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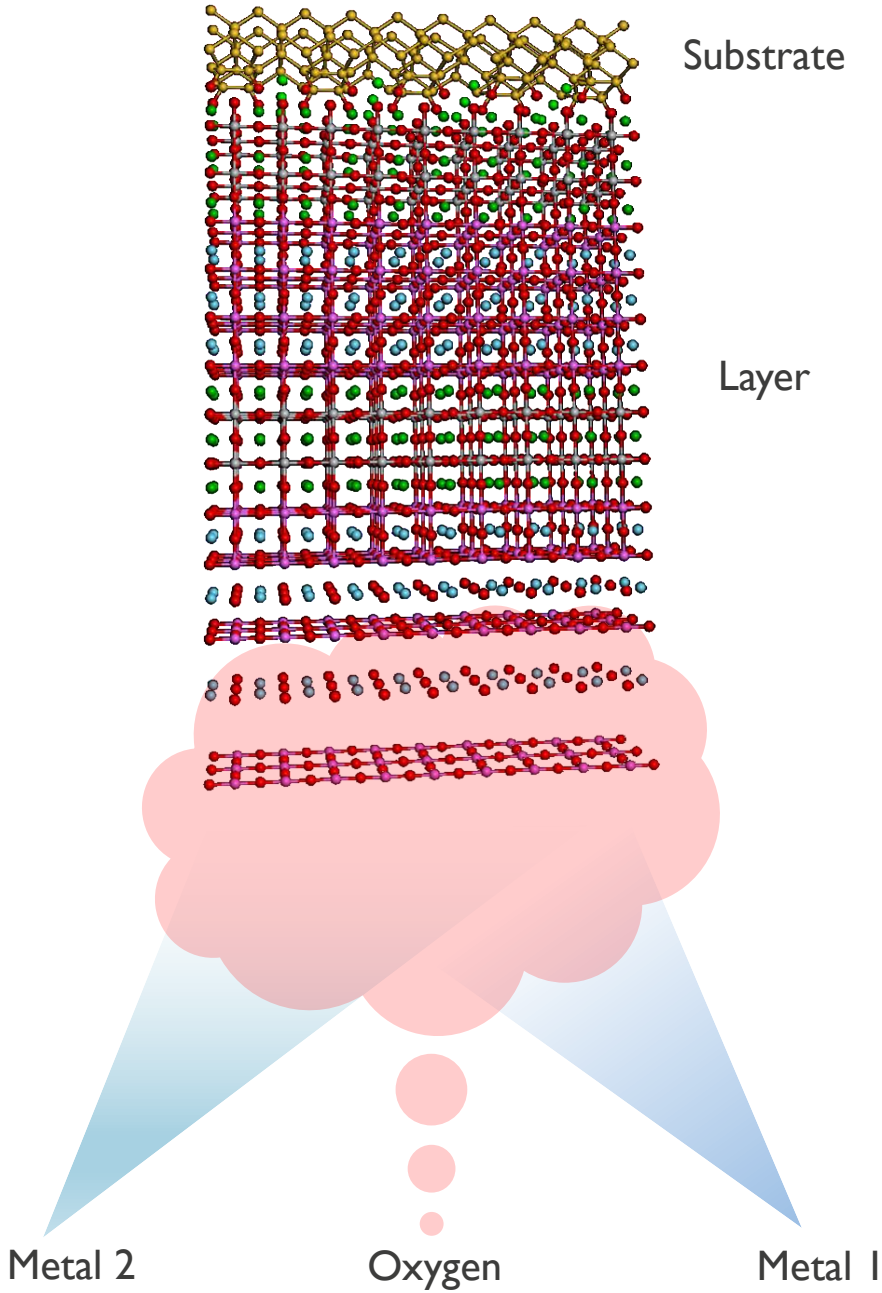
New challenges in applications

Prof. Dr. Clement MERCKLING

05/07/2021

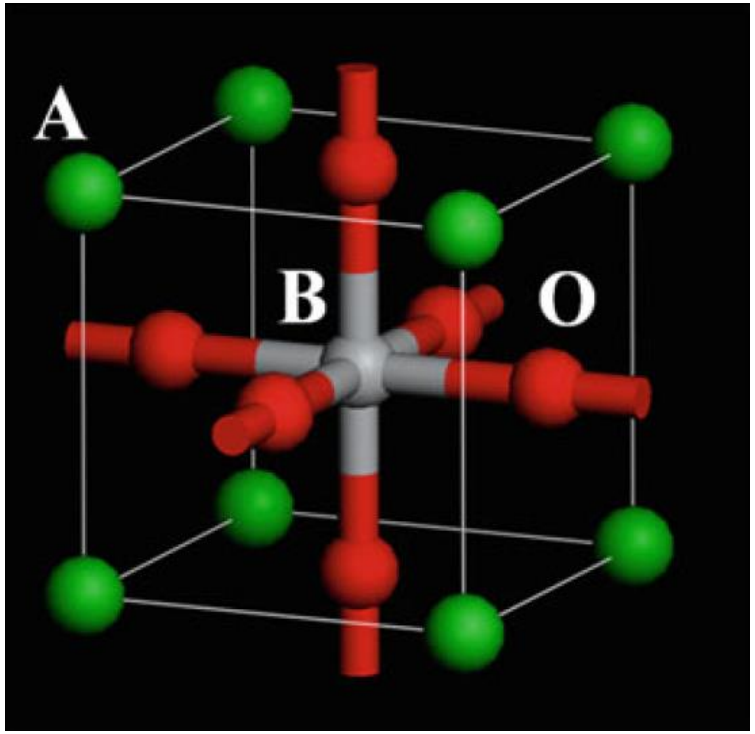
Outline

- Functional oxide materials ("Oxitronic")
  - Perovskite's materials
  - Properties / applications
- Monolithic integration on Si(001) though epitaxy
  - Thermodynamics
  - Buffer layer: $SrTiO_3$
  - Alternative options
- New challenges / new applications
  - Pockels materials: $BaTiO_3$
  - Topological materials: $BaBiO_3$
- Conclusions and perspectives



Functional oxide materials

Perovskite oxides



Cubic ABO_3 perovskite structure

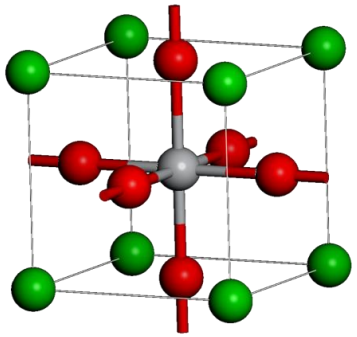
- The perovskite structure is very common among the transition metal oxides for compounds having chemical formula ABO_3.
- There is an extensive number of combinations of elements that form ABO_3 perovskite compounds with various electrical polarization, magnetism or electrical transport natures/properties.

Perovskite oxides

Perovskite (ABO_3)

AO plan

BO_2 plan



IA												IIIA	IVA	VA	VIA	VIIA	Noble
H	IIA							VIIIB			IB	IIB					He
Li	Be											B	C	N	O	F	Ne
Na	Mg	IIIB	IVB	VB	VIB	VIIB						Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	†	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	‡	Rf	Ha	Sg	Ns	Hs	Mt									

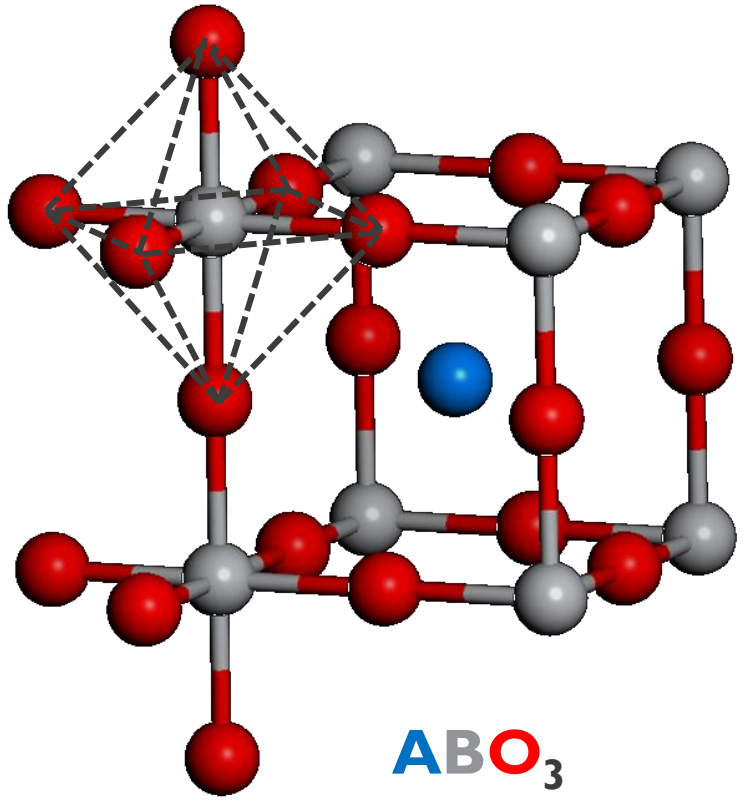
†	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
‡	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

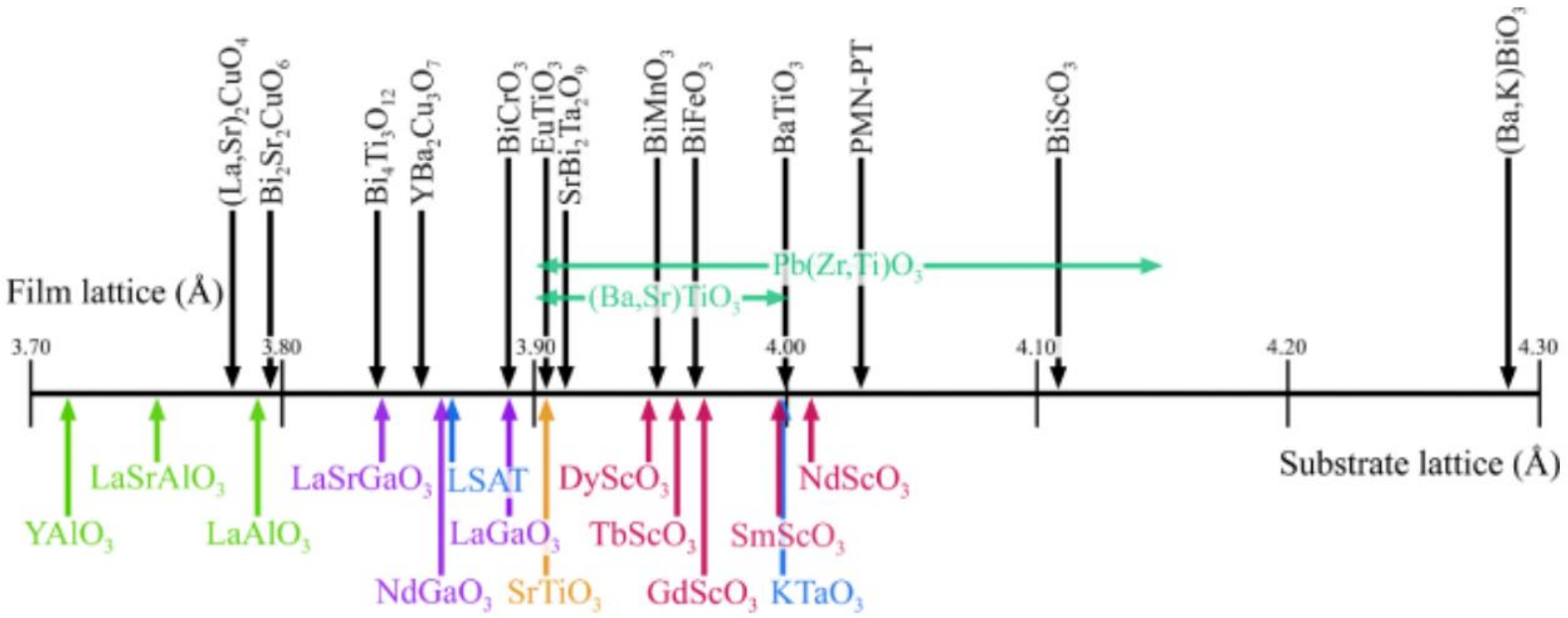
- A & B = cations
  - In general B has smaller radius
- O = anion

Perovskite oxides

Lattice parameter

$$a = 1.8836(r_B + r_O) + 1.4898\left[r_A + r_O\sqrt{2}(r_B + r_O)\right] - 1.2062$$



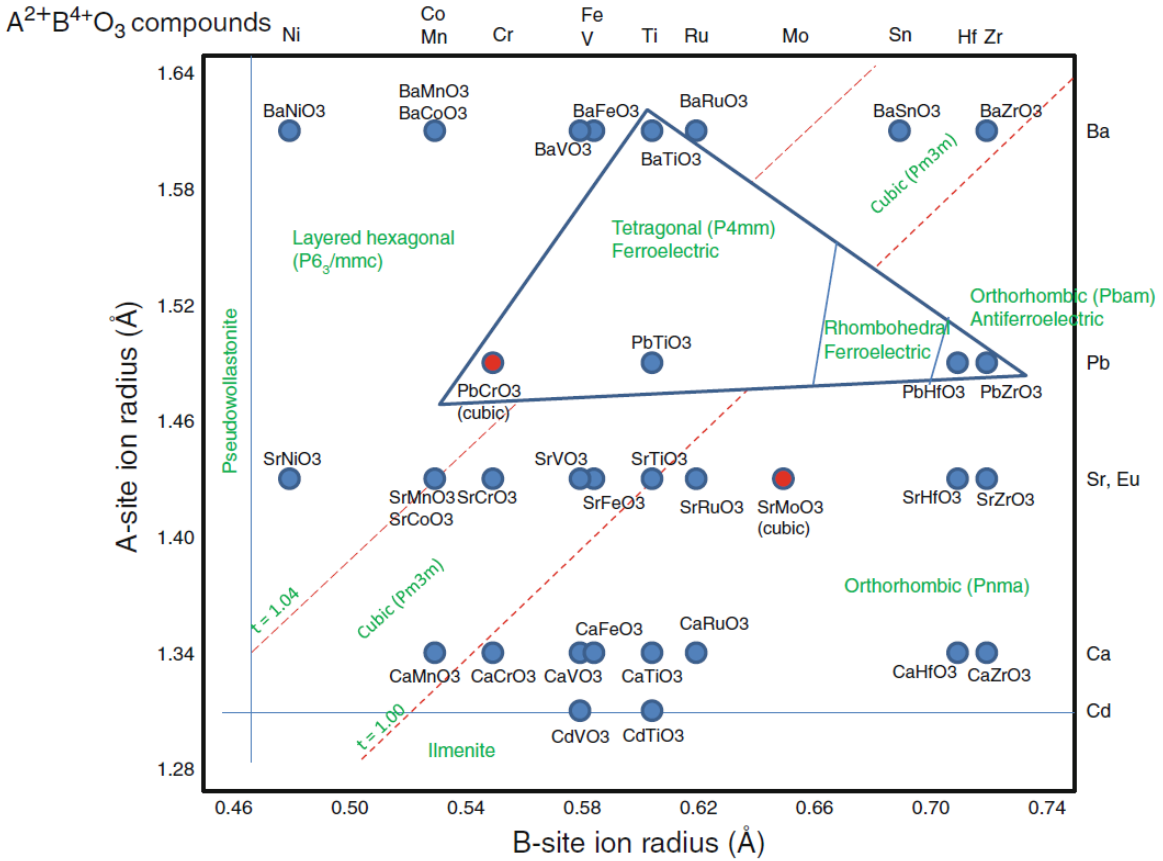


D. Schlom et al., J. Am. Ceram. Soc., 91; [8] 2429–2454 (2008)

- Perovskite lattice parameter formula based on ionic radii (empirical)
- Lattice parameters range between 3.7 Å and 4.3 Å
  - Maximum lattice parameter mismatch ~ 16%

Perovskite oxides

Crystal structures



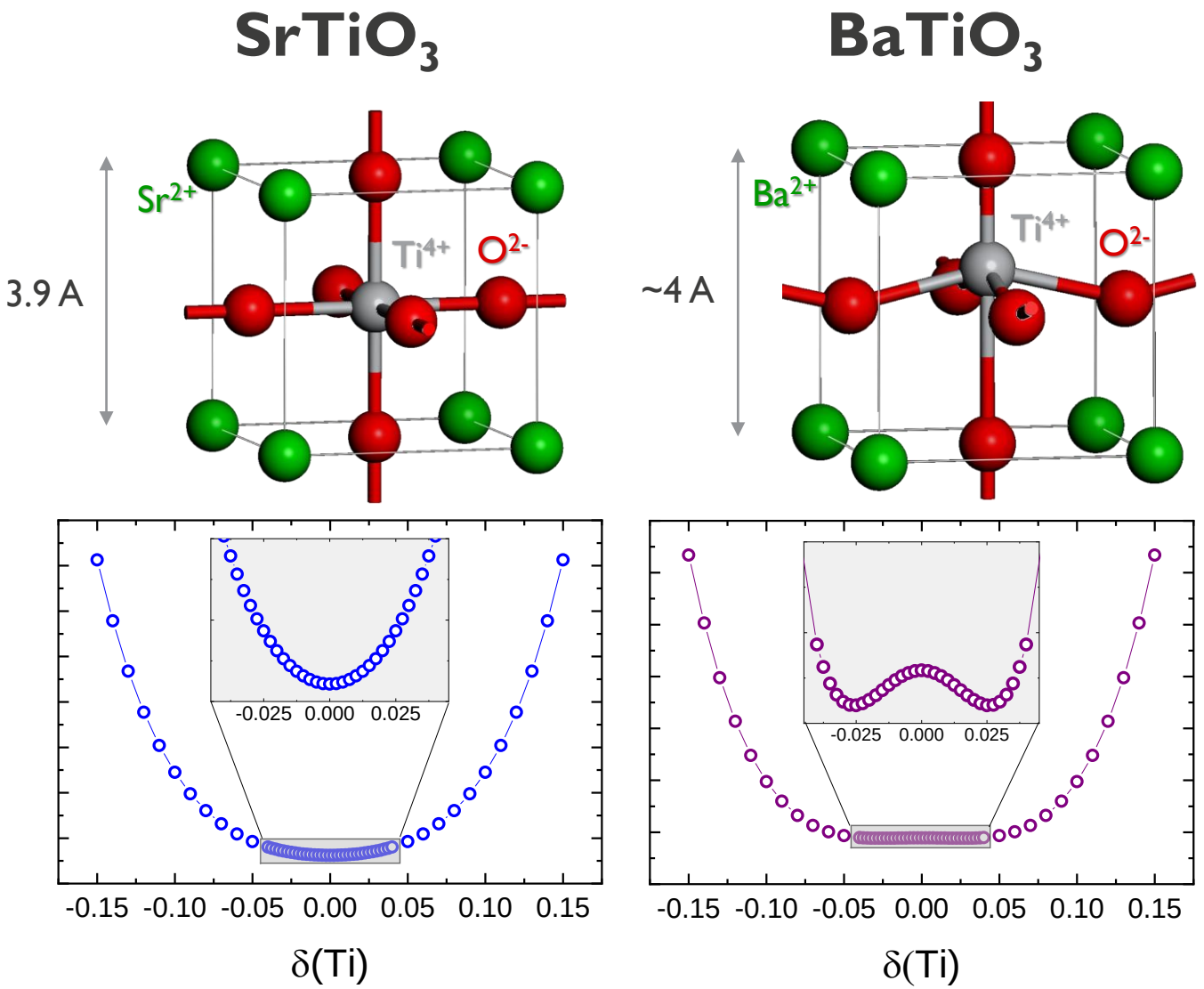
Crystal structure adopted by ABO_3 compounds at room temperature as a function of the ionic radii of the A and B ions for the case divalent A and tetravalent B cations.

