PHYSICAL REVIEW B **79**, 121101(R) (2009)

Direct observation of a repeatable change in electronic states with applied electric voltage pulses in the metal-insulator-metal structure

K. Azumi,[1] K. Aoyama,[1] S. Asanuma,[1] Y. Uesu,[1] and T. Katsufuji[1,2,3]
[1]*Department of Physics, Waseda University, Tokyo 169-8555, Japan*
[2]*Kagami Memorial Laboratory for Material Science and Technology, Waseda University, Tokyo 169-0051, Japan*
[3]*PRESTO, Japan Science and Technology Agency, Saitama 332-0012, Japan*

(Received 12 November 2008; revised manuscript received 22 December 2008; published 6 March 2009)

By the microspectroscopic imaging of optical reflectivity for the $La_{1-x}Sr_xFeO_{3-\delta}$ thin film with indium-tin-oxide electrodes, we observed that the shape of the conducting area between two electrodes is reversibly varied with applied electric voltage pulses and that causes a repeatable change in the electrical resistance between the electrodes. These results can be explained by the oxygen-ion migration with applied electric field, which induces a variation in the distribution of the Fe^{4+} ions in the thin film.

DOI: 10.1103/PhysRevB.79.121101 PACS number(s): 73.40.Rw, 71.30.+h, 73.50.Fq, 78.20.Jq

Switching behavior of electrical resistance in the metal-insulator-metal (MIM) structures attracts great interest because of its potential use as nonvolatile memories.[1–18] This nonvolatile and repeatable switching behavior is characterized by the change in the electrical resistance of insulating (poorly conducting) materials between two metallic electrodes after applied different directions or magnitudes of electric field. Recent studies[7–11,13,15–18] suggest that ion migration by electric field and a resulting change in the electronic states are responsible for the change in the electrical resistance in those systems. Regarding this issue, several experimental techniques have been employed, for example, conductivity mapping by an atomic-force microscope with a conducting cantilever[11] for directly detecting the repeatable change in the local electrical resistance or an x-ray absorption spectroscopy measurement[15,16] and a transmission electron microscope[17] for detecting the change in the electronic states before and after an applied electric field. However, there has been no report on the direct observation of the repeatable change in the electronic states by an applied electric field. In the present work, we directly observed a repeatable change in the electronic states associated with the migration of oxygen ions with electric field by means of microspectroscopic imaging technique.

To optically observe the change in the MIM structure, several issues have to be taken into account. First, since optical imaging technique requires that the area in which the oxygen ions migrate is exposed to air, the capacitor-type electrodes that sandwich the insulating thin film are not appropriate but the coplanar electrodes on top of the thin film are better. On the basis of this structure, the next issue to be considered is reducing the contact resistance between the insulating thin film and the electrode. If the contact resistance is substantially larger than the bulk resistance of the thin film itself, the electric field is applied only at the interface between the electrode and the film, and the ion migration driven by the electric field can occur only at a very limited spatial region, presumably much shorter than 1 μm from the electrodes. Accordingly, if we want to observe the oxygen-ion migration in the thin film in the way of optics, which requires the length scale of the object longer than the wavelength of light (typically 1 μm), the value of the contact resistance should be small enough, i.e., comparable to that of the bulk resistance, such that ion migration occurs over an sufficiently large spatial region.

Through the studies of the switching behavior on various thin films and electrodes, we found that the perovskite ferrite $La_{1-x}Sr_xFeO_{3-\delta}$ allows a large amount of oxygen defects δ, suitable to oxygen-ion migration in the crystal, and the combination with indium-tin-oxide (ITO) electrodes provides resistance values small enough (~several kΩ) for the measurement. Thus, $La_{0.33}Sr_{0.67}FeO_{3-\delta}$ thin film was deposited by pulsed laser deposition on the (001) $SrTiO_3$ substrate, following the method in Ref. 19, for the present study. Oxygen partial pressure and substrate temperature were varied as follows: 650 °C/0.15 Torr for "oxidized" samples and 800 °C/5×10^{-5} Torr for "reduced" samples. The thickness of the films was 40 nm. ITO electrodes were deposited on the oxidized samples by the same technique for 300 °C/0.02 Torr, as illustrated in Fig. 1(a). X-ray diffraction measurement indicates that all the thin films are homogeneous—judging from the width of the diffraction peak—and *c* axis oriented, and the *c* lattice constants are 3.87, 3.99, and 3.90 Å for the oxidized, reduced, and the sample with ITO, respectively. This result indicates that the sample with ITO electrodes is reduced during the deposition of ITO. Note that the lattice constant of bulk $La_{1/3}Sr_{2/3}FeO_3$ close to oxygen stoichiometry is 3.87 Å in the cubic setting.[20] A typical value of resistivity of the oxidized samples is 2×10^{-2} Ω cm and contact resistance is typically less than 10% of bulk resistance.

