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Patterning the two dimensional electron gas at the $LaAlO_3/SrTiO_3$ interface by structured Al capping

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We demonstrate an approach for patterning a quasi-two dimensional electron gas (q-2DEG) at the interface of $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) utilizing a structured Al capping layer. The capping of Al enables the formation of q-2DEG at the interface of 1–3 unit cells (uc) of LAO on STO, which was originally insulating before capping. The properties of the q-2DEG induced by the Al capping layer are essentially the same as those of q-2DEG without Al. Therefore, we can pattern q-2DEG by simply patterning the Al film on LAO (2 or 3 uc)/STO using a one-step liftoff process. Our approach circumvents the difficulty of direct patterning of oxide materials and provides a simple and robust patterning method for future device applications based on complex oxide interfaces. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4979784]

Oxide interfaces are of great interest in both fundamental science and applications because their relatively simple structures exhibit a series of abnormal physical properties. The interface of the insulating oxides $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) is one of the prototypical examples.[1] When more than 4 unit cells (uc) of LAO films are epitaxially grown on the TiO_2-terminated STO (001) substrates, a quasi-two dimensional electron gas (q-2DEG) confined in a few uc is developed at the LAO/STO interface.[2] A wide range of behaviors such as tunable spin-orbit coupling,[3,4] ferromagnetic order,[5] two-dimensional superconducting phase below 0.2 K,[6] coexistence of ferromagnetism and superconductivity,[7,8] and quantum Hall effect[9] have been observed in this interface, providing a rich playground for fundamental research and future device applications.

In order to develop electronic devices based on the q-2DEG at the LAO/STO interface, the patterning of the q-2DEG is highly required. The poor corrosion resistance and the high temperature deposition in an oxygen atmosphere of the oxide materials make them difficult to be patterned by traditional photolithographic and etching processes without altering the interface properties. Several methods for patterning the LAO/STO interface have been developed to overcome these difficulties. Previous studies used regular optical lithography to obtain a patterned amorphous LAO film on a 2-uc-thick epitaxial LAO layer. Then, the second epitaxially grown LAO layer with a thickness of more than 2 uc led to the conductive interface for the films without the amorphous LAO layer.[10] The problem of this technique is that the amorphous LAO may induce the conductive LAO/STO interface and result in the failure of the devices.[11] To resolve this problem, the AlO_x and amorphous $La_{7/8}Sr_{1/8}MnO_3$ (LSMO) films were used as the hard masks.[12,13] These approaches are needed for the growth of AlO_x and LSMO films and for chemically etching them to obtain a patterned structure before epitaxially growing the LAO layer. In these circumstances, the surface of the STO substrates may be contaminated by the AlO_x and LSMO films. Moreover, it is difficult to find a good selective etching recipe and achieve precise control of the patterned size using the chemical etching method. Besides these disadvantages, these approaches require multiple steps of the film growth and the liftoff process. In addition to these methods, an atomic force microscopy (AFM) tip by applying voltage can directly pattern the LAO (3 uc)/STO interface into structures down to a few nanometers. However, this technique is time consuming and clearly not applicable for large scale device production.

A conductive LAO/STO interface was initially observed when the thickness of the LAO layer is more than 4 uc.[2] The writing of the surface charge on the LAO surface or the deposition of other polar materials can reduce the LAO critical thickness down to 3 uc.[14,15] First-principles calculations predicted that a conductive interface at the LAO (2 uc)/STO interface can be obtained by capping the low work function materials such as Na, Al, and Ti.[16] This was recently demonstrated by the magnetotransport and X-ray absorption spectroscopy experiments for the LAO/STO interface capping with Co, where the LAO layer thickness is as thin as one uc.[17] However, the transport properties were the mixture of the LAO/STO interface and the Co layer due to the shunting effect. This is not ideal for the fundamental study and cannot be applied to the device applications. In this work, we found that the critical LAO thickness for the conducting LAO/STO interface can be reduced to 1 uc by capping the Al film. In our measurement method, the shunting connection of the Al capping layer is found to be negligible in contrast to the Co study. Equally important is that the obtained interface properties are essentially the same as the interface with more than 4 uc LAO. Based on these findings, the patterned structure of the Al capping layer can be transferred and resulted in the formation of the structured conductive LAO (1–3 uc)/STO interface. This pattern strategy is much simpler and more robust than other approaches.

