Growth and Surface Modification of LaFeO₃ Thin Films Induced By Reductive Annealing

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Abstract

The mixed electronic and ionic conductivity of perovskite oxides has enabled their use in diverse applications such as automotive exhaust catalysts, solid oxide fuel cell cathodes, and visible light photocatalysts. The redox chemistry at the surface of perovskite oxides is largely dependent on the oxidation state of the metal cations as well as the oxide surface stoichiometry. In this study, LaFeO_3 (LFO) thin films grown on yttria-stabilized zirconia (YSZ) was characterized using both bulk and surface sensitive techniques. A combination of *in-situ* reflection high-energy electron diffraction (RHEED), x-ray diffraction (XRD), and Rutherford backscattering spectrometry (RBS) demonstrated that the film is primarily textured in the [100] direction and is stoichiometric. High-resolution transmission electron microscopy measurements show regions that are dominated by [100] oriented LFO grains that are oriented with respect to the substrate's lattice. However, selected regions of the film show multiple domains of grains that are not [100] oriented. The film was annealed in an ultra-high vacuum chamber to simulate reducing conditions and studied by angle-resolved x-ray photoelectron spectroscopy (XPS). Iron was found to exist as Fe(0), Fe(II), and Fe(III) depending on the annealing conditions and the depth within the film. A decrease in the concentration of surface oxygen species was correlated with iron reduction. These results should help guide and enhance the design of LFO materials for catalytic applications.

Keywords: LaFeO_3 , lanthanum iron oxide, angle-resolved XPS, molecular beam epitaxy, perovskite

1. Introduction

LaFeO_3 (LFO) and $\text{LaFe}_{1-x}\text{M}_x\text{O}_3$ (where M = metal dopant) perovskite oxides can function as self-regenerating automotive exhaust catalysts[1], methane reformers to produce syngas[2], visible light photocatalysts[3], gas sensors[4,5], and as cathodes in solid oxide fuel cells (SOFCs)[6,7]. Iron-based perovskites are typically oxygen deficient[8,9], which in part explains the high oxygen mobility within the material[10] and its suitability for catalytic applications such as oxygen reduction and ion transport in SOFCs. For some of these applications, the surface stoichiometry and transitional metal oxidation state can have a substantial impact on the redox chemistry. Calculations have shown that oxygen reduction occurs preferentially on the FeO_2 -terminated LFO (010) surface rather than the LaO-type termination[11]. In addition, simulations suggest that the termination on LFO (001) can significantly affect Pd migration into the perovskite lattice, which can impact “intelligent catalysts” automotive exhaust catalysis[12]. Aside from the surface termination, atomic vacancies are also predicted to influence the chemistry of LFO catalysts. First-principle calculations indicate that CO adsorption on the LFO (010) surface can be significantly altered due to oxygen vacancies, where CO was found to donate charge on a stoichiometric surface and accept charge on an oxygen deficient surface[13]. Given the range of environments in which these materials operate, it is important to understand their surface properties under both oxidizing and reducing conditions.

The goal of this study was to evaluate the chemical stability of LFO films with angle-resolved x-ray photoelectron spectroscopy (XPS). Yttria-stabilized zirconia (YSZ) was chosen as a substrate due to the potential to characterize LFO/YSZ interfaces

which are relevant for SOFC applications[14]. The LFO thin film was processed and transferred into the analyzing chamber under ultrahigh vacuum (UHV) conditions to avoid contamination and to assist in unambiguous interpretation of the XPS spectra. Angle-resolved XPS studies highlight the substantial differences between the surface and bulk oxidation states and compositions for LFO.

2. Experimental Methods

A 60 nm thick LFO thin film was grown by molecular beam epitaxy (MBE) on (001)-oriented Y:ZrO₂ (YSZ) substrates. The YSZ substrate was loaded into an ultrahigh vacuum chamber and heated at 750 °C for 20 minutes in an oxygen partial pressure of 6.0×10^{-6} Torr prior to growth. La and Fe were evaporated from high-temperature effusion cells. Flux rates were calibrated using a quartz crystal microbalance (QCM) located at the substrate position and *ex-situ* Rutherford backscattering spectrometry (RBS) measurements[15]. During film growth the substrate temperature was 700 °C with an O₂ partial pressure of $\sim 5.0 \times 10^{-6}$ Torr. Reflection high-energy electron diffraction (RHEED) patterns were monitored during and after film growth.

