Quantun Materials: An introduction

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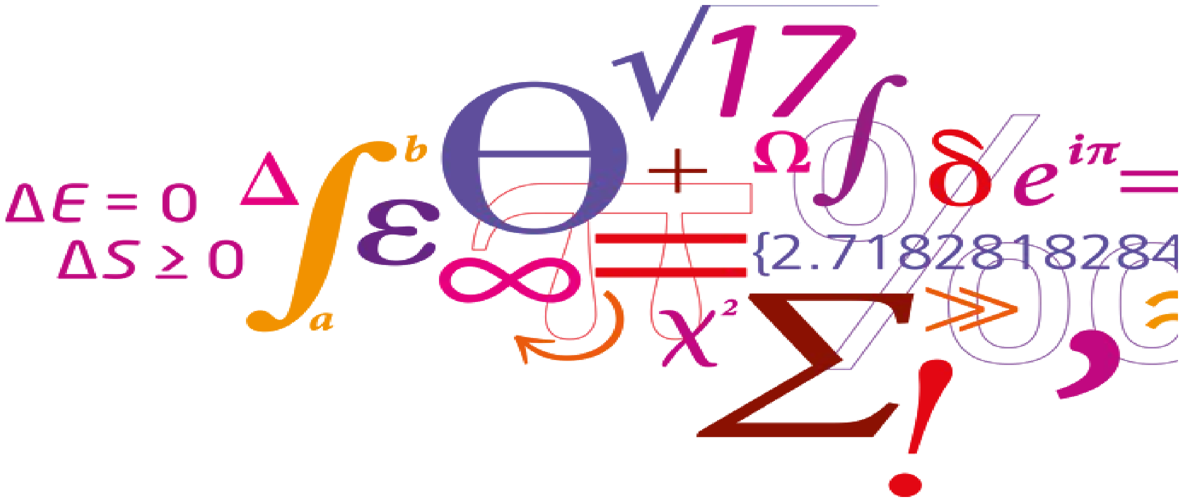


DTU Energy
Department of Energy Conversion and Storage

Outline

- 1. What are quantum materials
- 2. Materials and synthesis
- 3. Emergent functions at the interface between two oxide insulators

What are quantum materials ?

DTU

Quantum materials (QM)are solids with exotic physical properties, arising from the quantum mechanical properties of their constituent electrons; such materials have great scientific and/or technological potential.

Themes of modern quantum Materials:

Order and Symmetry; Topology;

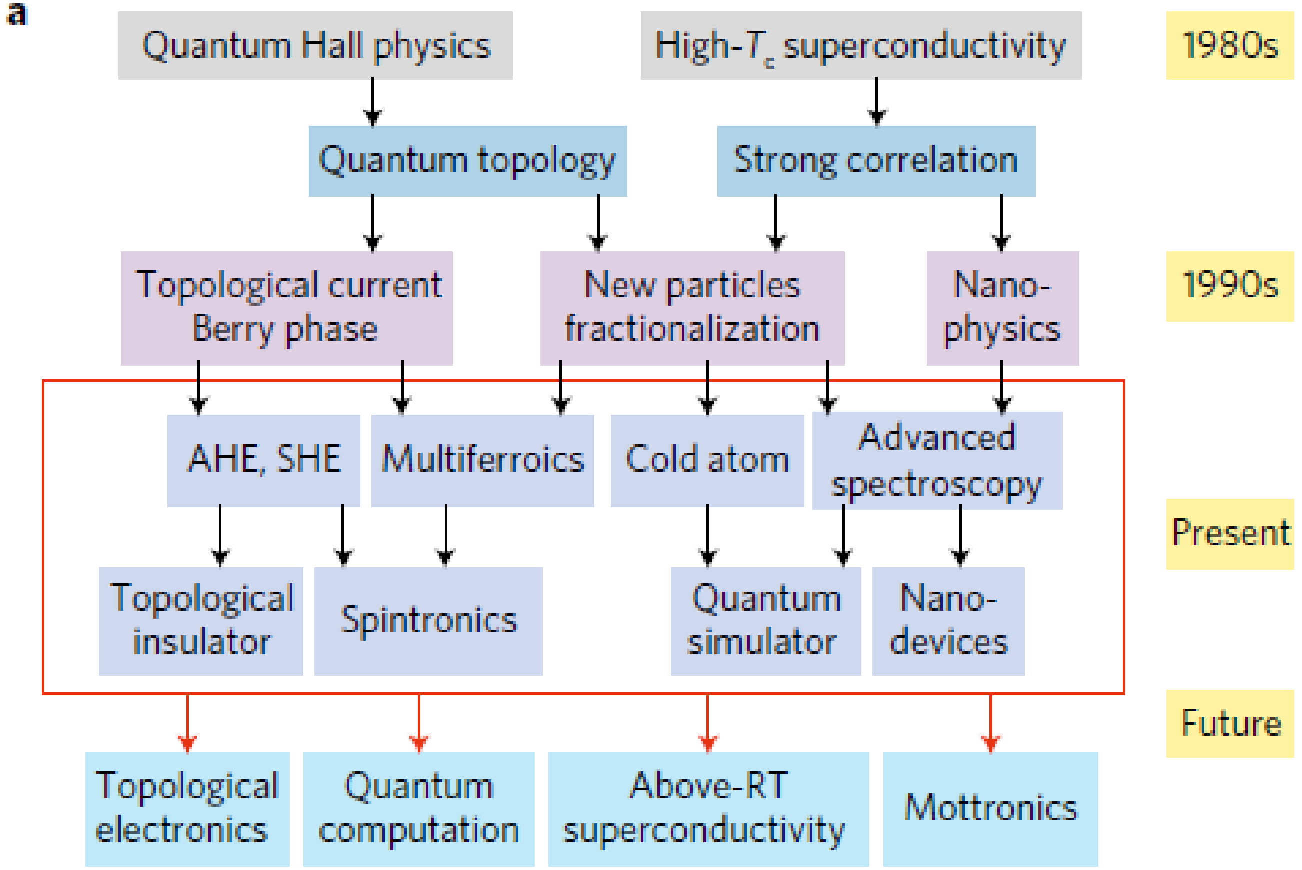
Entanglement; Correlations; Dynamics

REVIEW ARTICLES
PUBLISHED ONLINE: 25 SEPTEMBER 2017 | DOI: 10.1038/NPHYS4274
nature physics

Emergent functions of quantum materials

Yoshinori Tokura[1,2]*, Masashi Kawasaki[1,2] and Naoto Nagaosa[1,2]

Brief history of the research on physics of QM



editorial

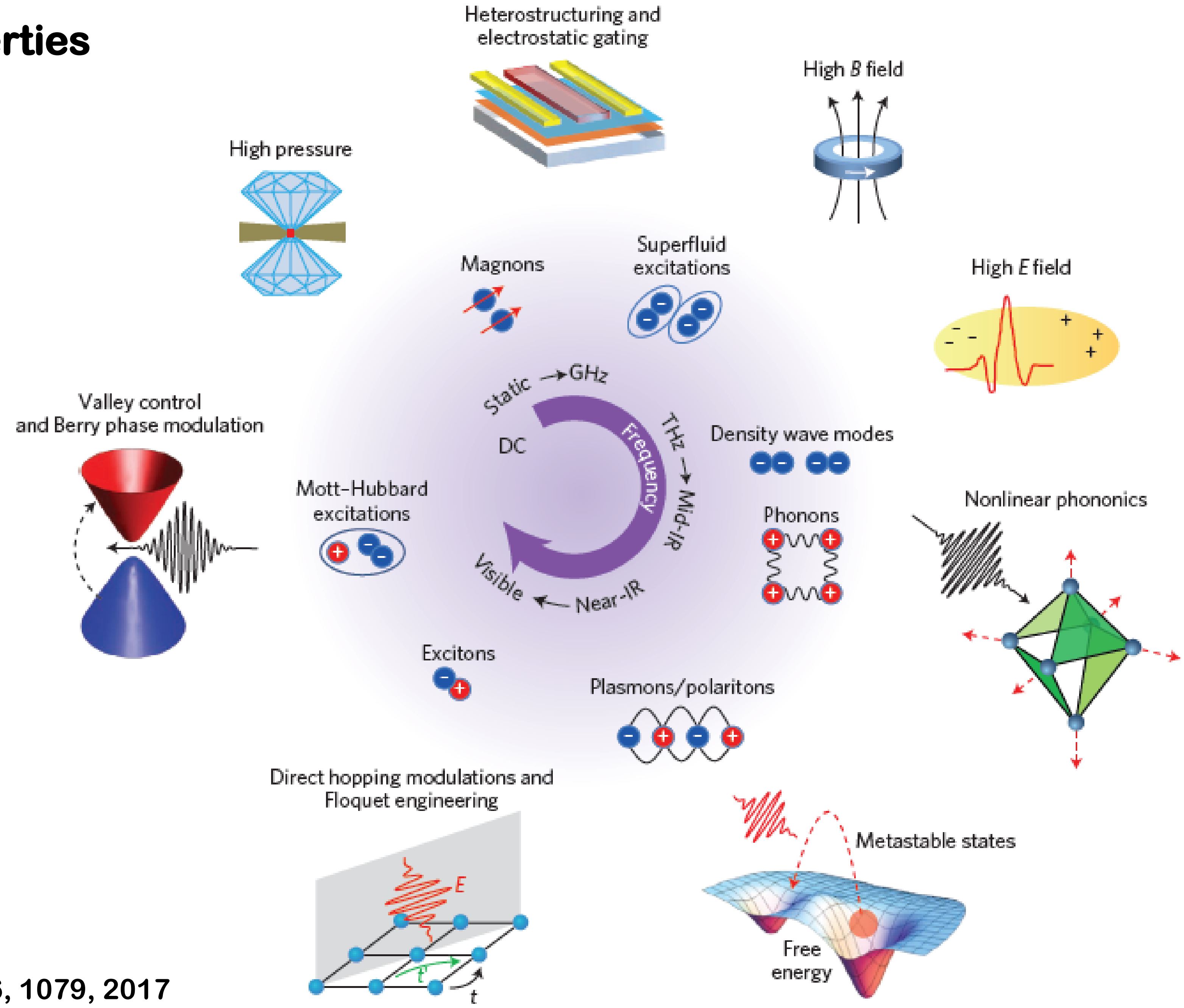
The rise of quantum materials

Nature Physics. 12, 105, 2016

Emergent phenomena are common in condensed matter. Their study now extends beyond strongly correlated electron systems, giving rise to the broader concept of quantum materials.

- ❑ Magnetism
- ❑ High temperature superconductors
- ❑ Topological Insulators
- ❑ **Oxide heterostructures**
- ❑ Van der Waals heterostructures
- ❑ Monolayer "transition-metal dichalcogenides”
- ❑ ….

The trend: on-demand properties

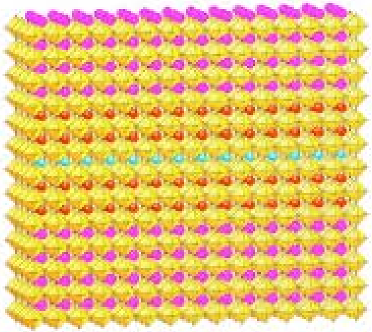


Basov et al. Nature Material, 16, 1079, 2017

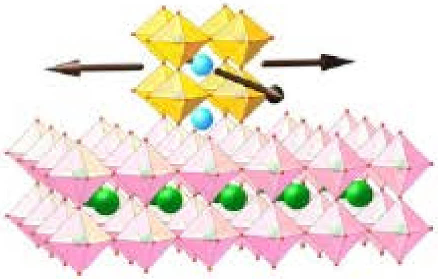
"Artificial" Quantum Materials

DTU

Interface Engineering

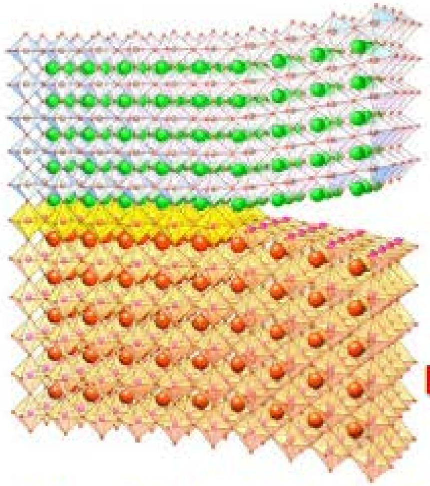


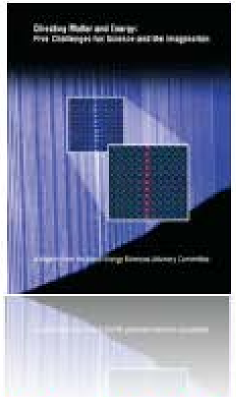
$(LaMnO_3)_{2n}$ / $(SrMnO_3)_n$



Strain Engineering

FeSe / $SrTiO_3$





$LaAlO_3$ / $SrTiO_3$

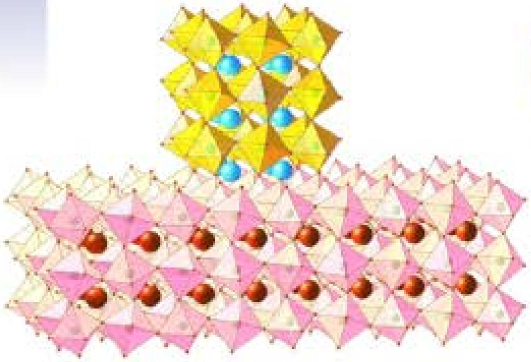
Bi_2Se_3 / EuS

Polarization Doping & Proximity Effects

(from juxtaposed competing

Bulk Quantum Materials

ARPES



Epitaxial Stabilization

$BaRuO_3$ / $SrTiO_3$

Ba_2RuO_4 / $GdScO_3$

Dimensional Confinement

$A_{n+1}B_nO_{3n+1}$: $(La,Sr)_2CuO_4$, Sr_2RuO_4, Sr_2IrO_4

D. Schlom et al.

My Reseach

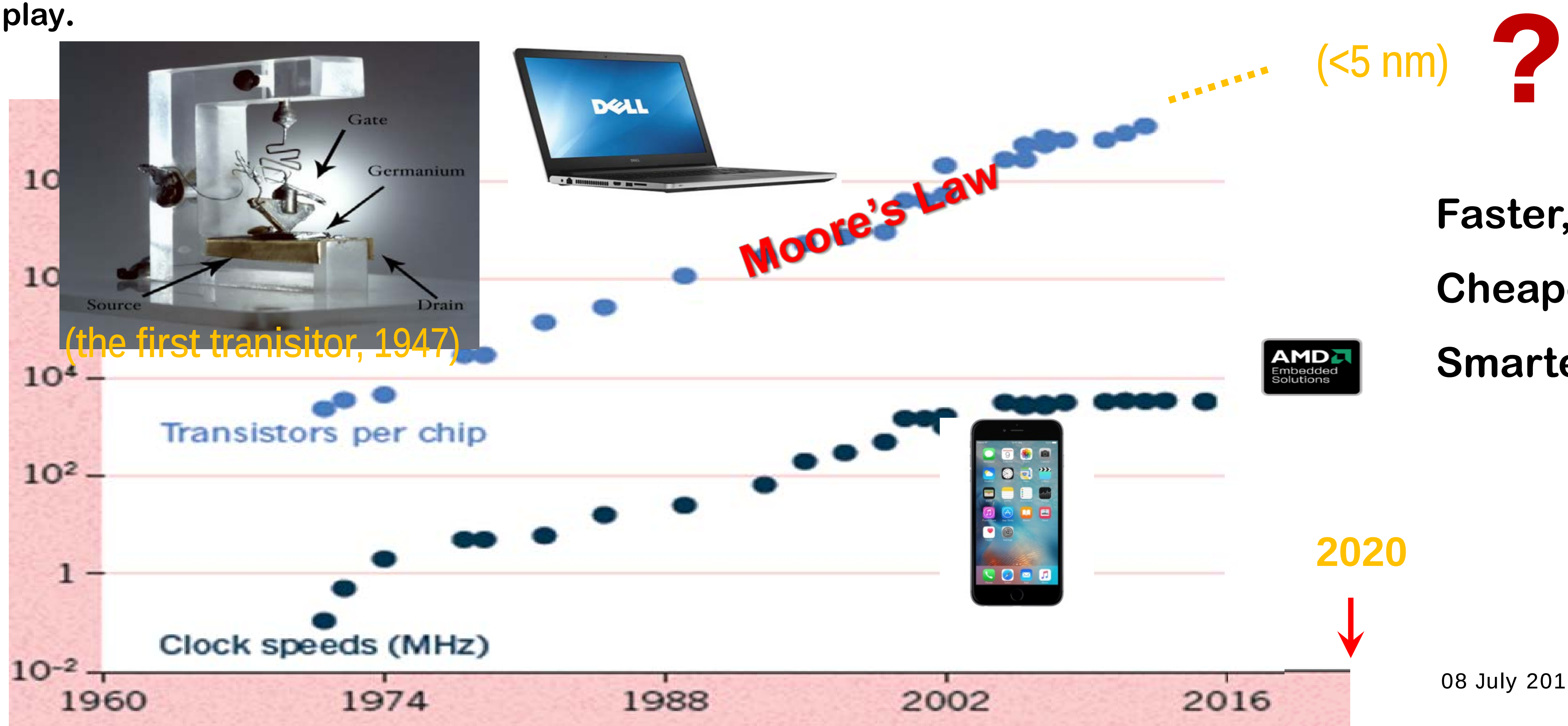
- Conducting Oxide Interfaces for Electronics

- Conducting Oxide Interfaces for Ionics and Electrocatalysts

Two Key Challenges of Current Semiconductor Technology

1. Material limit of Si is going to be meet

What will happen when continued scaling is no longer possible with silicon because quantum effects have come into play.



