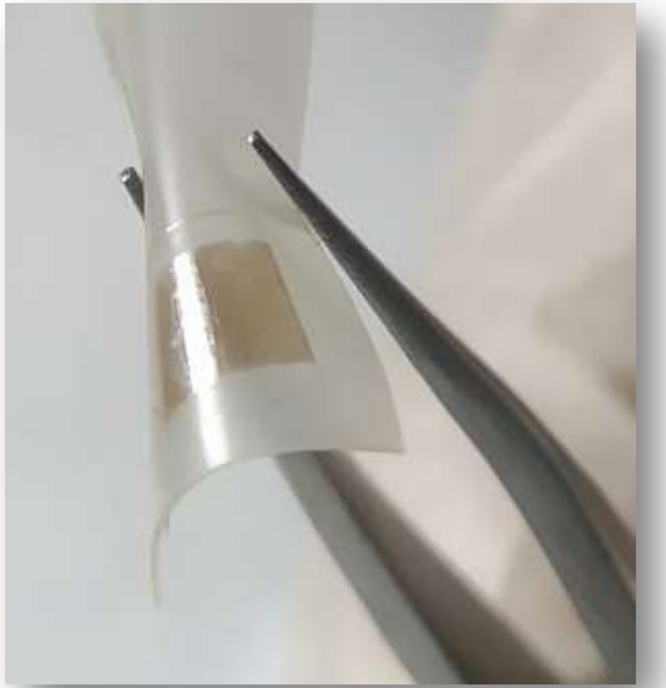
Freestanding functional oxide membranes



Mariona Coll
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ISOE2023 August 29- September 8

Outline

- Why free-standing oxides
- Preparation of free-standing oxides
  - Sacrificial Layer
- Challenges in the preparation
- Outlook/ perspective

Epitaxial complex oxides

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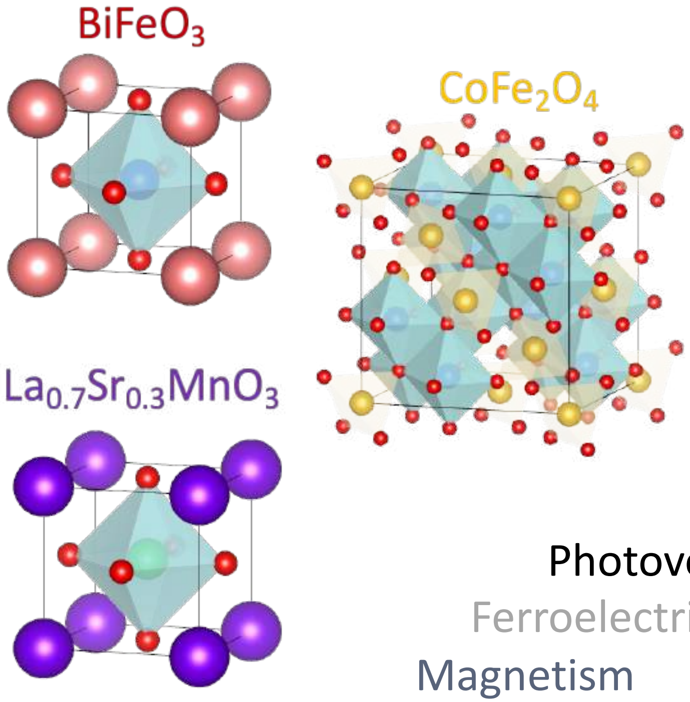
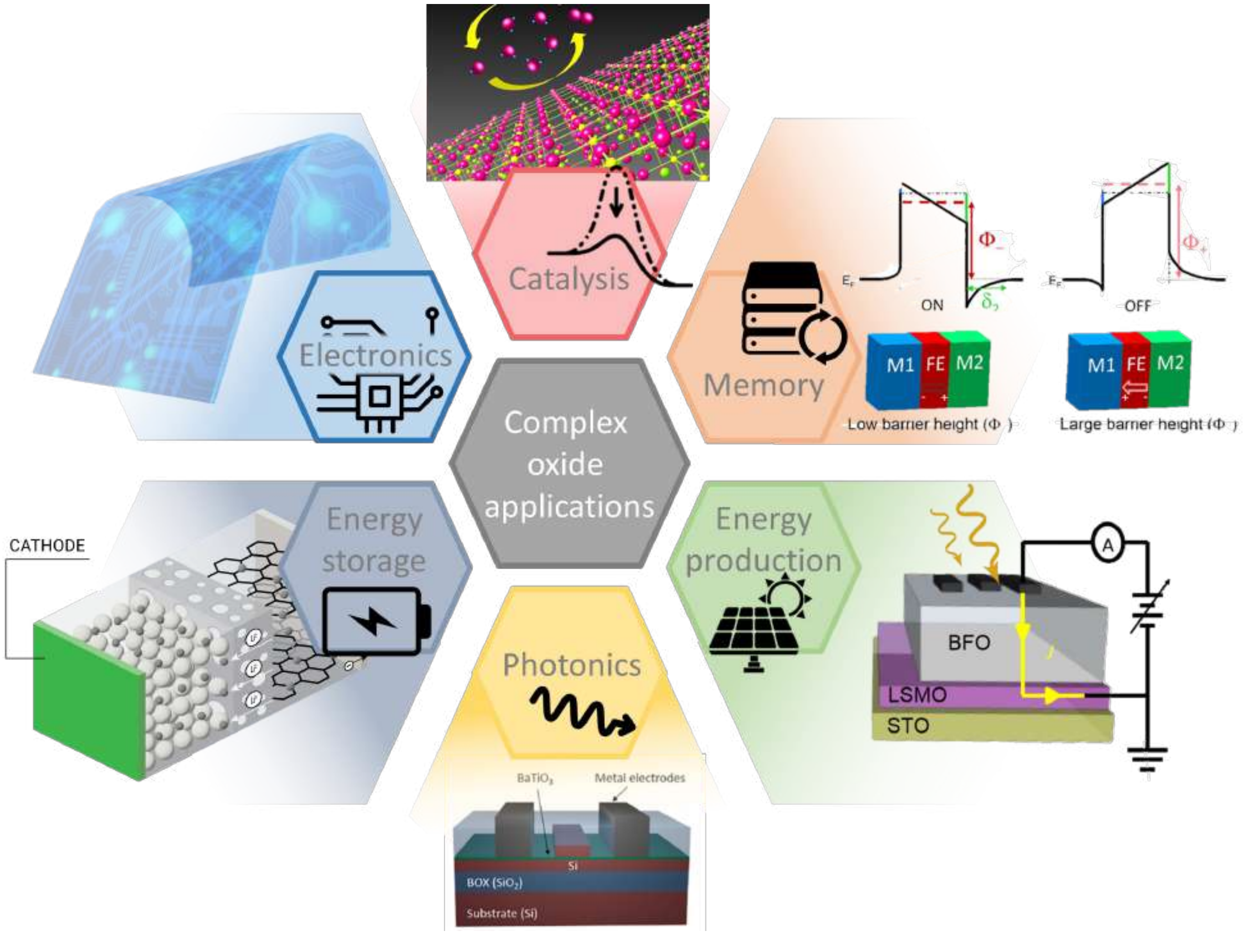
- ✓ Broad variety of structures
- ✓ Composition versatility
- ✓ (chemical, thermal, mechanical) stability
- ✓ Unique physical, chemical properties



Photovoltaic
Ferroelectricity
Magnetism
Superconductivity
Metal-insulator transitions
...



Appl. Surf. Sci., ***482***:1–93, 2019 Roadmap Towards Oxide Electronics

Free-standing complex oxides

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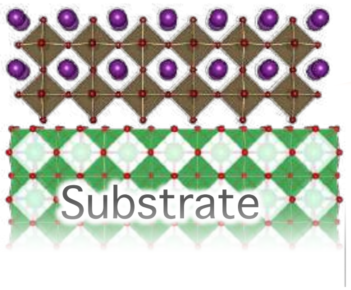
Epitaxial growth



Single-crystal Substrate

- Rigid
- Fragile
- limited availability
- Expensive

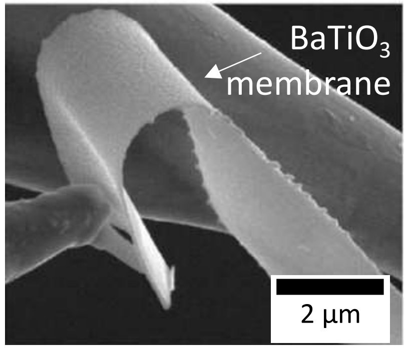
High Temperature treatment

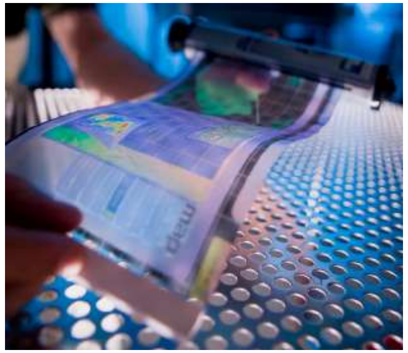
- limits substrate nature
- Thermodynamic compatibility of films

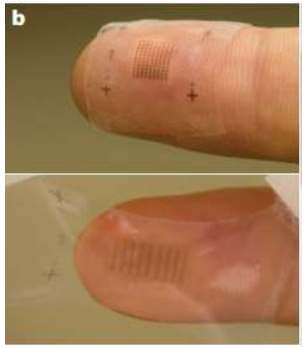
New opportunities

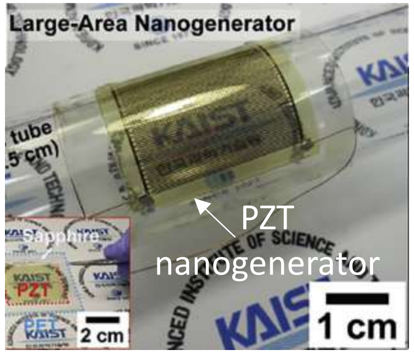
Epitaxial complex oxide membranes: new opportunities

- Integration into Si, polymers, 2D materials …









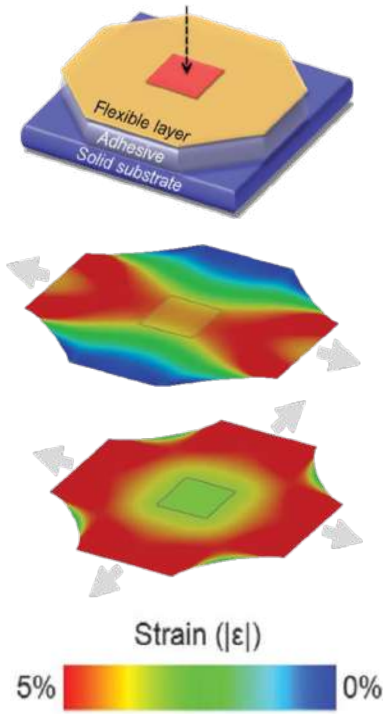
G Dong *et al.*, *Science* **366** (6464), 475-479, 2019

S Wang *et al.*, *Nature* **555** (7694), 83–88, 2018

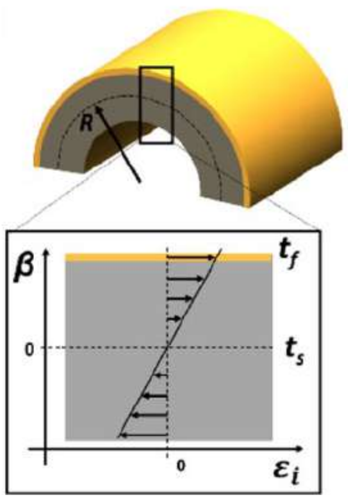
K Park *et al.*, *Adv. Mater.* **26**, 2514–2520, 2014

- Strain engineering

Stretching



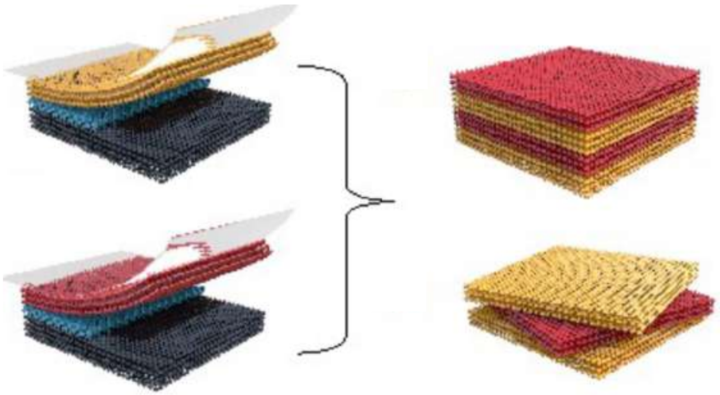
Bending



SS Hong *et al.*, *Science* **368** (6486), 71–76, 2020

FM Chiabrera *et al.*, *Ann. Phys.* **534**, 2200084, 2022

- New phenomena at artificial interfaces



Y Li *et al.*, *Adv. Mater.* **34**, 2203187, 2022

Outline

- Why free-standing oxides

- **Preparation of free-standing oxides**

  Sacrificial Layer

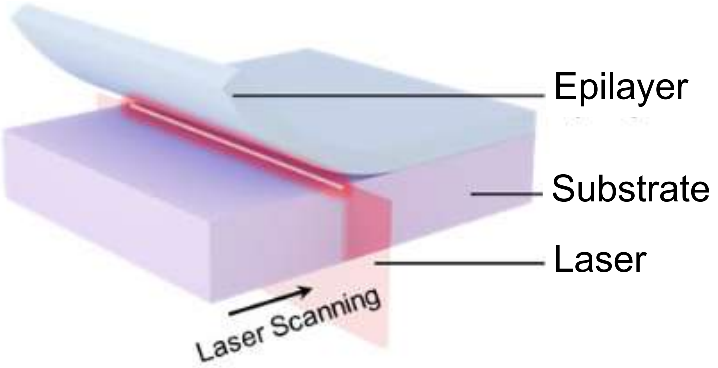
- Challenges in the preparation

- Outlook/ perspective

Freestanding epitaxial complex oxides: How to detach them from the substrate?

PHYSICAL TECHNIQUES

Laser lift-off

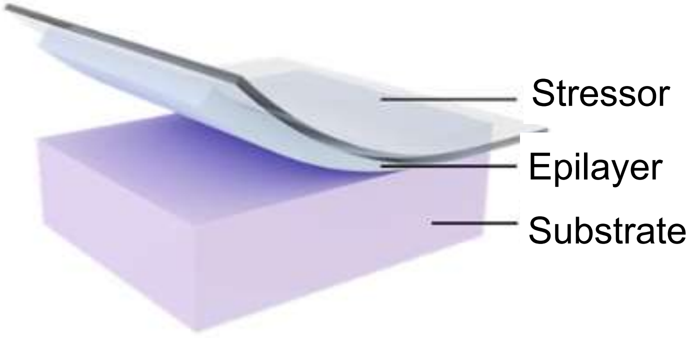


Transparent substrate
Bandgap of the film < bandgap laser

Limited number of suitable films
Rough surface
No reusable substrate

Ex: PZT//sapphire-->PET

Mechanical lift-off

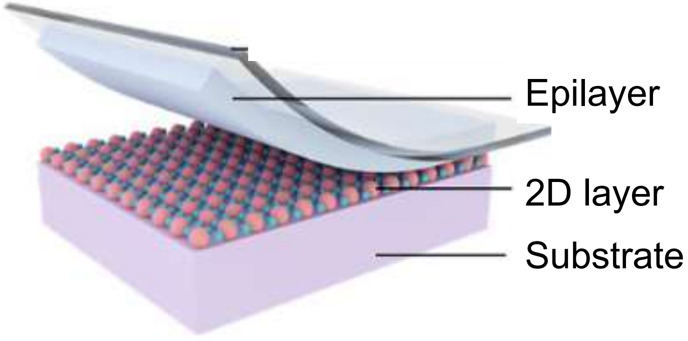


Weak interface bonding
Brute Force + stressor

Materials with weak bonding
Cracking

Ex: Ni/PMN-PT//SRO/STO

2D assisted lift-off



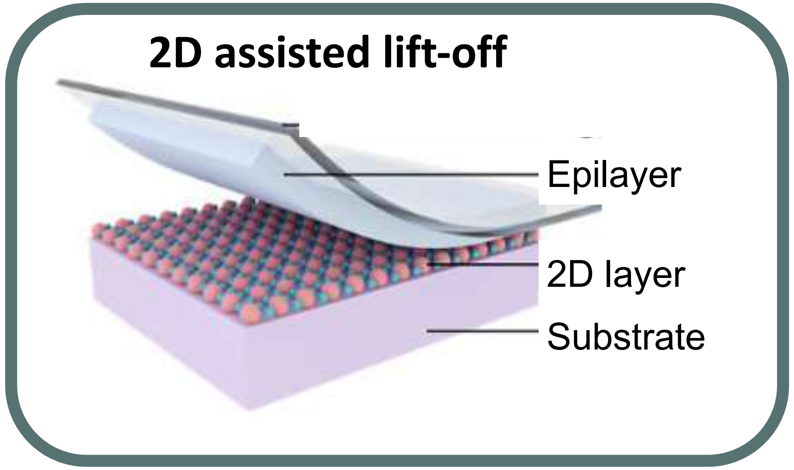
VdW 2D buffer layer
Exfoliation yield > mechanical lift-off

Residues of organic/metal
Film quality depends on graphene quality
Still challenging large areas