- Compounds on the lower right have an **orthorhombically** distorted perovskite structure.
- Compounds on the upper left have a **layered hexagonal** structure consisting partially of face-sharing octahedra.
- In the middle is a band of **cubic** perovskite materials. For highly polarizable A ions (Pb and Ba), ferroelectric-type distortions dominate.
- Materials with a too small A ion result in the *ilmenite* crystal structure while materials with a too small B ion result in the *pseudowollastonite* crystal structure

Origin of ferroelectric properties in $BaTiO_3$

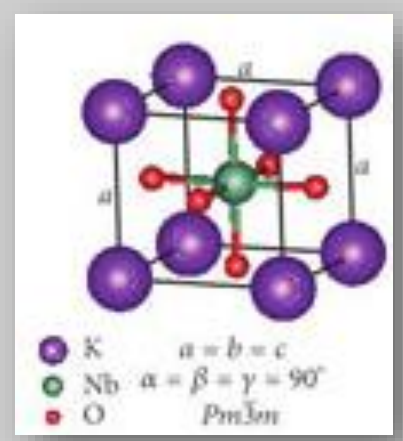
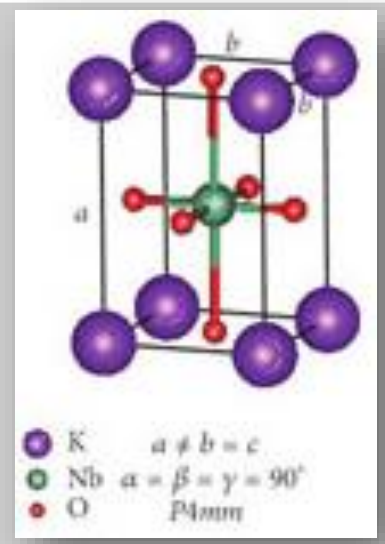
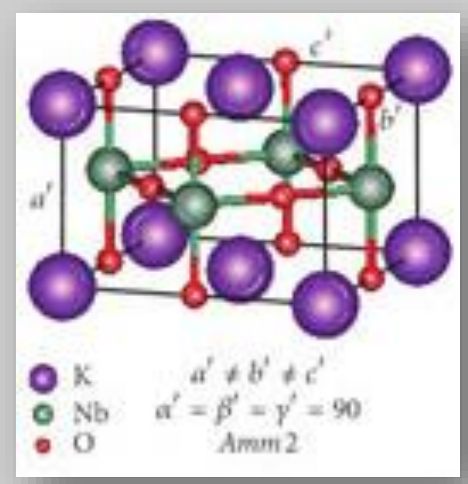
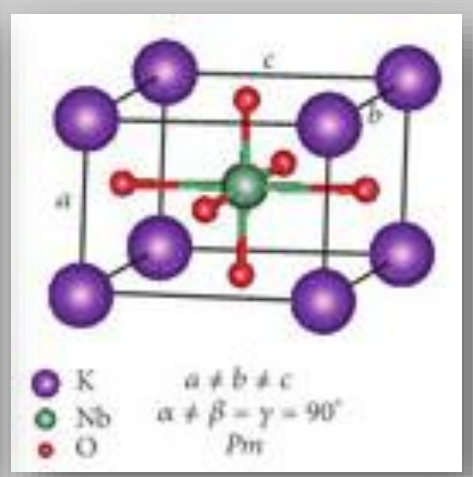
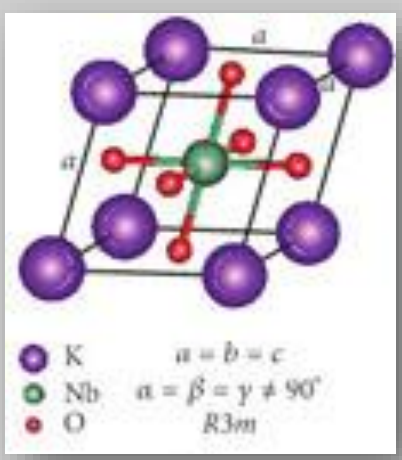
Perovskite ABO_3

- Stability of the perovskite structure depends on the relative ionic radii
  - In $SrTiO_3$: Ti-O bond ~ 1.95 Å
    - Typical bond length
      - Stable cubic structure
  - In $BaTiO_3$: Ti-O bond > 2.0 Å
    - Stretched bond length
      - Metastable structure
    - Atoms may displace slightly off its central position
  - As these ions carry electrical charges, any displacement will result in a net **electric dipole moment** : $BaTiO_3$ becomes a ferroelectric oxide...



Perovskite oxides

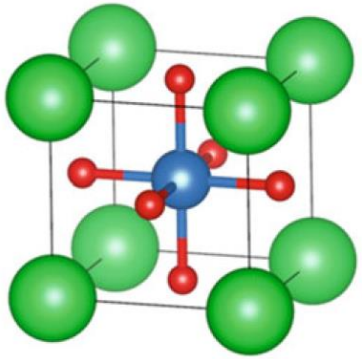
Crystal structures

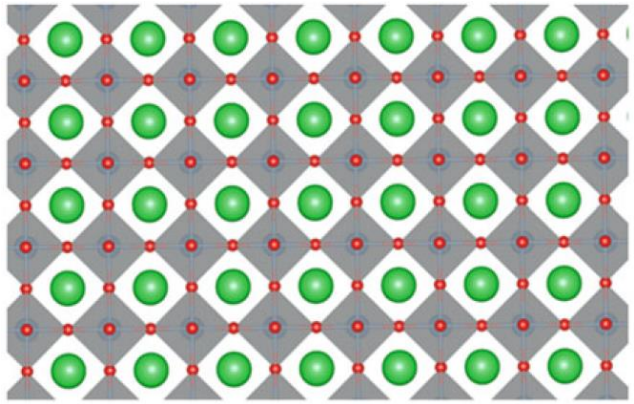
Cubic	Tetragonal	Orthorhombic	Monoclinic	Rhombohedral
				

- Perovskites structure with ABO_3 formula but **slight distortion** from the cubic lattice will induce new crystal structure
- Generally, in function of temperature, perovskite material can have cubic, tetragonal, orthorhombic, monoclinic and/or rhombohedral phases.

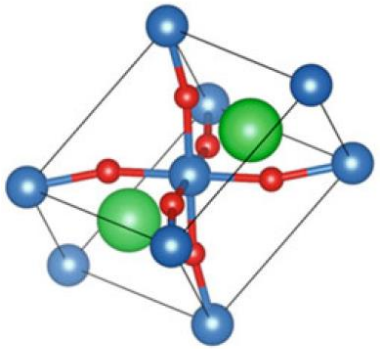
Perovskite oxides

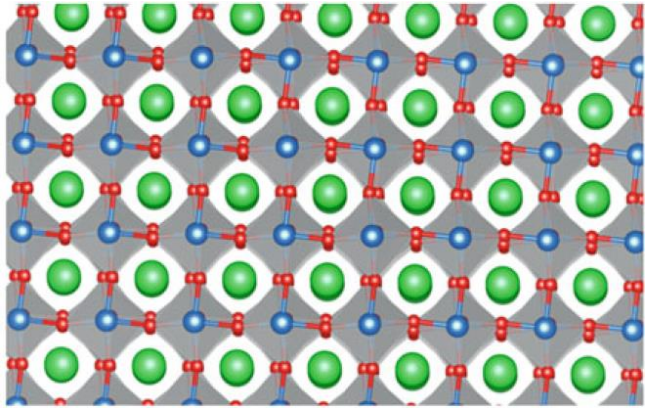
Crystal structures distortion



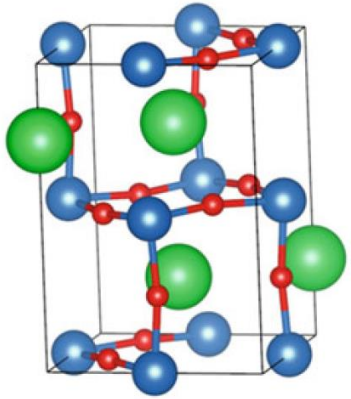


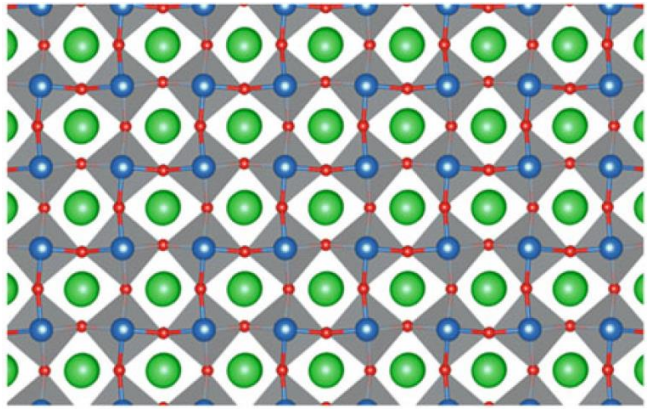
Unit cell and octahedral tiling for cubic (undistorted) perovskite with space group Pm3m





*Unit cell and **octahedral tiling** for rhombohedrally-distorted perovskite with space group R-3c*





*Unit cell and **octahedral tiling** for orthorhombically-distorted perovskite with space group Pnma*

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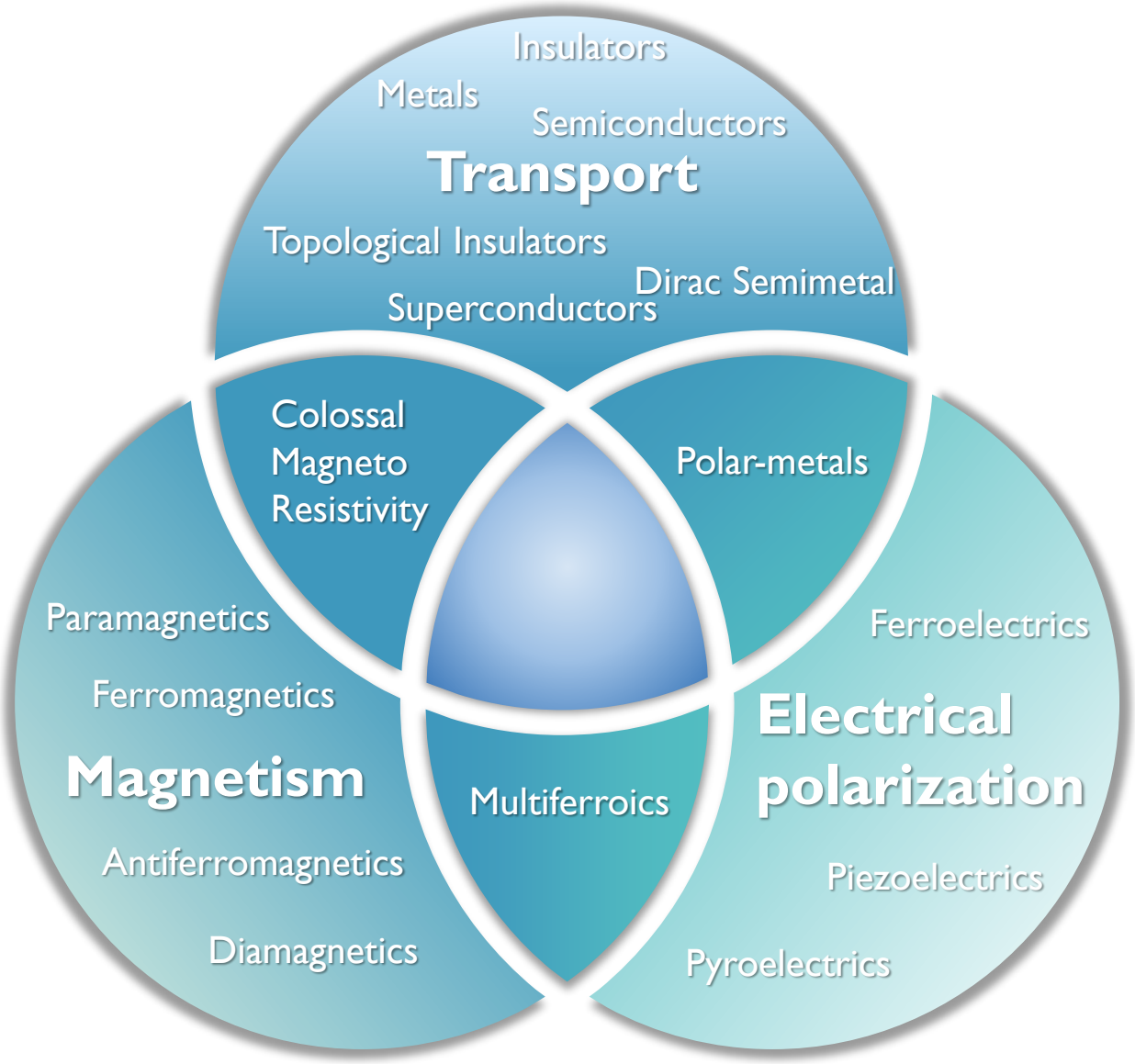
Functional oxides

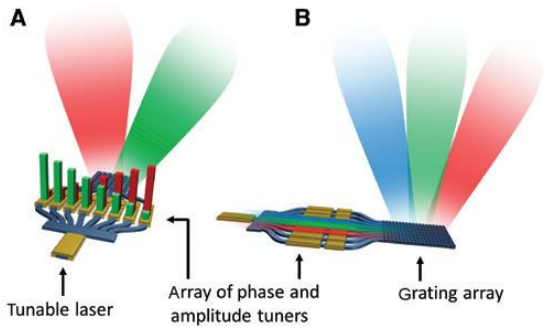
- Transport properties
  - Insulator / high-κ: $LaAlO_3$, $SrHfO_3$, $SrZrO_3$
  - Metals: $BaSnO_3$, $LaNiO_3$, $SrRuO_3$
  - Superconductors: $(Ba,K)BiO_3$
  - Topological insulators: $KBiO_3$, $BaBi(O,F)_3$
  - Dirac semimetals: $SrIrO_3$
  - Weyl semimetals: $SrRuO_3$
- Electrical polarization properties
  - Piezoelectric: $Pb(Zr,Ti)O_3$
  - Pyroelectric: $(Ba,Sr)TiO_3$
  - Ferroelectric: $BaTiO_3$
- Magnetic properties
  - Ferromagnetic: $(La,Mn)SrO_3$
  - Antiferromagnetic: $(La,Sr)FeO_3$
  - Multiferroic: $BiFeO_3$



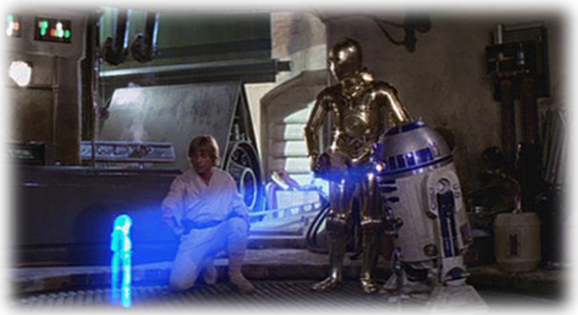
Combination of materials with various properties but with "similar" structures

Functional oxides

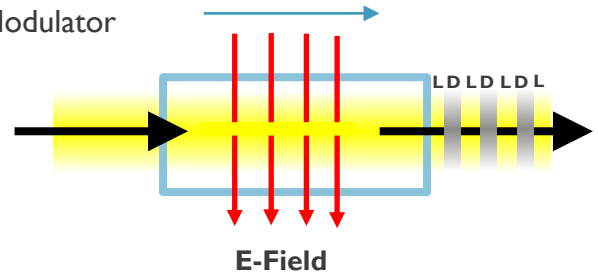
Applications

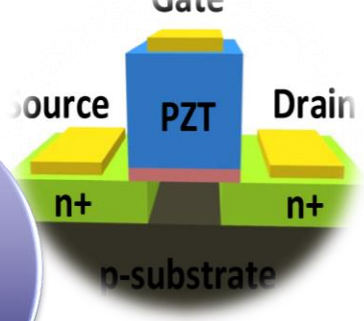


Video holography

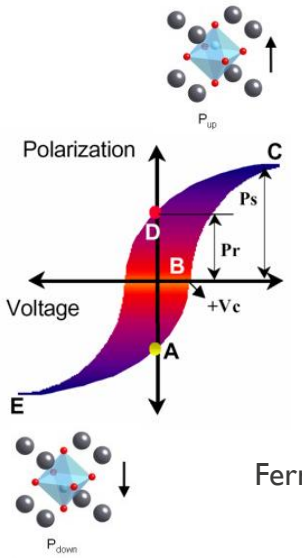


Optical Modulator

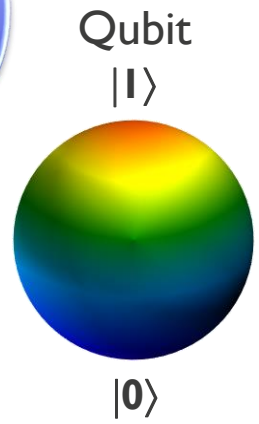




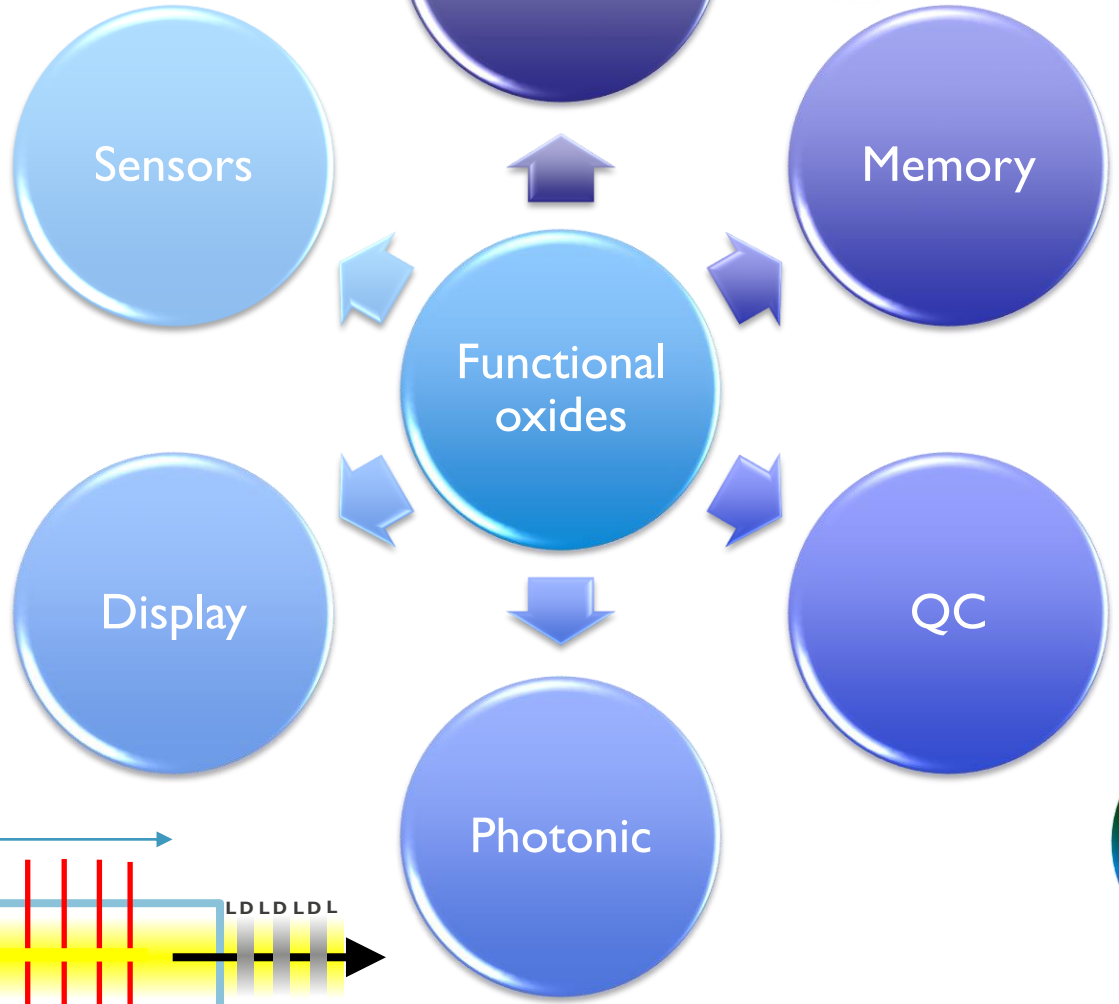
FeFET



Ferroelectric memory



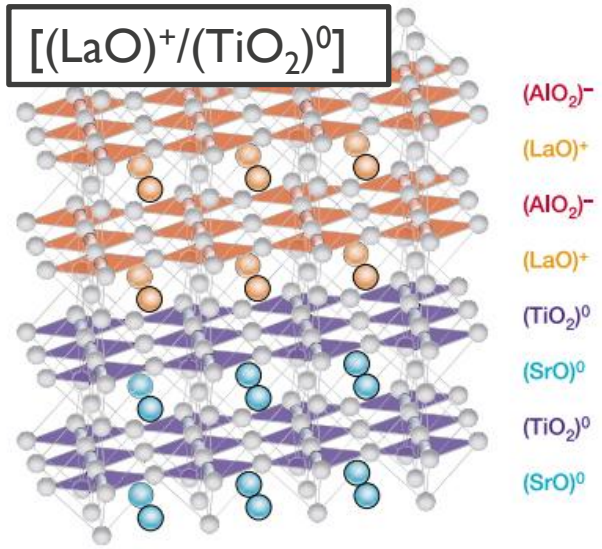
SC/TI

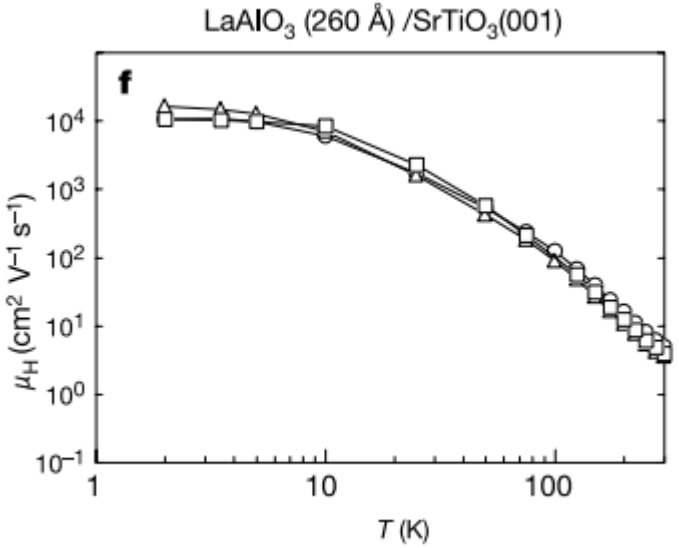


High-mobility 2DEG at the LAO/STO heterointerface

Ohtomo & Hwang, NATURE 427, 423 (2004)

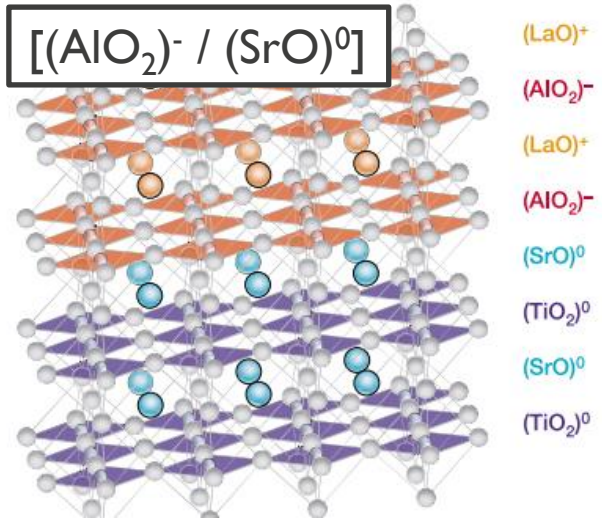
extra half electron
n-type interface
conducting





- The hole-doped interface is found to be **insulating** while the electron-doped interface is **conducting**, with extremely high carrier mobility exceeding **10 000 $cm^2V^{-1}s^{-1}$**.

extra half hole
p-type interface
insulating



- **Interface engineering** between two insulating perovskite oxides, $LaAlO_3$ and $SrTiO_3$, at an atomic scale.
- One interface presents an extra half **electron** $[(LaO)^+/(TiO_2)^0]$ or **hole** $[(AlO_2)^- / (SrO)^0]$ per two-dimensional unit cell, depending on the structure of the interface.