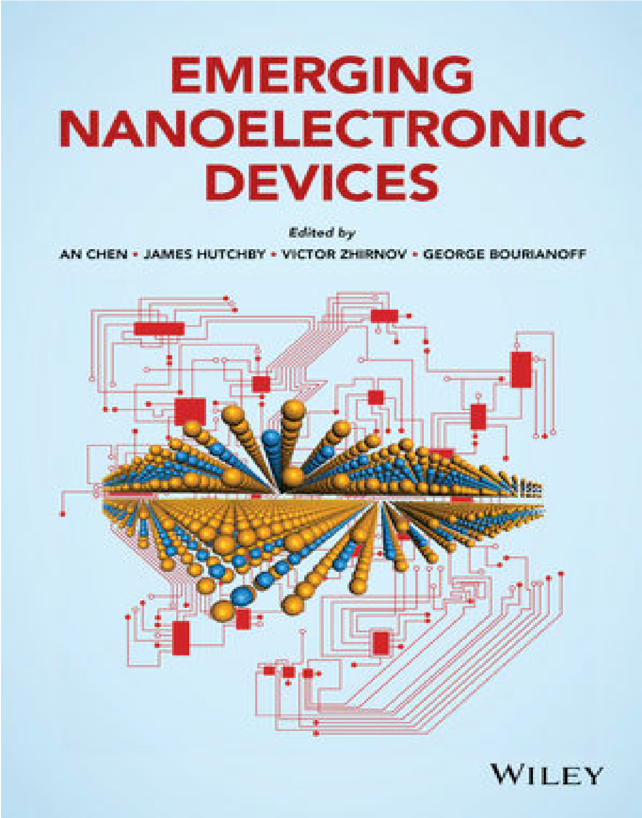
Faster,

Cheaper,

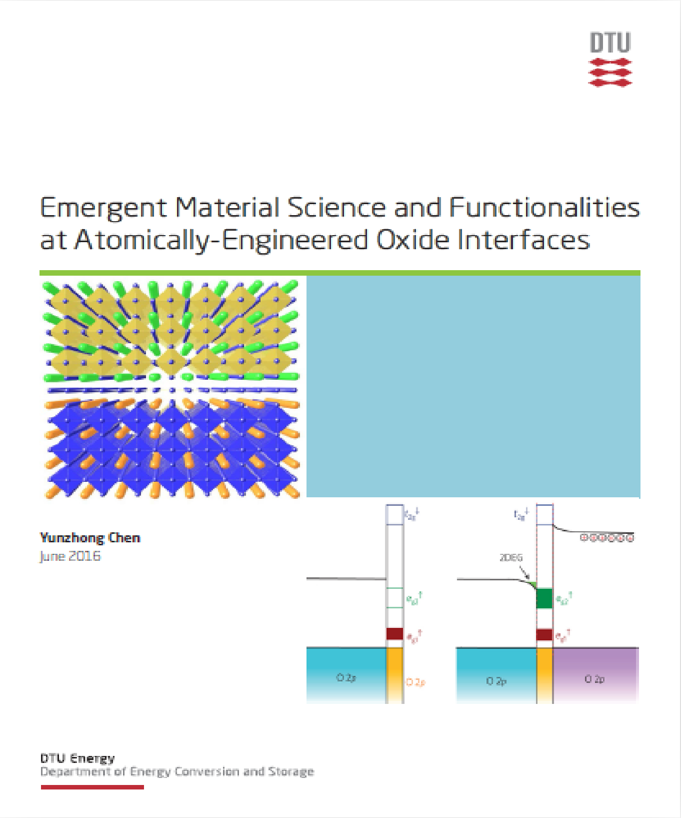
Smarter…

Beyond CMOS : Emergent Research Device Materials

Marked in 2007 edition of The International Technology Roadmap for Semiconductors



2015



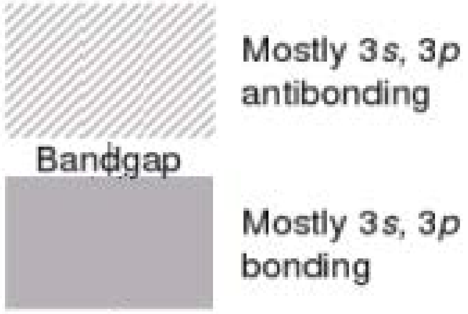
2016

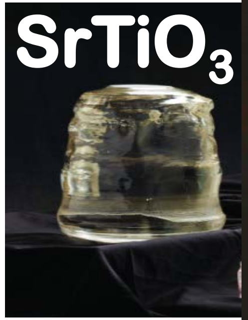
To develop a new generation of devices based on new physical principles ...

1. Oxide Electronics Emerge

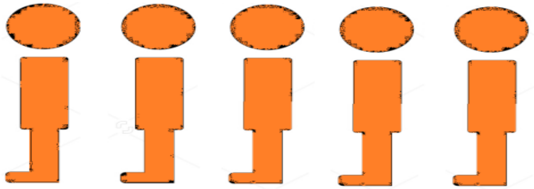
1.1 Why Oxides, compared to Si?

a. Rich Physics due to correlated electrons;





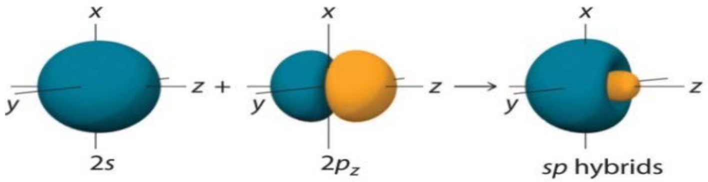
Electrons

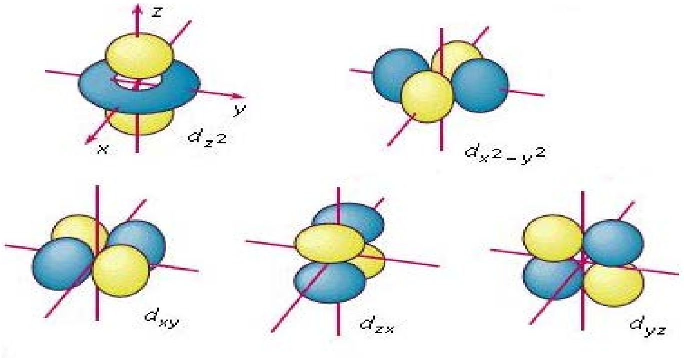


(Free)

(Correlated)

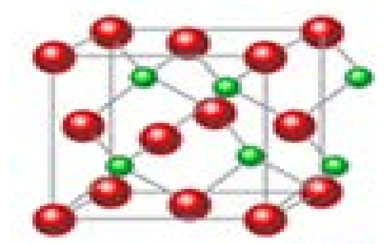
Orbitals



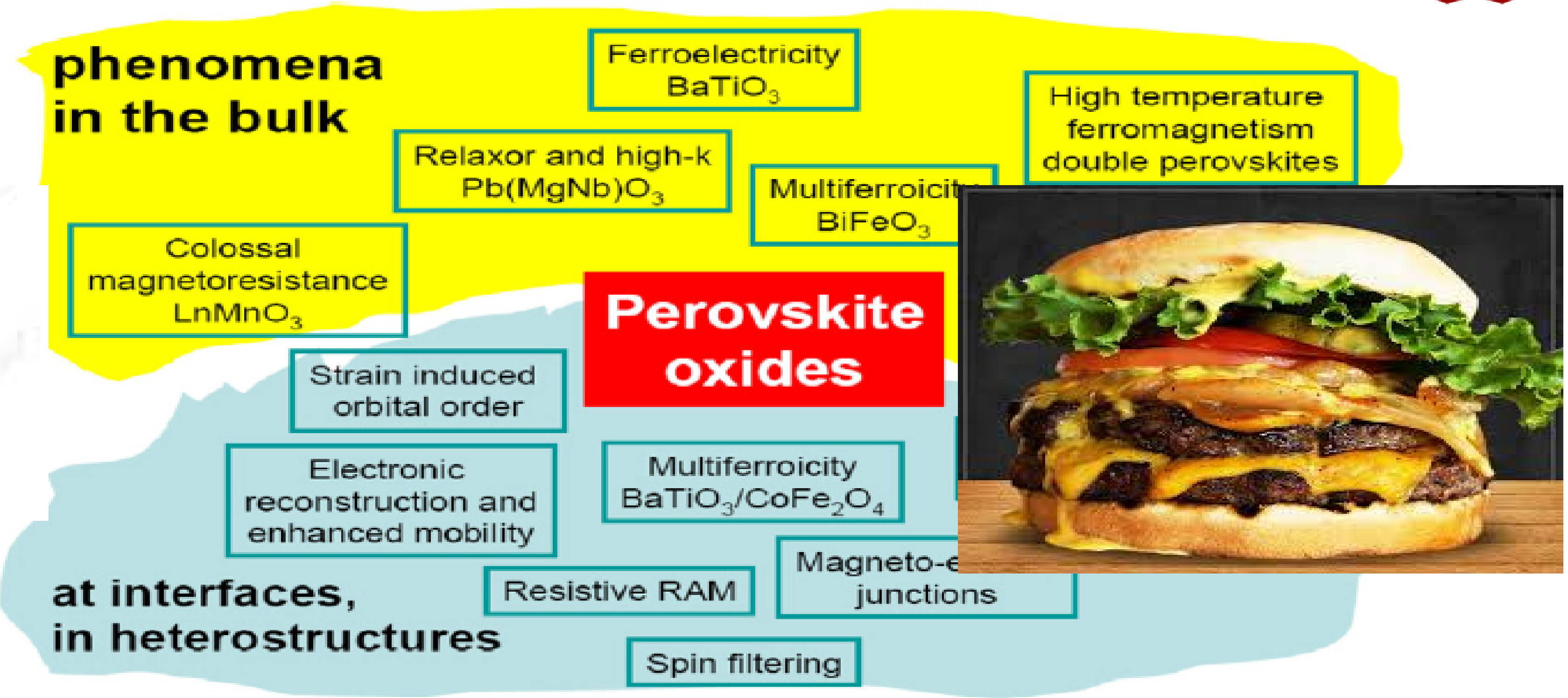


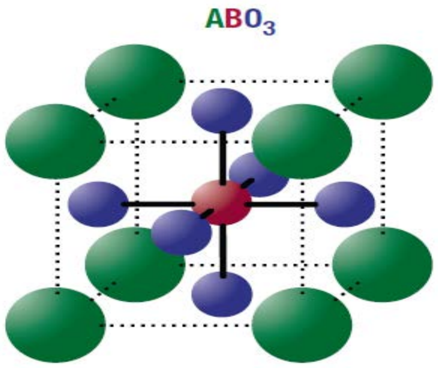
b. Multi-functions in compatible structures;

Silicon/III-V Compounds
(Semiconductor, Insulator)

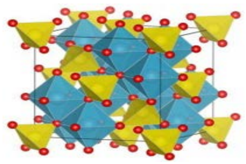


Diamond/zinc-blende

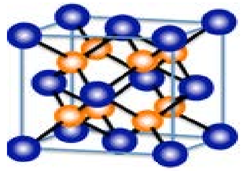




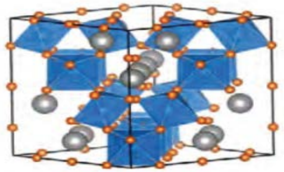
Perovskite



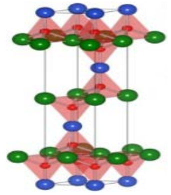
Spinel (AB_2O_4)



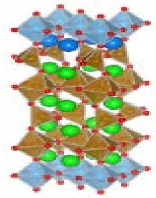
Fluorite (AO_2)



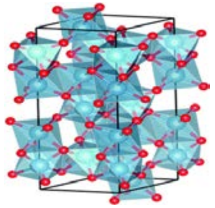
Pyrochlore ($A_2B_2O_7$)



Delafossite (ABO_2)



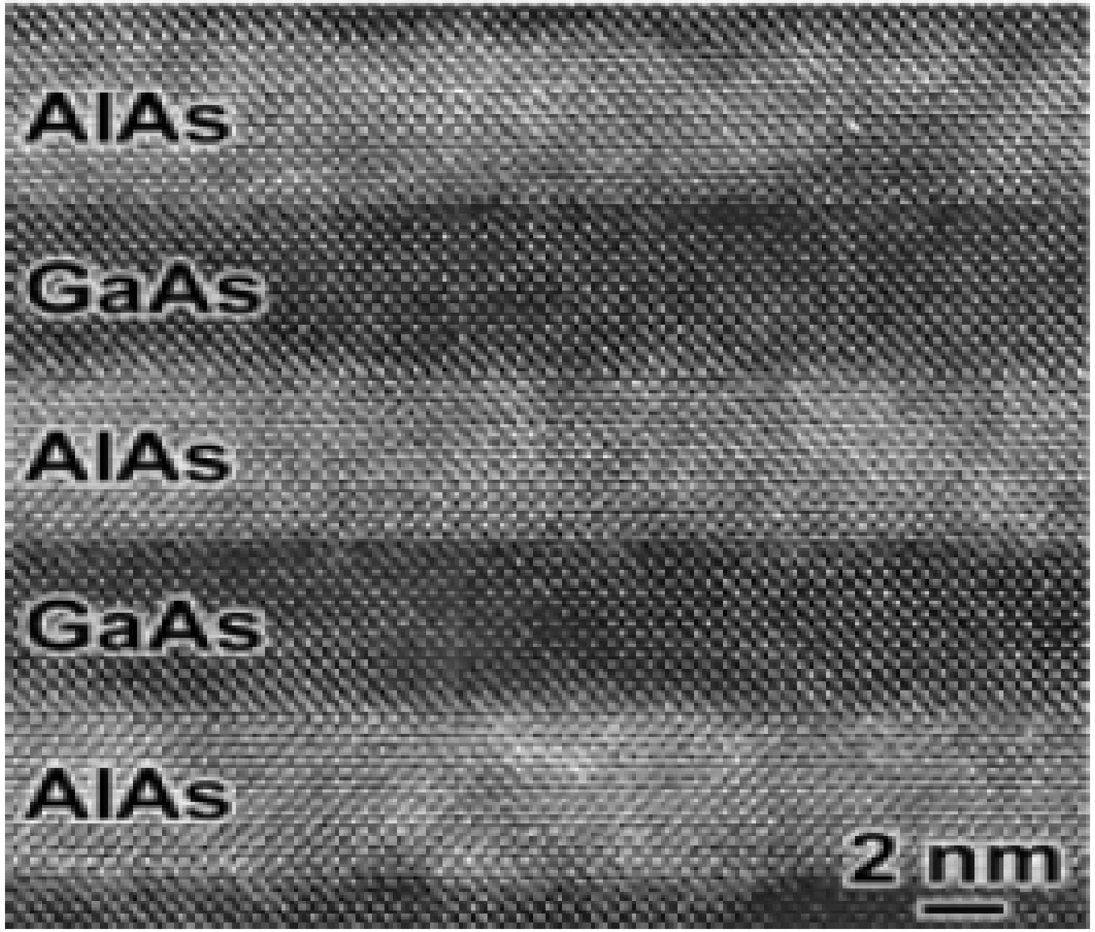
Brownmillerite ($ABO_{2.5}$)

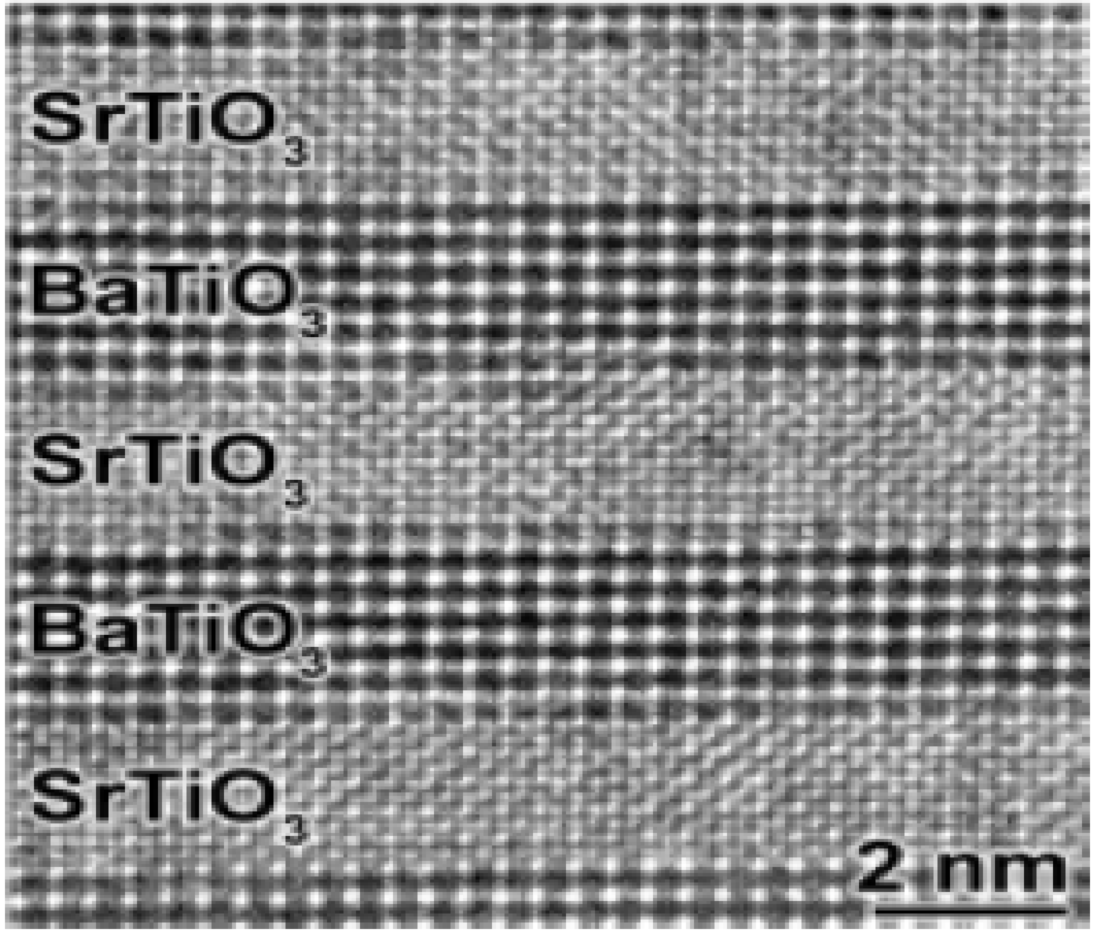


Corundum (A_2O_3)

