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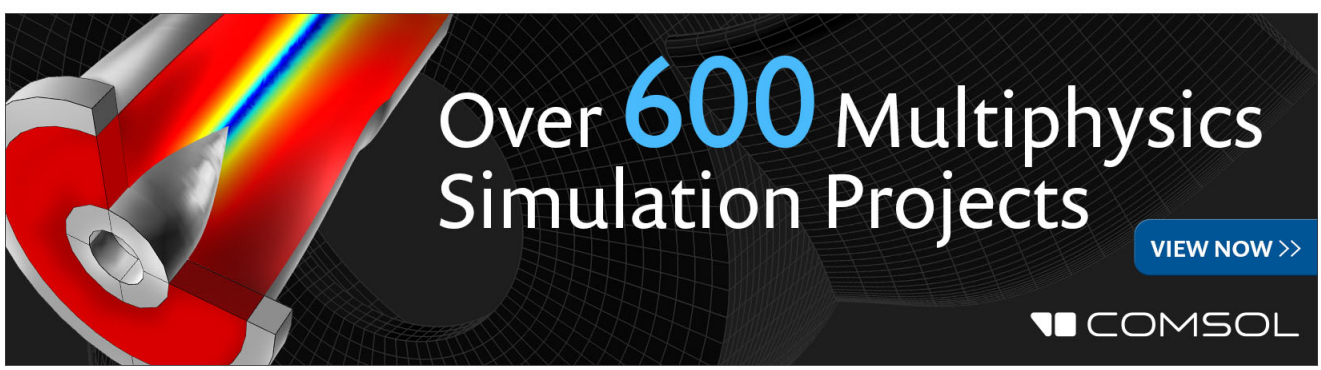

Visible light illumination-induced phase transition to the intermediate states between the metallic and insulating states for the $LaAlO_3/SrTiO_3$ interfaces

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Photoexcitation usually drives the $LaAlO_3/SrTiO_3$ interface from the insulating state into a totally metallic state, without experiencing any intermediate states. Here, we reported on an illumination-induced transition of the insulating $LaAlO_3$(3uc)/$SrTiO_3$ interface to a series of state between a totally insulating state and a totally metallic state. We found that appropriate light illumination can cause an insulator-to-semiconductor transition in the temperature range above ~150 K and an insulator-to-metal transition below ~60 K, while the original state recovers immediately after the removal of the illumination, without persistent photoconductivity as previously reported. Moreover, a remarkable resistive anomaly corresponding to the structural transition of $SrTiO_3$ at ~105 K appears, indicating a phase-transition-induced carrier density change. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4904460]

The two-dimensional electron gas (2DEG) at the $LaAlO_3/SrTiO_3$ (LAO/STO) interface has attracted intensive attentions in recent years,[1] and exotic phenomena including superconductivity,[2] magnetism,[3] gating effect,[4] and charge writing effect[5,6] have been observed. It thus provides a unique platform for emergent phenomenon exploration. An interesting observation is that the metallic 2DEG forms only when the LAO overlay exceeds a critical thickness, i.e., ~4 unit cells (uc).[4] As theoretically revealed, this is the threshold thickness for the electron transferring to the LAO/STO interface to screen the discontinuous electrical polarity at the interface.[4,7] In additional to the layer thickness of LAO, the oxygen pressure, P_O, for the deposition of the LAO layer also affects the conductivity of the interface. The interface is metallic when P_O is below 10^{-4} mbar, and undergoes a metallic to semiconducting transition below ~100 K when the oxygen pressure is increased to about 10^{-3} mbar. However, exposing the insulating interface to a ultra-violet or visible light, a metallic transition can be triggered.[8,9] As recently reported,[8,9] light illumination can result in a giant persistent photoconductive effect, the sheet conductivity grows by ~5 orders of magnitude,[8] and the original state cannot be recovered after the removal of the light unless a gating field was applied.[9] There are also attempts to build up the 2DEG by deposing a metal layer above the LAO overlayer[10] or by applying a gate field.[4]

