2016 MERIT Self-directed Joint Research

# Study of Ferromagnetism at the $LaAlO_3/CaTiO_3$ interface

Yoshihito Motoyui, Xiuyi Hou

**Authors**

Yoshihito Motoyui: A PhD student at Shin group, ISSP. He studies surface/interface magnetic domains by laser-excited photoelectron emission microscopy.

Xiuyi Hou: A PhD student at Lippmaa group, ISSP. He studies oxide thin films by pulsed laser deposition.

**Introduction**

At the $LaAlO_3/SrTiO_3$, the two dimensional metallic states are generated while both oxides are non-magnetic insulators in the bulk. Through charge transferring caused by the $LaAlO_3$ polarity, $3d^0$ electronic states of $Ti^{4+}$ transform $3d^{0.5}$ electronic states of $Ti^{3+}$ at the $TiO_2$ interfacial layer.[1] At this interface, the existence of ferromagnetism also had been reported in some experiments (e.g. SQUID).[2] However, it had been hard to detect it sensitively so that it made the magnetism unclear and unbelieved. Furthermore, the mechanism of the magnetism had been under discussion.

In these days, Motoyui succeeded to get the direct evidence of the magnetism through observation of uniform magnetic domain using laser-excited photoelectron emission microscopy (Laser-PEEM) which enabled high sensitive measurement to the interfacial states. Surprisingly, the ferromagnetism kept above room temperature. In this study, we tried to control the magnetism by replacement of cations and then understand the mechanism.

To understand simply, we started to consider the Stoner criterion, $D(E_F)\cdot I_{XC} \geq 1$. If the equation is satisfied, ferromagnetic phase can be stable. Here the stoner parameter $I_{XC}$ is constant in each ion.

Thus, it is expected that the exchange interaction gets much stronger if the $D$ ($E_F$) get much larger. In case of $CaTiO_3$, the 3d band width comes to be narrower than the width in $SrTiO_3$ because of the effect of rotation of $TiO_6$ octahedra in $CaTiO_3$. Therefore, the $D(E_F)$ gets larger than that in $SrTiO_3$. Actually, the criterion estimated by Gangulli[3]b was 1.22 in $LaAlO_3/CaTiO_3$ while it was 1.02 in $LaAlO_3/SrTiO_3$. For the estimation, ferromagnetism with a stronger interaction could exist in $LaAlO_3/CaTiO_3$ if the explanation is applied to the interfacial system. Furthermore, the calculation suggested that the charge transferred occurred in $LaAlO_3$($\geqq$5 uc)/$CaTiO_3$ and the criterion was satisfied in $LaAlO_3$($\geqq$15 uc)/$CaTiO_3$. That had been recognized as the critical thickness in $LaAlO_3/SrTiO_3$.

In spite of the expectation, $LaAlO_3/CaTiO_3$ thin film had never been made and studied.

For this background, Hou, who had studied the growing of oxides thin films, and Motoyui, who had observed magnetic domain in $LaAlO_3/SrTiO_3$, collaborated in this study. Hou prepared the sample, $LaAlO_3/CaTiO_3$ and Motoyui measured the sample to investigate the magnetism. This study was performed to discover the ferromagnetism in $LaAlO_3/CaTiO_3$, which had never been reported and to reveal the relationship between the magnetism and the electronic states.

**Methods**

$LaAlO_3/CaTiO_3$ thin films were grown by pulsed laser deposition. The $CaTiO_3$ (010) crystals (lattice parameter: a= 5.44Å, b= 7.64Å, c= 5.37Å) from Surface Net Gmbh were used as the substrates.

We investigated the magnetism by Laser-PEEM. In the machine, photoelectron which has information on electronic states can be detected through the electron lens system. Especially, our laser energy was so low (4.66 eV) that it cannot excites the electron of valence band but of the conduction band. For the interface, it is possible to detect the interfacial states selectively and sensitively. In microscopic mode, we can do microscopic photoelectrons imaging in real space. Switching the circular polarization of excitation laser, and taking the difference of those, we can observe the magnetic circular dichroism (MCD) image. Beside the photoelectrons spectra can be measured spectroscopic mode and band dispersion also can be observed in angle-resolved spectroscopic mode.

We used the superconducting quantum interference device (SQUID) as another way to investigate the magnetism.