C. Technology progress in oxide thin film growth

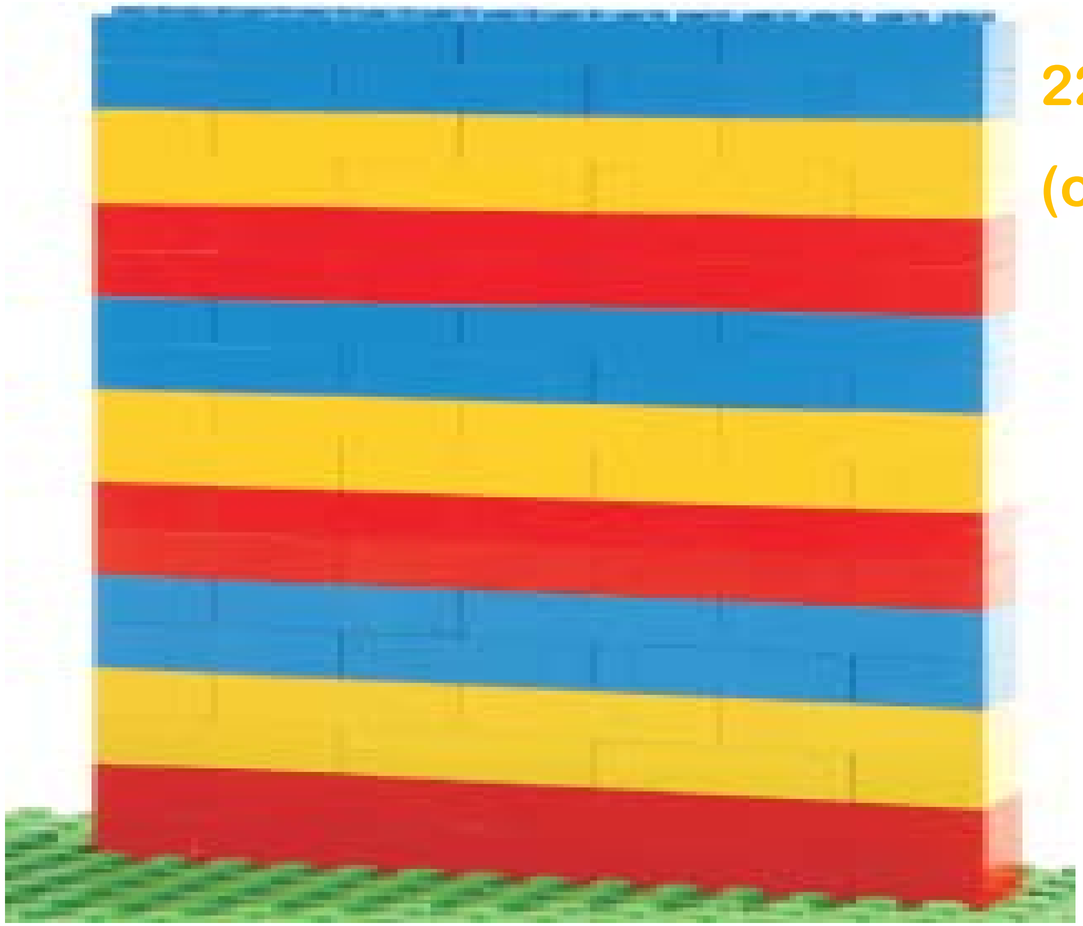
In the past two decades





D. G. Scholm *et al. J. Am. Ceram. Soc.* 91, 24298(2008)

Build up your own superlattice

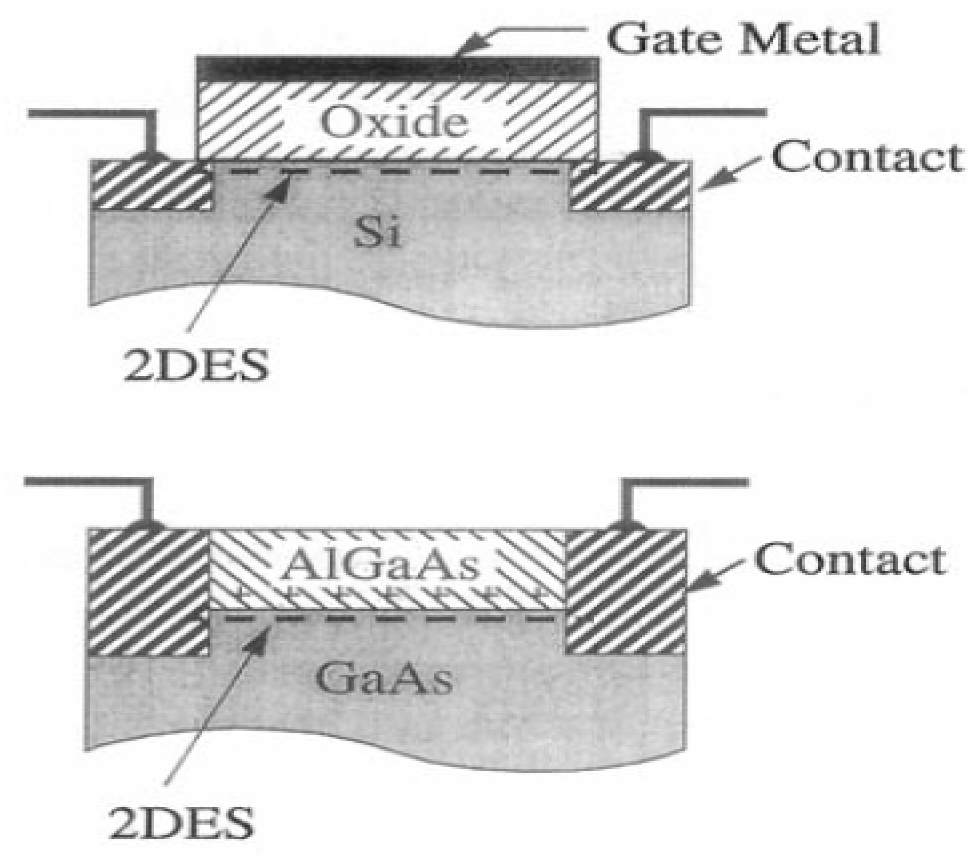


2272 perovskite oxides

(out of 2454 materials with perovskite structure)

Lego version of an oxide superlattice structure

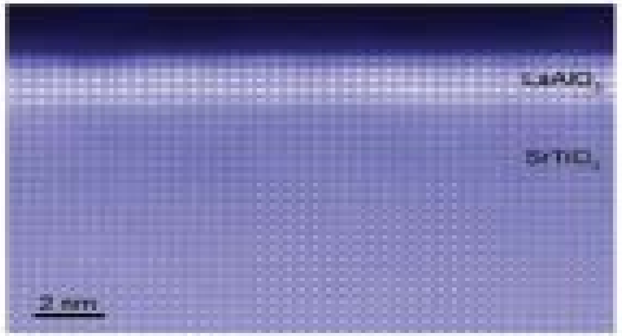
1.2 Conducting Interface is the device

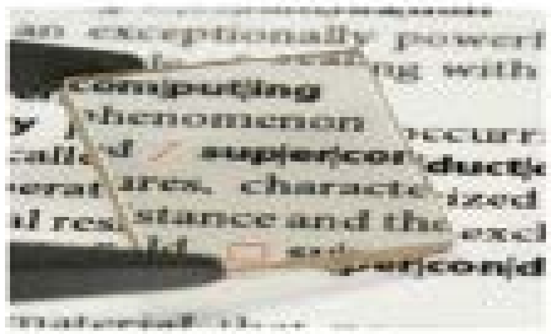


2DEGs in Si-based MOSFET

and GaAs/AlGaAs

A. Ohtomo and H. Y. Hwang, Nature, 427, 423





REVIEW

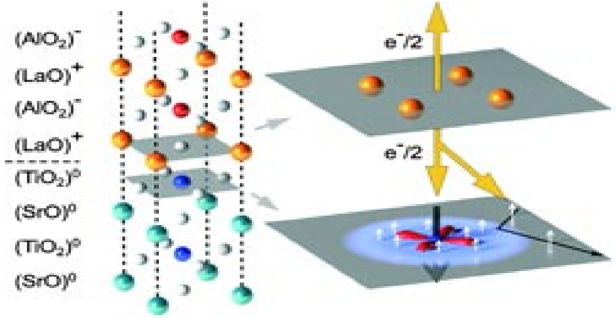
Oxide Interfaces—An Opportunity for Electronics

J. Mannhart[1*] and D. G. Schlom[2*] Science, 327, 1607, 2010

1.3 Oxide Interface remains in its infancy

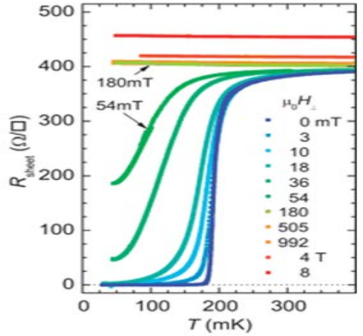
a . Novel physical properties and phenomena

Ferromagnetism, Superconductivity, metal-insulator transitions, large spin-orbital coupling…



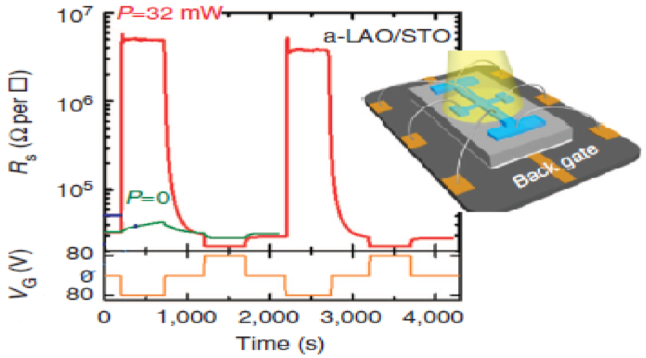
Magnetism

A. Brinkman *et al*, Nature Mater. 2007



Superconductivity

N. Reyren *et al.* Science, 2007

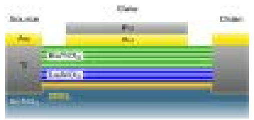


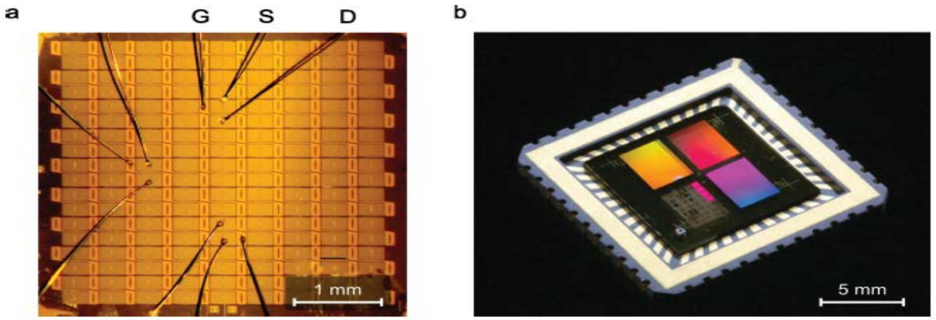
Visible light enhanced field effect

Y. Lei *et al.* Nature Commun, 2014

b. Demonstration of field effect transistors (FET)

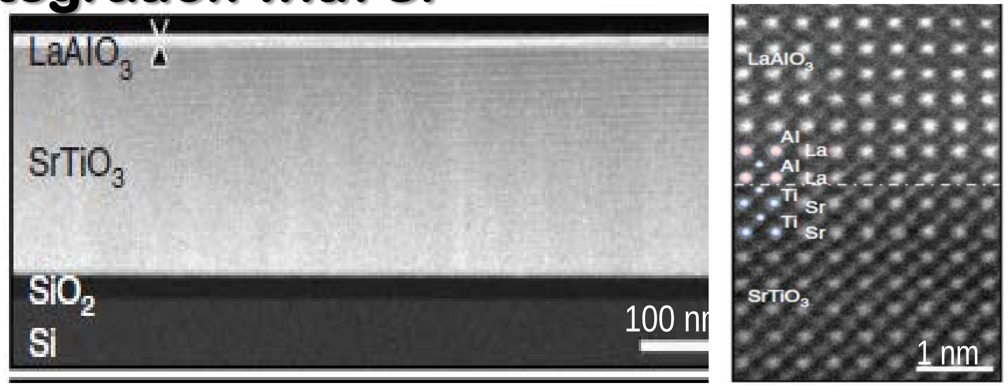
c. Integration with Si





Photograph of an array of LAO/STO FET and a chip carrying 700 000 FETs.

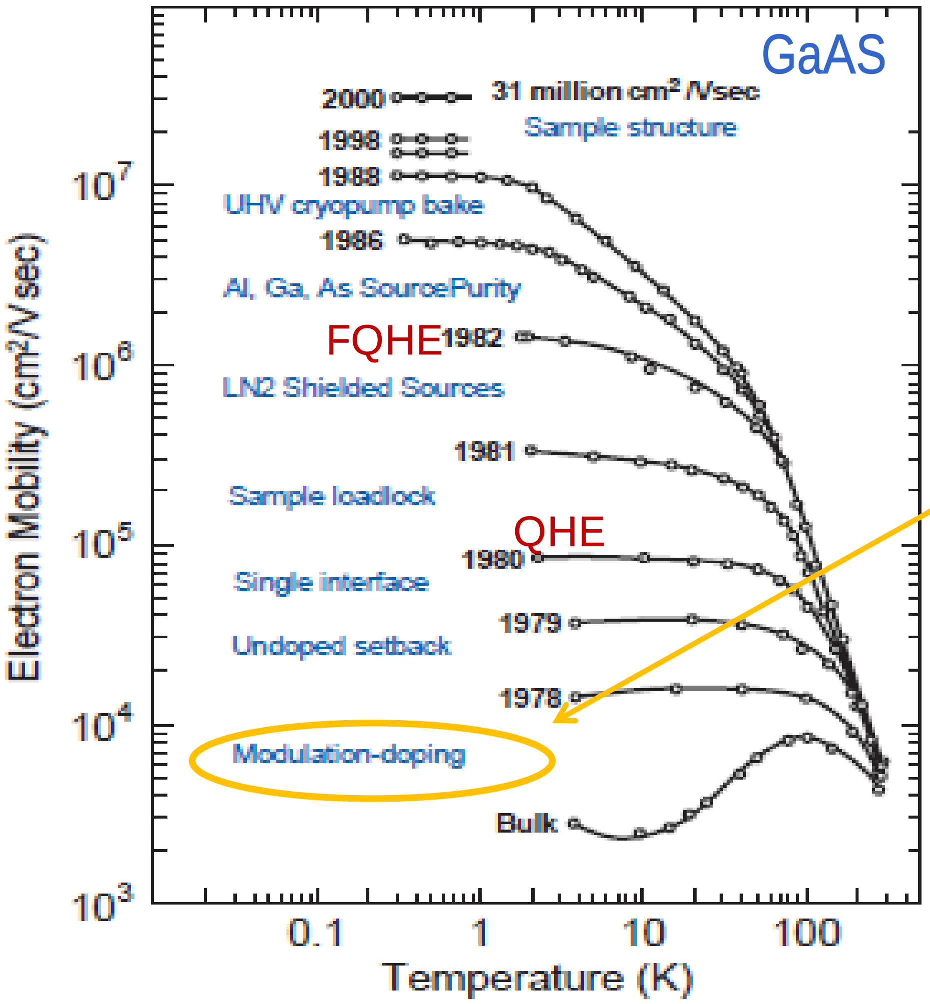
R. Jany *et al. Adv. Mater. Interfaces* 1, 1300031 (2014)



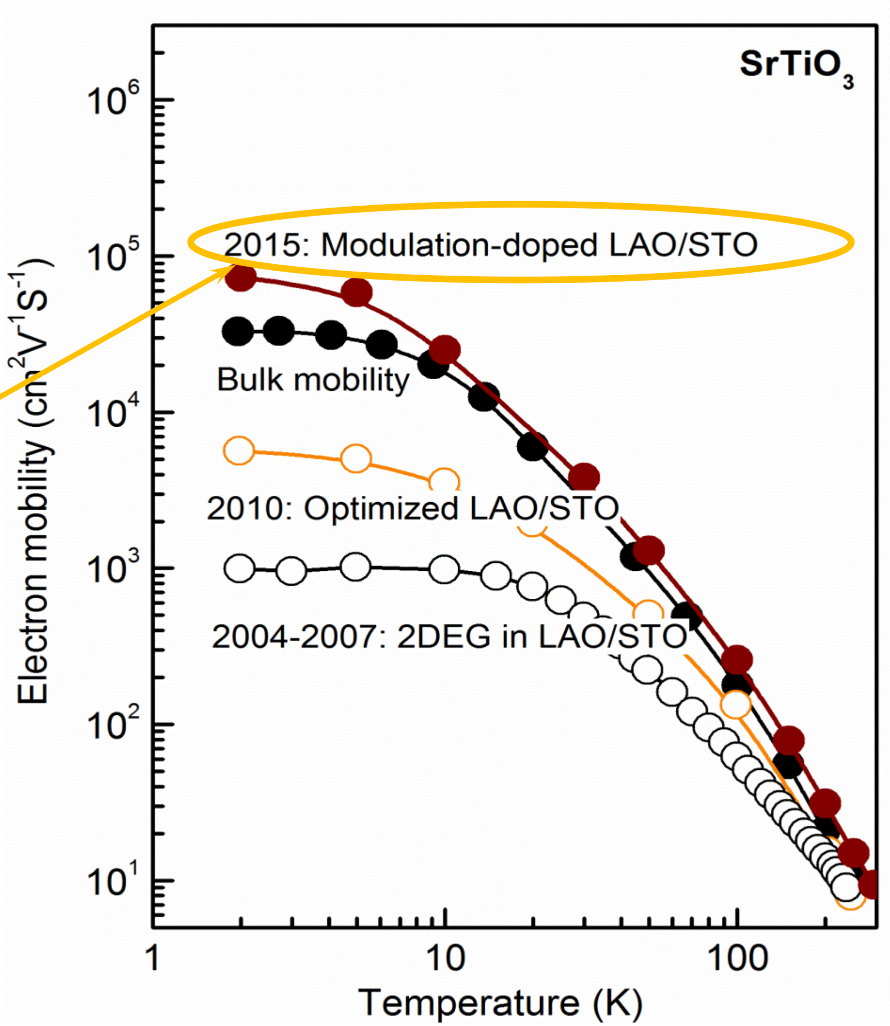
LAO/STO heterointerface on Si.

J.W. Park et al. Nature Commun. 1:94 ,1096 (2010)

One of the key challenges: improveing the cleanness of the interface.



History of improvements in the mobility of 2DEG in GaAs-AlGaAs heterostructure.



Mobility History of 2DEG in LAO/STO heterostructure

1.4 DTU's contributions

Quantum devices at oxide interfaces
(Detection of QHE at complex oxide interface)

Oxide interfaces for Energy
(Oxide interfaces for catalysts)

The realization of modulation-doping at oxide interfaces
(chrage transfer principle)

2DEG at amorphous interface

The first creation of 2DEG at a spinel/perovskite interface with record mobility.

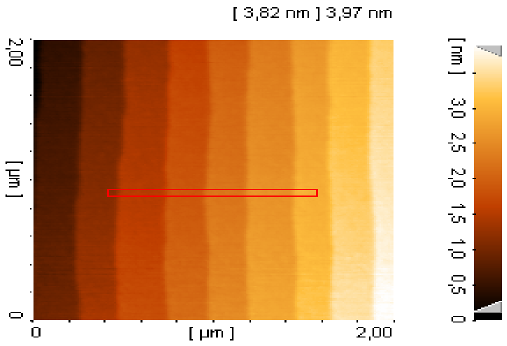
Creating 2DEGs by strain-induced polarization

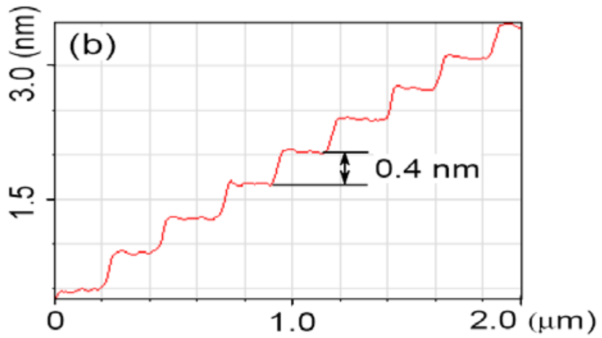
Exploration of new systems and Optimization

The origin of 2DEG at oxide interfaces
(Discovery of a new way to create 2DEGs at oxide interface by redox reaction,)

Experimental
Oxide Thin Film growth with atomical control at DTU Energy

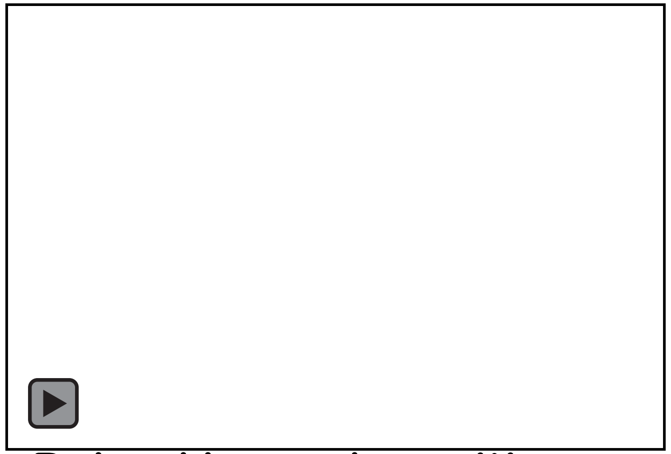
a. Atomically flat substrates



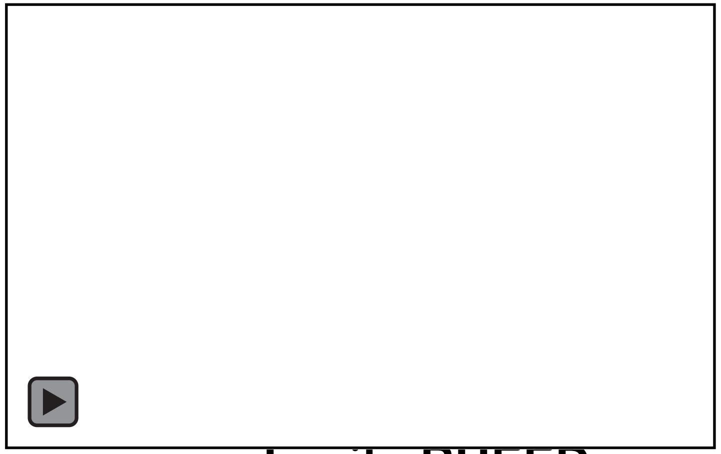


Regular flat terrace surface with terrace height of one unit cell (0.39 nm).