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Large scale integration of perovskites materials

$SrTiO_3$(001) substrate
Size: 1cm x 1cm
Cost: > 250 €

Si(001) substrate
Size: 300mm diameter
Cost: < 150 €

- Silicon integration (via epitaxy) is the only solution for future use of perovskite oxides ...

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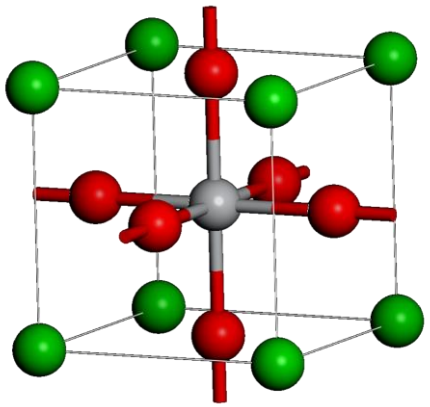
Monolithic integration though epitaxy

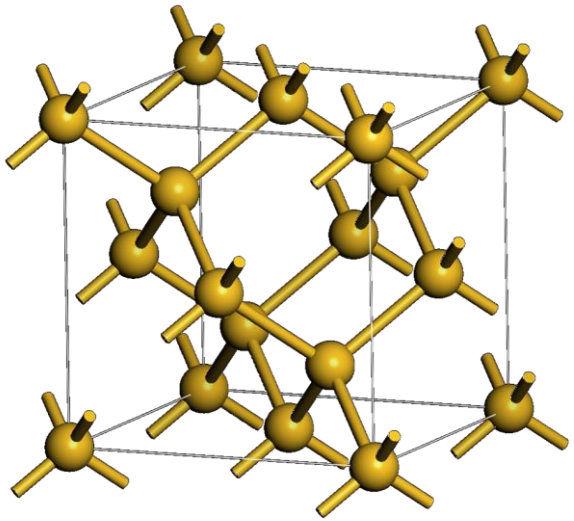
Epitaxial oxide challenges
ABO_3 vs. Si

- **Crystal structure** mismatch
  - Perovskite vs. Diamond

Perovskite (ABO_3)

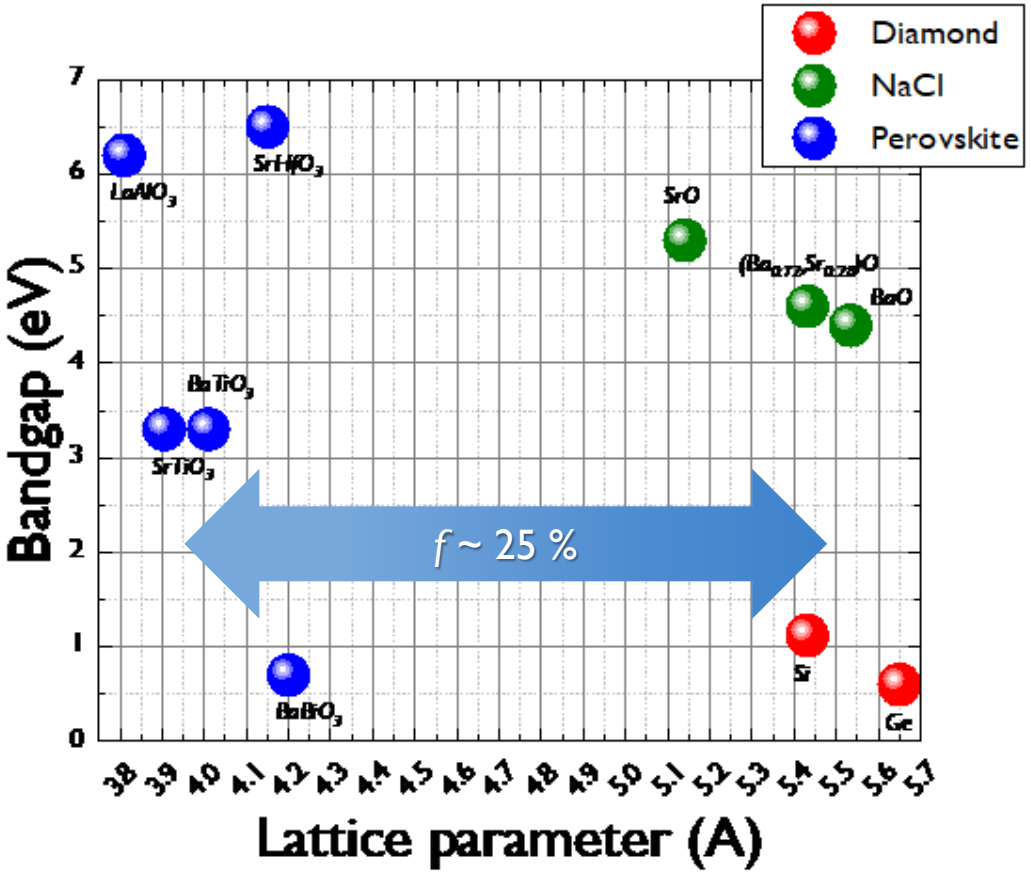


Diamond



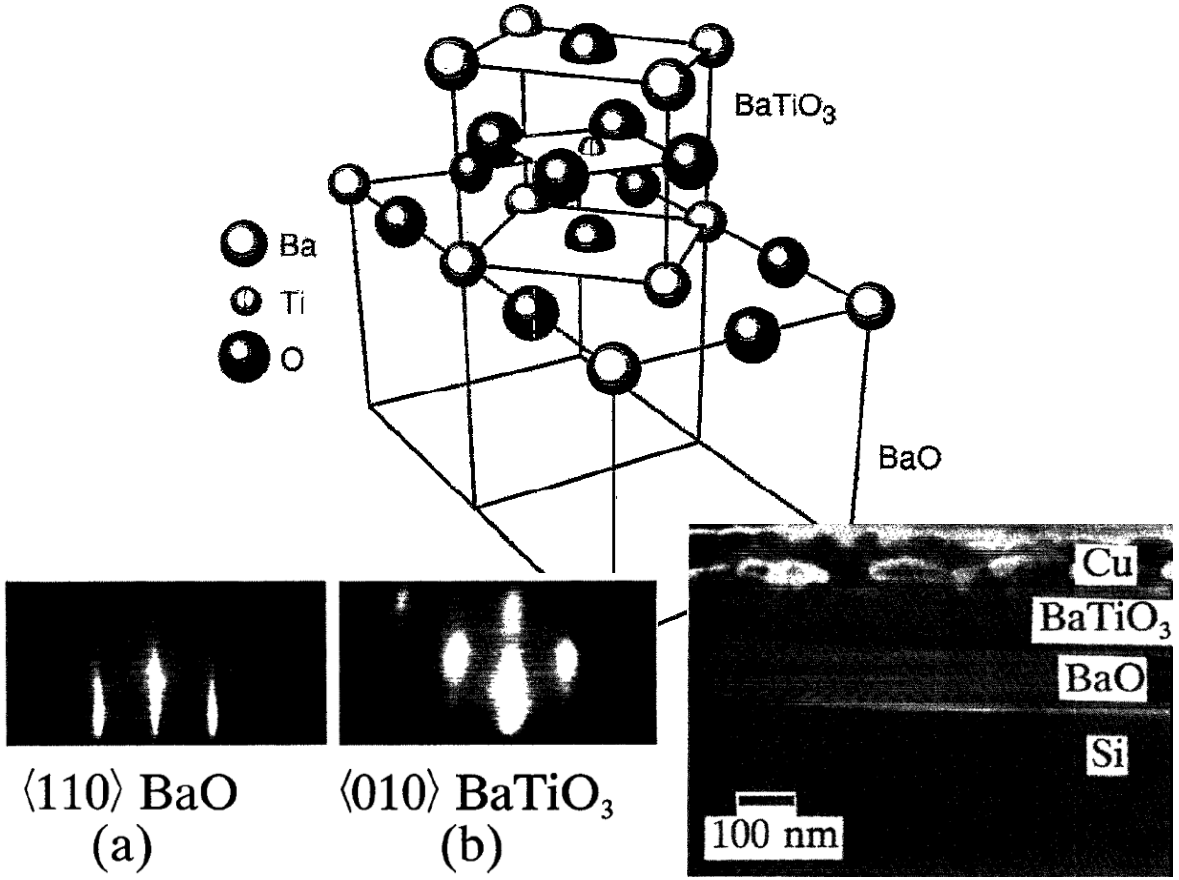
- **Chemical bonding** mismatch
  - Ionic bonds vs. Covalent bonds

- **Lattice parameter** mismatch

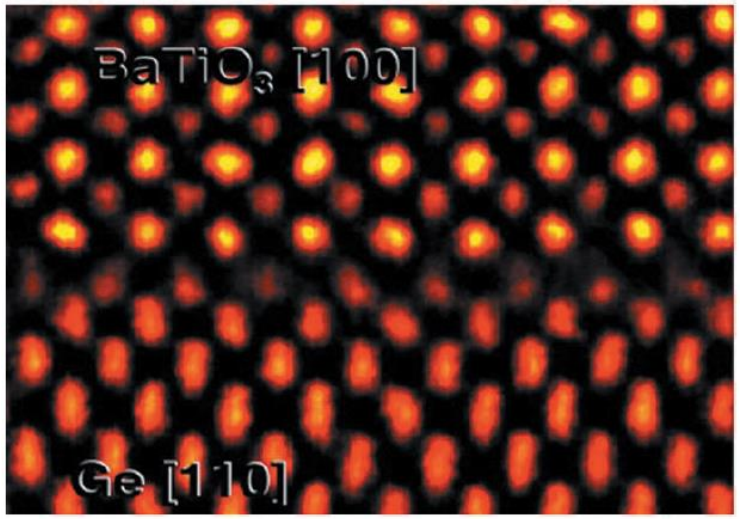


Pioneering work

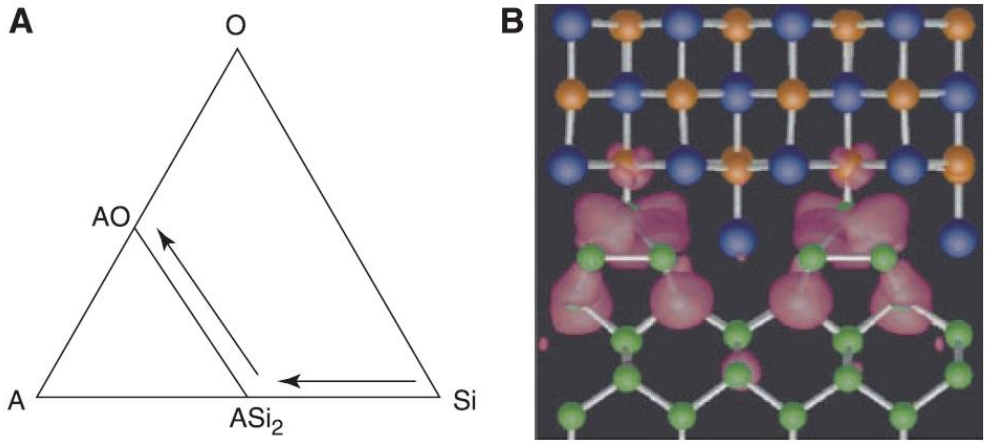
McKee et al., Oak Ridge Univ. (1990 ~ 2000)



Appl. Phys. Lett. **59**, 782 (1991)



Science 293, 468 (2001)

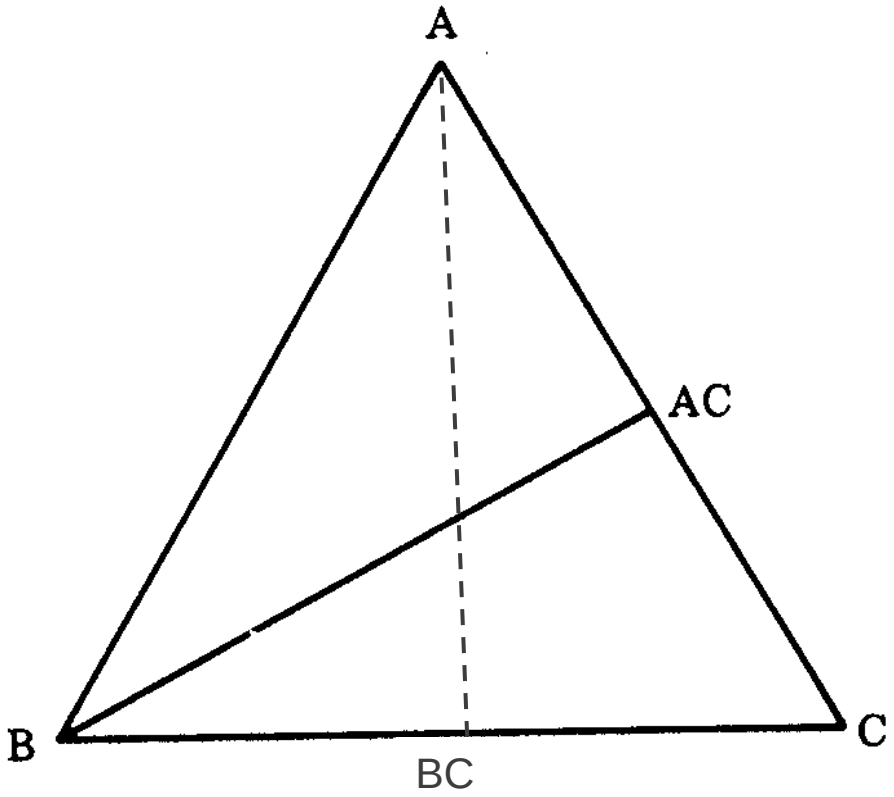


Science 300, 1726 (2003)

Thermal stability of M_xO_y/Si systems

- One of the important point was the thermal stability of the oxide with Si.

- Phase diagrams can provide valuable insight in this issue.
  - Diagram used to investigate the thermal stability of the different compounds in presence of each other (i.e. M, Si and O)
  - Stable (solid) tie line: thermodynamic stability between AC compound and B
  - Unstable (dashed) tie line: BC compound and A not thermodynamically stable

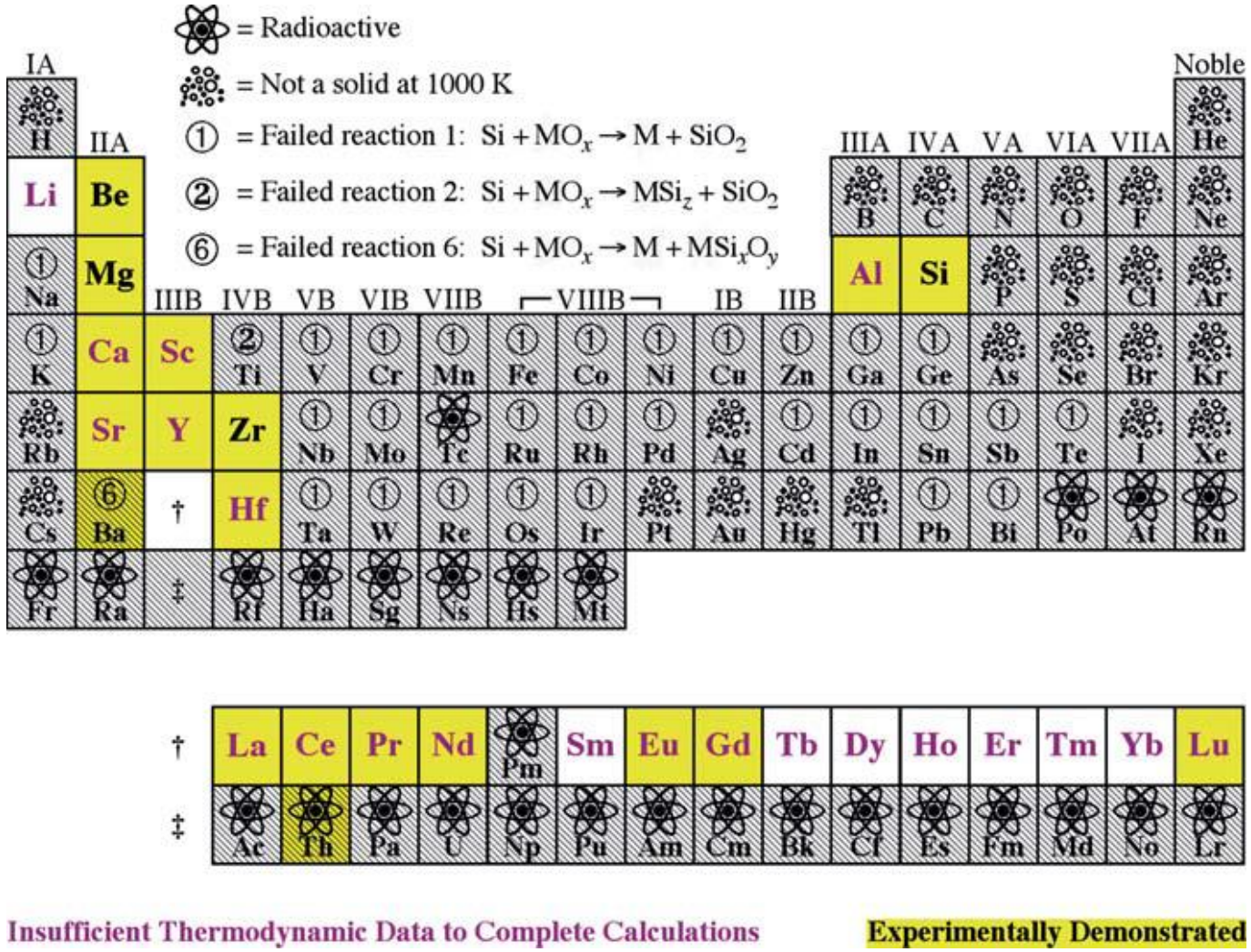


Schematics of a ternary-phase diagram: single tie line

Interface Engineering on Si

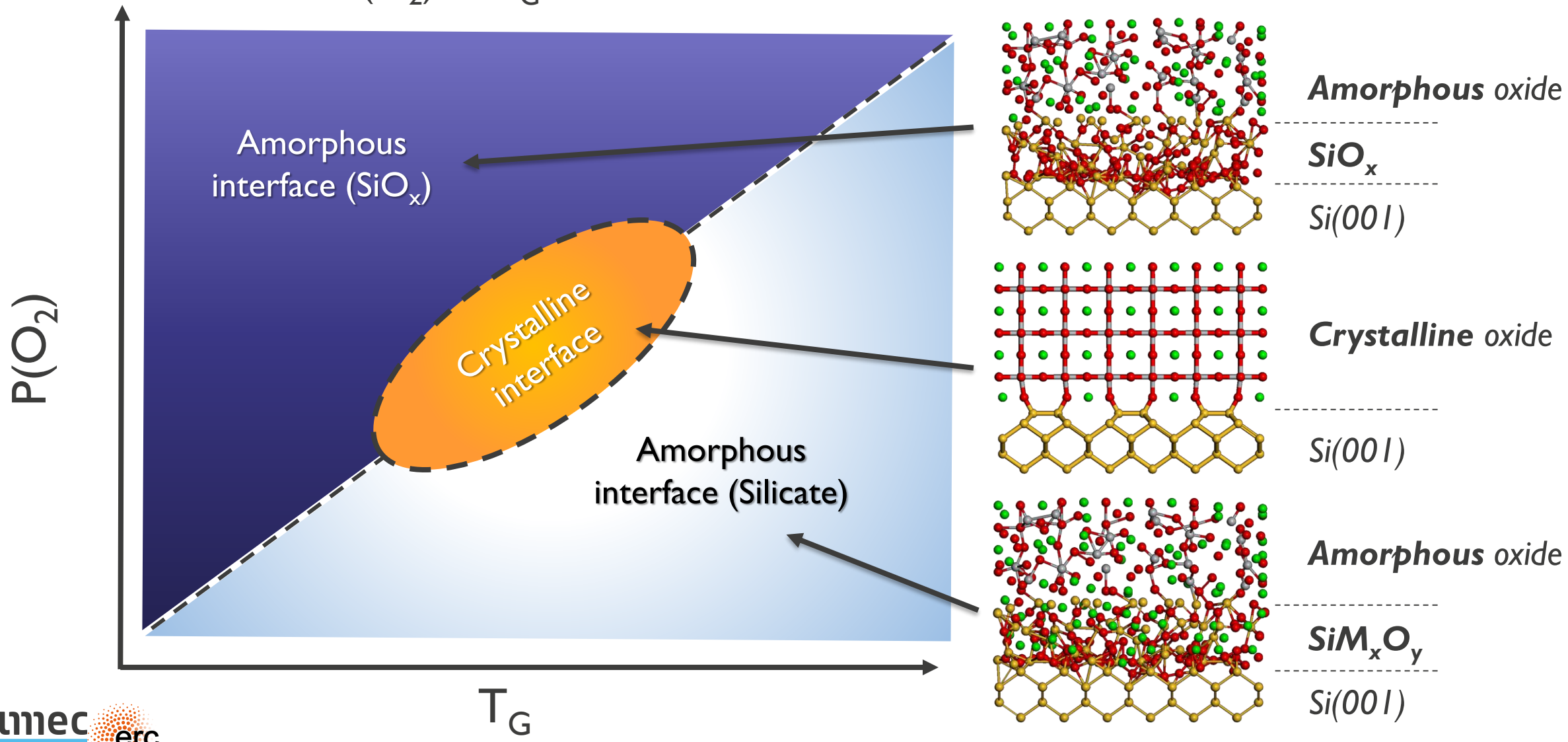
"A thermodynamic approach for interfacial layer screening" – *D.G. Schlom & J.H Haeni*

- Need for stable interface with Si
  - Controlled Metal – Si – Oxygen reactions
  - Thermodynamic approach compared with experimental demonstration
- The elements $\boldsymbol{M}$ having an oxide $\boldsymbol{MO_x}$ that has been experimentally demonstrated to be stable in direct contact with Si are underlined:
  - IV_A: (Si)
  - III_A: Al
  - II_A: Ca, Sr, Mg
  - III_B: Sc, Y
  - IV_B: Hf, Zr
  - Lanthanites: La, Ce, Pr, Gd, ...



