X-ray photoemission spectroscopy of La$_{0.67}$Ca$_{0.33}$MnO$_3$ films

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We have performed x-ray photoemission spectroscopy (XPS) on thin films of (001) and (200) oriented La$_{0.67}$Ca$_{0.33}$MnO$_3$ grown on (100) and (110) SrTiO$_3$ substrates by off-axis sputtering. The films were examined by XPS without exposing them to air. We have compared the core levels and the valence spectra between the two different orientations, as well as after the effects of air exposure and annealing in UHV. We find that the surfaces are very stable against exposure to air. Comparing the measured intensity ratios to a model for the uniform termination of the film shows the terminating layer to be MnO$_2$ for both the (001) and (200) oriented La$_{0.67}$Ca$_{0.33}$MnO$_3$ films.

I. INTRODUCTION

The colossal magnetoresistance (CMR) behavior seen in thin films of the lanthanum based manganese oxides [1] has resulted in a great deal of interest in thin film growth of the materials. X-ray photoemission studies have been carried out on these systems to understand the change in electronic structure as a function of doping. [2-4] Valence-band structure has also been studied for a La$_{0.65}$Ca$_{0.35}$MnO$_3$ film using angle-resolved photoemission; [5] however, there has been no x-ray photoemission spectroscopy (XPS) studies of the core states for thin films of these materials. In this paper, we present in situ and ex situ XPS measurements for films of La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) grown on SrTiO$_3$ substrates. We have examined how the core lines are affected by exposure to air and subsequent annealing in UHV, and we have compared our measured intensities to a quantitative model for the terminating surface of the films. We have also compared the differences between LCMO films grown on different orientations of SrTiO$_3$.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Our samples were grown by off-axis sputtering using a composite target of LCMO material mounted in a copper cup. The substrates were (100) and (110) oriented strontium titanate (SrTiO$_3$), silver-pasted onto a stainless steel substrate holder that was radiatively heated from behind by quartz lamps. Although there was no direct measurement of the holder temperature for the runs used in this study, previous runs (under nominally the same conditions) using a thermocouple clamped onto the front surface of the holder indicated a temperature of 670°C. The films were rf-sputtered at 80 W in a sputter gas composed of 80% Ar and 20% O$_2$ (as measured by flow meters) and at a total pressure of 13.3 Pa. These conditions gave deposition rates of $\approx$ 17 nm/hr, with film thicknesses being typically 50 nm. After deposition, the samples were cooled in 13.3 kPa of oxygen. After the samples had
cooled to below 100 C, the chamber was pumped out to below 10\(^{-4}\) Pa, and the samples were moved by a manipulator arm into an adjacent chamber that has the XPS analytical equipment. After the sample was placed into the XPS stage, the chambers were isolated, and the XPS chamber pressure evacuated below 3 \(\times\) 10\(^{-7}\) Pa. For characterization after exposure to air, the sample surfaces were cleaned by UHV anneals to 600 C. Such anneals are known to have a detrimental effect on the oxygen content in other perovskite materials (such as the high T\(_c\) superconductor YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\)). For the case of LCMO, we have seen in anneals on in situ films (not shown here) and in our ex situ film results (shown later) that such anneals do not cause any significant reduction in the measured oxygen levels.

The XPS spectra were taken at room temperature with a Vacuum Generators CLAM 100 analyzer using Mg K\(\alpha\) radiation (12 kV, 20 mA). The emission angle of the photoelectrons was 15° to the surface normal, unless otherwise stated. The pass energy was set to 50 eV, giving a full width at half maximum (FWHM) of 2.0 eV for a Pt 4f\(_{7/2}\) line. For the transmission function we use what is commonly seen in VG ESCALab detectors \((T(E_k) \propto 1/\sqrt{E_k})\), which are also 150° sector angle hemispherical analyzers.

The collected XPS peaks were fit by multiple Gaussian curves after subtracting away an S-shaped background \([6]\) to obtain the peak positions and peak areas. The energy scale for the system was calibrated using an ion-milled Pt foil sample, and has an absolute accuracy of ±0.5 eV and a relative energy accuracy of ±0.1 eV for all samples.