Crystallographic film orientation and film quality were investigated using high-resolution x-ray diffraction (HRXRD) with a Philips X'Pert Materials Research Diffractometer (MRD) equipped with a fixed Cu anode operating at 45 kV and 40 mA. A hybrid monochromator, consisting of four-bounce double crystal Ge (220) and a Cu x-ray mirror, was placed in the incident beam path to generate monochromatic Cu K α x-rays ($\lambda = 1.54056$ Å) with a beam divergence of 12 arc seconds.

RBS measurements were carried out using 2 MeV helium ions at normal incidence (full details of the accelerator setup can be found elsewhere[16]). The backscattering spectra were collected using a silicon surface barrier detector which was positioned at a scattering angle of 150° . The SIMNRA simulation program was used to model the experimental RBS spectrum collected in a random incident direction[17]. In these simulations, the sample was divided into several thin layers of variable thickness and composition. Experimental parameters such as incident ion energy, atomic number of the incident ion, scattering angles, solid angle of detection, and the total charge deposited by the incident beam were used to simulate the experimental spectrum. The composition profiles and film areal density (in units of atoms/cm²) were then varied until the best fit to the experimental data was obtained.

The LFO/YSZ samples were exposed to ambient air after synthesis and transferred into the XPS system, which is attached to an auxiliary processing chamber. The sample was fixed to a sample holder using molybdenum clips on top of a molybdenum heating plate. During heating, the molybdenum plate was biased and heated by electron beam bombardment of the backside of the plate. Flowing liquid nitrogen cooled the sample by means of conduction via the sample holder. A type-K thermocouple contacted the sample surface and was held in place by molybdenum clips.

In the auxiliary chamber the sample was initially heated to 600 °C in 1.0×10^{-6} Torr O₂ for 10 minutes to remove adventitious carbon and to fully oxidize the sample. For vacuum annealing, the sample was heated in 100 °C increments with a base pressure between $1.0\text{-}2.0 \times 10^{-9}$ Torr, and a 10 minute holding time at each

temperature. After cooling to room temperature the sample was transferred into the XPS chamber for analysis, and the vacuum annealing process was repeated up to 700 °C. The heating rate was 1-2 °C/sec, and the cooling rate was 2-4 °C/sec.

For XPS measurements monochromated Al K α x-rays were used along with an analyzer pass energy of 23.5 eV. All spectra were calibrated to the binding energy (BE) of the O 1s lattice oxygen peak at 530.0 eV[18]. PHI MultiPak software was used for atomic concentration quantification using the O 1s, Fe 3p, and La 4d core levels, while CasaXPS was used for peak fitting. The O 1s spectra were fit with a Shirley background and Gaussian-Lorentzian line shapes, with the peaks' Gaussian character set to 90%.

The mean escape depth (MED) of electrons at take off angles (θ) of 10° versus 45° are estimated to determine the relative surface sensitivity at each angle. The inelastic mean free path (IMFP) of Fe 2p_{3/2} electrons in LaFeO₃ was estimated to be 1.5 nm using the NIST Standard Reference Database 71[19] and TPP-2M equation[20], with values for the band gap and density of the compound taken from other experimental studies[21,22]. Ignoring the effects of elastic-electron scattering, the MED is equal to the IMFP multiplied by the sine of the take-off angle. For 10° and 45°, the MED is 0.3 and 1.0 nm respectively. However, because elastic-electron scattering is typically not negligible, MEDs may be as much as twice as large at near-grazing angles as values calculated using the formula above[23].