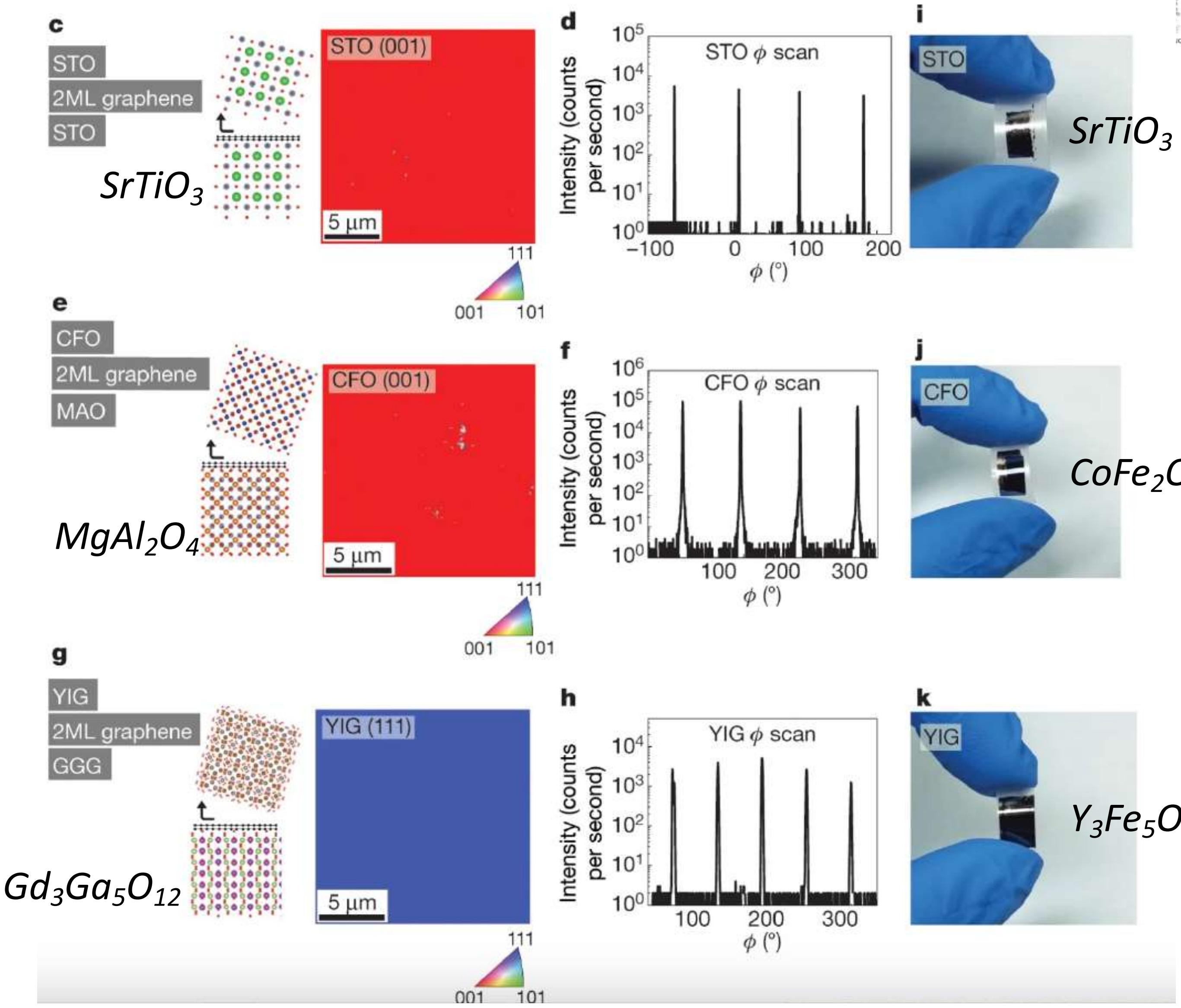
Ex: mica or graphene--> many oxides

L Dai *et al., J. Appl. Phys.* **132**, 070904, 2022

Freestanding epitaxial complex oxides: 2D assisted lift-off. Examples



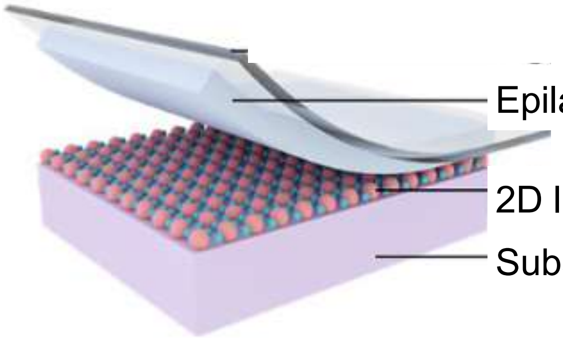
PLD



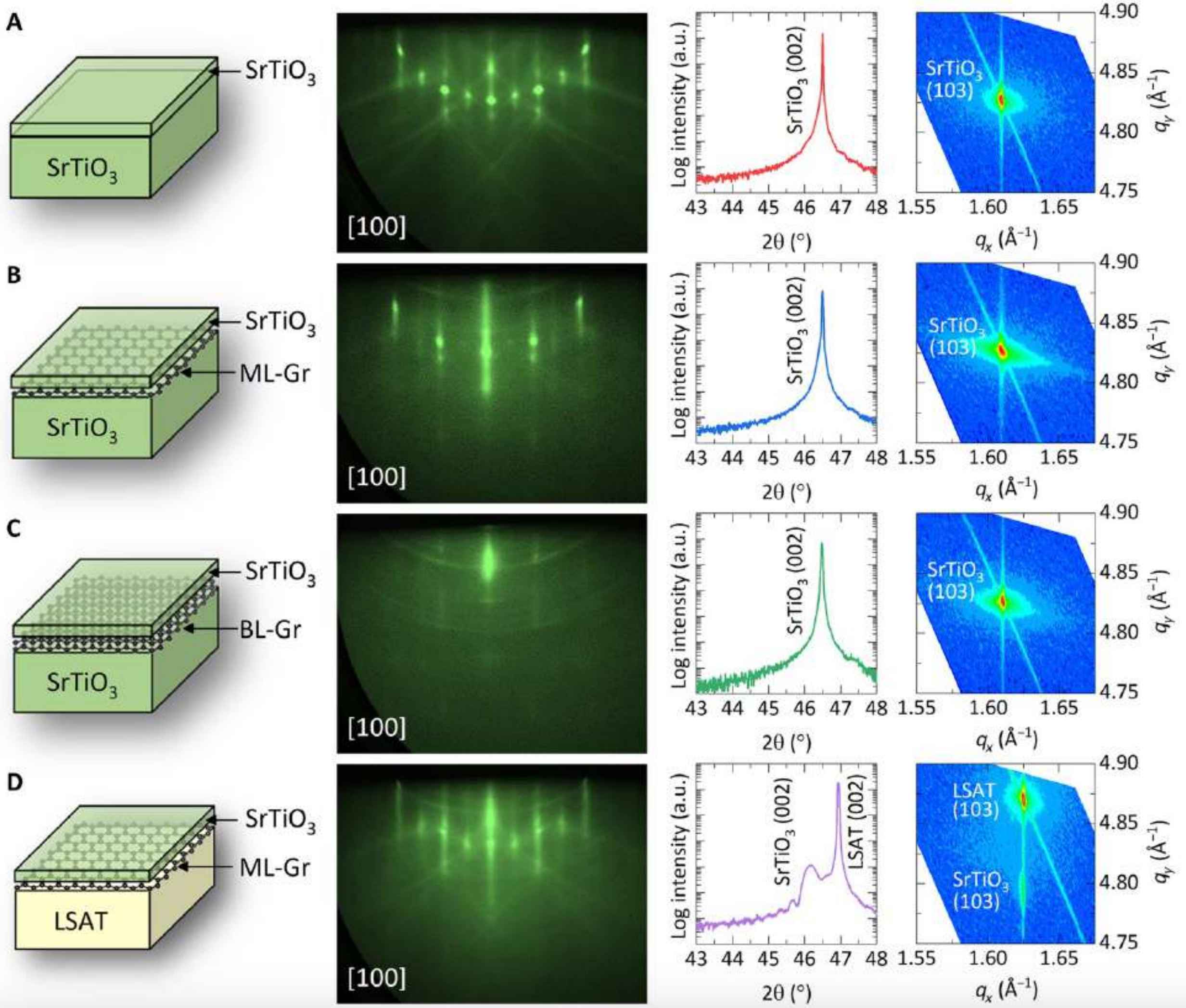
Kum et al. Nature, volume 578, pages 75–81 (2020)

Freestanding epitaxial complex oxides: 2D assisted lift-off. Examples

2D assisted lift-off



Hybrid-MBE



Freestanding epitaxial complex oxides: 2D assisted lift-off. Examples

Table 1. Reported complex-oxides and processes for remote epitaxy.

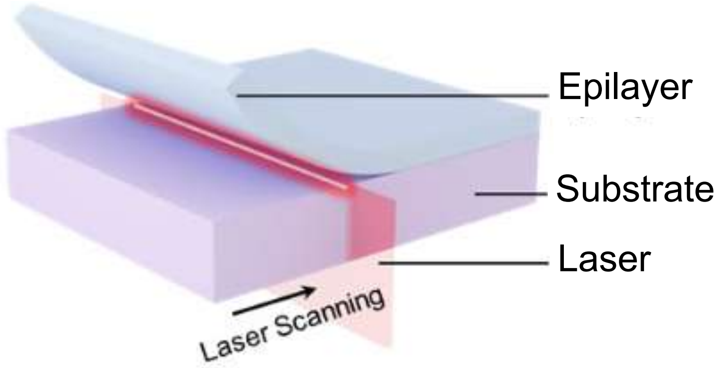
Grown epilayer	Substrate	2D interlayer	2D synthesis method	2D transfer method	Epitaxy tool	Comment	References
STO	STO	Bilayer graphene	Graphitization of SiC	Semi-dry	PLD	Bilayer graphene and ultra-thin buffer layer are needed	[58]
CFO	MAO	Bilayer graphene	Graphitization of SiC	Semi-dry	PLD	Bilayer graphene is needed	[58]
YIG	GGG	Bilayer graphene	Graphitization of SiC	Semi-dry	PLD	Bilayer graphene is needed Post-annealing about 850 °C to improve crystal quality	[58, 94]
BTO	STO	Monolayer graphene	Graphitization of SiC/CVD on Cu foil	Semi-dry/Wet	MBE	Graphene is immediately etched if ozone is used	[58]
VO_2	Al_2O_3	Monolayer graphene	CVD on Cu foil	Wet	PLD	Low exfoliation area yield (5%)	[84]
$LiNbO_3$	Al_2O_3	Monolayer graphene	CVD on Cu foil	Wet	PLD	There is no mention of exfoliation	[85]
STO	STO	Mono-/bilayer graphene	Direct CVD growth	—	PLD	Atomic layer etching is used Ultra-thin buffer layer is needed	[87]
VO_2	Al_2O_3	Bilayer graphene	CVD on Cu foil	Wet	Sputter	There is no mention of exfoliation	[86]
STO	STO	Monolayer graphene	CVD on Cu foil	Wet	MBE	Graphene is immediately etched if ozone is used regardless of buffer layer	[91]
BTO	Ge	Monolayer graphene	Direct CVD growth	—	PLD	Ge (110) substrate allows remote interaction	[88]
STO	STO	Bilayer graphene	CVD on Cu foil	Wet	MBE	Hybrid MBE is used	[92]
LSAT	STO	Monolayer graphene	CVD on Cu foil	Wet	MBE	Hybrid MBE is used	[92]

Phys. Scr. 98 (2023) 052002

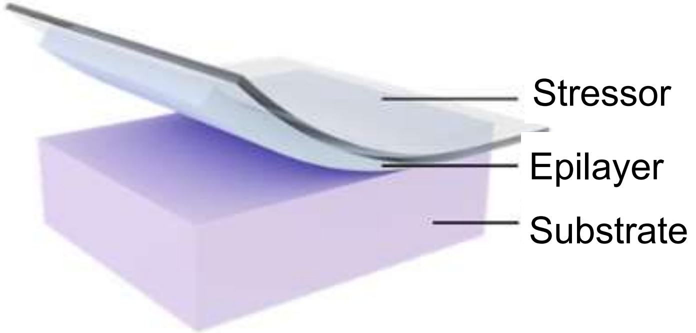
Freestanding epitaxial complex oxides: How to detach them from the substrate?

PHYSICAL TECHNIQUES

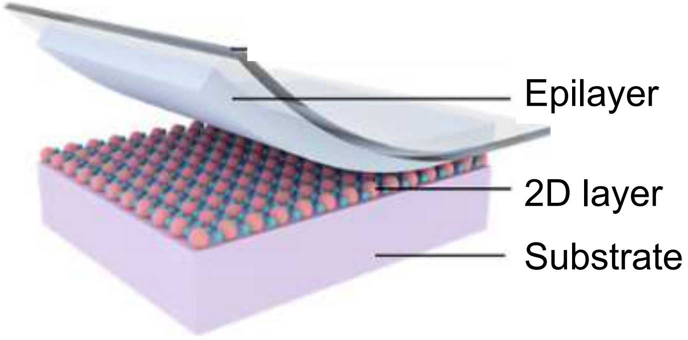
Laser lift-off



Mechanical lift-off



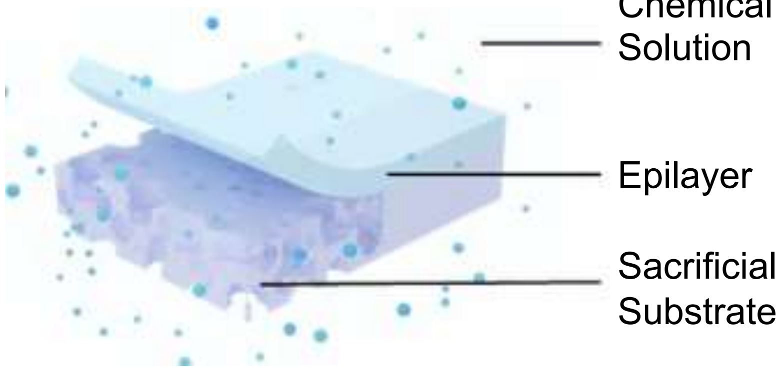
2D assisted lift-off



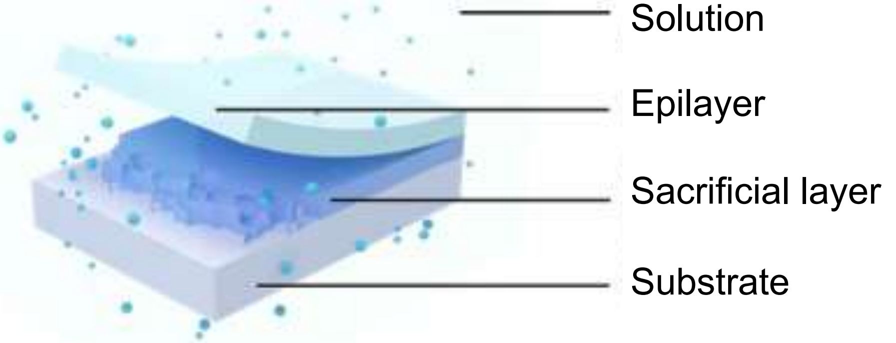
HS Kum *et al., Nature* **578**, 75–81, 2020

CHEMICAL TECHNIQUES

Substrate etching



Sacrificial layer



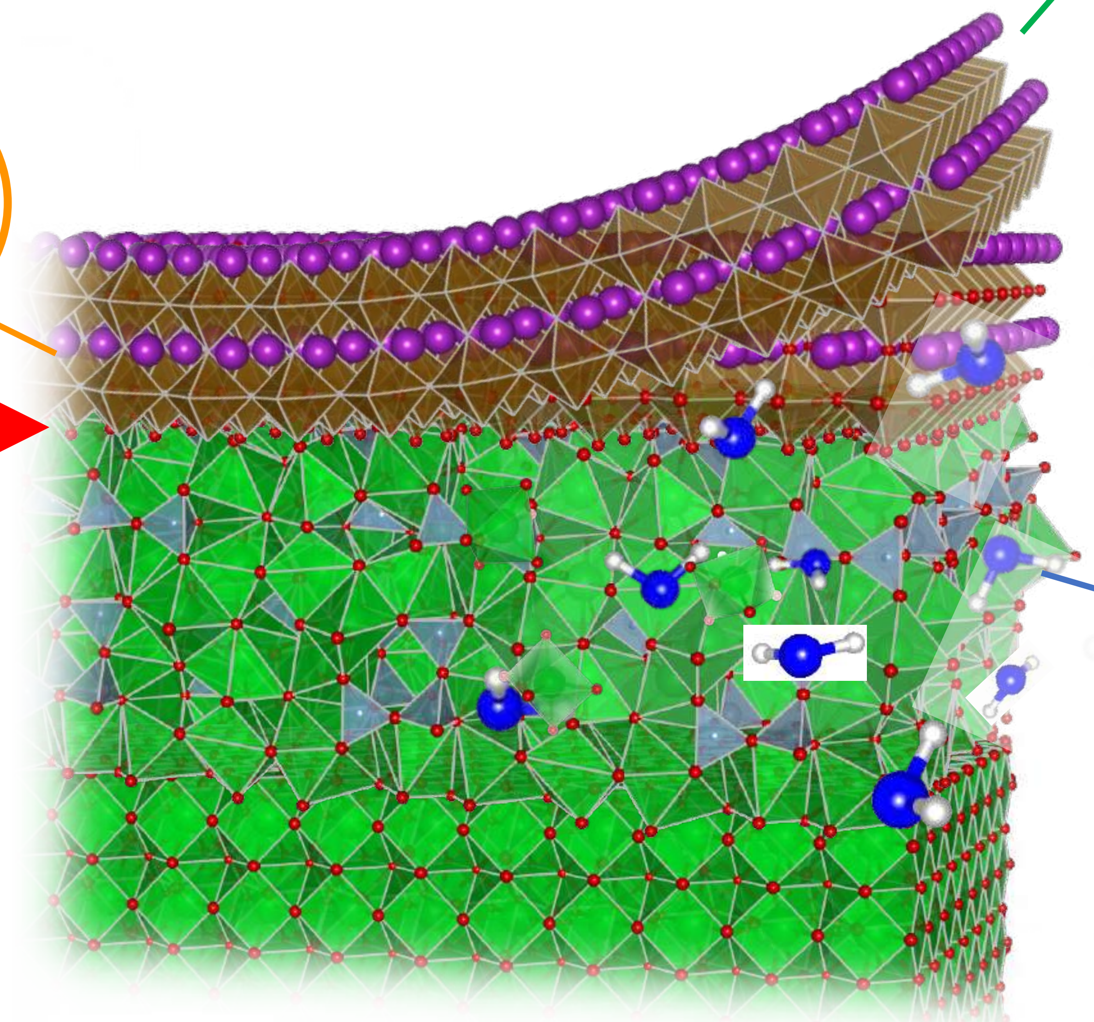
L Dai *et al., J. Appl. Phys.* **132**, 070904, 2022

Sacrificial

Oxide transfer
Towards device
fabrication

Functional
oxide
$CoFe_2O_4$
$La_{0.7}Sr_{0.3}MnO_3$
$BiFeO_3$
....

Epitaxy
Interdifusion
Sharp interface
Thickness
Functionality



Epitaxy, stoichiometry
Continuous film (crack and wrinckles free)
Interaction/adhesion with arbitrary substrates (polymer, semiconductors)

Sacrificial Layer

Selective etching

Epitaxy
Smooth Surface
Stability
Thickness

Sacrificial layers tested

Table 1.1: Sacrificial layer compositions for the preparation of freestanding epitaxial complex oxide films.

Sacrificial Layer	Substrate	Etching solution	Released epitaxial oxide
$La_{0.7}Sr_{0.3}MnO_3$	$SrTiO_3$ (001)	KI + HCl	$BaTiO_3$,[31,51] PZT, $CaTiO_3/SrTiO_3$ superlattice[29]
$SrRuO_3$	$SrTiO_3$ (001)	$NaIO_{4(aq)}$	LSMO[52]
$YBa_2Cu_3O_7$	$SrTiO_3$ (001)	HCl	LSMO[53]
$SrVO_3$	$SrTiO_3$ (001)	50 °C Water	$SrTiO_3$[54]
$SrCoO_{2.5}$	$SrTiO_3$ (001), (110), (111)	Weak acids	$SrRuO_3$[55]
MgO	$SrTiO_3$ (001)	$(NH_4)_2SO_{4(aq)}$	$CoFe_2O_4$[56]
BaO	$SrTiO_3$ (001)	RT Water	$BaTiO_3$, $SrTiO_3$[57]
$(Ca,Sr,Ba)_3Al_2O_6$	$SrTiO_3$ (001), (110), (111), $LaAlO_3$ (001)	RT Water	See 1.1.3 $Sr_3Al_2O_6$ (SAO) sacrificial layer

Pol Salles, PhD thesis, Unfolding the challenges to prepare epitaxial complex oxide membranes by chemical methods, University Autonoma Barcelona, Spain, April 2023

Sacrificial compatibility with epitaxial oxides

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CSIC Consejo Superior de Investigaciones Científicas

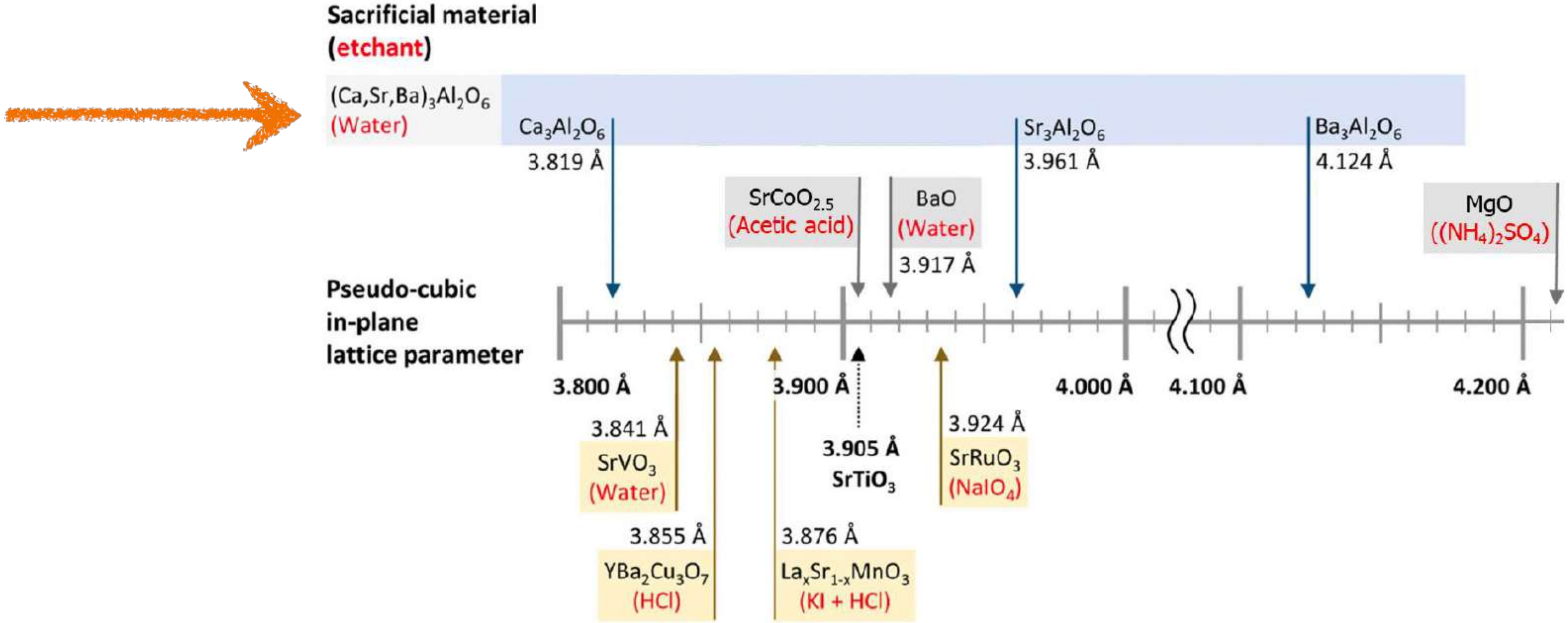
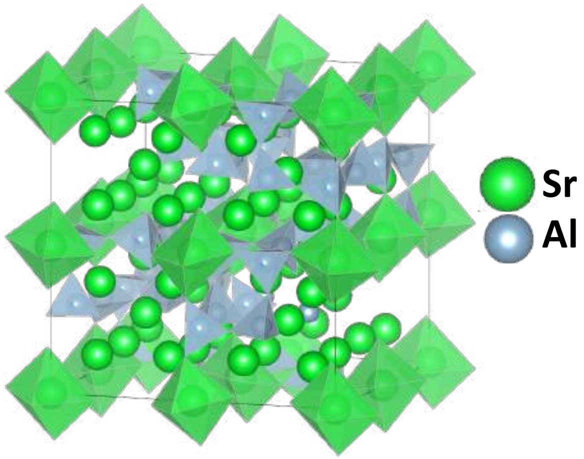


Figure 1.5: Compatible sacrificial layers with epitaxial complex oxides. Pseudo-cubic in-plane lattice parameters of the different sacrificial layer compositions included in Table 1.1. The yellow frames correspond to perovskites, the blue one corresponds to the $(Ca,Sr,Ba)_3Al_2O_6$ family and the grey ones to other alternative structures. $SrTiO_3$, as typical single-crystal substrate for the growth of epitaxial complex oxides, is depicted as reference. *Figure adapted from Ref.*[58].

