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# In-situ Manipulation and Imaging of Switchable Two-dimensional Electron Gas at Oxide Heterointerfaces

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The recent discovery of a two-dimensional electron gas (2DEG) at the interface between insulating perovskite oxides SrTiO3 and LaAlO3 was made possible by advances in atomic layer controlled growth. These advances have led to the creation of atomically-abrupt interfaces between novel complex oxide materials. It has been demonstrated that the conducting layer can be localized within a few nm of the interface, and that the carrier concentration can be altered with an electric field and/or lattice strain. We have created a strong interdisciplinary collaboration with the expertise in US and Korea required to attack the fundamental issues in this exciting, emerging field. This project is a collaborative effort to explore the fundamental scientific issues of the growth and novel properties of oxide hetero-interfaces. Specific tasks are (1) atomic layer epitaxial growth and characterization of switchable two-dimensional oxide heterointerface materials; (2) direct imaging of charge carrier densities by inline holography and electrical transport of 2DEG oxide hetero-interfaces. Our goal is to achieve an atomic-level understanding of the growth and characteristics of oxide hetero-interfaces, with advanced properties and new functionalities

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# "In-situ Manipulation and Imaging of Switchable Two-dimensional Electron Gas at Oxide Heterointerfaces"

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## Executive Summary

The recent discovery of a two-dimensional electron gas (2DEG) at the interface between insulating perovskite oxides $SrTiO_3$ and $LaAlO_3$ was made possible by advances in atomic layer controlled growth. These advances have led to the creation of atomically-abrupt interfaces between novel complex oxide materials. It has been demonstrated that the conducting layer can be localized within a few nm of the interface, and that the carrier concentration can be altered with an electric field and/or lattice strain. We have created a strong interdisciplinary collaboration with the expertise in US and Korea required to attack the fundamental issues in this exciting, emerging field. This project is a collaborative effort to explore the fundamental scientific issues of the growth and novel properties of oxide hetero-interfaces. Specific tasks are **(1) atomic layer epitaxial growth** and **characterization** of switchable two-dimensional oxide hetero-interface materials; (**2) direct imaging of charge carrier densities by inline holography and electrical transport** of 2DEG oxide hetero-interfaces. Our goal is to achieve an atomic-level understanding of the growth and characteristics of oxide hetero-interfaces, with advanced properties and new functionalities.

### *Atomic Layer Controlled Growth of Oxide Hetero-Interfaces*

We have designed and grown $LaAlO_3/SrTiO_3$ oxide hetero-interfaces and switchable 2DEG by using pulsed laser deposition atomic with *in-situ* reflection high-energy electron diffraction (RHEED). We have incorporated a differentially pumped high-pressure RHEED providing essential real-time monitoring and feedback to the growth process, and provide atomic-layer control of epitaxial oxide heterostructures at high oxygen partial pressure.

***Direct imaging of 2DEGs: Inline electron holography***

We have demonstrated that the inline electron holography can directly visualize the 2DEG at the both (001) and (111) LAO/STO interface. Taking an example of 2DEGs forming at LAO/STO interfaces with different crystal symmetry, we have shown that the selective orbital occupation and spatial quantum confinement of 2-DEGs can be resolved with sub-nm resolution using inline electron holography (Fig. 1). For the standard (001) orientation, the charge density map obtained by inline electron holography shows that the 2-DEG is confined to the interface with narrow spatial extension (~1.0 ± 0.3 nm in the half width). On the other hand, the 2DEG formed at the (111) interface shows a much broader spatial extension (~3.3 ± 0.3 nm) with the maximum density located ~2.4 nm away from the interface (Figs. 1b and d), in excellent agreement with density functional theory calculations. This orientation-dependent spatial confinement of 2DEGs results from the orbital-selective quantum confinement in the differently reconstructed subbands of Ti 3*d*–orbitals due to the crystal symmetry imposed orbital hierarchies on (001)- and (111)-oriented quantum well structures. Our results demonstrate the unprecedented capability of electron holographic charge imaging to probe interface-confined electronic systems. We have used this to reveal direct evidence that 2DEG properties can be controlled through the interface orbital configuration, paving the way toward interface orbital engineering of complex oxide systems.

