

Effects of thermal annealing in oxygen on the antiferromagnetic order and domain structure of epitaxial LaFeO₃ thin films

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Abstract

The antiferromagnetic order and domain structure of LaFeO₃ thin films, epitaxially deposited on LaAlO₃(001) substrates, were investigated by X-ray magnetic linear dichroism (XMLD) spectroscopy and spectromicroscopy, using the soft X-ray photoelectron emission microscopy (PEEM) beamline at the Advanced Light Source. In particular, we have examined the effects of thermal annealing in oxygen on the antiferromagnetic domains and spin orientation in the near surface region of such films. The recorded PEEM micrographs show AFM domains for all samples, though the domains are on average larger for the thermally annealed films. XMLD spectra recorded for different angles between the electromagnetic field vector and the film surface normal suggest a characteristic difference in the spin orientation between the as-grown (epitaxially strained) and the thermally annealed (strain relaxed) samples. While temperature-dependent measurements reveal little difference in Néel temperature between an as-grown and a fully relaxed film ($T_N=645$ K and 610 K, respectively), both are reduced compared to that of bulk LaFeO₃ ($T_N=740$ K).

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1. Introduction

Antiferromagnetic (AFM) thin films are an essential component of magnetic thin film structures used in devices such as magnetic sensors and the read heads in modern computer hard drives [1]. The antiferromagnet serves to pin the direction of magnetization of an adjacent ferromagnetic layer, thus acting as a magnetic reference in these devices. The phenomenon, commonly referred to as exchange anisotropy or exchange-bias [2], has yet to be fully understood and may place limitations on the implementation and performance of spin-polarized materials in future

memory and logic applications. Precise characterization and control of the interfacial magnetic structure is crucial to the development of thin film spin devices. The nanometer-to micrometer-sized AFM domains in thin films call for the application of a surface sensitive, high-resolution technique to image the magnetic domain structure. Soft X-ray absorption spectroscopy in combination with secondary electron emission microscopy provides the necessary spatial resolution and surface sensitivity for surface magnetic domain imaging.

Magnetic domain contrast arises from the dependence of the absorption coefficient, and thus of the secondary electron yield, on the relative orientation of the X-ray polarization and the orientation of the AFM axis. Using linearly polarized X-rays, Scholl et al. utilized this effect, known as X-ray magnetic linear dichroism (XMLD), to image the AFM domains in the near surface region of LaFeO₃ thin films

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grown on (100)- and (110)-oriented SrTiO₃ substrates [3,4]. These studies suggest that the AFM domains are seeded by the crystalline microstructure of the thin films, which is characterized by nanoscopic (10–100 nm) domains with their *c*-axis oriented along the [010] and [001] directions of the SrTiO₃ substrate. The authors also measured the AFM domain contrast to obtain a Néel temperature for the thin films ($T_N=670\pm 10$ K) lower than that of bulk LaFeO₃ ($T_N=740$ K). The observed reduction in T_N was attributed to epitaxial strain caused by the lattice mismatch.

In this study, we examine the effect of strain relaxation on the near surface AFM order and domain structure of epitaxial LaFeO₃ thin films. In particular, we compare the AFM domain contrast in XMLD spectromicroscopy images recorded at different temperatures on strained and relaxed films.

2. Experimental details

The samples investigated were ~150 nm thick LaFeO₃ films grown epitaxially on LaAlO₃(001) by reactive off-axis *rf* magnetron sputtering from a polycrystalline composite target [5]. X-ray diffraction analysis and cross-section transmission electron microscopy (TEM) show that the films grow [110]-oriented with twinned crystallographic domains, oriented with their *c*-axis along the [100] and [010] directions of the LaAlO₃ surface plane. The out-of-plane lattice constant was obtained from θ - 2θ X-ray diffraction and was determined to be $d_{110}=3.970$ Å for the as-grown films, corresponding to a 1.0% lattice expansion compared with bulk LaFeO₃ ($d_{110}=3.932$ Å).

