FLAG-ERA 2022 Project Workshop

March 21th 2022

Transferable two-dimensional correlated oxide layers

TO2DOX

FLAG-ERA JTC 2019. **Euro Flag ERA Call 2019**
FlagERA ERA-NET Cofund Horizon 2020 Programme
(1/1/2020- 31/1/2023)

1/4/2020 through 31/3/2023

extended through
31/12/2023

FLAG-ERA

FLAG–ERA JTC 2019 Full Proposal[1]

FLAG-ERA

Project Acronym

To2Dox

Project Full Title

Transferable two-dimensional correlated oxide layers

Sub-call: ☒ Graphene – Basic Research ☐ Graphene – Applied research and innovation ☐ HBP – Basic and applied research

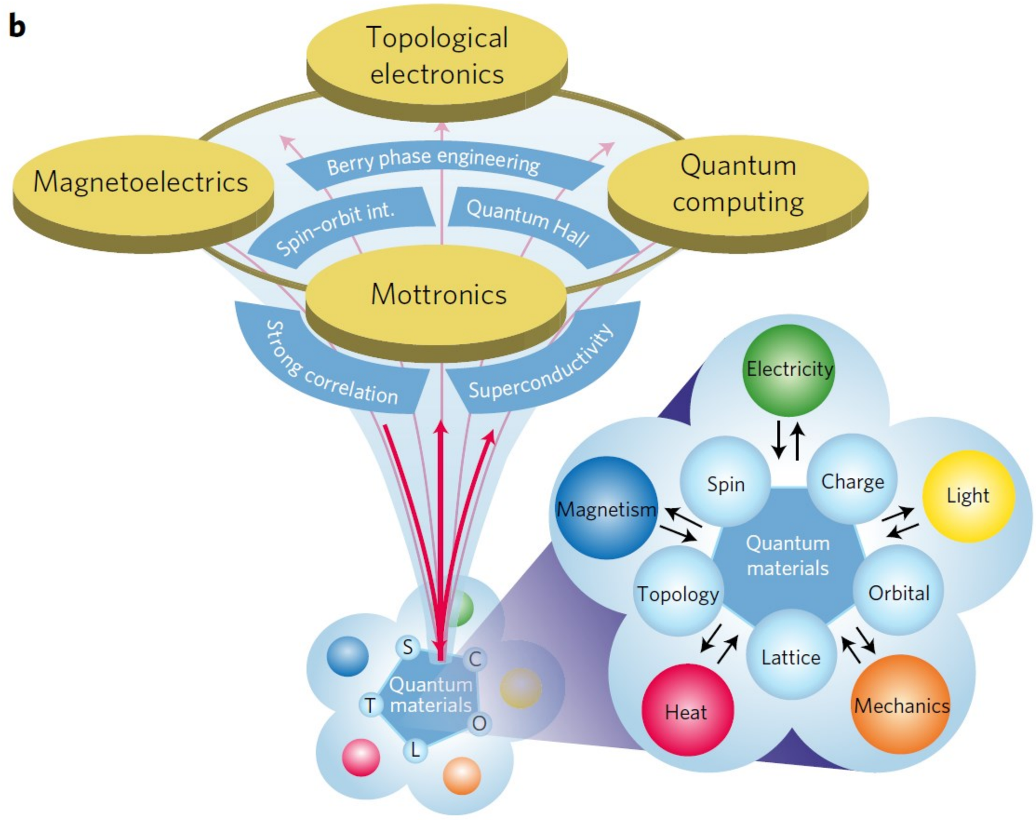
Main area within sub-call (*1, 2, 3…*): 5
Secondary area(s) (*If several, separate with commas*):
Duration: 36 months

Partners and participants involved in the realisation of the project

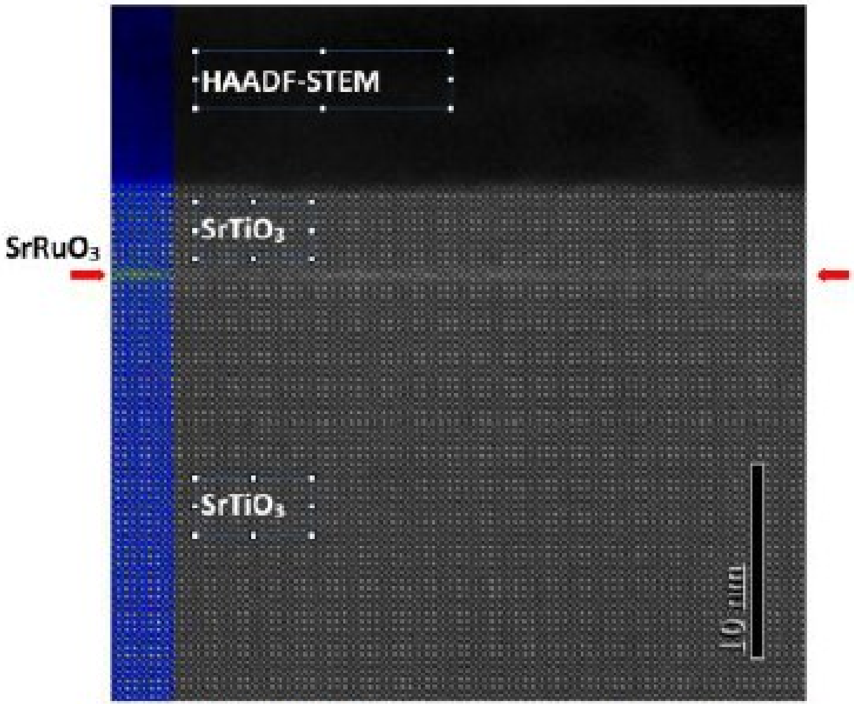
Partner Number	Country	Institution/ Department	Name of the Principal Investigator (PI)[2]	Name of the co-Investigators[3]	Other participants[4]
1 *Coordinator*	Spain	Univ. Complutense / Dpt. Materials Physics	Jacobo Santamaria	Carlos Leon	Alberto Rivera-Calzada. Maria Varela , 1 post doc
2	Spain	CSIC/ Inst. Ciencia de Materiales Madrid	Mar Garcia-Hernandez	Andres Castellanos-Gomez	1 postdoc
3	France	CNRS THALES/ Unite Mixte de Physique	Javier Villegas	Karim Bouzehouane	Anke Sander; Javier Briatico, 1 postdoc
4	Germany	Max Planck Institute fuer Festkoerper Forschung	Jochen Mannhart	NN	1 PhD student
5	Germany	Forschungszentrum Jülich/PGI-7	Regina Dittmann	Felix Gunkel	1 PhD student
6	Latvia	University of Latvia/ Inst. Solid State Physics	Sergei Piskunov	Eugene Kotomin	Yuri Mastrikov, 1 postdoc

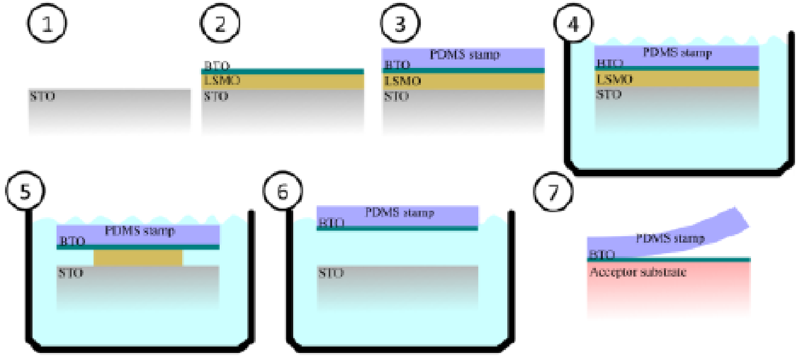
Transferable two-dimensional correlated oxide layers

To2Dox



adapted from Y. Tokura. Nature Physics 13 (2017)

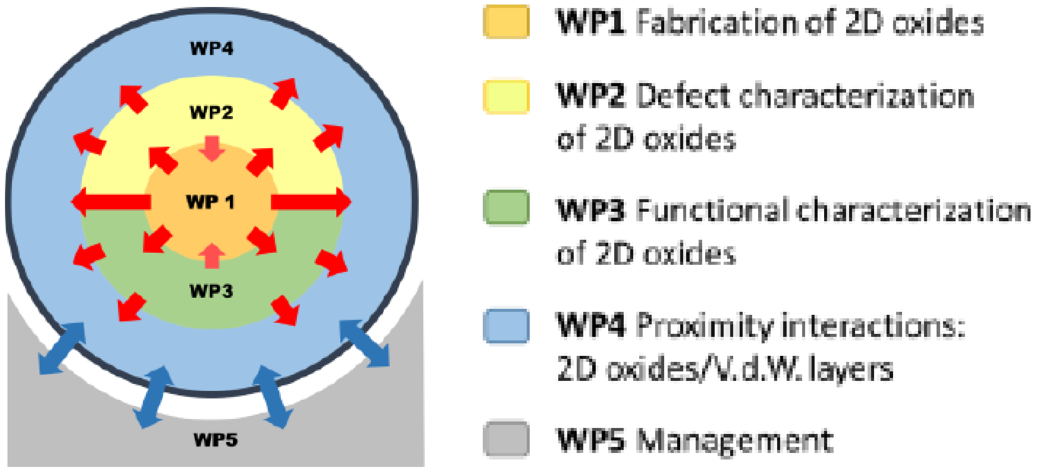




GANNT CHART		YEAR 1			YEAR 2			YEAR 3		
WPs	TASKs	M/ 1-4	5-8	9-12	13-16	17-20	21-24	25-28	29-32	33-36
WP1	T1.1				D1.1					
	T1.2				D1.1					
	T1.3					D1.2				
WP2	T2.1					D2.1			D2.2	
	T2.2					D2.1			D2.2	
	T2.3					D2.1			D2.2	
	T2.4					D2.1			D2.2 D2.3	
WP3	T3.1						D3.2			
	T3.2						D3.1			
	T3.3								D3.3	
WP4	T4.1								D4.1	
	T4.2									D4.2
	T4.3									D4.3
WP5	T5.1	D5.1 D5.4								
	T5.2					D5.5				D5.6
	T5.3	D5.2 D5.3								

Mile1 ▲ Mile2▲ Mile3▲

No of Mileston e	Delive ry month	WP involved	Title
M1	20	WP1, WP2, WP3	Fabrication of a new family of freestanding 2D correlated oxides
M2	28	WP2, WP3, WP4	Understanding the role of defects on the stability and properties of 2D oxides
M3	34	WP1, WP2, WP3, WP4	Identification of proximity effects at interfaces between 2D oxides and 2D VdW materials



Deliverable	Month of delivery	Title of deliverable
D1.1	14	Unit cell thick oxide layers with optimized properties
D1.2	20	Freestanding layers of correlated 2D oxides
D2.1	18	First report on structure and chemistry of defects in freestanding 2D oxides. Partial (preliminary) report will be delivered in month 12.
D2.2	32	Final report on defects structures of 2D oxides and their manipulation. Partial (preliminary)report will be delivered in month 24
D2.3	32	Final report on theoretical simulations of defects structures of 2D oxides. Preliminary reports will be delivered in months 12 and 24
D3.1	22	A freestanding ferroelectric $BaTiO_3$ layer
D3.2	24	Freestanding ferromagnetic $La_{0.7}Sr_{0.3}MnO_3$ and $SrRuO_3$ layers
D3.3	30	A freestanding $YBa_2Cu_3O_7$ superconductor
D4.1	32	Report on field effect modification of VdW layers with freestanding ferroelectrics
D4.2	34	Report on spin textures induced in 2D oxide ferromagnets by spin orbit proximity effect
D4.3	36	Report on superconducting proximity effect between a d wave superconductor and a topological insulator.