In addition to the XPS studies, the samples were characterized ex situ by standard \(\theta-2\theta\) x-ray diffraction scans, electrical resistivity measurements (using the van der Pauw method \([7]\)) for zero applied field, and magnetization measurements at low fields using a Quantum Design SQUID Magnetometer.

### III. RESULTS AND DISCUSSION

**A. Film properties**

On (100) and (110) SrTiO\(_3\) we get smooth, well-oriented LCMO films. In Figure 1 we show the x-ray diffraction patterns along the film growth direction for LCMO films on (100) and (110) SrTiO\(_3\). We find (001) LCMO on (100) SrTiO\(_3\), with a c-axis lattice constant of 7.60Å. For the LCMO film on (110) SrTiO\(_3\), we had to use x-ray diffraction in the plane of the film since it can be difficult to distinguish between the (200) and (112) LCMO reflections. What we find for this film is that it is oriented as (200) LCMO, with an a-axis lattice constant of 5.44Å. Furthermore, we find that the LCMO is oriented in the film plane with (001) LCMO || (001) SrTiO\(_3\) and (010) LCMO || (1\(\bar{1}\)0) SrTiO\(_3\), with b and c-axis lattice constants of 5.52 and 7.77Å, respectively. SEM micrographs (not shown) show no evidence of second phases or particulates. In Figure 2 we present the resistivity data in zero applied magnetic field and magnetization data (at 50 Oe) for the LCMO films on the two substrates. We see a maximum in resistivity near 200 K and a magnetic transition that occurs slightly above the resistivity peak in temperature.
B. XPS characterization

1. In situ vs. ex situ studies

Photoemission data for all the samples was collected around the Mn 2p doublet, the La 4d and 3d doublet, the O 1s, Ca 2p, C 1s, Mn 3p lines, and the valence region. In the following figures of XPS spectra, the core level spectra are shown along with their deconvolution into different Gaussian contributions. In Figures 3 and 4, we show scans around the location of the above core lines and valence region for a LCMO film on (100) SrTiO$_3$ after insertion into the spectrometer (A), after exposure to room air for approximately 5 minutes (B), and after annealing to 600 C for 1 hour in UHV (C). The curves are offset for clarity.

For the in situ measurement (A) we see no evidence of carbon on the surface of the film, therefore no cleaning procedures were needed for the in situ studies. The in situ surfaces have not undergone any ion milling or thermal cycling, and are thus representative of what would be used in further film processing. The O 1s line has a main peak at 529.1 eV with a broad satellite of $\approx 71\%$ intensity located at 529.5 eV. The Mn 2p$_{3/2}$ line is also composed of a low binding energy component at 641.3 eV and a high binding energy component with $\approx 90\%$ intensity at 643.3 eV. The spin orbit splitting of the Mn 2p lines is 11.7 eV, similar to that seen in MnO$_2$, but our binding energy is lower. The La 3d$_{5/2}$ line is well fit by a double Gaussian, with peaks at 833.7 eV and 837.4 eV, and with the high binding energy peak having 115 $\%$ of the intensity of the low peak. The La 3d series is very similar to that of La$_2$O$_3$, with our spin orbit splitting being 16.7 eV. However, as in the case of the Mn 2p lines, our binding energy is lower than that seen in La$_2$O$_3$. The Mn 3p line is similar to the Mn 2p$_{3/2}$ line, with a high binding energy component of 119$\%$ intensity of the low binding energy component, and with peak positions of 50.1 and 48.3 eV respectively. The La 4d doublet is composed of two spin-orbit doublets with binding energies of the 4d$_{5/2}$ line at 101.9 and 104.1 eV, with the higher binding energy component having 122% of the intensity of the lower component. The Ca 2p doublet, in contrast to the other lines, is well fit by a standard p-like doublet, with no need for satellite terms. The Ca 2p$_{3/2}$ line is located at 346.3 eV. Finally, the valence region shows contributions from the La 5p, O 2s, Ca 3p, and La 5s lines, as well as Mn-O bonding below 10 eV. We find overall good agreement when we compare the binding energies of our core levels to that seen by Taguchi et al. for bulk La$_{1-x}$Ca$_x$MnO$_3$. 