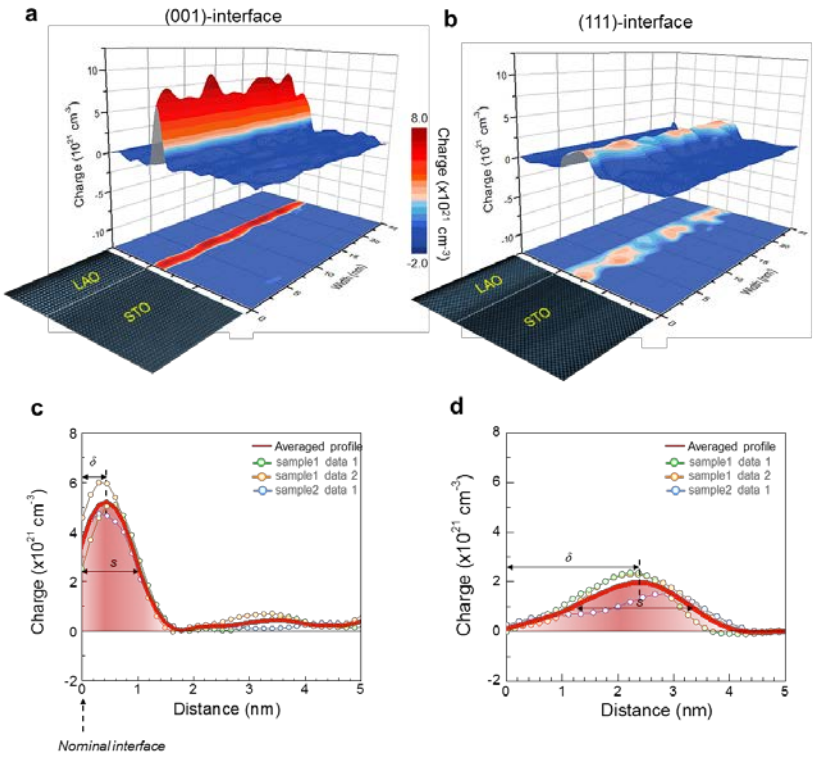


**Figure 1**. **Direct imaging of the 2DELs at oxide interfaces. a, b,** 2-D surface plot and projected map of the total charge density obtained by inline electron holography for the LAO/STO (001) and the (111) interfaces, respectively. HAADF STEM images are shown next to the charge density maps. **c, d,** 1-D electron density profiles obtained from the charge density maps. **c,** The red solid line corresponds to the averaged electron density profile. For the (001) interface, the density of the 2DEL ($n_e$) is 2.88 ± 0.39 × $10^{14}$ $cm^{-2}$. Its distribution shows that the spatial depth (denoted by *s*) is 1.0 ± 0.3 nm and the maximum density is slightly displaced from the interface by about 0.4 nm (denoted by $\delta$), which is within the range of measurement uncertainty. **d,** For the (111)-interfaces, the $n_e$ is measured to be 1.02 ± 0.01 × $10^{14}$ $cm^{-2}$. Its distribution has a spatial depth of $s$ = 3.3 ± 0.3 nm, and the maximum density is found at $\delta$ ~ 2.4 nm away from the interface.

***In situ inline electron holography***

We used a switchable ferroelectric polarization to modulate the electron concentration of the 2-DEG forming at a LAO/STO interface. Figure 2 shows the suggested experimental approach and the model structures in which the electron concentration of the *entire* 2-DEG is changed through the field effect by switching the ferroelectric polarization in the 15 u. c. strained STO layer on LSAT-buffered Nb-doped STO (Fig. 2c). The change in the electron concentration occurs due to the ferroelectric field effect that depends on polarization orientation. The switching is accomplished by applying a saturating electric field between the 2DEG layer and a Nb-doped STO substrate bottom electrode directly inside TEM.

As the first step toward direct modulation of the concentration/spatial width of 2DEG and its visualization through *in situ* electron holography, we constructed an experimental setup which enables direct application of electric fields to the LAO/STO interfaces (Fig. 2a). We used a commercial electrical biasing TEM holder (Nanofactory STM holder) and a separate *I-V* measurement system. For the exit-wave reconstruction of a through-focal series of TEM BF images, we used the QPt software (HREM Research) as well as the standard FRWR algorithm, as the former is suited better for *in situ* experiments because it requires only three defocused images. Using a focused ion beam (FIB), cross-sectional TEM specimens were made from the switchable 2DEG devices which incorporate strained STO as an active ferroelectric layer. By performing prior *I-V* and *P-E* measurements, we confirmed the LAO/STO interfaces hosts the regular 2-DEG and also that the strained STO layer is ferroelectric as we predicted.