We noted that most of the previous works focused on metallic or semiconducting interfaces,[8,9,11,12] and the effect of photoexcitation of visible light on insulating interface has been scarcely studied. In addition to this, in most of the previous reports only the illumination-induced variation of the sheet resistance was presented. The information on charge carriers such as carrier density and mobility, which is no doubt more important for a deep understanding of the transport mechanism of the oxide interface, was missing. Moreover, the photoconductivity was usually studied at the room temperature or, at most, at several selected temperatures.[8,9,11,12] From these data, it is difficult to know the whole temperature dependence of the photoconductivity. In this letter, the photoconductivity under different light powers was presented in the whole temperature range below 300 K. We found an illumination-induced transition of the insulating LAO(3uc)/STO interface to the intermediate state between a totally insulating state and a totally metallic state. We gave experimental evidence that the enhanced interface conduction is caused by extra charge carriers, whereas the carrier mobility keeps unaffected by illumination. We also observed strong influence of the structural transition of STO at ~100 K on the 2DEG, which was not reported before.

The sample was prepared by depositing a LAO layer, though pulsed laser deposition, on the TiO_2-terminated (001) STO substrate of the dimension of $5 \times 5\,mm^2$. The deposition temperature was 800 °C and the oxygen pressure was 10^{-5} mbar. The fluence of the laser pulses was 0.7 J cm^{-2}, and the repetition rate was 1 Hz. After deposition, the sample was *in situ* annealed in 200 mbar of O_2 at 600 °C for one hour, and then cooled to room temperature in the same oxygen pressure. The growth process was monitored by *in situ* reflection high energy electron diffraction (RHEED). Three samples with the LAO layer thicknesses of 2 uc, 3 uc, and 3.4 uc, respectively, were prepared. The standard four-probe technique was employed for resistance measurements, and ultrasonic Al-wire bonding was adopted for electrical contacts. The separation between two neighboring probes is 0.5 mm. The applied current for the resistance measurements was 1 μA. Hall effect was measured with an in-plane current of 1 μA in the field range from −1.6 T to 1.6 T. The laser beams with the wavelengths of 532 nm, 660 nm, 780 nm, 850 nm, and 980 nm, and the size of ~1 mm in diameter were employed for photoexcitation.

Figure 1(a) shows the sheet resistance of the LAO(3uc)/STO interface as a function of temperature, measured using different power levels but with a constant wavelength of

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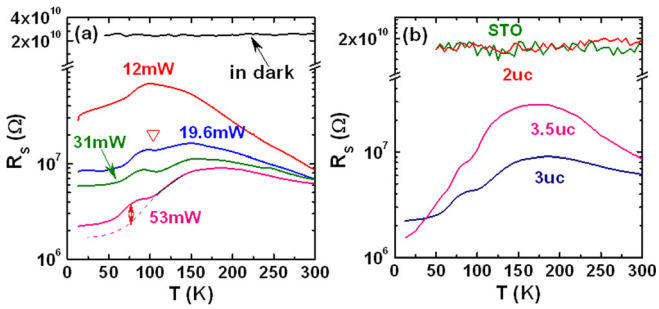

FIG. 1. (a) Sheet resistance as a function of temperature for the LAO(3uc)/STO heterointerface, measured when the sample is exposed to the lights with different powers but a constant wavelength of 532 nm. Red triangle indicates the resistive anomaly caused by a structural transition of STO. Dashed line mark the R_S-T curve without phase transition. (b) Sheet resistance as a function of temperature for the LAO/STO heterointerfaces with varied LAO layers. Light power is 53 mW and light wavelength is 532 nm.