b. Atomically In-situ control during film growth (PLD-RHEED)



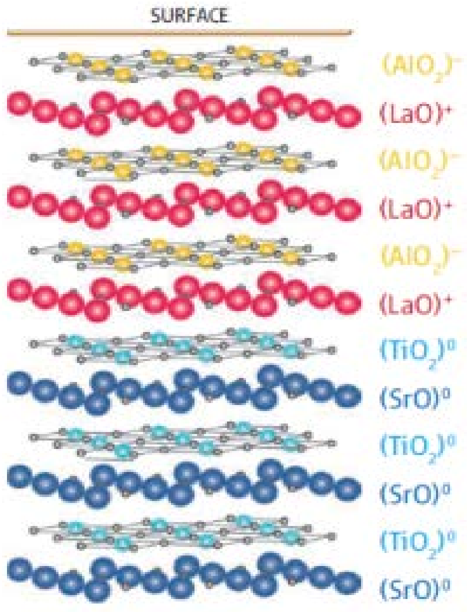
Pulsed laser deposition



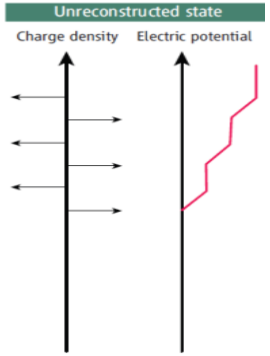
In-situ RHEED

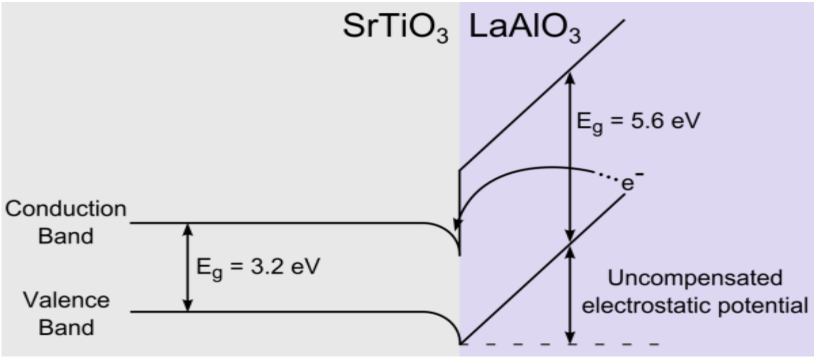
2. Creation of oxide 2DEG by redox reaction

2.1 10-year debates on the origin of 2DEG at LAO/STO interface



Intrinsic doping

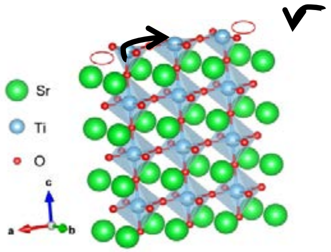


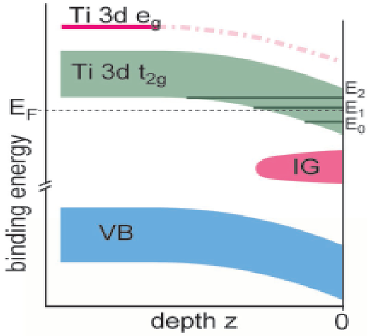


Polarization catastrophe

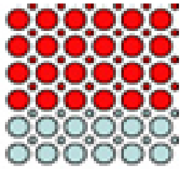
Extrinsic doping

Oxygen Vacancies



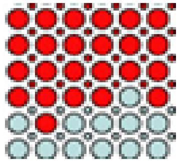


Cation intermixing (Interdiffusion of La into STO)



Sharp interface

vs

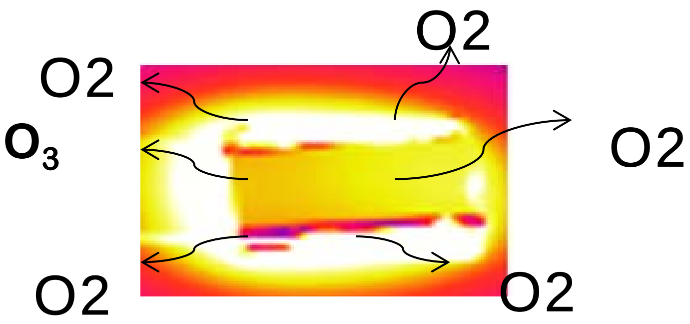


Intermixed interface

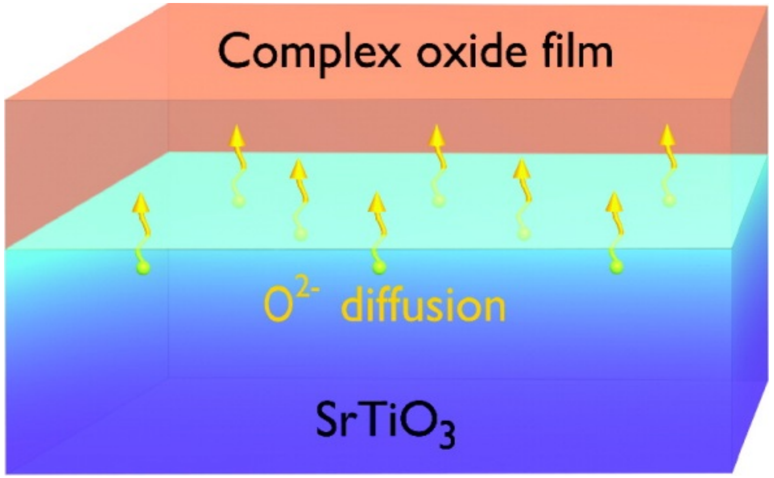
The key is to identify the right origin of the defects.

a. Oxide heterostructures are often grown at high temperatures, where ions exchange introduces the complexity

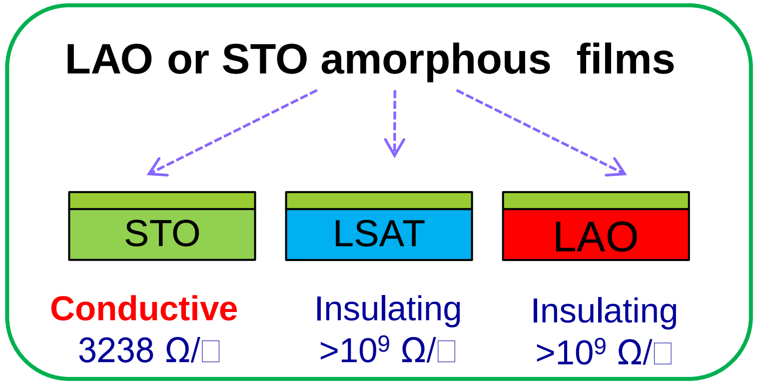
Heated $SrTiO_3$ in vaccum



b. Our finding: Room temperature redox reaction at oxide interfaces

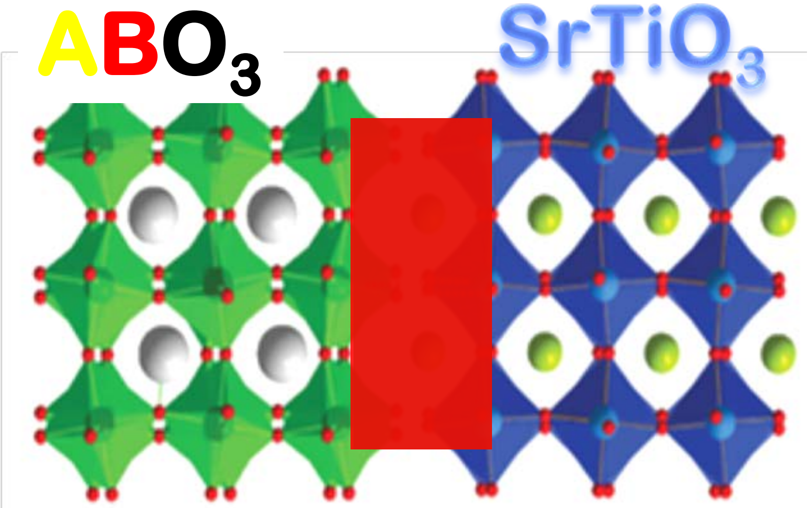


(No polarity, no thermal-induced oxygen conduction, no intermixing)

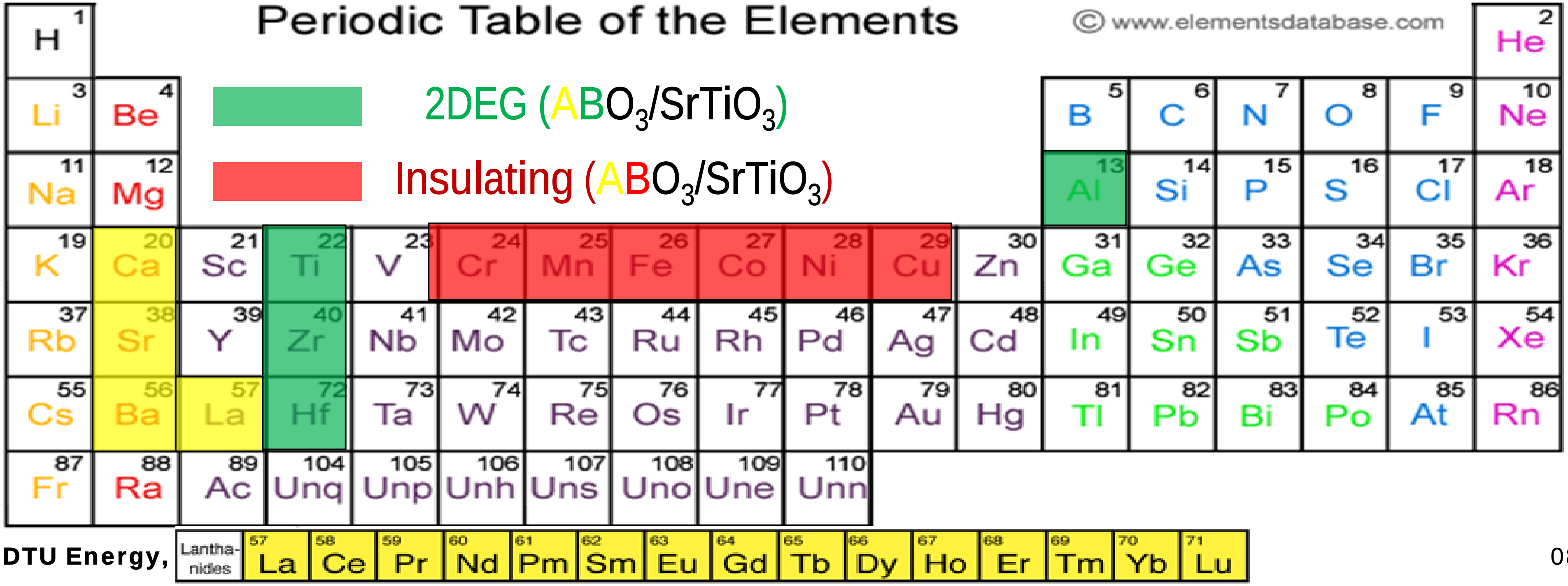


Y. Z. Chen *et al.* *Nano letters* 11, 3774 (2011)

All perovskite $ABO_3/SrTiO_3$ interfaces fit in Redox reactions regime

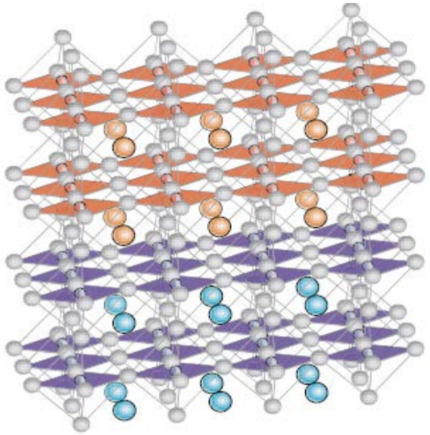


A powerful tool to design oxide 2DEG.



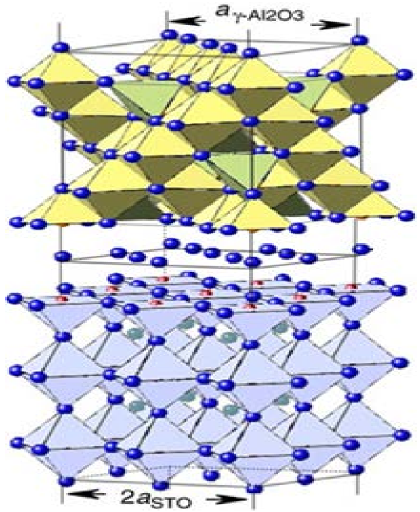
2. Materials of oxide 2DEGs

1. Polar oxide interfaces;



Ohtomo & Hwang
*Nature, **427**,* 423 (2004)

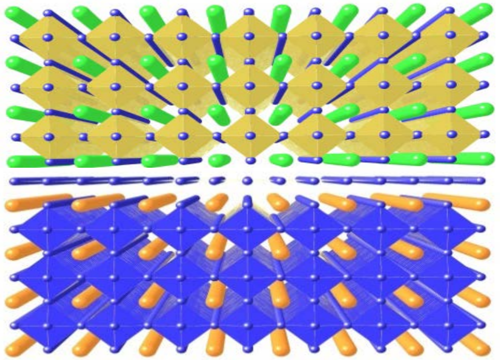
LaAlO3/SrTiO3



Chen *et al. Nature Commun.*
4, 1371 (2013)

Gamma-Al2O3/SrTiO3

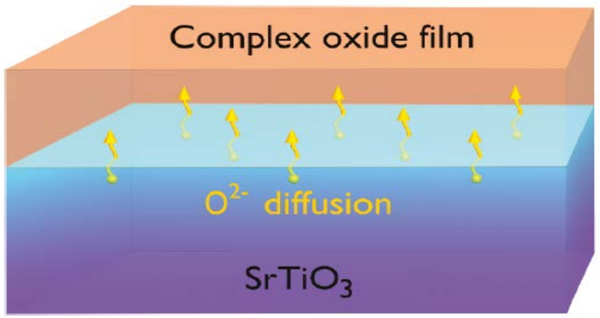
2. Nonpolar interfaces;



Chen *et al. Nano letters*
11, 3774 (2015)

CaZrO3/SrTiO3

3. Disordered structure



Chen *et al. Nano letters*
11, 3774 (2011)

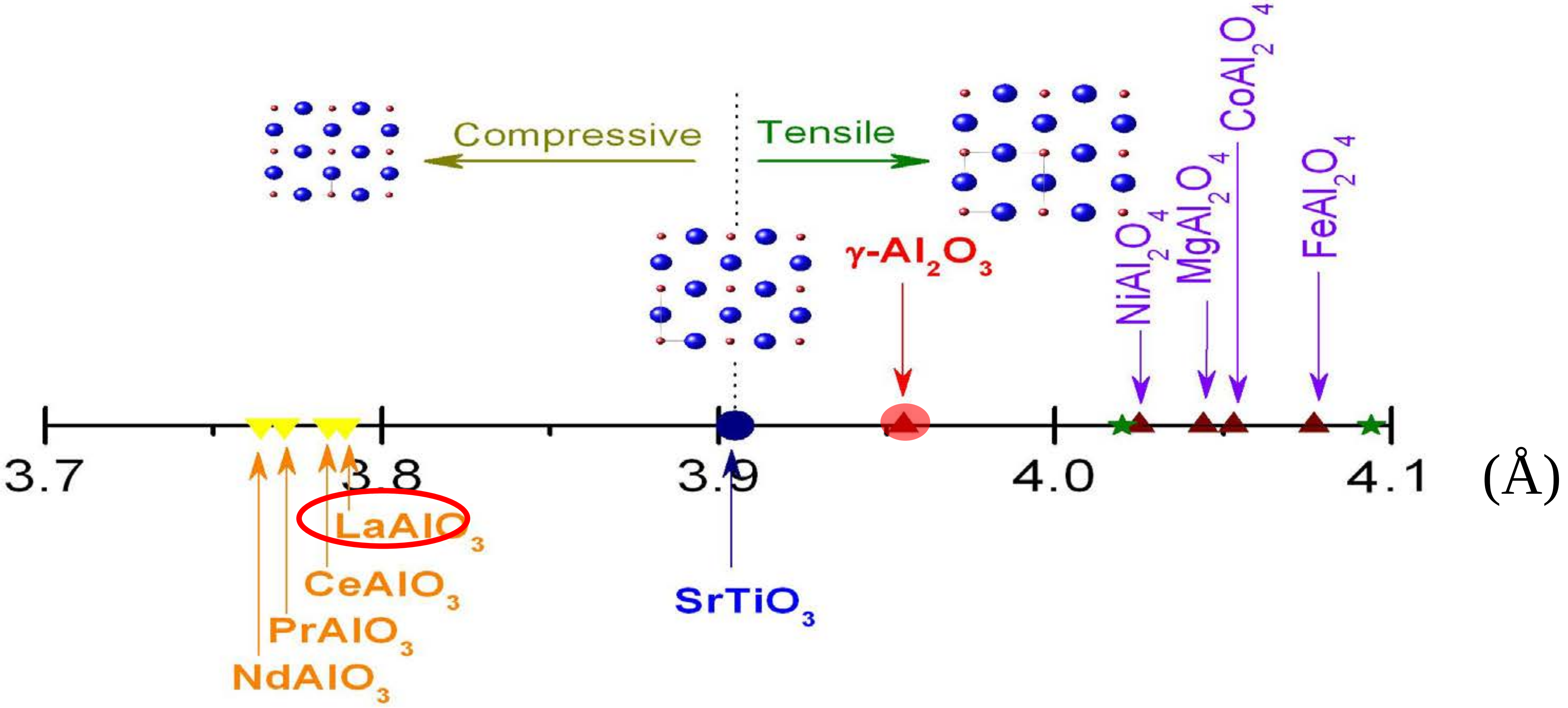
Amorphous-LaAlO3/SrTiO3

2DEG at GAO/STO interfaces (a system outperform any others)

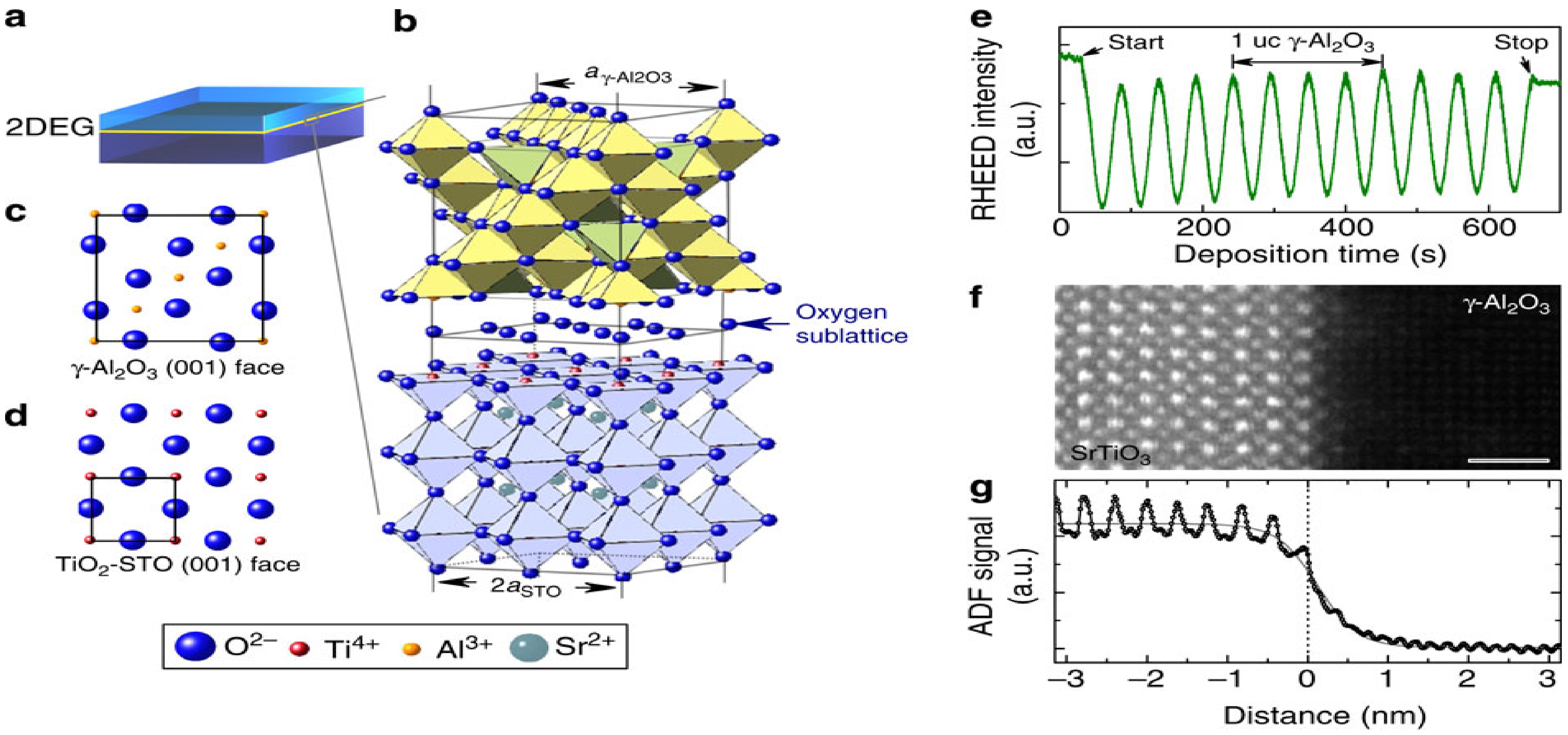
2DEG at GAO/STO interfaces (a system outperform any others)

2.1 Why Alumina (Al_2O_3)?

- Al-based oxides satisfy the criteria for interface redox reaction
- For Al-based oxides, gamma-Al_2O_3 matchs perfectly with STO.