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The 1–3 uc LAO layer was epitaxially grown on the TiO_2-terminated STO (001) substrate by pulsed laser deposition (PLD) at 750 °C and the oxygen pressure of 5×10^{-5} Torr, as schematically shown in Fig. 1(a). The detailed growth method can be found in our previous report.[15] The LAO (1–3 uc)/STO interface is insulating, and the resistance is beyond our measurement limit of 1 GΩ, consistent with previous reports.[2] A 5-uc-thick LAO layer was then homoepitaxially grown on the LAO surface through a shadow mask to define four rectangular pads, as schematically shown in Fig. 1(b). After the growth of two layers of the LAO film, the sample was annealed at an oxygen pressure of 1 atm and 550 °C for 4 h. These additional LAO layer defined areas with a total thickness of 6–8 uc, well above 4 uc of the critical thickness for the conduction interface, are conducting. They serve as four electrodes to contact with the insulating LAO (1–3 uc)/STO interface. Finally, an Al cross-bar structure patterned by standard optical lithography and lift-off processes was prepared onto the LAO layer, as schematically shown in Fig. 1(c). The Al film was deposited at room temperature by *e*-beam evaporation. The optical micrograph of the sample layout is shown in Fig. 1(d). The Al cross-bar is 300 μm wide and 20 nm thick. The Al wires were ultrasonically bonded to the pads of the LAO/STO interface, labeled as contacts 1, 2, 3, and 4 in Figs. 1(c) and 1(d). The structured Al layer was connected to contact wires by a silver paint to prevent the electrical contacting from the LAO/STO interface, labeled as contacts 5 and 6 in Figs. 1(c) and 1(d). For comparison, an unpatterned LAO (5 uc)/STO reference sample was fabricated under the same growth conditions.

Remarkably, we find that the LAO (3 uc)/STO interface covered by the Al film is no longer insulating. This is clearly evidenced by the linear current-voltage (*I-V*) behavior, shown in Fig. 2(a), measured at 2 K between the contacts 1 and 4. In contrast, the *I-V* curve measured between the 20-nm-thick Al capping layer (contact 5) and the LAO/STO interface (contact 1) exhibits strong non-linear behavior due to the current tunneling through the LAO layer. Moreover, we performed a non-local measurement on the 20-nm-thick Al strip: a small current applied between contacts 1 and 4 and a voltage measured between contacts 5 and 6. This non-local measurement yields the resistance of only 1.4 Ω, in

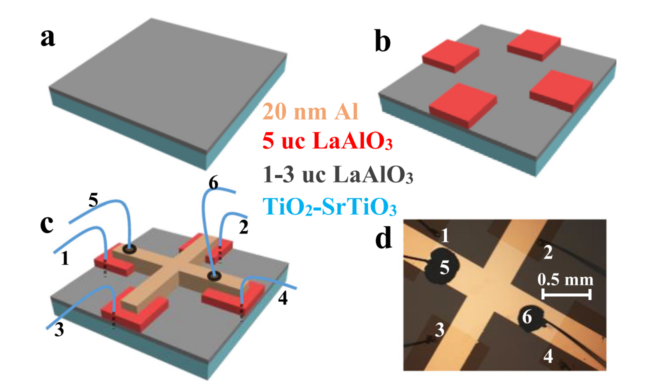

FIG. 1. Schematic of the patterning process of the LAO/STO interface. (a) Growth of 1–3 uc of the LAO layer on the TiO_2-teminated STO (001) substrate. (b) Growth of 5 uc of the LAO layer on the LAO surface through a shadow mask to define four rectangular pads. (c) Growth of the Al cross-bar structure defined by standard optical lithography and lift-off processes. (d) Optical micrograph of the final sample layout.

