



In-situ Charge-Density Imaging of Metamaterials from Switchable 2D electron gas

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14. ABSTRACT 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 also 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 2DEGs can be resolved with sub-nm resolution using inline electron holography. For in-situ biasing experiments in TEM, we prepared two model heterostructures of switchable 2DEG systems and performed in-situ STEM HAADF imaging of the heterostructure taken under various DC biases. The electric potential images and profiles were obtained from the reconstructed phase of transmitted electron beam after calibrating local thickness of TEM sample.						
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" *In-situ* Charge-Density Imaging of Metamaterials from Switchable 2D Electron Gas"

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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. We propose a collaborative effort to explore the fundamental scientific issues of the growth and novel properties of switchable 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 switchable 2DEG oxide hetero-interfaces *in situ*. 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 $\text{LaAlO}_3/\text{SrTiO}_3$ 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 2DEGs 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 2DEG is confined to the interface with narrow spatial extension ($\sim 1.0 \pm 0.3$ nm in the half width). On the other hand, the 2DEG formed at the (111) interface shows a much broader spatial extension ($\sim 3.3 \pm 0.3$ 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 3d-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. This work has been accepted for publication in *Nature Nanotechnology* (“Direct Imaging of the Electron Liquid at Oxide Interfaces” K. Song et al., in press, *Nature Nanotechnology* (2018))

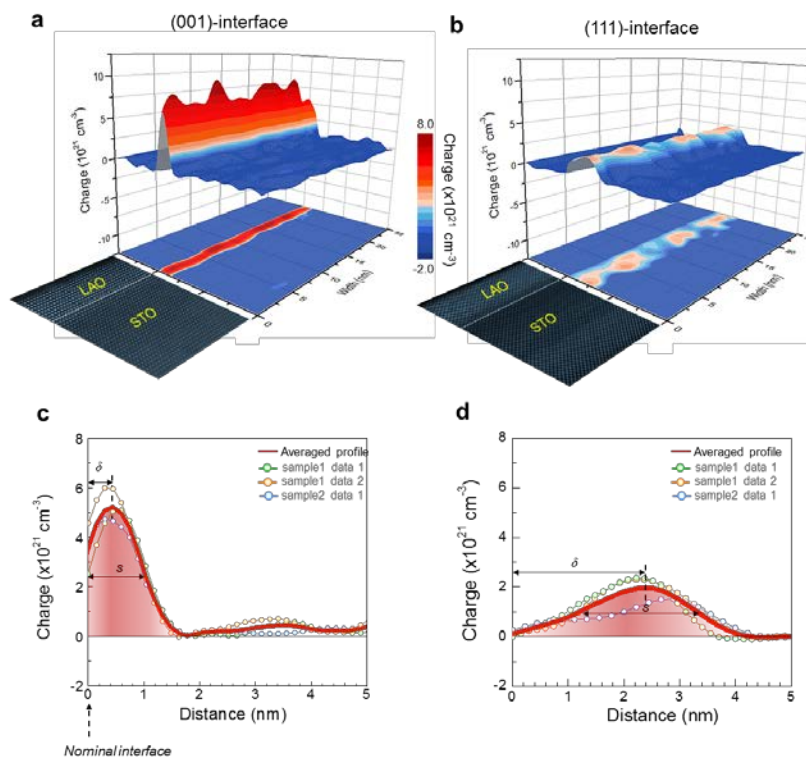


Figure 1. Direct imaging of the 2DELs at oxide interfaces. **a, b**, 2-D surface plot and projected map of the total charge density obtained by inline electron holography for the LAO/STO (001) and the (111) interfaces, respectively. HAADF STEM images are shown next to the charge density maps. **c, d**, 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 $2.88 \pm 0.39 \times 10^{14} \text{ cm}^{-2}$. 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 δ), which is within the range of measurement uncertainty. **d**, For the (111)-interfaces, the n_e is measured to be $1.02 \pm 0.01 \times 10^{14} \text{ cm}^{-2}$. Its distribution has a spatial depth of $s = 3.3 \pm 0.3 \text{ nm}$, and the maximum density is found at $\delta \sim 2.4 \text{ nm}$ away from the interface.