WP1. Fabrication and manipulation of freestanding layers of correlated TMOs.

Partner 4 MPI FF

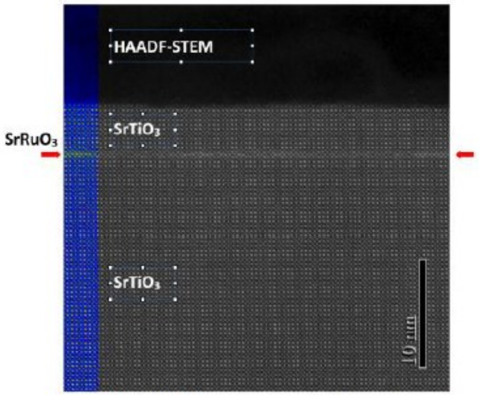
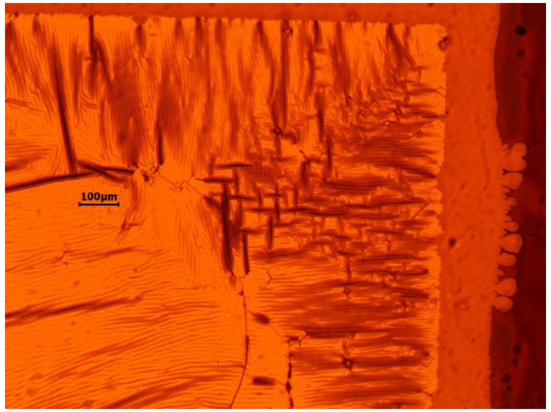
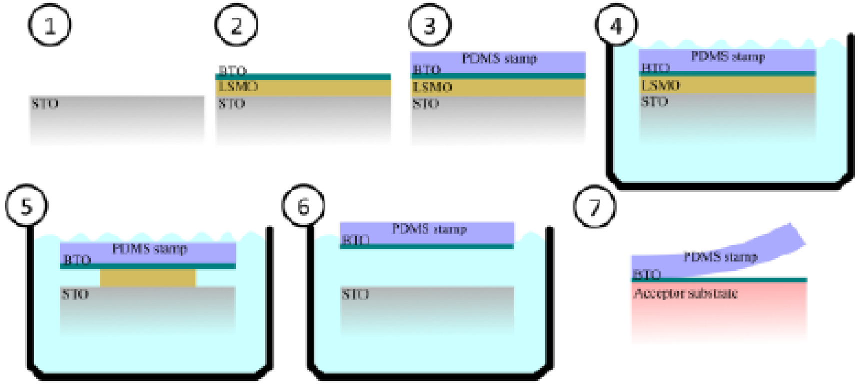


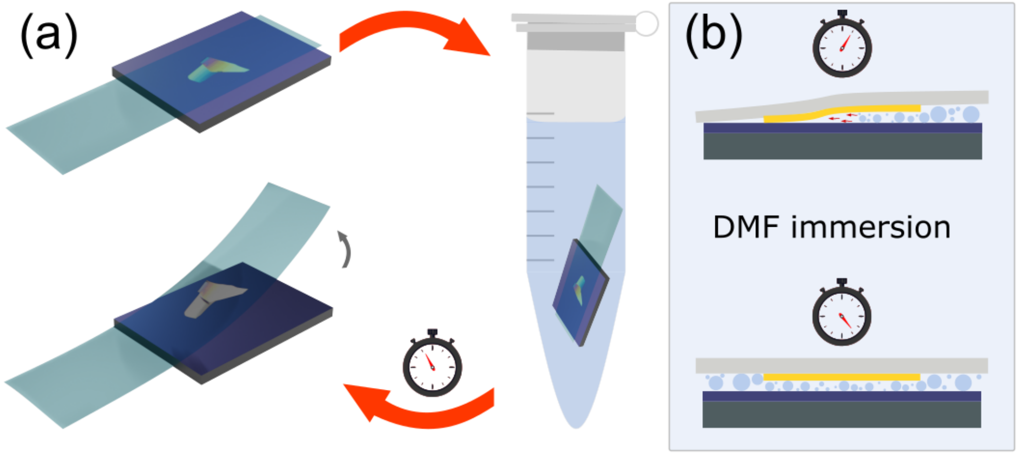
Figure 1. STEM cross-sectional cut through a unit-cell thick $SrRuO_3$ layer embedded in $SrTiO_3$. The sample has been grown by PLD.

Freestanding correlated oxides are a new family of materials with potentially interesting collective groundstates stable at room temperature

$BaTiO_3$







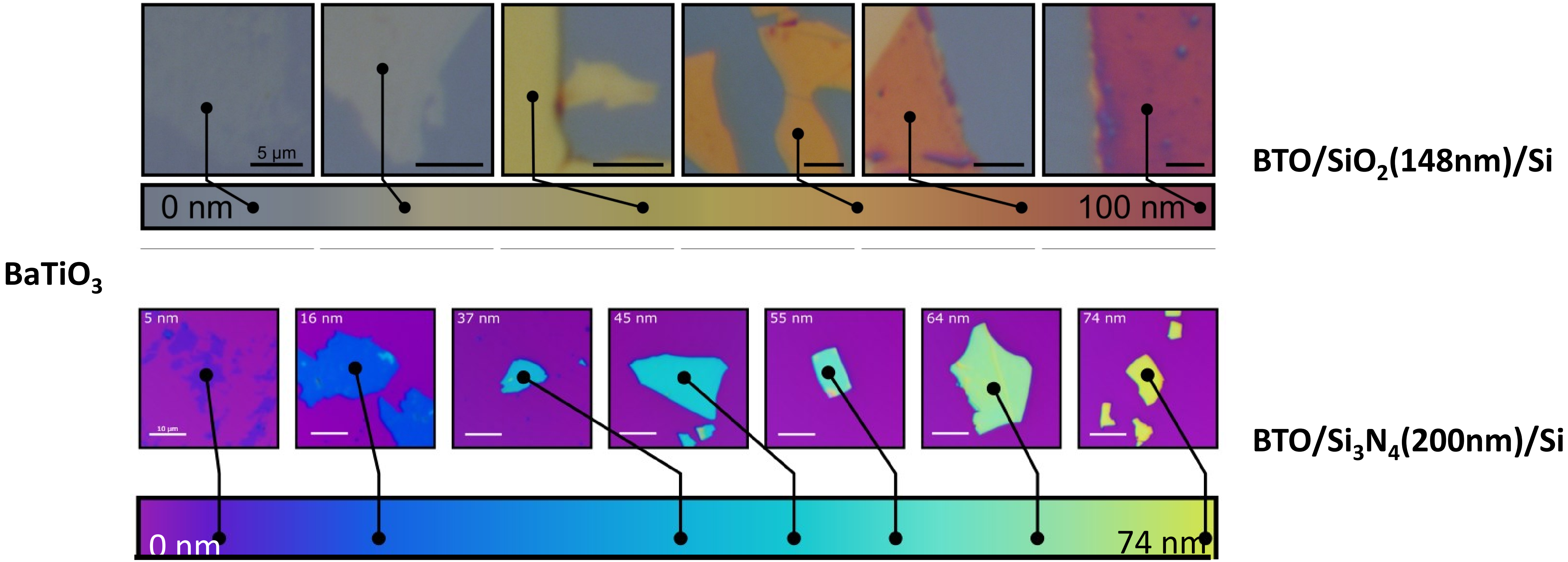
Deterministic BTO placement

Our procedure allows transferring the fabricated bilayers to different target substrates, including **TEM grids** for structural characterization.

D1.2 Freestanding layers of correlated 2D oxides

WP1. Fabrication and manipulation of freestanding layers of correlated TMOs.

Colour charts for BTO samples → optical thickness identification for different substrates