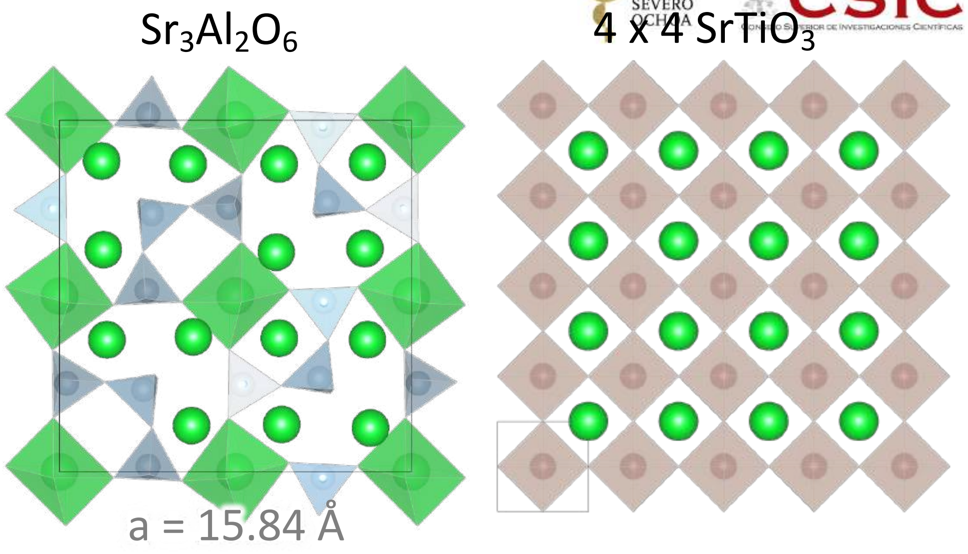
Pol Salles, PhD thesis, Unfolding the challenges to prepare epitaxial complex oxide membranes by chemical methods, University Autonoma Barcelona, Spain, April 2023

$Sr_3Al_2O_6$ (SAO) as sacrificial layer

- ✓ Similar cell parameters to $SrTiO_3$, $La_{0.7}Sr_{0.3}MnO_3$, $BiFeO_3$,… (epitaxial growth)
- ✓ Dissolved in **H_2O** (non-toxic, low-cost, soft)
- ✓ High versatility



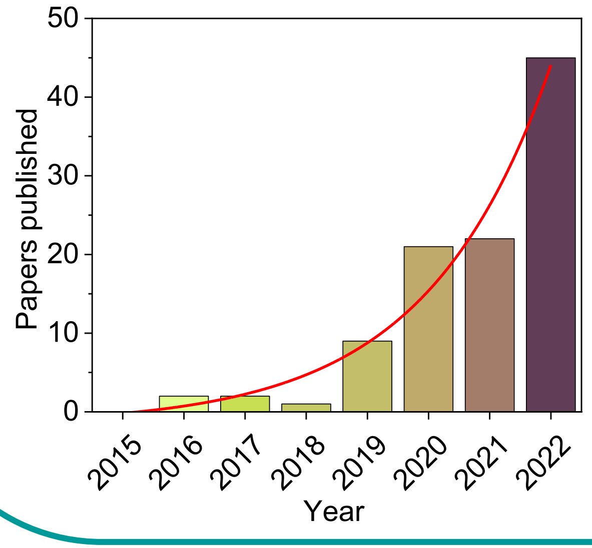
Pseudo-perovskite structure



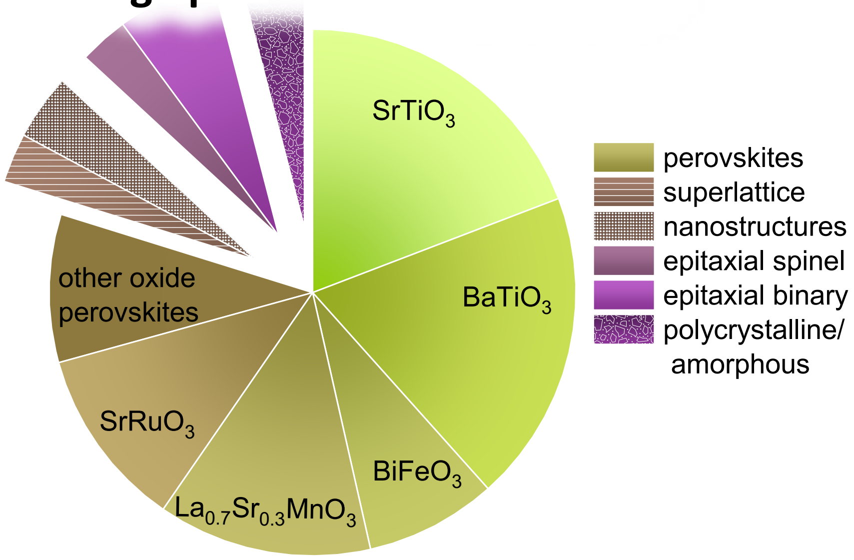
D Lu *et al.*, *Nat. Mater.* **15**, 1255–1260, 2016

STATE OF THE ART (Last update: 31st Dec 2022)

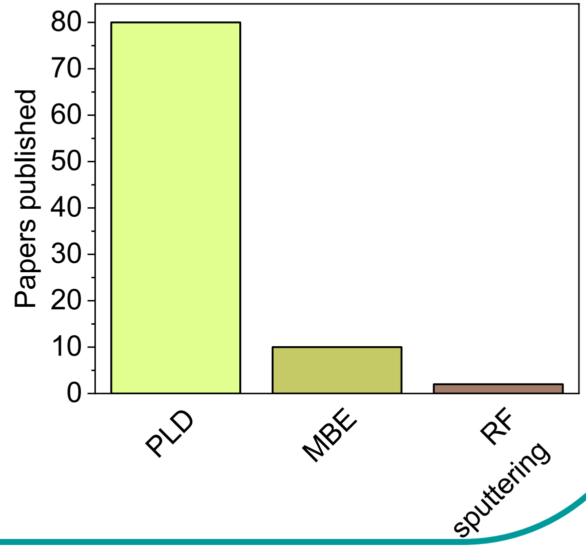
Papers published using SAO as sacrificial layer



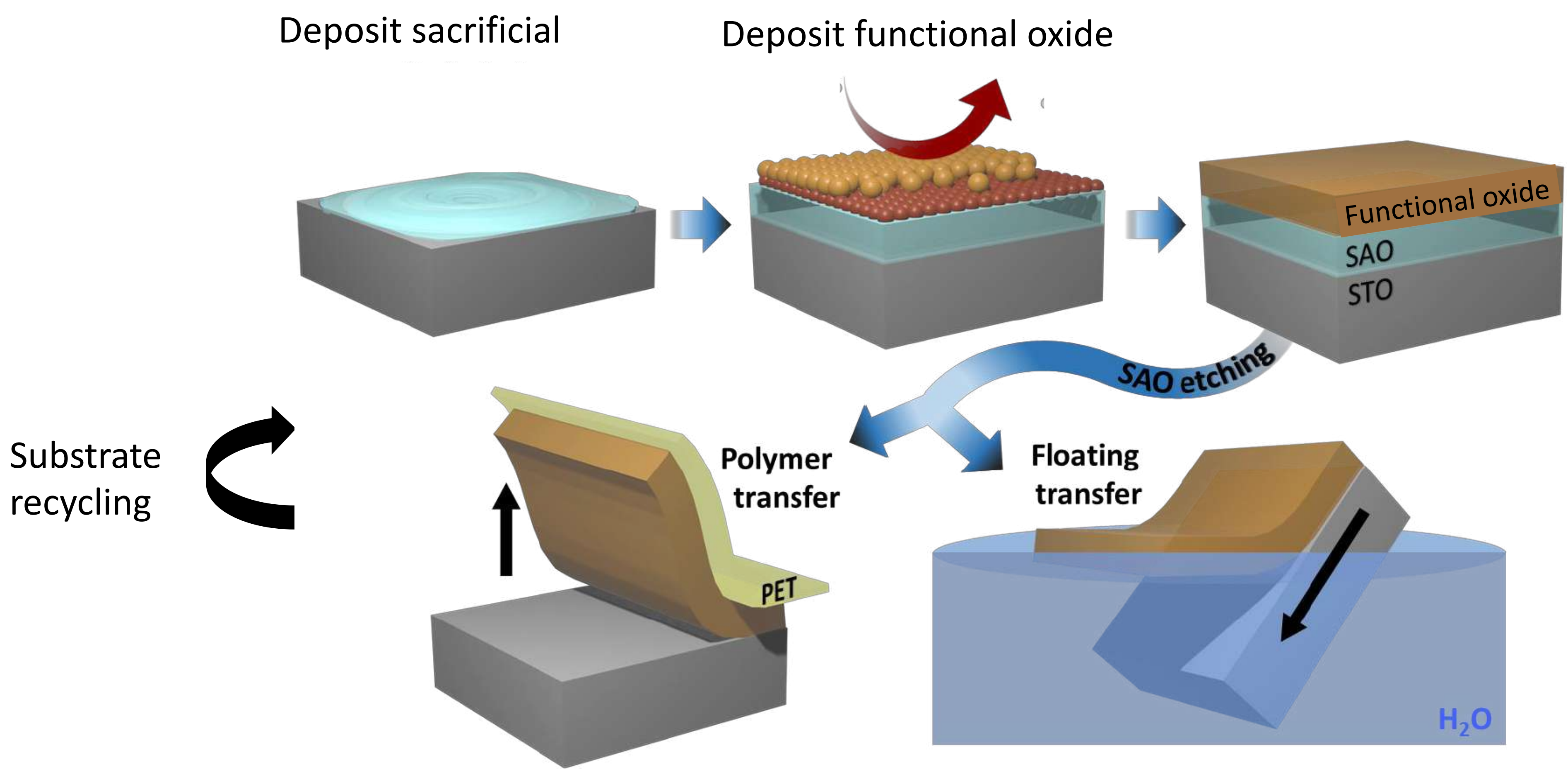
Freestanding epitaxial oxide structures



High-vacuum deposition techniques

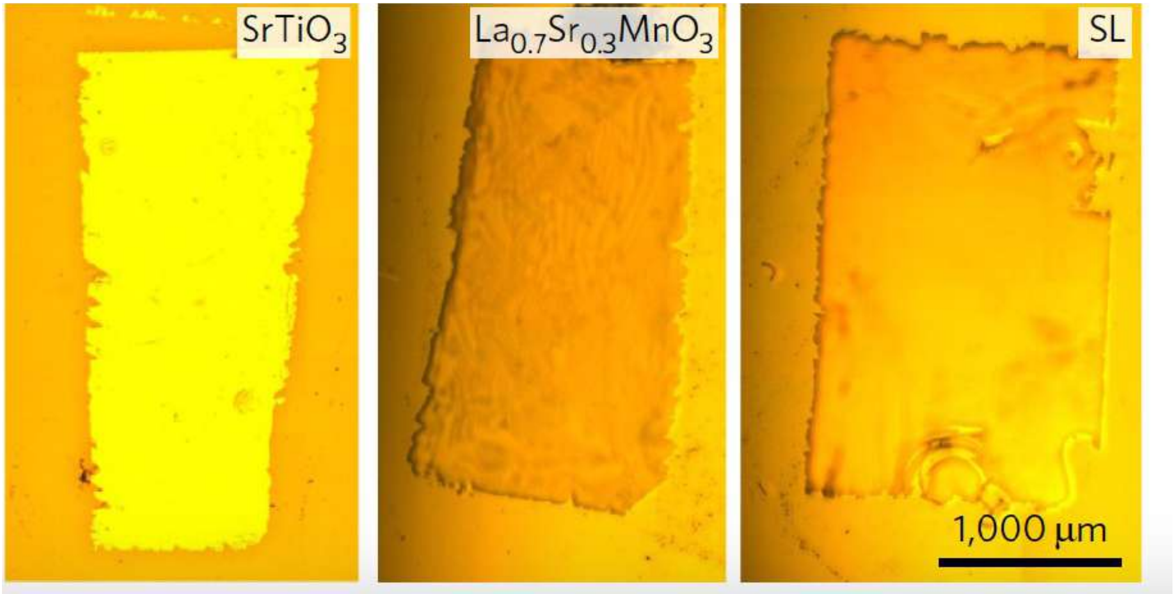


Schematic of the procedure to obtain functional oxide membranes...



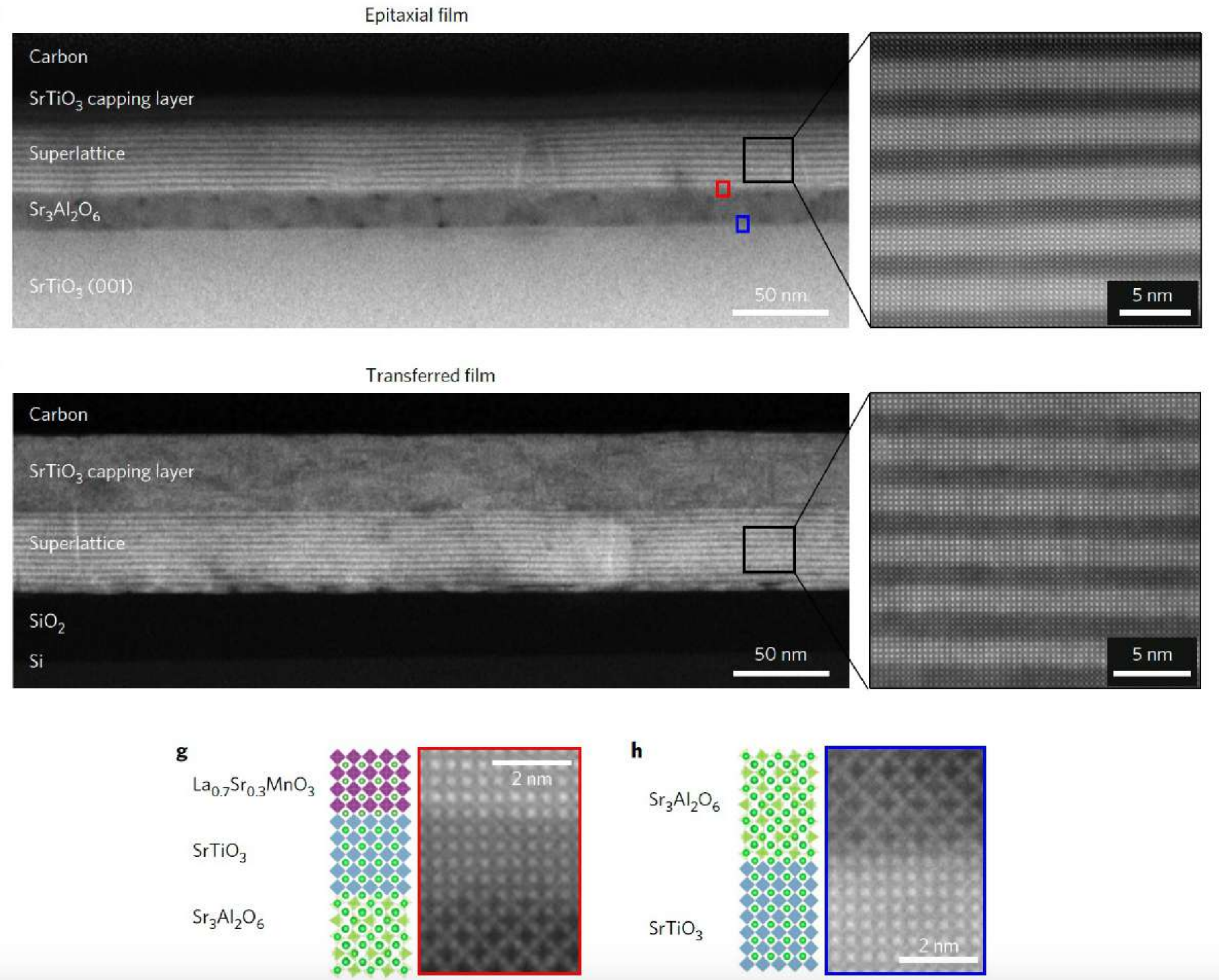
Synthesis of freestanding single-crystal perovskite films and heterostructures

80 nm 80 nm 5 u.c STO/5 u.c LSMO



Lu et al. Nature Materials volume 15, pages 1255–1260 (2016)

Synthesis of freestanding single-crystal perovskite films and heterostructures



Novel functionalities in freestanding oxides

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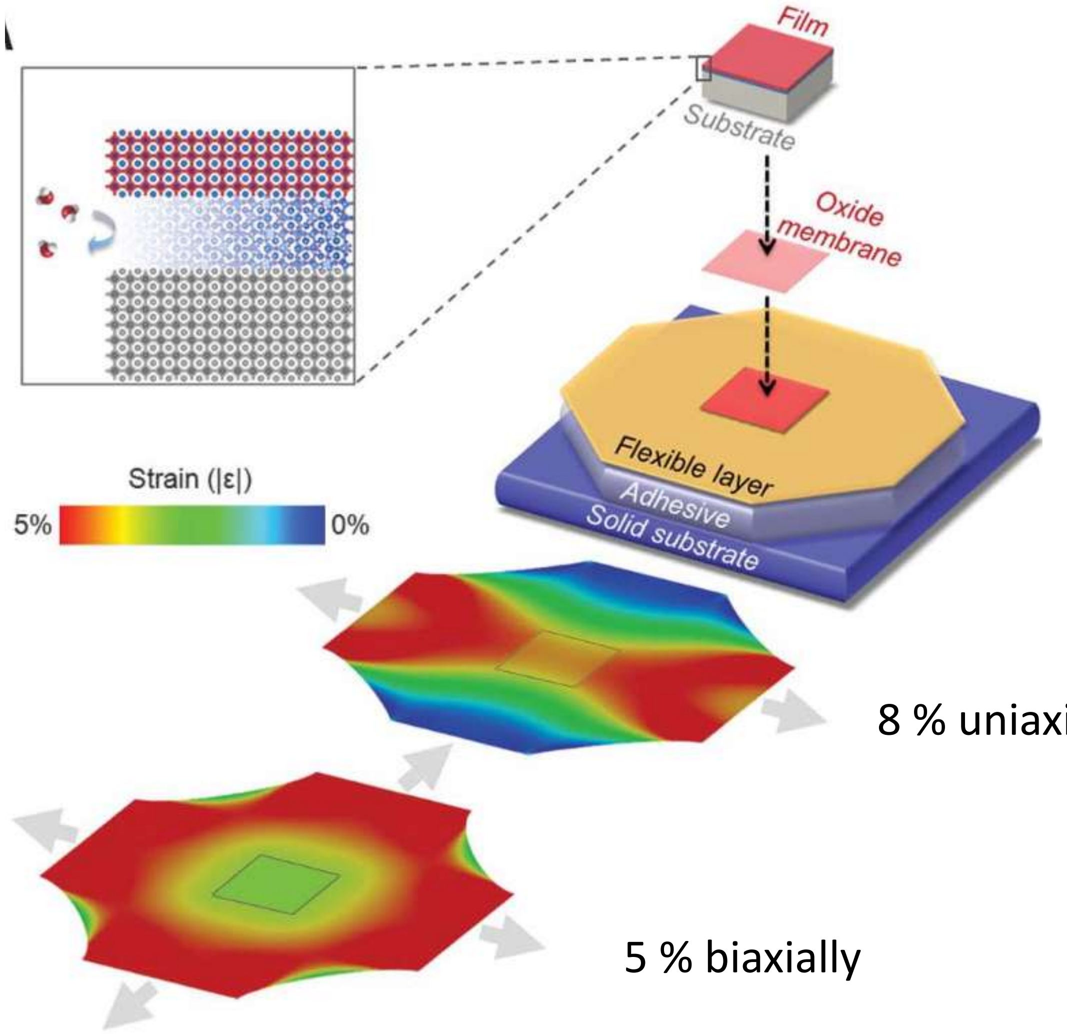
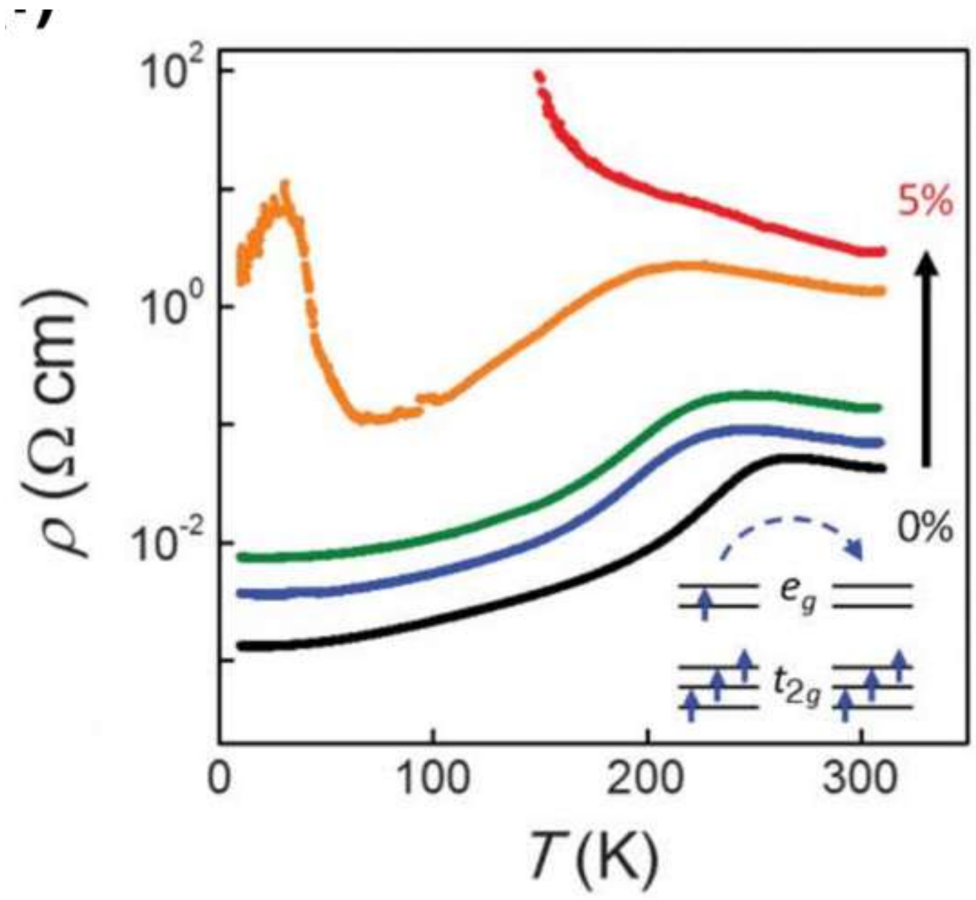
Extreme tensile strain states $La_{0.7}Ca_{0.3}MnO_3$:metallic vs insulating



