Vacancy assisted SrO formation on $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ surfaces – a synchrotron photoemission study

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Abstract

We present a systematic synchrotron radiation photoemission spectroscopy study of the interaction of O_2 with defective $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}(100)$ surfaces at low temperatures. First, the surface chemical evolution during low energy Ar^+ ion sputtering is investigated and is found to create oxygen vacancies. Subsequently, the interaction of the O_2 molecules with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}(100)$ surface is observed to create an insulating phase. We performed a detailed core-level peak-fitting analysis to identify the chemical nature of this phase and to probe the role of vacancies in the formation of this phase.

Keywords: XPS, SOFC, oxygen vacancy, thin film, Lanthanum Strontium Cobalt Ferrite, fuel cell cathode

1. Introduction

Understanding the surface chemistry of complex multi-element metal oxides is of fundamental scientific importance on account of the myriad of chemical processes they display at low dimensions and because of the possibility of exploiting their properties in energy generation and storage devices [1–4]. Transition metal perovskite oxides have the potential to allow the use of renewable energy on demand as they are widely used to promote the kinetics of oxygen electro-catalysis which can lead to the development of cost effective energy storage and conversion technologies [5–11]. However, the development of highly efficient devices is hampered by the lack of fundamental understanding at the molecular level of the mechanism of electro catalysis [12,13]. Prior studies show that understanding the electronic structure and surface chemistry can lead to the discovery of surfaces which possess superior electro catalytic activities [14,15]. Also one can tune the catalytic activity by modifying the perovskite surfaces by different means [9,16]. Solid oxide fuel cells (SOFC)

have the highest predicted and demonstrated efficiencies for chemical to energy conversion and their extensive use has the potential to provide a clean and efficient path to CO₂-neutral economies [17–19]. La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} (LSCF) is a perovskite oxide with mixed electronic and ionic conductivities which is commonly used as a cathode material for SOFCs [20]. LSCF is a potential candidate for intermediate to low temperature (IT-LT) SOFCs, where lowering the operating temperature could lead to their wide spread SOFC applicability [20]. Sr segregation at the surface while annealing leading to the formation of SrO and SrCO₃ has been reported previously [21,22]. This is detrimental to the device operation due to the insulating nature of these compounds and also as they reduce the effective area available for the oxygen reduction reaction at the LSCF surface [21,22]. X-ray Photoelectron Spectroscopy (XPS) is a powerful technique which can be used to study the surface chemistry by evaluating the electronic structure of the surfaces [23–25]. Literature shows that Ar⁺ ion sputtering can be used as a surface modification tool to pattern the surfaces as well as to create nanostructures with intriguing physical and chemical properties [26,27]. We report here a study of the reaction of oxygen molecules with sputter modified La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF-8228) surfaces using synchrotron XPS measurements.

Our study can be broadly divided into two separate themes. In the first, we systematically investigate the affects of Ar⁺ ion sputtering on the LSCF-8228 (100) surface and the chemical modification resulting from it. In the second, we report results obtained from studying the reaction of oxygen molecules with sputter-modified LSCF-8228 (100) at low temperatures.

2. Experimental

The photoemission measurements presented in this paper were carried out at the soft x-ray undulator beamline X1B at the National Synchrotron Light Source, Brookhaven National Laboratory. During data acquisition the chamber pressure was in the ultra high vacuum (UHV) range (10⁻¹⁰ Torr). Photoemission spectra were carried out on a hemispherical analyzer with monochromatic x-rays at 250 eV and 900 eV. The total resolution of these spectra is estimated to be 0.4 eV (FWHM) for the Sr 3*d* edge, and 0.7 eV (FWHM) for the oxygen and C 1*s*-edges. For the binding energy calibration Au 4*f* core levels of clean gold foil in electrical contact with the sample were used. For XPS core level peak-fitting voigt line shape was used and the background was assumed to be Shirley background. The FWHM values of the bulk peaks of O1*s* and La4*d* are respectively 1.4 eV, 1.39eV. The spin orbit splitting value of 1.7 eV was used Sr 3*d* peak. The calculated Inelastic Mean Free Path (IMFP) values for O1*s* and Sr3*d* signals are 8 Å and 13 Å