On these thin films, we employed a microspectroscopic imaging technique, by which we measured the spatial distribution of optical reflectivity with an applied electric field between the two electrodes. In the imaging mode of our measurement system, the spatial distribution of the optical reflectivity (R) of the monochromated light with a wavelength between 400 and 900 nm (3.1 and 1.4 eV) can be measured by a charge-coupled device camera with relative accuracy $\Delta R/R\sim5\times10^{-3}$ and with spatial resolution 2 μm. In the spectroscopy mode, the optical reflectivity spectrum for the area of typically 30×30 μm^2 was measured by using a Si or Ge photodiode as a detector, an optical chopper, and a lock-in amplifier between 400 and 1800 nm (3.1 and 0.7 eV)

©2009 The American Physical Society

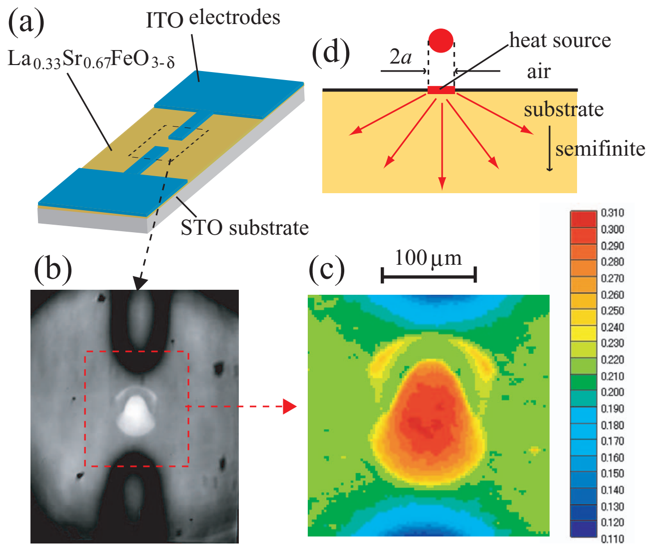

FIG. 1. (Color) (a) Schematic picture of the metal-insulator-metal structure. The dotted rectangular refers to the area observed under the microscope. (b) Microscopic image of the white area by unmonochromated light between two electrodes (up and bottom). (c) Optical reflectivity image (spatial distribution of optical reflectivity) by the light with a 500 nm wavelength for the same sample as that of (b). (d) Schematic picture of the diffusion of the heat produced within the thin film between the electrodes represented by the two-dimensional heat source in a circle with a radius *a*.

with relative accuracy $\Delta R/R \sim 1\times10^{-4}$. Microspectroscopic technique was applied also to the reflectivity measurement with a Fourier transform infrared spectrometer with a HgCdTe detector between 0.08 and 0.8 eV.

First, electric voltage pulses were applied between the two electrodes with gradually increased pulse height. At a certain pulse height and width, typically 50 V and 100 ms, a "white" area appears between the two electrodes. Figure 1(b) is a microscopic image of the white area between the two electrodes by unmonochromated light from a halogen lamp. The optical reflectivity image around the white area by the monochromated light with a wavelength of 500 nm is shown in Fig. 1(c). An area in the shape of an asymmetric ellipsoid with higher reflectivity than the other area by several percent can be observed.