532 nm. Without illumination, the interface is insulating with a sheet resistance exceeding 10 GΩ, consistent with reported results in the literature.[4] When exposed to light, the interface exhibits a different resistive behavior, semiconducting above ~150 K and metallic below ~70 K. In the temperature range between 70 and 150 K, it undergoes a broad semiconductor-to-metal transition upon cooling. This is in sharp contrast to the previous observations that the interface shows a tendency toward semiconducting at low temperatures when the oxygen pressure for sample preparation is slight high.[13] The sheet resistance of the STO substrate and the LAO(2uc)/STO interface was also measured (Fig. 1(b)), and it remains insulating even illuminated by the light of 53 mw, the highest power of our laser. This result strongly suggests that the illumination effect stems from the LAO/STO interface rather the STO substrate.

A further interesting observation is the appearance of a shoulder in the low temperature side of the broad resistance peak (marked by a triangle in Fig. 1(a)). This anomaly was not observed in the totally metallic LAO/STO interface. This, as will be discussed later, could be ascribed to the cubic-tetragonal structural transition of the STO substrate, thus is the unambiguous evidence of influence of the structural transition on 2DEG.

To obtain the photocarrier concentration, we measured the Hall resistance, R_{xy}, under different applied magnetic fields. Without illumination, the interface is insulating, and the Hall effect is undetectable. Linear R_{xy}-H curves are obtained when exposing the sample to light (Fig. 2(a)), signifying the appearance of free charge carriers. The R_{xy}-H slope is negative, indicating the electron nature of the charge carriers, and monotonically declines with the increase of light power P, manifesting a steady growth of the carrier density with P. Fig. 2(b) shows the deduced carrier density, n_S, as a function of light power. n_S increases from $\sim 6.4 \times 10^{12}$ to $\sim 9.1 \times 10^{12}\,\mathrm{cm}^{-2}$ as P grows from ~12 to ~53 mW. Fascinatingly, metallic conduction, which usually requires that $n_S \gg 1 \times 10^{13}\,\mathrm{cm}^{-2}$,[13] appears even for a n_S of $\sim 6.4 \times 10^{12}\,\mathrm{cm}^{-2}$ in the present sample. This result indicates that the interface scattering in the present sample may not be as strong as that occurred in the sample with a thick LAO layer: this is possible when the band bending at the LAO/STO interface is smooth, and it leads to a spreading of the 2DEG. The spreading of the 2DEG has two different effects on charge transport. It will cause a reduction of carrier overlap, disfavoring charge transport. Simultaneously, it will depress interface scattering, favoring charge transport. We noticed that metallic 2DEG can be formed for the conventional semiconductor interface at very low carrier densities, 10^{11}–10^{12} cm^{-2} (Ref. 14). This implies that the reduced overlap in this density range has not severely affected charge transport. In this case, the reduced interface scattering may play the dominant role.