**Results & Discussion**

(1) Sample fabrication

We searched the condition to create a flat surface at first because Laser-PEEM measurement is a surface sensitive technique. Substrates were annealed in the vacuum chamber at several oxygen pressure and temperatures, and we found that annealing substrates for 10 min at $P_{O2}$=1 × $10^{-3}$ Torr, $T_{sub}$=850° C was best condition (see Fig. 1). After annealing process, $LaAlO_3/CaTiO_3$ thin films were deposited at $P_{O2}$=1 × $10^{-5}$ Torr, $T_{sub}$=750° C. We grew four samples with different film thicknesses: 2 unit cell (uc), 5 uc, 15 uc, and 30 uc to observe thickness dependences.

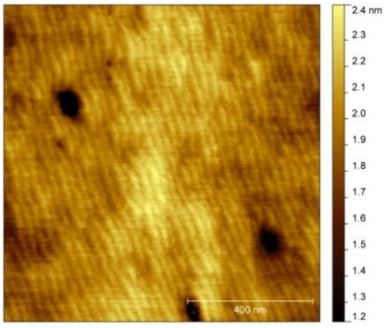


**Fig. 1 $CaTiO_3$ surface after annealing process (1000nm × 1000nm)**

(2) SQUID measurements

At first, SQUID measurements were performed at room temperature. Fig. 2 shows that the magnetization as a function of the magnetic field of each sample after diamagnetic components from $CaTiO_3$ bulk were subtracted. The ferromagnetic-like hysteresis loops could not be observed, but the slight magnetization saturated around 2000 Oe were detected ($\sim 5\times10^{-7}\ emu$) in all samples. That signal has no $LaAlO_3$ thickness dependence so that there are two possibilities of the signal. One is cation vacancies-induced ferromagnetism in deficient $CaTiO_3$ bulk [4]. Another one is from some magnetic impurities during measurements or growing sample. Even so, SQUID has low sensitivity to the nano-scale magnetization so that the signal has been buried in magnetism of bulk or impurities. That is why interfacial ferromagnetism cannot be observed. Therefore, we should not determine the absence of the interfacial ferromagnetism and should check those in high sensitive technique. Hence, we performed the measurements in Laser-PEEM.

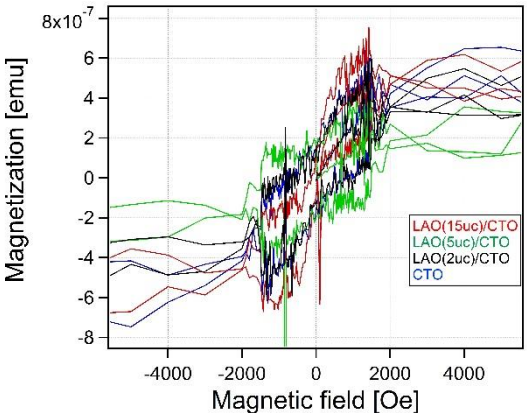


**Fig. 2 M-H curve in SQUID after diamagnetic subtraction.**

(3) Magnetic domain imaging in Laser-PEEM

Twin domain

At first, the structural twin domains could be observed as follows. Fig. 3 (b), (c) show micro-meter order domains. The domains could not be observed in raw image (Fig.3 (a)) but could be observed in CD or LD images. Essentially, these are due to breaking some reversal symmetry. In $CaTiO_3$ substrate, it is known that the crystal structure is octahedral and it forms twin domains. From this fact, we guess that the micro-meter order domains are structural twin domains. Exactly, the domains seem to align parallel to a- or b-axis of the sample.