We measured the spectra of optical reflectivity for the white area and the other area of the thin film. As shown in Fig. 2(a), the value of optical reflectivity is higher between 0.1 and 3 eV for the white area than the other area. We also measured the reflectivity spectra of the thin films of $La_{0.33}Sr_{0.67}FeO_{3-\delta}$ deposited in different oxygen partial pressures, as shown in Fig. 2(b). The thin film grown in oxidizing atmosphere has higher reflectivity than that grown in reducing atmosphere. We made Lorentzian fitting of the four reflectivity spectra [the white area of the sample, the other area of the sample, the oxidized film, and the reduced film] by assuming four Lorentzians (~0.5, 1.5, 2.5, and 4.3 eV) and by taking account of the multiple reflections within the thin film.[22,23] The results of the fitting for the reflectivity spectra are shown in Figs. 2(a) and 2(b) by dashed lines, and the optical conductivity spectra reproduced from the obtained parameters are shown in Fig. 2(c).

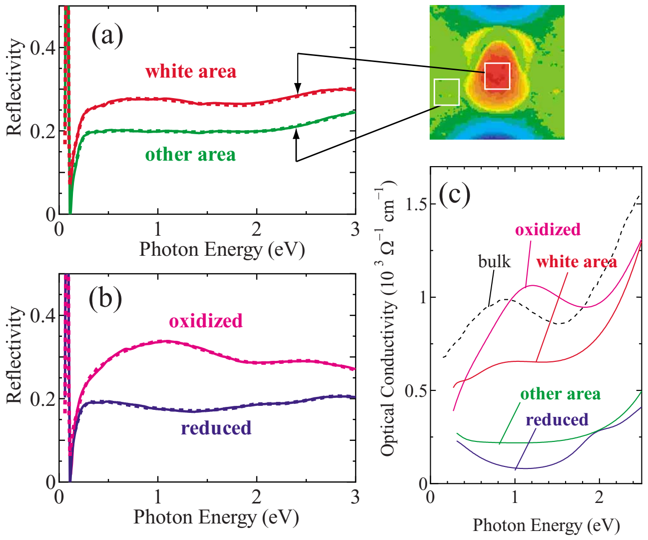

FIG. 2. (Color online) (a) Reflectivity spectra for the white area and the other area of the sample (solid lines). The dashed lines correspond to the result of the Lorentzian fitting. The position of the arrows corresponds to the photon energy used for the reflectivity imaging. (b) Reflectivity spectra of $La_{0.33}Sr_{0.67}FeO_{3-\delta}$ deposited in the oxidized atmosphere and reducing atmosphere (solid lines). The dashed lines correspond to the result of the Lorentzian fitting. (c) Optical conductivity spectra derived by the Lorentzian fitting for the four samples shown in (a) and (b). The optical conductivity spectrum of bulk $La_{1/3}Sr_{2/3}FeO_3$ (dashed line) is from Ref. 21.

The optical conductivity spectrum of the oxidized sample in Fig. 2(c) resembles that of the bulk $La_{1/3}Sr_{2/3}FeO_3$ single crystal[21] shown by a dashed line, except for the overall shift of the spectrum to higher energy by ~0.3 eV.[24] This similarity of the spectrum and the similar lattice constant between the oxidized film and the bulk sample indicate that the oxygen content of the oxidized film is most close to stoichiometry among the four samples. The comparison of the four spectra suggests that the "white" area of the sample between the electrodes is more stoichiometric (i.e., has less oxygen deficiency) than the other area. Such a difference of the spectral weight in the optical conductivity with different amounts of oxygen deficiency can be attributed to the different amounts of the Fe^{4+} ions in the sample. Indeed, the spectral weight below 3 eV increases with increasing x almost linearly for the bulk single crystals of $La_{1-x}Sr_xFeO_3$.[25] It should be pointed out that in various transition-metal oxides, the change in the spectral weight of optical conductivity with doping barely depends on how the doping is made either by cation substitution or oxygen offstoichiometry.[26,27] Therefore, we estimated the amount of oxygen deficiency δ for each $La_{0.33}Sr_{0.67}FeO_{3-\delta}$ thin film by obtaining the spectral weight of optical conductivity below 2.5 eV and comparing it with the linear relation between the spectral weight and the number of Fe^{4+} for $La_{1-x}Sr_xFeO_3$ single crystals.[25] The result is as follows: δ=0.04 for the oxidized sample, δ=0.10 for the white area between the electrodes, δ=0.25 for the other area, and δ=0.27 for the reduced sample.