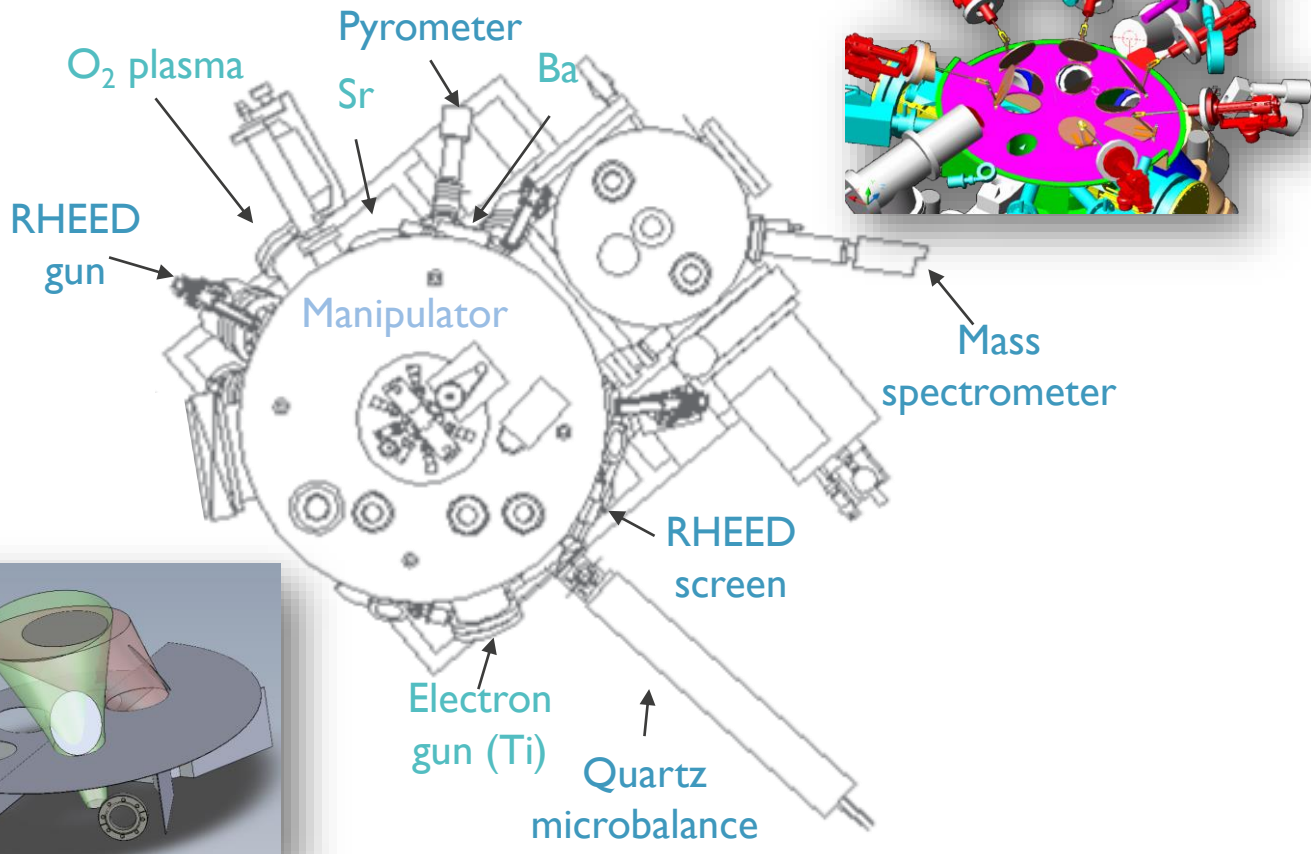
Epitaxial oxide challenges

Si interface control: $P(O_2)$ vs. T_G



Epitaxial Strategy
Molecular Beam Epitaxy

- Molecular Beam Epitaxy (MBE)
  - In-situ analysis growth technique
  - Precise flux controlling at atomic level



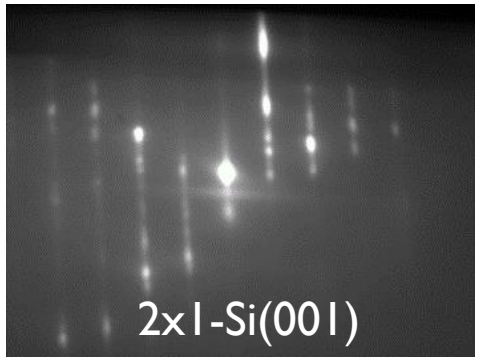
- RIBER MBE49 200mm Tool @ imec
  - 2” to 8” substrates
  - Ba, Sr, Bi, Ti, Hf, Zr, CaF_2, Al_2O_3
  - O_2 & N_2 remote plasma
  - *in-situ* characterizations
    - RHEED
      - Crystalline state

- In-situ quartz microbalance
  - Flow rate calibration

- Mass spectrometers (x6)
  - Evaporation control

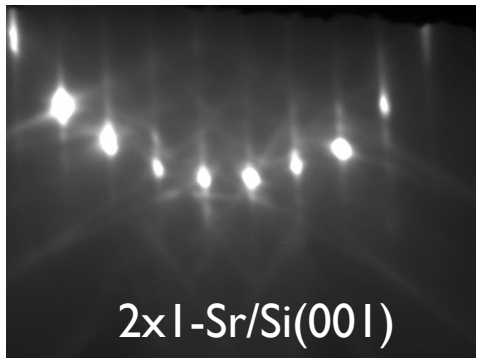
½ ML Sr Submonolayer engineering of Si(001)

Si(001)

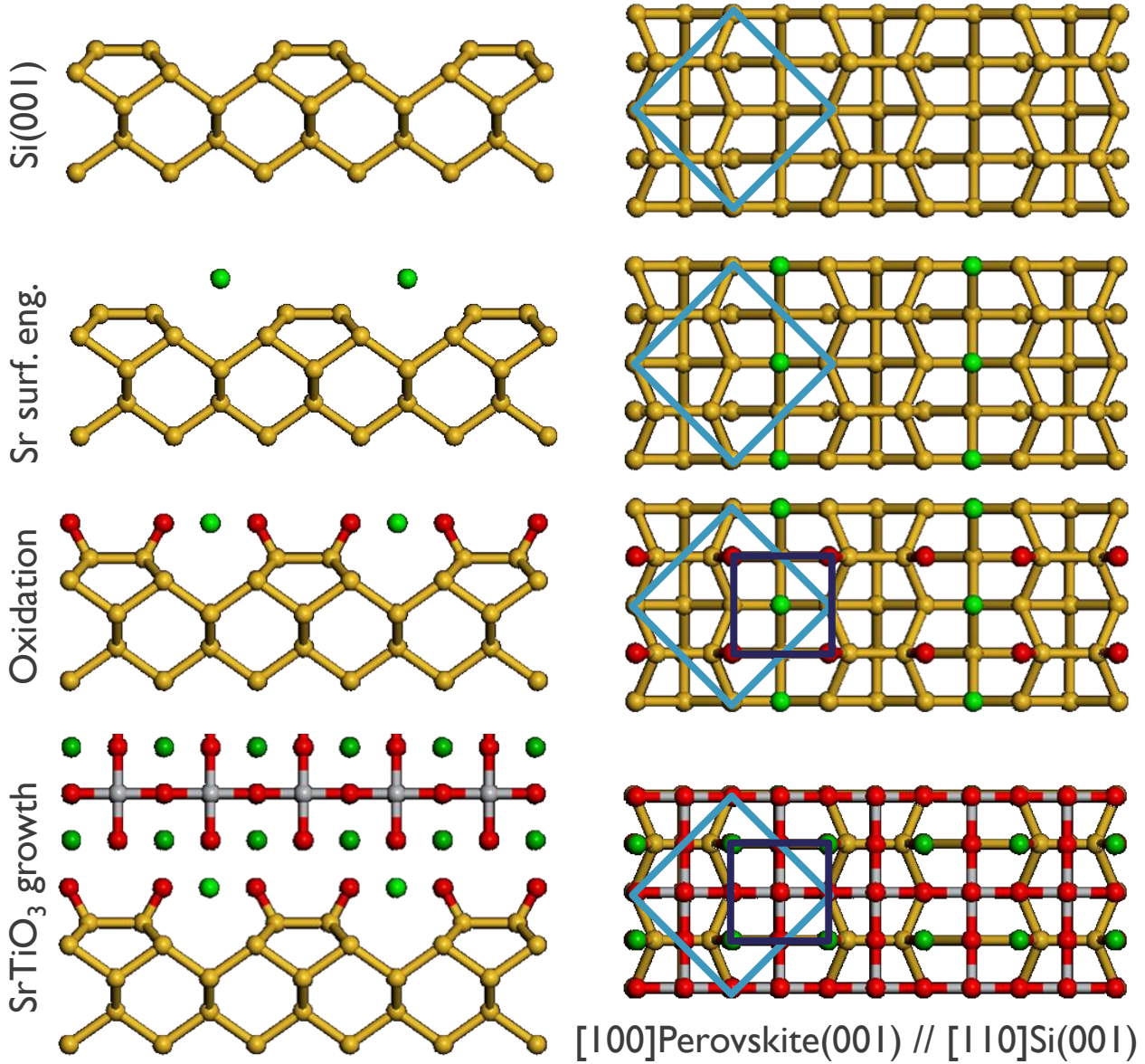


Dimerized Si(001) surface

0.5 ML Sr
Si(001)

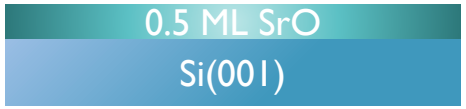


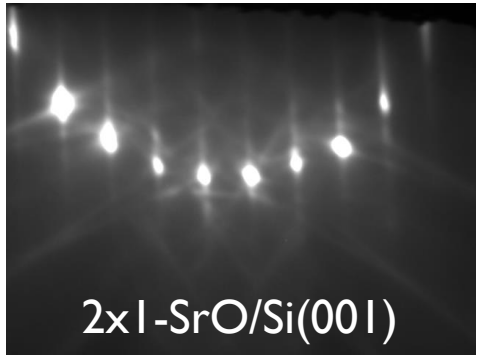
½ ML Sr-Terminated Surface

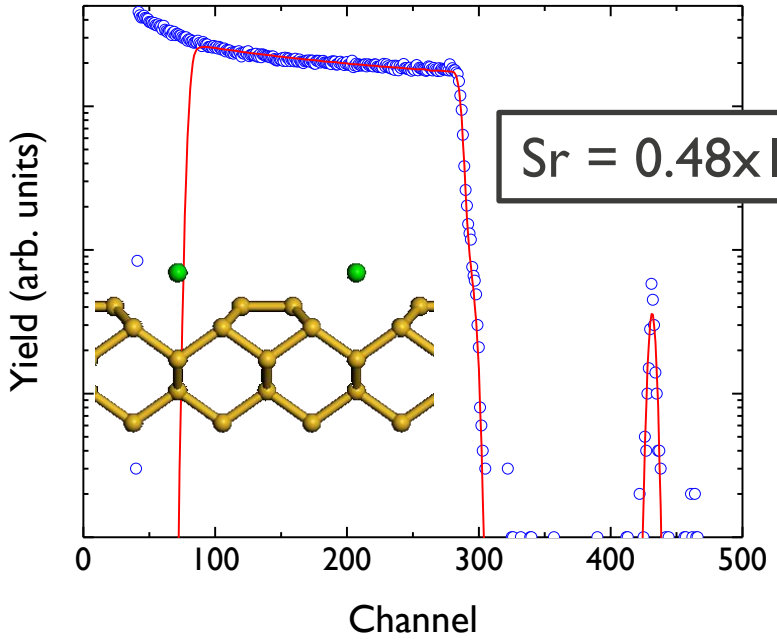


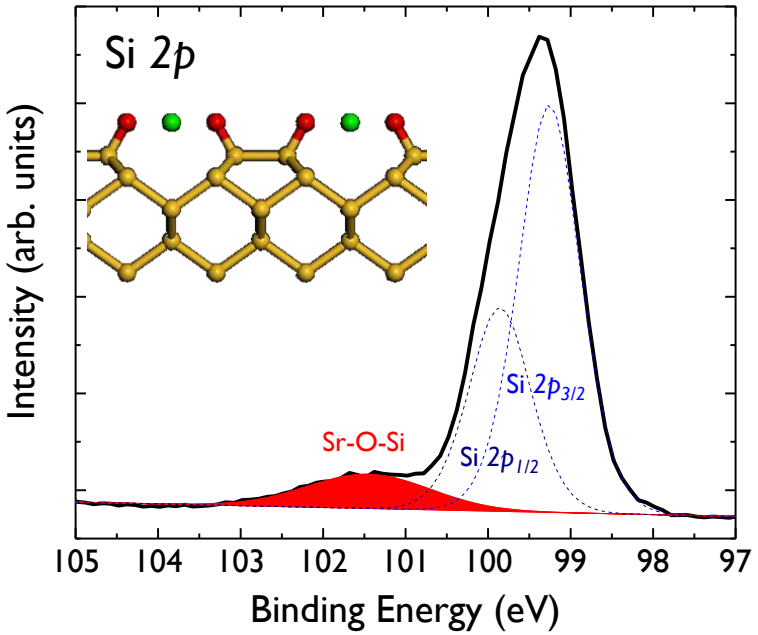
SrO Interfacial Layer

½ ML SrO/Si(001)







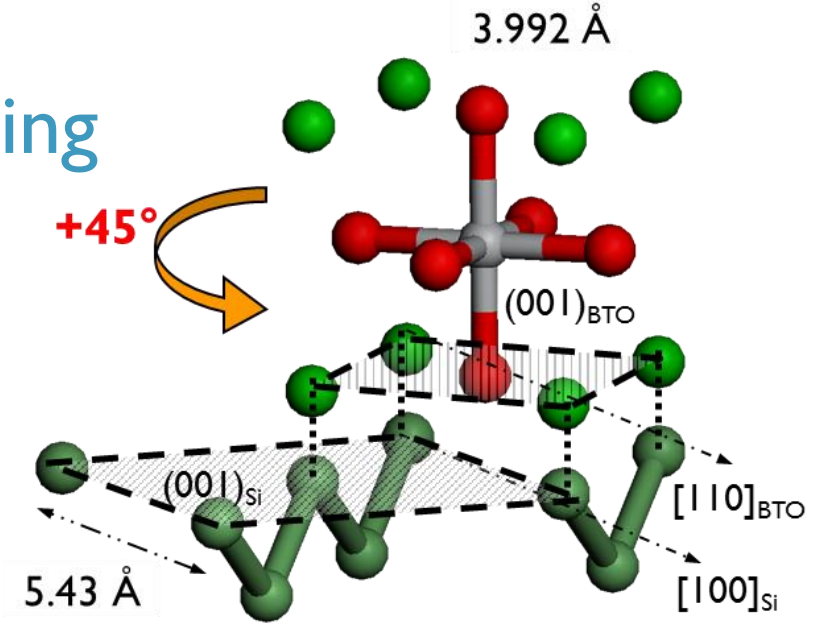


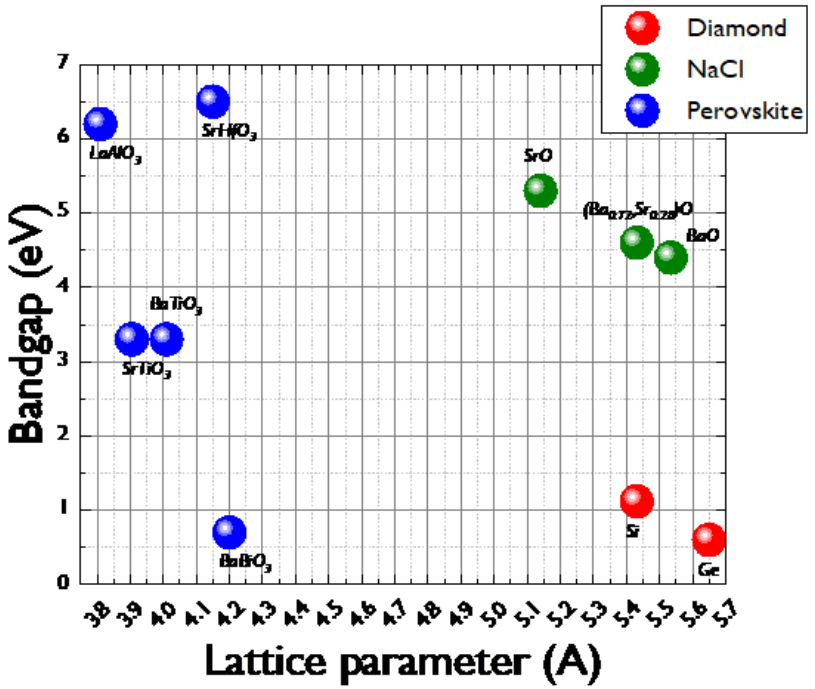
- A stable and natural oxidation barrier for Si(001) surface
  - 2x1 surface reconstruction preserved
- Atomic concentration measured by RBS
  - 0.48×10^{15} at/cm^2 = ½ ML
- Ultra thin Sr-O-Si interfacial layer measured by AR-XPS

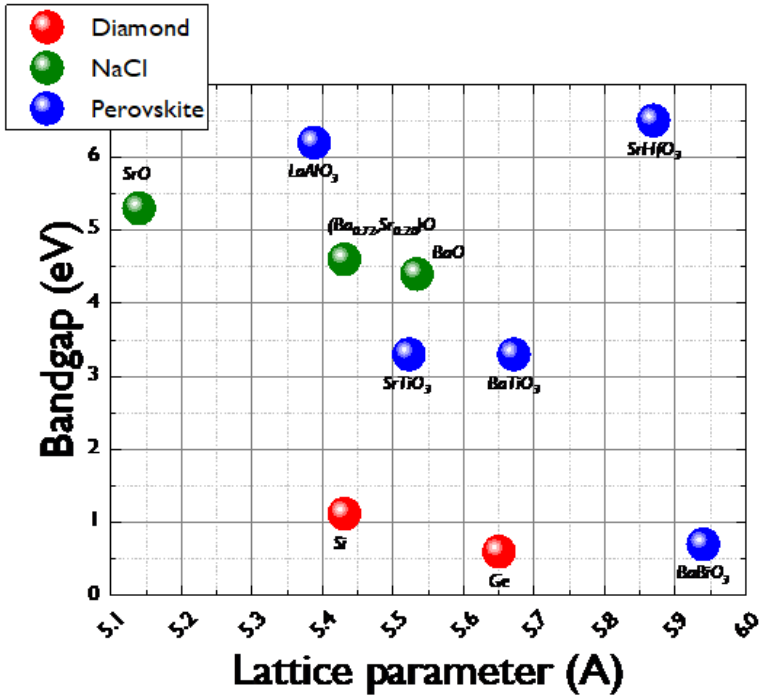
Epitaxial Strategy: Oxide/Si Interface Engineering

Alkaline Submonolayer

- Alkaline Submonolayer (Mg, Ca, Sr, …)
  - Oxidation Barrier: stable "Si – O – Alkaline" interface
  - Crystal Template: 45° Lattice rotation
  - [100]Perovskite(001) // [110]Si(001)
    - Effective lattice mismatch reduction

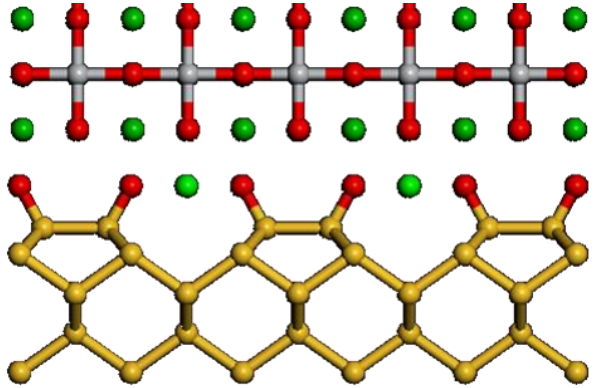






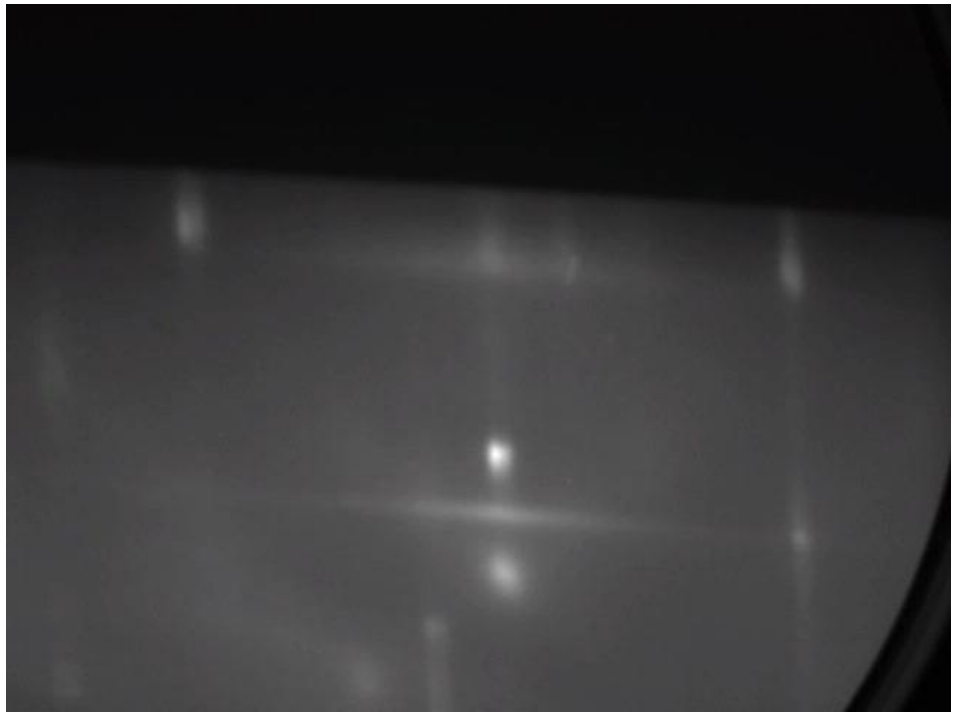
$SrTiO_3$/Si(001) pseudo substrate: the key

$SrTiO_3$ buffer: the trick ....