8 % uniaxially

5 % biaxially

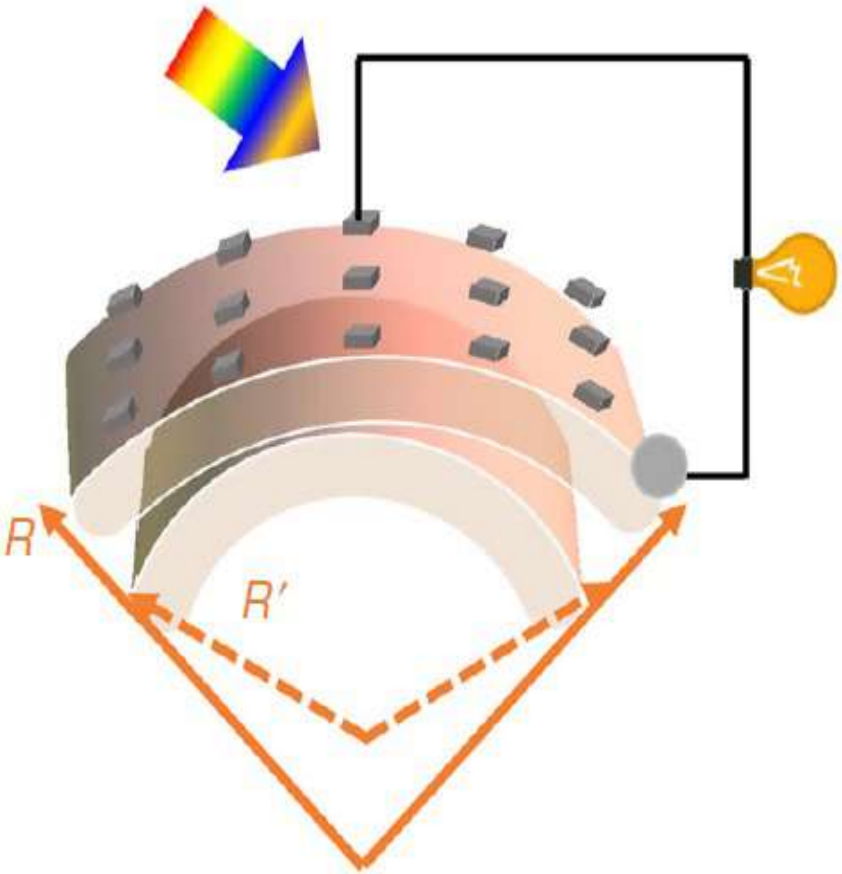


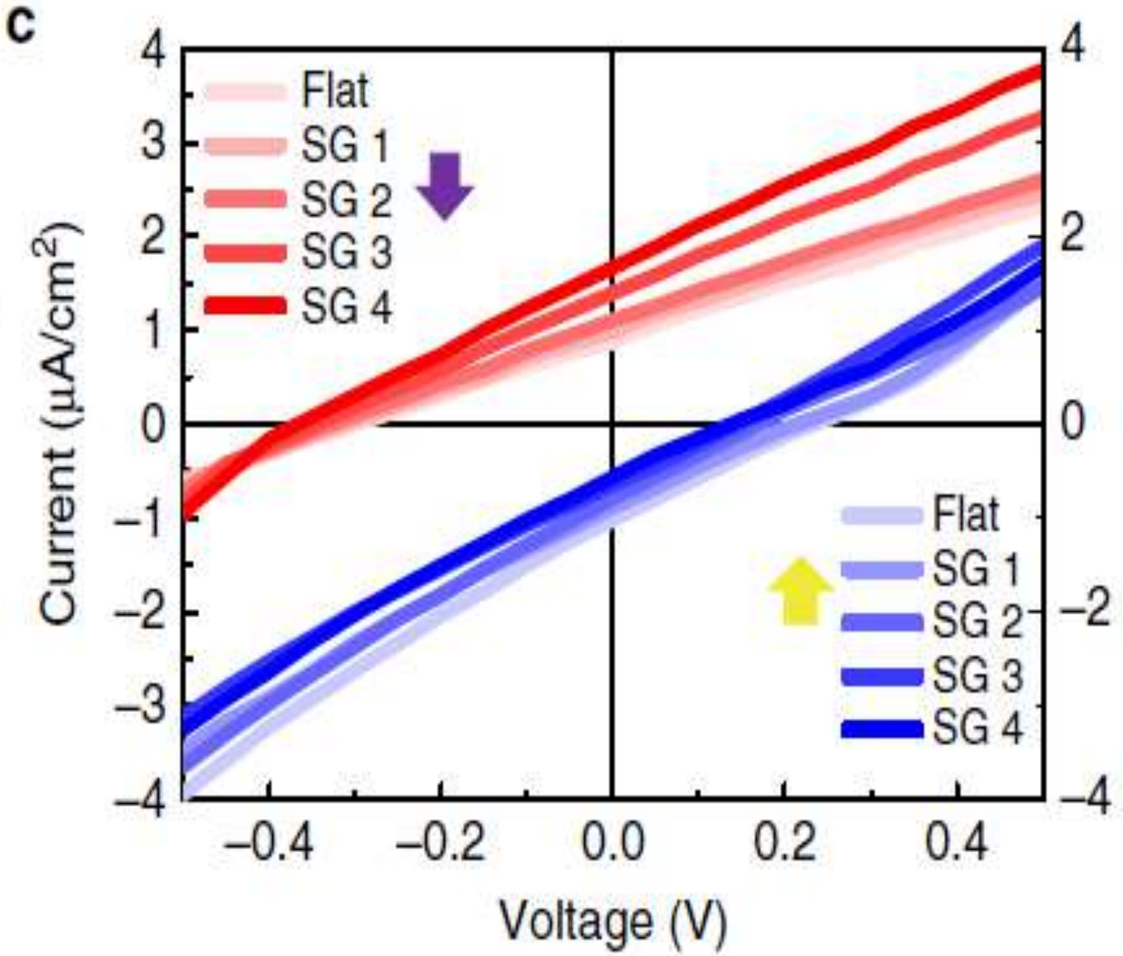
Hong et al. ,Science 368,71–76 (2020)

Offers opportunity to investigate how extreme strain affects properties

Novel functionalities in freestanding oxides

- Flexoelectricity by BFO bending: controllable photoconductance





non uniform lattice distortion--> strain gradient: multilevel photoconductance

R Guo *et al., Nat. Commun* **11**, 2571, 2020

Novel functionalities in freestanding oxides

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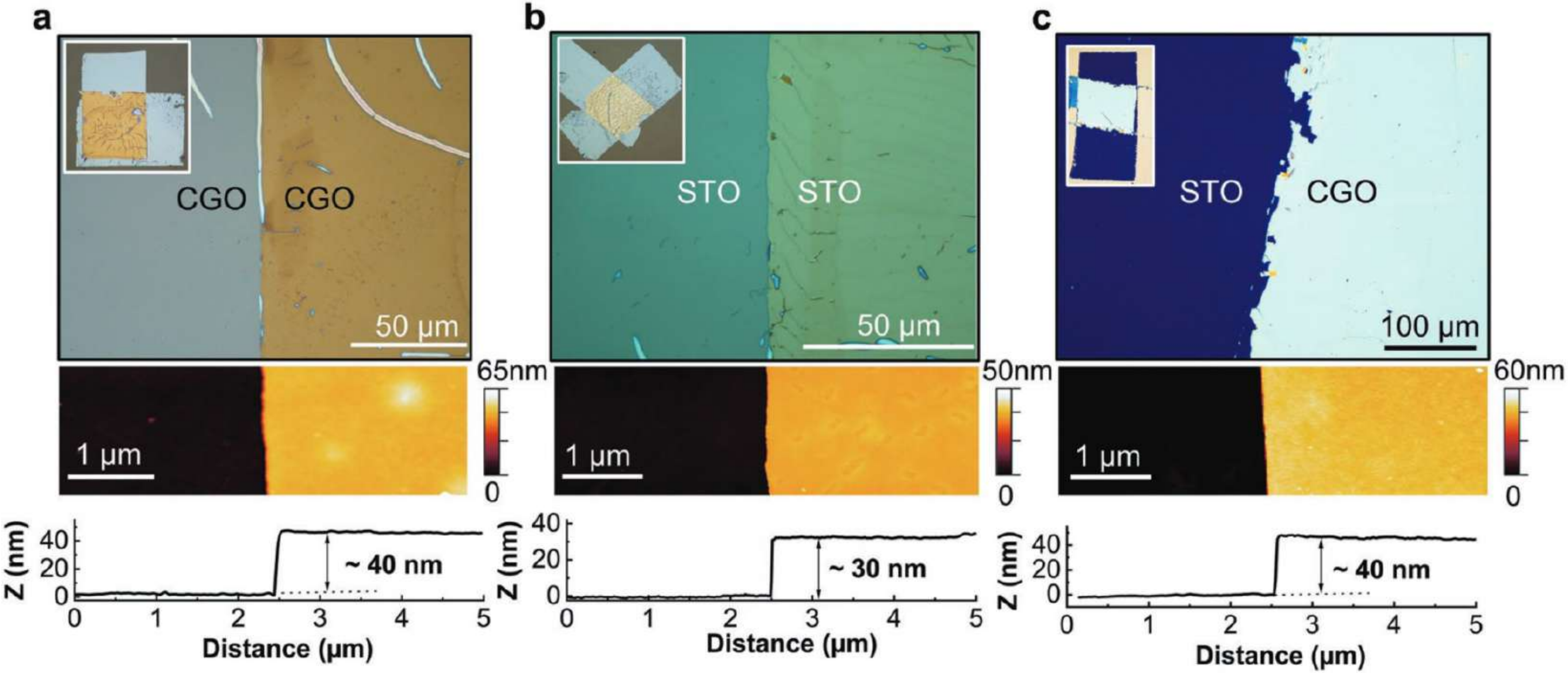
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

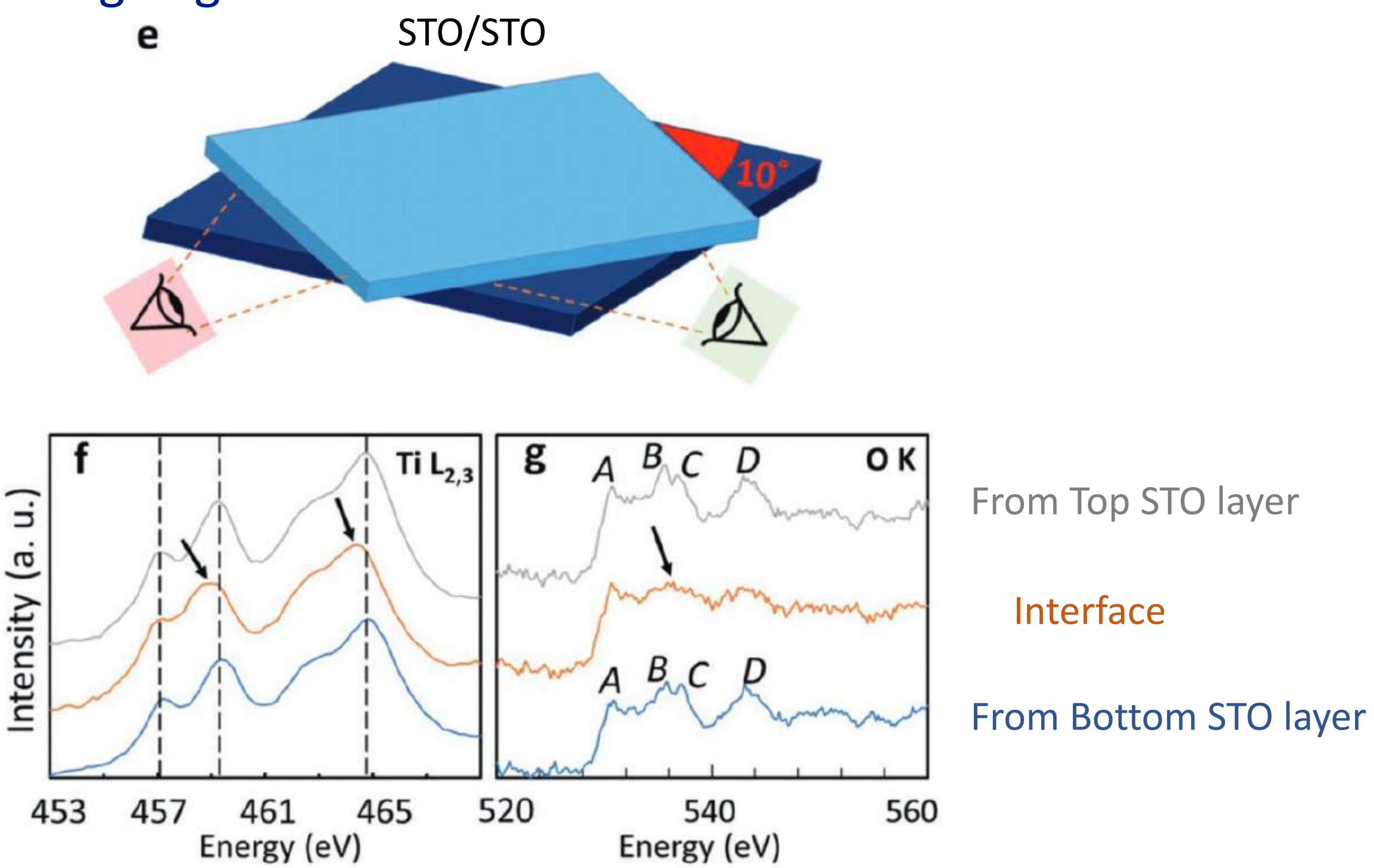
- Artificial interfaces+ twisting angle



Adv.Mater.2022, 34, 2203187

Novel functionalities in freestanding oxides

- Artificial interfaces+ twisting angle



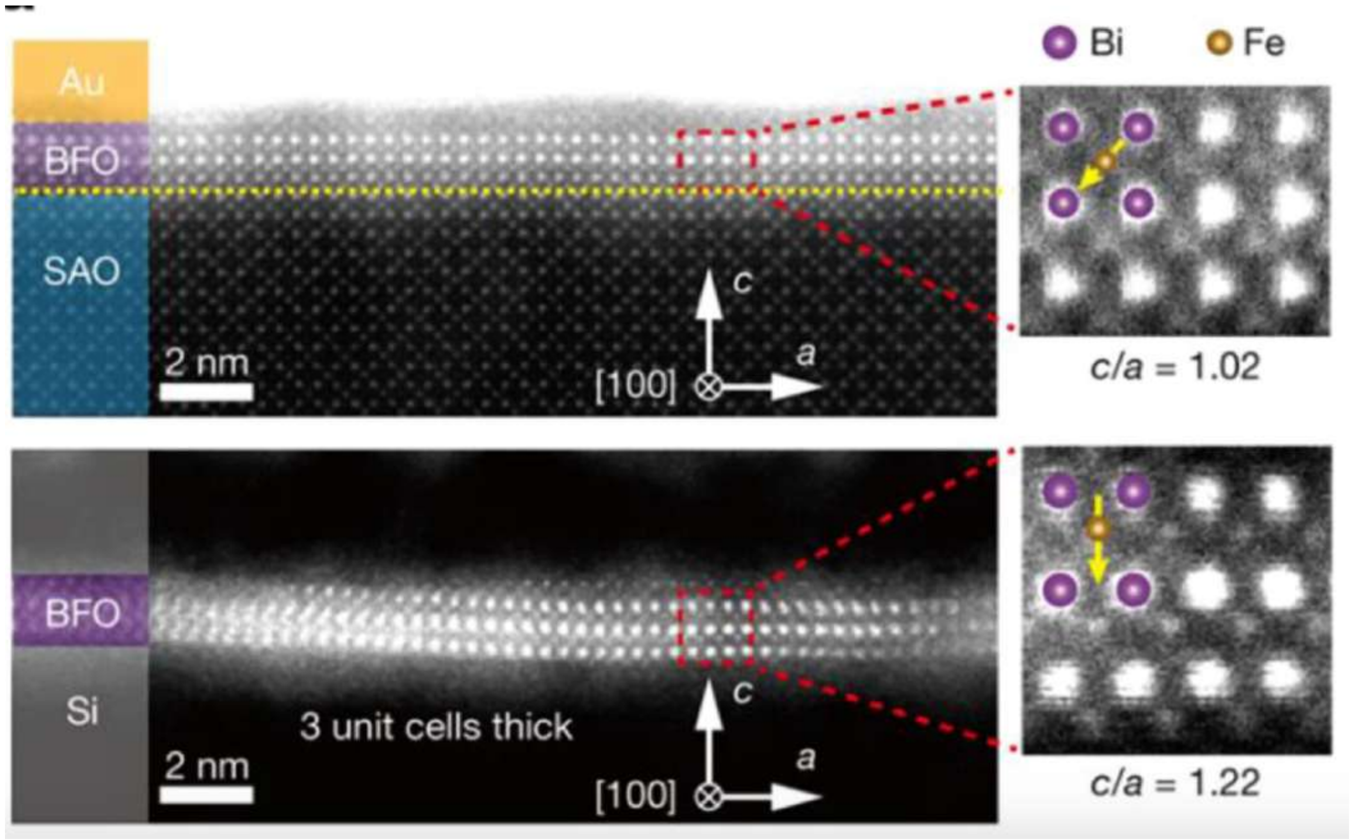
"twisting" yields anisotropic oxygen ion diffusion @ STO/STO stack with twist angle θ. Otherwise isotropic in bulk (001)-STO

Preference for oxygen vacancies--> strategy to manipulate diffusion properties of Vo in perovskite oxides