For the case of a 5 minute exposure to room air (B), we see the appearance of a carbon line at 285 eV, indicating the presence of hydrocarbons on the surface, along with a reduction in intensity of the remaining lines. Comparing the lines to those for the in situ case (A), we do not see a great deal of modification in the line shapes. A numerical comparison shows the greatest modification to be in the O 1s line, where there is an increase of 30% in the relative intensity of the high binding energy component compared to the low binding energy peak. For the valence structure, a peak near 9-10 eV is usually associated with contamination. We do not observe a change in this region after exposing the sample to air; however it may be that this peak does not have a significant cross section for Mg K$\alpha$ radiation. After annealing the film to 600 C in UHV (C), we see a reduction in the carbon level, and again, no major modification in the line shapes. What we find most interesting about this series is...
that the surface of the LCMO film seems very robust and does not undergo a rapid reaction under exposure to room air.

2. Surface layer issues

In XPS studies on the high temperature superconductors, \[9\] it was customary to assign the high binding energy component seen in the core lines with a surface layer having a different chemical environment than the bulk. By making XPS measurements at different angles to the surface normal, it is possible to distinguish bulk and surface contributions to a photoemission line. We have compared scans of the La 3d\(_{5/2}\), Mn 2p\(_{3/2}\), O 1s, and La 4d lines at two different angles, \(\theta\), where \(\theta\) is the angle between the sample normal and the plane defined by the x-ray source and detector. Due to limitations of the sample holder, the maximum angle we were able to use was 45\(^\circ\). In Figure 5 we show a comparison for the O 1s line for our \textit{in situ} film (A). What we find here is true for the other lines: there is very little change in the lineshape as one goes to different angles. If either component were a surface feature, we would have expected at least a 60% change in relative intensity ratio of the two components. Even for the case of the LCMO film exposed to air for 5 minutes (B), where we saw an increase in the relative intensity of this high binding energy peak for the O 1s line and would interpret it as a possible surface component, we find that there is very little change between the 0\(^\circ\) and 45\(^\circ\) spectra. This implies that the high binding energy components are not due to surface layers, and instead are representative of the bulk of the LCMO material.

3. Effects of different orientations and termination study

We also performed \textit{in situ} XPS measurements for the LCMO film grown on (110) SrTiO\(_3\). What we observe first for this film is that the core lines are nearly identical to our LCMO film on (100) SrTiO\(_3\), with only the relative intensity ratios varying. So rather than present the curves for this sample, we instead look at the variation in intensity ratios, which are presented in Table 1. To study the variation quantitatively, we use the model of Frank et al. \[10\] (applied here to the case of LCMO) which models the XPS intensities as being due to a perfect termination of the film surface and takes into account the contribution from each layer. For the crystal structure of LCMO we used data from LaMnO\(_3\) based structures \[11,12\] and our values of the lattice parameters. For the films on (100) SrTiO\(_3\) we use a sequence of layers along the (001) direction, which gives a .../O/Mn/O/La\(_{0.67}\)Ca\(_{0.33}\)O/... sequence. However, in our calculation, the difference between this more exact sequence compared to the approximate sequence .../MnO\(_2\)/La\(_{0.67}\)Ca\(_{0.33}\)O/... is not significant, so we have used the latter sequence. We then have two possible configurations, \(S_{(001)}1\) (MnO\(_2\)/La\(_{0.67}\)Ca\(_{0.33}\)O/...) and \(S_{(001)}2\) (La\(_{0.67}\)Ca\(_{0.33}\)O/MnO\(_2\)/...). For the film on (110) SrTiO\(_3\) we also have only two possible configurations for (100) oriented LCMO, \(S_{(100)}1\) (La\(_{0.67}\)Ca\(_{0.33}\)MnO/O\(_2\)/...) and \(S_{(100)}2\) (O\(_2\)/La\(_{0.67}\)Ca\(_{0.33}\)MnO/...). The values for photoelectron cross sections and inelastic mean free path are taken from the usual sources. \[13,14\] The calculated values of relative intensities for a specified termination layer were then compared to the experimental values and the termination layer varied to minimize \(\chi^2\), where
\[
\chi^2 = \frac{1}{N} \sum_i \frac{(R_{i,m} - R_{i,p})^2}{R_{i,m}},
\]

(1)

with \(N\) the number of ratios compared, \(R_{i,m}\) the measured intensity ratio and \(R_{i,p}\) the predicted intensity ratio for peak \(i\). The results of this analysis are shown in Tables II and III for the LCMO films on different orientations of SrTiO\(_3\), where we also compare the intensity ratios to what would be expected for a random matrix.