A heretofore unexplored heterointerface between two oxide insulators of **Spinel γ-Al_2O_3** and **Perovskite $SrTiO_3$**



Y. Z. Chen *et al. Nature Communications,* 4:1371, 2394 (2013)

A short note:

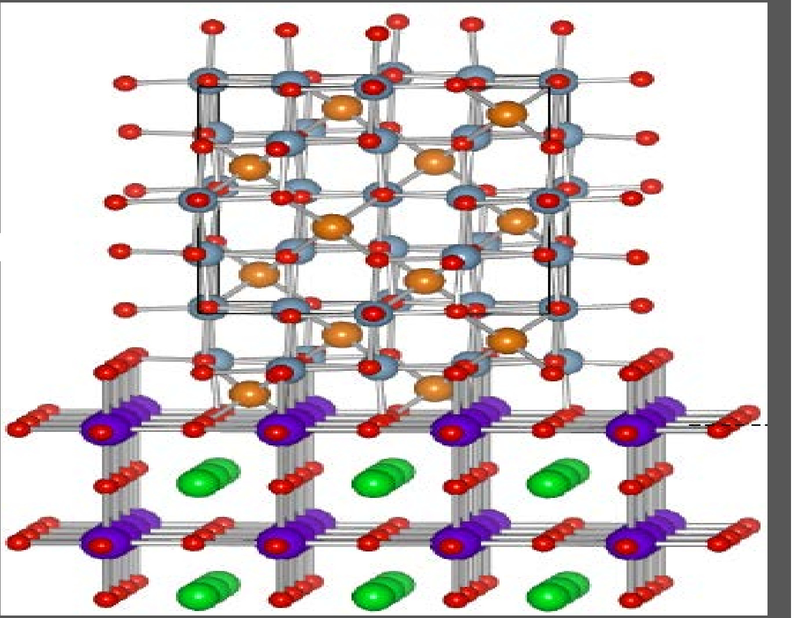
Our γ-Al_2O_3/$SrTiO_3$

1. **New system with perfect lattice match;**
   Perovskite/spinel rather than perovskite-type in

2. **Clear 2D character;**
   not quasi-2DEG any more.

3. **Highest mobilities;**

4. **Common and cheap materials (without La)**

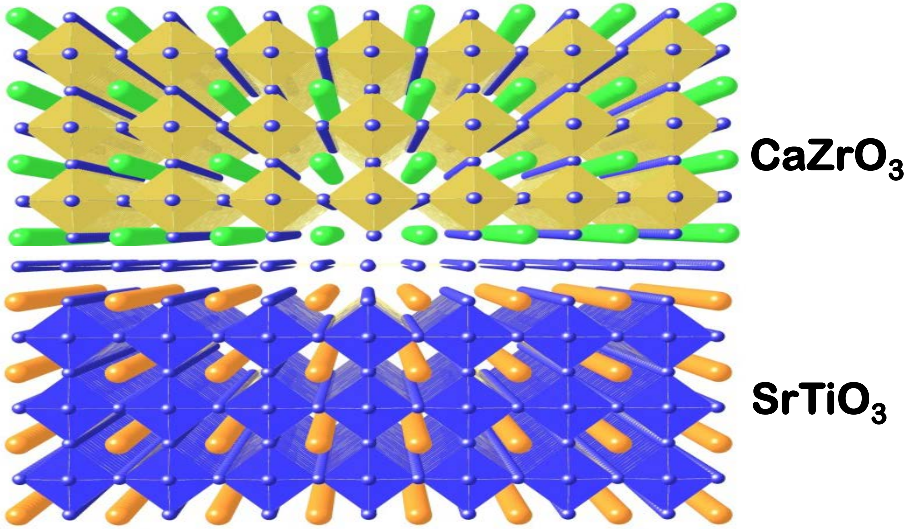


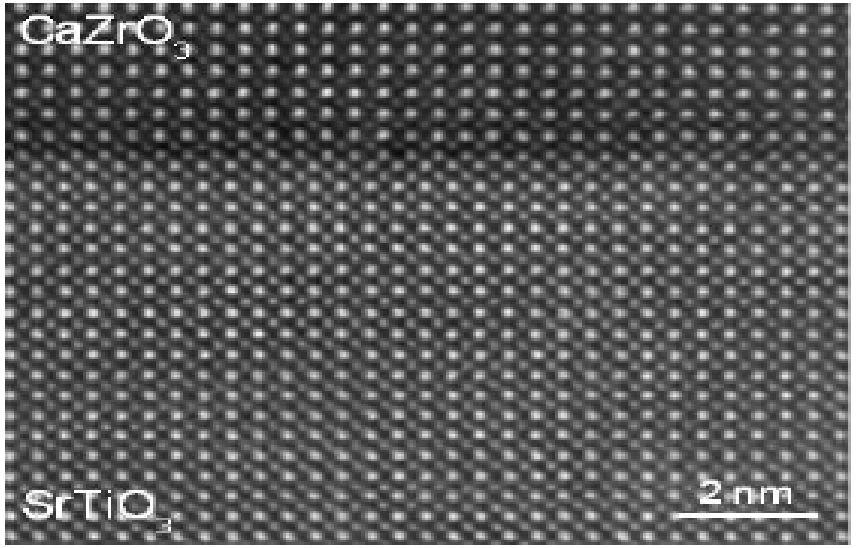
OXIDE INTERFACES

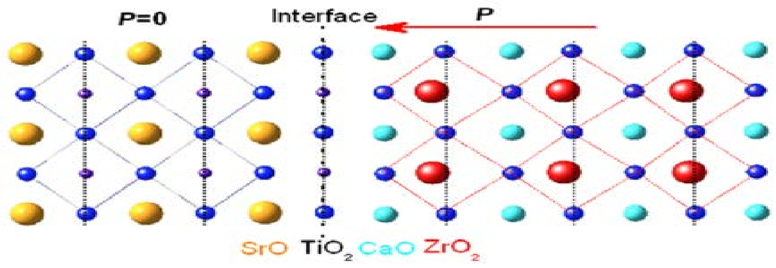
Mismatched lattices patched up

NATURE CHEMISTRY | VOL 8 | APRIL 2016 | www.nature.com/naturechemistry

Use proven principle to create 2DEGs at oxide interfaces.





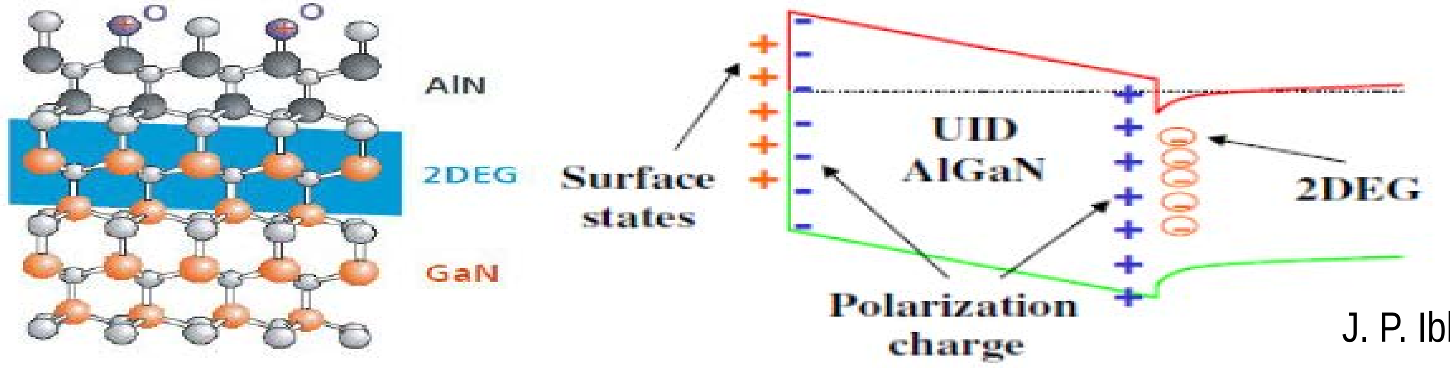


Y. Z. Chen *et al. Nano Lett.* **15**, 1849 (2015)

Polarization near the interface.

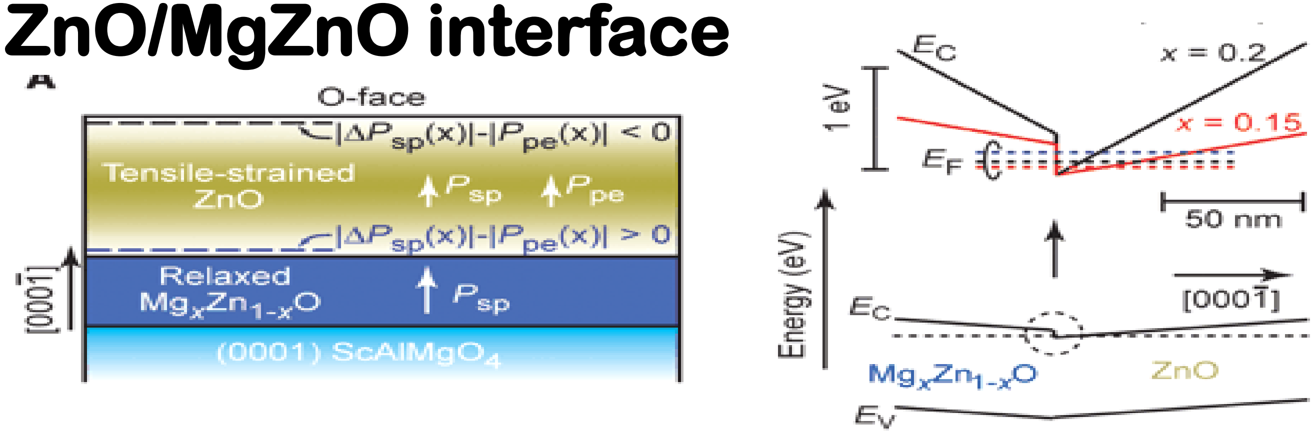
Proven principle to create 2DEGs at semiconductor interfaces:
Such as the piezoelectric polarization effect

a. Semiconductor interface (AlGaN/GaN)



J. P. Ibbetson *et al.* APL 77, 250 (2000).

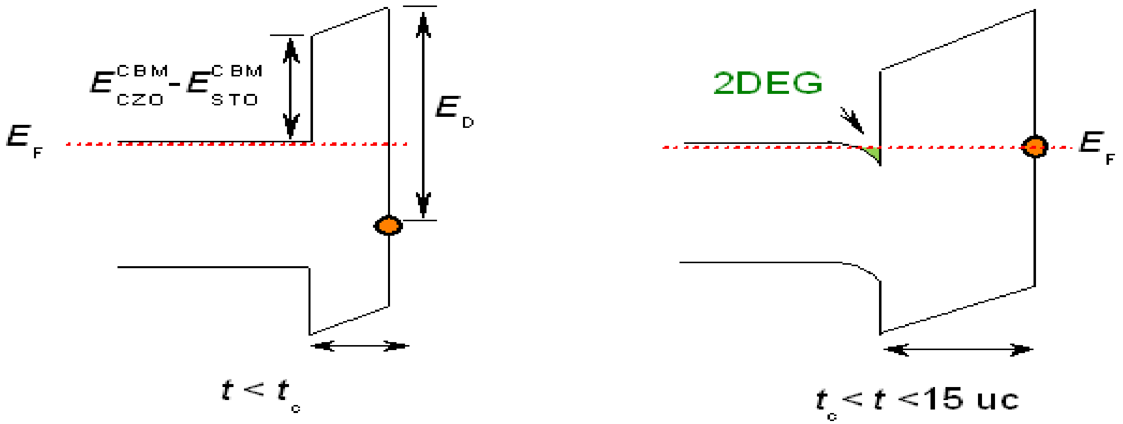
b. ZnO/MgZnO interface

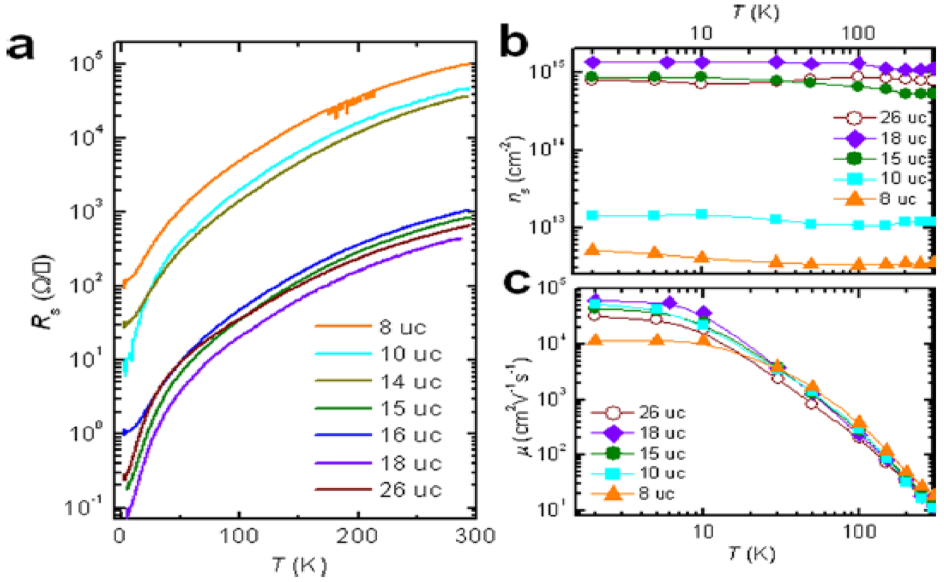


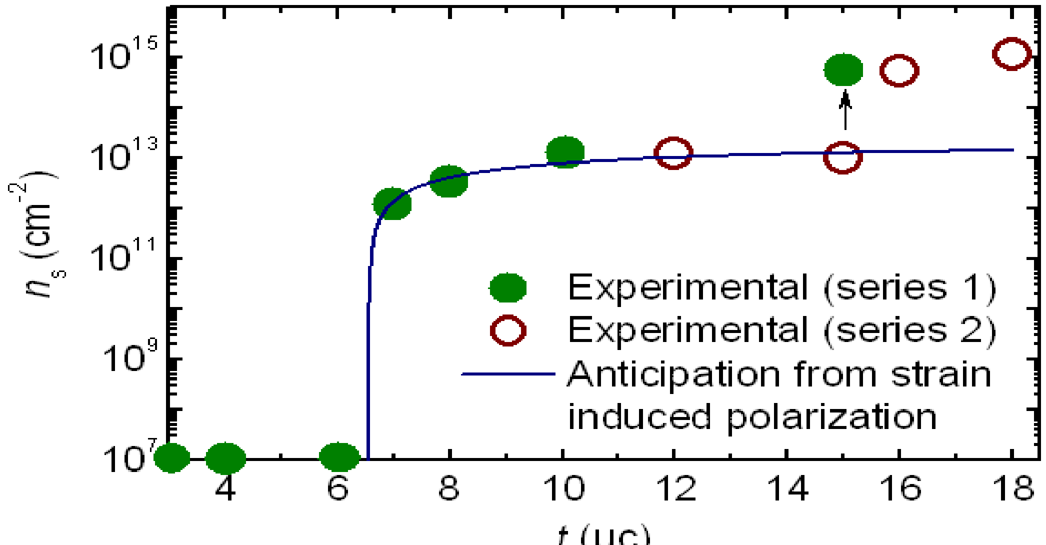
A. Tsukazaki ***et al. Science*** **315, 1388 (2007)**

c. Complex oxide interface: CZO/STO

Polarization effect dominates the interface conduction of $CaZrO_3$/STO







$$t_c = \left[E_D - \left(E_{CBM}^{CZO} - E_{CBM}^{STO}\right)\right]\varepsilon_0\varepsilon_{CZO} \Big/ eP_{CZO}$$