- Different strategies for STO growth on Si
  - 2 steps: LT deposition + recrystallization
  - Different buffers: ½ ML SrO -> few nm (Ba,Sr)O
  - Direct STO epitaxy onto Sr-Si(001)

- @ imec: direct STO epitaxy onto Sr-Si(001)
  - T_G ~ 300 C & $P(O_2)$ < 2e-7 Torr
  - Smooth "Si-to-STO" transition by RHEED
  - Strong streak diffractions lines from STO at early stage without amorphization step

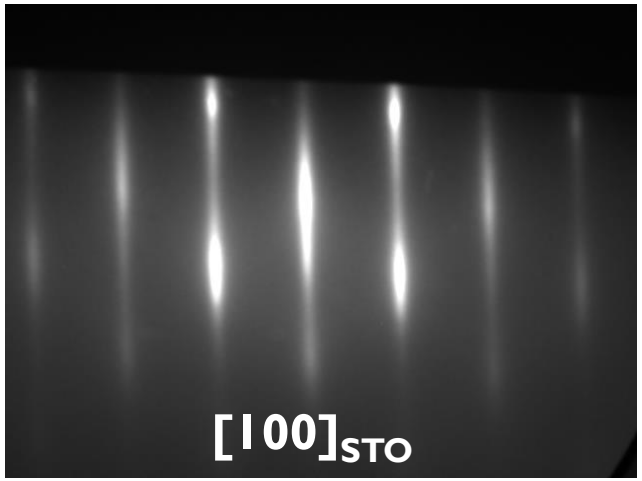


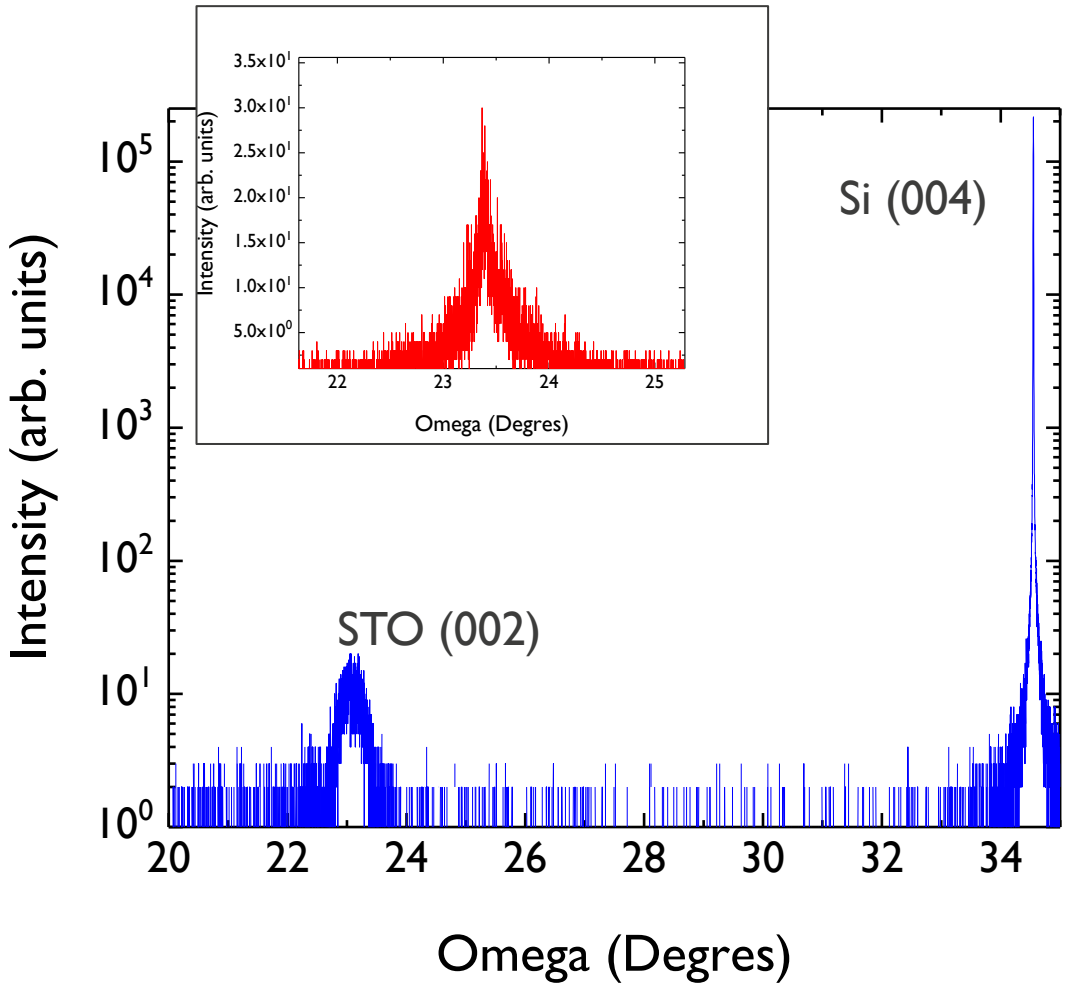
High Quality $SrTiO_3$

Low temperature epitaxy on Sr-Si(001)

- Excellent STO pseudo-substrate quality for functional oxides integration on Silicon
  - Monocrystalline oxide
  - (002) FWHM < 0.2°

20MLs (~8nm)

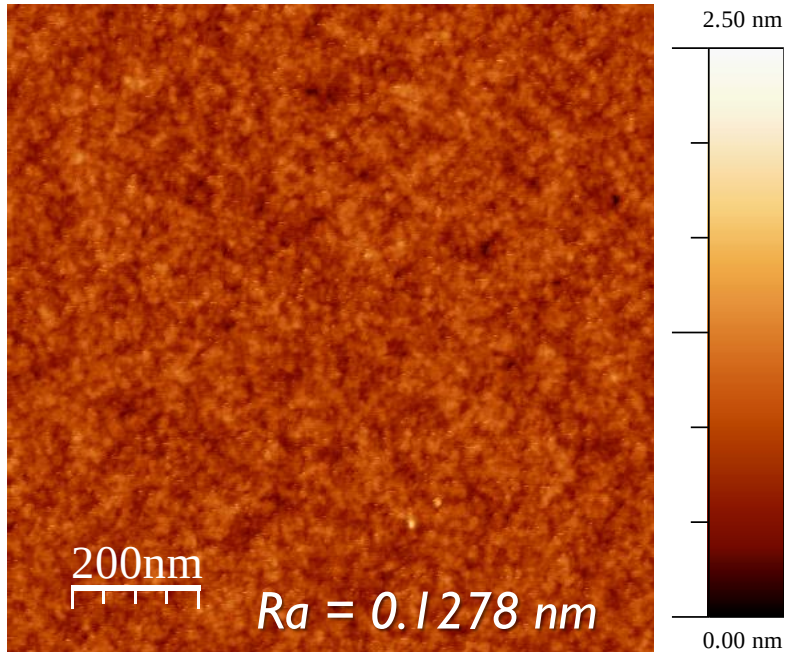


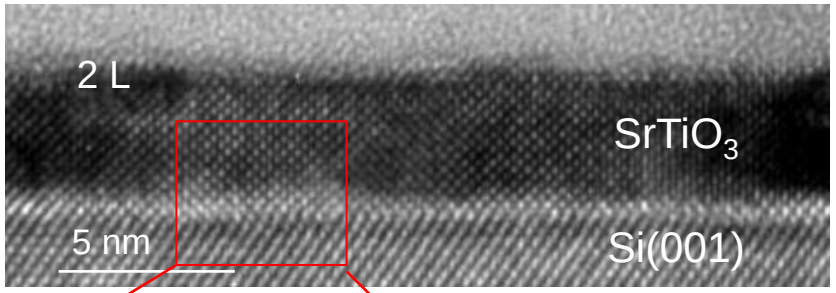


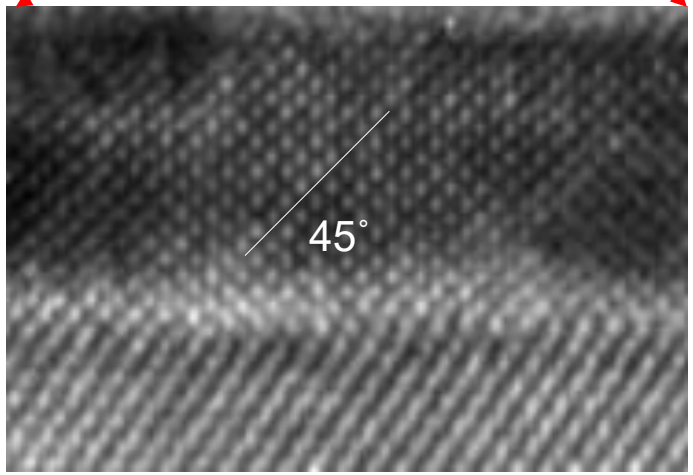
High Quality $SrTiO_3$

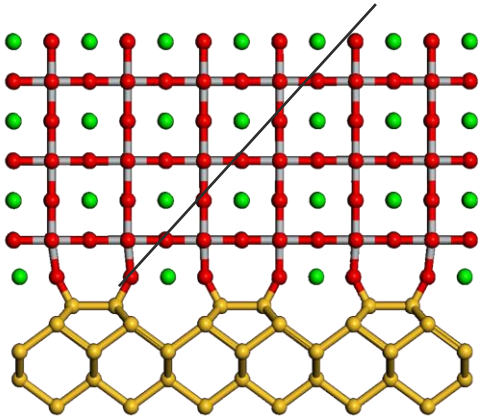
Low temperature epitaxy on Sr-Si(001)

- Excellent STO pseudo-substrate quality for functional oxides integration on Silicon
  - RMS < 0.2 nm
  - Sharp Si/STO interface



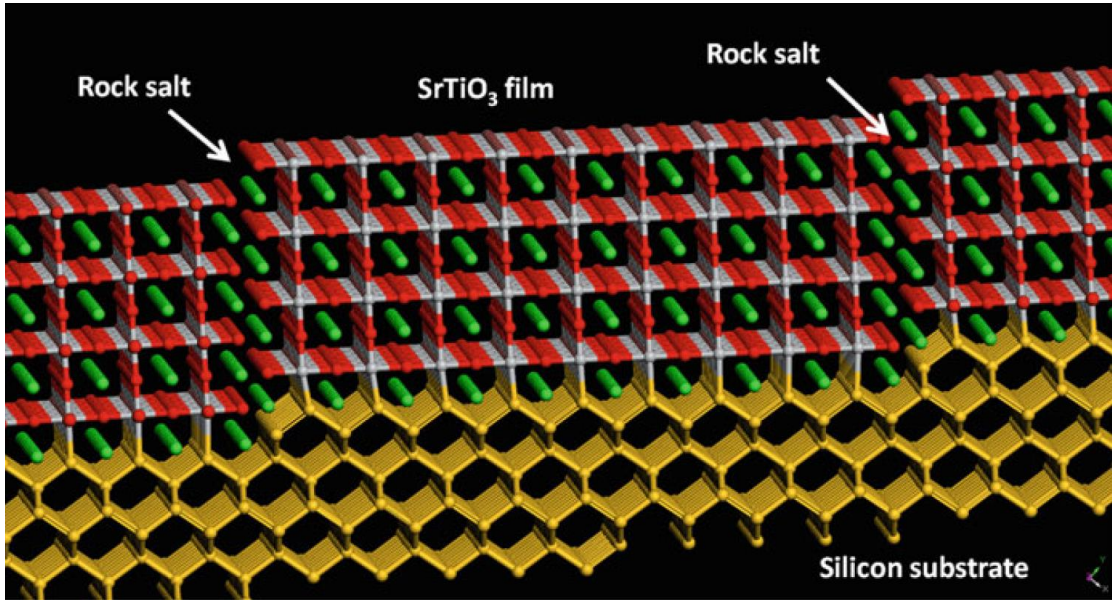




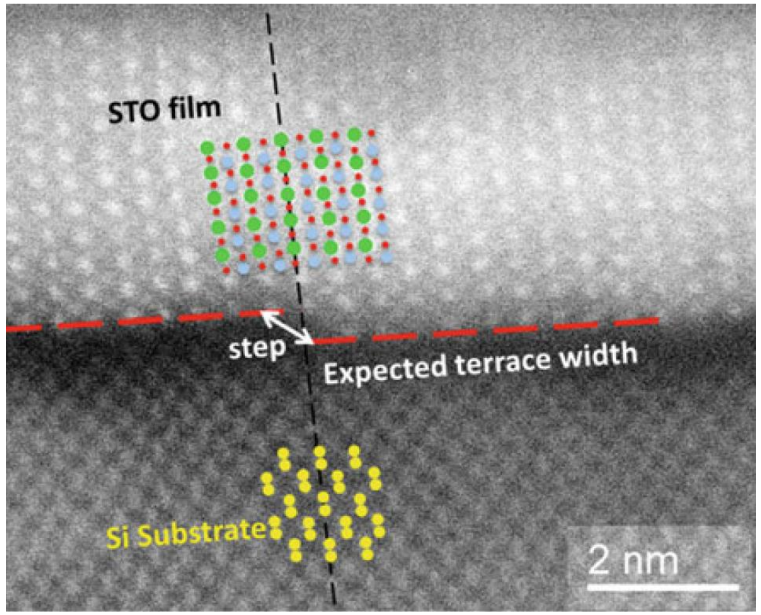


Defects in perovskites

Anti-phase domains



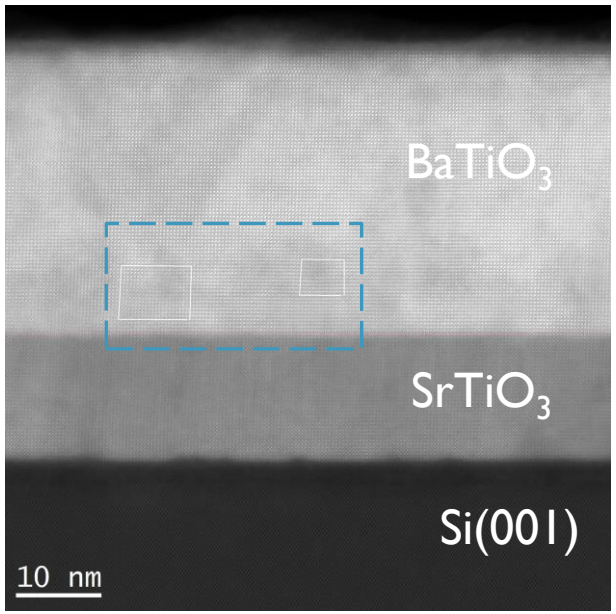
Domain walls at step edges can be healed using the formation of quasi Ruddlesden-Popper layers

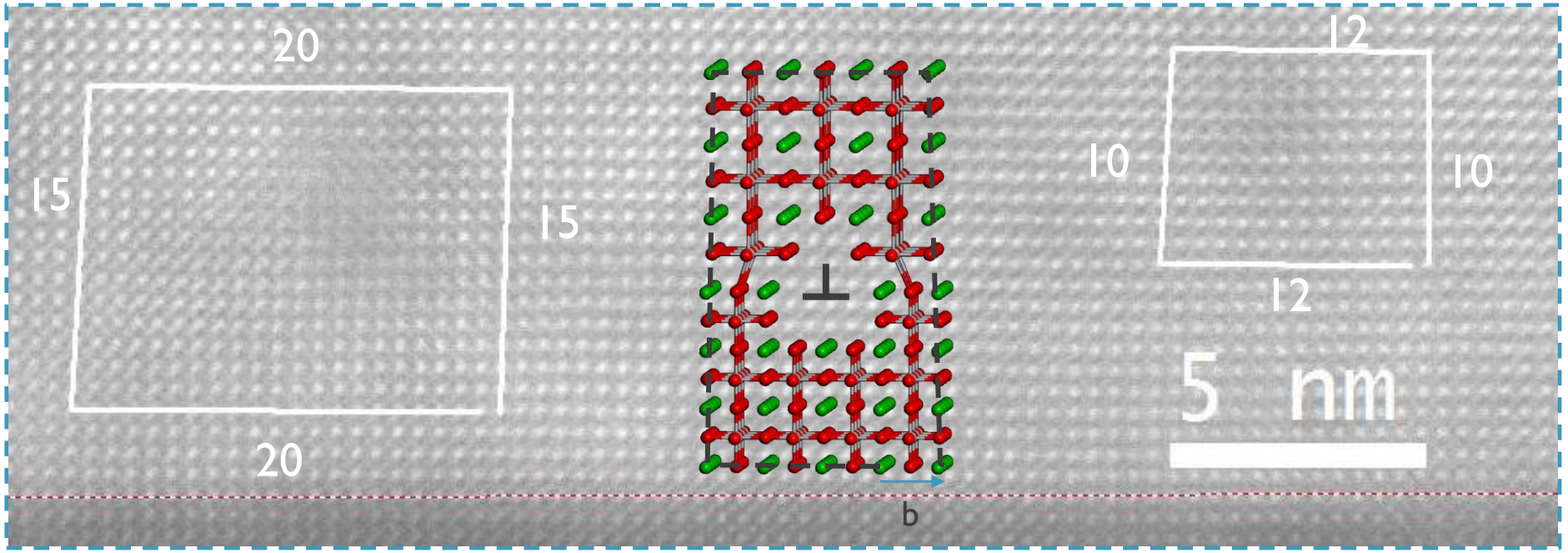


Scanning transmission electron micrograph of STO grown on 4° miscut vicinal Si(100). (Image courtesy of D. J. Smith).

Defects in perovskites

Misfit dislocations



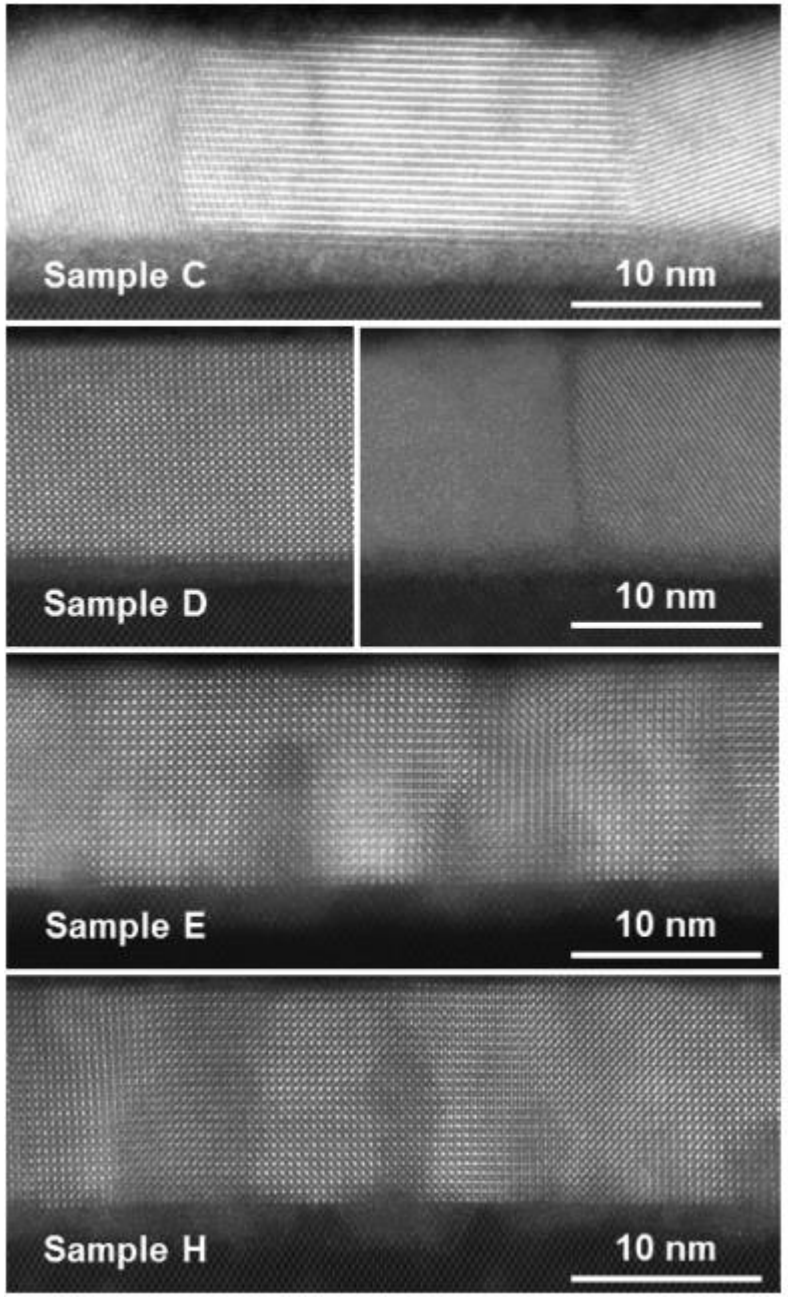


- Strain relaxation via misfit dislocations
- Edge dislocations
  - Burger vector: b = $a_{BTO}\langle 100\rangle$ = 3.995 A

Defects in perovskites

Importance of stoichiometry

- The Sr/Ti stoichiometry in crucial, any slight variation would drastically influence the layer crystallinity and generate high defect density or amorphous / polycrystalline phases.