respectively. This gives an average sampling depth of about 3.2 nm for the measurements performed here. The asymmetry value for the peaks is kept at zero. Samples were sonicated in isopropyl alcohol and tantalum strips were used to ground the sample surface. Samples were radiatively heated through their mount using a tungsten filament and the power supplied to the filament was monitored using a constant voltage/current power supply. A K-type thermocouple in contact with the surface was used to calibrate the temperature. For both Ar sputtering and oxygen dosing a constant pressure valve was used to maintain a steady pressure of gas inside the chamber. For Ar⁺ sputtering an Ar partial pressure of 5.0×10^{-5} Torr was used with beam energy of 500 eV. For oxygen dosing the valve was set to get a pressure of 1.0×10^{-8} torr which was maintained for 80 min resulting in surface oxygen dosage about 48 L (Langmuir). The sample is annealed in the oxygen gas at different temperatures and after each annealing cycle the sample was quenched by abruptly turning off the heating and was cooled in oxygen before the photoemission measurements were carried out. The LSCF samples used in the present study were single crystalline thin films of 250 nm thickness grown using pulsed laser deposition (PLD) on NdGaO₃ substrate at an oxygen partial pressure of 10 mTorr and substrate temperature 550°C.

3. Results and discussions

3.1 LSCF-8228 (100) – Surface modification

3.1.1 XPS survey scan

LSCF-8228 (100) surface was subjected to several cycles of Ar⁺ ion sputtering for a duration of 5 min each. Sample was sputtered for total sputtering time of 30 min. After each sputtering event, XPS measurements were carried out. Fig. 1 shows the XPS survey scan obtained from the LSCF-8228 (100) surface at x-ray beam energy of 900 eV and different core-level peaks are marked. From Fig. 1 it is clear that the intensity of the C 1s peak changes drastically with sputtering time. Finer scans of the C 1s core levels are plotted in the inset, for clarity. We find that after 5 min of Ar⁺ ion sputtering the C 1s integrated intensity diminishes to about half of that obtained on the pristine LSCF-8228 (100) surface. After 10 min of sputtering the C 1s core level photoemission intensity becomes below the detection limit of the instrument. The position of the C 1s peak observed corresponds to a binding energy (BE) of 284.6 eV which could be due to organic contaminants as the samples were cleaned with isopropyl alcohol [28]. The formation of SrCO₃ at higher operating temperatures has been widely reported to be a possible cause for device deterioration of SOFCs [21,22]. Our XPS spectra doesn't show any contribution related to SrCO₃.

In Fig. 1 regions of Sr 3d and La 4d peaks are clearly marked and show apparent relative changes in their intensities. These are further quantitatively analyzed by computing the fractional compositions of these elements. The cross section values for these calculations are used from Ref. [29] which for Sr 3d is 0.3312 Mbarn at 900 eV and La 4d is 0.2749 Mbarn at 900 eV. The intensity values (evaluated as peak area considering a linear

Fig. 1: shows the photoemission survey scans taken at X-ray beam energy of 900eV from pristine as well as sputtered LSCF-8228 (100) surfaces. And in the inset the C1s XPS core level scans obtained from pristine as well as sputtered LSCF-8228 (100) surfaces are shown for different sputtering times.

background and simple Gaussian fit) obtained from Fig. 1 are thus normalized by dividing with cross-section values of the respective elements to calculate $I_{Sr}/(I_{Sr}+I_{La})$ and $I_{La}/(I_{Sr}+I_{La})$ where I_i represents the normalized intensity of element i , and these are plotted versus sputtering time in Fig. 2. Trend lines are drawn to guide the eye. From Fig. 2 it can be seen that the amount of Sr on the LSCF-8228 (100) surface decreases linearly with sputtering time which saturates after 20 min of sputtering. This is associated with a linear rise in the value of fractional intensity of La 4d. This result indicates that the as loaded pristine LSCF-8228 (100) film has an excess Sr layer on the surface. The samples used in the present study have been grown using PLD at a substrate temperature of 550 °C and in an oxygen partial pressure of 10 mTorr. Our results are in line with the previous report which suggests that growing

PLD films at an oxygen partial pressure lower than the ambient pressure may lead to surfaces that are higher in Sr-containing secondary phases [30]. Thus from Fig. 2 it can be understood

Fig. 2: Fractional intensity ratios of Sr and La obtained from photoemission survey scans from LSCF-8228 acquired at 900eV X-ray beam energy are plotted versus sputtering time in min. The intensities of La and Sr were first normalized with respective cross-section values.

that the effect of sputtering is to remove Sr from this layer as indicated by the reduction in the Sr 3d fractional intensity and the increase in the fractional intensity of La 4d being brought about by the removal of Sr over layers. At 20 min in Fig. 2 both the curves of fractional intensities of La and Sr saturate, where the Sr 3d signals show an average value of 0.17 and the La 4d signal shows an average value of 0.83 at the plateau. These values are close to the bulk stoichiometric values of LSCF-8228 samples used in the present study, *viz.* La(0.8) and Sr(0.2), which also evidences the excess Sr present on the surface [29]. Thus after 20 min the surface is sputtered uniformly preserving the stoichiometry which also validates the choice of low beam energy of 500 eV used in the present study to keep the effect of sputtering mild and uniform.