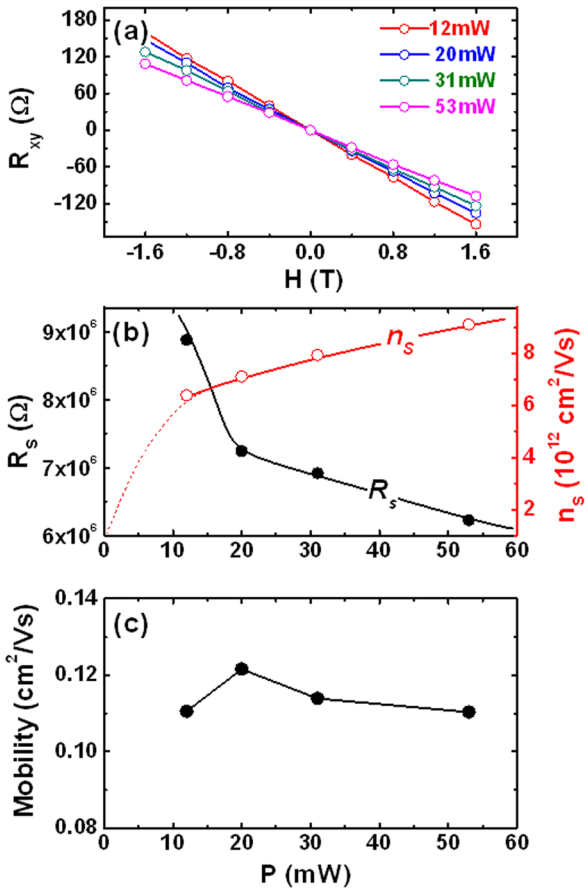

FIG. 2. (a) Hall resistance as a function of magnetic field, measured at the room temperature with different power levels ($\lambda = 532$ nm). Labels in the figure mark the power of light. (b) Correspondence between sheet resistance and carrier density. (c) Carrier mobility deduced from the data in (a) and (b). Solid lines are guides for the eye.

Based on the data in Figs. 1(a) and 2(a), the mobility of the charge carrier can be estimated. It is $\sim 0.11\,\mathrm{cm}^2/\mathrm{V\ s}$ at the room temperature, and is nearly independent of light power (Fig. 2(c)). It is lower than the modest values for metallic conduction, probably due to the semiconducting character of the interface at the room temperature.

A further analysis shows that the semiconducting behavior can be well described by $R_S = R_0 T \exp(E_a/k_B T)$ (case (a)) or $R_S = R_0 \exp(E_a/k_B T)$ (case (b)), where E_a is the activation energy and k_B is the Boltzmann constant (Figs. 3(a) and 3(b)). We cannot determine the exact form due to the narrow temperature span of the semiconducting behavior. Whatever, the electronic transport at the LAO/STO interface proceeds in the form of electron hopping. Considering the Jahn-Teller distortion of the interfacial TiO_6 octahedron at the LAO/

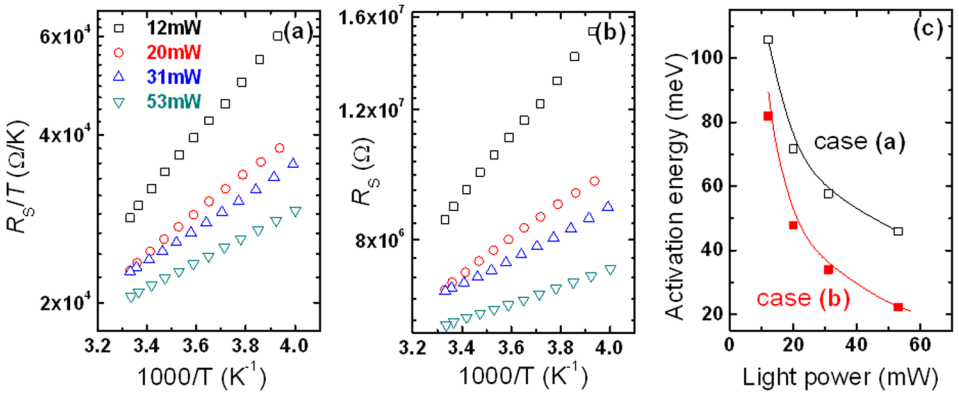

FIG. 3. (a) and (b) An Arrhenius plot of the sheet resistance in the temperature range above the semiconducting transition. (c) Deduced activation energy as function of light power. Cases (a) and (b) are activation energies deduced from the *R-T* relations in (a) and (b), respectively. Solid lines are guides for the eye.

STO interface as theoretically predicted,[13] small polaron conduction is possible. A simple calculation indicates that the activation energy is 105 meV (82 meV for case (b)) for the light of 12 mW (Fig. 3(c)), which is the typical value for polaron hopping.[15] With the increase of light power, E_a monotonically decreases, implying a competition between the polaron effect and metallic conduction. With the decrease of temperature, phonon scattering weakens, leading to an increase in carrier mobility. When the hopping rate for the charge carrier is so high that it cannot be followed by the octahedron distortion, a metallic transition occurs.