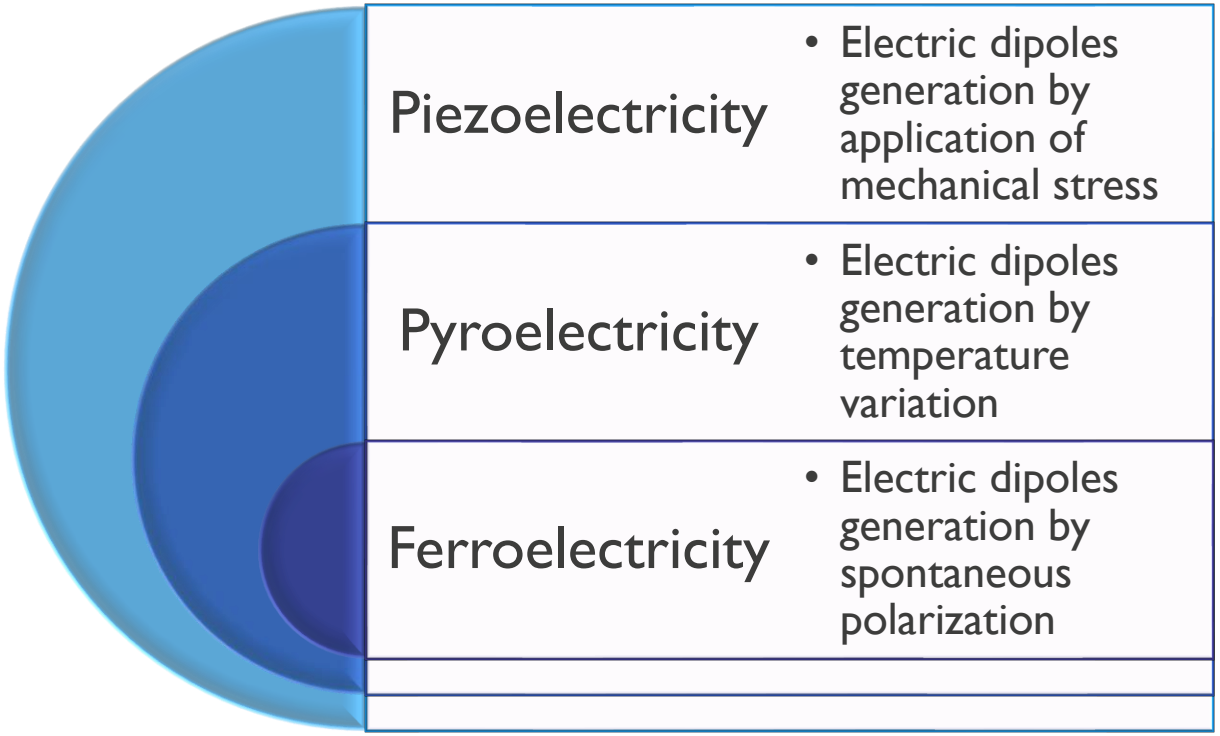
G. Saint Girons et al., Chem. Mater. 2016, 28, 5347−5355

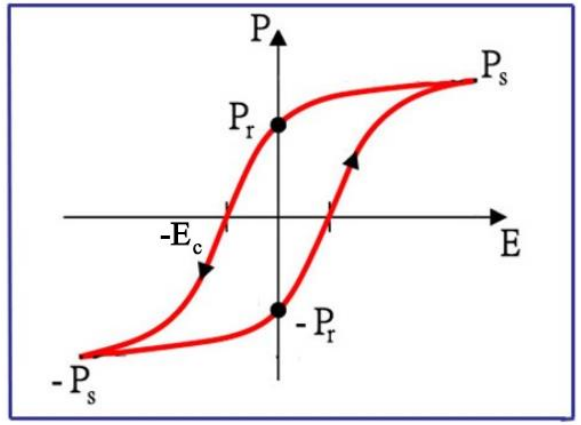
New challenges / new applications

Pockels materials : $BaTiO_3$

Ferroelectricity
Definition

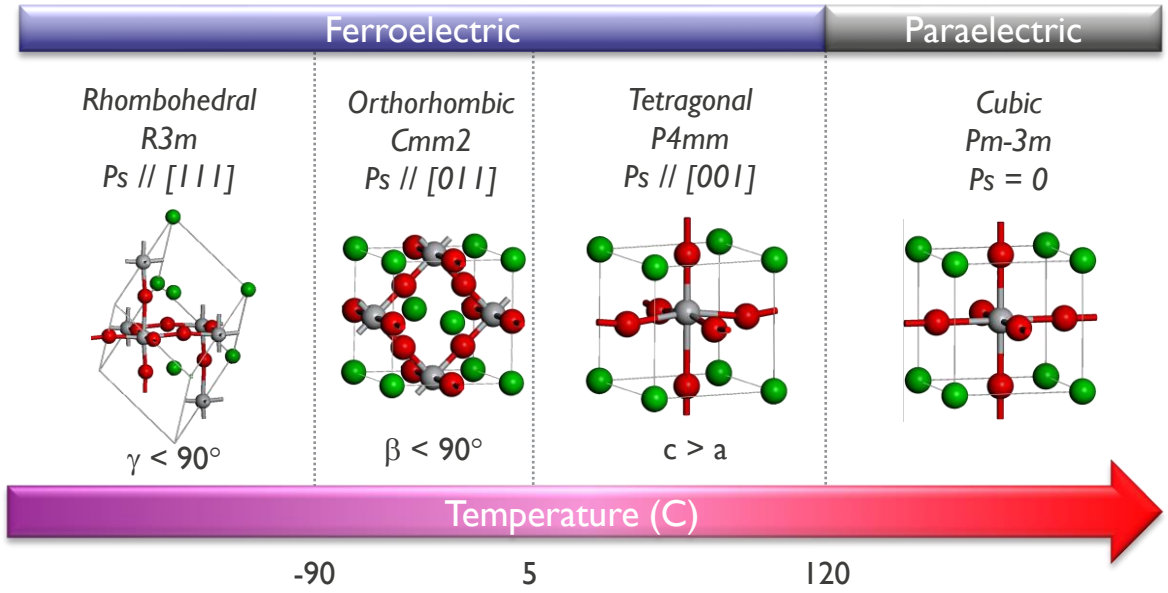
- Ferroelectric: material that shows spontaneous and reversible dielectric polarization (P_s)
  - Sub-family of pyro- and piezoelectric materials
  - Internal electric dipoles can be forced to change direction by application of an external electrical field
    - Ferroelectric Hysteresis Loop
  - The electric dipoles are physically linked to the intrinsic properties of the ferroelectric material.

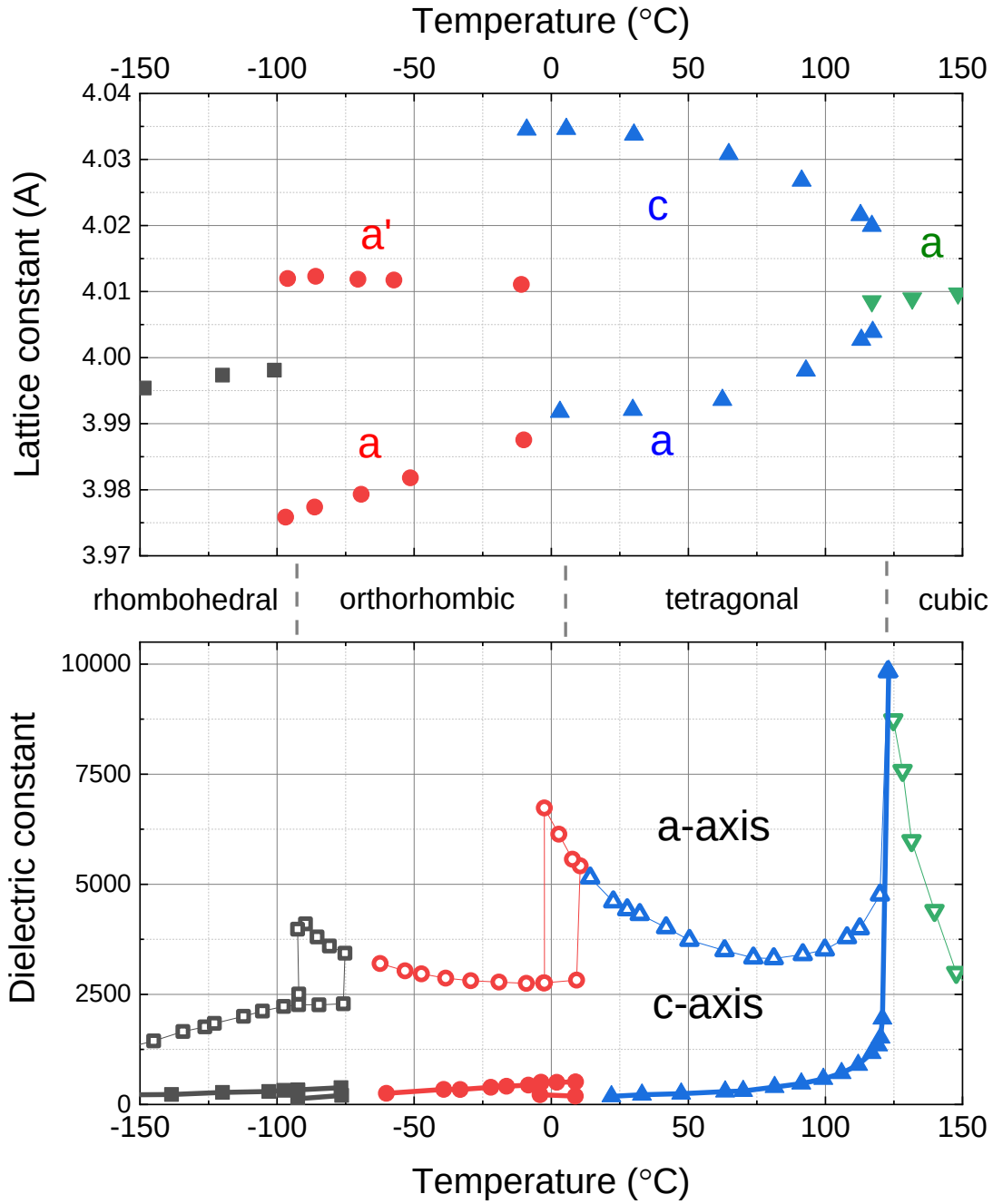




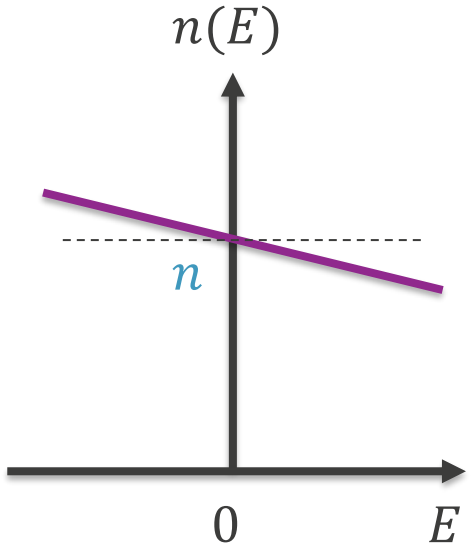
$BaTiO_3$
Structural properties

- Strong temperature dependence
  - Crystalline phases
  - Lattice parameter
  - Dielectric constant
  - Polarization properties

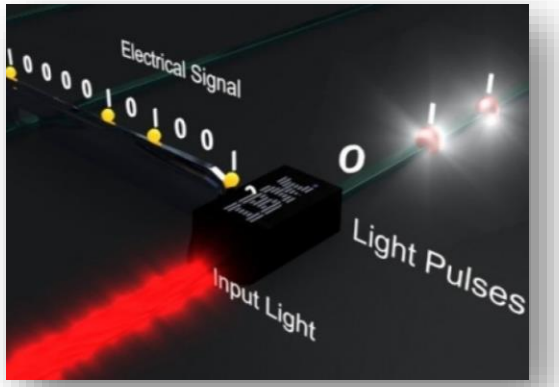




Electro-Optical effect



- E-O effect is the change of refractive optical index (n) of a material induced by an external electric field
- Ideal for **fast** light modulation
- Applications / devices
  - Photonic
    - Optical modulator
  - Beam forming
    - Lidar
  - Display
    - Video holography



Optical modulators (IBM)


Lidar (Bosch)


Video holography (Samsung)

Fundamentals

- Change of the refractive index

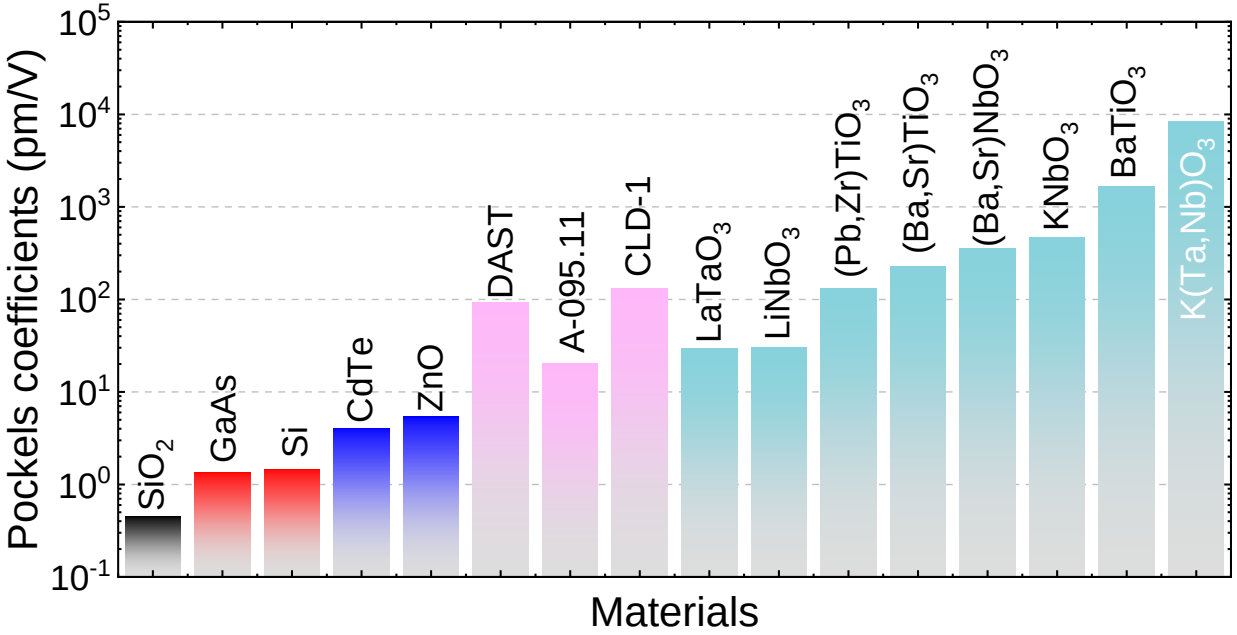
$$n(E) \approx n - \frac{1}{2} r n^3 E - \frac{1}{2} R n^3 E^2$$

  - **Pockels** effect (with r the Pockels coeff.)
    - Figure of Merit (FOM) of the Pockels effect as $FOM_{Pockels} = n^3 r$
  - **Kerr** effect (with R the Kerr coeff.)

- Polarization-optic effect: change of the optical index as function of the induced polarization in the materials

$$r_{ijk} = \varepsilon_0 f_{ijm} (\varepsilon_{mk} - \delta_{mk})$$

Polarization-optic coef. *Dielectric constant* *Dielectric loss*



- Large electro-optic effects would be observed in materials with:
  - **large polarization-optic response**.
    - Organic polymers
    - Organic crystals
  - **large dielectric constant**
    - Ferroelectric oxides (KNO, BTO, ...)

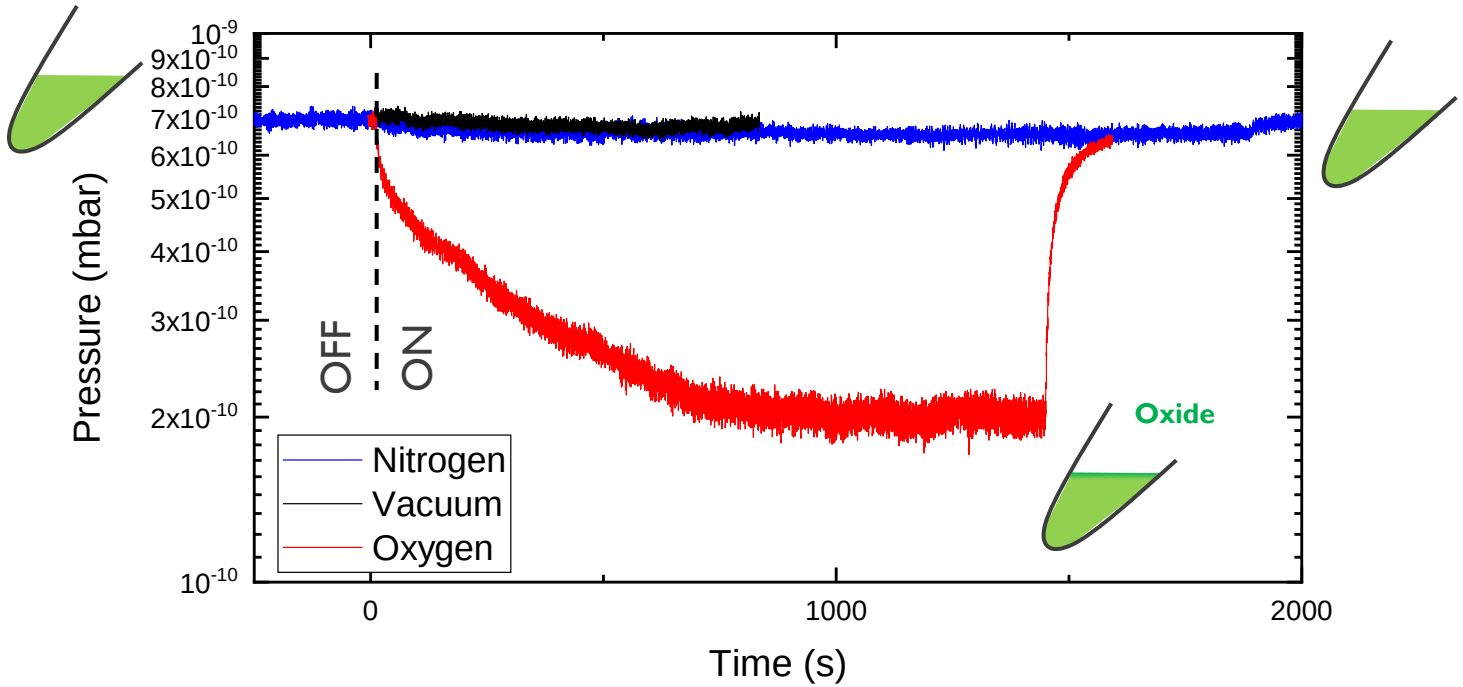
imec KU LEUVEN erc

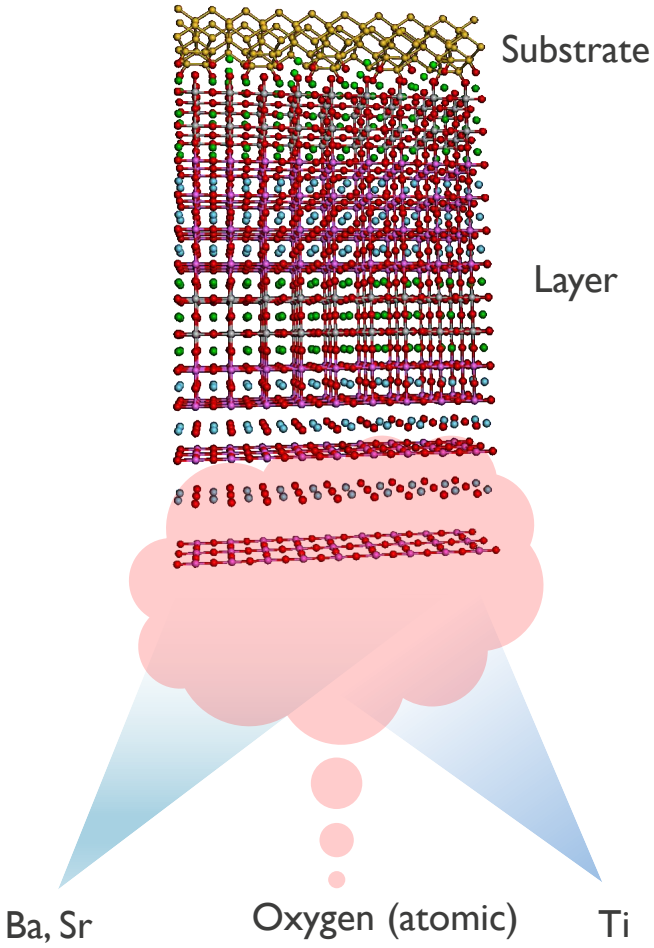
Material down selection

MATERIALS	r (pm/V)	n (633 nm)	ε (low freq.)	$f\varepsilon_0$	FOM (n^3r)
INORGANIC MATERIALS					
• $LiNbO_3$	r_{33} = 31.8	2.2	28	1.1	338
• $KNbO_3$	r_{33} = 467	2.2	300	1.56	4 972
• $BaTiO_3$	r_{42} = 1640	2.37	2500	0.65	21 830
ORGANIC CRYSTALS					
• DAST	92	2.5	5.2	21.9	1 435
ORGANIC POLYMERS					
• A-095.11	20	1.66	2.8	11.1	92
• CLD-1	130	1.65	3.5	52	584

- **$LiNbO_3$** (substrate) is well developed and is already used in high-bandwidth optical communication systems but has low EO properties
- **Organic materials** have high EO coefficient but unresolved problems of thermal and optical stability
- **$BaTiO_3$** compares favorably with both $LiNbO_3$ and organic materials with respect to several of the figures of merit for electro-optic devices but is hardly available in substrates

