Magnetic origin in Ba(Fe$_{1-x}$Zr$_x$)O$_{3-\delta}$ single-crystal films on SrTiO$_3$ substrates

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Introduction
Coupling between magnetic and electric polarizations has attracted considerable attention, due to a possible application in spintronics devices, sensors, information storage media and so on [1]. Under these circumstances, we have intensively studied on one of the ABO$_3$-type oxide, Ba(Fe$_{1-x}$Zr$_x$)O$_{3-\delta}$ (BFZO) single crystalline films that exhibit dielectric and ferromagnetic-like natures even at room temperature. Then, we revealed that the Zr substitution, especially for the $x=0.8$ and 0.9 samples, enhanced the ferromagnetic spin alignment of the Fe ions, although the tetravalent Zr ions were thought to be nonmagnetic [2]. However of this, the detailed mechanism of the enhancement of the ferromagnetic spin alignment still remains to be uncertain. In order to clarify this, we investigated the spatial distribution and valence states of the Fe ions in the BFZO thin films, which may significantly correlate with their magnetic behavior.

Results and Discussion
The single crystalline Ba(Fe$_{1-x}$Zr$_x$)O$_{3-\delta}$ ($x=0.6$-$0.9$) thin films were deposited on (100) SrTiO$_3$ substrates by pulsed laser-beam deposition. Figure 1 shows the Fe$^{2+}$ core level XPS spectra for the $x=0.8$ sample, using a synchrotron soft-X-ray radiation of $h\nu=2100$ and 3100 eV. As clearly indicated, the peak with higher binding energy significantly stands out with increasing the radiation energy. Bocquet et al. investigated the electronic structure of the Fe$^{4+}$ perovskite oxide SrFeO$_3$ by XPS, and they concluded that the large increase in charge at the Fe site leads to a chemical shift to a higher binding energy. Hence, these results suggest that the Fe ions in the majority part of the film excepting the most outer surface can be considered to have the tetra valent state. In addition, the peak positions of the Fe$^{2+}$ core level spectra for the $x=0.6$-$0.8$ BFZO samples significantly are shifted toward the larger binding energy side as the $x$ value increases. This simply means that the Zr substitution is thought to cause the change in the valence state from Fe$^{4+}$ to Fe$^{2+}$ ions due to the high oxydizability of Zr. Accordingly, the enhancement of ferromagnetic ordering in the present samples can be ascribed to the increasing in the relative number of the ferromagnetically superexchange coupling of Fe$^{4+}$-O-Fe$^{4+}$.

It should be noted here that the diffused contrast due to the presence of the strain field with an average diameter of 5-10 nm were patchily observed in the in-plane high resolution TEM micrographs. In addition, it was found that the Fe/Zr ratio in such regions was significantly larger than the averaging values of the whole film. Consequently, it can be speculated that the Fe$^{4+}$ ions substantially occupied the B-sites of the Perovskite structure in these regions.

In conclusion, the enhanced ferromagnetic ordering observed in the BFZO samples, can be ascribed to the Zr substitution that may preferentially produces the tetravalent Fe ions due to the high oxydizability of Zr. In addition, the spatially separated regions of the Fe-rich BFZO exhibiting the behavior of the ferromagnetic superexchange coupling of Fe$^{4+}$-O$^2-$Fe$^{4+}$ may form within the BFZO thin film. Incorporation of these two factors should lead to the enhanced ferromagnetic nature of the samples.

References

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