For the films on (100) SrTiO\(_3\), we see a clear preference for the films terminating in a MnO\(_2\) configuration. The scans taken at 45° also show a significant enhancement of the Mn and O signal levels, which would imply a MnO\(_2\) surface layer. However, what we see for all the samples on (100) SrTiO\(_3\) is a significantly higher O 1s/La 3d\(_{5/2}\) ratio than that predicted, even for case (C) for which the specimen was annealed in UHV to 600 C. If we assume that the top layer has an enhanced oxygen content, we would require an increase in the oxygen level of 150% to get agreement with our measured values. Clearly this is not reasonable. Requiring a higher oxygen content throughout the film does not give a more reasonable picture, especially in consideration of the fact that our films are oxygen-deficient as shown by annealing them in oxygen. The reason for the substantially increased O 1s signal level is not understood.

For the film on (110) SrTiO\(_3\) we find that the values of \(\chi^2\) for the S(100) models are much poorer than those for the S(001) models on (100) SrTiO\(_3\), and that the random model gives a better agreement. If we compare to the models for (001) oriented LCMO, however, we find that the best fit is with the S(001)1 termination, or the MnO\(_2\) layer. This would not be expected given the observed orientation of the film, and would seem to imply that the MnO\(_2\) layer is an energetically favorable free surface. What maybe happening is that the Mn atoms tend to form a MnO\(_2\) terminating layer, causing a distortion in the layers near the top surface, which might explain the low value of \(\chi^2\) found for these fits. Attempts to model a MnO\(_2\) layer artificially placed onto a (100) oriented LCMO film also gave good results, but not better than that seen for the S(001)1 termination.

In Figure 6 we present detailed scans of the valence region for our \textit{in situ} films on (100) SrTiO\(_3\) and (110) SrTiO\(_3\). For the film on (100) SrTiO\(_3\) we see two dominant contributions near 4 and 6.5 eV. The data are similar to that seen by Chainani et al. \cite{1} for La\(_{1-x}\)Sr\(_x\)MnO\(_3\), but are less similar to the data on a La\(_{0.65}\)Co\(_{0.35}\)MnO\(_3\) film taken at 50 eV photon energy by Zhang et al. \cite{2} In that work the dominant peak was seen at 5.8 eV compared to our 6.5 eV. Zhang et al. also see a high binding energy shoulder at 7.8 eV. For the film on (110) SrTiO\(_3\) we see that there is a loss of intensity at the peak positions seen for the film on (100) SrTiO\(_3\). It might be initially assumed that the change in the spectrum is due to the different crystal orientation. However, in light of the results from the termination study it is more likely that what we are seeing here is the result of the distortion present in the top surface as it orders in a MnO\(_2\) structure. If the Mn atoms come from deeper layers, the local distortion in the Mn-O bonds may result in a smearing of the local density of states, resulting in a valence curve as seen on (110) SrTiO\(_3\).
IV. CONCLUSIONS

We find from quantitative analysis of XPS data that in situ films of LCMO on both (100) and (110) SrTiO$_3$ terminate with MnO$_2$ layers, even though the film on (110) SrTiO$_3$ has an orientation clearly different than the film on (100) SrTiO$_3$. We do not see any significant difference in the binding energies between the two different films, but only a variation in the relative intensity ratios for the core levels. There is a change in the valence structure, which we feel is due to a possible distortion in the top surface of the LCMO film grown on (110) SrTiO$_3$. Exposure to air for 5 minutes and subsequent annealing at 600 C in UHV does not significantly modify the shape of the core levels or the valence structure. Comparing scans at 0$^\circ$ and 45$^\circ$ to the surface normal shows that the core level peaks are not composed of a surface and bulk component, but are representative of the bulk.

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FIG. 1. X-ray diffraction scans along the film normal for LCMO films grown on (a) (100) SrTiO$_3$ and (b) (110) SrTiO$_3$. The reflections due to the substrate are labeled by s.