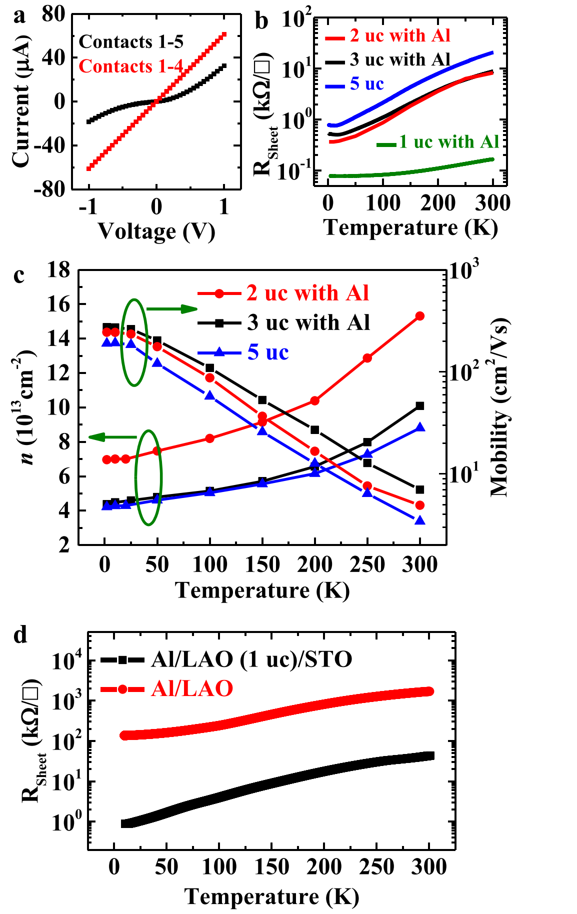

FIG. 2. (a) *I-V* curves of the LAO/STO interface with Al capping measured between contacts 1 and 5 (black line) and the LAO layer measured between contacts 1 and 4 (red line) measured at 2 K. The contacts are labeled in Fig. 1(d). (b) Temperature dependence of the sheet resistance of LAO (1–3 uc)/STO with patterned Al capping and LAO (5 uc)/STO. (c) Temperature dependence of the carrier density and the mobility of LAO (2 uc and 3 uc)/STO with patterned Al capping and LAO (5 uc)/STO. (d) Temperature dependence of the sheet resistance of Al (1 nm)/LAO (1 uc)/STO and Al (1 nm)/LAO samples.

comparison to the resistance of ∼100 Ω for this Al strip (see supplementary materials). This result demonstrates that the current tunneling into the Al layer is negligible when the current flows in the LAO/STO interface. Therefore, the transport properties are dominated by the LAO/STO interface when it is measured between the contacts of 1, 2, 3, and 4. It can be seen that our experimental geometry is superior to the previous report in which the resistance is the parallel resistance of the Co overlayer and the LAO/STO interface.[17] Our approach allows us to investigate the intrinsic transport properties of the interface without the contamination of the metallic overlayer.

For comparison, we prepared and measured the unpatterned LAO (5 uc)/STO reference sample in the van der Pauw geometry. Figure 2(b) presents the temperature dependence of the sheet resistance of LAO (2 and 3 uc)/STO with the patterned Al capping and LAO (5 uc)/STO reference sample. The Al capped samples show metallic behaviors, similar to the reference sample without Al. All the samples exhibit the sheet resistance minima at about 15 K, which has been attributed to both the weak localization[18] and the Kondo effect.[5]

These results are consistent with the previous report in which the samples were grown under the similar conditions.[5,19] Moreover, we varied the Al capping layer thickness from 3 to 60 nm. The Al resistance varies more than one order of magnitude from ~500 Ω to 10 Ω and is much smaller than the interface resistance of 100 kΩ at room temperature. However, the interfaces capped with different Al-thickness films exhibit similar behavior (see supplementary material). This result strongly confirms that the measured transport properties of the Al-capped LAO/STO interface are from the LAO/STO interface rather than the Al overlayer. The sheet carrier concentration n and the mobility of all the samples measured by the Hall effect as functions of temperature are shown in Fig. 2(c). n and the carrier mobility of the Al capped samples exhibit a similar trend and similar values to the LAO (5 uc)/STO sample, meaning that the Al-capping-induced conducting LAO/STO interface possesses similar physical properties to the regular thick LAO/STO interface. We note that the mobility of our sample is ~273 and 7 cm^2/Vs at 2 and 300 K, respectively. These values are relatively small. This might be due to the *ex situ* annealing (see supplementary material), which removes the oxygen vacancies in LAO to electrically separate the LAO/STO interface from the Al overlayer.[20] Unlike the approaches of patterning the LAO/STO interface by the hard mask, our patterning procedure is very simple and can cooperate with the standard semiconductor production process.

