Correlation of high temperature x-ray photoemission valence band spectra and conductivity in strained LaSrFeNi oxide on SrTiO₃(110)

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Reversible and irreversible discontinuities at around 573 and 823 K in the electric conductivity of a strained 175 nm thin film of (La_{0.8}Sr_{0.2})_{0.95}Ni_{0.2}Fe_{0.8}O_{3-δ} grown by pulsed laser deposition on SrTiO₃ (110) are reflected by valence band changes as monitored in photoemission and oxygen *K*-edge x-ray absorption spectra (XAS). The irreversible jump at 823 K is attributed to depletion of doped electron holes concomitant with reduction of Fe³⁺ toward Fe²⁺, as evidenced by oxygen and iron core level soft XAS, and possibly of a chemical origin, whereas the reversible jump at 573 K possibly originates from structural changes. © 2009 American Institute of Physics.

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Epitaxial strain in films provides opportunities for the miniaturization of systems, devices, and components. There is an increasing interest in epitaxy of oxide ceramic systems.¹ Under biaxial strain, SrTiO₃ can develop a high temperature (HT) ferroelectric phase,² and permit a larger dopant Nb concentration than bulk phases.³ In-plane compressive strain seems to push away apical oxygen from CuO₂ planes in superconductors, increasing *T_c*.⁴ The charge ordering temperature in Pr_{0.5}Ca_{0.5}MnO₃ was enhanced by epitaxial film growth.⁵ Valence band properties of epitaxial LaSrFe-oxide (LSF) films have been extensively studied with photoemission and oxygen core level spectroscopy.⁶ Critical limits are reached in thin films when temperature activated diffusion destroys the discrete structure of multilayer assemblies. Oxygen vacancy formation⁷ and ordering⁸ must also be taken into account. We present here a thin film study on (La_{0.8}Sr_{0.2})_{0.95}Ni_{0.2}Fe_{0.8}O_{3-δ} (LSFN), which belongs to the class of multiferroic, strongly correlated electron systems.⁹ Our interest in HT properties of LSF is motivated by their suggested use as cathodes in intermediate temperature solid oxide fuel cells, where addition of Ni causes a substantial increase in conductivity.¹⁰ Such materials may have a wider range of applications such as in spintronics,⁹ and their HT properties could possibly play a role in *under the hood* applications in automotive technology.

175 nm thick films and high quality, black luster surface were pulsed laser deposited on single crystal SrTiO₃ (110)

(*a*=0.3905 nm) from a LSFN feed target for 45 min at 773 K and 10 mTorr oxygen base pressure, and then *in situ* annealed with 250 Torr oxygen. Kiessig oscillations were detected with a high resolution Seifert diffractometer. Structure analysis was carried out with a Philips X'pert diffractometer equipped with a Cu target.

Photoemission spectra (PES) were collected at BL 8–1 at Stanford Synchrotron Radiation Lightsource in ultrahigh vacuum (UHV) of 2.1×10⁻⁹ Torr after careful surface cleaning at 623 K and monitoring volatilization of adsorbates with survey scans. After cooling to 323 K, the film was heated to 831 K while spectra were recorded at 60 eV for various *T*. Arrived at 831 K, the film was flashed to 1023 K for 5 min and returned to 828 K. During cooling, spectra were recorded until *T*=344 K. The film was then reddish translucent. Oxygen *K*-edge and iron *L*-edge x-ray absorption spectra (XAS) of the as-deposited and annealed film were recorded by target current detection at Beamline 9.3.2, Advanced Light Source, Berkeley, in UHV of 1.0×10⁻¹⁰ Torr base pressure at 300 K. Spectra were collected from 510–550, 700–750, and 800–880 eV in steps of 0.1 eV with energy resolution of around Δ*E*/*E*~1/10 000. Four-point dc conductivity as a function of *T* was obtained (computer controlled Keithley 2400 sourcemeter, Keithley 2700 multimeter¹¹) in a muffle furnace at ambient pressure.

The sharp double peaks (*K*_{α1} and *K*_{α2}) in the x-ray diffractogram (XRD) (Fig. 1) at around 32.45°, 67.8° are identified with the (110) and (220) substrate (*S*) Bragg reflections.^{12,13} Reflections at 31.4° and 31.8° are from the as-deposited (black) and the annealed (red) film. The film grows to a large extent commensurate with the substrate in

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FIG. 1. (Color online) Diffractogram of LSFN powder (P, blue with indexed reflections), and as-deposited (F, black) and annealed (F, red) thin films. The left inset shows in magnification substrate (110) peaks (s) at about 32.45° , and the film (110) reflections between 31° and 32° , respectively. Left inset shows reflectometry Kiessig oscillations (filled symbols with cubic spline), modeled with a 175 nm film (thin drawn line).