Adv.Mater.2022, 34, 2203187

Novel functionalities in freestanding oxides

- Approaching the monolayer limit



Rhombohedral

clamping effect removed

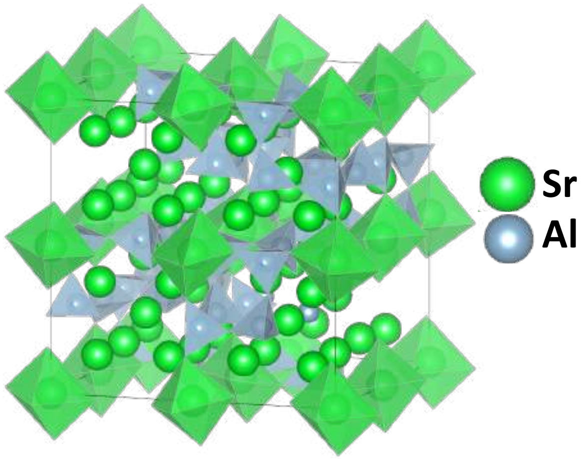
P_{op} = 140 μC/cm^2

Enhanced tetragonality

*D. Ji et al. Nature **2019**,570, 87*

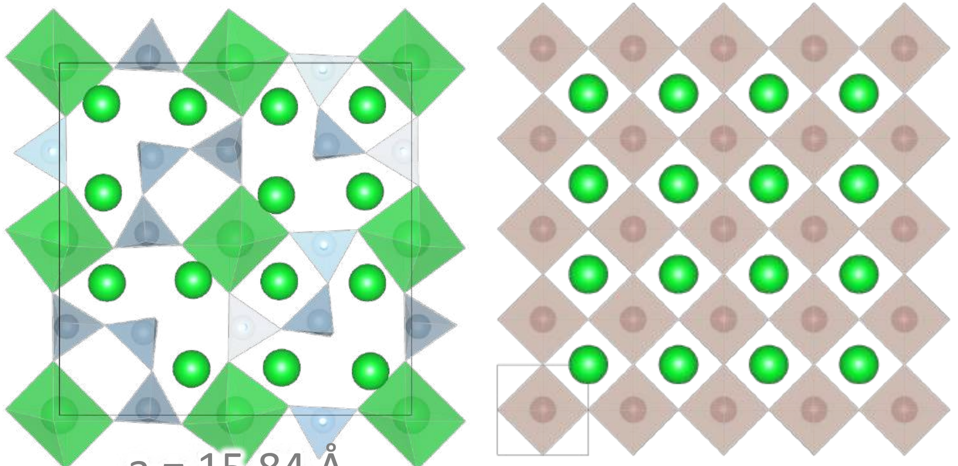
$Sr_3Al_2O_6$ (SAO) as sacrificial layer

- ✓ Similar cell parameters to $SrTiO_3$, $La_{0.7}Sr_{0.3}MnO_3$, $BiFeO_3$,… (epitaxial growth)
- ✓ Dissolved in **H_2O** (non-toxic, low-cost, soft)
- ✓ High versatility



Pseudo-perovskite structure

$Sr_3Al_2O_6$ 4 x 4 $SrTiO_3$



a = 15.84 Å

D Lu *et al.*, *Nat. Mater.* **15**, 1255–1260, 2016

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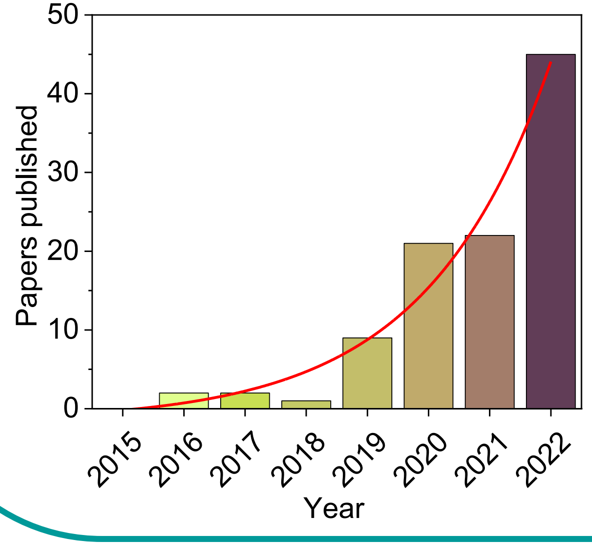
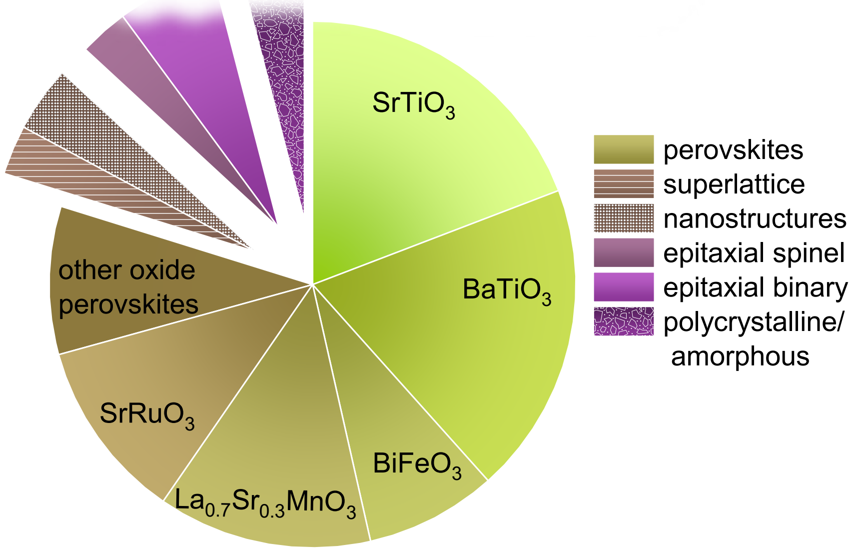
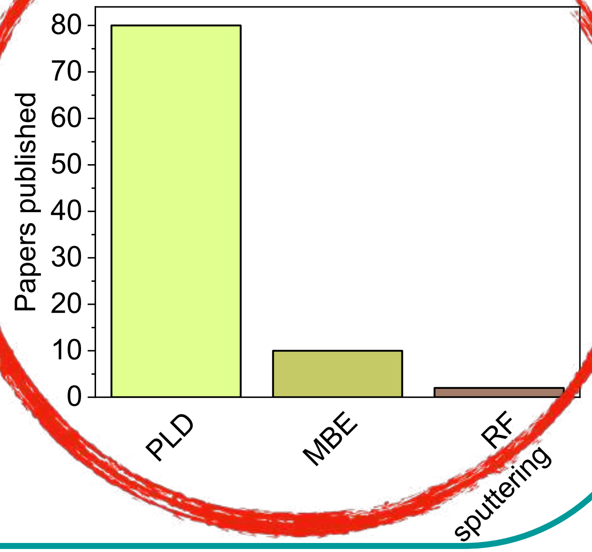


Freestanding epitaxial oxide structures



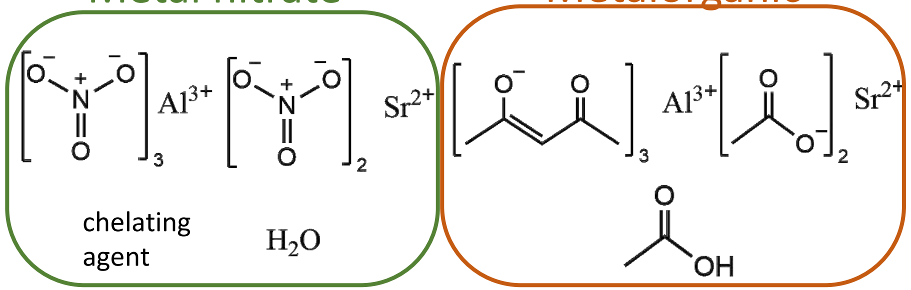
High-vacuum deposition techniques

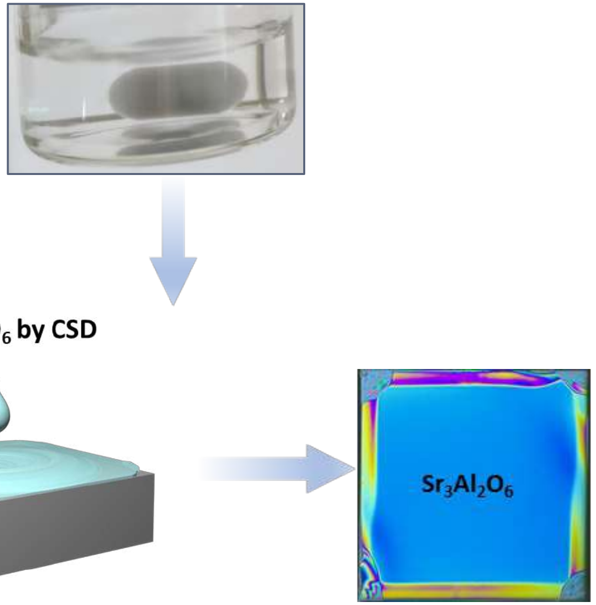


$Sr_3Al_2O_6$ by chemical methods

Pol Sallés

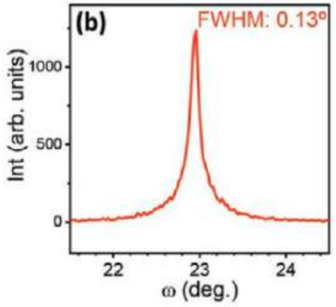
Metal nitrate / Metalorganic



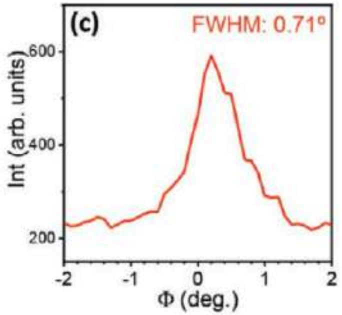


- Metal nitrate vs. metalorganic precursors
- Solvents (H_2O, acetic acid)
- Chelating agent

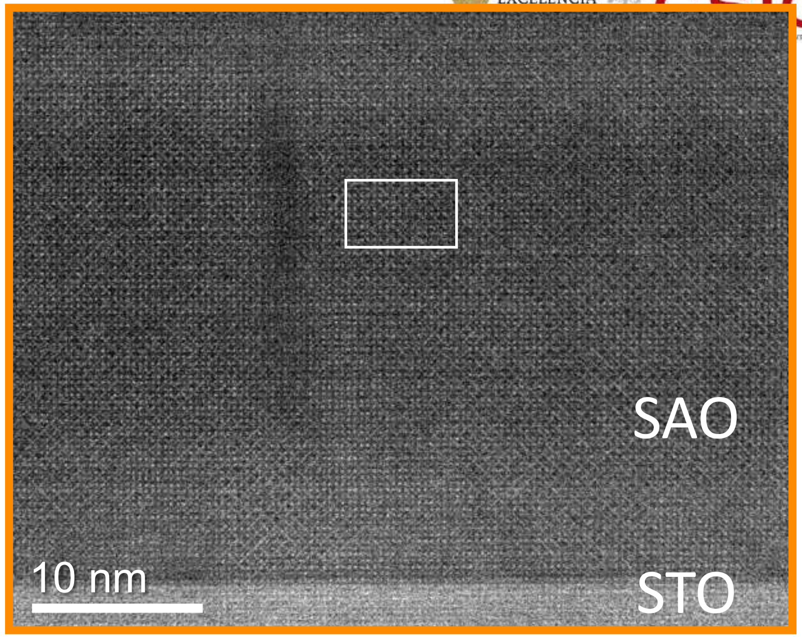
$\Delta\omega$ (008)SAO

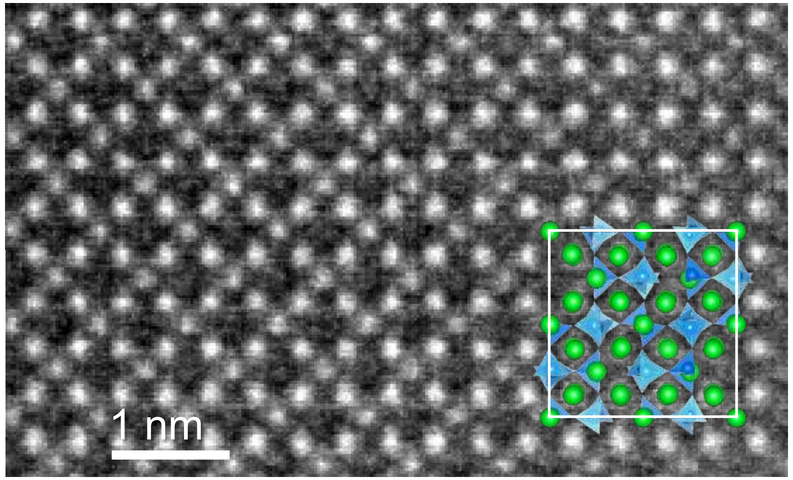


$\Delta\theta$(660)SAO



Epitaxial growth - HR-TEM cross-section





P. Salles, I. Caño, M. Coll et al. Adv. Funct. Interfaces, 2001643 (2021)

Outline

- Why free-standing oxides

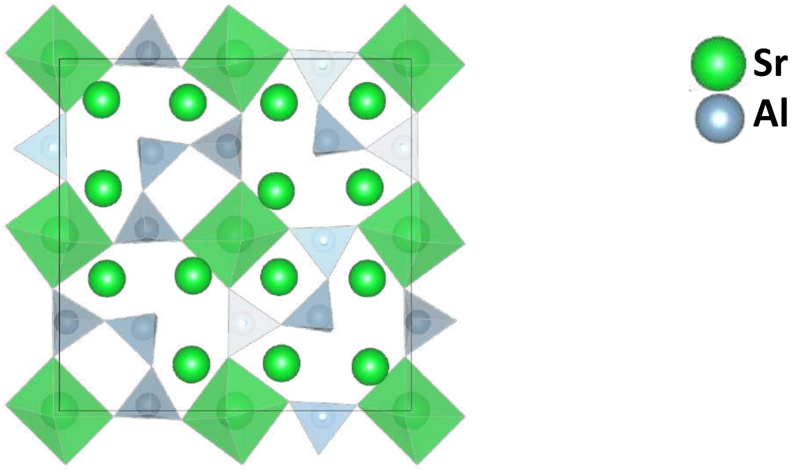
- Preparation of free-standing oxides

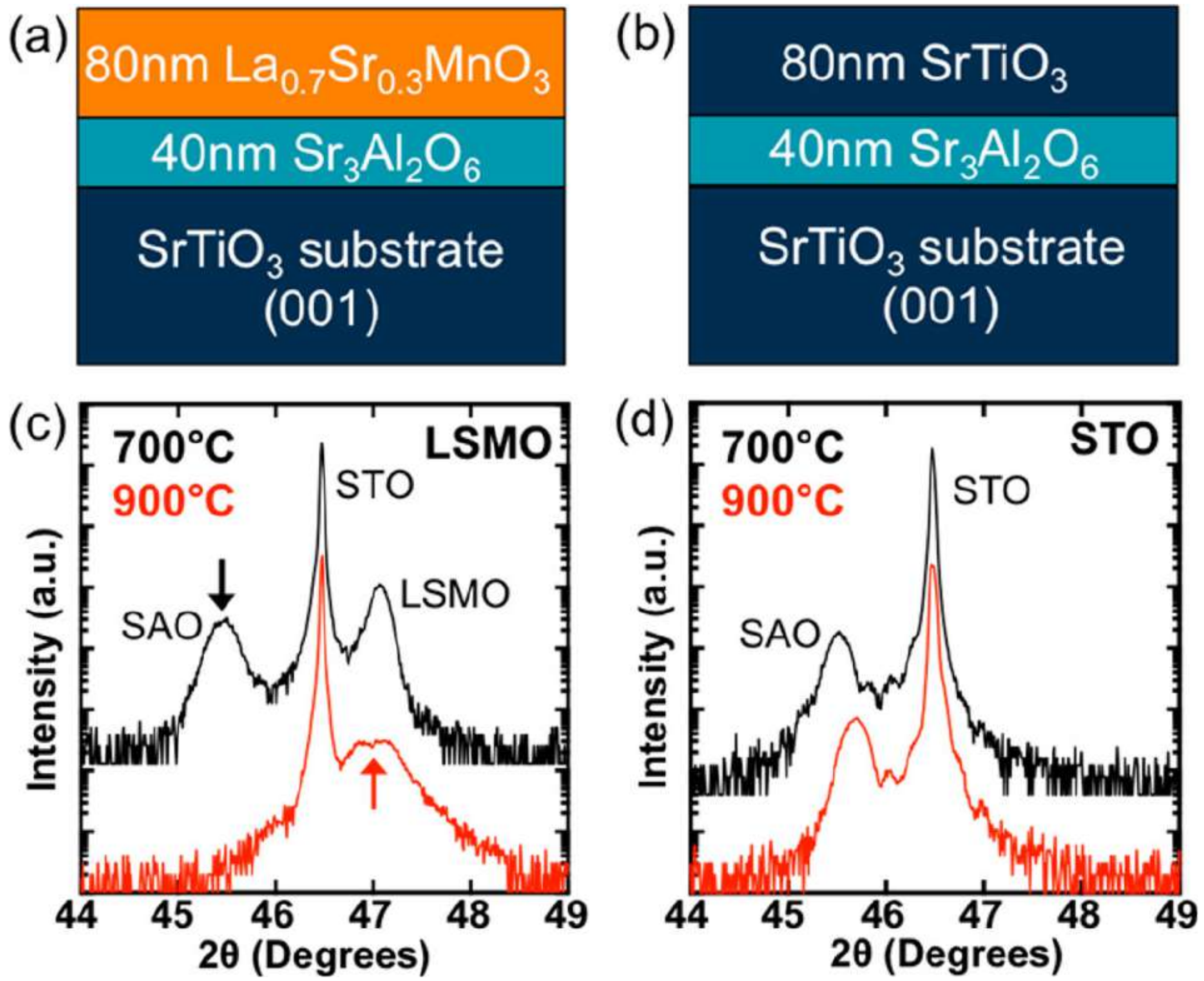
- **Challenges in the preparation**

  Oxide/Sacrificial interface
  Exfoliation

- Outlook/ perspective

Challenges : Oxide/ SAO interface



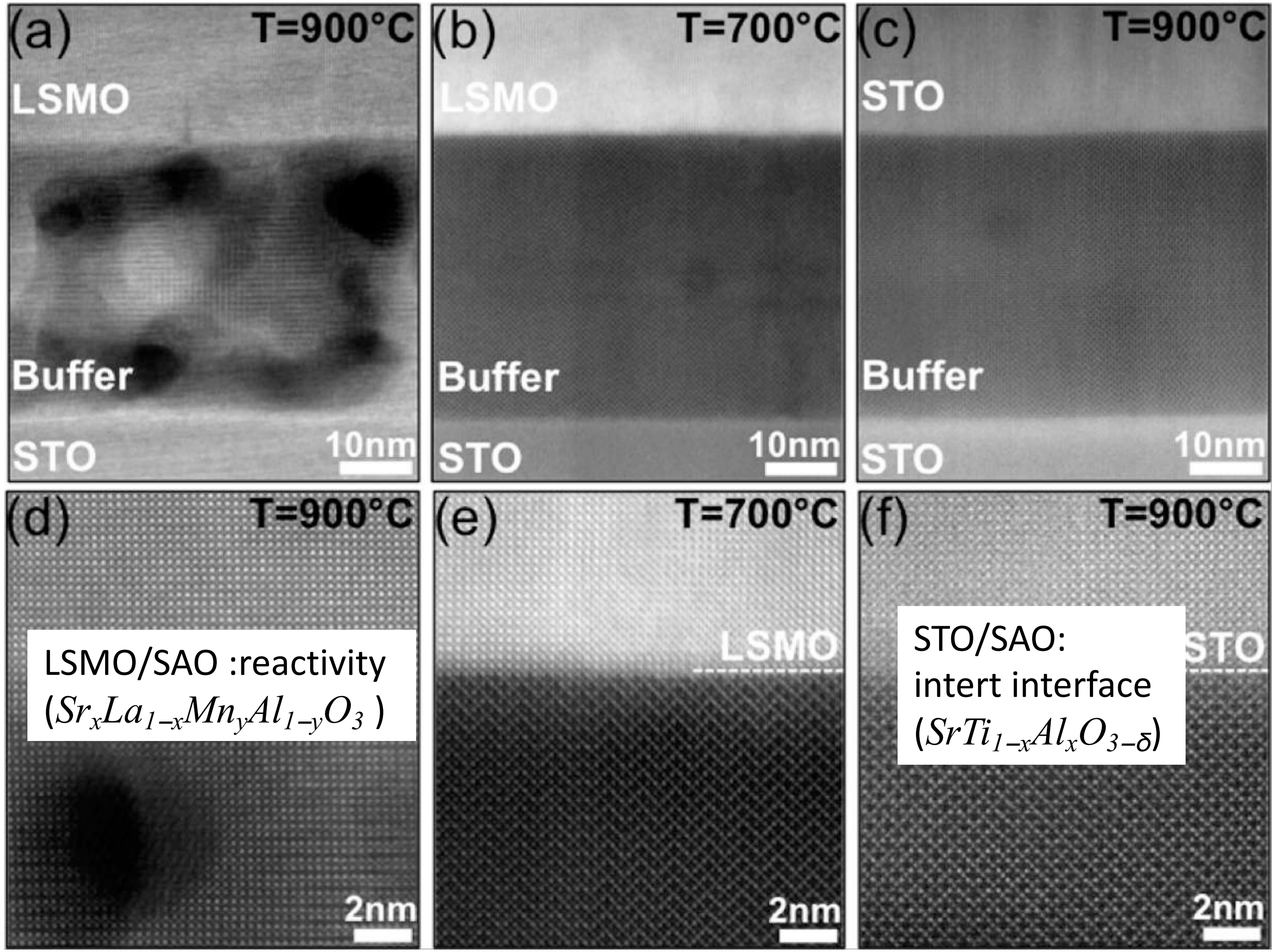


Temperature + composition

Adv. Mater. Interfaces, 2017, **4**, 1700155

ACS Appl. Mater. Interfaces 2017, 9, 1, 54–59

Challenges : Oxide/ SAO interface



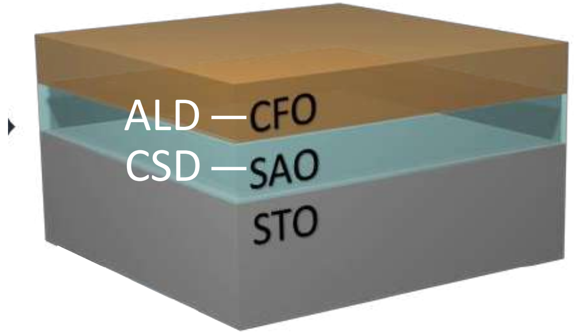
LSMO/SAO :reactivity
($Sr_xLa_{1-x}Mn_yAl_{1-y}O_3$)