When the LAO layer is only 1 uc thick, the tunneling resistance of the LAO layer is too small, leading to a significant shunting current flow in the Al overlayer. The sheet resistance is mainly contributed by the Al layer, shown in Fig. 2(b). It is difficult to separate the conductive interface from the 20-nm-thick Al layer experimentally. To avoid this problem, we deposited 1 nm Al, in which the sheet resistance is relatively large, on LAO (1 uc)/STO and a bare LAO substrate simultaneously. The sheet resistance of Al (1 nm)/LAO (1 uc)/STO is more than one order of magnitude smaller than that of Al (1 nm)/LAO between 10 and 300 K, shown in Fig. 2(d). This result suggests that the transport properties of Al (1 nm)/LAO (1 uc)/STO are dominated by the conductive LAO/STO interface and the LAO critical thickness is reduced down to 1 uc.

One of the mechanisms proposed for the appearance of the q-2DEG at the LAO/STO interface is the charge reconstruction, in which the electrons transfer from the LAO surface to the interface to overcome the electrostatic potential divergence built in the polar material LAO. This mechanism explains well the appearance of the conducting interface beyond the LAO critical thickness of 4 uc. In fact, the first-principles theoretical calculations and experimental results show that the built-in potential in LAO is significantly reduced after capping with metallic capping layers.[16,21] This means that the critical LAO thickness cannot be reduced with the Al capping layer according to the charge reconstruction mechanism. The interfacial interdiffusion occurred in the vacuum growth is another possible mechanism to induce the mobile carriers.[22,23] As the Al films were deposited at room temperature, the interfacial interdiffusion at the LAO/STO interface during the Al growth is unlikely. The redox reaction between Al and LAO can induce the oxygen vacancies. The thinner the LAO thickness is, the more the oxygen vacancies at the surface diffuse into the LAO/STO interface. In fact, the carrier density of LAO (1 uc)/STO capped by Al is measured to be about $2.5 \times 10^{13}\,cm^{-2}$ (see supplementary material), which is larger than the calculated carrier density based on the model considering work function.[21] This means that other factors such as the surface reaction induced oxygen vacancies may play an extra role in the formation of q-2DEG with an ultrathin LAO layer.

The surface state of LAO is intimately correlated with the LAO/STO interface properties. First-principles calculations reveal that the metallic capping on the LAO/STO surface alters the electrostatic boundary conditions and hence the electronic properties of the interface.[16] The work function of the metallic capping layer plays a major role among all the factors. Indeed, it was experimentally found that the carrier density at the LAO (5 uc)/STO interface increases to $7.5 \times 10^{13}\,cm^{-2}$ after capping the Al layer, which is attributed to the charge transfer from Al to the interface as the Fermi level of Al is higher than that of the q-2DEG.[21] This mechanism plays an important role in 1–3 uc thick LAO as well. In addition to Al, we have studied several other metallic capping layers on LAO (3 uc)/STO, including Ti, Co, Au, and Pt. We found that all these metals cannot induce the conductive interface. The charge transfer effect could be very weak or even does not occur for Co, Au, and Pt because the work function of these metals is more than 0.5 eV larger than that of Al. As a result, the interfaces remain insulating. Although the work function of Ti is comparable with that of Al, the conductive interface is not observed for Ti either. It may be because other factors such as the chemical bond between the metal and the surface AlO_2 layer and the type of metal come into play. In fact, the theoretical calculations show that the Al capping layer transfers more charges than the Ti capping layer.[16] We note that it was reported that Co can reduce the LAO critical thickness (Ref. 17). Co was deposited by magnetron sputtering in previous work[17] instead of *e*-beam evaporation in our work. The evaporated Al by the *e*-beam has thermal kinetic energy ($\ll$1 eV). In sputtering, the kinetic energy of Co could be up to 100 eV. It is conceivable that the high-kinetic-energy Co could strongly diffuse into and react with LAO, resulting in the significant change in the LAO/STO interface properties. Indeed, the different material properties fabricated by the *e*-beam and sputtering have been observed in the magnetoresistance effect in the Pt/$Y_3Fe_5O_{12}$ system.[24]

To further confirm the patterning of the q-2DEG, we fabricated three channels with the Al lateral size of 100, 200, and 300 μm on LAO (3 uc)/STO. These three channels are fabricated on the same substrate to reduce the sample-to-sample variation. The sample structure is described in supplementary materials. Figure 3(a) shows the resistance as a function of temperature for these three channels. The resistances at 10 and 300 K are extracted from Fig. 3(a) to plot in Figs. 3(b) and 3(c). The resistance is clearly inversely proportional to the Al strip width, confirming that the q-2DEG is confined by the shape of the Al overlayer.