Atomic flux vs. environment in Oxide-MBE

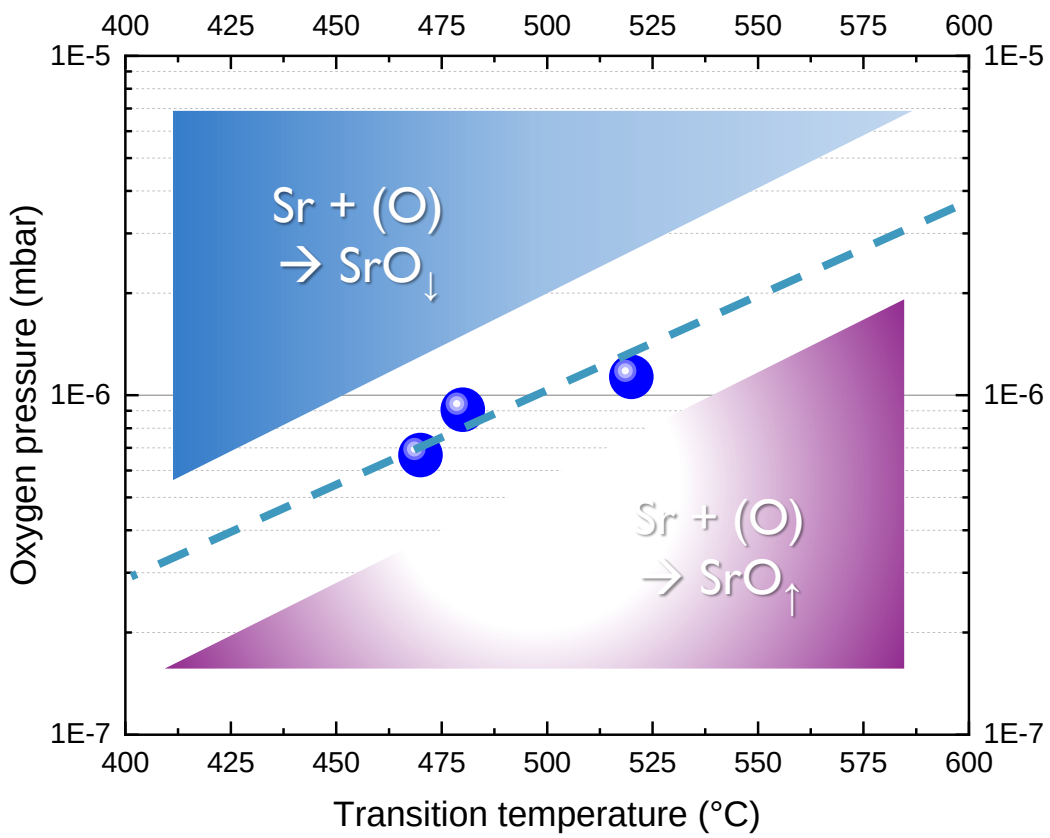




- Characterize the elemental partial pressure by XBS in function of the environment: UHV, O_2, N_2
- Similar behavior for Sr, Ba and Ti metallic sources
- In oxygen ambient, native oxide is formed in surface of the metal impacting the molecular beam, and function of the source temperature and oxygen pressure

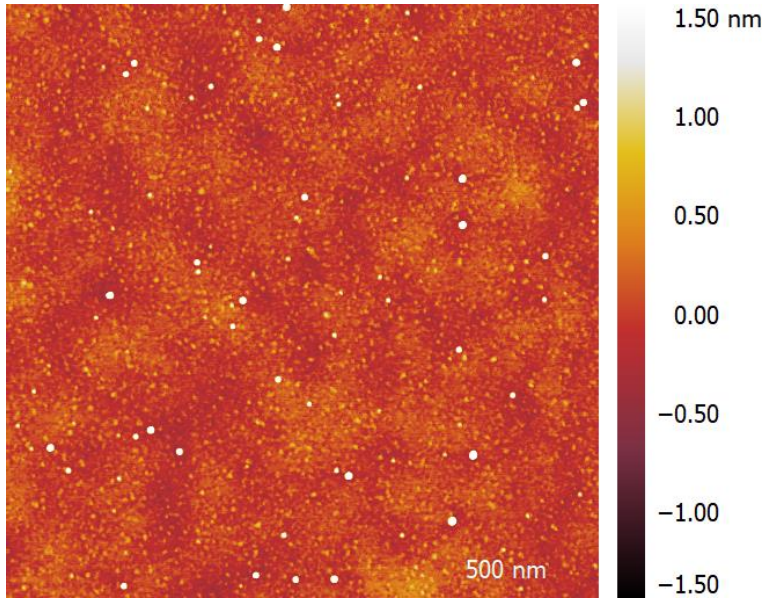
Atomic flux dependence with oxygen

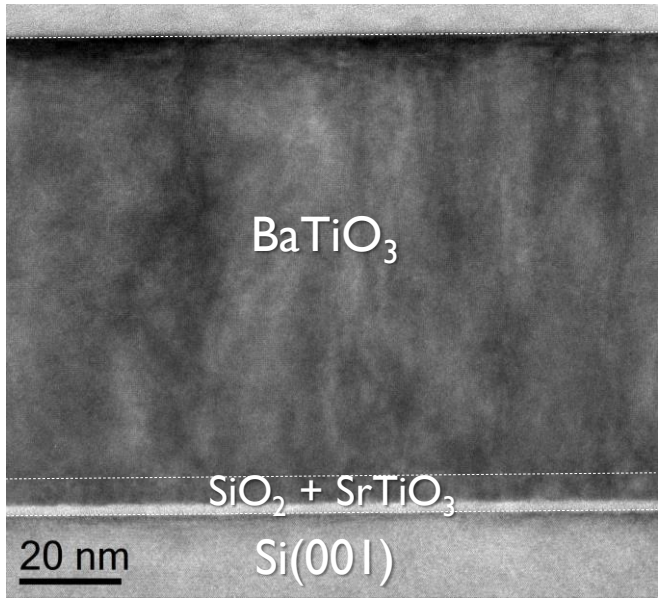
Transition temperatures of strontium

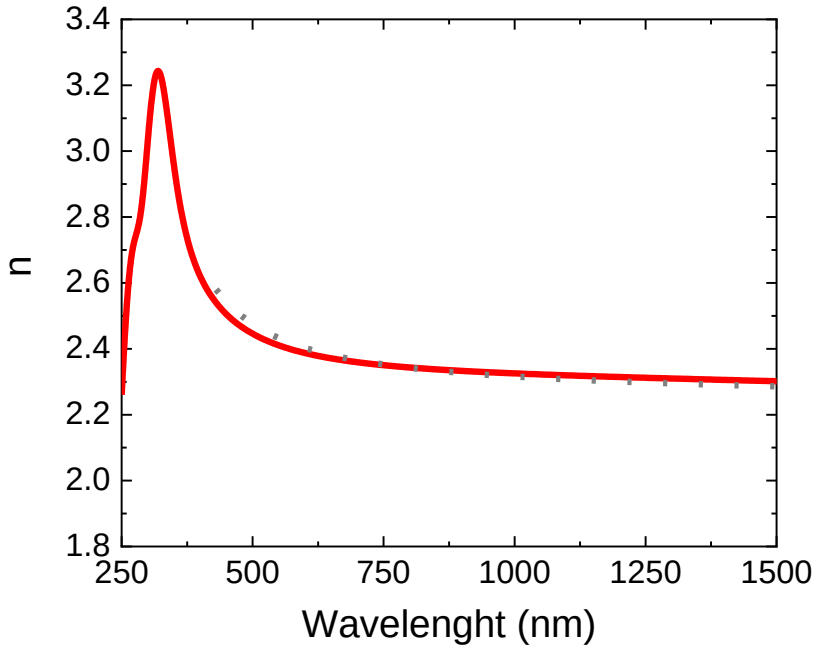


- Transition temperatures (metal dependent) at which the oxidation effects are negligible
- 2 growth windows in MBE:
  - Low growth rate (preferred for crystallinity) but need to apply a **temperature gradient** during growth
  - High growth rate (not favorable for crystalline quality) without temperature gradient during growth
- Stoichiometry control during full $SrTiO_3/BaTiO_3$ thickness is a key challenge !!!

MBE $BaTiO_3$ / $SrTiO_3$ / Si(001) heterostructure





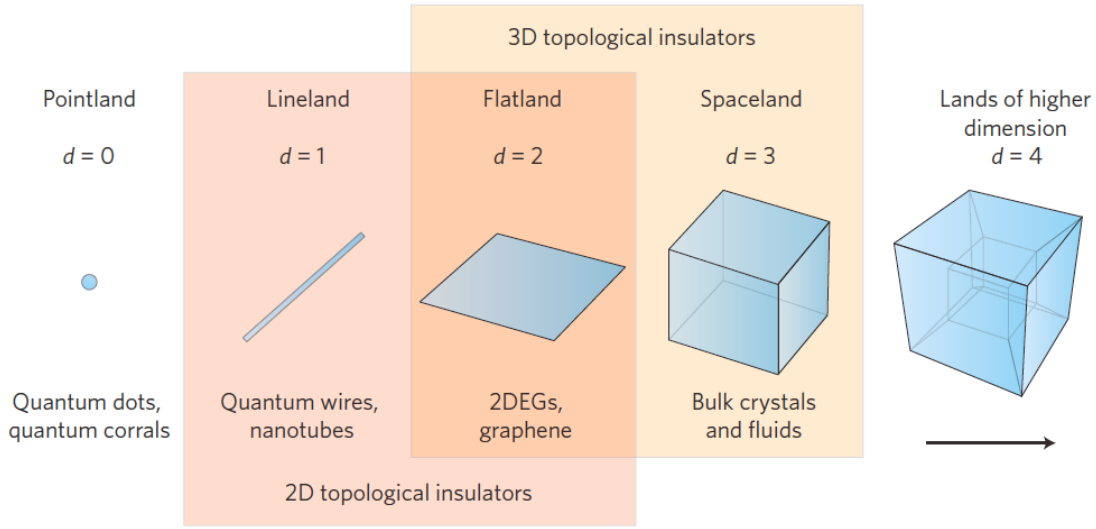


- Ultimate $BaTiO_3$ quality with Ba gradient stochiometric $BaTiO_3$
  - Atomically smooth BTO achieved
  - Monocrystalline heterostructure with low defectivity
  - Optical response similar with bulk properties
  - Large Pockels coefficient > 200 pm/V

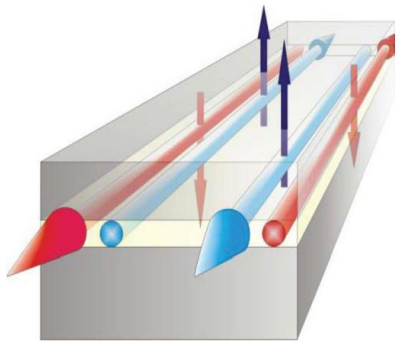
Topological materials: $BaBiO_3$

Topological insulators

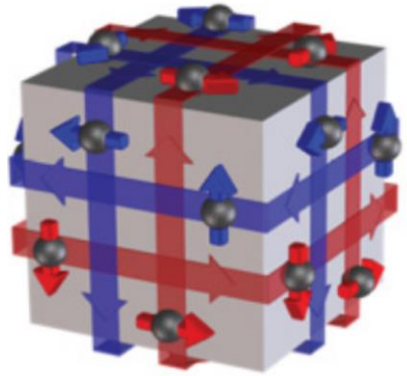
- A topological insulator is an **insulating material** that allows electric charge to flow along its **boundary** in spin-polarized channels that are **topologically protected** from impurity scattering.
- The physics of topological insulators involves interactions between **hosts** of dimension d and **boundaries** of dimension $d-1$.
- Topological insulators can be subdivided into two classes: three-dimensional (3D) and two-dimensional (2D) systems. The former exhibits a 2D metallic surface with a 3D bulk insulator, while the latter 2D system consists of 1D gapless conductive edge channels with an insulating 2D area.



H. C. Manoharan, Nature Nanotechnology, Vol. 5, 2010, p. 477

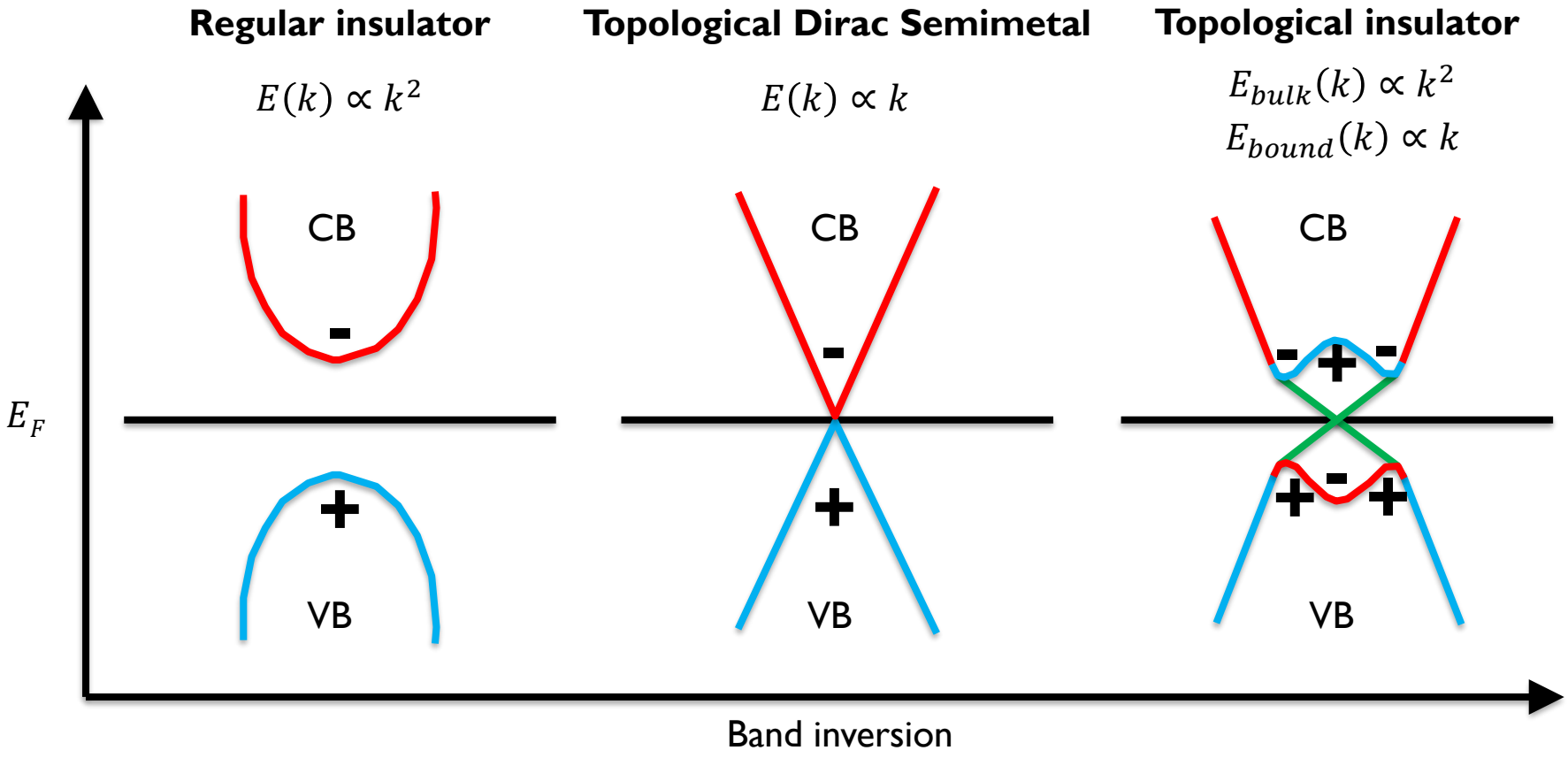


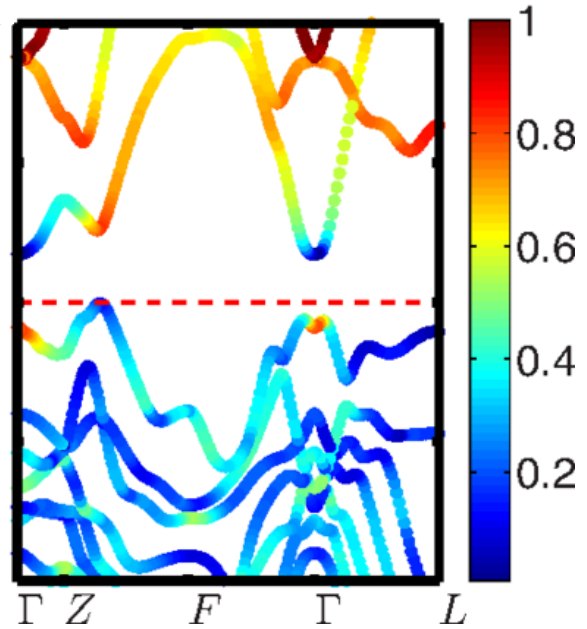
2D TI's



3D TI's

Band structure evolution with band inversion

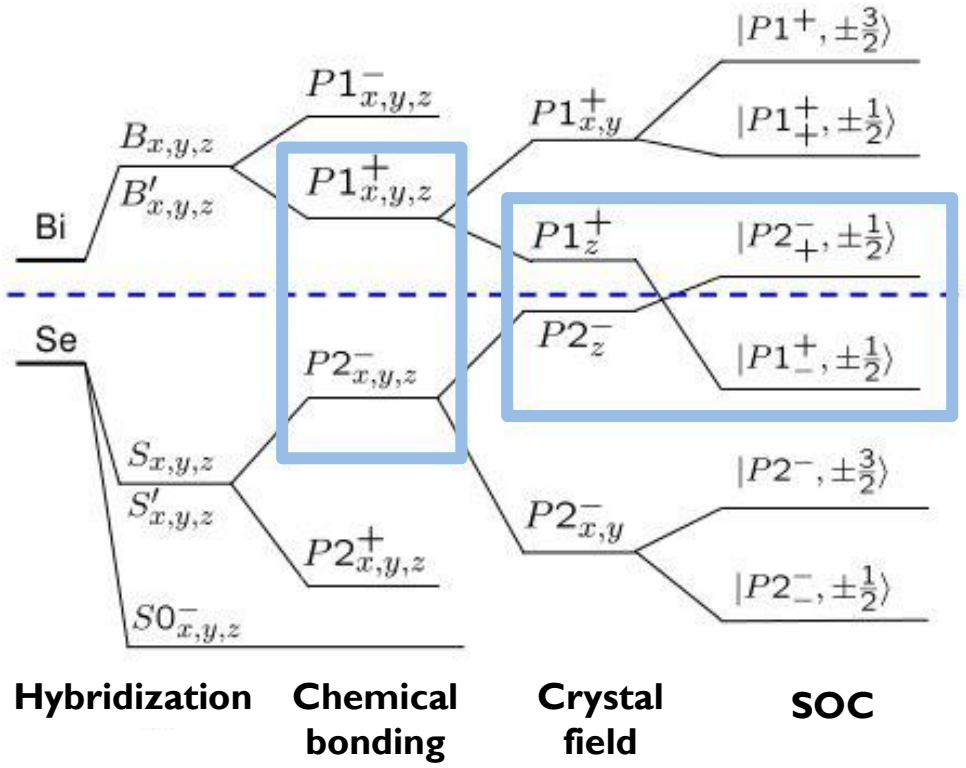


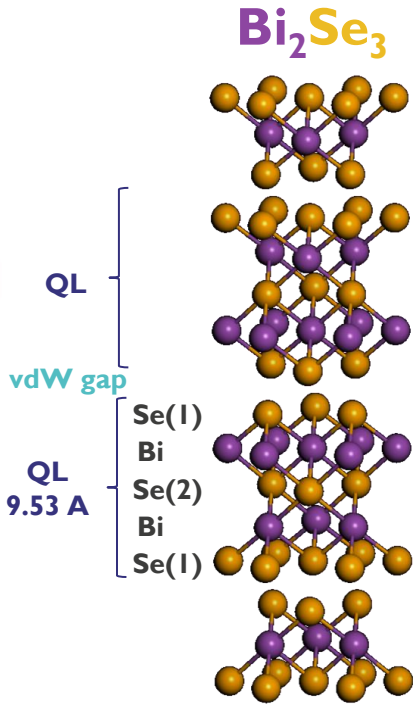


Bi_2Se_3 band structure

Band inversion in Bi_2Se_3

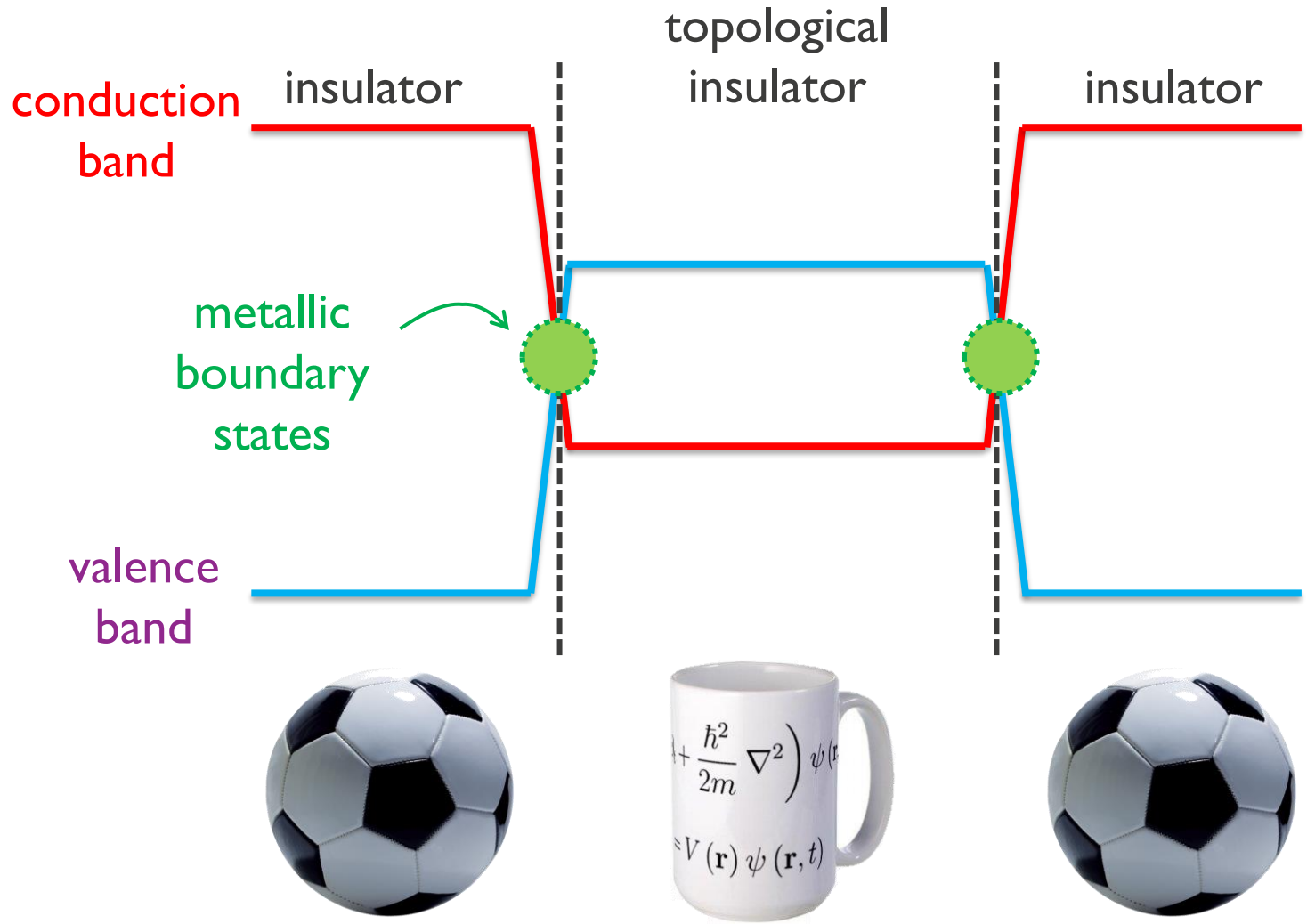
- It is accepted that **band inversion** could be induced by **spin–orbit coupling (SOC)** but may also occur when the strength of some other external parameter such as structural distortion increases.
- In the case of Bi_2Se_3 compounds, without spin–orbit coupling (SOC), the "conduction band" is majorly made of Bi p_z orbitals and the "valence band", is made of Se p_z orbitals.
- The spin–orbit coupling (SOC), induce conduction band that has contributions from the band that made the valence band originally and vice versa. This is called a band inversion.