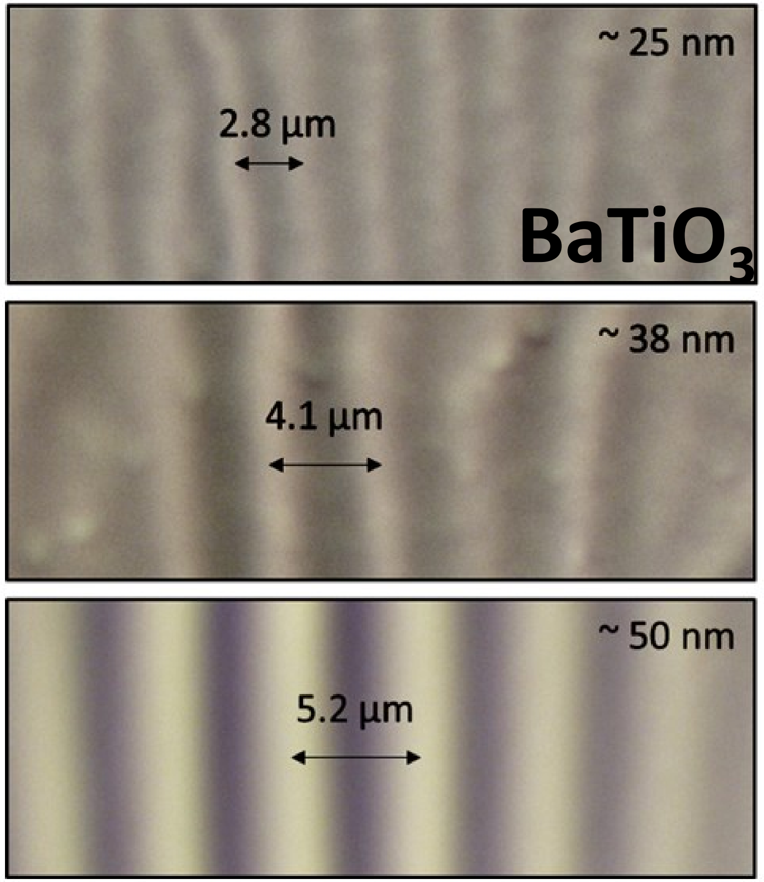


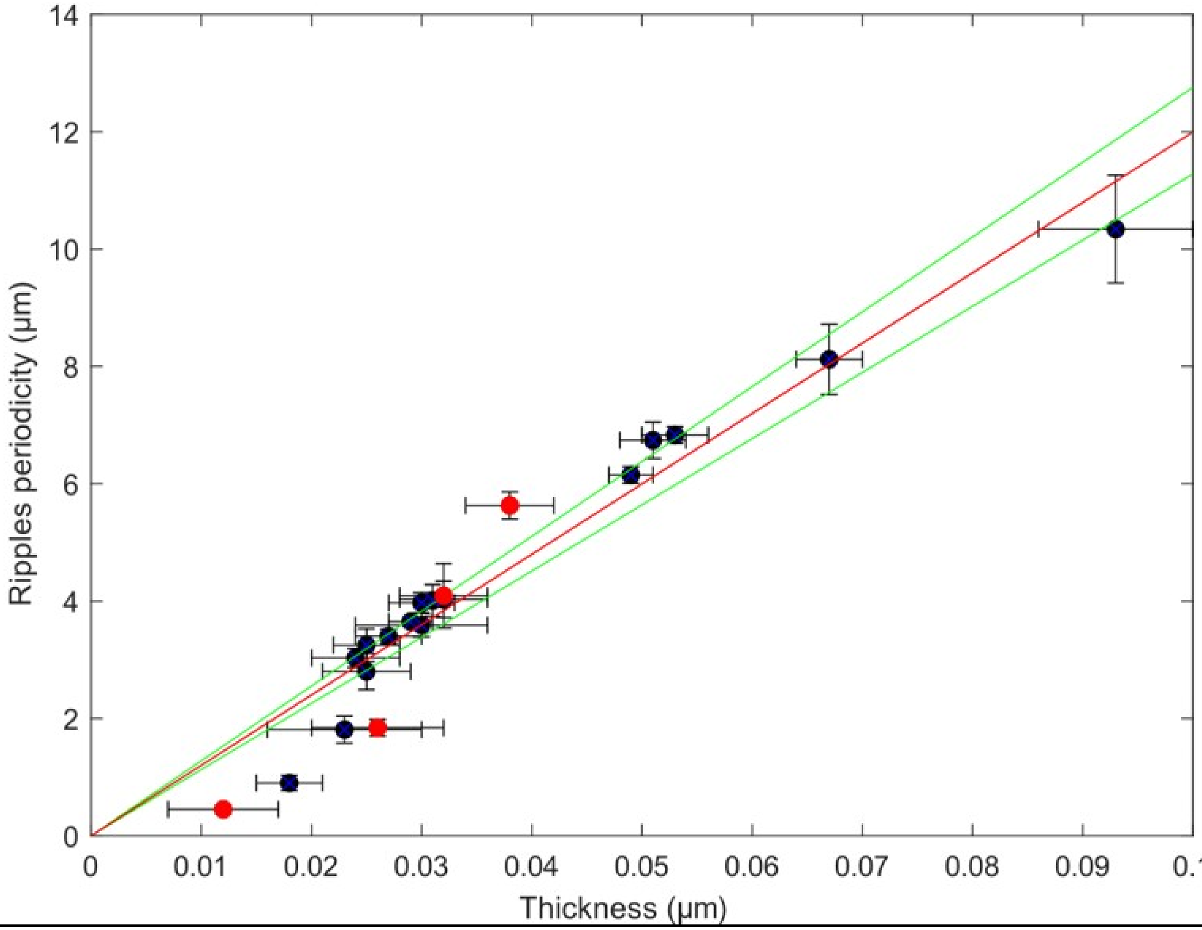
S. Puebla, et al (in preparation)

D1.1 Unit cell thick epitaxial oxide layers

D1.2 Freestanding layers of correlated 2D oxides

Partner 2 CSIC





$$E_f = 3\left(\frac{\lambda}{2\pi h}\right)^3 \frac{1-\nu_f^2}{1-\nu_s^2} E_s$$

$E_{f/s}$ – *Young´s modulus film/substrate*

$\nu_{f/s}$ – *Poisson ratio film/substrate*

λ – *Ripples periodicity*

h – *Film thickness*

Measured Young's modulus BTO flakes : 13±1 GPa

**Young's modulus BTO_{bulk}: ~67 GPa

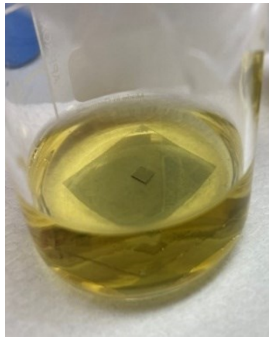
Ref: IEEE 5th International Symposium on Micro Machine and Human Science proceedings 1994, p.75

S. Puebla, V. Rouco et al .. A. Castellanos (in preparation)

D3.1 A freestanding ferroelectric BaTiO3 layer

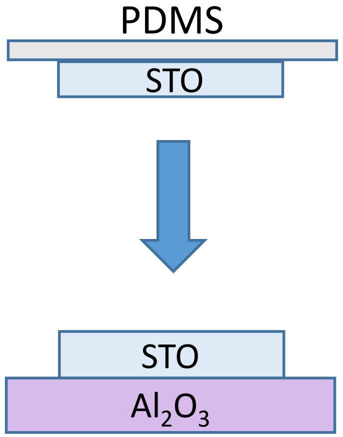
Sucessful exfoliation and transfer of $SrTiO_3$ lamellae

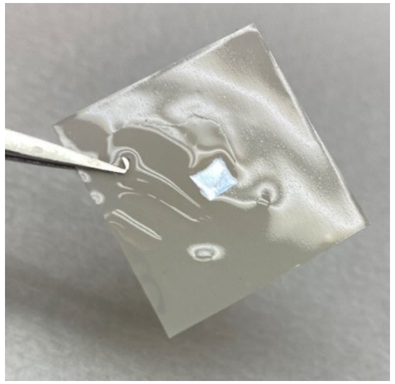
Partner 5 FZJ PGI 7

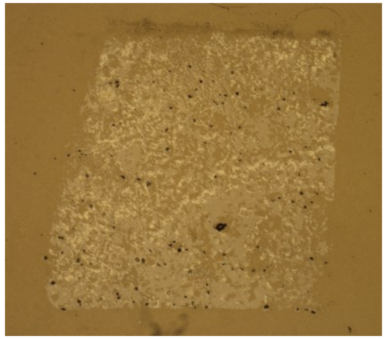


- ✓ $SrTiO_3$ grown on $LaSrMnO_3$ sacrifial layer
- ✓ Sacrificial layer is etched

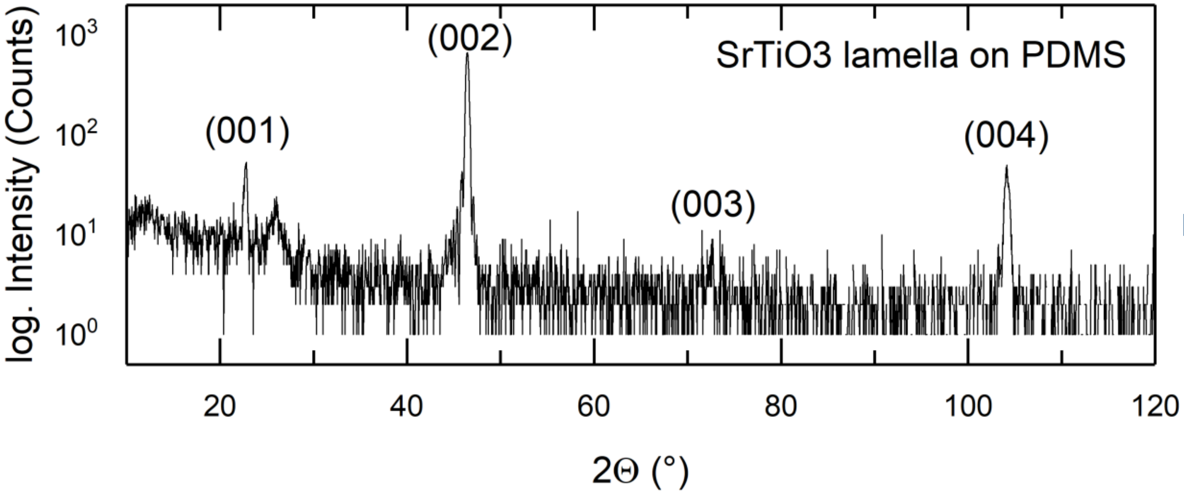
Free-standing $SrTiO_3$ on PDMS

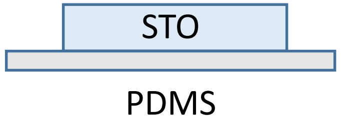


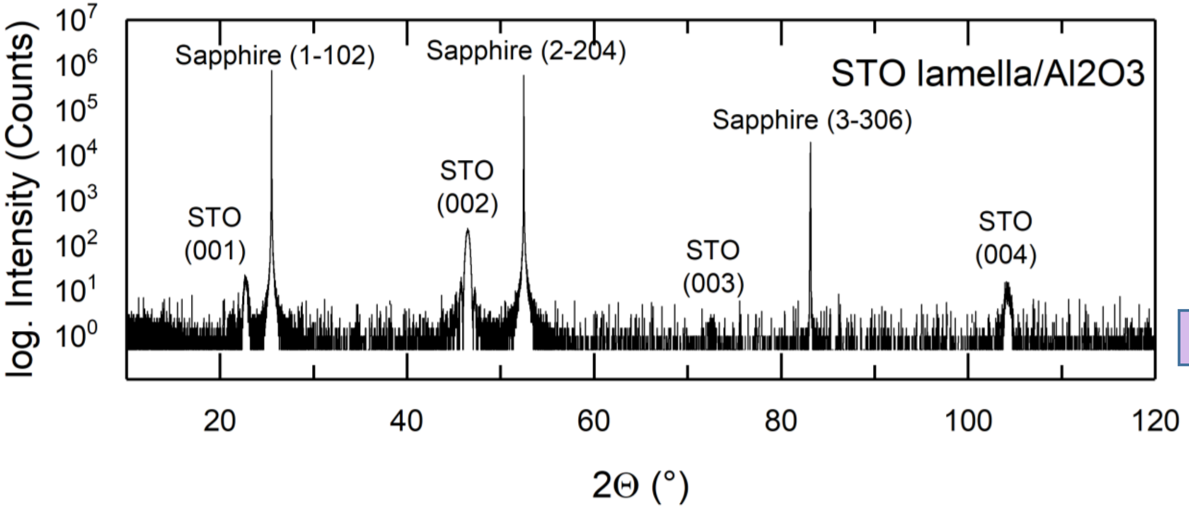




$SrTiO_3$ transfer to Al_2O_3



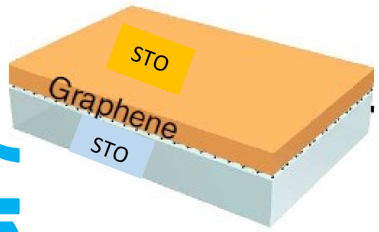




- ✓ $SrTiO_3$ is successfully detached from the STO substrate and transfered to the Al_2O_3 single crystal
- ✓ XRD and XPS analysis confirm the transfer of a crystalline $SrTiO_3$ layer