Two of the three LaFeO₃ thin films prepared for the present study were annealed in oxygen for 6 h at 900°C and 36 h at 1000 °C, respectively. Following this annealing, the LaFeO₃ out-of-plane lattice parameter was measured at $d_{110}=3.946$ Å and $d_{110}=3.939$ Å, respectively, which is evidence of strain relaxation upon this thermal processing. The data are corroborated by cross-section TEM analysis of the oxygen-annealed films, showing strain relaxation by the introduction of uniformly distributed plane dislocations at the film/substrate interface [6]. Both the as-grown and the thermally annealed samples were found to be of good crystalline quality, as demonstrated by rocking curve measurements and Rutherford backscattering spectroscopy, which showed excellent channelling properties for these films [7].

The XMLD spectromicroscopy measurements were carried out with the soft X-ray photoelectron emission microscope (PEEM2) at the Advanced Light Source [8]. Monochromatic, linearly polarized X-rays were incident on the LaFeO₃ film at an angle $\Theta=60^\circ$ with the film surface normal and the electric field vector \vec{E} oriented parallel to the sample surface. Fig. 1a and b plot the X-ray absorption spectra of the Fe $L_{2,3}$ edge obtained from dark and bright AFM domains (cf. Fig. 1c) of the fully relaxed sample.

The AFM domain images were obtained by dividing the PEEM image recorded at 721.5 eV (peak A) by one