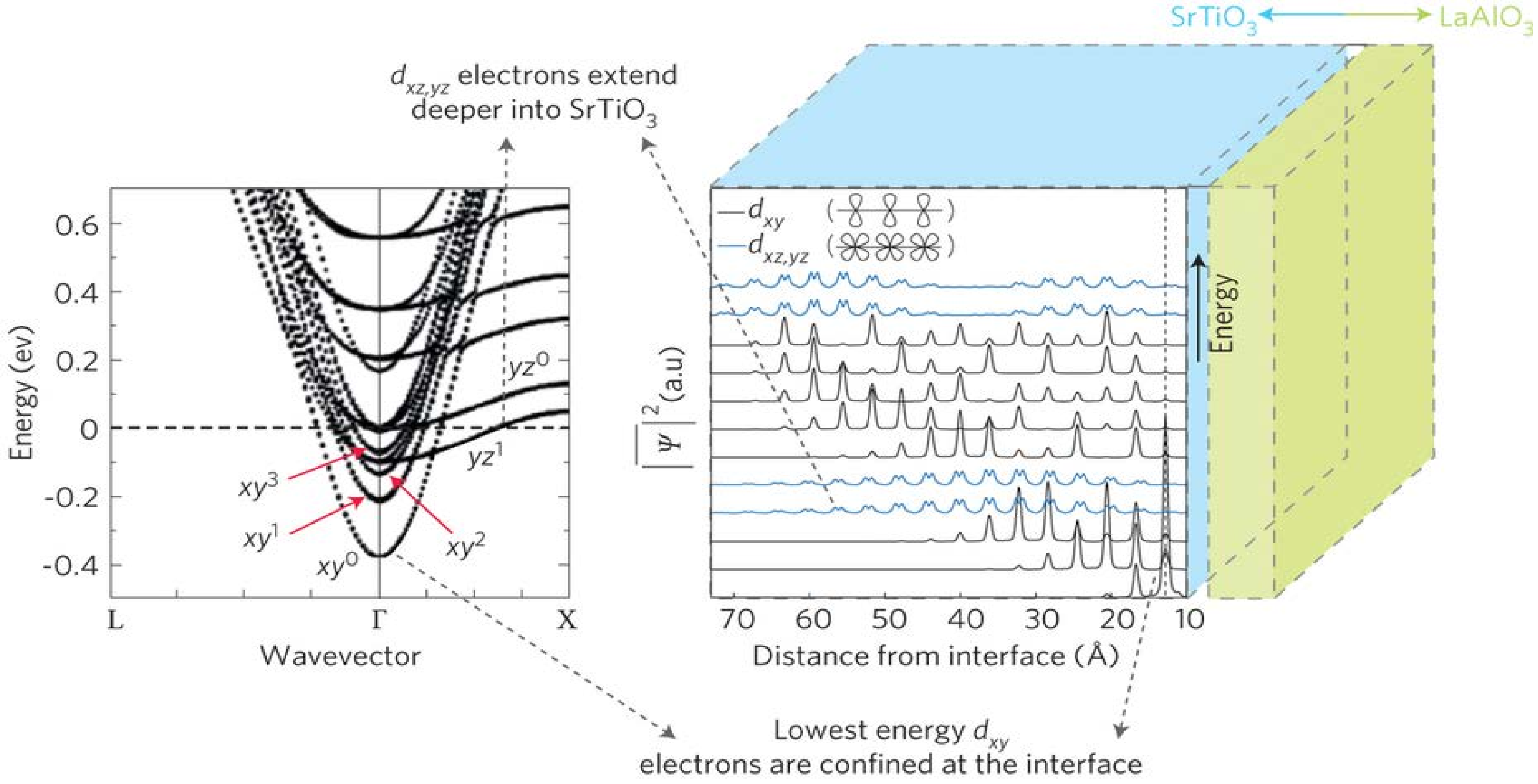
$$en_s = P_{CZO}/(1 - t_c/t)$$

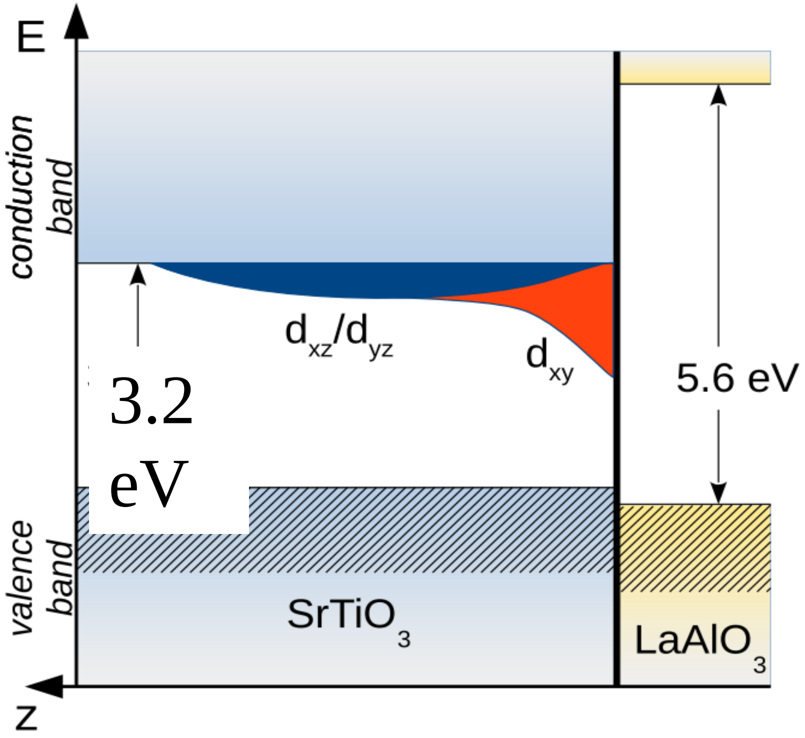
P_{CZO}=2.3 × 10^{13} e/cm^2=3.5 μCcm^{-2},

t_c=6.5 uc

Y. Z. Chen *et al. Nano Lett.* **15**, 1849 (2015)

A common problem for STO 2DEL

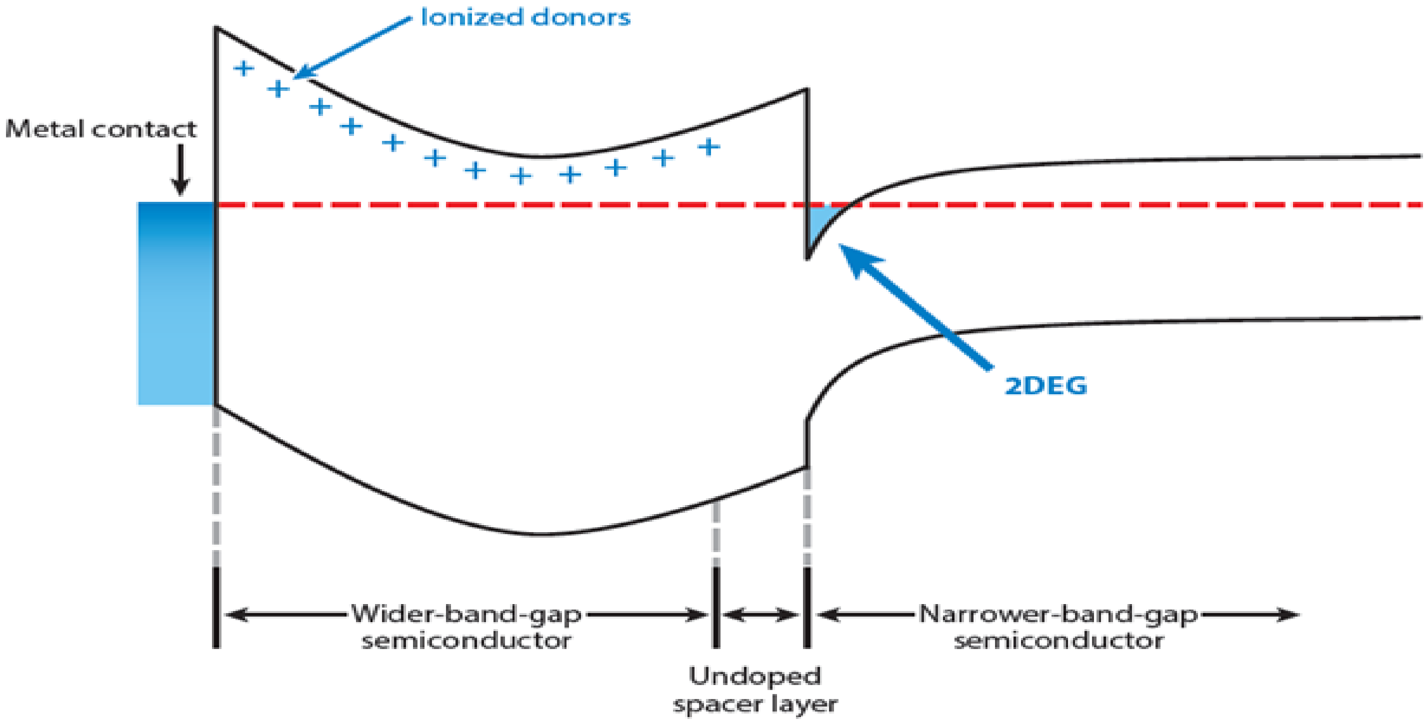




M. Gabay & J-M Triscone. ***Nature Phys.*** 9, 610 (2013).

How to further increase the electron mobility of complex oxide interface?

Modulation doping in semiconductors



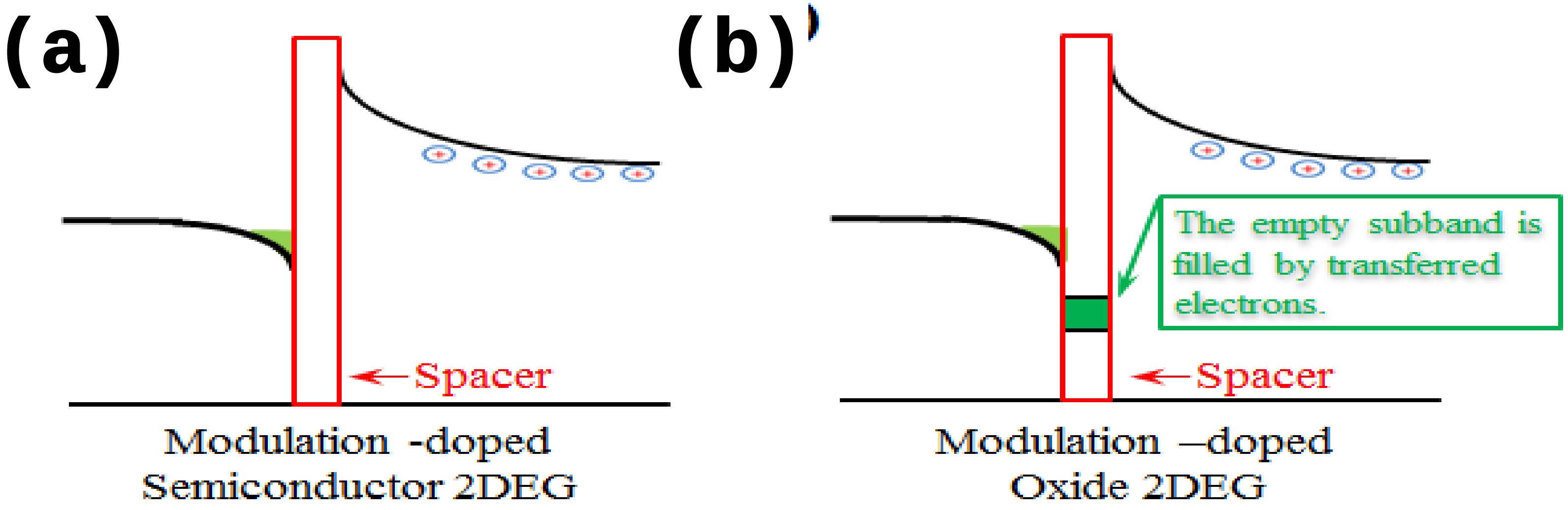
Semiconductor Interfaces

Complex Oxide Interfaces

No mobility gains at oxide interfaces!

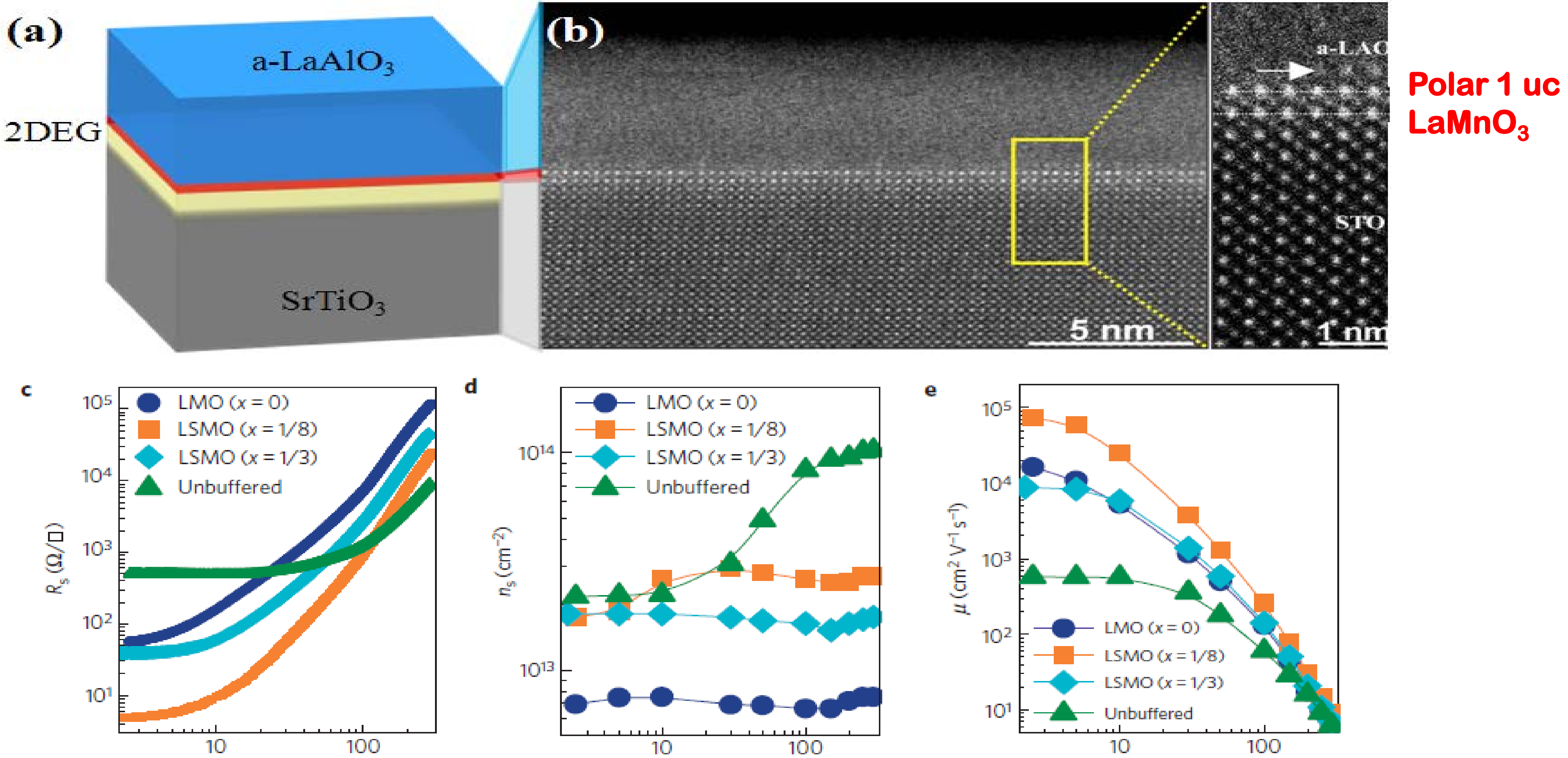
S. Stemmer, S. J. Allen, Ann. Rev. Mater. Res. **44**, 151 (2014)

Strategy: Use an electron sink to trap the heavy/slow electrons.



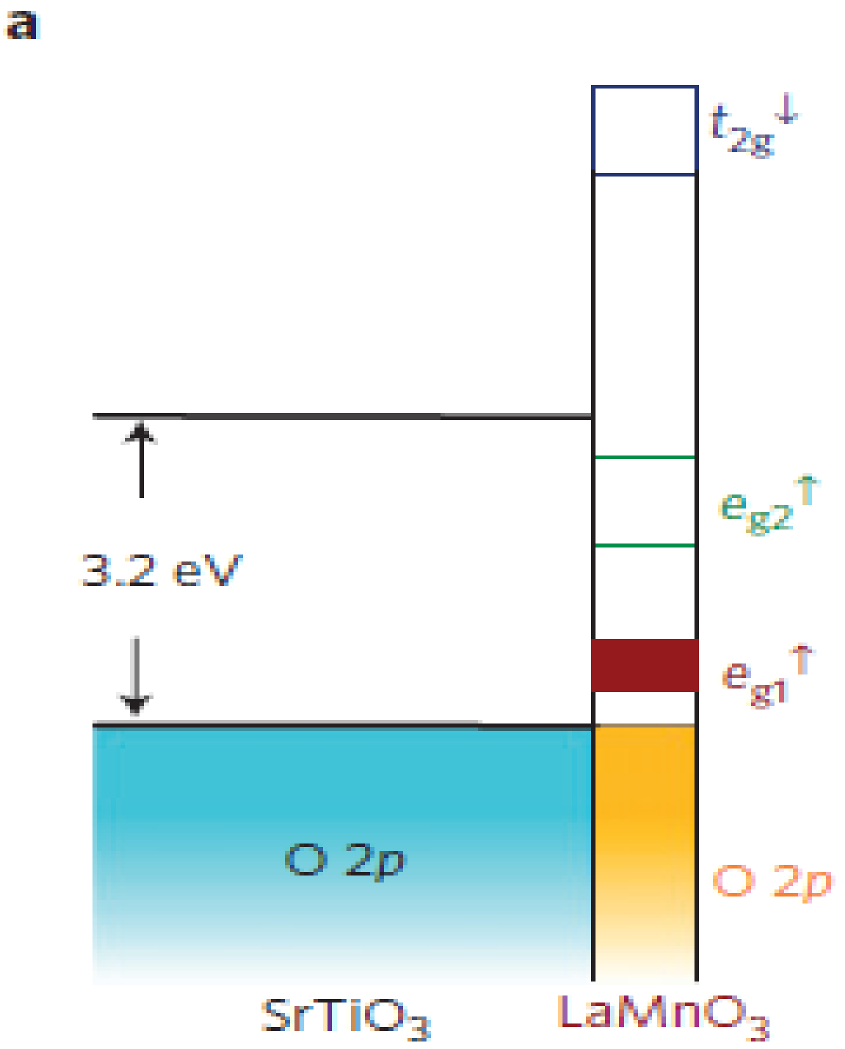
A single unit cell buffered oxide interface:

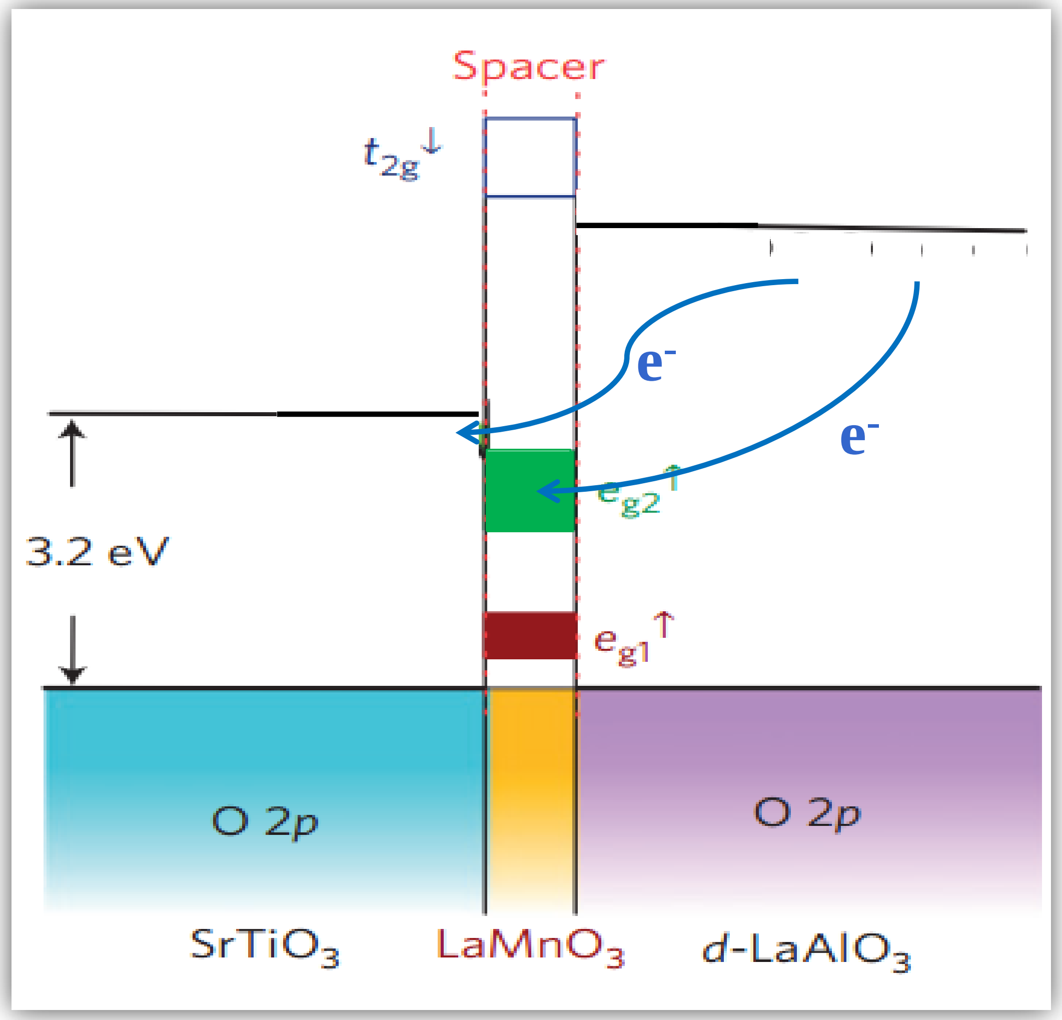
The first effective modulationg doping at complex oxide interfaces.