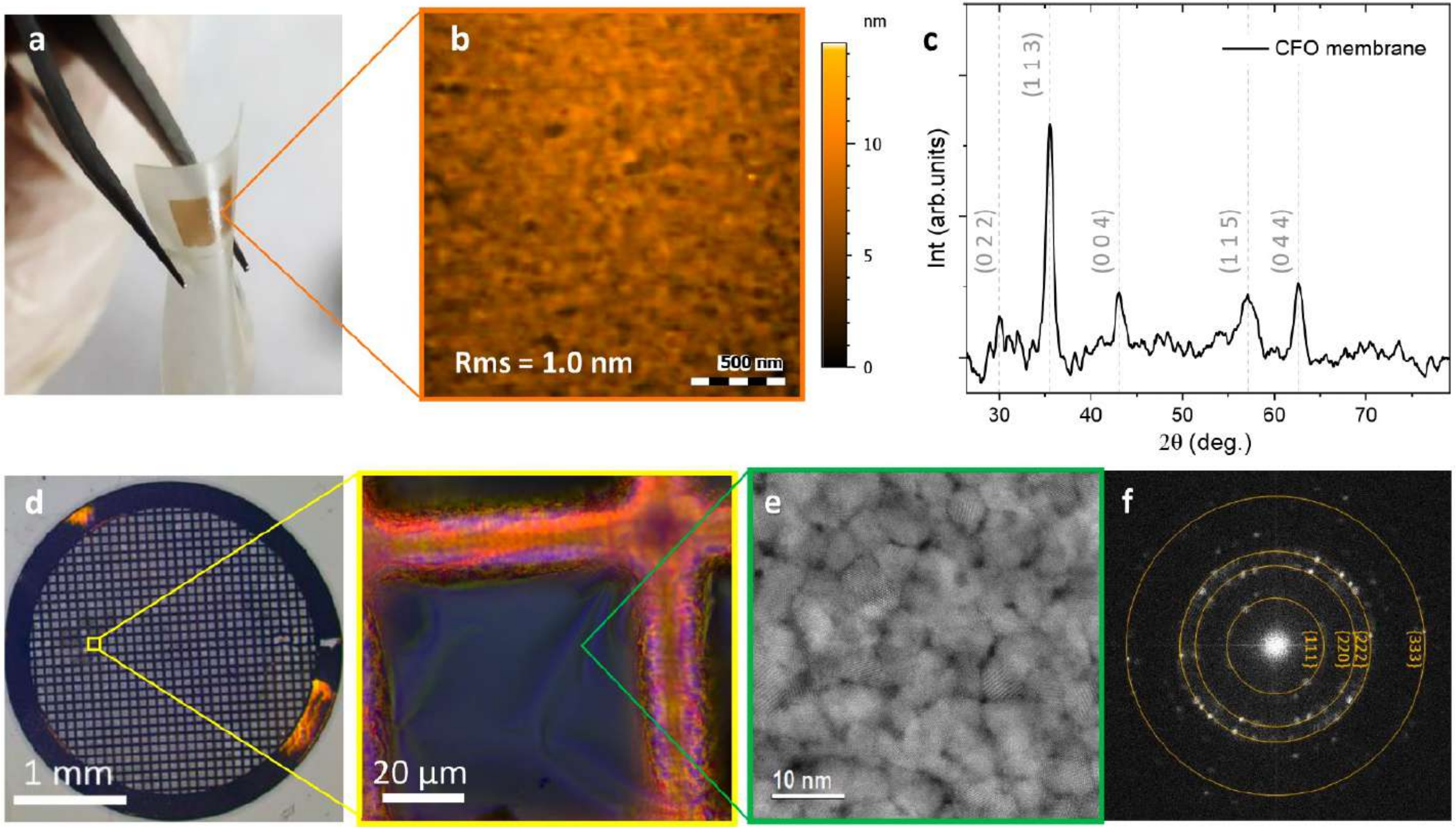
STO/SAO:
intert interface
($SrTi_{1-x}Al_xO_{3-\delta}$)

ACS Appl. Mater. Interfaces 2017, 9, 1, 54–59

Challenges : Oxide/SAO interface

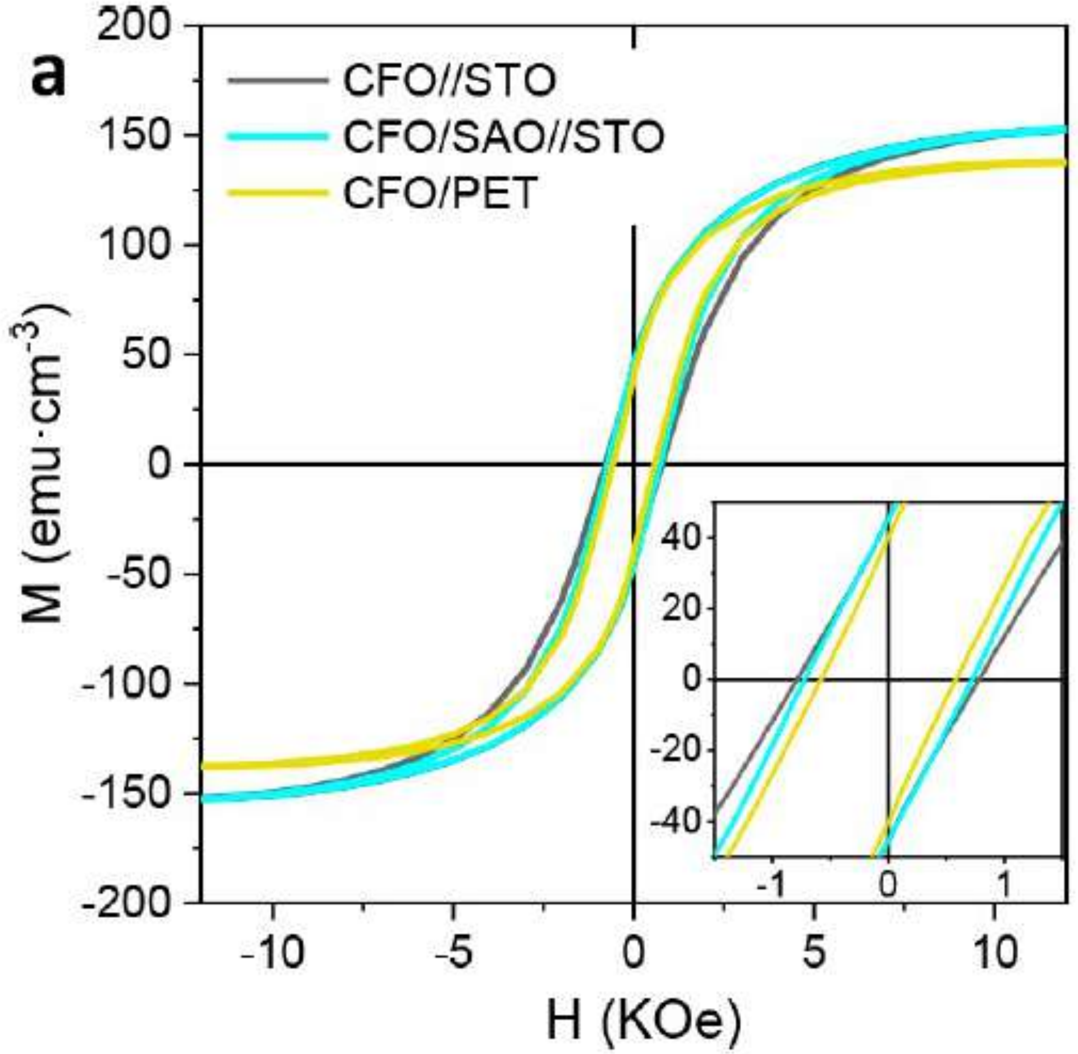
Bendable Polycrystalline and Magnetic $CoFe_2O_4$ Membranes : all chemical





P. Salles, MC et al. ACS Appl. Mater. Interfaces 2022, 14, 12845−12854

Bendable Polycrystalline and Magnetic $CoFe_2O_4$ Membranes



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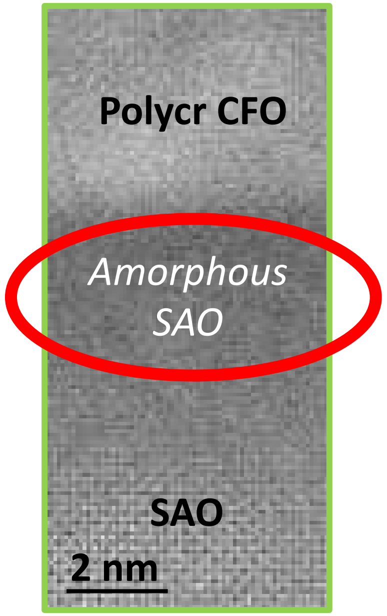
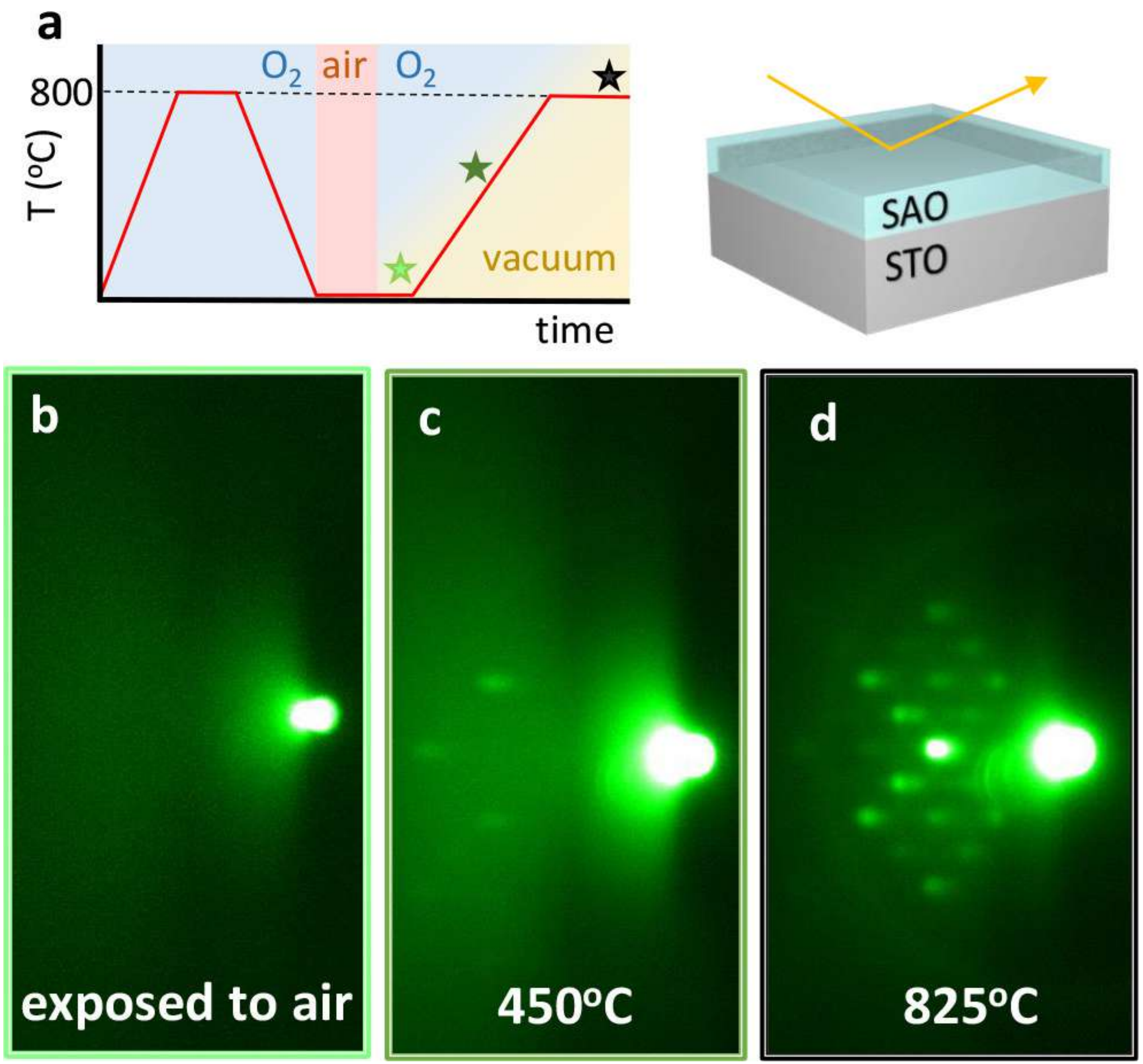
Challenges : Oxide/SAO interface

Exposure to air/humidity



annealing in vacuum

Recover crystallinity

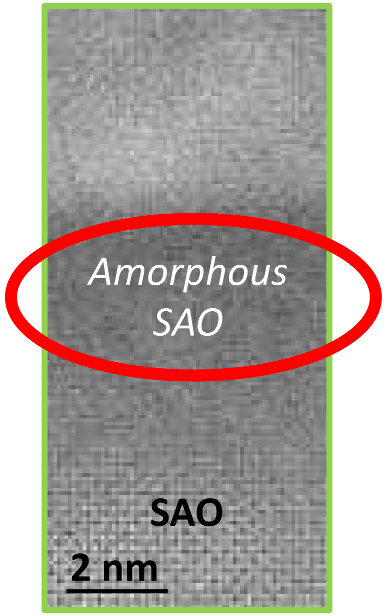


P. Salles, MC et al. ACS Appl. Mater. Interfaces2022, 14, 12845−12854

Challenges : Oxide/SAO interface

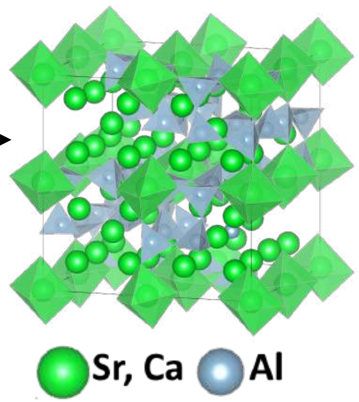
Cation engineering in SAO

Cation	Electronegativity	Ionic radius (pm)	a (Å)	a/4 (Å)
Sr^{2+}	0.95	132	15.84	3.96
Ca^{2+}	1.00	114	15.26	3.81



Cation engineering the sacrificial layer:

$Sr_{3-x}Ca_xAl_2O_6$ (SC_xAO)

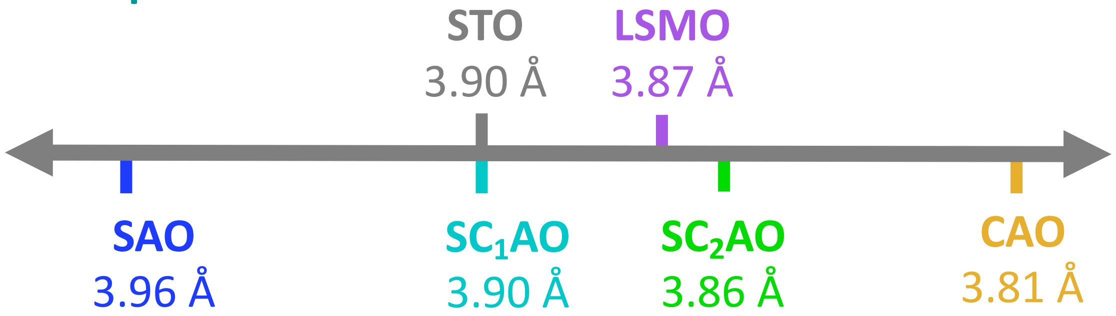


Reactivity with H_2O

Al - O : covalent bond

Sr, Ca - O : Ionic bond

Lattice parameters

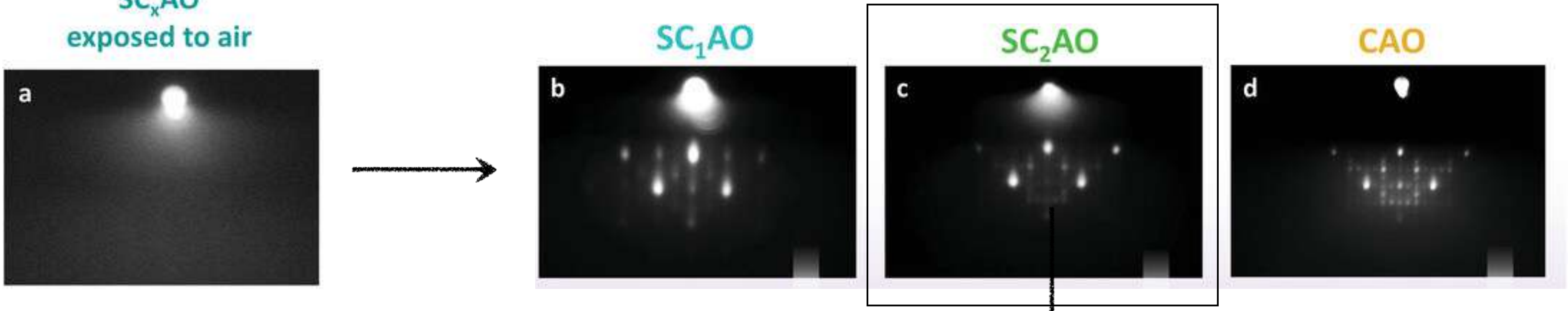


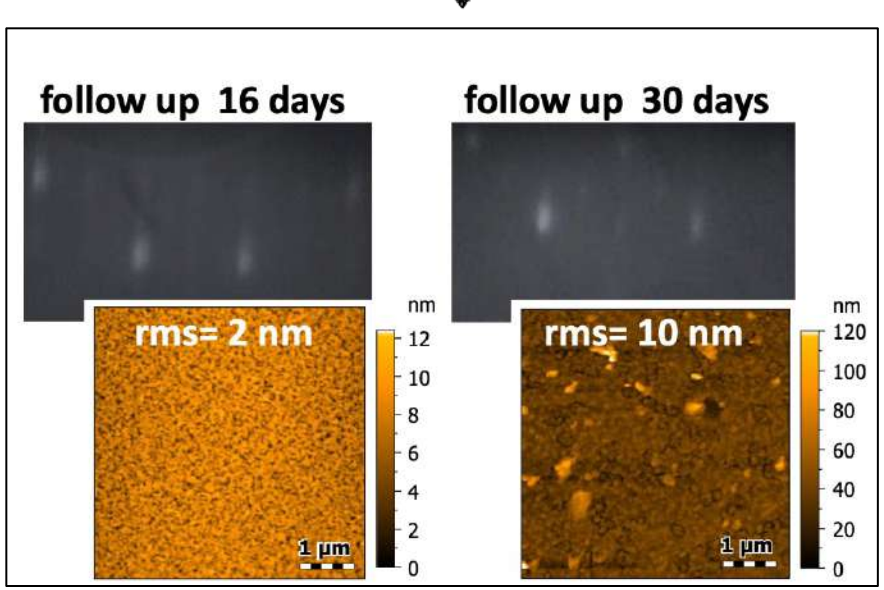
P Salles, MC *et al.*, *Advanced Functional Materials* **2023**. *2304059*