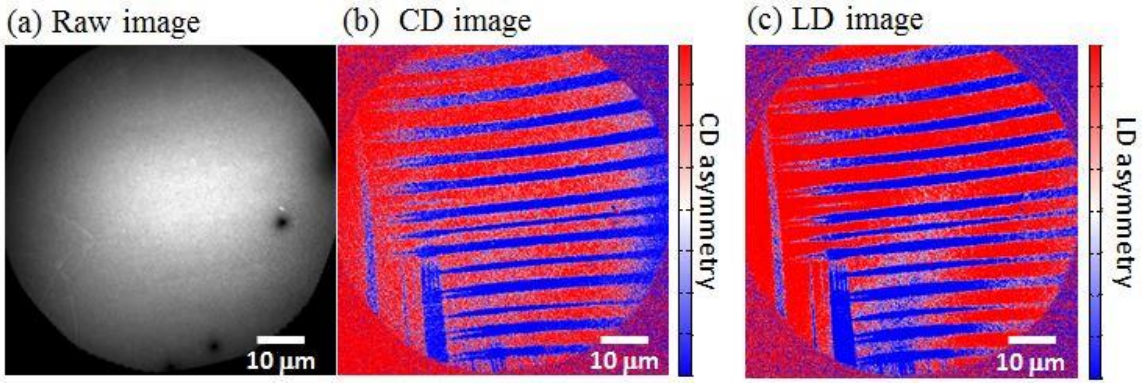


**Fig. 3 (a)raw image, (b)CD image, (c)LD image of $LaAlO_3$(15 uc)/$CaTiO_3$**

Magnetic domain

Subsequently, we discuss the ferromagnetic signal of CD images. Fig. 4 shows the CD images on every thickness samples. As shown above, the twin-domain could be observed in each CD images (Fig. 4 (a)-(c)). In order to exclude the components from twin domain, we selected observed areas which were inside domains but not on the boundary. Fig. 4(e)-(h) show CD images which were magnified in the areas marked on Fig. 4(a)-(c). In addition, the CD signals from twin domains are subtracted. The subtracted CD signal should represent the intrinsic ferromagnetic signal.

Broadly speaking, domain structures can be observed on 15 uc sample (Fig. 4(e), (f)). On the other hand, there are no domains for 2 and 5 uc samples (Fig.4 (g), (h)). That indicates there is the $LaAlO_3$ thickness dependence as reported in $LaAlO_3/SrTiO_3$. However, the critical thickness in this case (5 uc$<T\leq$15 uc) could be much thicker than it in case of $LaAlO_3/SrTiO_3$ (4 uc). That is consistent with Ganguli's report.

To analyze quantitatively the domain size and MCD asymmetry, Fig 5 shows the auto-correlation length and averaged CD asymmetries in CD domains. On the whole, it looks there is the thickness dependence as above. In the results of 2 uc sample, the analyzed data include some noise and non-uniformity in machine's detector so that the CD asymmetry and auto-correlation have been overestimated. For 15 uc sample, conversely, the size and CD asymmetry are appropriate to consider ferromagnetic domain. They are 45 nm and 0.8 %.