The resistive anomaly at ~105 K deserves special attention. As well established, the STO experiences a structural transition at ~105 K, leading to a growth of the *c/a* ratio from 1 to 1.00056. The resulted changes in lattice strain will affect the carrier density in the conduction channel. According to Bark *et al.*,[16] 1% contraction of the in-plane lattice will decrease the carrier density by $\sim 4 \times 10^{13}\,\mathrm{cm}^{-2}$. Based on this result, a charge transfer of $\sim 2.2 \times 10^{12}\,\mathrm{cm}^{-2}$ out of the conduction channel is expected when the sample is cooled through this phase transition temperature. For the typical metallic sample, the carrier density is generally in the order of $\sim 3 \times 10^{13}$, much higher than $\sim 2.2 \times 10^{12}\,\mathrm{cm}^{-2}$. This is why no effects of phase transition have been identified from the transport behavior there. For our samples, the total carrier density is $6\text{–}8 \times 10^{12}\,\mathrm{cm}^{-2}$, comparable to $\sim 2.2 \times 10^{12}\,\mathrm{cm}^{-2}$. Extrapolating the R_S-T curve through the transition temperature of STO, we obtained the dashed line below the measured curve in Fig. 1(a). A simple estimation indicates that the phase-transition-induced resistance change is $\Delta R_S \sim 30\%$. Thus the corresponding carrier density reduction will be $\Delta n_S \sim 2.4 \times 10^{12}\,\mathrm{cm}^{-2}$ if this resistance growth is exclusively caused by Δn_S, close to the expected value $2.2 \times 10^{12}\,\mathrm{cm}^{-2}$.

To reveal the influence of illumination history, the sheet resistance was further measured while repeating the light on-off operations. As shown in Fig. 4(a), the response of the resistance to light illumination is instantaneous: R_S drops from above 10^{10} Ω down to 10^6 Ω in one second, the time scale of our laser. Different from the previous reports,[8,9] no memory of the illuminated state is observed: the R_S returns to 1.5×10^9 Ω in one second after removing the light, and recovers completely in ~14 s. As a result, the R_S switches between two stable states as the light is turned on and off. Obviously, the excited electrons may mainly come from the in-gap states of STO since the photon energy is lower than the band gap of STO, and they will be driven to the interface by the interfacial potential barrier, spatially separated from the parent donor defects. This is the general explanation of the persistent photoconductivity.[8] The absence of persistent photoconductivity in our sample indicates that the oxygen vacancies in STO may concentrate on the LAO/STO interface, situating in an interfacial layer of a few nanometers. As a consequence, the spatial separation of the excited electrons with their parent donor defects is not severe, and recombination is much easier.

An interesting observation is that the conduction channel is extremely sensitive to light illumination, and even a low power of 3 mW can produce a dramatic reduction in R_S (Fig. 4(b)). This result indicates that the illumination-induced R_S decrease has the character of phase transition. An unexpected result is that the resistance saturates at a value of 1.8×10^6 Ω when the light power exceeds ~50 mW instead of continuously decrease. It is possible that the in-gap states have been exhausted above the light of 50 mW.

Further insight can be obtained from the dependence of the illumination effect on light wavelength. In Fig. 5(a) we show sheet resistance as a function of wavelength, recorded at $T = 12$ K in the lights of the same power $P = 53$ mW but different wavelengths. It shows a weakening of the efficiency of the light in depressing sheet resistance with wavelength. The 532-nm light is most effective, while the 980-nm light is the most ineffective. The most rapid decrease in illumination efficiency occurs between 780 nm and 850 nm (Fig. 5(b)). This result indicates that the threshold photon energy to excite the extra carriers is ~1.4 eV.