As a next step, the voltage pulses with the opposite polarity were applied. First, the electric pulses with 60 V height and 100 ms width were applied. As shown in Fig. 3(a), the

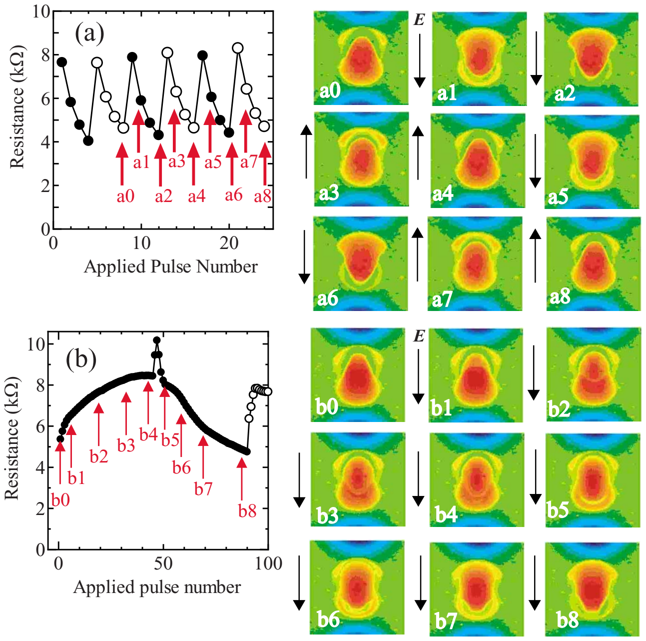

FIG. 3. (Color online) (a) Left panel: change in the electrical resistance between the electrodes associated with the application of the electric voltage pulses. The pulse height and width were fixed to 60 V and 100 ms, but the polarity was changed after four pulses with the same polarity had been applied. Arrows show the timing when the reflectivity images were measured. Right panels: change in the reflectivity images by the monochromated light with a wavelength of 500 nm measured simultaneously with the resistance measurement. The arrows correspond to the polarity direction of the applied electric voltage. (b) Same as (a) except for the pulse width (10–20 ms).

shape of the “white” area changes in such a way that the wide side of the asymmetric ellipsoid moves to the opposite side of the electrodes. It should be noted that the direction of the movement is opposite to the direction of the electric field. Together with this shape change, the electrical resistance between the two electrodes also changes, as shown in Fig. 3(a). These changes in the shape of the white area and the electrical resistance are reversible and repeatable with the polarity change in the voltage pulses.

To see these changes more precisely, the shorter voltage pulses (10–20 ms) with the same polarity were successively applied. As seen in Fig. 3(b), during the variation in the shape of the white area with applied electric pulses, the value of the electrical resistance takes the maximum in the “intermediate” state with an approximately symmetric shape of the white area between the electrodes (b4 and b5). When further voltage pulses are applied and the asymmetric shape becomes the mirror reflection of the original one, the resistivity comes back to the original low value (b8). These results indicate a clear correlation between the shape change in the white area and the electrical resistance.[28]

According to the result of bulk $La_{1-x}Sr_xFeO_{3-\delta}$, a larger amount of Fe^{4+} leads to lower electrical resistivity in this series of compounds. Thus, the white area with a smaller amount of oxygen deficiencies is electrically more conductive than the other area, resulting in the different values of electrical resistance between the two electrodes with the different shape of the white area. The lower electrical resistance when the white area is in the asymmetric shape can be explained by the lower contact resistance arising from the conducting (white) area touching the ITO electrode, as exemplified in Fig. 3 (b8).

Next, let us discuss the origin of the shape change in the white area with applied electric pulses. Since the white area moves to the opposite direction of the electric field, negatively charged objects are responsible for the shape change, and thus, it is most likely that oxygen ions move to the opposite direction of the electric field. This phenomenon is the same as the oxygen-ion conduction observed in various oxides. From the distance over which the oxygen ion moves ($l \sim 100\ \mu\text{m}$), the height ($V=60$ V) and the width ($t=100$ ms) of the electric pulse, the distance between the two electrodes ($d \sim 100\ \mu\text{m}$), and the relation $l=\mu Vt/d$; the mobility μ of the oxygen ions in this compound is estimated as $1.7\times10^{-5}\ \text{cm}^2/\text{V s}$. From the relation $\sigma=nq\mu$, where n is the density of mobile oxygen vacancies given by the difference of δ in the white and the other areas, and q is the charge of an oxygen ion ($2e$), the ion conductivity σ of this sample is estimated as $1.4\times10^{-2}\ \text{S cm}^{-1}$. This value is comparable to that of yttria-stabilized zirconia known to exhibit high oxygen-ion conductivity, at higher than room temperature, typically 500 °C.[29]