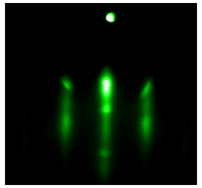
Remote epitaxy of $SrTiO_3$ on graphene

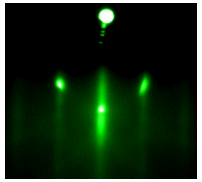
Partner 5 FZJ PGI 7

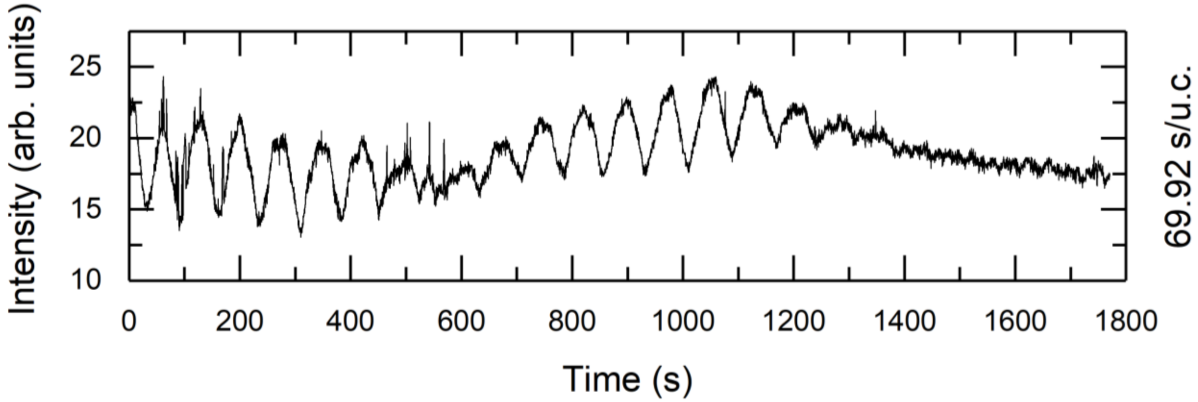


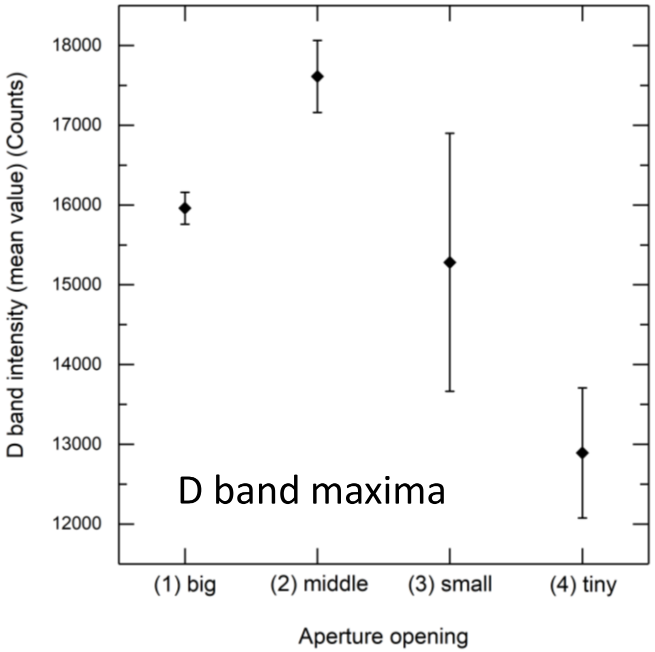
Challenge: Damage of the graphene during oxide growth by PLD

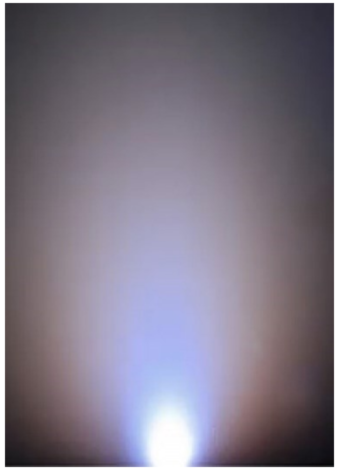
Solution: Confinement of the plume by inert gas or by the laser aperture

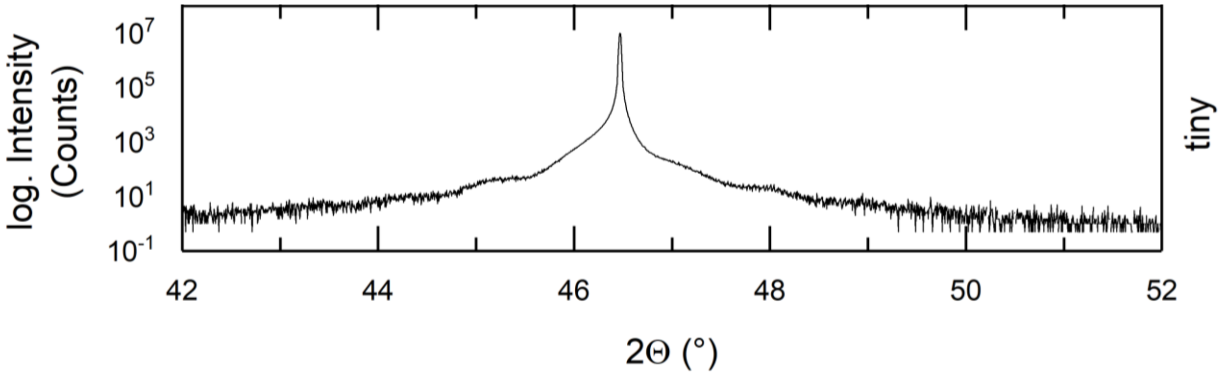










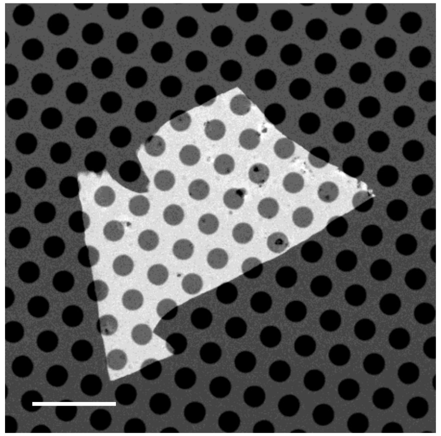


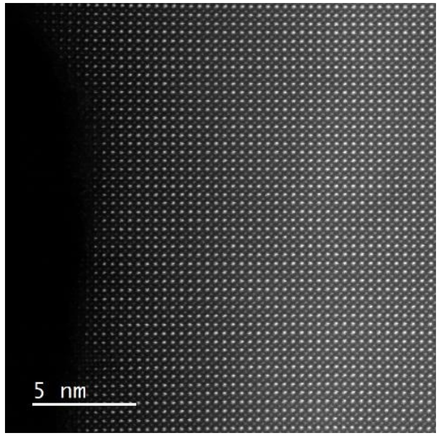
Raman spectroscopy: D band intensity is lowest for the smallest laser aperture

- ✓ High quality $SrTiO_3$ is grown on graphene
- ✓ Damage of graphene (D-band) can be minimised by plume confinement

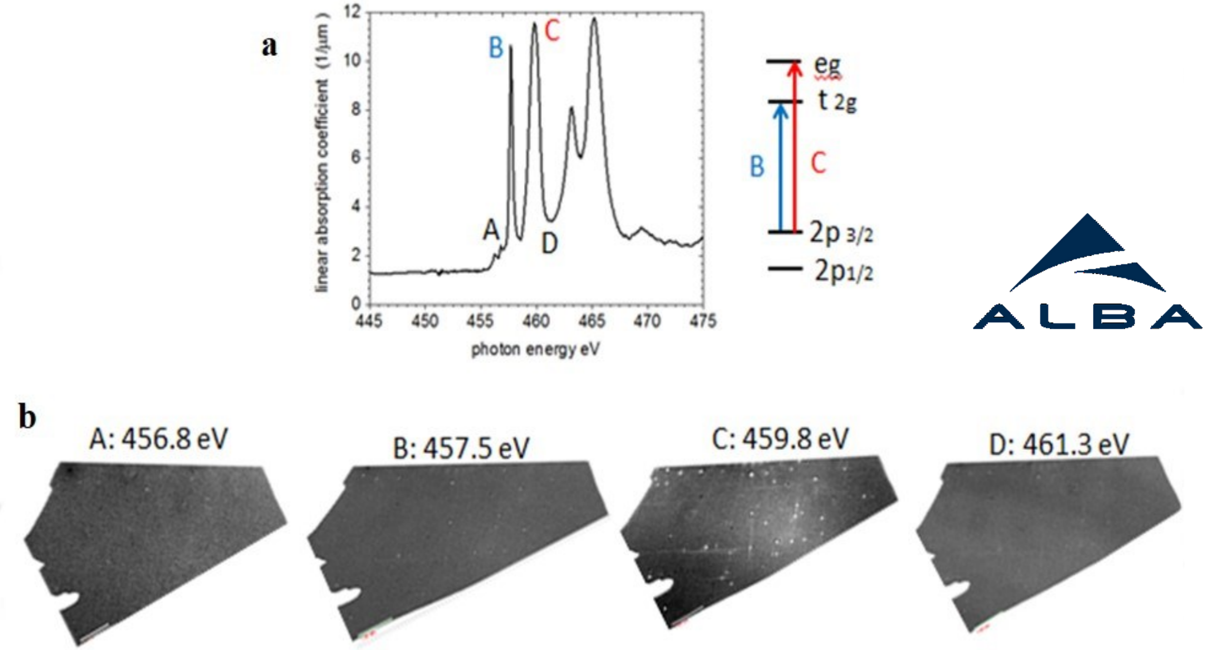
WP. 2. Study of the defect chemistry and structure of freestanding 2D oxide layers.

