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Crystal Growth of Electronic Ferroelectric, $YbFe_2O_4$ Film

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Abstract: In order to realize the ultra fast switching of the electric polarization, crystal growth of electronic ferroelectric, $YbFe_2O_4$ film was investigated. The film was deposited on *c*-oriented Al_2O_3 substrate using pulsed laser deposition method. Well oriented film was fabricated although the mixture phase of hexagonal (h-) $YbFeO_3$, Yb_2O_3, Fe_3O_4 was obtained. Pole figures indicated the growth of well-crystalline h-$YbFeO_3$, which has quite similar crystal structure to that of $YbFe_2O_4$. Crystal structure of improved film will be discussed.

1. Introduction

Much effort has been made to design functional materials with multi-ferroicity. If the ferroelectricity arises from the configuration of 3*d* electrons having different valence states, the direct coupling is expected between the ferroelectricity and magnetic property. Moreover, the electronic origin has advantages in the energy and the speed for the switching, compairing to the ordinal ferroelectrics.

RFe_2O_4 (R = rare earth ions) had been proposed as a candidate of such materials [1]. RFe_2O_4 is composed of doubly stacking iron triangular layers (*W*-layer) separated by single rare-earth triangular layer (*R*-layer) (Fig. 1). The equal amounts of Fe^{2+} and Fe^{3+} exist on the triangular lattices and the charge- and magnetic-orderings take place. The magnetic ordering is known to exhibit ferri-magnetism and the charge ordering is proposed to generate ferroelectricity [1]. If each *W*-layer consists of Fe^{2+} rich Fe-layer and Fe^{3+} rich Fe-lyer, each *W*-layer has microscopic electric polarization and their in-phase stacking generates ferroelectricity. As this ferroelectricity arises from electronic configuration, it has been called “electronic ferroelectricity” [2].

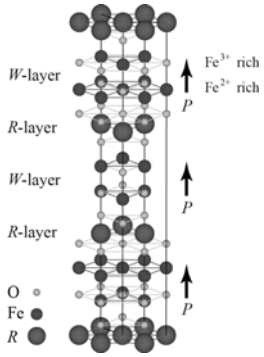

Fig. 1
Crystal structure of RFe_2O_4.

Although the existense of the electronic ferroelectricity had been questioned for recent decades [3], we scceeded in proving it by electric measurements and x-ray diffraction experiments [4,5]. We showed a clear polarization hysteresis loop as a function of applied electric field (*P*-*E* loop) in $YbFe_2O_4$. The ferroelectric transition temperatures were determined as 300 K and 100 K from the pyroelectric current measurements. As these temperatures are in good agreement with the developping teperature of the charge ordering, we concluded that the charge ordering is responsible for the ferroelectricity.

However, we found that the ferroelectric charge ordering coexist with antiferroelectric charge ordering, which is a little more stable. Therefore the majority phase was observed as the antiferroelectric in bulk. Although we also found that the electric field cooling enhances the formation of the ferroelectric phase [4,5], simple method to get single ferroelectric phase is required for the application.

One of the routes is to fabricate the thin film because thin film has the advantage in controlling the lattice parameter. The change of the lattice parameter may generate the difference in the electric interaction between iron ions. In this study, we investigated the crystal growth of $YbFe_2O_4$ film using pulsed laser deposition (PLD) method.

2. Experimental detail

A thin film was deposited on Al_2O_3(0001) at 730ºC by PLD method using KrF excimer laser (energy density = 2.5 J/cm^2, repetation rate = 1 Hz). During the deposition process, oxygen gas was flowed and the pressure was 7.2 x 10^{-5} Pa. The surface molohology was observed by atomic force microscope (AFM) (SII). The crystal strucuture was investigated from x-ray diffraction experiments (2θ-θ scan and pole figure) and depth profile of the atmic concentration using x-ray photoelectron spectroscopy with ion beam etching (ESCA-3400).

3. Results and Discussion

Fig. 2 shows the AFM images of the film surface. The surface consisted of 1 μm size of triangle shape grains. The step-terrace strucuture was observed in each grain although the height of the step was as high as ~5 nm.

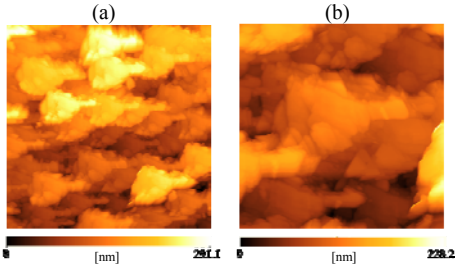

Fig. 2 AFM images of the film surface. (a) 5 x 5 μm, (b) 2 x 2 μm.

Fig. 3 shows the 2θ-θ x-ray diffraction pattern of the film. Three kinds of phase were obtained; hexagonal (h-) $YbFeO_3$, Yb_2O_3 and Fe_3O_4. h-$YbFeO_3$ consists of alternating stacking of Fe-layer and Yb-layer, which is quite similar crystal structure to that of $YbFe_2O_4$. Although $YbFe_2O_4$ phase was not obtained, all phases were well oriented, which is consistent with the layered structure on the surface (Fig. 2).