Engineered *d*-LAO/STO samples exhibit a strongly suppressed n_s and Mobility typically is higher than 10 000 $cm^2V^{-1}s^{-1}$ at 2 K (current record, μ=73000 $cm^2V^{-1}s^{-1}$).

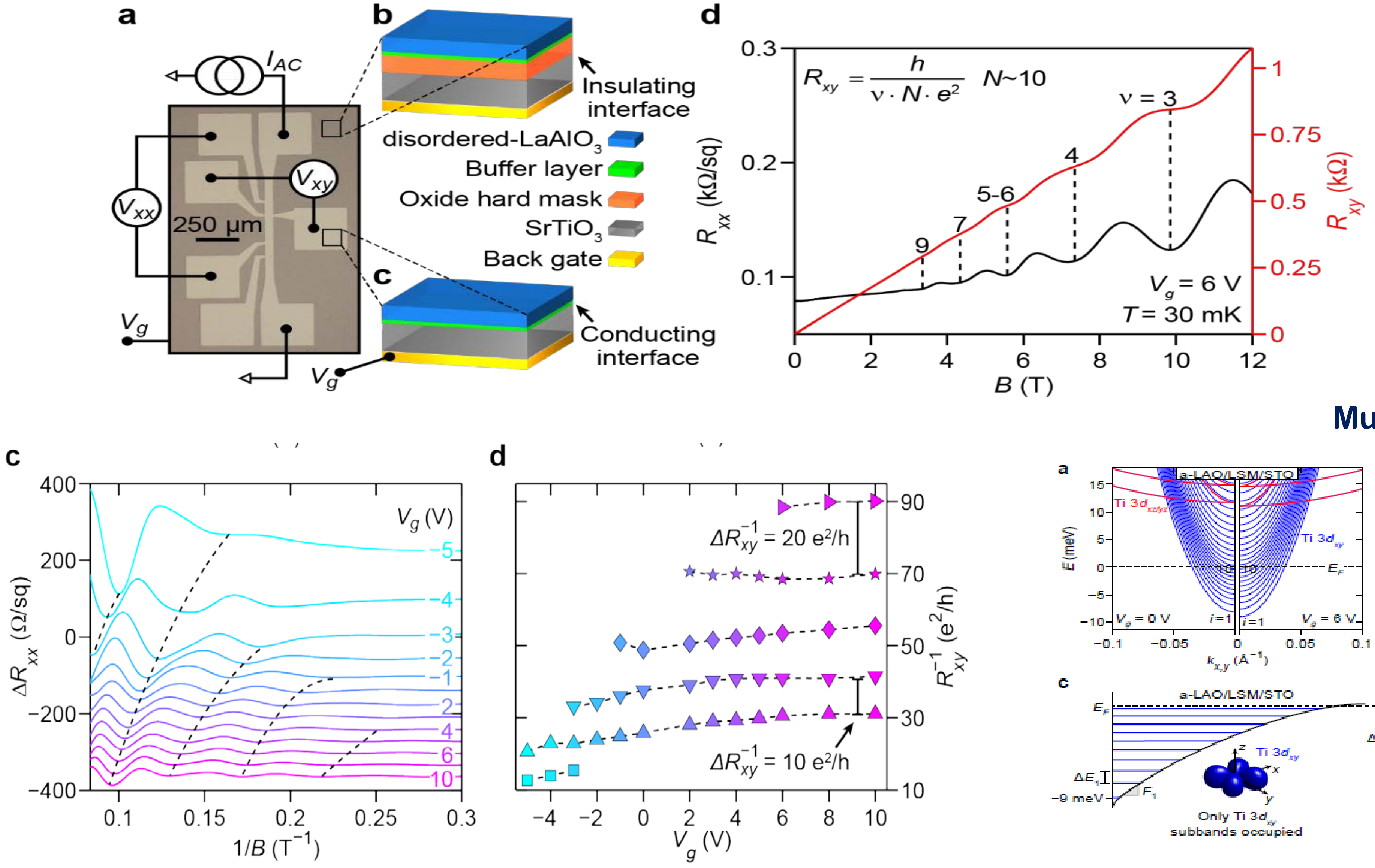
Charge transfer induced modulation doping.