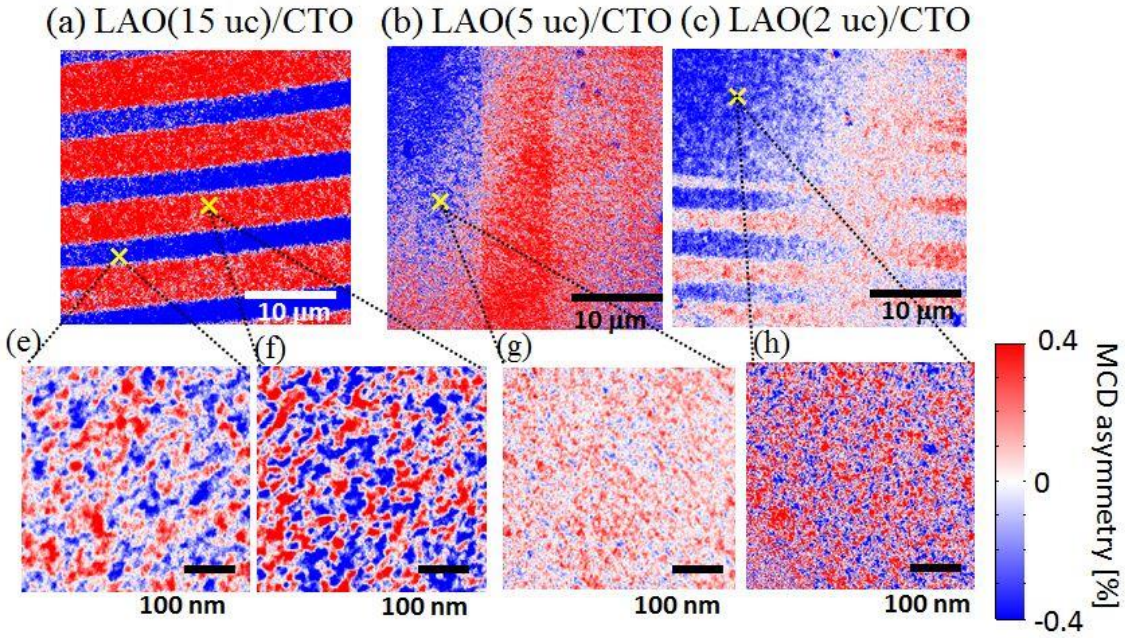


**Fig. 4 Magnetic imaging of the $LaAlO_3/CaTiO_3$**

**(a)~(c) CD image in $LaAlO_3$ (15, 5, 2 uc)/$CaTiO_3$, field of view (FoV) is 30 μm**

**(e)~(h) magnified CD images on marks, FoV is 500 nm**

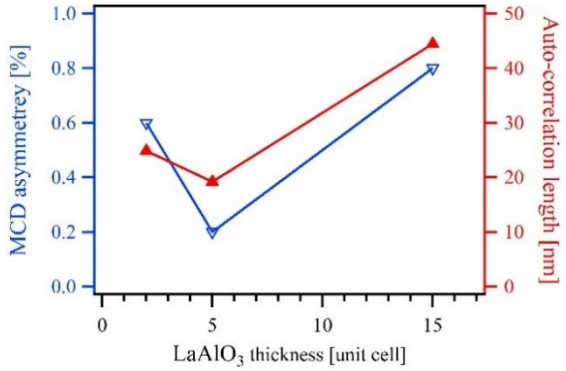


**Fig. 5 $LaAlO_3$ thickness dependence of MCD asymmetry and auto-correlation length**

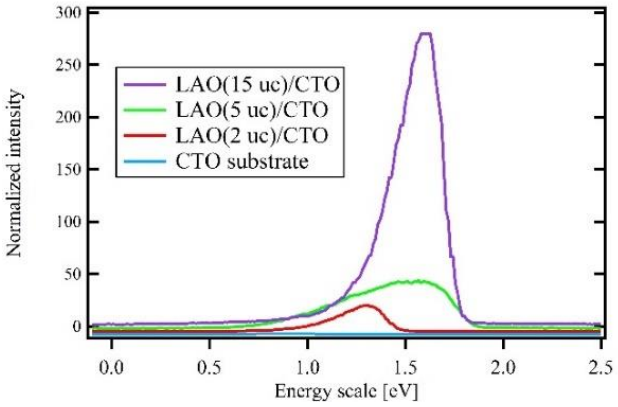


**Fig.6 Photoelectron spectra in each $LaAlO_3$ thickness samples.**

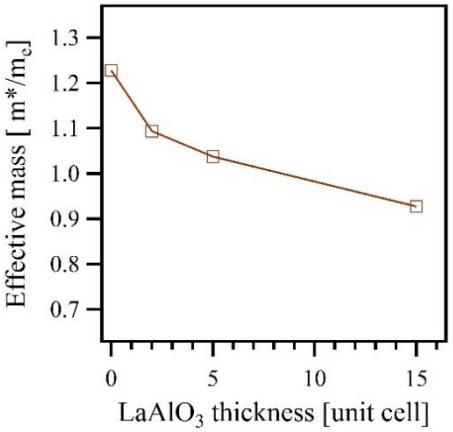


**Fig. 8 Effective masses in each $LaAlO_3$ thickness samples.**

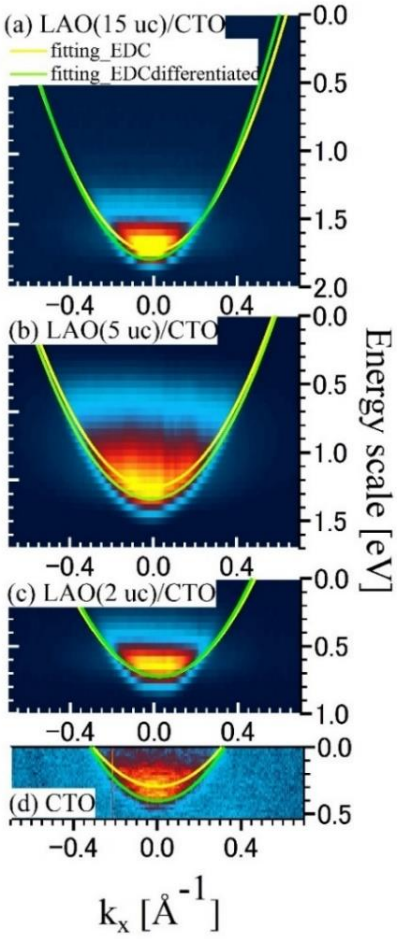


**Fig.7 Band dispersions in each $LaAlO_3$ thickness samples in ARPES**

(4) Spectroscopic measurements

Secondly, we performed photoelectron micro-spectroscopy to investigate electronic states on each thickness samples and relationship between the states and the results of magnetic imaging. Fig.6 shows the photoelectron spectra which were measured at the same spots as Fig.4 (e)-(h). In this study, Fermi energy could not be determined so that the horizontal axis in the graph indicates just energy scale.

In increasing $LaAlO_3$ thickness, the energy width of the spectra gets deeper and the intensity of photoelectron also gets stronger. There are crucial differences between 15 uc sample and 2 or 5 uc samples. That can be explained by the amount of charge transferring by $LaAlO_3$

polarity.

Comparing $LaAlO_3/CaTiO_3$ with $CaTiO_3$ which was measured as the reference, it is found that the photoelectron intensity in the substrate is 100 times weaker and is assumed to be attributed to deficient-$CaTiO_3$ bulk. It suggests that the photoelectrons detected in magnetic imaging are not from the bulk, but also dominantly from the interface where charge transferring occurs.

Finally, we performed angle-resolved photoelectron spectroscopy in order to know the detailed electronic states. Fig. 7 shows the results in 15, 5, 2 uc samples and $CaTiO_3$ substrate. Clear band dispersions like conduction bands could be observed in each sample. The dispersions are isotropic in $k_x$-$k_y$ plane (not shown here) so that they are determined as $d_{xy}$ orbit. The result means the 3d states are certainly generated by $LaAlO_3$ layers.