It is remarkable that the pattern of the Al overlayer can define the q-2DEG at the LAO/STO interface. Compared with other techniques to pattern the LAO/STO interface, our strategy needs only one-step photolithography and a lift-off

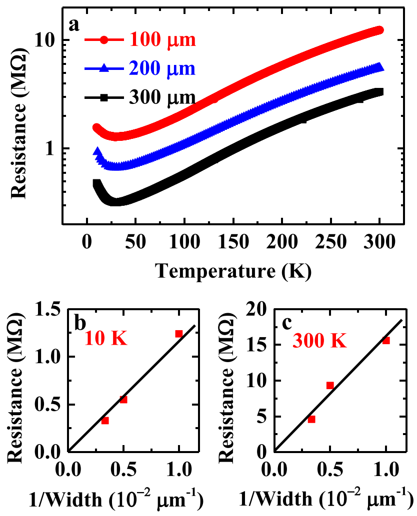

FIG. 3. (a) Temperature dependence of the resistance of LAO (3 uc)/STO capped by Al with the width of 100, 200, and 300 μm. Width dependence of the resistance of the patterned q-2DEG at (b) 10 K and (c) 300 K.

process and does not require any hard mask and etching process. The properties of the obtained q-2DEG are almost the same as those of the thick LAO layer on STO. In principle, our approach is applicable to the e-beam lithography technique to narrow down the sample size to the nanometer range to obtain oxide-based low-dimensional structures such as quantum dots. Using our approach, the study of the q-2DEG at the nanoscale could become more convenient and speedy.

Furthermore, we have compared the magnetoresistance (MR) of the Al/LAO (3 uc)/STO sample with that of the LAO (5 uc)/STO sample. As shown in Fig. 4, the MR behaviors of both the samples exhibit two regions: a positive MR below about 3 T and a negative MR above 3 T. These "M" shaped MR curves have been reported in LAO/STO interfaces. The negative MR is attributed to the weak localization (WL), associated with the suppression of backscattering in the theory of quantum transport. In contrast, the positive MR is attributed to the weak antilocalization (WAL), associated with the enhancement of backscattering.[25,26] These behaviors have been frequently reported in the LAO/STO interface with more than 4 uc LAO. Our results indicate that the Al capping layer induced q-2DEG has the same electronic properties as the ones obtained with thick LAO on STO and without the Al capping layer.

In conclusion, we have demonstrated that the Al capping layer induces q-2DEG at the LAO/STO interface for LAO thicknesses below 4 uc. The transport properties of the q-2DEG with a reduced LAO thickness are almost the same as those of the LAO(>4 uc)/STO sample. Accordingly, the patterned Al overlayer can be transferred into the LAO/STO interface to form structured q-2DEG. The advantage of this approach is that it avoids the direct patterning of the oxide layer and the resolution is limited by the metallic film patterning only and can in principle reach the nanoscale. This robust and simple patterning method opens a route towards the development of spintronic and quantum devices based on the complex oxide interface.

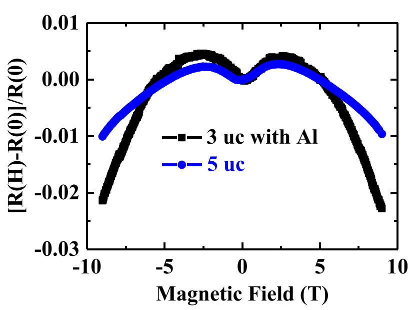

FIG. 4. The magnetoresistance of LAO (3 uc)/STO with Al capping and the LAO (5 uc)/STO reference sample measured at 2 K.

See supplementary material for the transport properties of the Al capping layer, influence of the Al thickness on the LAO/STO interface, effect of the annealing process on the mobility, carrier density of Al (1 nm)/LAO (1 uc)/STO, and sample structure to study the width dependence of the patterned q-2DEG.