Transmission electron microscopy (TEM) was performed using a probe-corrected FEI Titan 80-300 operated at 300 kV. High angle annular dark field scanning TEM

(HAADF-STEM) images were collected with an inner angle >50 mrad. Cross-sectional samples were obtained using an FEI Helios Dual beam focused ion beam and scanning electron microscope (FIB/SEM) equipped with an Omniprobe micromanipulator, with a final cleaning at 2 kV[24].

3. Results and Discussion

The crystalline structure of the as-grown LFO film was examined by θ - 2θ XRD. The out-of-plane θ - 2θ scan is shown in Fig. 1. LFO has a distorted perovskite crystal structure (i.e., orthorhombic) with $a = 5.556$ Å, $b = 5.565$ Å, and $c = 7.862$ Å[25], while YSZ has a cubic fluorite crystal structure with $a_o = 5.139$ Å[26]. In the XRD data there are two strong reflections that can be attributed to the (002) and (004) planes of YSZ at 34.89° and 73.63° , respectively. Two additional peaks centered at 32.31° and 67.55° are associated with reflections of LFO (200) and (400) planes. The absence of peaks related to other planes in the XRD spectrum in combination with in-plane XRD measurements (not shown) suggests that the LFO films are primarily oriented along the [100] direction. The positions of the XRD reflections give out-of-plane lattice parameters of 5.540 Å for LFO and 5.140 Å for YSZ. These data indicate that the LFO films were compressed by -0.30% relative to bulk LFO in the [100] direction (normal to the substrate surface).

HAADF-STEM data from a vacuum-annealed LFO/YSZ film are shown in Fig. 2, where much of the LFO film appeared highly oriented but other orientations were also observed. Most of the LFO grains have a [100] orientation with respect to the YSZ [001]

orientation, however there is evidence of various degrees of rotation. A high-resolution image of one region is shown in Fig. 2(a). Here the LFO is observed along the YSZ [001] zone axis and periodic edge dislocations are seen at the YSZ-LFO interface every 12 YSZ atomic planes, which gives an estimate of the lattice mismatch equal to ~8%. This value is in good agreement with the expected bulk mismatch between the LFO [010] and YSZ [010] (8.3%). Although the [100] orientation of LFO was dominate for these films, other grain orientations were also observed. The cross section shown in Fig. 2(b) illustrates the intersection of three LFO grains with different orientations. There were also frequently small mis-oriented grains along the LFO/YSZ interface at grain boundaries, all consistent with columnar growth. The TEM and XRD are each consistent with the indistinct reflection high-energy electron diffraction (RHEED) patterns observed during and after film growth (a post-growth RHEED pattern is shown in Fig. 3). This large lattice mismatch helps explain the spotty reflection high-energy electron diffraction (RHEED) patterns observed during and after film growth. The pattern suggests the growth proceeded by an island mode, where three dimensional clusters coalesce to form a two dimensional layer.

RBS spectra collected in channeling and random directions from the as grown sample are shown in Fig. 4(a). The leading edge of the Y/Zr plateau for the random direction spectra are shifted to lower energy due to ion energy loss when passing through the LFO film. SIMNRA was used to calculate the random spectrum and these results are shown in Fig. 4(a). The stoichiometry of the film was consistent with $\text{La:Fe:O} = 1:1:3$ by comparison of the experimental RBS spectra to calculated spectra for a 52 nm thick film.

A small energy window at the center of the La channeling spectrum was used to calculate the minimum yield ($\chi_{\min}$) for La. Another small energy window near the substrate Zr edge was used to calculate the minimum yield for Zr in the substrate. The minimum yield is the ratio of the yield in the channeling direction to that for a random direction. For the film, $\chi_{\min}$ for La is calculated to be 24%. This minimum yield is relatively high compared to the minimum yield measured from high quality epitaxial films (usually lower than 4%). This increase is likely due to the multiple grains and possibly disordered grain boundaries in the film as also shown in the TEM image in Fig. 2(b). Similarly, the minimum yield for the YSZ substrate ($\chi_{\min}$ for Zr = 21%) was also high compared to a bare YSZ substrate ($\chi_{\min} = 4.9\%$)[27], possibly due to dechanneling effects associated with the multiple grains and disordering the grain boundaries.