Partner 1 UCM





- We transfer a freestanding BTO flake into a porous SiN membrane. Flakes have 10s of microns size.
- Atomic resolution Z-contrast STEM images show some small defect structures at the surface of the transferred flake.
- The edge of the flake is atomically sharp

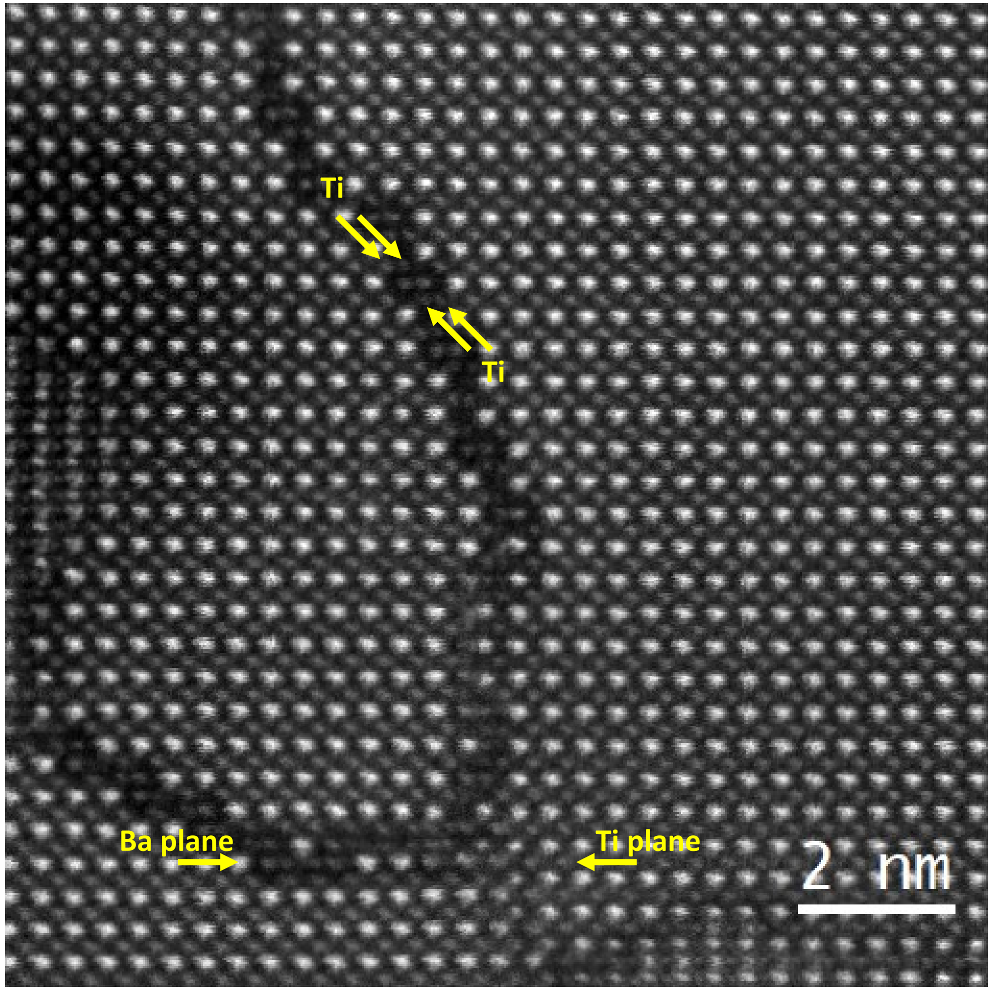


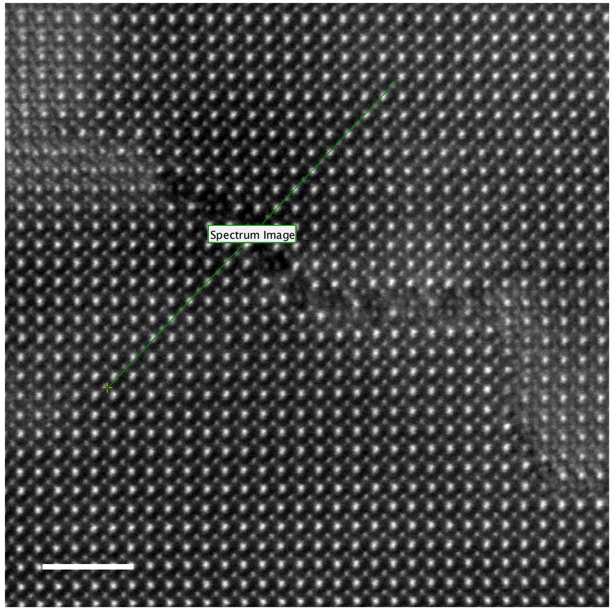
ALBA

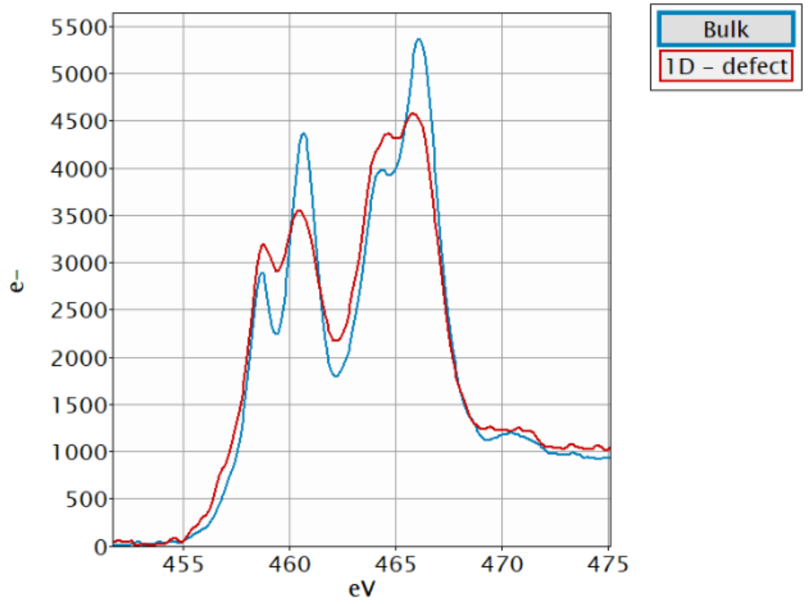
At the white spots the transition probability of the $2p_{3/2} \rightarrow e_g$ transition, and to less extent that of $2_{p3/2} \rightarrow t_{2g}$, are diminished compared with those at the rest of the crystal.

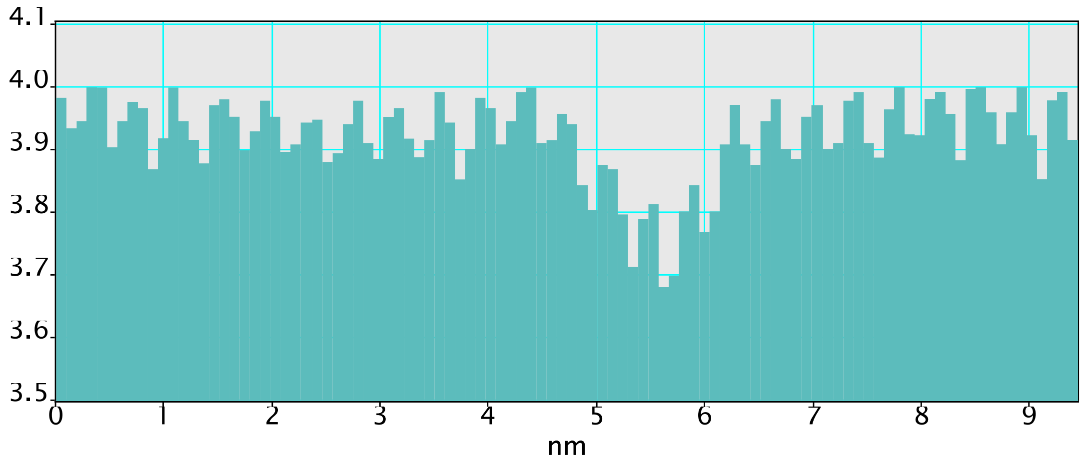
Release of strain is expected to produce a new defect zoology which is interesting to examine both experimentally and theoretically

1D defects – STEM - EELS





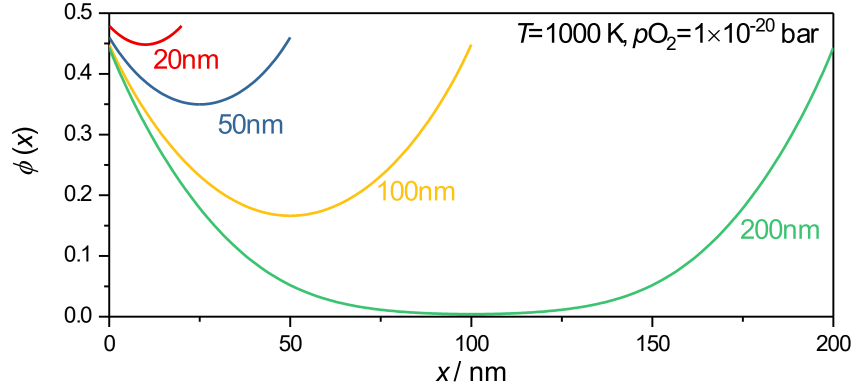




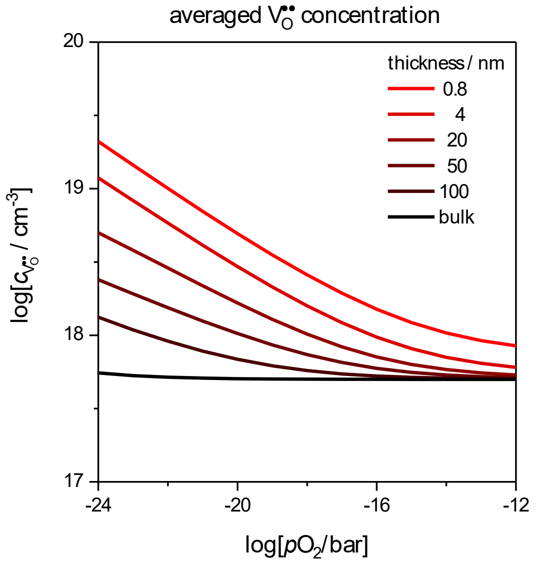
- We find 1D defects at the flake with extra Ti atoms
- EELS analysis at the 1D defect shows a Ti reduction to 3.8 oxidation state