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[1] A. Ohtomo and H. Y. Hwang, Nature **427**, 423 (2004).
[2] S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, and J. Mannhart, Science **313**, 1942 (2006).
[3] M. Ben Shalom, M. Sachs, D. Rakhmilevitch, A. Palevski, and Y. Dagan, Phys. Rev. Lett. **104**, 126802 (2010).
[4] A. D. Caviglia, M. Gabay, S. Gariglio, N. Reyren, C. Cancellieri, and J. M. Triscone, Phys. Rev. Lett. **104**, 126803 (2010).
[5] 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, Nature Mater. **6**, 493 (2007).
[6] 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).
[7] J. A. Bert, B. Kalisky, C. Bell, M. Kim, Y. Hikita, H. Y. Hwang, and K. A. Moler, Nat. Phys. **7**, 767 (2011).
[8] L. Li, C. Richter, J. Mannhart, and R. C. Ashoori, Nat. Phys. **7**, 762 (2011).
[9] F. Trier, G. E. D. K. Prawiroatmodjo, Z. Zhong, D. V. Christensen, M. von Soosten, A. Bhowmik, J. M. G. Lastra, Y. Chen, T. S. Jespersen, and N. Pryds, Phys. Rev. Lett. **117**, 096804 (2016).
[10] C. W. Schneider, S. Thiel, G. Hammerl, C. Richter, and J. Mannhart, Appl. Phys. Lett. **89**, 122101 (2006).
[11] Z. Q. Liu, C. J. Li, W. M. Lü, X. H. Huang, Z. Huang, S. W. Zeng, X. P. Qiu, L. S. Huang, A. Annadi, J. S. Chen, J. M. D. Coey, and T. Venkatesan, Phys. Rev. X **3**, 021010 (2013).
[12] N. Banerjee, M. Huijben, G. Koster, and G. Rijnders, Appl. Phys. Lett. **100**, 041601 (2012).
[13] F. Trier, G. E. D. K. Prawiroatmodjo, M. Von Soosten, D. V. Christensen, T. S. Jespersen, Y. Z. Chen, and N. Pryds, Appl. Phys. Lett. **107**, 191604 (2015).
[14] C. Cen, S. Thiel, G. Hammerl, C. W. Schneider, K. E. Andersen, C. S. Hellberg, J. Mannhart, and J. Levy, Nature Mater. **7**, 298 (2008).
[15] Y. J. Shi, S. Wang, Y. Zhou, H. F. Ding, and D. Wu, Appl. Phys. Lett. **102**, 071605 (2013).
[16] R. Arras, V. G. Ruiz, W. E. Pickett, and R. Pentcheva, Phys. Rev. B **85**, 125404 (2012).
[17] 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, Nature Commun. **5**, 4291 (2014).
[18] T. Schneider, A. D. Caviglia, S. Gariglio, N. Reyren, and J. M. Triscone, Phys. Rev. B **79**, 184502 (2009).
[19] G. Herranz, M. Basletić, M. Bibes, C. Carrétéro, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzić, J.-M. Broto, A. Barthélémy, and A. Fert, Phys. Rev. Lett. **98**, 216803 (2007).

[20]C. Cancellieri, N. Reyren, S. Gariglio, A. D. Caviglia, A. Fête, and J.-M. Triscone, Europhys. Lett. **91**, 17004 (2010).
[21]Y. Zhou, Y. J. Shi, S. W. Jiang, F. J. Yue, P. Wang, H. F. Ding, and D. Wu, Appl. Phys. Lett. **108**, 231603 (2016).
[22]P. R. Willmott, S. A. Pauli, R. Herger, C. M. Schlepütz, D. Martoccia, B. D. Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca, and Y. Yacoby, Phys. Rev. Lett. **99**, 155502 (2007).
[23]W. Siemons, G. Koster, H. Yamamoto, W. A. Harrison, G. Lucovsky, T. H. Geballe, D. H. A. Blank, and M. R. Beasley, Phys. Rev. Lett. **98**, 196802 (2007).
[24]N. Vlietstra, J. Shan, V. Castel, B. J. van Wees, and J. B. Youssef, Phys. Rev. B **87**, 184421 (2013).
[25]S. Hikami, A. I. Larkin, and Y. Nagaoka, Prog. Theor. Phys. **63**, 707 (1980).
[26]F. J. Wong, R. V. Chopdekar, and Y. Suzuki, Phys. Rev. B **82**, 165413 (2010).