In situ inline electron holography

For *in-situ* biasing experiments in TEM, we prepared two model heterostructures of switchable 2DEG systems (Fig. 2). The first system (sample A) is comprised of a LAO/STO interface with 2DEG and SrRuO₃ (SRO) top electrode. DC bias was applied to the SRO top electrode while the conductive Nb-doped STO substrate was electrically grounded. In the second system (sample B), a switchable BaTiO₃ (BTO) ferroelectric layer is added on top of the LAO to modulate the density of 2DEG through the ferroelectric field effect. Upon polarization reversal by electric field, a change in the 2DEG density is expected to arise due to the electrostatic screening of polarization charges that depend on polarization orientation.

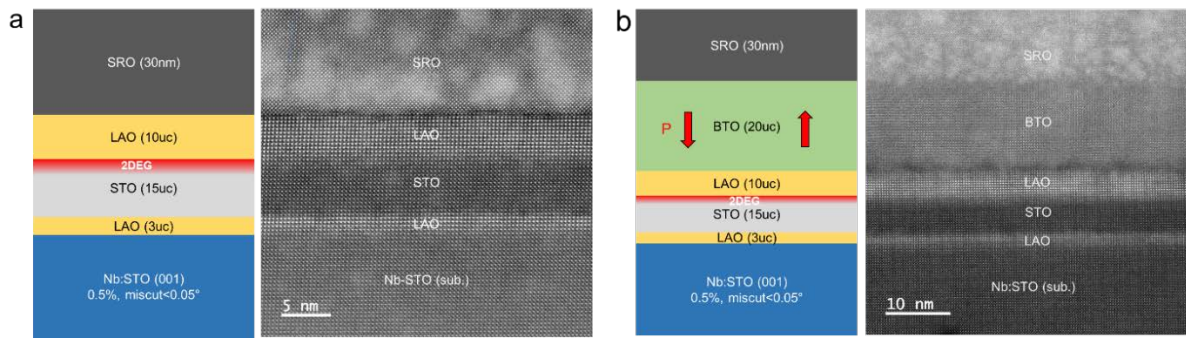


Figure 2. Two model structures of switchable 2DEG systems for in-situ inline electron holography. (a) SRO/LAO/STO/LAO/Nb-STO heterostructure (sample A) for electrostatic backgating of the 2DEG at the LAO/STO interface. (b) SRO/BTO/LAO/STO/LAO/Nb-STO heterostructure for ferroelectric field effect-controlled 2DEG charge density.

TEM samples for *in-situ* biasing experiment were prepared with focused ion beam (FIB) (Fig. 3). A thin lamella was lifted out and fixed onto a Si MEMS chip, then further milled for electron transparency in the low energy Ga⁺ ion beam FIB. An electrical biasing circuit for electric field application across the LAO/STO interface was constructed by cutting electrical isolation trenches. Inline holography, STEM imaging and EELS characterization were carried out *in-situ* in the TEM while varying DC bias was applied to the SRO top electrode.

