Observation of Fe/BaTiO₃ Interface State by X-Ray Absorption Spectroscopy*

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Electric field-induced change of magnetic properties in ferromagnetic Fe thin film grown on a ferroelectric BaTiO₃ (BTO) substrate is studied by means of x-ray absorption spectroscopy. We find that a few nm Fe oxide layer exists at the Fe/BTO interface when the Fe thickness is 8 nm, in which the film shows in-plane magnetization. The x-ray magnetic circular dichroism analysis reveals that the coercive field, H_c , of Fe shows a hysteresis behavior as a function of the electric field, and larger H_c is observed at $\sim \pm 3$ kV/cm. On the other hand, it is found from the extended x-ray absorption fine structure analysis that the Fe-O bond distance shows a similar electric field dependence to that of H_c , and shorter distance is observed at $\sim \pm 3$ kV/cm. Therefore, it is assumed that the H_c strongly depends on the ferroelectric domain structure of BTO, and larger H_c is observed for the multi-domain structure. We suppose that shrinking of the Fe-O distance caused by the domain formation leads to an enhancement of H_c due to the island-like localization of the interface Fe oxide. [DOI: 10.1380/ejsnt.2015.139]

Keywords: X-ray absorption spectroscopy; Extended X-ray absorption fine structure (EXAFS); Field effect; Magnetic films; X-ray magnetic circular dichroism (XMCD)

I. INTRODUCTION

Electric field-induced magnetization switching has a great potential to reduce the energy consumption in the magnetization switching process. The idea to control magnetization by an electric field has been proposed as a multiferroic concept [1]. For instance, BiFeO₃ has been extensively investigated as one of the most promising multiferroic materials. Unfortunately, the temperature at which such materials show the multiferroic property is usually much below the room temperature in the case of single compound materials. On the other hand, it was reported that the coercive field of a ferromagnetic Fe thin film grown on a ferroelectric BaTiO₃ (BTO) substrate changes when a voltage is applied between the Fe film and the bottom of the substrate even at room temperature [2, 3]. More recently, it was reported that the magnetic moment of Fe film can be controlled by the polarization reversal of BTO at room temperature [4, 5]. Since the mechanism of the voltage-induced effects on the magnetic properties has not been clearly understood, we have performed the x-ray magnetic circular dichroism (XMCD) and extended x-ray absorption fine structure (EXAFS) measurements for the Fe thin films grown on the BTO substrate, and observed the change in the interface state induced by polarization reversal of the substrate.

II. EXPERIMENTAL

Fe films were grown by electron bombardment evaporation in a high vacuum chamber, in which the BTO(001) single crystal substrate temperature was kept at 373 K for improving epitaxy under the tetragonal phase. The tetragonal BTO and bcc Fe have a good lattice matching ($\sim 1.4\%$), and layer-by-layer growth is expected [3].

FIG. 1. XMCD-hysteresis curves measured at Fe L_3 absorption edge of 8 nm Fe thin film on the BTO substrate at different electric fields, E .

A Au cover layer was deposited on the film to make an electric contact to the film, and the voltage of ± 1 kV was applied during the measurement between the film surface and the bottom of the substrate. BTO is known to exhibit a lattice expansion along the applied electric field and the polarization direction is assumed to be perpendicular to the sample plane.

Fe L -edge XMCD spectra were taken at the soft x-ray undulator beamline BL-16A of the Photon Factory, Japan (KEK-PF) [6]. All the XMCD spectra were recorded at room temperature in the fluorescence-yield mode. The polarization switching between opposite circular polarizations was applied to the XMCD measurement [7, 8]. The XMCD measurements were performed in an applied mag-

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FIG. 2. Electric field dependence of the residual magnetization, M_0 (a), and the coercive field, H_c (b). The electric field is changed from 10 kV/cm, as indicated by the arrows.

FIG. 3. XMCD spectra of 8 nm Fe film on the BTO substrate measured at the electric field of 10, 0 and -10 kV/cm.

FIG. 4. Fourier transforms of the Fe K -edge EXAFS function $k^2\chi(k)$ of 8 nm Fe film on the BTO substrate.

netic field of 500 Oe. The applied magnetic fields were parallel and antiparallel to the x-ray propagation direction. We adopted the grazing incidence configuration for the XMCD measurements, in which the angle between the surface normal and the x-ray beam, θ , was 60°.

The Fe K -edge EXAFS spectra were measured at the bending magnet beamline BL-12C of KEK-PF. All the spectra were recorded at room temperature in the fluorescence-yield mode with a 19-element solid-state detector. The EXAFS spectra were taken at normal incidence configuration at $\theta = 0^\circ$, in which the in-plane structural information was sensitively detected.

III. RESULTS AND DISCUSSION

Figure 1 displays the XMCD-hysteresis curves measured at Fe L_3 absorption edge (707.5 eV) of 8 nm Fe thin film on the BTO substrate at different electric fields, E . All the curves show small squareness ratio, which indicates that the Fe film shows weak in-plane magnetic anisotropy. Under such magnetic conditions, the magnetic domain structure of Fe could be influenced by the ferroelectric domain structure of the BTO substrate.