Surprisingly, it was found that the band curvatures got gradually larger in increasing $LaAlO_3$ thickness. The effective masses were estimated by fitting (Fig. 8). The effective masses got smaller in thicker samples. Although it is true that the band reconstructions occurs in $d_{xy}$ and $d_{xy,yz}$ when the states become two dimensional[5], continuous band transforming has never been known. For 15 uc sample, in which the domain could be observed, the mass was smallest (~0.92).

**Summary**

In this study, we succeeded in growing the $LaAlO_3/CaTiO_3$ thin film samples which were enough flat and high quality to generate interfacial states.

From observing ferromagnetic domain in Laser-PEEM, the existence of the ferromagnetic states was first-discovered. Our data suggest that there are critical thicknesses($5\ \text{uc} < T \leqq 15\ \text{uc}$). Investigating the electronic states in micro-spectroscopy, it is confirmed that the interfacial states are generated by charge transferring in $LaAlO_3$ layers. Furthermore, in increasing the LaAlO3 thickness, the interfacial states increase significantly and the effective mass get smaller.

For magnetism, it is consistent with the calculation by Ganguli that the ferromagnetism can appear when much charge transferring occurs. However, the cause for the change of effective masses requires further investigation, for example, transports measurement and further studies are needed in order to elucidate the detailed relationship between the electronic states and the magnetism.

**Acknowledgement**

The authors wish to acknowledge our supervisors Professor Shik Shin and Professor Mikk Lippmaa, ISSP, for their agreements and supporting.

The authors wish to acknowledge our second supervisors, Professor Masaaki Tanaka,

department of Electrical engineering and information systems and Professor Masashi Kawasaki, department of applied physics, for helping our study through reports and discussion

Finery, the authors wish to acknowledge MERIT program for giving us the budget, opportunity and view to collaborate.

**Reference**

[1] A. Ohtomo & H.Y. Hwang, *Nature* **427**, 423 (2004).

[2] Ariando *et al*., *Nat. Commun.* **2**, 188(2011).

[3] N. Ganguli and P. J. Kelly, *Phys. Rev. Lett.* **113**, 127201 (2014).

[4] L. Sun *et al*., *IEEE Transactions on Magnetics* **50**, 2303404 (2014).

[5] N. C. Plumb *et al*., *Phys. Rev. Lett.* **113**, 086801 (2014).