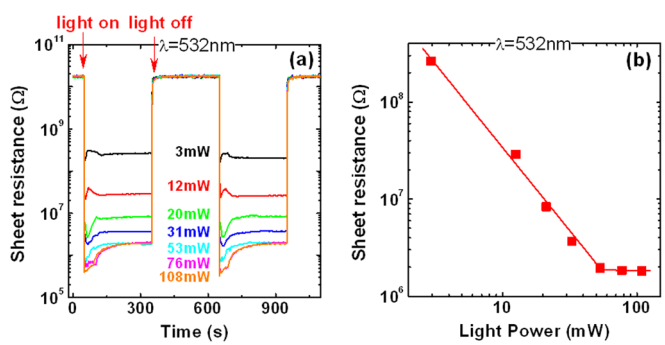

FIG. 4. (a) Resistance response to the light illumination ($\lambda = 532$ nm), measured at a fixed temperature of 12 K. (b) Sheet resistance as a function of light power. Solid line is a guide for the eye.

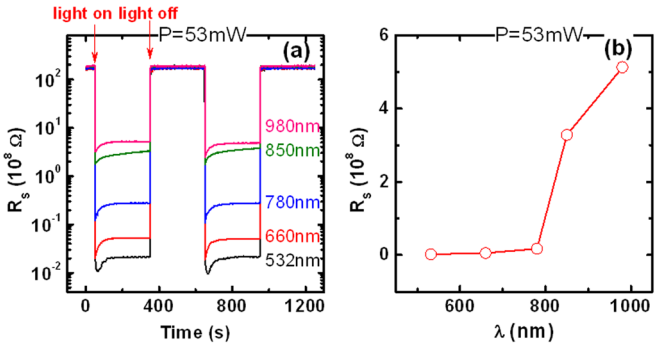

FIG. 5. (a) Resistance response to light illumination, measured at a constant temperature of 12 K. Light power is fixed at 53 mW while the wavelength varies between 532 nm and 980 nm. (b) Sheet resistance as a function of wavelength. Solid line is a guide for the eye.

There is experimental evidence for the presence of oxygen vacancies at the LAO/STO interface, appearing accompanying the outward diffusion of the oxygen ions from the STO substrate during the deposition of the LAO overlayer.[17,18] Cathode-luminescence measurements[19,20] have shown the presence of a strong blue light signal peaked at 460 nm, which is ascribed to electronic traps within the band gap associated with oxygen vacancies at the interface. It has been well established that the oxygen vacancies tend to aggregate into V_O-Ti-V_O chains with two shared electrons, yielding in-gap states.[21,22] The in-gap states have been directly detected by Wang *et al.*[23] in a LAO/STO structure prepared under high vacuum (10^{-6} mbar). It is found that these states form a energy band ~1.7 eV below the conduction of band of STO. Obviously, the in-gap states will be excited when the sample is exposed to the light with a photon energy above 1.4 eV if the band width is ~0.6 eV, leading to the insulator-to-semiconductor (metal) transition. In fact, deep level traps 1.3 eV below the conduction of the STO have been directly detected,[24] consistent with our results. Since the interfacial potential is so shallow, the excited electron fall into the trapped states immediately when the light is switched off, and the original resistive state recovers.

In summary, the effects of photoillumination on the LAO/STO interfaces have been studied, and an illumination-induced transition of the insulating $LaAlO_3$(3uc)/$SrTiO_3$ interface to a series of intermediate state between a totally insulating state and a totally metallic state has been obtained. Different from the previous reports, the original state recovers immediately after the removal of the illumination, without persistent photoconductivity. The presence of a threshold photon energy for the illumination effect, ~1.4 eV, indicates the dominative role of the photoexcitation of the in-gap states in this process. The present work demonstrates a feasible tuning of the 2DEG by photoexcitation.