Normalized angular yield curves for La in the film and Zr in the substrate are shown in Fig. 4(b). The energy regions that were used to calculate the minimum yields were also used to extract the angular yield curves. The solid line through the points is provided to guide the eye. Aligned (channeling RBS) spectra were collected at the beginning and at the end of each angular yield scan to check for any possible sample damage. No significant damage was observed during these measurements. In general both angular yield curves show very narrow angular widths. Since the variation of yield as a function of polar angle is similar for both La and Zr, most of the atomic columns of La in the film are parallel to the atomic columns of Zr in the substrate.

Fe 2p core level and valence band XPS spectra measured with take-off angles of 10° and 45° from samples with different heating treatments are shown in Fig. 5. These include after the film was oxidized at 600 °C, and after heating in vacuum to 400 °C and

700 °C. With regard to the La 3d and O 1s core level spectra, no major changes were observed for La with respect to take-off angle or heating, with the main La 3d_{5/2} peak remaining virtually unchanged at 834.6 eV. The O 1s spectra will be discussed in more detail below.

Little change occurs in the Fe 2p spectra after annealing for $\theta = 45^\circ$, with the exception of a very slight broadening of the main Fe 2p_{3/2} peak on the low BE side. Initially, the BE of the Fe 2p_{3/2} peak was at 710.9 eV after oxidation indicating that iron was present in the Fe³⁺ oxidation state[28]. After annealing in UHV, some of the Fe³⁺ was reduced to Fe²⁺, which has a characteristic Fe 2p_{3/2} BE position near 709.0 eV[26]. Much more substantial changes can be seen after annealing in the $\theta = 10^\circ$ spectra. At this grazing emission angle, the broadening in the Fe 2p_{3/2} is more pronounced, with Fe reduction clearly evident at 400 °C. Heating to 700 °C induced further Fe reduction to Fe⁰. The increased peak intensity at 706.9 eV and 720.0 eV are indicative of iron metal[29], and thus a mixture of Fe³⁺, Fe²⁺, and Fe⁰ was present at the surface after this heating treatment. This presence of iron metal is also correlated with the increased density of states near the Fermi level seen in the valence band spectra. In other studies where LaFeO₃ was reduced in hydrogen atmosphere it was observed that Fe³⁺ reduced directly to Fe⁰ without a Fe²⁺ intermediate[30,31]. The presence of Fe²⁺ in this work shows that Fe reduction can proceed sequentially and that Fe²⁺ is stable under certain conditions, which could impact LFO's use in catalytic applications as the altered Fe oxidation state would be expected to modify LFO's oxygen reduction reaction activity[32].

Coincident with formation of Fe⁰ after heating to 700 °C, the Fe concentration decreases substantially at the surface as seen in Fig. 6, with a resultant increase in La concentration. A surface termination change might partially explain this result. Calculations have shown that for LaFeO₃ (001) the LaO termination is thermodynamically favored versus the FeO₂ termination under UHV conditions at 727 °C[12]. XPS analysis has also shown a temperature-dependent switch in the termination of LaAlO₃[33], which was believed to stem from oxygen deficiencies in the first atomic layer. Another possibility is that the surface decomposed into Fe metal and La₂O₃ with Fe diffusion into the bulk. A possible mechanism is given by

No substantial change in the La 3d_{5/2} BE is expected in this case due to the similar BEs of the core level in La₂O₃[27,34] and LFO. The absence of an accompanying change in the La 3d spectra suggests that the reduced Fe may be nucleating in small metal particles. The loss of O₂ is consistent with the O 1s peak fitting results discussed below, where the surface oxygen peak decreased with increasing annealing temperature. An additional complicating factor is the decrease in unit cell volume that would result from decomposition and the attendant increase in surface roughness, which could particularly affect the XPS results at the low take-off angle[35].

Peak fitting results are shown in Fig. 7 for the O 1s spectra. Initially the oxidized, θ = 45° spectrum was fit using three components, one fixed at BE = 530.0 eV which was assigned to lattice oxygen and two other peaks, with all three constrained to have the same full width at half maximum (FWHM). These peak assignments were then

used to fit the remaining spectra while allowing for changes in peak areas and surface oxygen BE, with the FWHM allowed to vary by ± 0.05 eV.