3.1.2 Oxygen 1s

Fig. 3 shows the results obtained by analyzing the O 1s XPS core-level spectra on LSCF-8228 film surface at 900 eV where we have used XPS multi-peak fitting core-level analysis to decompose the spectra into its constituent components. The XPS background is

modelled using Shirley-type background and a Voigt function is used to model the components of the spectra, which is carried out using the XPSPeak peak fitting software

Fig. 3: (a), (b) and (c) respectively shows the peak-fitted O 1s core level spectra from LSCF-8228 film acquired at X-ray beam energy of 900eV from pristine LSCF sample, 15min sputtered surface and 30min sputtered surface. (d) shows the fractional area of the constituent components of the O1s peak plotted verses sputtering time.

package [31]. Fig. 3(a) shows the fit of the O 1s spectrum from pristine LSCF-8228 surface which can be separated into two components occurring at BEs of 528.7 eV and 531.3 eV. By

measuring the angular dependence of the intensity of ejected photo-electrons and also based on previous reports the lower BE peak can be ascribed to the bulk component and the high BE component to surface component [32,33]. The FWHM of the surface component is larger than the bulk component. This is likely due to carbon related contamination contributions to the peak. The precise chemical identity of surface contaminants cannot be resolved within the current dataset. We observe that when the surface is sputtered the surface component is removed or modified and a new component is observed at a binding energy of 530.7 eV. We have previously observed a similar component in O 1s spectra obtained from the LSCF surface annealed in oxygen gas which showed temperature dependence and was ascribed to the formation of oxygen vacancies [32]. Thus the new peak observed after sputtering is assigned to the formation of oxygen vacancies in the LSCF-8228 film upon sputtering. What we see as vacancy component is the chemically shifted bulk component. Oxygen vacancies are positively charged which modifies (reduces) the kinetic energy of ejected photo-electrons from the oxygen atoms in the vicinity of the vacancy. Thus a new peak at high binding energy side is formed which is labelled as vacancy component. A representative fit of a spectrum after 15 min of sputtering is shown in Fig. 3(b). As the sputtering time is increased, we do not observe any prominent changes in the O 1s spectra other than a relative increase in the peak corresponding to oxygen vacancies which can be seen in the spectra after 30 min of sputtering, shown in Fig. 3(c). So as to understand the quantitative changes in the different components of the O 1s spectra during the sputtering study, the fractional areas (component-area/total-area of all the peaks) of the components are plotted in Fig. 3(d) against the sputtering time, with trend lines drawn to guide the eye. In Fig. 3(d) curve I represents the contribution from the vacancy peak and the curve II that from the bulk peak. The first data point from each data set is excluded from drawing the trend lines as they correspond to the pristine surface and in the next sputtering event the surface peak is modified or removed to give rise to a peak corresponding to vacancies. Fig. 3(d) show that the oxygen vacancies on the LSCF-8228 film surface increases linearly with sputtering. Thus the effect of Ar ion sputtering on the LSCF surface is to create defects which are oxygen vacancies and which linearly increase with sputtering time. To elucidate the effect of the formation of oxygen vacancies on the A-site environment, we have subsequently performed detailed peak fitting analysis on Sr 3d XPS core level spectra.

3.1.2 Strontium 3d

In Fig. (4) we show representative fits to spectra of Sr 3d obtained from the LSCF-8228 surface at an x-ray beam energy of 250 eV. Fig. 4(a) is the Sr 3d spectrum from the

pristine surface and consists of two distinct features with a weak shoulder on the low BE side. This spectrum could be fitted with two sets of Sr $3d_{5/2}$ and Sr $3d_{3/2}$ doublets where the spin

Fig: 4: Shows the deconvoluted Sr 3d photoemission core level scans from LSCF-8228 film acquired at X-ray beam energy of 250 eV. (a) corresponds to the spectra obtained from the pristine sample and (b) is the scan observed on 30min sputtered surface.