Discrete defect model for free standing oxides

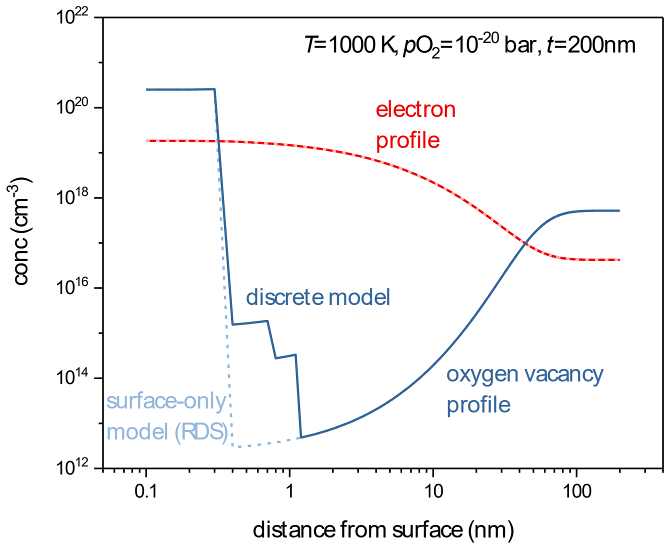
Partner 5 FZJ PGI 7



electronic band bending in thin oxide lamellae



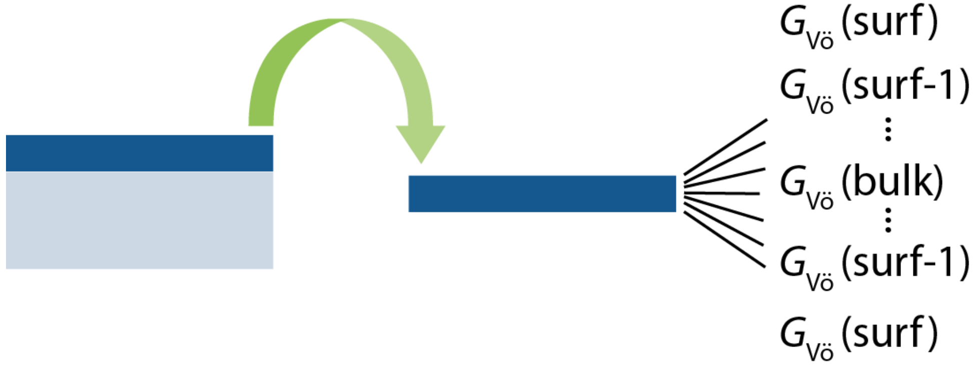
enhanced defect concentrations



discrete defect concentration profiles

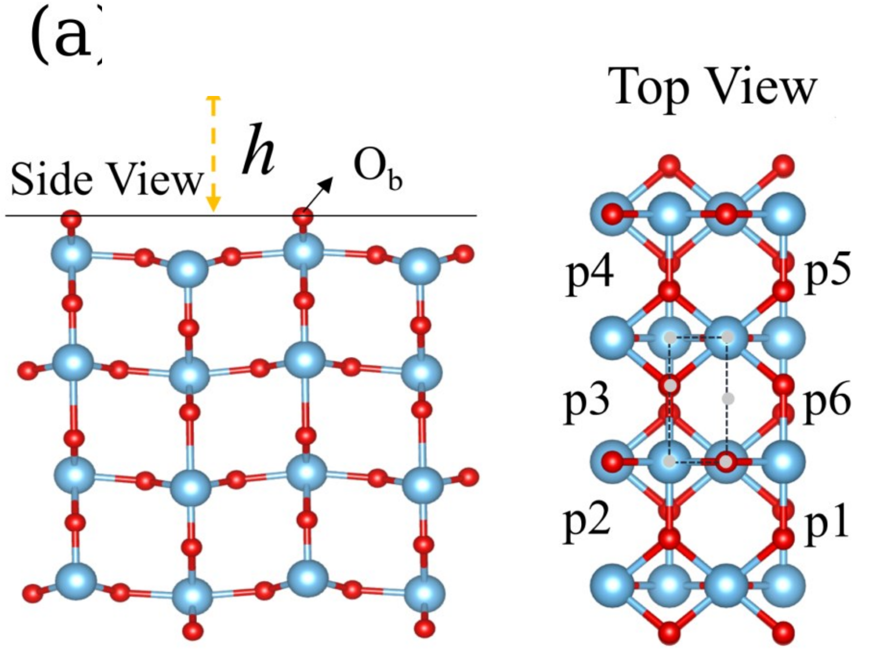
Requirement for finite size effect:

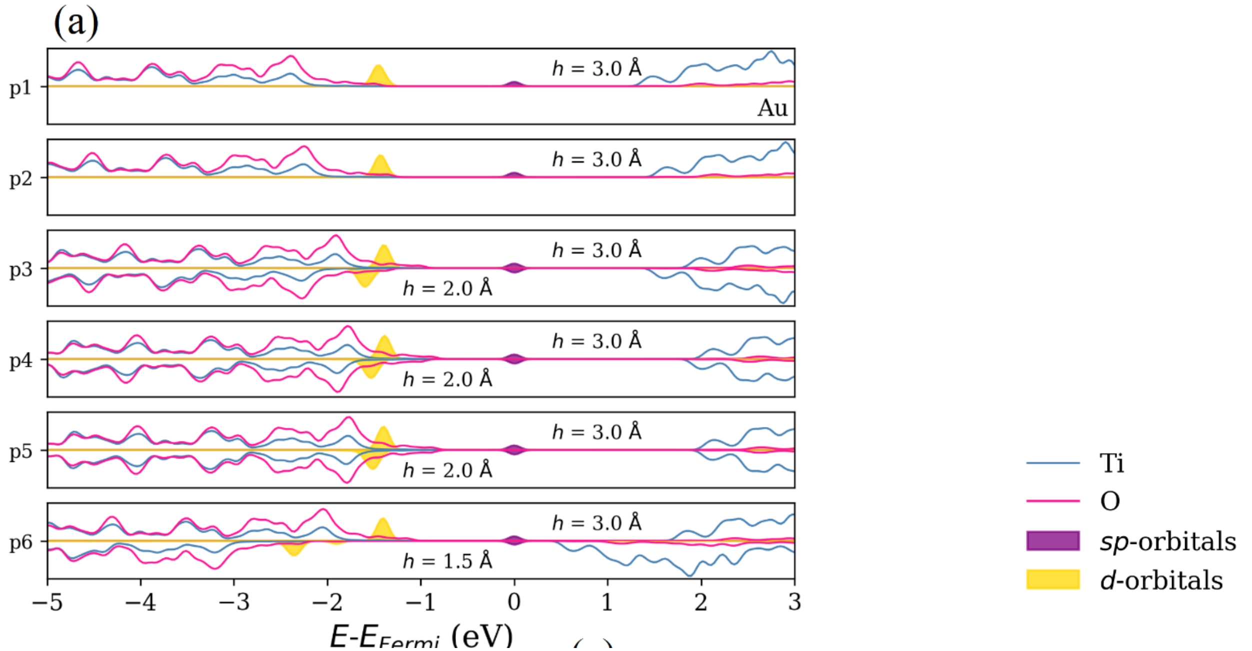
$$\Delta G_{V_O^{\cdot\cdot}}(x) > 2e\varphi(x)$$



First principles simulations of defect structures at TiO_2 (110) surface: Predictions from RT-TDDFT calculations

Partner 6 SSI UL





Real-time -dependent density functional theory (RT-TDDFT) calculations are performed to analyze the optical property and charge transitions on the rutile TiO_2 (110) surface.

- L. L. Rusevich, M.Tyunina, E.A. Kotomin N. Nepomniashchaia & A. Dejne **Sci. Rep. (2021) 11:23341**
- RI Eglitis, EA Kotomin, AI Popov, SP Kruchinin, R Jia **J Low Temperature Physics 48 (1), 80-88 (2022)**
- Maksim Sokolov et al. **Catalysts 2021, 11, 1326**.

D2.1 First report on structure and chemistry of defects in freestanding 2D oxides.

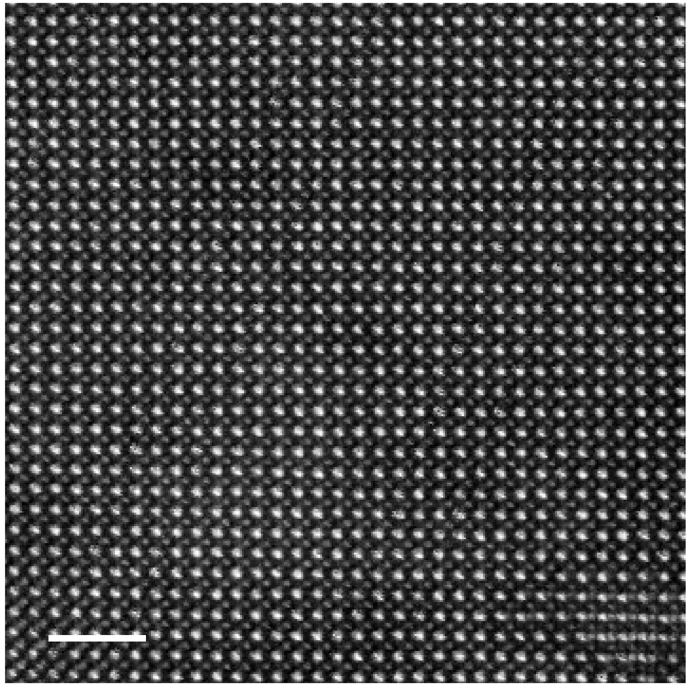
WP 3. Characterization of new electronic groundstates in freestanding 2D oxides.

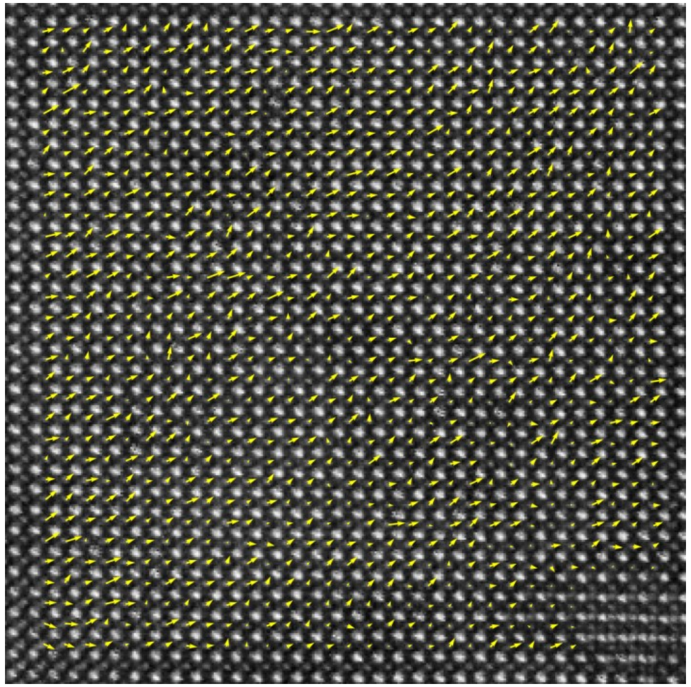
Functional response of freestanding oxides may vary compared to the “substrate –supported” counterparts.
Are correlated states stable in freestanding form?

Polarization on single film

Partner 1 UCM

Single films show homogeneous in-plane polarization





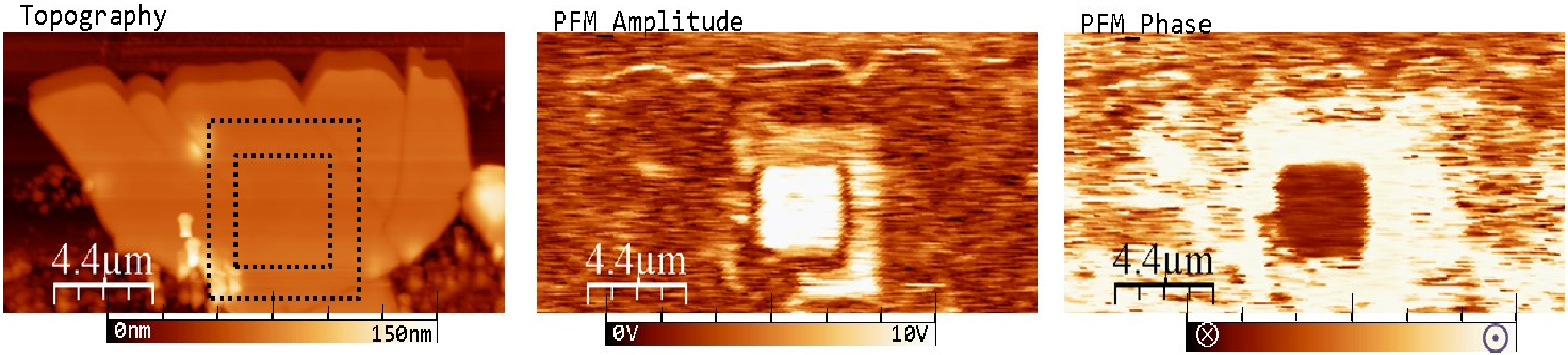
Ti displacement from center Ba sublattice

Mean (Px) = 0.16 Å
Mean (Py) = 0.10 Å

WP 3. Characterization of new electronic groundstates in freestanding 2D oxides.