(110) orientation (left inset). The peak at 31.4° is identified with the film (110) reflex (F), and shifted in the annealed film toward larger 2θ , suggesting film growth with expanded interlayer distance (1.73 Å), i.e., tensile perpendicular strain and lateral compressive strain, larger than the corresponding bulk material (1.70 Å), relaxing to 1.72 Å after annealing. For comparison, the XRD of LSFN powder (blue with indexed peaks, Fig. 1) looks similar to SrTiO_3 .¹³ Reflectometry Kiessig oscillations account for quality growth of the film and were modeled with 175 nm thickness (upper right inset).

Not shown here, scanning electron micrographs from the 1300 K annealed film show oblate, recrystallized microcrystals (1–2 μm wide, 150 nm thick) steeping out of the film. Within the detection limits, energy dispersive x-ray analysis and x-ray photoelectron spectroscopy did not show interdiffused Ti from the substrate to the film surface, suggesting that the film is thick enough to cover the substrate, and that compressive lateral strain in the as-deposited film provides an effective diffusion barrier. At 870 eV, an L_2 XAS peak for Ni was found.

Figure 2 displays the valence band PES during heating from 296 to 831 K, and subsequent cooling to 344 K. The peak assignment is the same as in Refs. 6 and 14, with the e_g band arising from doped holes in least-squares fit below -2.0 eV. Two sets of spectra mutually overlap well, i.e., those for heating to $296 \text{ K} < T < 723 \text{ K}$, representative to the fully strained film, and spectra for $831 \text{ K} > T > 344 \text{ K}$, representing to the partially relaxed film. Between 723 and

FIG. 2. (Color online) Left: normalized and energy corrected PES for the heating (left set; 296–723 K) and cooling (right set, 831–344 K). Right: magnified ranges of PES intensity near E_F during heating and cooling for quantitative intensity analysis.

FIG. 3. (Color online) Comparison of conductivity (lower three open symbol curves, solid filled bullet curves) and intensity of the PES spectra (upper left; connected circles with error bars) near the Fermi energy (-1.4 eV). Dip in PES intensity is paralleled by dip in conductivity at around 550 K.

831 K, still in the heating half cycle, there is drastic spectral change, i.e., the lower T spectra have their overall intensity maximum (t_{2g}) at -3.8 eV, whereas for $T=831$ K, that maximum is at about -5.0 eV. The e_g band shoulder at -1.9 eV is particularly pronounced for $T=296$ K. A second shoulder, left from the maximum, is observed at about -5.0 eV for $296 \text{ K} < T < 723 \text{ K}$. Here, no shift is observed. This shoulder coincides with the maximum of the spectrum of the $T=558$ K maximum (t_{2g}). While the spectra at 831 and 828 K have not as sharp maxima as those from lower T , the spectra at 831 K (last heating temperature) and all cooling temperatures look similar. Hence, a significant transition has taken place at $T > 723$ K during heating, but before flashing to 1023 K. These spectra still correspond to the strained film. Note that after the spectrum for 831 K was recorded, the film was flashed for 5 min to 1023 K; this stage represents the relaxed film. Hence, the drastic spectral change between 723 and 831 K cannot be attributed to the flashing to 1023 K. Inspection of all spectra near the Fermi energy E_F from $-2.0 \text{ eV} \leq E \leq -1.0 \text{ eV}$ shows systematic intensity variation with T , which we determined at an arbitrary energy of -1.4 eV and plotted for comparison in Fig. 3 reflecting the heating and cooling cycle. The PES intensity has a maximum at around 573 K, and then rapidly decreases during further heating at around 723–823 K. Upon cooling, it keeps declining, but passes an intermediate maximum at around 523 K.