Challenges : Stability of SAO

Cation engineering

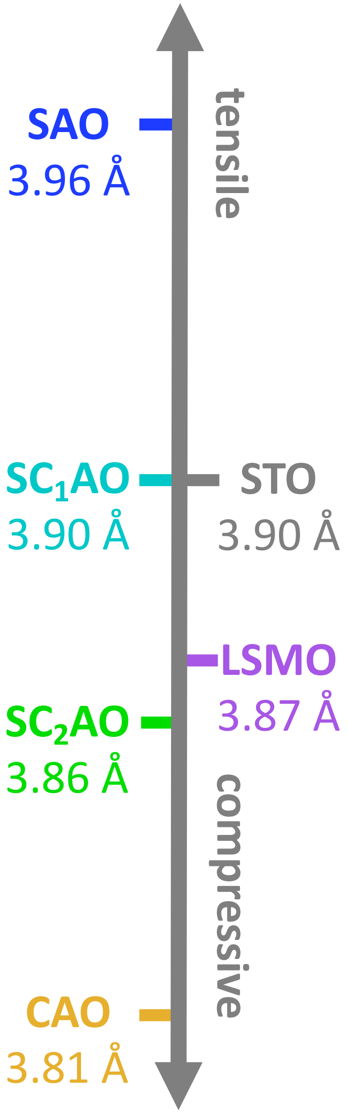
SC_xAO
exposed to air

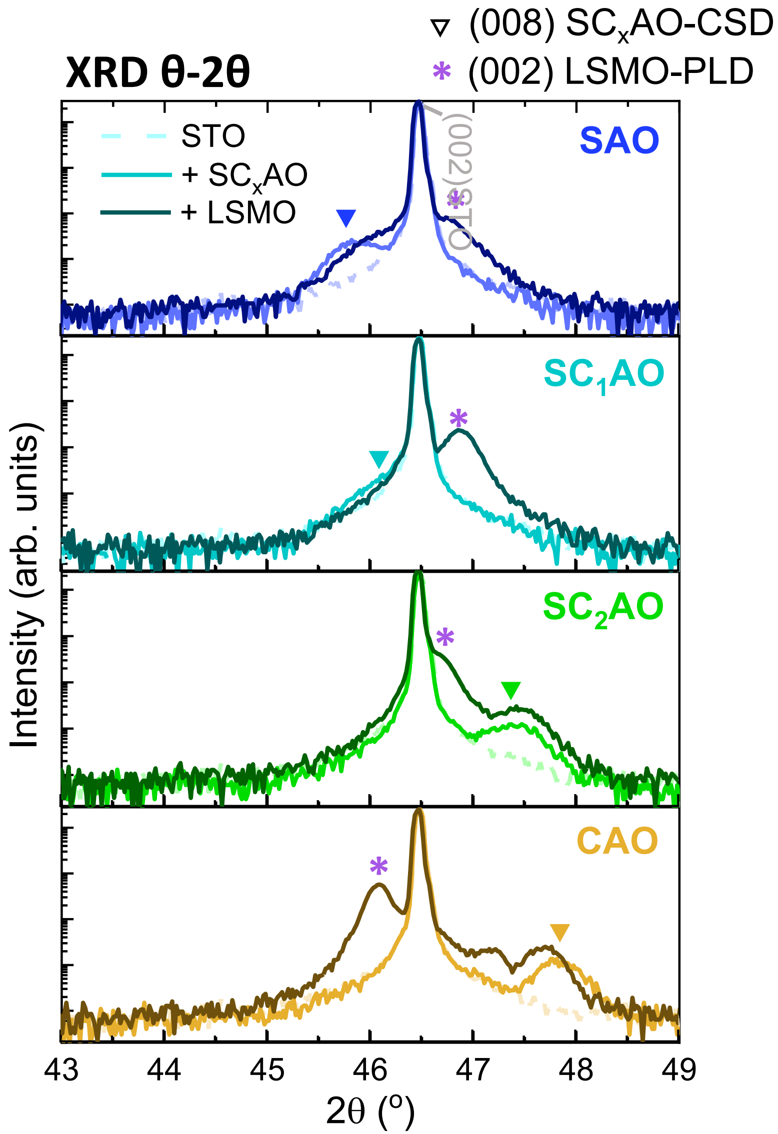


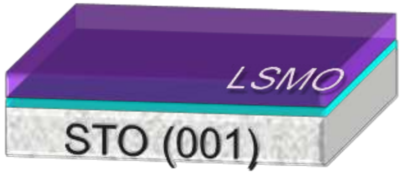


Adv. Funct. Mater.2023, 2304059

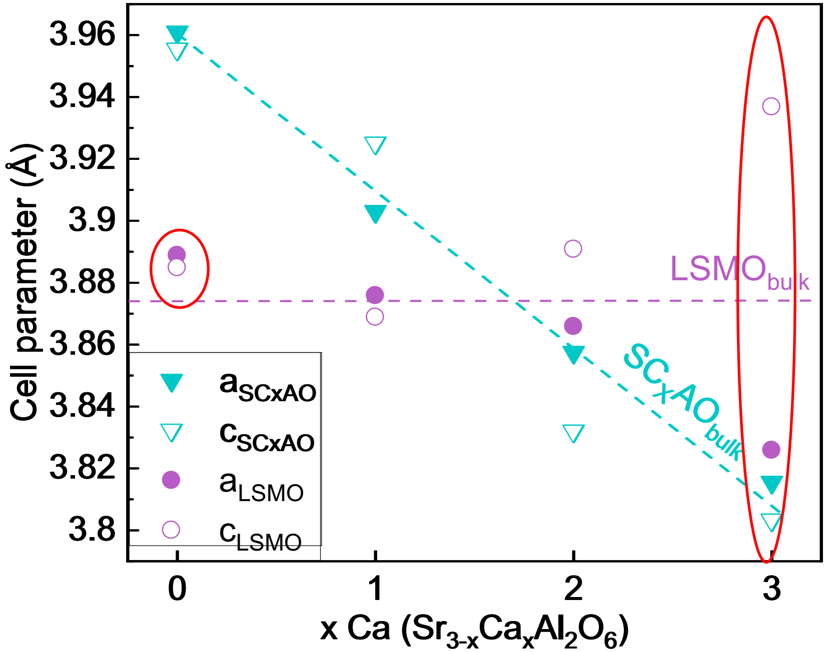
LSMO/SC_xAO//STO: XRD structure analysis







Lattice parameters from Reciprocal Space Map (RSM)



- Relaxed LSMO grown on SAO and SC_1AO
- In-plane compressive strain for LSMO grown on SC_2AO and CAO

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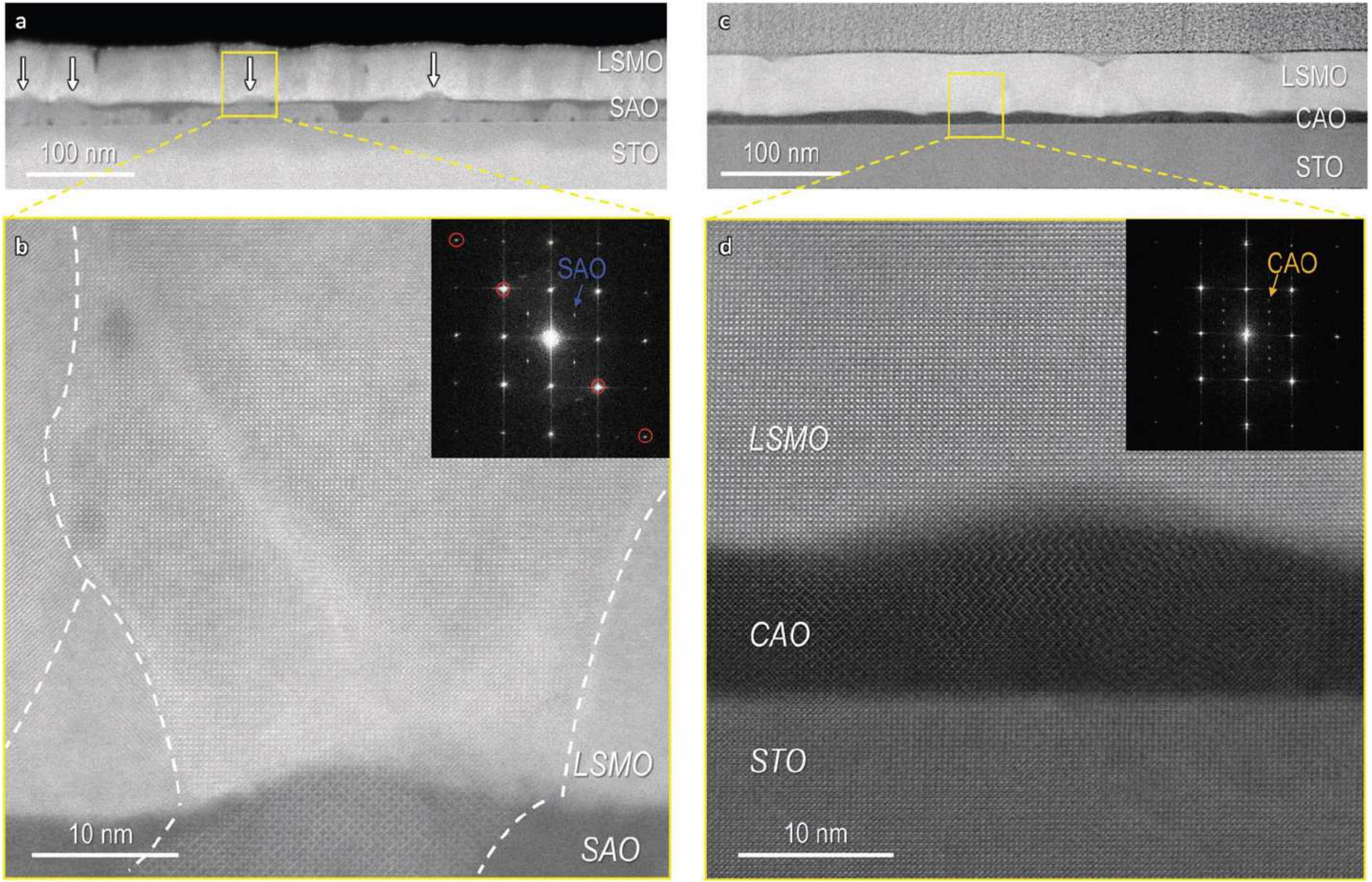

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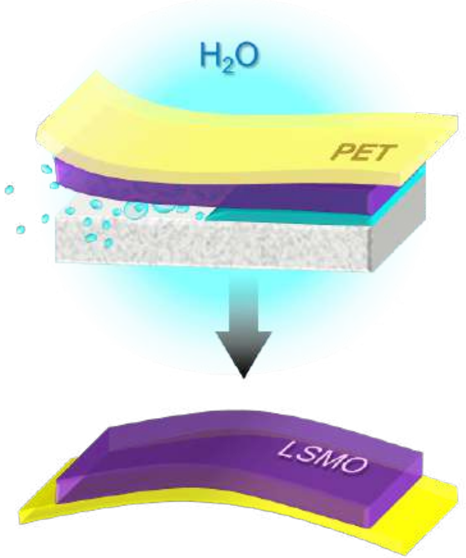
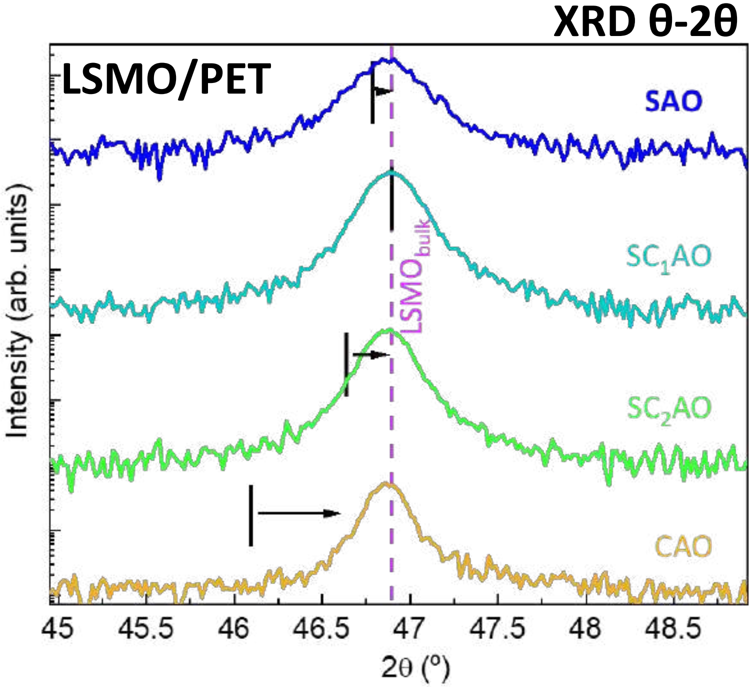
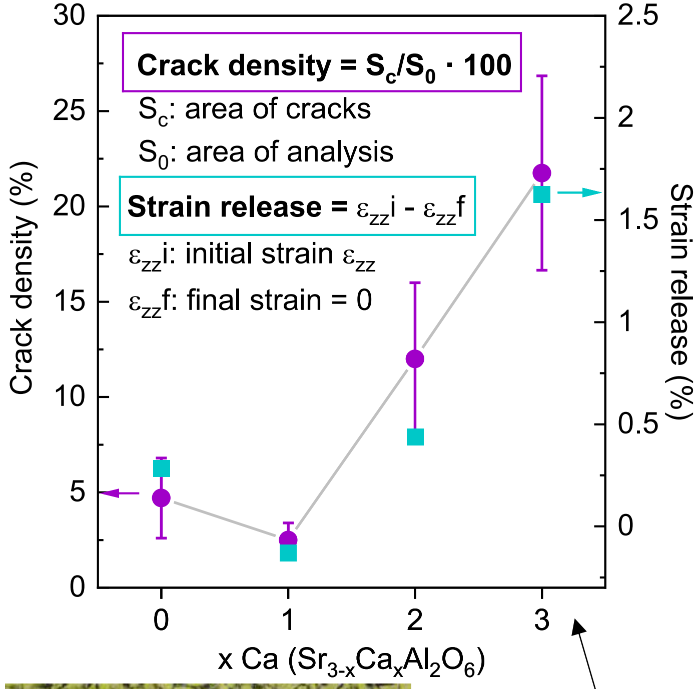
LSMO membranes on PET: strain release

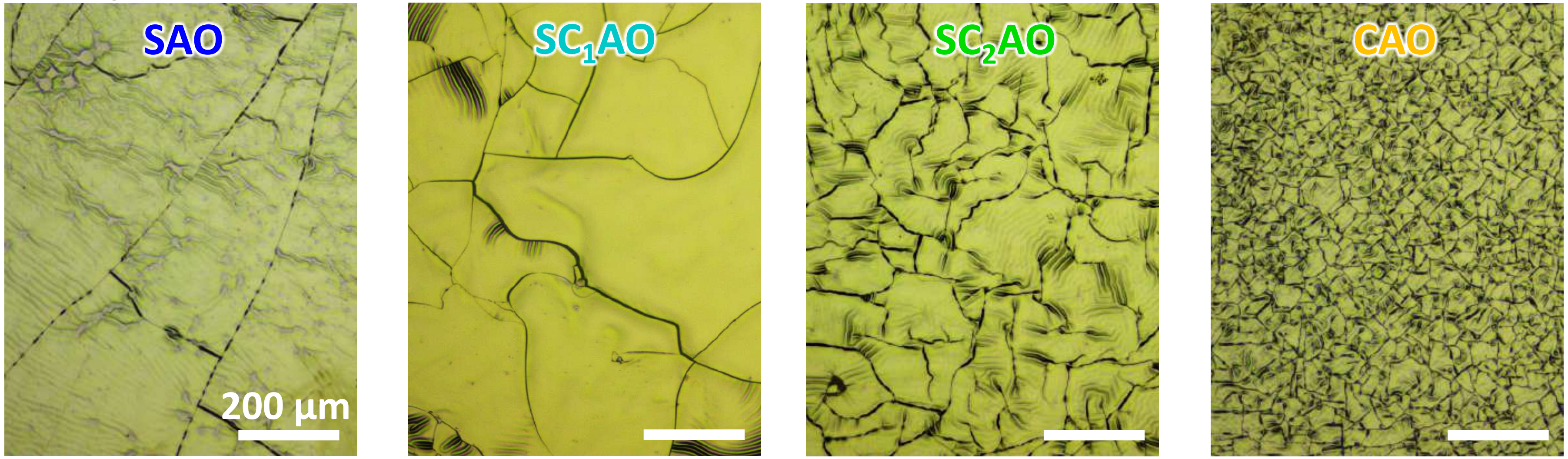






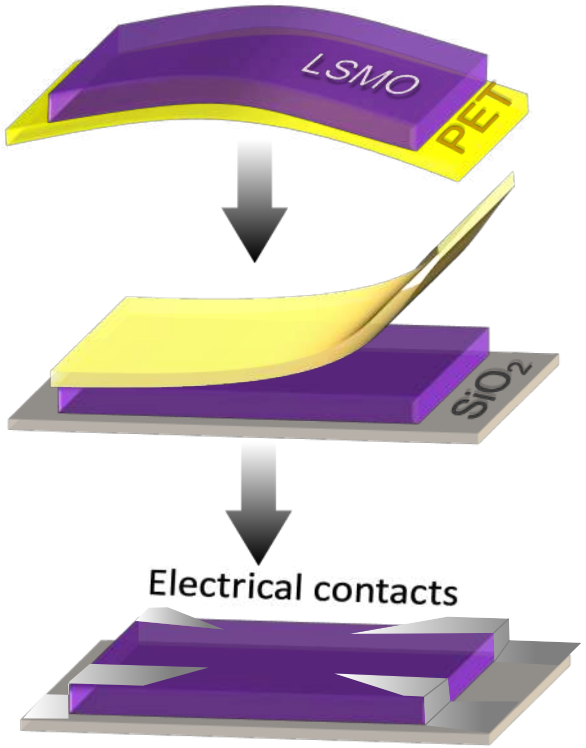
Crack density ∝ strain released

LSMO/PET

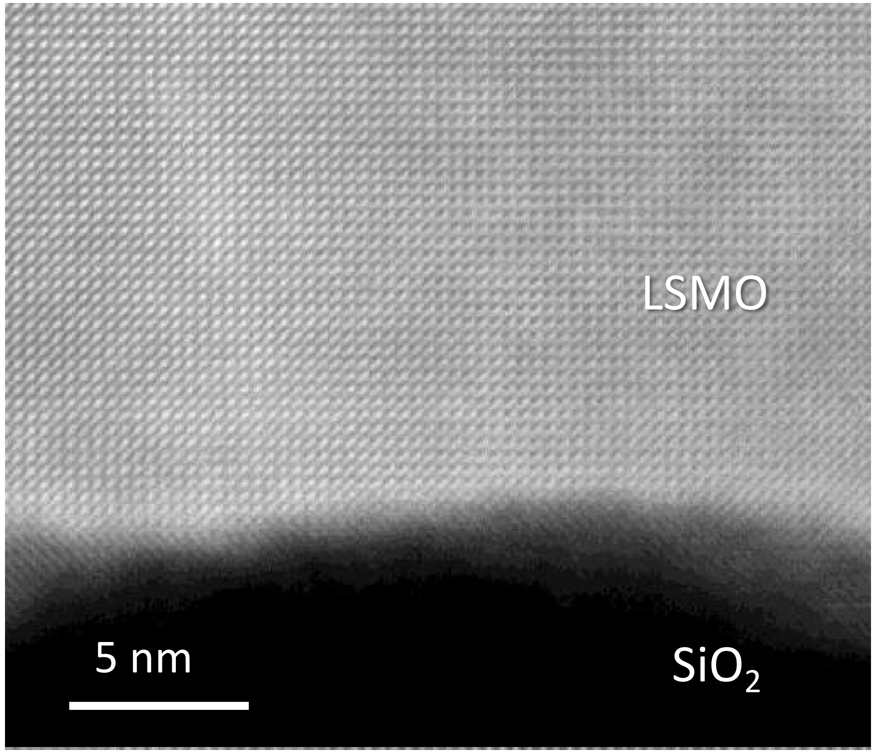


P Salles, MC *et al.*, *Advanced Functional Materials* **2023**. *2304059*

LSMO electrical transport ρ(T)



STEM cross-section



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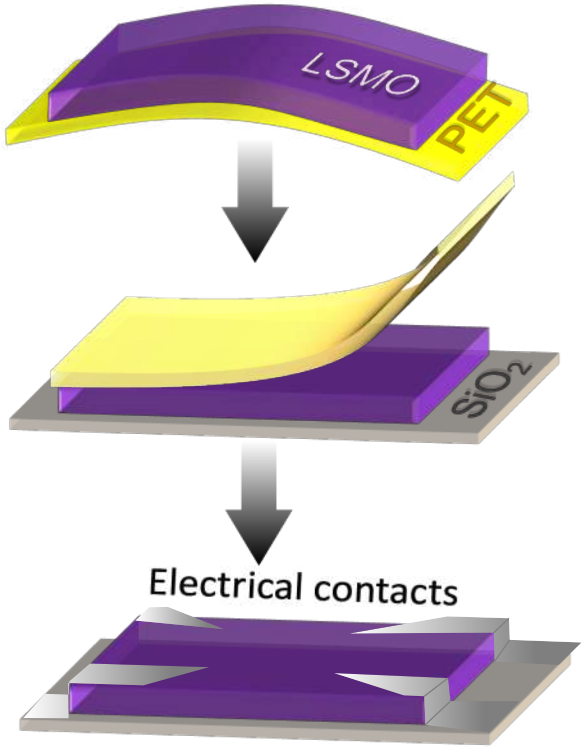
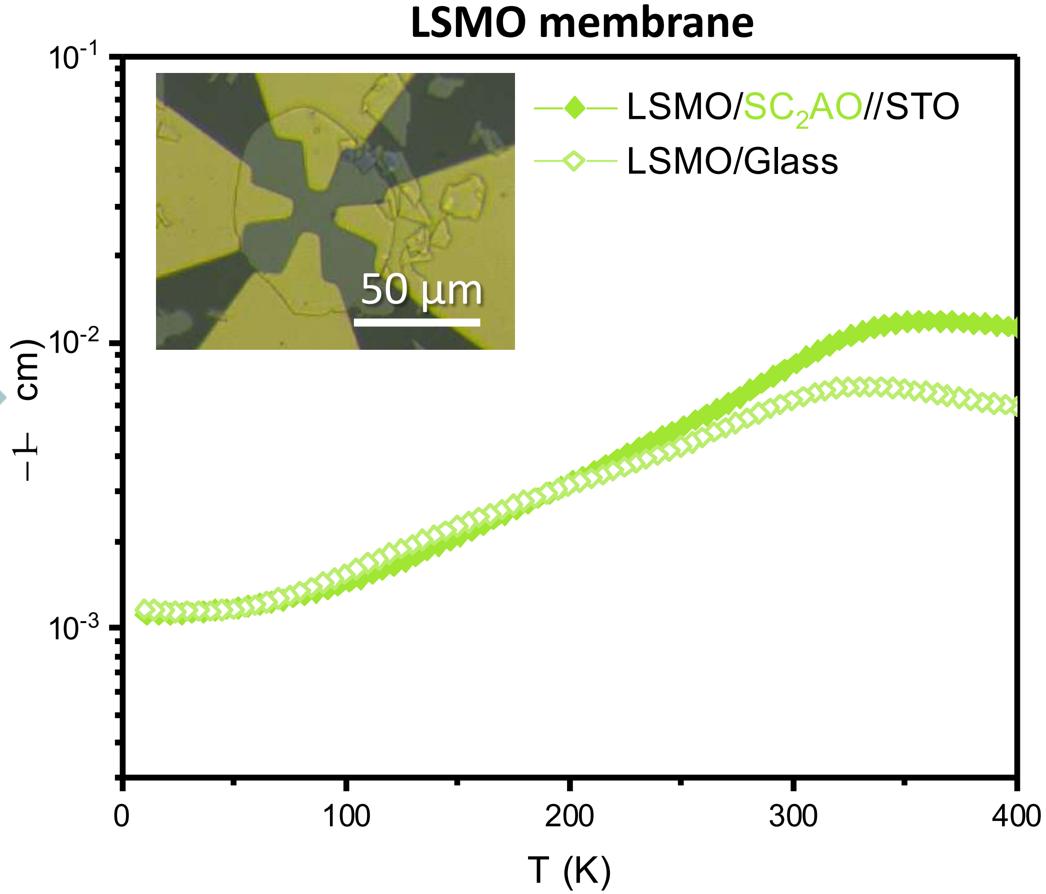
LSMO electrical transport ρ(T)





- ρ(T) of LSMO membrane presents small variations after release.