For the O 1s $\theta = 45^\circ$ spectra there are virtually no changes in the peak fits for the three sample conditions besides a downward shift of 0.25 eV of the highest BE peak after annealing. This peak is located 1.9-2.2 eV greater than lattice oxygen and comprised $\sim 3\%$ of the total peak area, while the other high BE shoulder is located ~ 1.0 eV higher than lattice oxygen and accounted for $\sim 15\%$ of the total O 1s peak. The O 1s spectra at the lower take-off angle are visibly broader than those obtained at larger take-off angles due to the increased peak areas of the higher BE components. The highest BE component decreased from 11% to 6% with annealing, while the intermediate O 1s feature decreased from 37% to 19%. The fact that the area of these peaks increases for the smaller take-off angle indicates that they are related to surface oxygen species. Although annealing in UHV can create surface oxygen vacancies[36], it is unlikely that these peaks are related to regions that have oxygen deficiencies as the peak areas decrease with annealing rather than increase. Given the BE difference of the highest BE peak and lattice oxygen and the peak's relatively small peak area, the high BE peak is attributed to low level adsorption of background gases. No signature for carbon was present during XPS analysis, so water and/or molecular oxygen adsorbed during sample cooling and transfer are the most likely species. The intermediate oxygen peak is then attributed to a surface oxygen species, consistent with the higher BEs seen for surface oxygen in perovskites[37,38]. The decrease in peak area upon annealing of this intermediate peak is then related to the surface dynamics discussed above, namely the altered stoichiometry and decomposition.

4. Conclusion

The growth of LFO on YSZ(001) was primarily oriented in the [100] direction as judged by XRD, RBS, and TEM data, however the film was not single crystalline due to the existence of several different crystalline domains observed in HRTEM images. A relatively high channeling yield compared to epitaxial films resulted from the multicrystalline nature of the LFO film. The large lattice mismatch between LFO and YSZ may prevent epitaxial, defect-free growth. After film growth, significant differences were detected with angle-resolved XPS between the surface and bulk of the LFO film, with a surface oxygen species present at higher concentration in the grazing-emission spectra. Annealing the film in UHV resulted in the sequential reduction of Fe cations, from Fe^{3+} to Fe^{2+} to Fe^0 . A greater degree of reduction took place at the surface, and the formation of Fe^0 likely resulted from surface decomposition. The redox properties of the LFO surface were sensitive to the experimental annealing conditions. This sensitivity suggests that appropriate methods may be developed to control the surface properties to suit a particular gas sensing or catalytic application.

Acknowledgements

The authors gratefully acknowledge support from the Semiconductor Research Corporation under contract number 2013-OJ-2438.001 and the Center for Sustainable Materials Chemistry, which is supported by the US National Science Foundation under grant number CHE-1102637. S.A.C. and M.A.H. were supported by BES, Division of

Chemical Sciences, Geosciences, and Biosciences. The research was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. B. Flynn and G. Herman acknowledge financial support from SRC Contract Number 2013-OJ-2438.

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Figures

Fig. 1 - XRD pattern of LFO(100) grown on YSZ(001) at 700 °C.

Fig. 2 - HAADF-STEM images at different locations of the LFO/YSZ film.

Fig. 3 – Post-growth RHEED pattern of LFO(100) grown on YSZ(001) at 700 °C.

Fig. 4 - (a) Channeling and random RBS spectra along with the SIMNRA calculated result for the as-grown LFO film on YSZ. (b) Normalized angular yield curves from La in the film and Zr in the substrate. In both cases, the incident energy of the helium beam was 2 MeV and the scattering angle was 150° .

Fig. 5 - 10° (top) and 45° (bottom) emission spectra from LFO/YSZ film oxidized and annealed in vacuum

Fig. 6 - Atomic concentrations from 10° (left) and 45° (right) emission spectra of LFO/YSZ film

Fig. 7 - Peak fits of O 1s spectra.