orbit splitting is found to be 1.7 eV and the branching ratio 1:0.66 [33]. As in the case of the analysis of the O 1s spectra, the low binding energy doublets at 132.9 eV (Sr $3d_{5/2}$) and 134.6 eV (Sr $3d_{3/2}$) represent the bulk components whereas the doublets at BEs of 134.0 eV (Sr $3d_{5/2}$) and 135.7 eV (Sr $3d_{3/2}$) represent the surface components. The spin orbit splitting value, branching ratio and FWHM of the peak components were fixed for analyzing the Sr 3d spectra obtained from the sputtered LSCF-8228 sample. Fig. 4(b) shows representative spectra obtained after 30 min of sputtering, where as in the case of pristine sample the peak is separated into two doublets of Sr $3d_{5/2}$ and Sr $3d_{3/2}$. After sputtering the important thing we observe is the shift of the high energy doublet towards the low bulk doublet by about 0.4 eV. Thus there is a chemical environmental modification of the high energy (surface) peak as

indicated by the chemical shift. The effect of sputtering, as described above, is to create oxygen vacancies in the LSCF film and this shift observed in the Sr 3*d* component could be a result of the modification of the Sr 3*d* core-level by oxygen vacancies through interaction of Sr with vacancies (Sr-vacancy interaction) owing to their opposite charges which we will discuss in more detail below.

We also acquired La 4*d* XPS core-level scans at different stages of sputtering but did not observe any appreciable changes in the spectra, in contrast to the Sr 3*d* spectra. The analysis of the La 4*d* states is complicated by the spin orbit splitting, occurrence of satellites and also an overlap with Co 3*s* states, which prevented us from separating the spectrum into constituent bulk and surface components [34–36]. For the x-ray beam energies available at the X1B beam-line at Brookhaven National Lab where the present experiment was carried out, the Co and Fe peaks were buried inside secondary electron noise, forbidding any detailed analysis.

3.2 Oxidation of sputtered LSCF-8228 (100) surface

In the second set of experiments a freshly prepared, clean LSCF-8228 sample was loaded into the UHV chamber and continuously sputtered for 30 min with an Ar ion beam. The sputtered LSCF was annealed at different temperatures in O₂ gas at a partial pressure of 1×10^{-8} Torr for a duration of 80 min such that the surface oxygen exposure was ≈ 48 L (Langmuir). XPS measurements were performed on the pristine sample, sputtered surface and after each annealing cycle.

3.2.1 Oxygen 1s

Fig. 5(a) shows the O 1*s* XPS core-level spectra observed at different stages of the sputtering and oxidation experiments. In Fig. 5(a) curves I, II, III and IV respectively show the O 1*s* spectra from pristine, 30 min sputtered surface, annealed in O₂ gas at 100 °C and at 150 °C respectively. As described above, the spectra from the pristine sample can be separated into surface and bulk components whereas the spectrum from the sputtered surface represents has bulk and vacancy components. Annealing of the sputtered sample in O₂ gas at 100 °C as seen by curve III in Fig. 5(a) does not produce any appreciable change in the O 1*s* spectrum. On the other hand, at 150 °C [curve IV, Fig. 5(a)] the spectrum is prominently different, and is shown separately in Fig. 5(b). Annealing at 150 °C is marked by an increase in the overall width of the spectrum [Fig. 5(b)] and the spectra can be fitted with three components. The first peak on the lowest B.E is bulk peak, the peak next to bulk peak is due to vacancies and the third peak at the highest binding energy would be described below. The formation of vacancies on the LSCF with annealing has been seen previously [32] and thus

there may be an additional creation of vacancies than that from the sputtering of the surface. Any further heating of the LSCF sample at temperatures higher

Fig. 5: Deconvoluted XPS core level scans of O 1s from the oxidation study of sputtered LSCF-8228 film acquired at X-ray beam energy of 900eV. In (a), curves I, II, III and IV respectively shows the spectrum from pristine, 30 min sputtered and from surface exposed to oxygen at 100°C and 150°C. (b) Shows the deconvolution of O1s spectrum obtained from the LSCF-8228 surface exposed to oxygen dose at 150°C.

than 150 °C in O₂ gas resulted in the sample surface becoming charged, which prohibited any further XPS measurements. This sample charging indicates the formation of an insulating phase on the surface which results in the accumulation of unbalanced positive charges as the photoelectrons leave the surface. Yu *et al.* describe two possible mechanism for the formation of SrCO₃ on LSCF surface which both require CO₂ [22]. As these experiments were carried out under UHV conditions, any significant amount of carbon on the surface was completely sputtered off and based on the analysis of the Sr 3d described below we ascribe the third component observed in the O 1s spectra to the formation SrO which being insulating supports the observed insulating surface phase transition. To further validate the formation of SrO we describe below the analysis performed on the Sr 3d core-level spectra.