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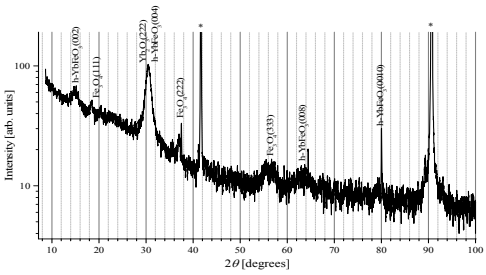

Fig. 3 2θ-θ x-ray diffraction pattern of the film. The asterisk indicates the peak arising from the Al_2O_3 substrate.

In order to understand the in-plane orientation of the film, pole figures were obtained. Fig. 4 shows the pole figures around (a) 2θ = 30º, 40º, (b) 15º, (c) 35º and 65º. Comparing 2θ values of powder diffraction patterns [6-8], the origin of the observed peaks can be estimated as follows; Al_2O_3 for 2θ = 40º, h-$YbFeO_3$ for 2θ = 15º, Yb_2O_3 for 2θ = 30º, and Fe_3O_4 for 2θ = 35º and 65º.

As shown in Fig. 4(a), Al_2O_3 substrate showed two peaks having 120º angle between each other, which is consistent with the three-fold axis. Around 2θ = 15º, h-$YbFeO_3$ showed only one peak in the angle area showed in Fig. 4(b), indicating the existence of the three fold axis. As the φ position is the same as that of Al_2O_3, it is indicated that h-$YbFeO_3$ had the same orientation as that of Al_2O_3. The existence of the clear three-fold axis suggests the well-crystalline h-$YbFeO_3$ film. Around 2θ = 30º, Yb_2O_3 showed doubly splitting peaks around 30º tilting point to Al_2O_3 in-plane, indicating that the Yb_2O_3 grew with lower symmetry and in-plane tilting angle of 30º to Al_2O_3 (Fig. 4(a)). Around 2θ = 35º and 65º, Fe_3O_4 showed two sets of six peaks, indicating the existence of two kinds of grains having in-plane tilting angle of 30º to each other (Fig. 4(c)). The intensity of one set of peaks was a little lower at the same φ position as that of Al_2O_3, indicating that the majority Fe_3O_4 grains have 30º of in-plane tilting angle to Al_2O_3. The six fold axes may indicate some stacking faults of Fe_3O_4. The two sets of peaks suggest that Fe_3O_4 phase appeared twice during the growing process due to the change of the growing condition or lattice matching with neighboring layers having different phases.

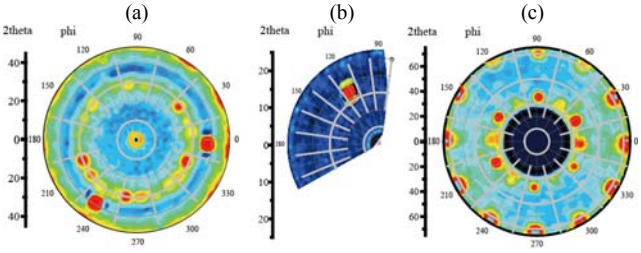

Fig. 4 pole figures around (a) 2θ = 30º, 40º, (b) 15º, (c) 35º and 65º.

In order to investigate the relation between the growing phase and growing condition or lattice matching, depth profile of the atomic concentration was obtained. Fig. 5 shows the etching time dependence of the atomic concentration ratio of Fe/Yb. The Fe:Yb ratio was 1:1 at the initial stage of the growth. With increasing the growing time, the Fe:Yb ratio increased to 2 and decrease to 1. At the final stage, the Fe:Yb ratio increased toward 2 again. This result suggests the formation of h-$YbFeO_3$ at the initial stage followed by the sccessive growths of Fe_3O_4 and Yb_2O_3. At the final stage Fe_3O_4 may have grown again.

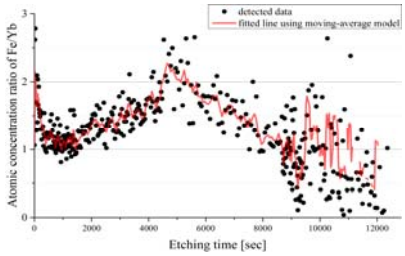

Fig. 5 Depth profile of the atomic concentration ratio of Fe/Yb. The data was fitted using moving-average model.

As for the average Fe/Yb ratio, it was smaller than 2 in total. This result suggests that Fe atom vaporization during deposition due to its lower vapor pressure than Yb. The quite low back pressure during the deposition may have enhanced the vaporization of Fe atom by keeping the collision speed high to the substrate. The inactive gas is required to increase the back pressure and decrease the collision speed. Another way to get $YbFe_2O_4$ phase may be to decrease the oxygen partial pressure. The pole figures indicated that the two kinds of iron oxides showed quite different crystalline; h-$YbFeO_3$ showed much more good crystalline than Fe_3O_4. Although the crystal structure is of course included as one of the origins of this difference, the valence of Fe ions may also responsible for the difference. The average varence of Fe ion in Fe_3O_4 is +8/3, which is lower than +3 in h-$YbFeO_3$. As that of $YbFe_2O_4$ is +5/2 and lower than Fe_3O_4, its stable oxygen partial pressure may be lower.

4. Summary

The crystal growth of $YbFe_2O_4$ film was investigated using PLD method. Well-oriented mixture phase of h-$YbFeO_3$, Yb_2O_3 and Fe_3O_4 was obtained. The crystal structure of improved film will be discussed.

5. References

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