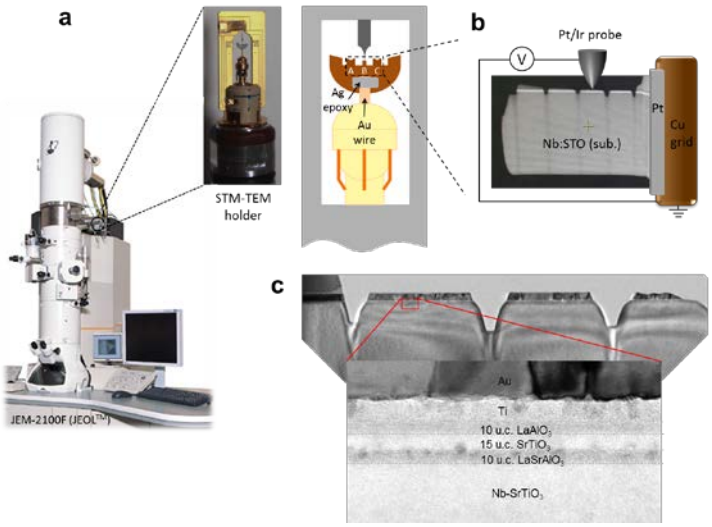


**Figure 2. *In situ* electron holography imaging of the switchable 2-DEG at LAO/STO interface.** (a) TEM (JEM-2100F, JEOL) and an electrical biasing TEM holder (STM-holder, Nanofactory) used for *in situ* electron holography. (b) TEM sample prepared by using FIB for electrical biasing in TEM. A conducting Nb-doped STO substrate is attached to the electrically grounded Cu grid. (c) TEM image showing the structure of a switchable 2-DEG device. The Pt/Ir probe installed in the TEM holder is brought into contact with the Au top electrode. When a voltage is applied to the Au electrode, an electric field is induced across the LAO/STO interface where the 2DEG is formed. The ferroelectric polarization of 15 u. c. STO layer is used to modulate the concertation and spatial extension of 2DEG via ferroelectric field effects.

We performed a series of *in situ* electron holography experiments to optimize the TEM sampling process and also the TEM imaging condition for the exit-wave reconstruction. The FIB prepared TEM samples suffered from a large leakage current. The large leakage current limited the application of electric field across the LAO/STO interface. We adopted low energy $Ga^{+}$ ion milling strategy to remove the surface damage layers which are the main cause of the leakage current. After several attempts of optimization, the leakage current could be suppressed sufficiently to induce an *effective* electric field acting across the LAO/STO interface region (refer to Fig. 3d). We obtained total 9 defocused TEM images at each voltage step in 1 V interval. Representative *in situ* electron holography data is shown in Fig. 3. The *R*-factor of all reconstructed data was below 5%. While all data show zero potential in the electrically grounded Nb-STO substrate, the potential at the top electrode does not match the applied voltage. Furthermore, a large voltage drop was observed at the Au/Ti interface, which might be caused by electric-field driven Ti layer oxidation from the adjacent LAO layer. In addition, different background potential i.e., mean inner potential, of the different materials make the interpretation of data complicated. Nonetheless, the results are promising in that our approach can induce an effective field across the LAO/STO interface to drive the ferroelectric field effects for the modulation of 2-DEG. In the next year, we will modify the model structure by replacing the top electrode with an oxide material (e.g., $SrRuO_3$) and calibrate the background potential and the dielectric constants of the corresponding materials used in the model structure.

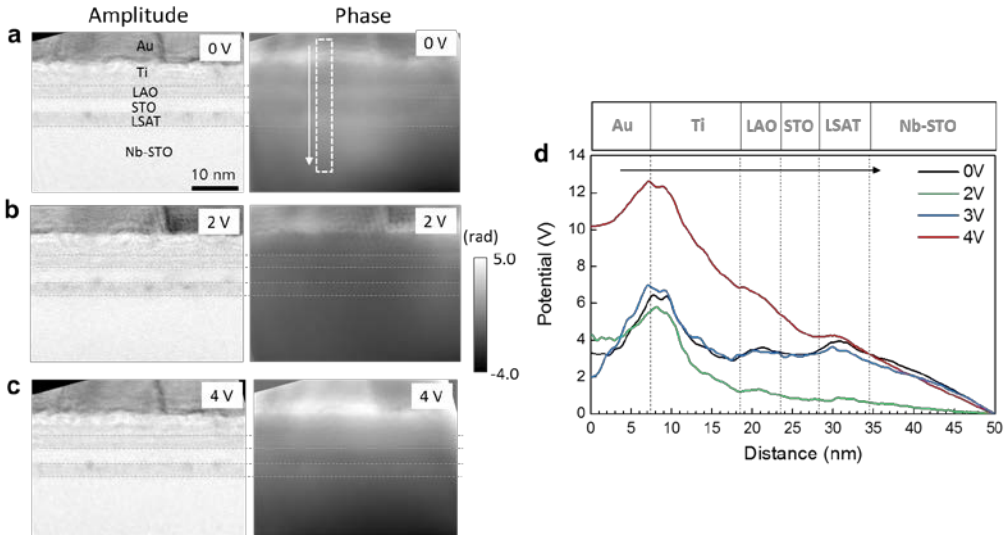


**Figure 3. Reconstructed amplitude and potential maps obtained by *in situ* electron holography.** Amplitude and phase maps obtained by the exit-wave reconstruction of a through-focal series TEM images under the applied voltage of: (a) 0 V; (b) 2 V; (c) 4 V. (d) Profile of the potential across the LAO/STO interface from the Au top electrode to the Nb-STO substrate. Note that the Nb-STO substrate was grounded.