Functional response of freestanding oxides may vary compared to the “substrate –supported” counterparts.
Are correlated states stable in freestanding form?

Piezoelectric Force Microscopy→ Switching of ferroelectric domains



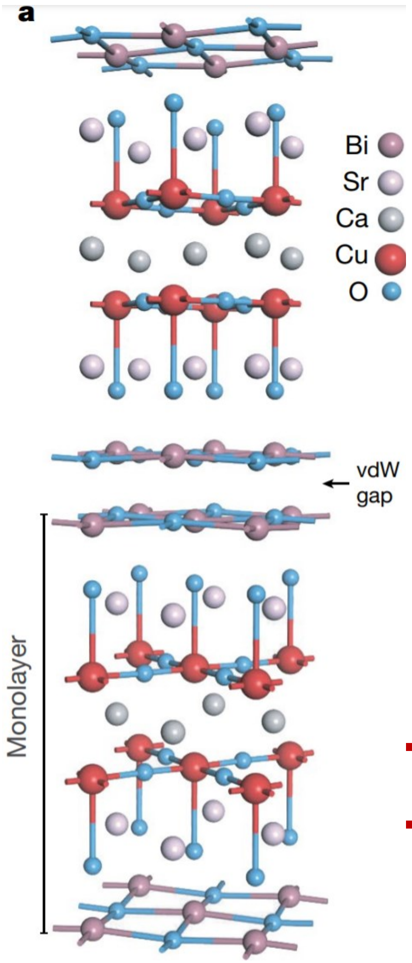
Freestanding BTO/Gold substrate

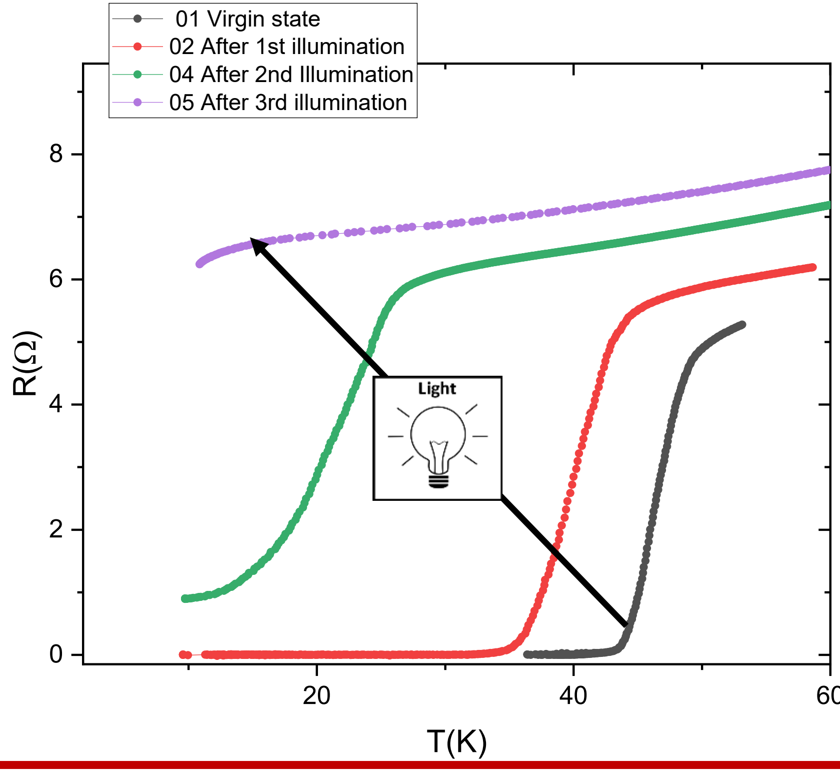
D3.1 A freestanding ferroelectric BaTiO3 layer

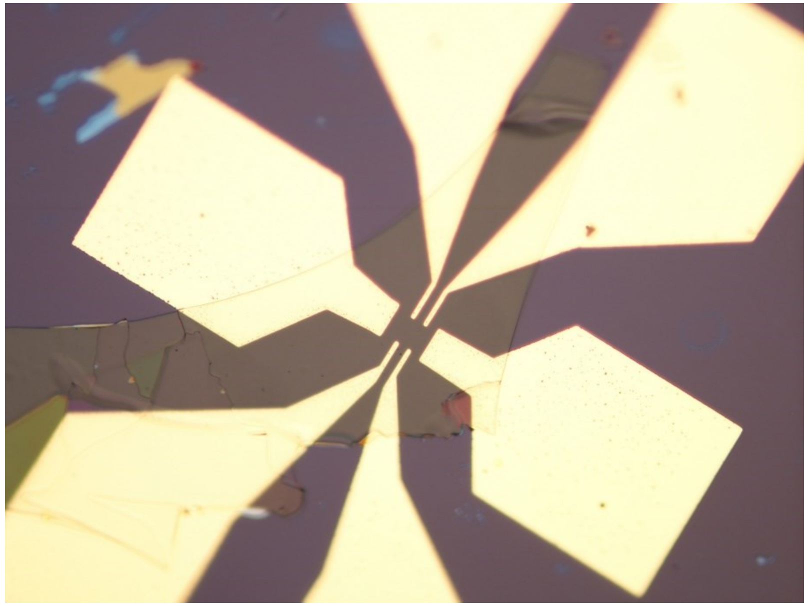
WP 3. Characterization of new electronic groundstates in freestanding 2D oxides.

Partner 3 UMR CNRS Thales

Functional response of freestanding oxides may vary compared to the “substrate –supported” counterparts.
Are correlated states stable in freestanding form?







Experiments with BSCCO (2212)

Changes of oxygen ordering? Does illumination change the Cu coordination number?

- R. El Hage …J. Santamaria J. E Villegas **Nature Electronics (under consideration)**
- D. Sanchez-Manzano … J. E Villegas and J. Santamaria **Nature Materials 21, 188 (2022)**
- Myoung Y Woo, …. J. Santamaria and J. E. Villegas **Nature Comms. 12:3283 (2021)**

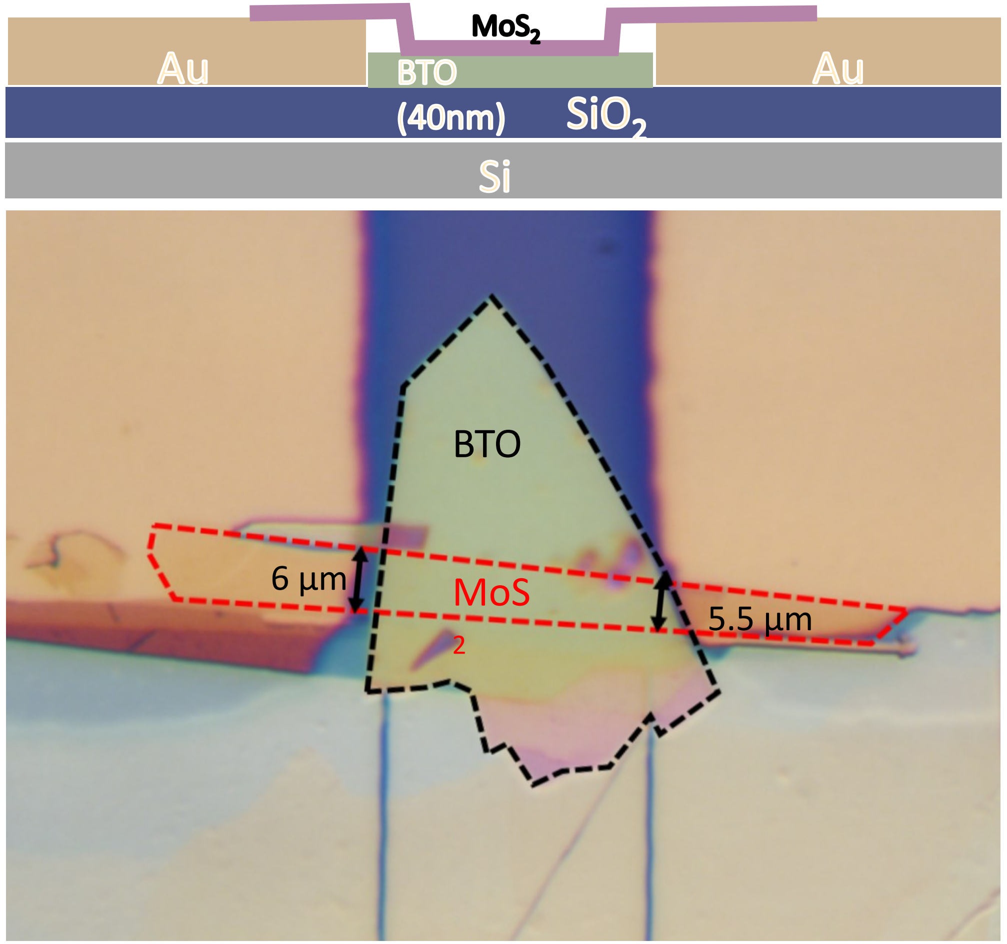
D3.3 A freestanding YBCO BSSCO superconductor

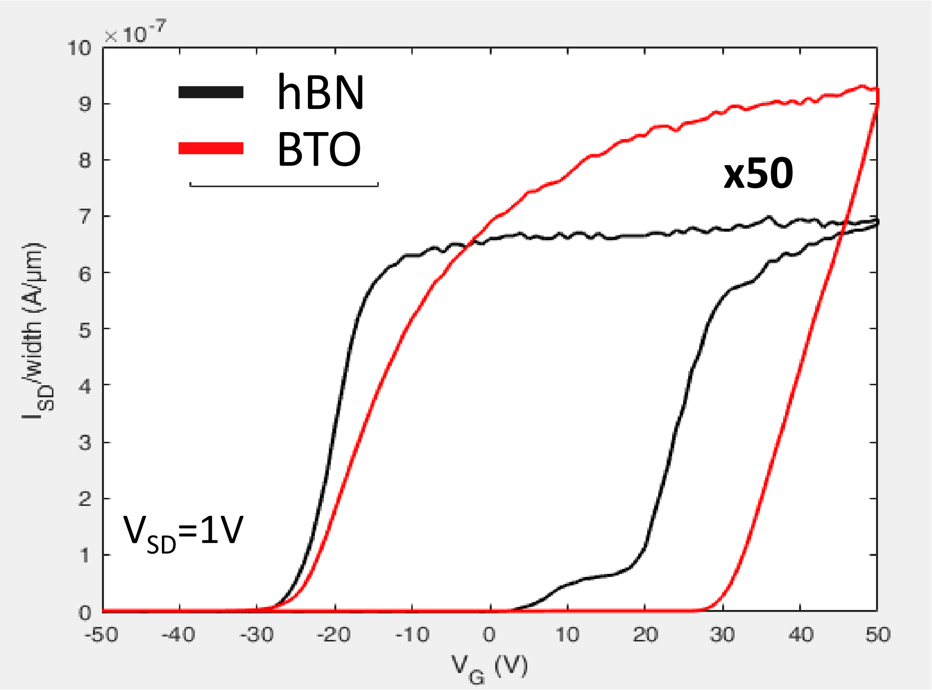
WP 4. Exploratory study of proximity interactions at interfaces between 2D correlated oxides and 2D van der Waals materials

Exciting new proximity phenomena with vdW materials can be anticipated.