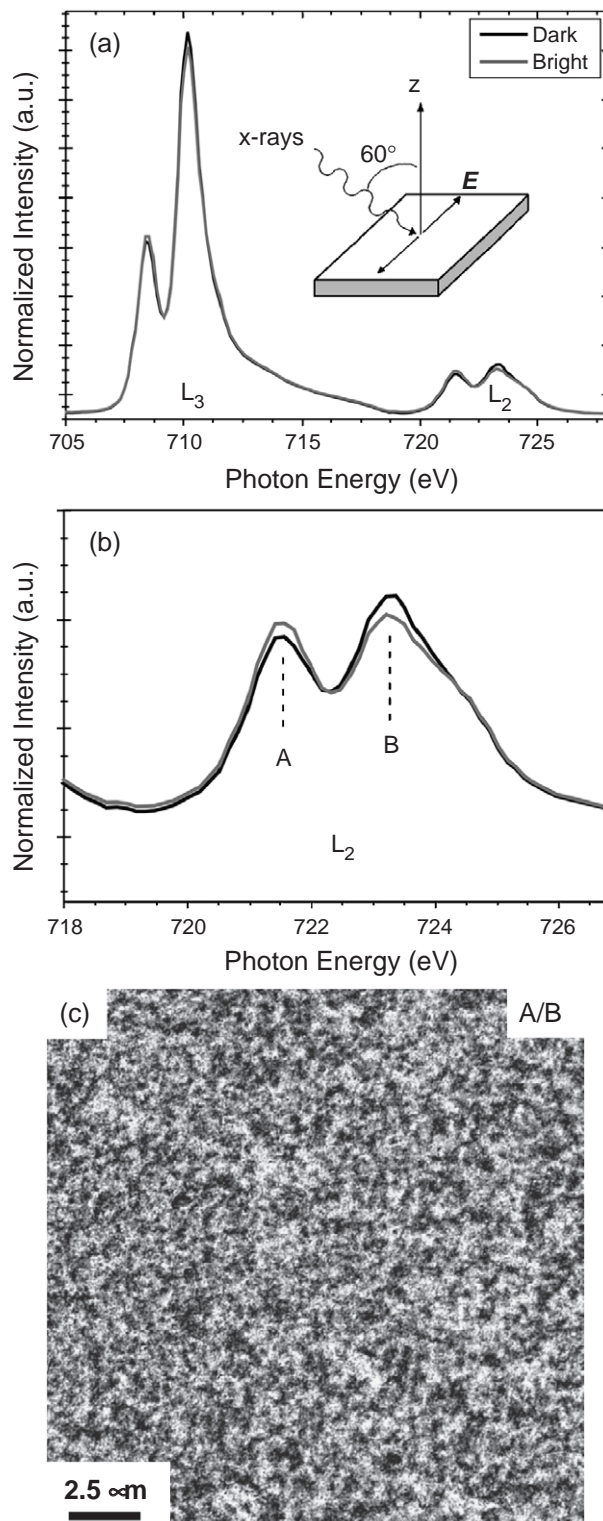


Fig. 1. (a) Total electron yield Fe $L_{2,3}$ edge X-ray absorption spectra of a fully relaxed LaFeO₃ thin film grown epitaxially on LaAlO₃(001). The measurement geometry is shown in the insert. The two spectra (bright vs. dark) were acquired from AFM domains with a different relative orientation of the magnetic axis and the electric polarization vector \vec{E} and show clear evidence of XMLD, cf. expanded view (b) of the Fe L_2 resonance. (c) XMLD image showing the AFM domain structure of the fully relaxed LaFeO₃ film sample. The two PEEM images, divided to obtain the domain contrast, were acquired at $A=721.5$ eV and $B=723.2$ eV, respectively.

recorded at 723.2 eV (peak *B*). The contrast arises from a different angle between the X-ray polarization vector and the local AFM axis. We also measured X-ray absorption spectra of the as-grown and the thermally annealed films for different angles of incidence, θ . Linearly polarized X-rays with the electric field vector parallel to the AFM axis enhances the intensity of peak *B* in the near edge X-ray absorption spectrum in Fig. 1b relative to peak *A*. Spectra recorded at different polar angles thus provide information on in-plane orientation vs. canting of the AFM axis.

3. Results and discussion

Fig. 2 displays divided (*A/B*) PEEM micrographs of the as-grown (a) and the fully relaxed sample (b), both measured at ambient temperature. By visual inspection, we see that the AFM domains of the annealed sample are characteristically larger than those of the as-grown film. Cross-section TEM images of annealed films support the anticipation that the twinned crystallographic domains of the as-grown film grow larger in size upon thermal annealing at 1000 °C. This finding supports the conclusion reached by Scholl et al. [3] that the AFM domains are seeded by the crystalline microstructure of the LaFeO₃ thin films.

The Fe *L*₂ PEEM images acquired at *A*=721.5 eV of the fully relaxed sample (Fig. 3a) show the presence of scattered triangle-shaped precipitates with their edges coherently aligned along low-index crystallographic directions of the LaAlO₃ substrate. Atomic force microscopy images of this sample (Fig. 3b) confirm the presence of such precipitates, protruding ~100 nm out of the LaFeO₃ film surface and ~700–800 nm wide at the base. Similar images of as-grown samples show that these films have a smoother surface with an order of magnitude lower rms surface roughness. Selected X-ray absorption data are insufficient to precisely ascertain the composition of these precipitates. The reduced contrast from the precipitates relative to the film matrix may be due to field emission from these sharp protrusions.

The XMLD effect depends on the X-ray polarization through the angle θ between the electric field vector \vec{E} and the magnetic axis, and on temperature through the magnetic

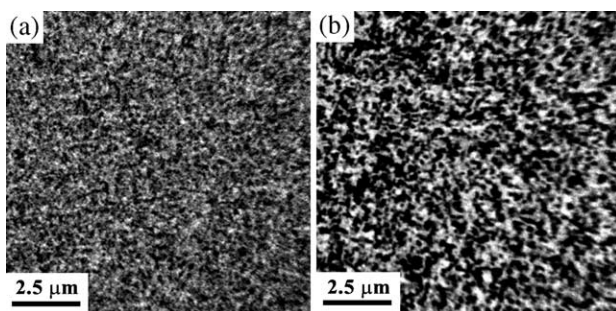


Fig. 2. *A/B* XMLD images showing the AFM domain contrast of an as-grown (a) and a fully relaxed (b) LaFeO₃ thin film on LaAlO₃(001). Both images were obtained at room temperature.

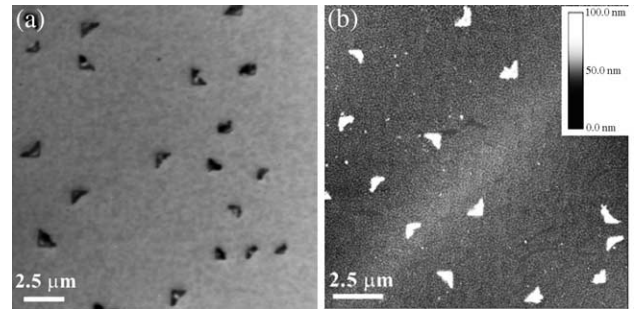


Fig. 3. Comparison of a PEEM image (a) and an atomic force microscopy image (b) of the fully relaxed LaFeO₃ thin film surface, showing characteristic triangular precipitates protruding up to 100 nm from the surrounding film matrix.

