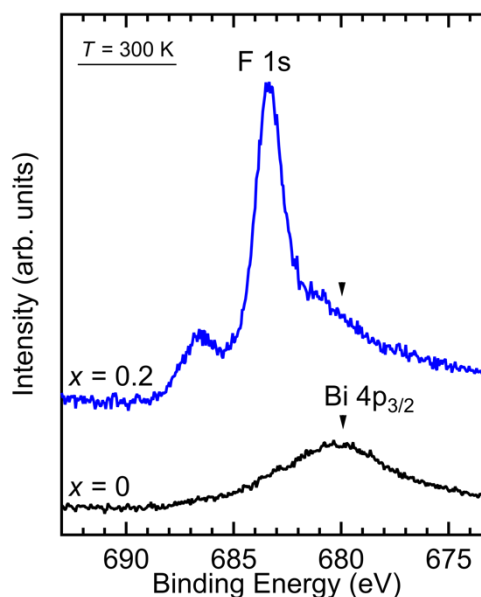


Fig. 1: F 1s and Bi 4p_{3/2} core-level XPS spectra of the fluorinated Bi_{1-x}Ba_xFeO_{3-x/2} ($x = 0, 0.2$) acquired at 300 K.

Figure 2 shows the Fe 2p core-level XPS spectra of Bi_{0.8}Ba_{0.2}FeO_{2.9} precursor and fluorinated Bi_{1-x}Ba_xFeO_{3-x/2} ($x = 0, 0.1, 0.2, 0.3, 0.4$) films. Each core-level spectrum is characterized by an Fe 2p_{1/2}–Fe 2p_{3/2} doublet and a weak satellite located between the doublet peaks; the positions of these peaks were unaffected by fluorination. The Fe 2p satellite peak and its position is known to be very sensitive to the Fe oxidation state [3]. A comparison of the spectra in Fig. 2 with previously reported XPS spectra of various

Fe oxides of Ref. 3 revealed that Fe exists in its trivalent oxidation state in the precursor and fluorinated films. It was also confirmed that the $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_{3-x/2}$ precursor films with other compositions have trivalent Fe ions. Thus, it can be concluded that topochemical fluorination at 200 °C does not affect the Fe oxidation state.

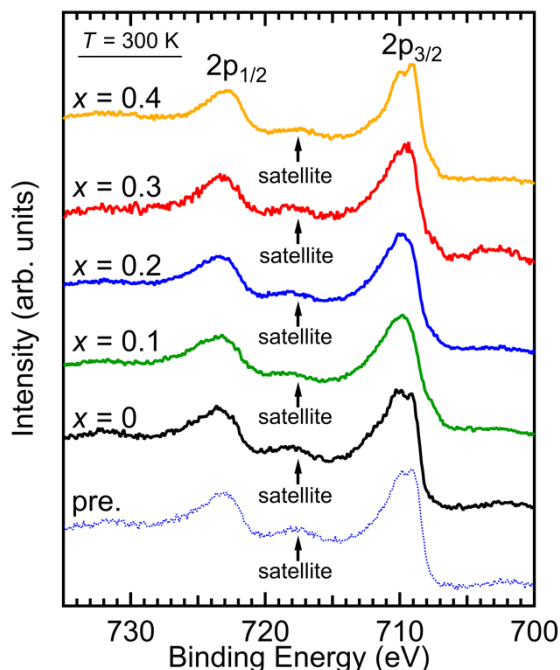


Fig. 2: Fe 2p core-level XPS spectra of $\text{Bi}_{0.8}\text{Ba}_{0.2}\text{FeO}_{2.8}$ precursor and fluorinated $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_{3-x/2}$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) films acquired at 300 K.

Figure 3 shows the valence band spectra of the $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_{3-x/2}$ ($x = 0.1, 0.2, 0.3$) precursor and fluorinated films. These spectra have been normalized to the maximum peak heights. According to density of states predicted by the density functional theory calculations [2], the structures *A* and *B* can be derived from O 2p bonding states and Fe 3d bonding states, respectively. In addition, in Fig. 3(b) and 3(c), the spectra of the fluorinated films have new spectral structure *C*: ~6 eV for $x = 0.2$ and ~5.5 eV for $x = 0.3$, respectively. This new state is due to the 2p bonding states associated with fluorine, which has a higher electronegativity than oxygen. Furthermore, for $x = 0.2$ and $x = 0.3$ fluoride films, attenuation of the structure *A* was observed. The degree of attenuation is greater for $x = 0.3$, which has a higher fluorine content, to the extent that the valence band maximum appears to shift to a higher region (Fig. 3(c)). These results suggest that the valence band change of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_{3-x/2}$ films by fluorination is different depending on their composition, and the change is larger in the more fluorine-rich films.

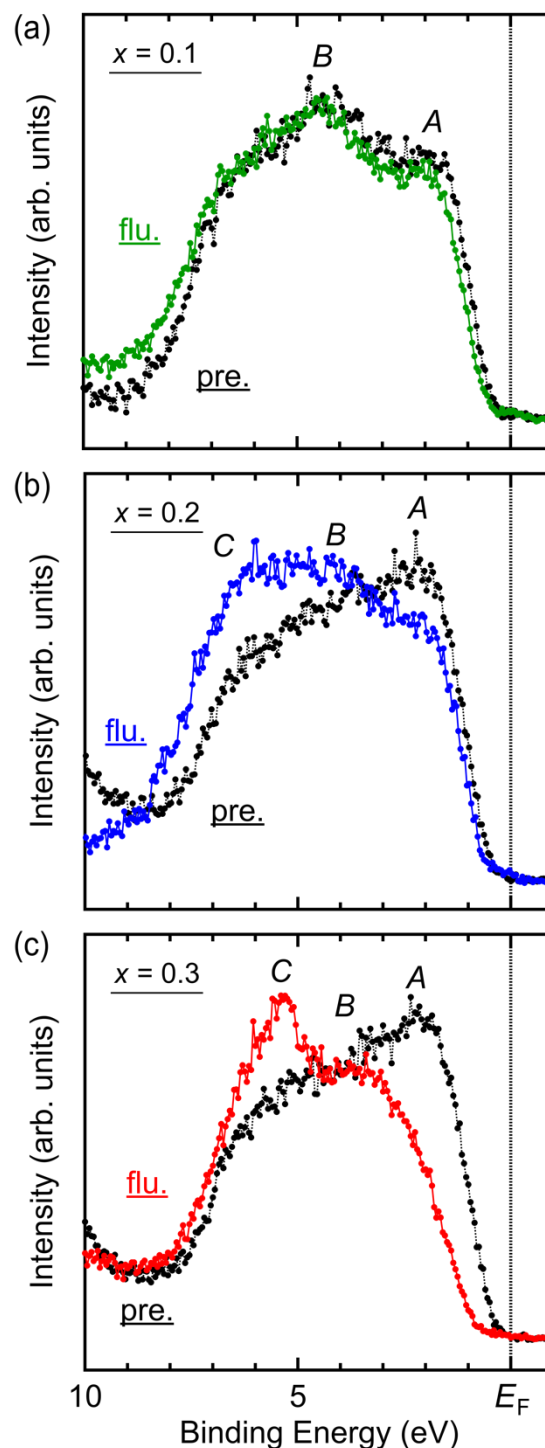


Fig. 3: Valence band XPS spectra of the precursor and fluorinated $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_{3-x/2}$ (a) $x = 0.1$, (b) $x = 0.2$, and (c) $x = 0.3$ films acquired at 300 K.

References

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