The film conductivity σ is shown in three subsequent scans for $295 \text{ K} \leq T \leq 1298 \text{ K}$, along with σ of a sintered slab from LSFN powder. Scan 1 exhibits an overall semiconducting-like profile. The conductivity at 295 K increases convex to 773 K, and then steeply increases to about 1073 K. After cooling to 300 K, the scan was repeated and a maximum at 1223 K was identified. Here, T did not exceed 1298 K. Scan 2 follows the global trend of scan 1, while scan 3 shows strong deviations. The conductivity increases steeply convex to around 550 K, where it abruptly decreases steplike. At 598 K, σ then increases concave to about 10.6 kS/m and remains at this value. Obviously, after two cycles to HT of 1073–1298 K, the film does not regain its original maximum σ , but remains at a plateau. Close inspection of σ around 573 K shows a slight saddle for scan 1, which develops to an undulation in scan 2, and to a step in scan 3. In this range, scan 2 shows concave growth, matching that of scan 3 very well, with the exception of a constant shift by around 2.0 kS/m up to 823 K. Here, the conductivity of scan 2 shows a sharp discontinuity of around $\Delta\sigma=5.0$ kS/m, not observed in the other scans. Scan 1 also shows slight deviation from the typical exponential increase of the conductivity

FIG. 4. (Color online) Left—oxygen XAS of films. Green arrow at 525 eV indicates the position of the realized (upper spectrum) and missing (lower spectrum) hole doped e_g states. Right—iron L -edge XAS (open symbols) and multiplett simulation (solid line).

of LSFN at ambient and intermediate T . A relative maximum and minimum around 573 K, as with scan 2 and scan 3 are not observed, but an inflection point around 598 K, at which the convex conductivity switches to an intermediate concave trend until it reaches 623 K. At 673 K, the convex characteristic is recovered in scan 1.

The correlation of the peculiarities in the relative PES intensity and the conductivity variation versus T in Fig. 3 is obvious (i) with respect to the initial increase and final decrease of σ and PES intensity from ambient T to 523 K, (ii) with respect to the intermediate maxima around 573 K, as highlighted with red circles in Fig. 3, and (iii) with respect to the jump feature at ~ 823 K for scan 2 during heating and the PES intensity starting at cooling, indicated by the vertical red line in Fig. 3. The extent of agreement is actually overwhelming, given the different physical mechanisms for PES and conductivity measurements. Similar observations were recently made on a monolithic single crystal,¹⁴ underlining that metal oxides can be meaningfully studied *ex situ* with PES and correlated with bulk transport properties. We believe that the features described in ii and iii are caused by minute phase transitions in the LSFN, first of which is reversible. Such phase transitions can influence electron orbitals and thus impact the conductivity.¹⁵ While the complexity of phase transitions may increase with decreasing film thickness,¹⁶ they might not even be detected in monolithic materials. The conductivity profile of the sintered slab has no peculiarities, except for an almost unnoticeable step at 486 K with $d\sigma/dT > 0$ for $T < 486$, and $d\sigma/dT < 0$ for $T > 486$ K. The conductivity profile of the slab is shifted by around 200 K toward lower T , and its maximum is below that of the strained film.

The change in σ during annealing scan 2 to scan 3, the change in the XRD, the PES intensities, and color change show that the film undergoes severe pathogenesis. The conductivity in LSF is based on electron holes doped by the Sr substitution, which manifests in an extra peak from a spin-up e_g orbital in the prepeaks of the oxygen XAS, in addition to the spin down t_{2g} and e_g bands (fitted in Fig. 4 with three pseudo-Voigt functions of 1.1, 1.2, and 1.2 eV width using WINXAS program), which are known for LaFeO_3 .¹⁷ While the spectrum of our as-deposited film has a distinct such e_g peak at 525 eV, it is absent for the annealed film, Fig. 4, revealing that annealing caused chemical changes in the film that removed the electron holes. Our multiplett simulation¹⁷ of the Fe L -edge spectra (Fig. 4) shows that Fe in the as-deposited

film is predominantly Fe^{3+} , whereas the annealed film has around 70% Fe^{3+} and 30% Fe^{2+} . Electron holes in the as-deposited film may be brought about by minute amounts of Fe^{4+} . Annealing causes reduction of the Fe^{3+} toward Fe^{2+} by oxygen loss, suggesting that electron holes are removed by annealing, and σ decreases accordingly. We could not make such estimate with respect to the Ni because their L_3 edge overlaps with the La $M_{4,5}$ absorption edge.

It remains open to what extent strain changed the film properties. The T range in which σ varies has a direct effect on the transport, potentially caused by lateral compression and vertical expansion of the film lattice. Strain may influence the density of states so that the semiconducting type conductivity is suppressed, for example by less overlap of O ($2p$) orbitals with the Fe and Ni ($3d$) orbitals, unless thermal activation sets in. Systematic studies on structure, conductivity, and valence bands with x-ray spectroscopy on films with varying substrates and film thickness would likely shed more light on the entanglement of transport, electronic structure, and epitaxial strain in films.

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