This high-temperature condition is satisfied owing to the self-heating effect by the flow of electrical current through the resistive thin film. In this experiment, 60 V voltage was applied to the thin film with approximately 6 kΩ resistance, and thus, 0.6 W power was produced from the thin film with the thickness 40 nm and with a typical length scale 100 μm along the plane. Here, the thin film can be regarded as a two-dimensional heat source on the surface when estimating its temperature. From the thermal conductivity $\kappa=0.112\ \text{W/cm K}$, the specific heat $c_p=0.544\ \text{J/g K}$, and the density $\rho=5.12\ \text{g/cm}^3$ of $SrTiO_3$; it can be estimated that for $t=100$ ms, a typical width of the electric pulses, the heat produced on the surface penetrates over $\lambda=\sqrt{\kappa t/\rho c_p} \sim 600\ \mu\text{m}$. This length λ is much larger than the length scale of the area where heat is produced (100 μm). Accordingly, it can be assumed that three-dimensional diffusion of heat into the substrate reaches a stationary state ($t\rightarrow\infty$ limit). When a power p is supplied to the inside of a circle with a radius a on the surface of the material, and the heat flows into the semifinite material with the thermal conductivity κ [Fig. 1(d)], the temperature increase in the surface within the circle is given by $\Delta T=p/\pi\kappa a$ in the stationary state.[30] With the values of $p=0.6$ W, $2a=100\ \mu\text{m}$, and $\kappa=0.112\ \text{W/cm K}$, ΔT becomes ~340 K.

This temperature increase is compatible with the high ionic conductivity required for the shape change in the white area between the electrodes. Furthermore, this temperature increase is enough to oxidize the oxygen-deficient $La_{0.33}Sr_{0.67}FeO_{3-\delta}$ to yield the “white” area (oxidized area) by the initial application of electric pulses. We speculate that when the white area appears in the initial process (forming process), oxygen comes from air and migrates into the sample; whereas during the repeatable switching process with an applied electric voltage, oxygen migration occurs only within the thin film. Such a tunable and reversible control of oxygen contents by electric field can be a useful technique for the study of the phenomena sensitive to carrier doping, for example, metal-insulator transitions and superconducting transitions, in oxide materials

Self-heating by electric current and resulting oxygen-ion migration can explain the quite efficient switching in the MIM structure with a thin film and capacitor-type electrodes, in which the switching occurs in the filamentary path between the electrodes,[5,11,14,17] since (1) the length scale in which heat is produced (parameter a) becomes so small (typically the radius of the filamentary path) so that the temperature increase ($\Delta T = p/\pi\kappa a$) can be large enough even with small electric power (p) and (2) the length scale over which the oxygen ions have to move (l) is also substantially reduced (typically the thickness of the film), resulting in the much shorter pulse width ($t = ld/\mu V$) needed to induce the switching.

We thank Y. Tokura for showing us the unpublished data of $La_{1-x}Sr_xFeO_3$ single crystals. We also thank A. Sawa, Y. Ogimoto, and S. S. Saxena for fruitful discussions. This work was partly supported by a Grant-in-Aid for Scientific Research (B) from MEXT of Japan.

---

[1] R. Waser and M. Aono, Nature Mater. **6**, 833 (2007).

[2] S. Q. Liu, N. J. Wu, and A. Ignatiev, Appl. Phys. Lett. **76**, 2749 (2000).

[3] A. Beck, J. G. Bednorz, Ch. Gerber, C. Rossel, and D. Widmer, Appl. Phys. Lett. **77**, 139 (2000).

[4] Y. Watanabe, J. G. Bednorz, A. Bietsch, Ch. Gerber, D. Widmer, A. Beck, and S. J. Wind, Appl. Phys. Lett. **78**, 3738 (2001).