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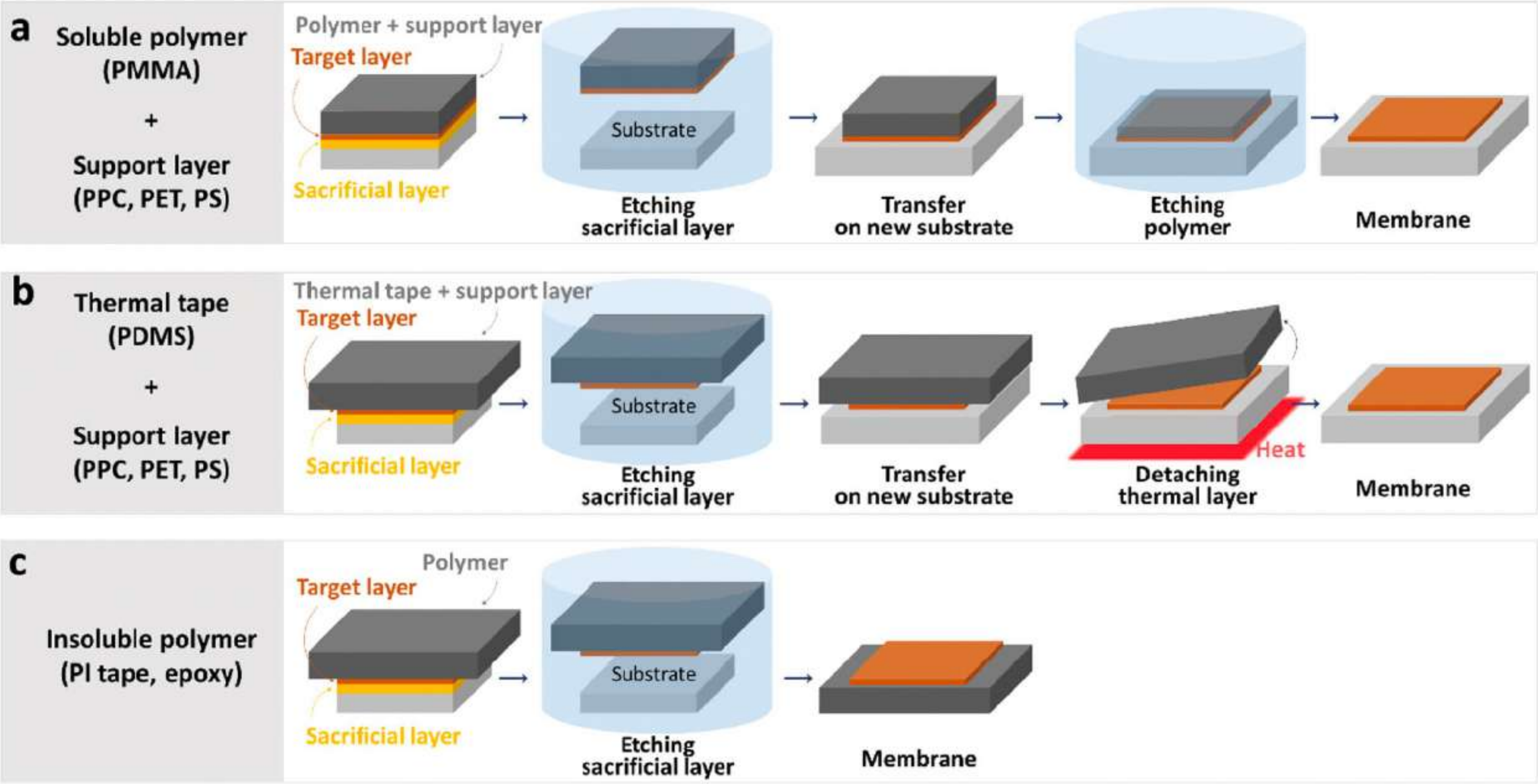
Challenges : Exfoliation



Solvents
Not easy to fully eliminate polymers
Polymer cellulose (CAB) might be an alternative

Residues and cracks might be introduced

Cannot be transferred to another platform

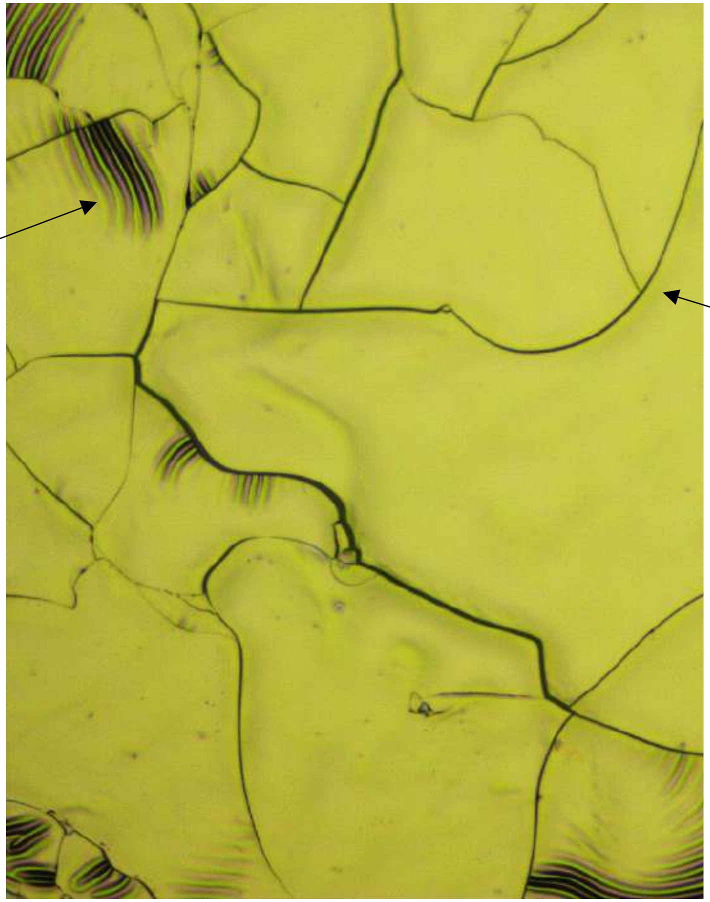
Ann. Phys. (Berlin) 2022, 534, 2200084

Zhang, J.L. MacManus-Driscoll et al. Nano-Micro Lett. (2021) 13:39

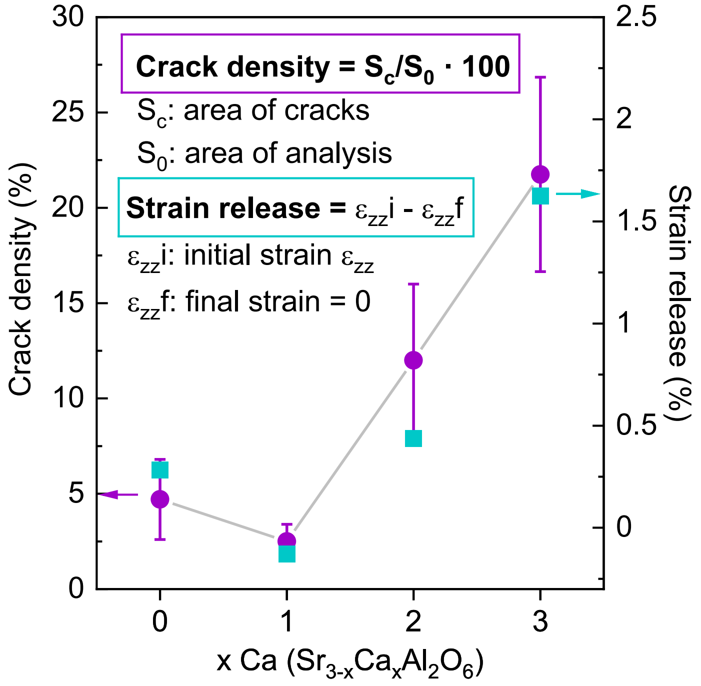
Challenges : Exfoliation

Typical defects

wrinkles



cracks

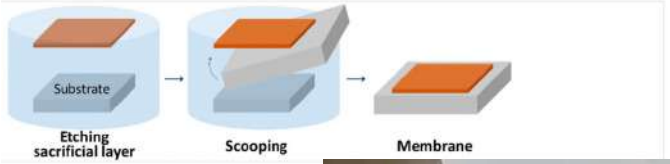


attributed to the stress during the releasing of the sup-port layer

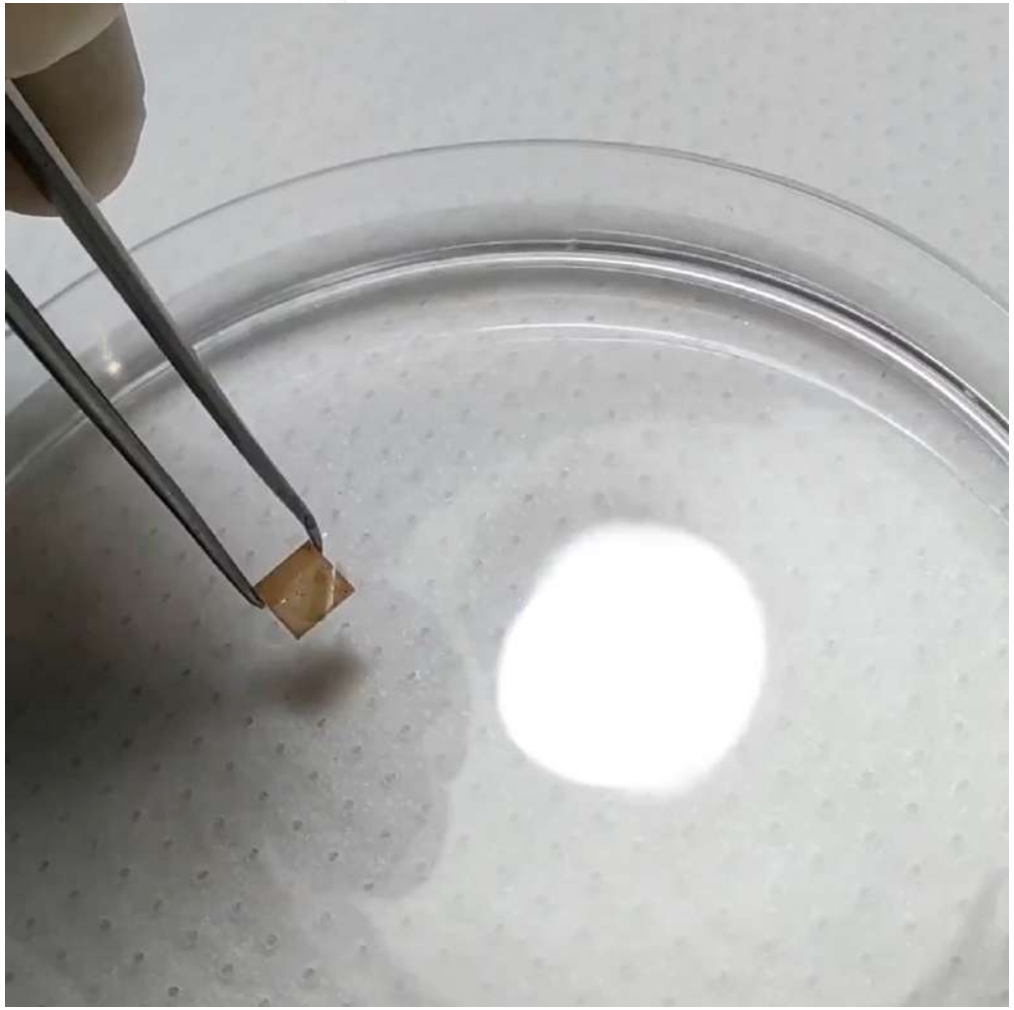
P Salles et al., *Advanced Functional Materials* **2023**; Wang et al. *Crystals* **2020**, 10(9), 733

Challenges : Exfoliation

Scooping



Mechanical stability...



P. Salles et al., ACS Appl. Mater. Interfaces ***14****, 12845−12854, 2022*

Outline

- Why free-standing oxides
- Preparation of free-standing oxides
- Challenges in the preparation
- **Outlook/ perspective**

Outlook

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EXCELENCIA SEVERO OCHOA
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

- Many new sacrificial layer composition and structures are yet to be developed (garnet and spinel not optimized)
- Understanding of how to transfer large defect-free membrane size is still needed in the short term
- Creation of novel electronic and photonic devices with superior performance: engineer properties and structure : strain-bending; artificial heterostructures, magic angle , 2D...
- Operando probes combined with theoretical studies to better elucidate the behavior of freestanding

*David Pesquera et al 2022 J. Phys.: Condens. Matter **34** 383001*
Chiabrera et al. Ann. Phys.(Berlin)2022,534, 2200084 (1 of 20)

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Collaborators

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Germany

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CHEMOX TEAM-ICMAB

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Karla Mena

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ICMAB INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA
EXCELENCIA SEVERO OCHOA
CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

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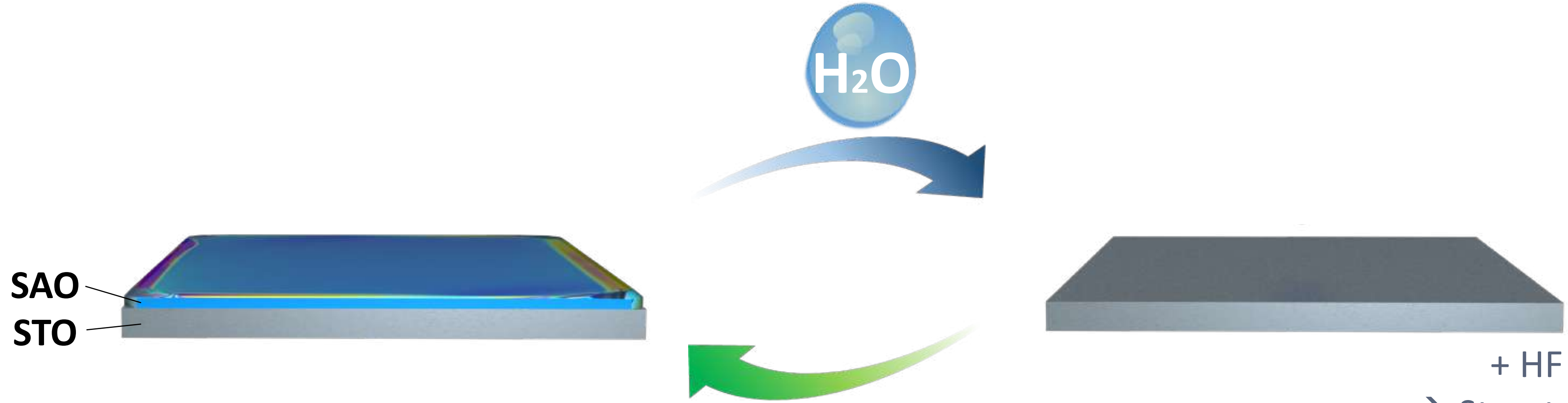
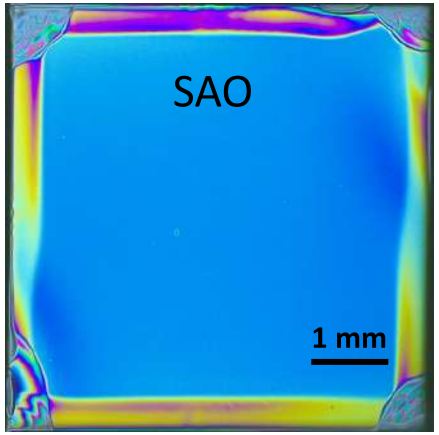
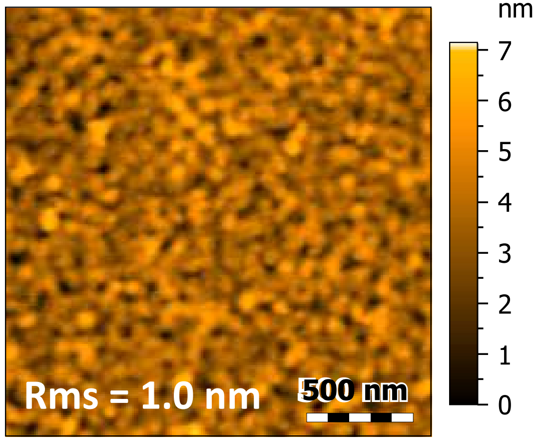
Characteristics of optimized SAO//STO epitaxial film

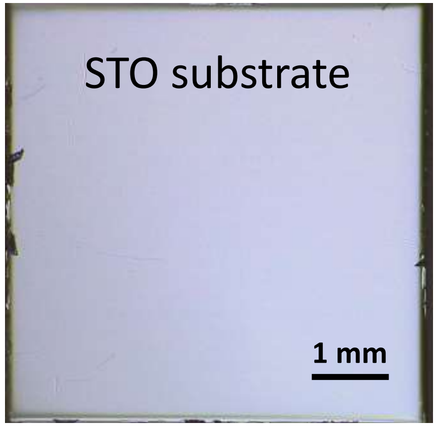


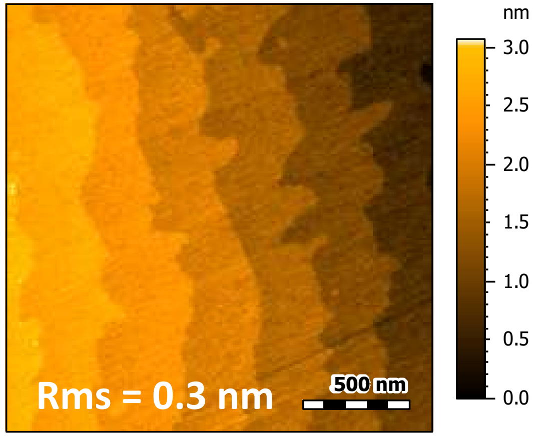
+ HF treatment
→ Step-terrace structure



AFM







✓ **Epitaxy and smooth surface**

✓ **Dissolved in H_2O**
✓ **Substrate recycling**

P. Salles *et al.*, *Adv. Mater. Interfaces* **8** 2001643, 2021