moment $\langle M^2 \rangle_T$, which vanishes above T_N . The intensity is given by

$$I(\theta, T) \propto (3\cos^2\theta - 1)\langle M^2 \rangle_T$$

Angle-dependent Fe *L*_{2,3} near edge X-ray absorption spectra measured at different angles of incidence $\theta=0-70^\circ$ unveil a distinct difference in the AFM order between the as-grown and the thermally annealed samples. The Fe *L*₂ absorption spectra of the as-grown sample, displayed in Fig. 4, shows that the intensity of peak *B* increases monotonically

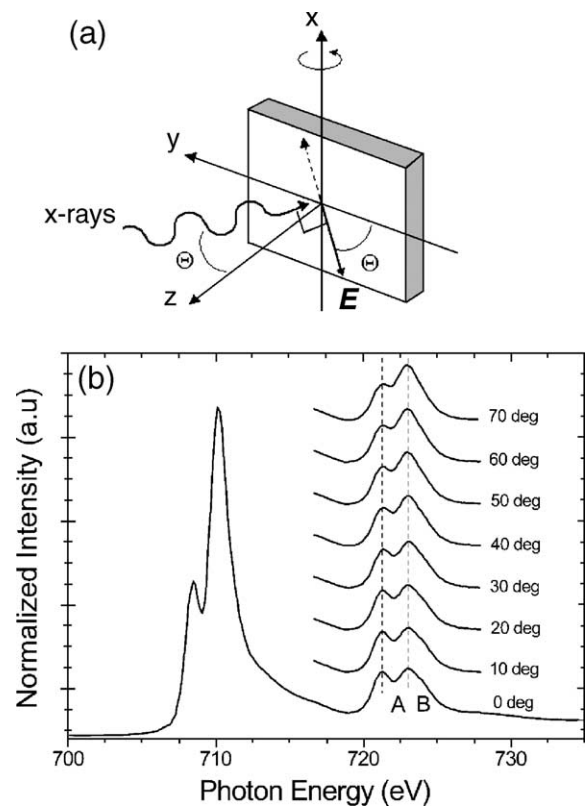


Fig. 4. (a) Measurement geometry for angle-dependent measurements of the XMLD in our LaFeO₃ thin films. (b) The recorded Fe *L*_{2,3} edge X-ray absorption spectra of the as-grown sample. The intensity of peak *B* of the *L*₂ resonance is seen to increase relative to peak *A* with increasing angle of incidence, θ , suggesting a canted orientation of the AFM spin axis.

cally with increasing Θ , relative to peak *A*. This result suggests that the spin orientation of the AFM domains is canted with respect to the LaFeO₃ film surface. No such trend was observed for the thermally annealed samples, for which the relative intensity of peaks *A* and *B* remained virtually constant as we changed the angle of incidence, Θ , suggesting a different AFM spin orientation in the near surface region of these films.

XMLD images obtained at different temperatures from 298 K to 623 K show that the AFM domain contrast is strongly reduced at elevated temperatures, cf. the images of the as-grown sample in Fig. 5a. Quantification of the domain contrast, which is a measure of $\langle M^2 \rangle_T$, was performed using a fast Fourier transform to obtain the