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[1]H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, Nat. Mater. **11**, 103 (2012) and the references therein.
[2]N. Reyren, S. Thiel, A. D. Caviglia, L. F. Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Rüetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, and J. Mannhart, Science **317**, 1196 (2007).
[3]A. Brinkman, M. Huijben, M. van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. van der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, Nat. Mater. **6**, 493 (2007).
[4]S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, and J. Mannhart, Science **313**, 1942 (2006).
[5]Y. W. Xie, C. Bell, T. Yajima, Y. Hikita, and H. Y. Hwang, Nano Lett. **10**, 2588 (2010).
[6]Y. W. Xie, C. Bell, Y. Hikita, and H. Y. Hwang, Adv. Mater. **23**, 1744 (2011).
[7]H. Chen, A. M. Kolpak, and S. Ismail-Beigi, Adv. Mater. **22**, 2881 (2010).
[8]A. Tebano, E. Fabbri, D. Pergolesi, G. Balestrino, and E. Traversa, ACS Nano **6**, 1278 (2012).
[9]H. L. Lu, Z. M. Liao, L. Zhang, W. T. Yuan, Y. Wang, X. M. Ma, and D. P. Yu, Sci. Rep. **3**, 2870 (2013).
[10]E. Lesne, N. Reyren, D. Doennig, R. Mattana, H. Jaffrès, V. Cros, F. Petroff, F. Choueikani, P. Ohresser, R. Pentcheva, A. Barthélémy, and M. Bibes, Nat. Commun. **5**, 4291 (2014).
[11]A. Rastogi, J. J. Pulikkotil, and R. C. Budhani, Phys. Rev. B **89**, 125127 (2014).
[12]N. Y. Chan, M. Zhao, N. Wang, K. Au, J. Wang, L. W. H. Chan, and J. Dai, ACS Nano **7**, 8673 (2013).
[13]M. Huijben, A. Brinkman, G. Koster, G. Rijnders, H. Hilgenkamp, and D. H. A. Blank, Adv. Mater. **21**, 1665 (2009) and the references therein.
[14]K. Hirakawa, H. Sakaki, and J. Yoshino, Phys. Rev. Lett. **54**, 1279 (1985).
[15]M. B. Salamon and M. Jaime, Rev. Mod. Phys. **73**, 583 (2001).
[16]C. W. Bark, D. A. Felker, Y. Wang, Y. Zhang, H. W. Jang, C. M. Folkman, J. W. Park, S. H. Baek, H. Zhou, D. D. Fong, X. Q. Pan, E. Y. Tsymbal, M. S. Rzchowski, and C. B. Eom, Proc. Natl. Acad. Sci. U.S.A. **108**, 4720 (2011).
[17]Y. Z. Chen, N. Pryds, J. E. Kleibeuker, G. Koster, J. R. Sun, E. Stamate, B. G. Shen, G. Rijnders, and S. Linderoth, Nano Lett. **11**, 3774–3778 (2011).
[18]Z. Q. Liu, C. J. Li, W. M. Lu, X. H. Huang, Z. Huang, S. W. Zeng, X. P. Qiu, L. S. Huang, A. Annadi, J. S. Chen, J. M. D. Coey, T. Venkatesan, and Ariando, Phys. Rev. X **3**, 021010 (2013).
[19]A. Kalabukhov, R. Gunnarsson, J. Börjesson, E. Olsson, T. Claeson, and D. Winkler, Phys. Rev. B **75**, 121404 (2007).
[20]D. Kan, T. Terashima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa, and M. Takano, Nat. Mater. **4**, 816 (2005).
[21]D. D. Cuong, B. Lee, K. M. Choi, H. S. Ahn, S. Han, and J. Lee, Phys. Rev. Lett. **98**, 115503 (2007).
[22]F. Cordero, Phys. Rev. B **76**, 172106 (2007).
[23]X. Wang, J. Q. Chen, A. R. Barman, S. Dhar, Q.-H. Xu, T. Venkatesan, and Ariando, Appl. Phys. Lett. **98**, 081916 (2011).
[24]M. Meevasana, P. D. C. King, R. H. He, S.-K. Mo, M. Hashimoto, A. Tamai, P. Songsiriritthigul, F. Baumberger, and Z.-X. Shen, Nature Mater. **10**, 114–118 (2011).