[5] C. Rossel, G. I. Meijer, D. Bremaud, and D. Widmer, J. Appl. Phys. **90**, 2892 (2001).

[6] A. Baikalov, Y. Q. Wang, B. Shen, B. Lorenz, S. Tsui, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, Appl. Phys. Lett. **83**, 957 (2003).

[7] S. Tsui, A. Baikalov, J. Cmaidalka, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, C. W. Chu, L. Chen, and A. J. Jacobson, Appl. Phys. Lett. **85**, 317 (2004).

[8] K. Aoyama, K. Waku, S. Asanuma, Y. Uesu, and T. Katsufuji, Appl. Phys. Lett. **85**, 1208 (2004).

[9] A. Sawa, T. Fujii, M. Kawasaki, and Y. Tokura, Appl. Phys. Lett. **85**, 4073 (2004).

[10] S. Seo, M. J. Lee, D. H. Seo, S. K. Choi, D.-S. Suh, Y. S. Joung, I. K. Yoo, I. S. Byun, I. R. Hwang, S. H. Kim, and B. H. Park, Appl. Phys. Lett. **86**, 093509 (2005).

[11] K. Szot, W. Speier, G. Bihlmayer, and R. Waser, Nature Mater. **5**, 312 (2006).

[12] M. Hamaguchi, K. Aoyama, S. Asanuma, S. Uesu, and T. Katsufuji, Appl. Phys. Lett. **88**, 142508 (2006).

[13] X. Chen, N. Wu, J. Strozier, and A. Ignatiev, Appl. Phys. Lett. **89**, 063507 (2006).

[14] Y. Ogimoto, Y. Tamai, M. Kawasaki, and Y. Tokura, Appl. Phys. Lett. **90**, 143515 (2007).

[15] G. I. Meijer, U. Staub, M. Janousch, S. L. Johnson, B. Delley, and T. Neisius, Phys. Rev. B **72**, 155102 (2005).

[16] M. Janousch, G. I. Meijer, U. Staub, B. Delley, S. F. Karg, and B. P. Andreasson, Adv. Mater. (Weinheim, Ger.) **19**, 2232 (2007).

[17] G.-S. Park, X.-S. Li, D.-C. Kim, R.-J. Jung, M.-J. Lee, and S. Seo, Appl. Phys. Lett. **91**, 222103 (2007).

[18] Y. B. Nian, J. Strozier, N. J. Wu, X. Chen, and A. Ignatiev, Phys. Rev. Lett. **98**, 146403 (2007).

[19] H. Wadati *et al.*, Phys. Rev. B **71**, 035108 (2005).

[20] P. D. Battle, T. C. Gibb, and P. Lightfoot, J. Solid State Chem. **84**, 271 (1990).

[21] T. Ishikawa, S. K. Park, T. Katsufuji, T. Arima, and Y. Tokura, Phys. Rev. B **58**, R13326 (1998).

[22] O. S. Heavens, *Optical Properties of Thin Solid Films* (Dover, New York, 1965).

[23] The parameters for the 4.3 eV Lorentzian were obtained from the optical conductivity spectrum of the $La_{1/3}Sr_{2/3}FeO_3$ single crystal (Ref. 21) and fixed in the fitting. The value of $\epsilon_\infty = 5$ (the high-frequency limit of the real part of the dielectric constant) was also obtained from the data of the single crystal.

[24] This blue shift of the spectrum is probably caused by the tensile strain from the $SrTiO_3$ substrate. The Fe-Fe distance is enlarged by 1% in the thin film along the plane, and this results in the decrease in the transfer integral of d electrons and the enhancement of the correlation gap.

[25] S. K. Park and Y. Tokura (unpublished).

[26] M. A. Quijada, D. B. Tanner, F. C. Chou, D. C. Johnston, and S.-W. Cheong, Phys. Rev. B **52**, 15485 (1995).

[27] C. C. Homes, J. M. Tranquada, Q. Li, A. R. Moodenbaugh, and D. J. Buttrey, Phys. Rev. B **67**, 184516 (2003).

[28] See EPAPS Document No. E-PRBMDO-79-R13908 for a different type of change in the reflectivity image on a different type of sample structure. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html

[29] H. Inaba and H. Tagawa, Solid State Ionics **83**, 1 (1996).

[30] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, New York, 1959).