Partner 2 CSIC

Device fabrication → FET configuration using BTO flake as gate dielectric



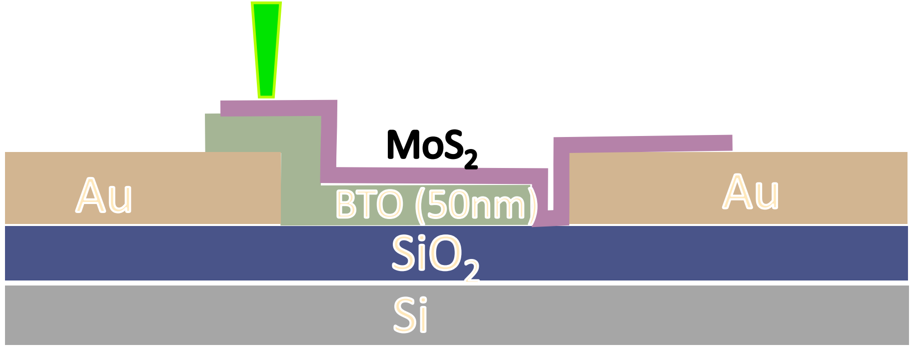


$\mu_{hBN} = 0.8\ cm^2V^{-1}s^{-1}$ $\boxed{\mu_{BTO} = 15\ cm^2V^{-1}s^{-1}}$

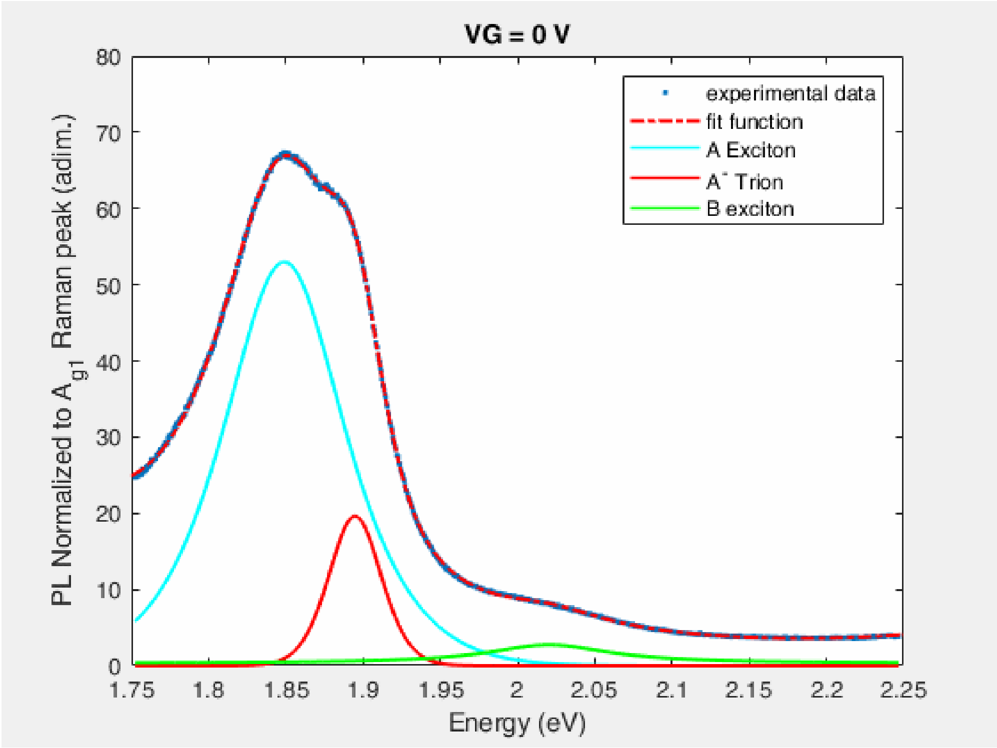
S. Puebla, V. Rouco et al…. A. Castellanos (in preparation)

D4.1 Report on FE modification of VdW layers with freestanding BTO

Device fabrication → Field effect control of MoS_2 optical emission



PL spectra of MoS_2 modified by BTO gating



D4.1 Report on FE modification of VdW layers with freestanding BTO

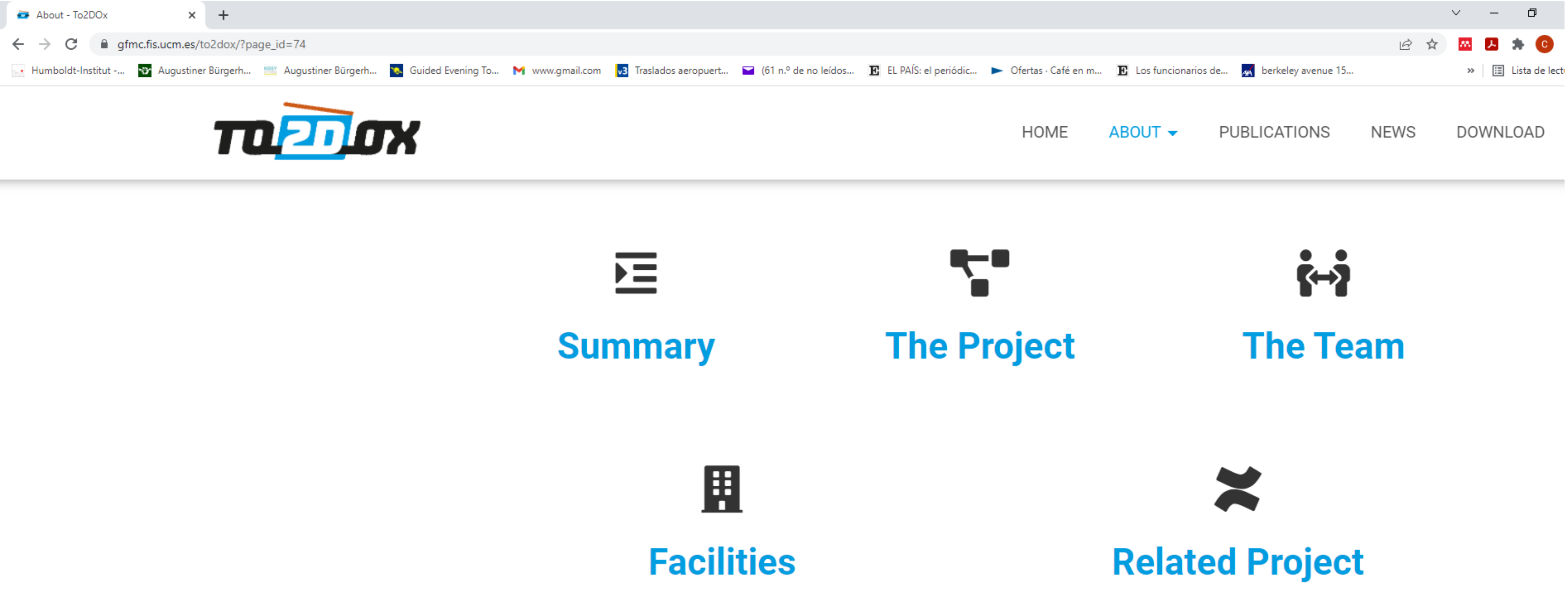
Management. RRI.

WP 5	Project management, dissemination and exploitation of results and Communication with the Graphene Flagship. Leader: Mar Garcia-Hernandez (ICMM-CSIC).	Start month 1	End month 36

Deliverable	Month of delivery	Title of deliverable
D5.1	2	Project's website.
D5.2	3	Data Management Plan (DMP).
D5.3	4	Project's database.
D5.4	4	Dissemination and Exploitation of the results plan (DERP).
D5.5	19	Intermediate Report.
D5.6	36	Final Report.

- We have asked and obtained a cost-ineffective a **project extension** until December 2023
- **Gender** balance (2 node leaders are female researchers)
- The **Project management Board PMB** (formed by the PI of the different nodes of the consortium) has delivered a **Data Management Plan**,
- The **Dissemination and Communication Board DCB** has elaborated a **Publication protocol; With a data tracking system**
- A **project Webpage** has been delivered

https://gfmc.fis.ucm.es/to2dox/



Transferable two-dimensional correlated oxide layers

To2Dox

Progress Meeting held (1/03/2022)

1/4/2020 through 31/3/2023

GANNT CHART		YEAR 1			YEAR 2			YEAR 3		
WPs	TASKs	M/ 1-4	5-8	9-12	13-16	17-20	21-24	25-28	29-32	33-36
WP1	**T1.1**				**D1.1**					
	T1.2				**D1.1**					
	T1.3					**D1.2**				
WP2	**T2.1**					**D2.1**			**D2.2**	
	T2.2					**D2.1**			**D2.2**	
	T2.3					**D2.1**			**D2.2**	
	T2.4					**D2.1**			**D2.2** **D2.3**	
WP3	**T3.1**						D3.2			
	T3.2						D3.1			
	T3.3								D3.3	
WP4	**T4.1**								**D4.1**	
	T4.2									**D4.2**
	T4.3									**D4.3**
WP5	**T5.1**	**D5.1** **D5.4**								
	T5.2					**D5.5**				**D5.6**
	T5.3	**D5.2** **D5.3**								

Mile1 ▲ Mile2▲ Mile3▲

- L. L. Rusevich, M.Tyunina, E.A. Kotomin N. Nepomniashchaia & A. Dejne The electronic properties of $SrTiO_{3-\delta}$ with oxygen vacancies or substitutions **Sci. Rep. (2021) 11:23341**
- RI Eglitis, EA Kotomin, AI Popov, SP Kruchinin, R Jia Comparative ab initio calculations of $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, and $SrZrO_3$ (001) and (111) surfaces as well as oxygen vacancies **J Low Temperature Physics 48 (1), 80-88 (2022)**
- Extremely long-range, high-temperature Josephson coupling across a half-metallic ferromagnet D. Sanchez-Manzano … J. E Villegas and J. Santamaria **Nature Materials 21, 188 (2022)**

Relation with Graphene Flagship. Work package 3

(To2Dox is Ass. Member of the Graphene Flagship)

- **Deterministic placement** of freestanding layers has been implemented in partners laboratories
- Methodology for **Assembling heterostructures** combining freestanding layers

CONCLUSIONS:

- We have delivered fabrication protocols of **freestanding BTO and STO** layers on arbitrary substrates.

- We have characterized the **mechanical and ferroelectric properties of the BTO free standing layers**.

- We have characterized the superconducting properties and the effect of **illumination of BSCCO freestanding layers**.

- We have produced the first **heterostructures BTO/ 2D VdW materials in FET devices** and have started to explore systematically their transport and optical properties. There is path for improvement by making devices in vacuum and improve the interfaces

NEXT STEPS

- PLD growth of water solvable buffer layers
- Superconductor devices
- Magnetic freestanding layers. Proximity to superconductors
- Defect characterization