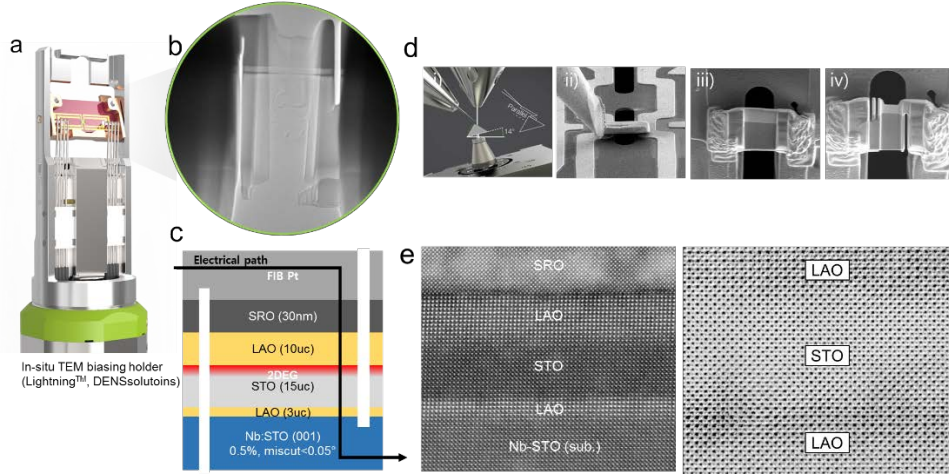


Figure 3. TEM sample preparation for *in-situ* biasing of switchable 2DEG systems. (a) TEM biasing holder. (b) TEM image of sample prepared by FIB. (c) Schematic showing the electrical connections of the device. The top SRO electrode together with Pt layer is connected to the left metal pad and the Nb-STO substrate to the right metal pad by cutting trenches for electrical isolation of one electrode from each contact. (d) FIB procedure for TEM sample preparation. (e) STEM HAADF and ABF images of the LAO/STO interface.

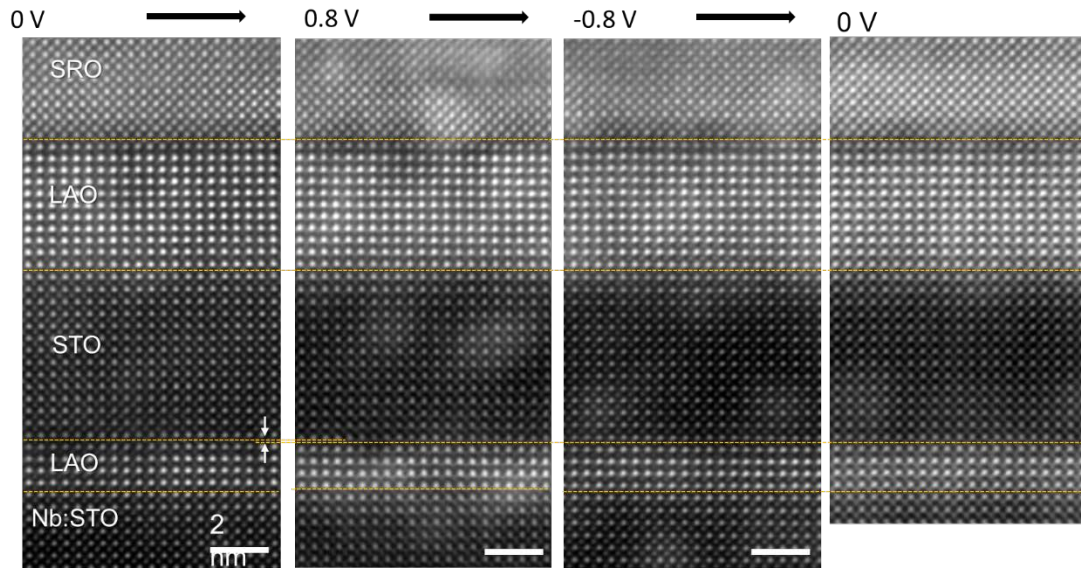


Figure 4. STEM HAADF images of sample A under applied biases. (a) 0V, (b) 0.8 V and (c) -0.8 V.

In-situ STEM HAADF images of the heterostructure (sample A) taken under various DC biases are shown in Fig. 4. With the application of bias, it is observed that the interfaces become rough and diffuse, particularly at the interfaces with the LAO layers, which indicates inter-diffusion of cations between adjacent layers. In addition, bright particle-like features appeared in the heterostructure. The insulating oxide LAO layer in our model heterostructures likely behaves as a “solid electrolyte” since the layer is just a few unit cells thick, allowing ion transport under an applied bias. We attribute this to the strongly field-dependent activation energies for the formation and migration of oxygen vacancies,

which decreases rapidly for electric field strengths greater than 1 MV cm^{-1} . With typical 1 V applied voltages and films of a few nanometers thick, the applied electric field in the active region of a device easily exceeds 1 MV cm^{-1} . At such strong fields the formation of oxygen vacancy and/or cation intermixing can occur at the interfaces.