Figure 2 shows the electric field dependence of the residual magnetization, M_0 (a), and the coercive field, H_c (b). The electric field is changed from $E = 10$ kV/cm, as indicated by the arrows in the figure. Both M_0 and H_c show the maximum at $\sim \pm 3$ kV/cm, and the hysteresis behavior is observed. Indeed, it is known that the ferroelectric domain of BTO under the tetragonal phase shows multi-domain structure after going through the zero-field during the polarization reversal. We assume that the coercive field of Fe increases because of the multi-domain formation, which obstructs the movement of the magnetic

domains. Figure 3 displays the XMCD spectra of 8 nm Fe film on the BTO substrate. No significant difference by the polarization reversal is observed in the spectra. This result indicates that the change in M_0 and H_c by the polarization reversal is not caused by the change in the electronic state of Fe itself, but by the ferroelectric-domain structure of the BTO substrate. Because it is expected that the domain structure of BTO affects the crystal structure of Fe film, we apply Fe K -edge EXAFS structural analysis to the film.

Figure 4 shows Fourier transforms of the Fe K -edge EXAFS function $k^2\chi(k)$ of 8 nm Fe film on the BTO substrate. For all the spectra, a large peak at a distance of ~ 1.6 $\text{\AA}$, which correspond to the Fe–O bond, is observed. Moreover, other peaks appear at ~ 2.0 and 2.5 $\text{\AA}$, and they come from the Fe–Fe scattering. This suggests that there exists a Fe oxide other than the Fe metal phase, and this could be formed by the hybridization between Fe and BTO at the interface. Indeed, some theoretical works predict the hybridization between the Fe–Ti $3d$ states and O $2p$ states at the Fe/BTO interface [4, 9, 10], and the existence of interfacial Fe oxide layer has been proposed [4, 5], however, direct evidence has not been shown.

We further analyze the EXAFS data in order to obtain quantitative structural parameters. EXAFS curve fittings are performed by IFEFFIT package [11, 12] in k space after the inverse Fourier transform for the nearest Fe–O and Fe–Fe contributions. The EXAFS spectra of the FeO and bcc Fe clusters calculated by FEFF8 code [13] are used as a theoretical standard for the Fe–O and Fe–Fe bonds, respectively. Please note that the fitting procedure for the nearest neighbors does not need to consider the long range structures nor the chemical state of the standard, so that the obtained result does not depend on the chem-

FIG. 5. Deviation of the in-plane bond distances for Fe–O (a) and Fe–Fe (b), as a function of the electric field, E . The electric field is changed from $E = -10$ kV/cm, as indicated by the arrows.

FIG. 6. Coordination number of the Fe–O bond as a function of the electric field, E .

ical species of the clusters. Figure 5 shows the deviation of the in-plane bond distances for Fe–O (a) and Fe–Fe (b), as a function of the electric field, E . Please note that the electric field is changed from $E = -10$ kV/cm, as indicated by the arrows in the figure, and the deviation is estimated by setting the first point as a standard. The rate of change of the distance with respect to the electric field is larger for the Fe–O bond compared to the Fe–Fe one. This means that the local structure of the interfacial Fe oxide can be easily affected by the ferroelectric-domain structure of the BTO substrate. Furthermore, the response to the electric field is much similar to that of M_0 and H_c as shown in Fig. 2. That is, the in-plane bond distances for Fe–O shows a hysteresis behavior and it shows shorter distance at $\sim \pm 3$ kV/cm. These results indicate that the in-plane Fe–O distance is shorter when H_c is larger, in which the multi-domain structure in the BTO substrate is formed. On the other hand, the Fe–O

distance is larger in the case that H_c is smaller, in which BTO shows single domain like structure. In former situation, the lateral connection of the Fe oxide over the grain boundary must be weak, and the island-like localization is expected. We suppose that the localization of the interface Fe oxide leads to an enhancement of H_c of Fe. Finally, we roughly estimate the thickness of the interface Fe oxide. Figure 6 shows the electric field dependence of the coordination number (CN) for the Fe–O bond. CN is found to be ~ 0.75 regardless of the electric field. Because typical Fe oxides are tetrahedrally or octahedrally coordinated, obtained CN is $\sim 15\%$ of that expected for the fully oxidized film. Therefore, $\sim 15\%$ of Fe is supposed to be oxidized, so that the thickness of the interface Fe oxide is estimated to be a few nm. Although the chemical state of the interface oxide is not discussed, this component plays a key role in the field-induced effect of remaining ferromagnetic Fe.

IV. CONCLUSION

We have investigated the electric field-induced change of magnetic properties in ferromagnetic Fe thin film grown on the ferroelectric BTO substrate by means of x-ray absorption spectroscopy. We have observed a few nm Fe oxide layer at the Fe/BTO interface at the Fe thickness of 8 nm, in which the film showed in-plane magnetization. XMCD analysis revealed that the coercive field, H_c , of Fe showed a hysteresis behavior as a function of the electric field, and larger H_c was observed at $\sim \pm 3$ kV/cm. On the other hand, it was found from the EXAFS analysis that the Fe–O bond distance showed a similar electric field dependence to that of H_c , and shorter distance was observed at $\sim \pm 3$ kV/cm. Therefore, it was assumed that the H_c strongly depends on the ferroelectric domain structure of BTO, and larger H_c was observed for the multi-domain structure. We suppose that shrinking of the Fe–O distance caused by the domain formation leads to an enhancement of H_c due to the island-like localization of the interface Fe oxide.

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