3.2.2 Strontium 3d

Sr 3d spectra obtained from the LSCF-8228 (100) surface at different stages of the oxidation experiment are shown in Fig. 6(a). Curves I, II, III and IV in Fig. 6(a) respectively show the Sr 3d spectra obtained from the pristine 30 min, sputtered, that annealed in oxygen at 100 °C and at 150 °C. As discussed above, the spectra from the pristine sample can be separated into surface and bulk components whereas the sputtered surface includes a component which is chemically shifted compared with the bulk doublets. As in the case of the O 1s core-level spectra, the Sr 3d spectra after annealing in O₂ at 100 °C doesn't show

Fig. 6: Shows the Sr 3d core level spectra obtained in the LSCF oxidation study of sputtered LSCF-8228 film acquired at X-ray beam energy of 250eV. In (a), curves I, II, III and IV respectively shows the spectrum from pristine, 30min sputtered and from surface exposed to oxygen at 100°C and 150°C. (b) Shows the deconvolution of Sr3d spectrum obtained from the LSCF surface exposed to oxygen dose at 150°C.

any appreciable changes, as indicated by curve III, Fig. 6(a). However, after annealing at 150 °C in O₂ gas there is a marked increase in the width of the Sr 3d spectrum indicating an additional component and the spectrum is shown alongside its constituent components in Fig. 6(b). The additional shoulder that develops is best fitted with another doublet to account for the increase in the width of the spectrum. Considering the insulating nature of the LSCF-8228 surface when annealed in O₂ gas at temperatures higher than 150 °C, and in line with the analysis of the O 1s described above and the arguments presented there, this additional doublet can be ascribed to that arising from SrO formation [37,38]. It has to be noted that though we cannot exclude the possibility of some weak charging on the O 1s and Sr 3d spectra IV in Fig. 5 and Fig. 6 respectively, it doesn't conclusively and simultaneously explain both the O1s and Sr 3d spectra. In the following, we discuss the role of vacancies in the formation of the insulating SrO phase on the LSCF-8228 film surface.

3.3 SrO formation – role of vacancies

The main effect of sputtering on the surface is to generate defects which are oxygen vacancies, the quantity of which is found to increase with sputtering time. We have also observed a chemical shift of the Sr surface component upon sputtering. Crumlin. *et al.*, have proposed that because of the opposite charges of the vacancies and Sr, there could be an interaction between the two and the surface vacancies could be driving the Sr from the LSCF lattice towards the surface region, creating a Sr-enriched surface layer [30]. The chemically shifted Sr component observed in the present study could correspond to this Sr enriched layer

and the chemical shift indicates the Sr-vacancy interaction. Our previous results [32] obtained by studying the reaction of O_2 molecules with LSCF at low temperatures showed an

Fig. 7: The schematic showing different processes observed during the sputtering of LSCF-8228 (100) surface and that during the annealing of sputtered LSCF in O_2 gas at different temperatures.

insulating phase at temperature of 300 °C whereas in the present work the insulating phase is formed at a much lower temperature of 150 °C. This lowering of temperature can be explained as follows. In the case of only annealing the sample without sputtering, vacancies form at a certain temperature above room temperature. But when the surface is sputtered before annealing, vacancies are formed prior to the heating process, which help to head start Sr-vacancy interaction. And annealing the sputtered surface further helps in creation of vacancies promoting the formation of Sr enriched near surface layer. This facilitates the SrO formation. The observed mechanism is schematically summarized in Fig. 7 where the different processes and effects observed during sputtering and oxidation are depicted.

4. Summary and conclusions

Considering the importance of understanding the surface chemistry of complex metal oxides and the possibilities of Ar ion sputtering as a surface modification tool, we have carried out a systematic investigation of the reaction of O_2 molecules with the sputtered LSCF-8228 (100) surface. We first described the results of our systematic study of the chemical modification of LSCF surface during sputtering and then discussed the results of the reaction of sputtered LSCF with O_2 molecules at low temperatures using synchrotron photoemission spectroscopy. We find that the surface contaminant carbon species can be completely removed by sputtering for a short duration of 10 min with 500 eV Ar ion beam.

PLD grown samples at O₂ partial pressures lower than the ambient are found to have Sr-excess overlayers, which were found to be sputtered first. Ar ion sputtering is found to create oxygen vacancies in the LSCF film, whose concentration increases with sputtering time. Analysis of the Sr core levels shows evidence for the interaction between vacancies and Sr. An insulating phase is observed to form on the LSCF-8228 surface when annealed in O₂ gas at 150 °C and this phase is identified to be SrO. The low temperature formation of SrO is found to be facilitated by the formation a Sr enriched near surface layer which results from the Sr-vacancy interaction. We believe that the results from the present work obtained by carrying out *in-situ* reaction experiments would contribute towards the understanding of changes in surface chemistry and surface phase composition in SOFC cathode materials.

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Figure(1)

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