The electric potential profiles across the LAO/STO interface (sample A) at the applied voltages of -0.8 V and +0.8 V are shown in Fig. 5. The electric potential images and profiles were obtained from the reconstructed phase of transmitted electron beam after calibrating local thickness of TEM sample. While the potential of the conductive Nb-STO substrate and the STO layer hosting the interfacial 2DEG remained almost the same under electric bias, the potential of the LAO layers and the STO top electrode changed significantly. This indicates that defect-induced structural changes occurred in these layers. Particularly in the LAO layers, the oxygen EELS K-edge structure shows energy shifts, indicating oxygen vacancy formation and subsequent migration (Fig. 6). In support of this the out-of-plane strain maps show compressive strain in the LAO layers. This implies that oxygen vacancies are formed and migrate away from the LAO layer.

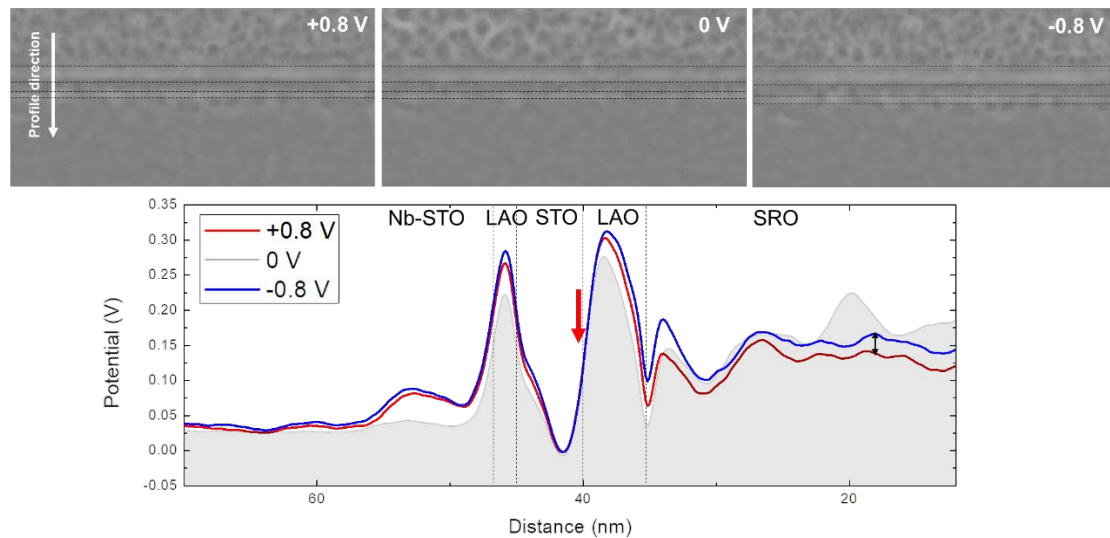


Figure 5. 2D electric potential images and 1-D profiles across the LAO/STO interface (sample A) obtained under the applied biases of -0.8 V and +0.8 V. No significant potential change is observed at the STO side of the LAO/STO interface (red arrow) where the 2DEG exists. However there are several regions which exhibit local potential variations in response to the applied bias, i.e. near interface region of Nb-STO, LAO layer and SRO top electrode. We associate these changes with oxygen vacancy formation and migration.

