

XPS Study on Charge Ordering type Ferroelectric YbFe₂O₄ Thin Films

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Introduction

Recently, rare-earth iron oxide system RFe₂O₄ (R=rare earth Dy to Lu and Y) has received much attention as novel ferroelectrics. RFe₂O₄ has a rhombohedral crystal structure consisting of an alternate stacking of triangular lattices of rare-earth, iron and oxygen. An equal amount of Fe²⁺ and Fe³⁺ ion occupy crystallographically equivalent sites. Therefore, a charge interaction between iron ions, Fe²⁺ and Fe³⁺, leads to charge ordering state on the triangle lattice. Recently, Ikeda et al. reported the ferroelectricity by the charge ordering in LuFe₂O₄.¹ This finding is quite interesting from both physical and engineering points of view. However, it is reported that RFe₂O₄ phase is stable at extremely low oxygen partial pressure ($3.9 \times 10^{-6} \sim 1.2 \times 10^{-9}$ torr) and high temperature ($\sim 1200^\circ\text{C}$). Therefore exact control of oxygen partial pressure and quench are required to synthesize RFe₂O₄.

We have attempted to synthesize RFe₂O₄ in thin film form, because it can be expected that epitaxial effect on the thin film growth encourage the formation of RFe₂O₄ at more moderate condition and RFe₂O₄ thin films are useful for device application. In this study, we focused on the thin film growth of YbFe₂O₄, which can be synthesized at high oxygen pressure compared to other RFe₂O₄.

Experiments

YbFe₂O₄ thin films were grown on YSZ(111) single crystal substrates by pulsed laser deposition method. The crystal structure was characterized using x-ray diffraction and reciprocal space mapping. The mixed valence state of Fe ions (Fe²⁺/Fe³⁺) was evaluated using x-ray photoelectron spectroscopy (XPS).

Results and Discussion

The phase diagram of Yb₂O₃-Fe₂O₃-Fe system indicates that YbFe₂O₄ is synthesized at high temperature and reductive atmosphere. Therefore, the deposition was carried out over 800 °C and at low oxygen partial pressure ($\sim 1 \times 10^{-9}$ torr). As a result, it was found that YbFe₂O₄ thin films are obtained on YSZ substrates at a growth temperature of 900 °C which is 300 °C lower than the temperature where YbFe₂O₄ is thermodynamically stable. A large area reciprocal space mapping for the YbFe₂O₄ thin films is shown in Fig. 1. The diffraction spots from the films are identified as YbFe₂O₄ and growth orientation relationship of YbFe₂O₄ [0001]//YSZ [111] and YbFe₂O₄ [11-20]//YSZ [1-10] was determined.

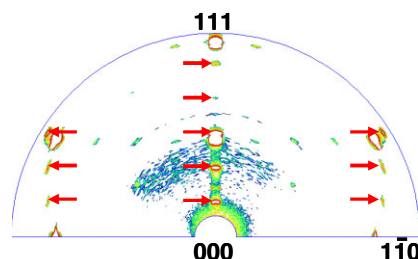


Fig. 1 Large area reciprocal space mapping for the YbFe₂O₄ thin film on a YSZ(111) substrate (Arrows indicate diffraction spots from YbFe₂O₄)

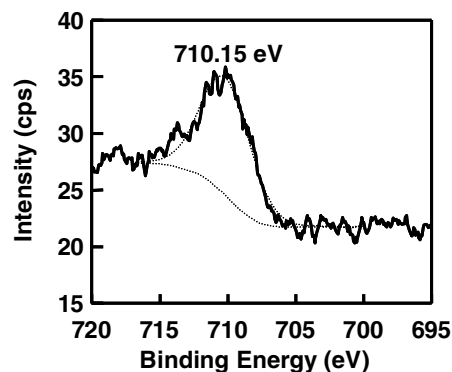


Fig. 2 Fe 2p_{3/2} core level XPS spectrum for the YbFe₂O₄ thin film.

To reveal the valence state of Fe ions, Fe 2p_{3/2} core level is evaluated using a synchrotron soft x-ray radiation of $h\nu=3100$ eV. The result is shown in Fig. 2. The Fe 2p_{3/2} core level is reported at 709.5 eV for Fe²⁺ and at 711.0 eV for Fe³⁺.² As can be seen in the XPS spectrum, Fe 2p_{3/2} core level of the YbFe₂O₄ thin films is not separated from each other but are positioned between these two values. Moreover, Fe 2p_{3/2} core level of 710.15 eV is close to the reported value of that for LuFe₂O₄ ceramic (710.2 eV). Therefore this results indicates that the valence state of Fe ions in the YbFe₂O₄ thin films is mixture of Fe²⁺ and Fe³⁺. Further investigations to reveal the ratio of Fe²⁺ and Fe³⁺ is in progress to characterize the oxygen nonstoichiometry, which has a large effect on the ferroelectricity of YbFe₂O₄.

References

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