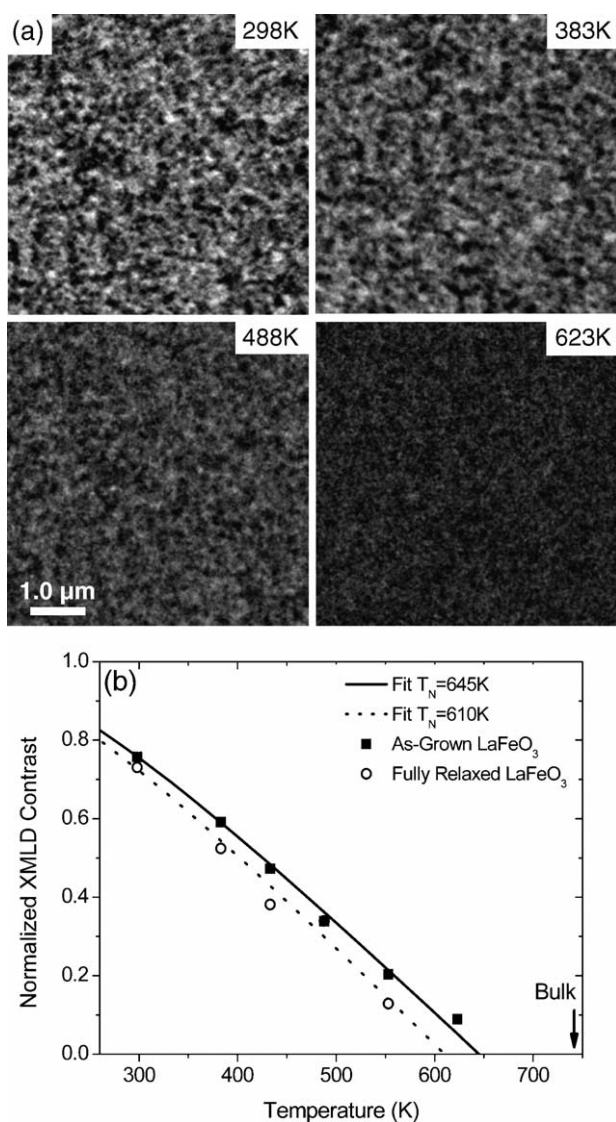


Fig. 5. (a) XMLD images recorded at four different substrate temperatures for the as-grown LaFeO₃ sample on LaAlO₃(001). (b) XMLD contrast numbers for the as-grown (solid squares) and fully relaxed (open circles) LaFeO₃ samples as a function of temperature, along with fits to $\langle M^2 \rangle_T$ from mean field theory, plotted as solid and dotted lines. These fits give an estimate for the Néel temperature of 645 K and 610 K, respectively.

power spectrum $[\log_{10}(\text{FFT})^2]$ of the XMLD micrographs, subtracting the noise background, and plotting the result as a function of temperature. Fig. 5b plots a compilation of the XMLD contrast number as a function of temperature for the as-grown (filled squares) and the fully relaxed (open circles) film samples. The solid and dotted lines represent fits of the data to $\langle M^2 \rangle_T$ from mean field theory. These fits give values of $T_N=645 \pm 10$ K for the as-grown sample and $T_N=610 \pm 10$ K for the fully relaxed sample, significantly reduced from the bulk value, $T_N=740$ K. This finding conflicts with the conjecture made by Scholl et al. [3], that the measured reduction in Néel temperature for LaFeO₃ thin films is due to epitaxial strain. If this was the case, we would expect the fully relaxed sample to have a T_N that approaches the bulk value. With the present film thickness of ~ 150 nm, which is considerably larger than the 40 nm thick films of LaFeO₃ used in the previous experiment of Scholl et al. [3], we agree with these authors that the reduced Néel temperature cannot be explained as a finite size effect. The PEEM experiment selectively probes the AFM order and domain structure at the sample surface with a $1/e$ sampling depth of 2–3 nm, as determined by the escape length of the secondary electrons produced in the Auger decay of the soft X-ray excited core holes. We suggest that the reduced T_N in thin films can be explained by a defect-related perturbation of the exchange interaction or possibly an inherent effect of the broken symmetry at the film surface.

4. Conclusion

We have investigated the impact of thermal annealing in an oxygen ambient at temperatures up to 1000 °C on the antiferromagnetic order and domain structure of LaFeO₃ thin films grown epitaxially on LaAlO₃(001). Such annealing proved to cause relaxation of epitaxial strain in these films. The AFM domains observed by XMLD spectromicroscopy were found to be larger for the thermally annealed samples, probably seeded by changes in the film crystalline microstructure. In addition, a characteristic difference exists in the orientation of the AFM axis between the as-grown and the thermally annealed films. Temperature-dependent measurements of the AFM domain contrast showed that while T_N of all thin film samples is reduced relative to that of bulk LaFeO₃, no appreciable difference exists between T_N of epitaxially strained and relaxed films. These results indicate that strain cannot explain the reduction of T_N , and we attribute this finding to a change of the exchange interaction near the film surface.

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