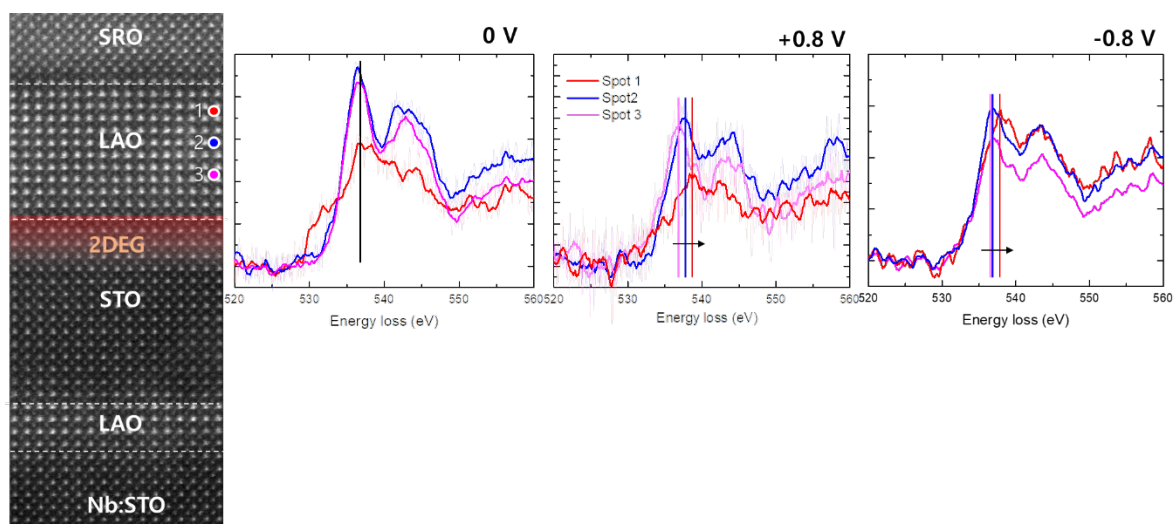


Figure 6. STEM EELS O-K edge of sample A under applied biases of 0V, 0.8 V and -0.8 V. The chemical shift of the first sub-peaks is indicated by arrow.

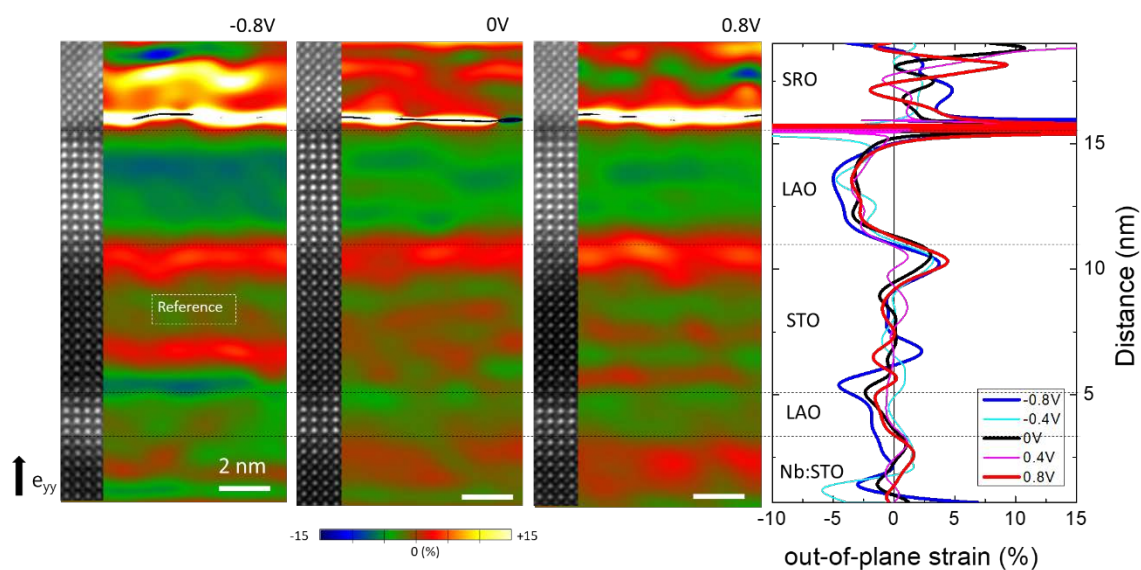


Figure 7. Out-of-plane strain maps and profiles obtained by STEM HAADF images under applied biases of 0V, 0.8 V and -0.8 V. The strain map shows changes in the lattice plane spacing along the growth direction. The LAO layers show compressive strain at -0.8 V, implying oxygen vacancy formation and migration.