**List of Publications and Significant Collaborations that resulted from your AOARD supported project:**

**a) papers published in peer-reviewed journals,**

1. "Reversible Tuning of Two-dimensional Electron Gases in Oxide Heterostructures by Chemical Surface Modification" H. Lee, N. Campbell, S. Ryu, W. Chang, J. Irwin, S. Lindemann, M. K. Mahanthappa, M. S. Rzchowski, and C. B. Eom, *Applied Physics Letters*, **109**, 191604 (2016)
2. "Electro-mechanical response of top-gated $LaAlO_3/SrTiO_3$" Feng Bi, Mengchen Huang, Chung-Wung Bark, Sangwoo Ryu, Sanghan Lee, Chang-Beom Eom, Patrick Irvin and Jeremy Levy, J. Appl. Phys. **119**, 025309 (2016)
3. "Emergence of Room-Temperature Ferroelectricity at Reduced Dimensions", D. Lee, H. Lu, Y. Gu, S.-Y. Choi, S.-D. Li, S. Ryu, T. R. Paudel, K. Song, E. Mikheev, S. Lee, S. Stemmer, D. A. Tenne, S. H. Oh, E. Y. Tsymbal, X. Wu, L.-Q. Chen, A. Gruverman, C. B. Eom, *Science*, **349**, 1314 (2015)
4. "Real-time and *in situ* monitoring of sputter deposition with RHEED for atomic layer controlled growth" J. P. Podkaminer, J. J. Patzner, B. A. Davidson and C. B. Eom, APL Mater. 4, 086111 (2016);
5. "*In situ* TEM observations of the resistance switching by electrochemical redox reactions at a metal/oxide interface". Kyungjoon Baek, Sangsu Park, Jucheol Park, Young-Min Kim, Sang Ho Oh, accepted for publication in *Nanoscale* (2016). DOI: 10.1039/C6NR06293H

**d) conference presentations without papers,**

1. "TEM Techniques for Charge, Strain and Polarization Mapping", Sang Ho Oh, Invited talk, SpectroNanoscopy 2015 Workshop, September 2-4, 2015, Jeju, Korea.
2. "In situ TEM Switching of Non-volatile Memory Devices", Sang Ho Oh, Invited talk, DPG Spring Meeting, March 6-11, 2016 Regensburg, Germany.

**e) manuscripts submitted but not yet published**

1. "Direct imaging of the electron liquid at oxide interfaces", Kyung Song, Sangwoo Ryu, Hyungwoo Lee, Si-Young Choi, Tula R. Paudel, Christoph T. Koch, Mark S. Rzchowski, Evgeny Y. Tsymbal, Chang-Beom Eom and Sang Ho Oh, *manuscript in preparation for submission to Nature Nanotechnology* (2016).
2. "Strain undulation in Nonpolar InGaN/GaN Quantum wells", Ja Kyung Lee, Kyung Song, Christoph T. Koch, Woo Young Jung, Dmitry Tyutyunnikov, Tiannan Yang, Jong Kyu Kim, Chan Gyung Park, Peter A. van Aken, Long-Qing Chen, Young-Min Kim, Sang Ho Oh, submitted to *Advanced Functional Materials* (2016).

**f) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.**

We have developed research collaboration with Igor Altfeder and Andrey Voevodin at AFRL at Dayton, OH. They have been looking on a development of interfacial 2DEG using their UHV-STM with and without electrostatic gate voltage to determine the evolution of 2DEG charge density. This investigation is important for understanding oxide-based 2DEG field effect transistors and complimentary with this project. The Eom group at UW-Madison

designed and provided symmetric n-type 2DEG bilayer heterostructures prepared by atomic layer engineering method. The AFRL group observed surface conductivity which is the indicator of 2DEG presence. We published a coauthored paper as a result of this collaboration.

"Scanning tunneling microscopy of an interfacial two-dimensional electron gas in oxide heterostructures" Igor Altfeder, Hyungwoo Lee, Jianjun Hu, Rachel D. Naguy, Alp Sehirlioglu, Amber N. Reed, Andrey A. Voevodin, and Chang-Beom Eom, *Phys. Rev. Letts.*, **93**, 115437 (2016)