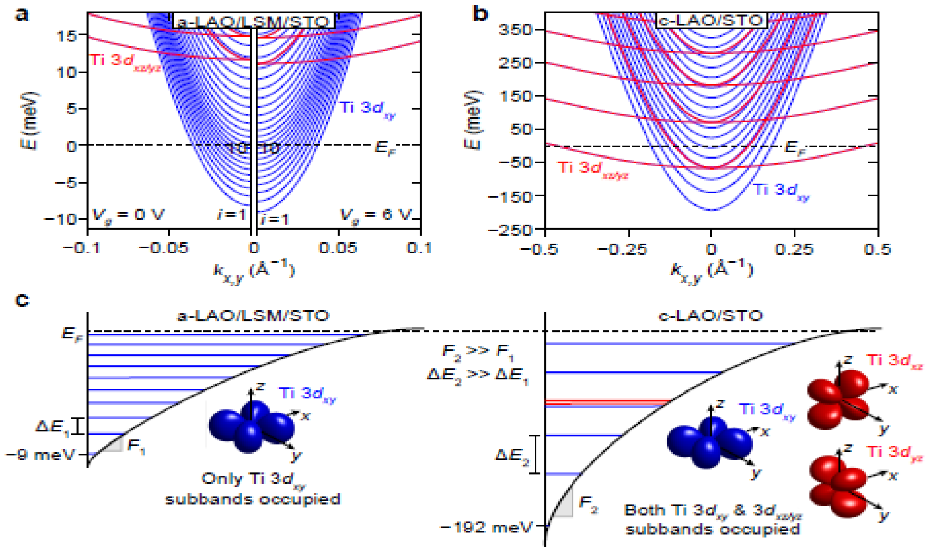


Y. Z. Chen et al. ***Nature Mater.*** 14(8), 801-806 (2015).

Impact: The observation of Quantum Hall effect at complex oxide interfaces



Multiple quantum wells nature

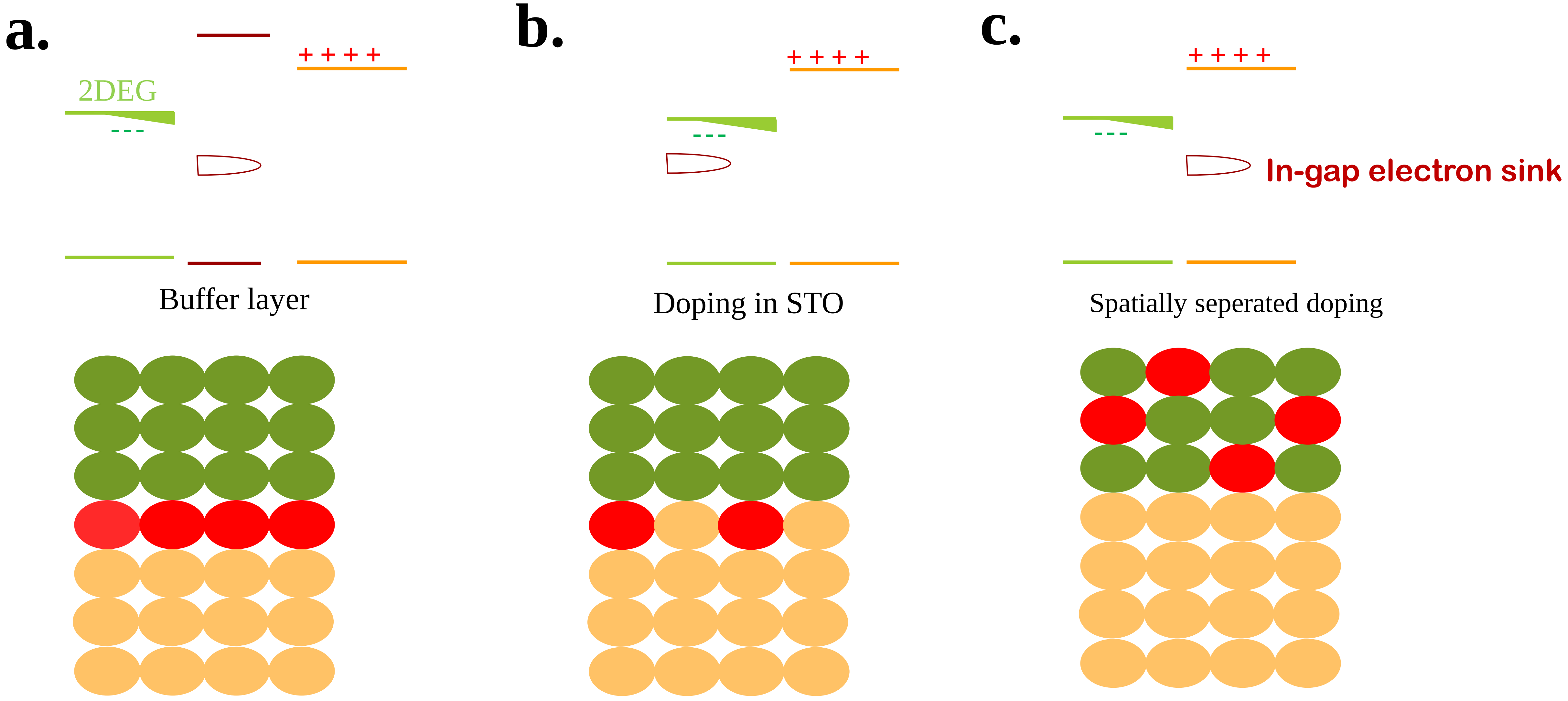


DTU Energy, Technical University of Denmark

F. Trier, Y. Z. Chen et al. Phys. Rev. Lett. (2016)

4. Other research:

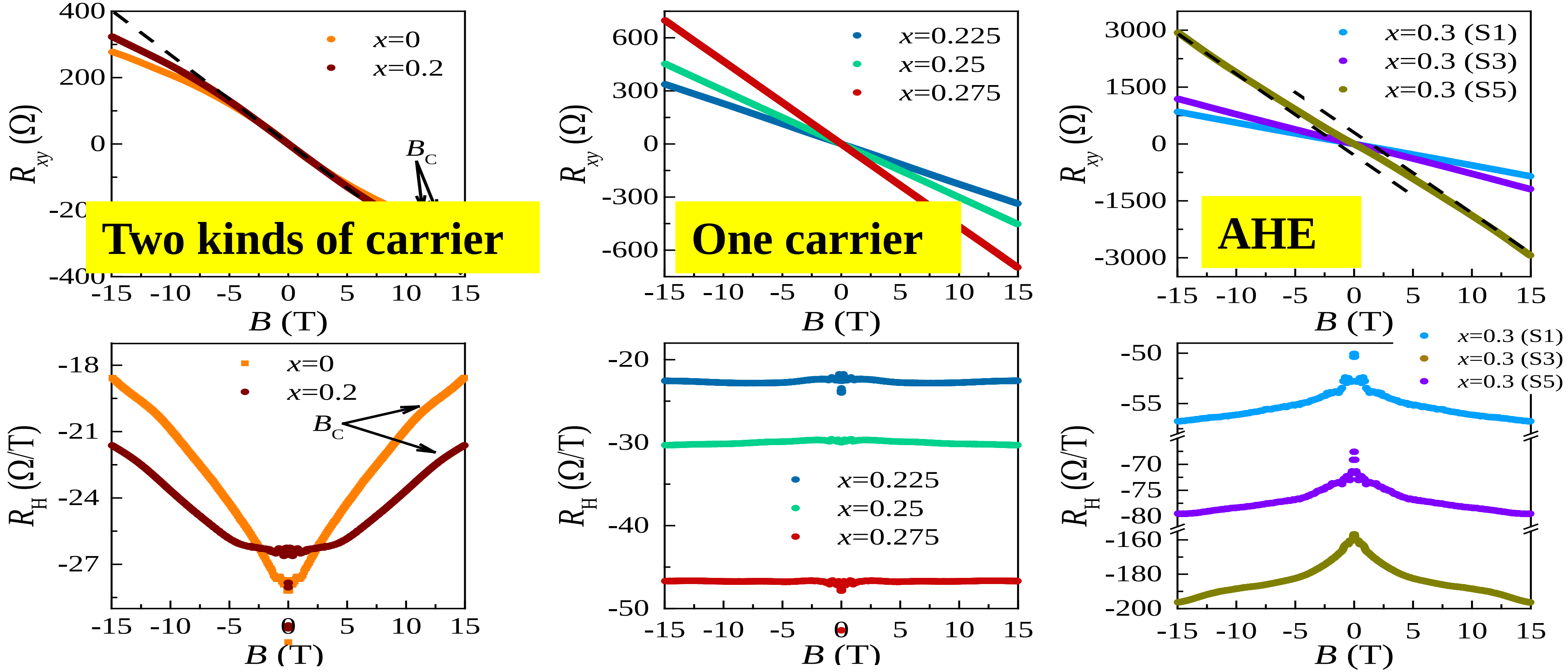
4.1 Three ways to modulation doping

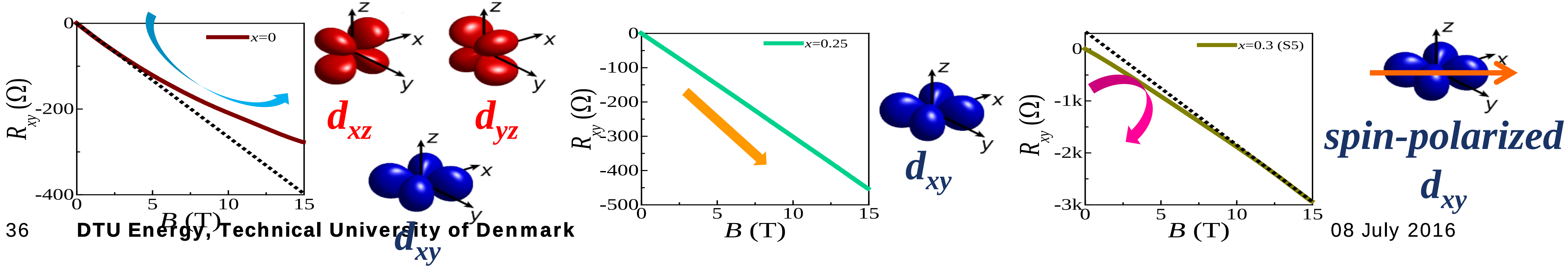


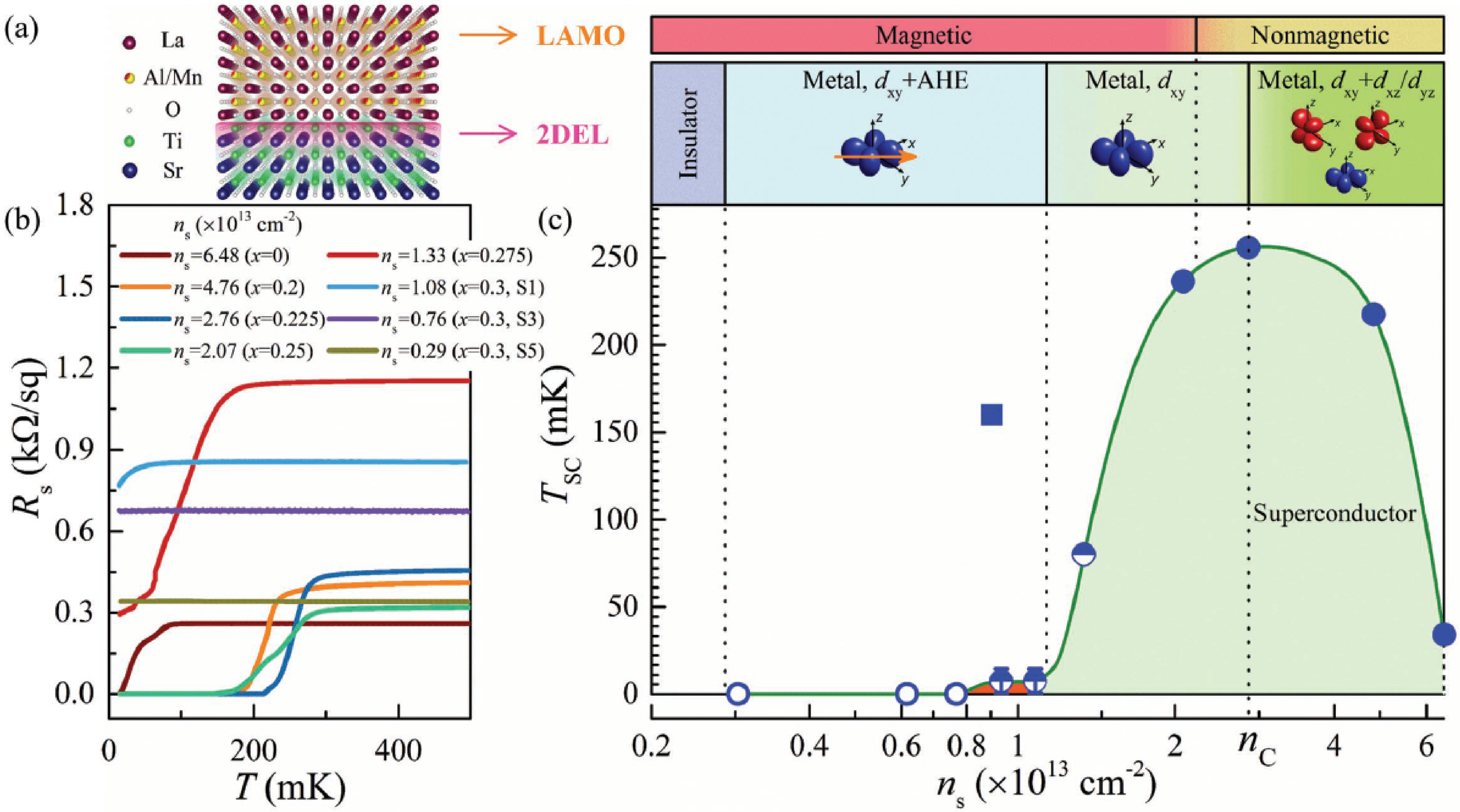
Transport Properties

Hall Resistance

Hall coefficient

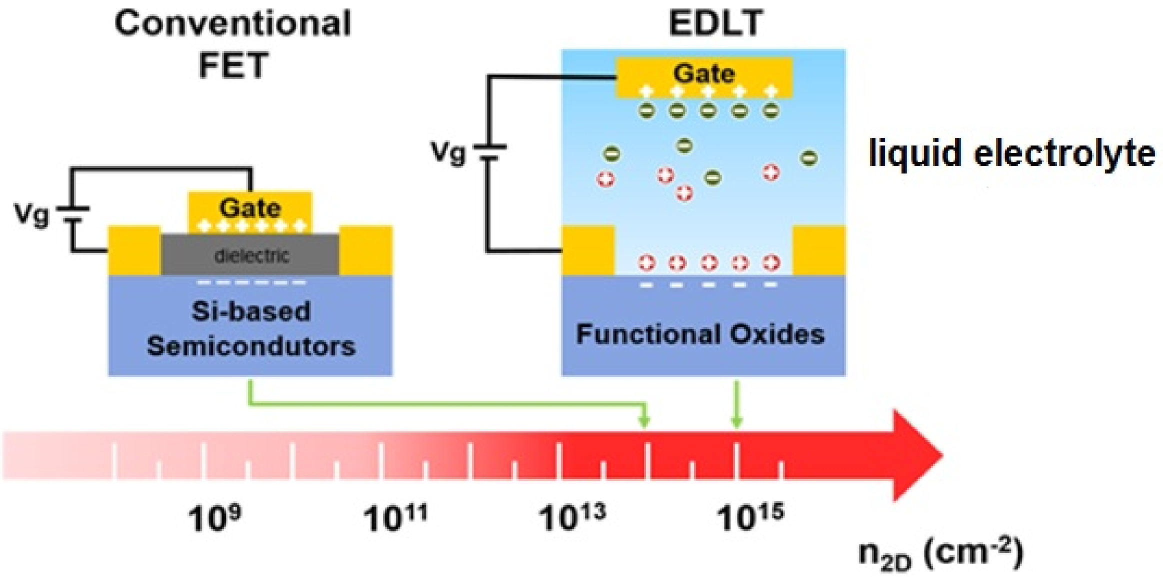


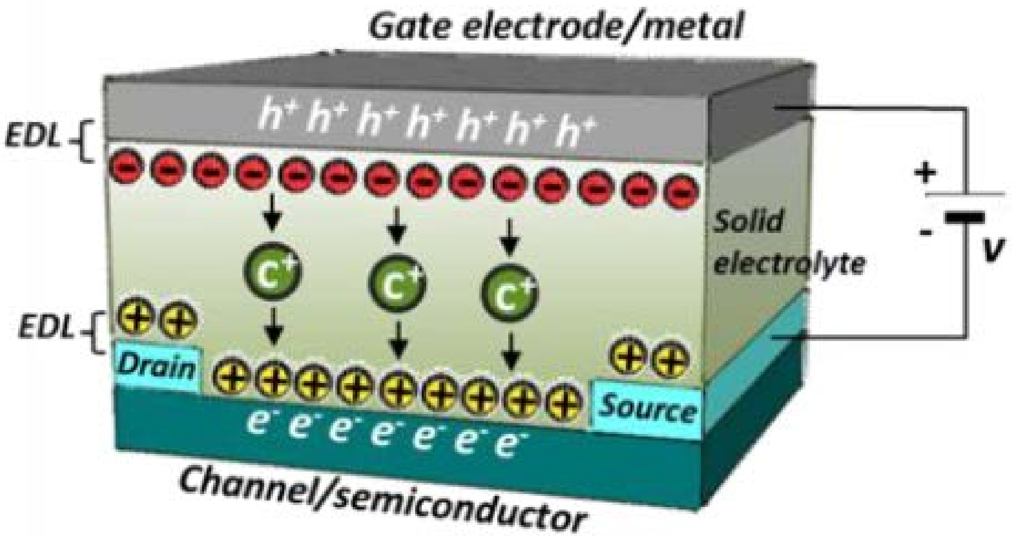




Gan *et al.* Adv. Mater. 2019

4.3 ionic gating



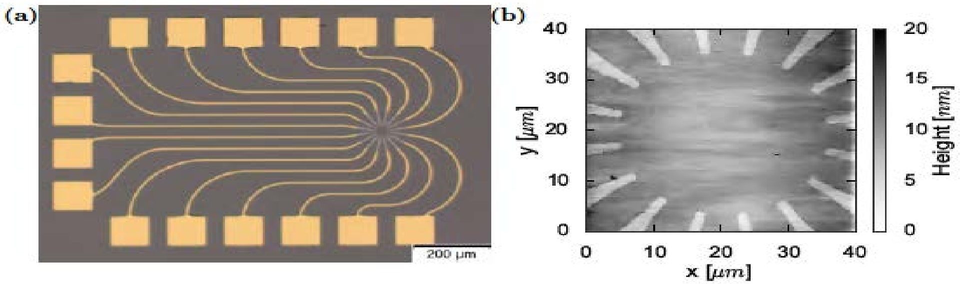


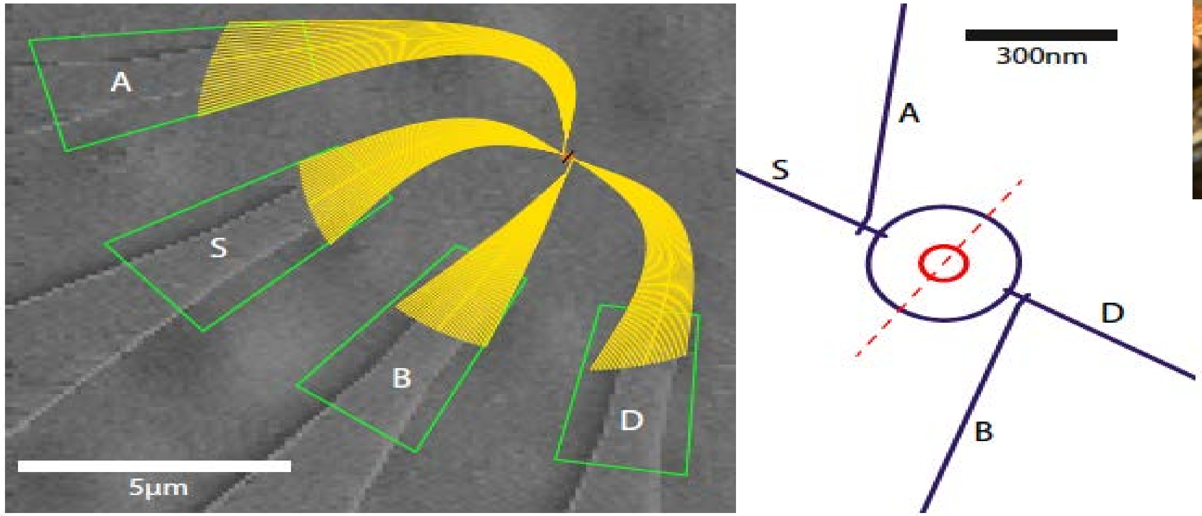
Moving from liquid electrolyte to solid electrolyte

W. Niu et al. **Nano Lett. 17**, 6878-6885 (2017)

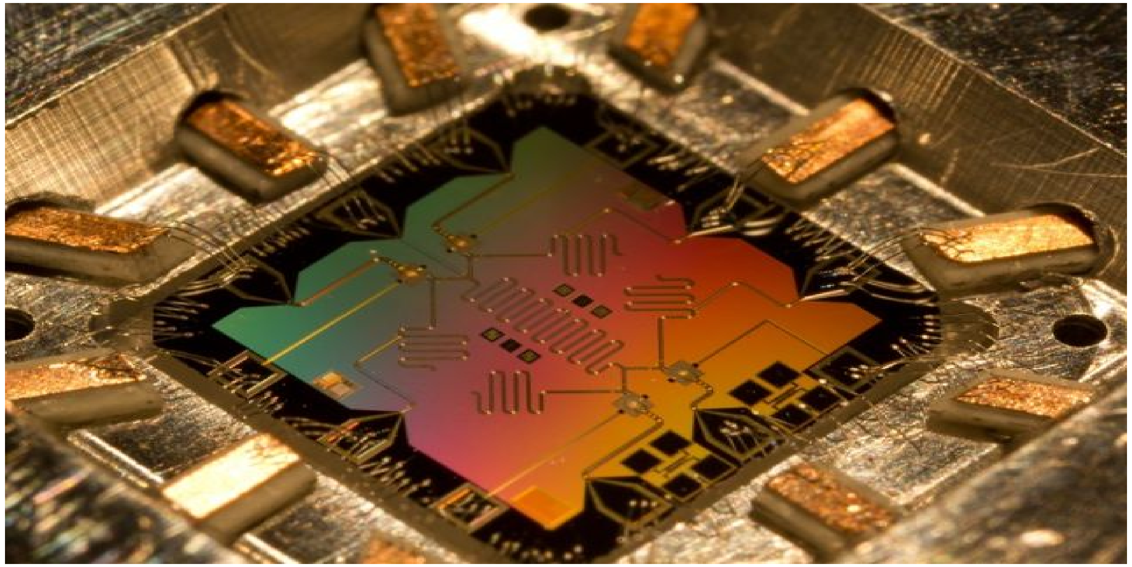
5. Perspective on Future Applications

5.1 Quantum devices with strongly-correlated electrons at oxide interfaces.





Merlin V. Soosten et al.



IBM's quantum processor

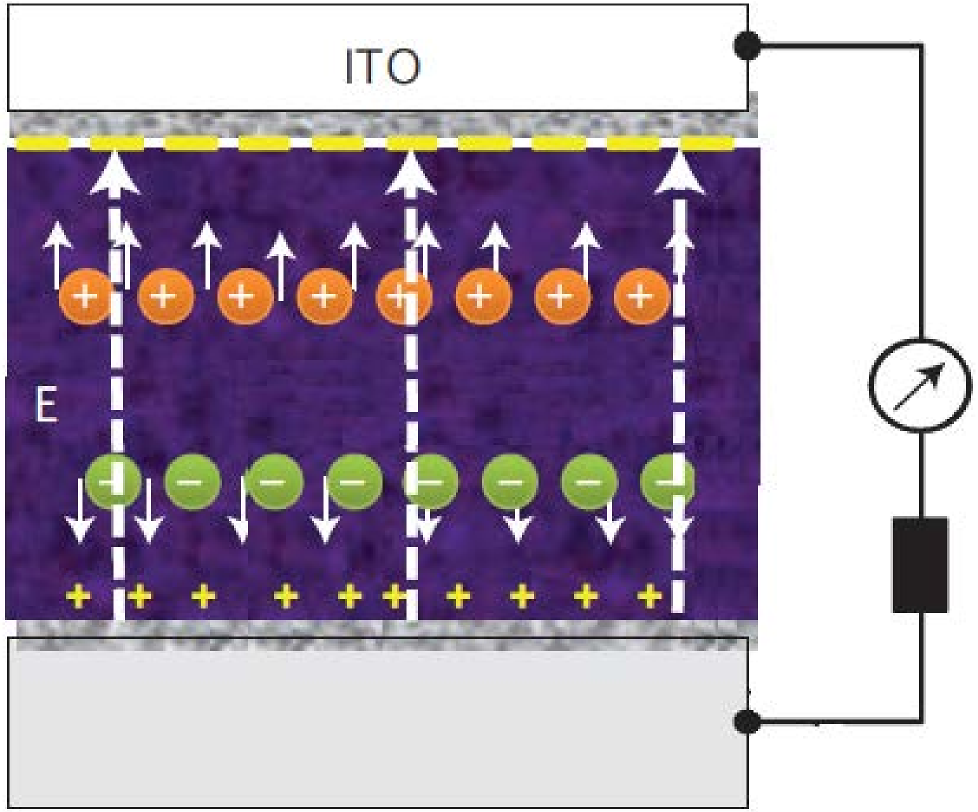
5.2 It is time to think big!

In 20-30 years

How to cope with the intermittency of renewable energy sources?

Emerging technology: Ferroelectric solar cells

Key benefits of Ferroelectric light absorber



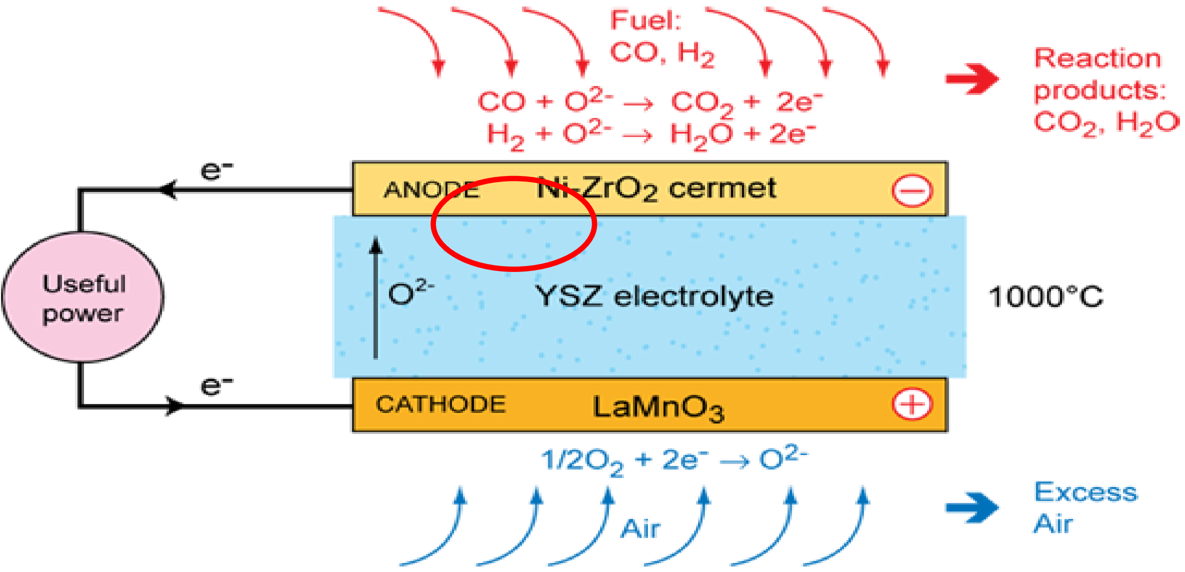
1. Internal fields in ferroelectric materials reduce recombination.

   The effective electric field in a ferroelectric material is around one order of magnitude higher than in a p–n junction.

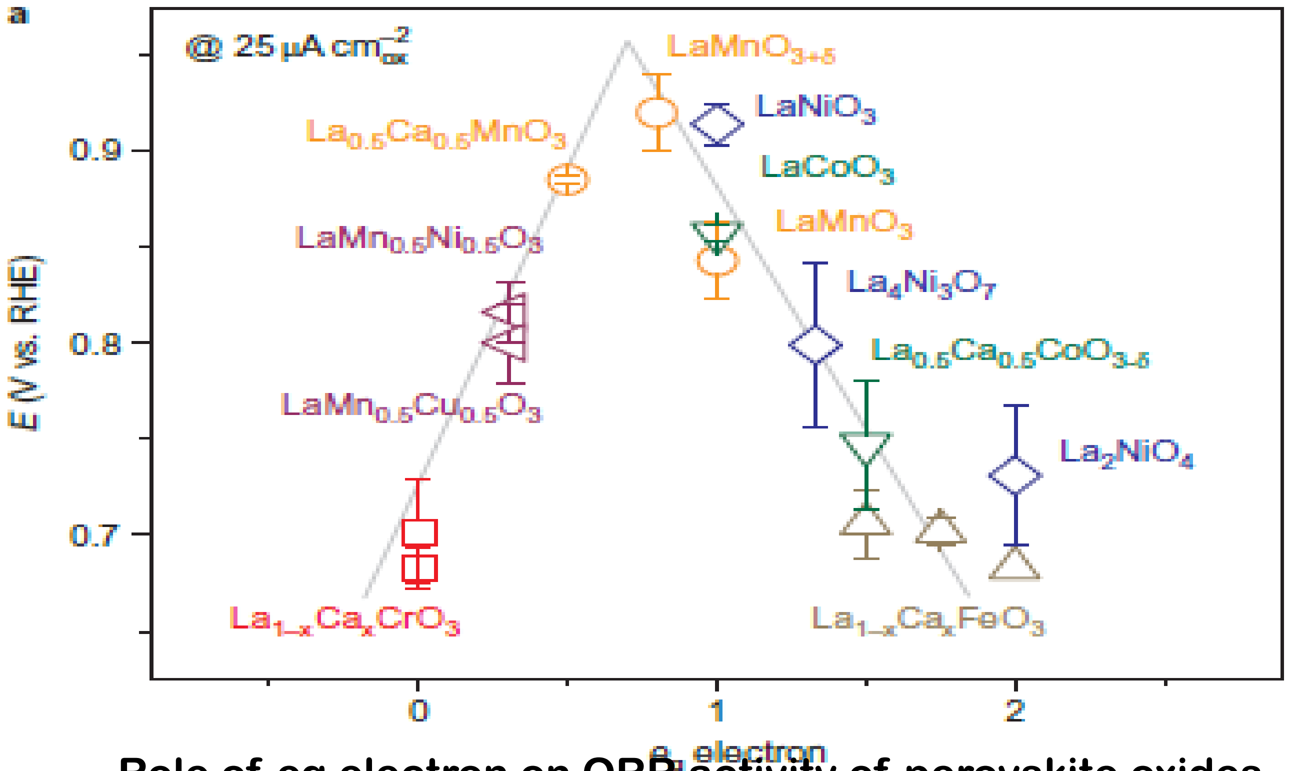
2. Ferroelectric materials can achieve extremely high open circuit voltags (V_{oc}).

5.2 Artificial oxide interfaces as electrocatalysts

The search for highly active and abundant transition-metal-oxide catalysts to replace platinum.



Solid oxide fuel/electrolysis cells



Role of eg electron on ORR activity of perovskite oxides

PROGRESS REPORT

Perovskite Oxide Interfaces

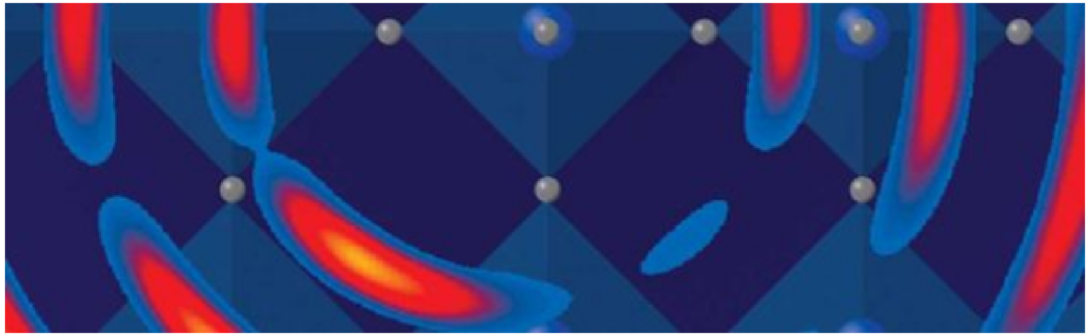
ADVANCED MATERIALS INTERFACES

www.advmatinterfaces.de

Progress and Perspectives of Atomically Engineered Perovskite Oxide Interfaces for Electronics and Electrocatalysts

Yunzhong Chen and Robert J. Green**

scientists working on a variety of problems at the frontiers of physics, materials science and engineering. The properties of these systems are uniquely defined by quantum mechanical effects that remain manifest at high temperatures and macroscopic length scales.



https://www.nature.com/collections/ydsxkfvwws/

Thank you.