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

a) papers published in peer-reviewed journals,

1. “Direct Observation of Two-Dimensional Hole Gas at Oxide Interfaces” H. Lee, N. Campbell, J. Lee, T. J. Asel, T. R. Paudel, H. Zhou, J. W. Lee, B. Noesges, J. Seo, B. Park, L. J. Brillson, S. H. Oh, E. Y. Tsymbal, M. S. Rzchowski, and C. B. Eom, in press *Nature Materials*, (2018)
2. “Direct Imaging of the Electron Liquid at Oxide Interfaces” Kyung Song, Sangwoo Ryu, Hyungwoo Lee, Tula R. Paudel, Christoph T. Koch, Bumsoo Park, Ja Kyung Lee, Si-Young Choi, Young-Min Kim, Hu Young Jeong, Mark S. Rzchowski, Evgeny Y. Tsymbal, Chang-Beom Eom, Sang Ho Oh, in press, *Nature Nanotechnology* (2018)
3. “Direct Imaging of Sketched Conductive Nanostructures at the LaAlO₃/SrTiO₃ Interface” Zhanzhi Jiang, Xiaoyu Wu, Hyungwoo Lee, Jung-Woo Lee, Jianan Li, Guanglei Cheng, Chang-Beom Eom, Jeremy Levy, Keji Lai, *Appl. Phys. Letts.* **111**, 233104 (2017)
4. “Strain-induced Indium Clustering in Non-polar InGaN 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, *Acta Materialia* **145**, 109 (2018)
5. “*In situ* TEM observation on the interface-type resistive switching by electrochemical redox reactions at a TiN/PCMO interface”, Kyungjoon Baek, Sangsu Park, Jucheol Park, Young-Min Kim, Hyunsang Hwang, Sang Ho Oh, *Nanoscale* **9**, 582 (2017).
6. “Sharpened VO₂ phase transition via controlled release of epitaxial strain” Daesu Lee, Jaeseong Lee, Kyung Song, Fei Xue, Si-Young Choi, Yanjun Ma, Jacob Podkaminer, Dong Liu, Shih-Chia Liu, Bongwook Chung, Wenjuan Fan, Weidong Zhou, Jaichan Lee, Long-Qing Chen, Sang Ho Oh, Zhenqiang Ma, Chang-Beom Eom, *Nano Letters*, **17**, 5614 (2017).
7. “*In-situ* Probing of Coupled Atomic Restructuring and Metallicity of Oxide Heterointerfaces induced by Polar Adsorbates” S. Ryu, H. Zhou, T. R. Paudel, J. Irwin, J. P. Podkaminer, C. W. Bark, D. Lee, T. H. Kim, D. D. Fong, M. S. Rzchowski, E. Y. Tsymbal and C. B. Eom, *Appl. Phys. Lett.* **111**, 141604 (2017)
8. 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. *Appl. Phys. Lett.* **109**, 191604 (2016)
9. “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 Materials* **4**, 086111 (2016)

10. “Electro-mechanical response of top-gated LaAlO₃/SrTiO₃” 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)

d) conference presentations without papers,

Sang Ho Oh, “Direct Imaging of the Electron Liquid at Oxide Interfaces”, BIT’s 5th Annual Congress of Analytix-2017, Fukuoka, Japan, March 23, 2017.

e) manuscripts submitted but not yet published

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

Chang-Beom Eom and Sang Ho Oh visited AFRL and gave a seminar on July 18, 2017. They also met and discussed potential collaboration with scientist and postdocs. Dr. Donald L. Dorsey at AFRL was the host.

Dr. Don Dorsey followed up after the visit by email. “I had a discussion with our electron microscopist, Dr. Mahalingam, and he was very impressed by the in-line electron holography approach. We would be very interested in comparing our future electron holography results (we are just now initiating this capability) with your inline approach on the same sample. We hope to have some good results within a year and will get back to you on this.”

Chang-Beom Eom also developed collaboration with Dr. Brandon Howe and Amber on TiN thin films. AFRL sent sputtered TiN thin films to UW-Madison for NH₃ annealing (which was developed by Eom group) to improve the electrical properties. “Very cool that we’ve found some common ground to collaborate on and I look forward to visiting you sometime in October. (Amber you are welcome to join as well - he has a VERY impressive lab).”