FIG. 2. (a) Electrical resistivity and (b) relative magnetization vs. temperature for LCMO films grown on (100) SrTiO$_3$ and (110) SrTiO$_3$.
FIG. 3. XPS spectra and peak fit analysis of (a) C 1s and La 4s, (b) O 1s, (c) Mn 2p\textsubscript{3/2}, and (d) La 3d\textsubscript{5/2} lines. Spectra are shown for (A) an *in situ* film, (B) after exposure to air for 5 minutes, and (C) after annealing to 600 C in UHV. All are for LCMO on (100) SrTiO\textsubscript{3}.

FIG. 4. Same as Figure 3 but for (a) Mn 3p, (b) La 4d, (c) Ca 2p, and (d) the valence region.

FIG. 5. XPS spectra around the O 1s line for the *in situ* film on (100) SrTiO\textsubscript{3} (A) taken at 0\textdegree and 45\textdegree relative to the surface normal.

FIG. 6. XPS spectra in the valence region for *in situ* LCMO films grown on (100) and (110) SrTiO\textsubscript{3}. The curves are offset for clarity.

| Sample | \(\text{Mn}^{2p_{3/2}}\)/La 3d\textsubscript{5/2} | \(\text{O}^{1s}\)/La 3d\textsubscript{5/2} | \(\text{Ca}^{2p}\)/La 3d\textsubscript{5/2} | \(\text{La}^{4d}\)/La 3d\textsubscript{5/2} | \(\text{Mn}^{3p}\)/La 3d\textsubscript{5/2} |
|--------|-----------------|----------------|----------------|----------------|----------------|
| (A) *In situ* on (100) SrTiO\textsubscript{3} | 0.51 | 0.45 | 0.087 | 0.26 | 0.050 |
| (B) *Ex situ* on (100) SrTiO\textsubscript{3} | 0.49 | 0.49 | 0.11 | 0.28 | 0.054 |
| (C) 600 C UHV (100) SrTiO\textsubscript{3} | 0.49 | 0.46 | 0.098 | 0.27 | 0.051 |
| *In situ* on (110) SrTiO\textsubscript{3} | 0.54 | 0.56 | 0.13 | 0.28 | 0.063 |

| Model | \(\text{Mn}^{2p_{3/2}}\)/La 3d\textsubscript{5/2} | \(\text{O}^{1s}\)/La 3d\textsubscript{5/2} | \(\text{Ca}^{2p}\)/La 3d\textsubscript{5/2} | \(\text{La}^{4d}\)/La 3d\textsubscript{5/2} | \(\text{Mn}^{3p}\)/La 3d\textsubscript{5/2} | \(\chi^2\)(A) | \(\chi^2\)(B) | \(\chi^2\)(C) |
|-------|-----------------|----------------|----------------|----------------|----------------|-----------|-----------|-----------|
| \(S_{(001)}^1\) | 0.51 | 0.35 | 0.091 | 0.23 | 0.079 | 0.0090 | 0.014 | 0.0109 |
| \(S_{(001)}^2\) | 0.35 | 0.27 | 0.083 | 0.20 | 0.058 | 0.028 | 0.035 | 0.028 |
| Random | 0.44 | 0.32 | 0.094 | 0.24 | 0.077 | 0.012 | 0.018 | 0.014 |

| Model | \(\text{Mn}^{2p_{3/2}}\)/La 3d\textsubscript{5/2} | \(\text{O}^{1s}\)/La 3d\textsubscript{5/2} | \(\text{Ca}^{2p}\)/La 3d\textsubscript{5/2} | \(\text{La}^{4d}\)/La 3d\textsubscript{5/2} | \(\text{Mn}^{3p}\)/La 3d\textsubscript{5/2} | \(\chi^2\) |
|-------|-----------------|----------------|----------------|----------------|----------------|-----------|
| \(S_{(100)}^1\) | 0.41 | 0.28 | 0.081 | 0.20 | 0.062 | 0.044 |
| \(S_{(100)}^2\) | 0.43 | 0.33 | 0.086 | 0.21 | 0.066 | 0.031 |
| Random | 0.44 | 0.32 | 0.094 | 0.24 | 0.077 | 0.028 |
| \(S_{(001)}^1\) | 0.51 | 0.35 | 0.091 | 0.23 | 0.079 | 0.021 |
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