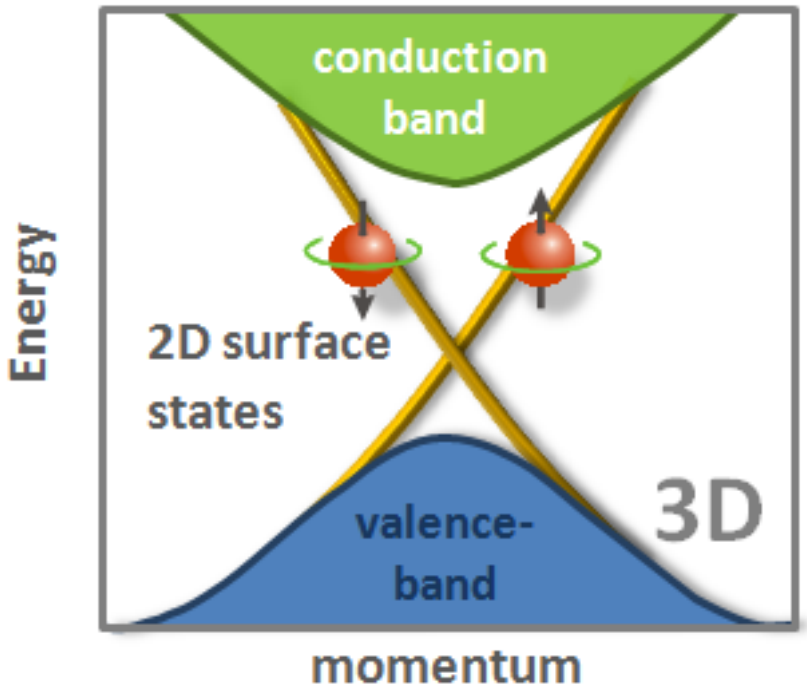
Topological insulators

- Materials properties which are invariant under topological transformations property are known as **topological materials**.
- Metallic states are formed by **topology effect**.



Topological insulators

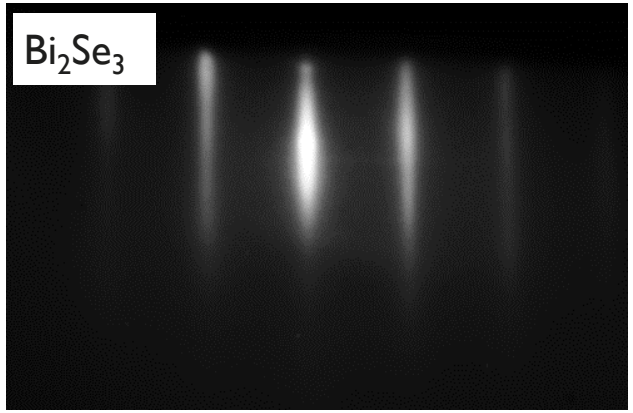
- The research area of topological insulators experienced a major extension when the concept was generalized to **3D materials**.
- Since then, the number of possible materials belonging to the class of topological insulators has steadily increased. However, **only a few materials have been experimentally confirmed** to be a 3D topological insulator.
- 3D topological insulators have a linear energy dispersion of quasi-relativistic Dirac fermions with **locked electron-spin and momentum** within the band gap formed by the 3D bulk states.

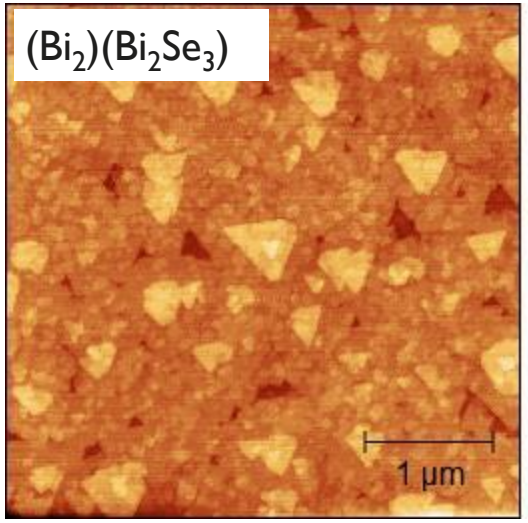


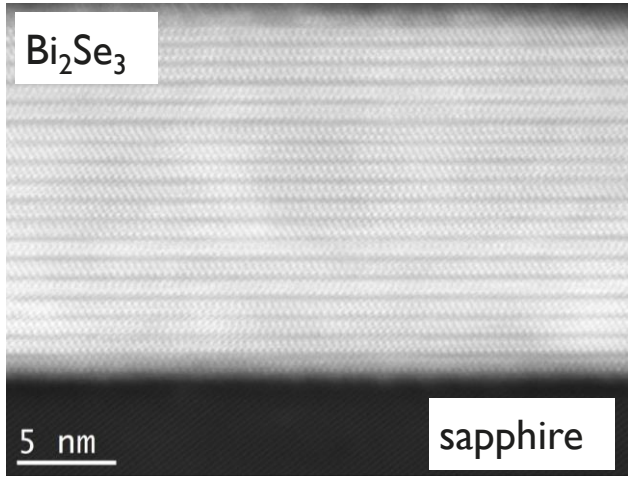
Schematics of the band structure of a 3D topological insulator with surface states within the band gap.

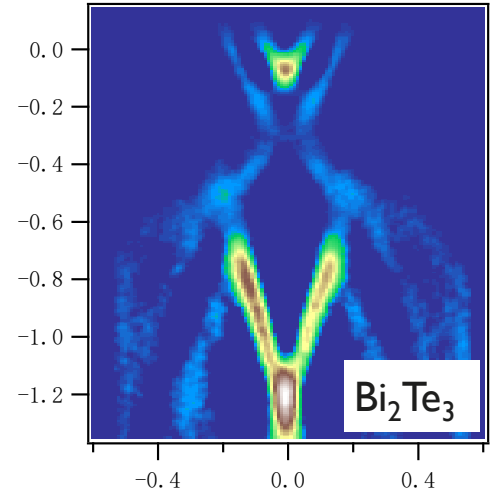
TI thin films: structural quality

- 3D TI can be grown using **MBE technique** on various substrates (e.g. Sapphire, Si(111), III-V(111), Graphene, ...)
- Surface morphologies and thickness dependent electronic structures are properties characterized by RHEED, Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM) and Transmission Electron Microscopy (TEM).
- Topological states can be experimentally demonstrated by imaging the **electronic band structure** using Angle Resolved Photoelectron Spectroscopy (ARPES).





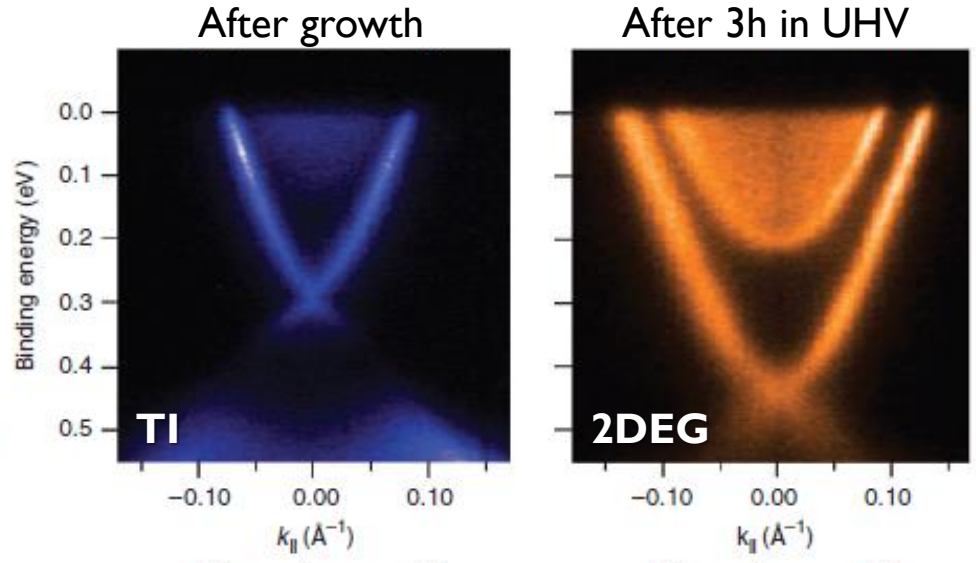


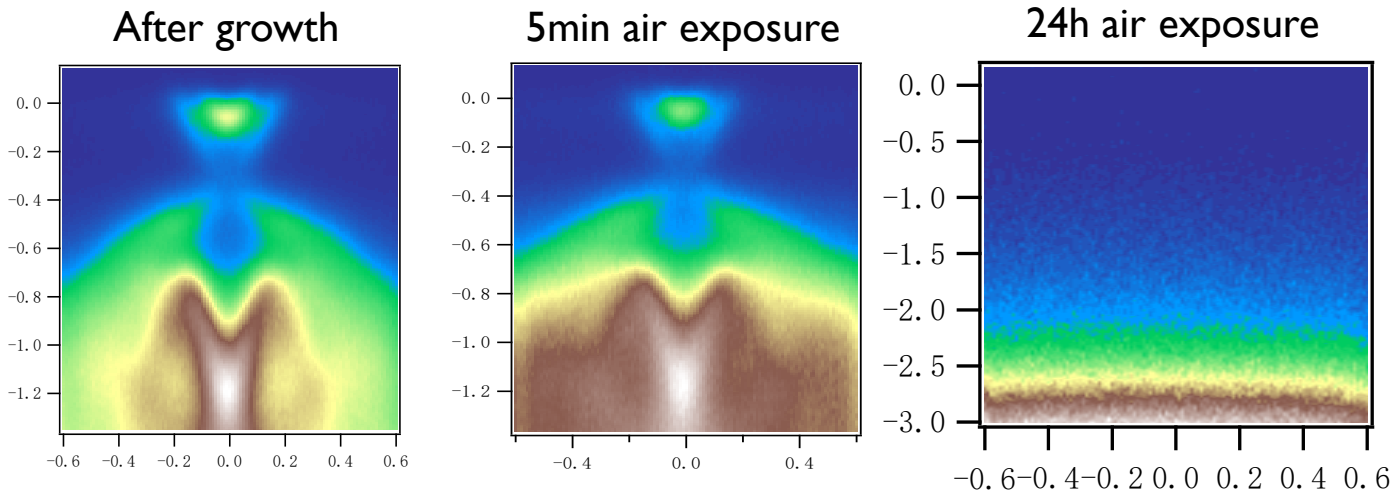


RHEED, AFM, TEM and ARPES analysis of 3D-TIs @ imec

Stability and ageing effects

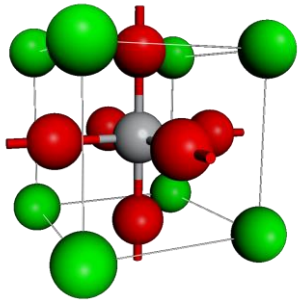
- Defects like group-VI vacancies (Se, Te, ...) makes these layers **very reactive** to environment (even in UHV ...), especially air whereby oxygen will diffuse easily through the vacancies network and oxidize the TI surface, ...
- Layer **stability and ageing effects** of these V_2VI_3 compounds whereby the thin film properties change over time, are also crucial problems that need to be further addressed...





Outlooks

Novel functional oxides for quantum technologies



European Research Council

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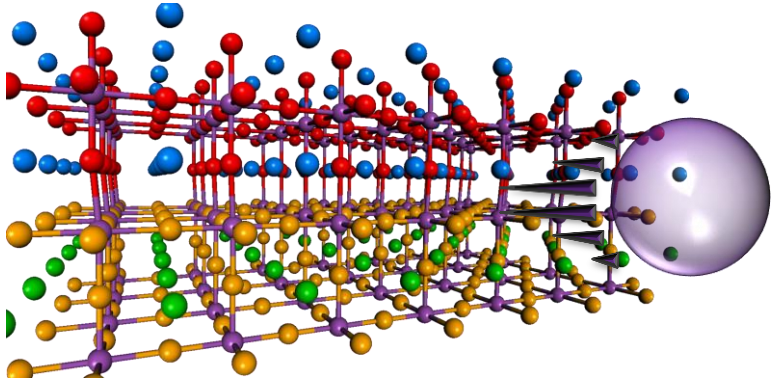
ERC Consolidator 2019

September 2020 – September 2025

Novel **O**xides and **T**opological **I**nterfaces for quantum**C**omputing **E**lectronics (NOTICE)

"Materials Towards Fault-Tolerant Qubits"



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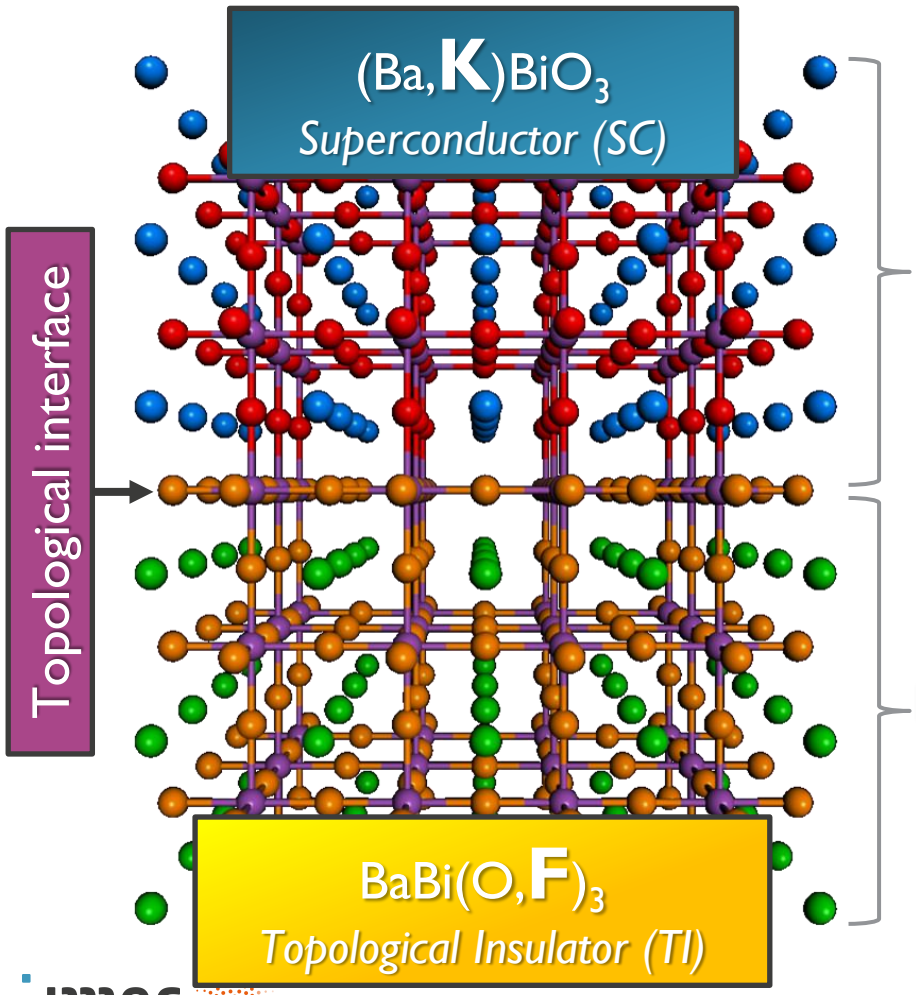
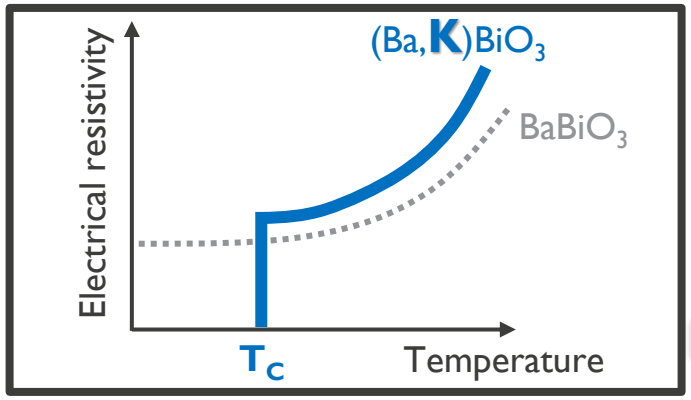
NOTICE project overview

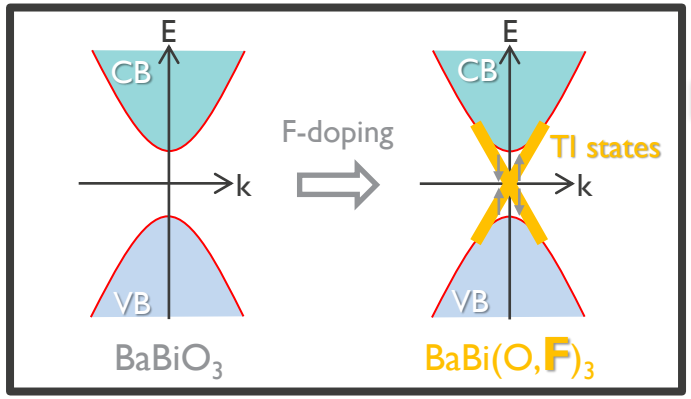
Molecular Beam Epitaxy [= flexibility & atomic control]



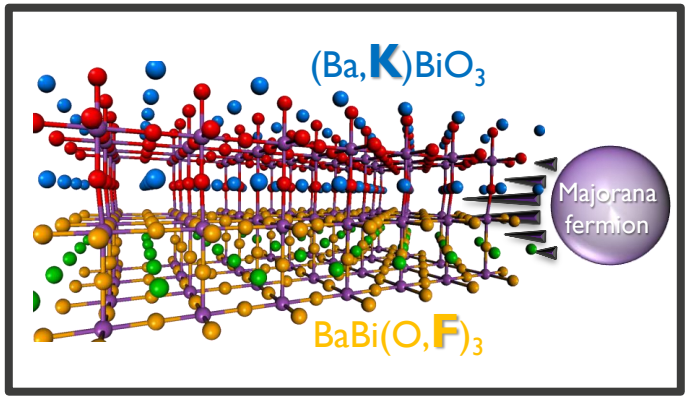
1b. SC perovskite



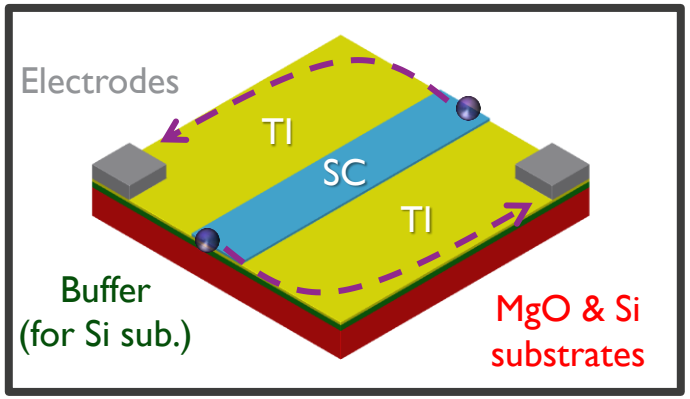
1a. TI perovskite



2. TI/SC interface



3. Majorana qubit



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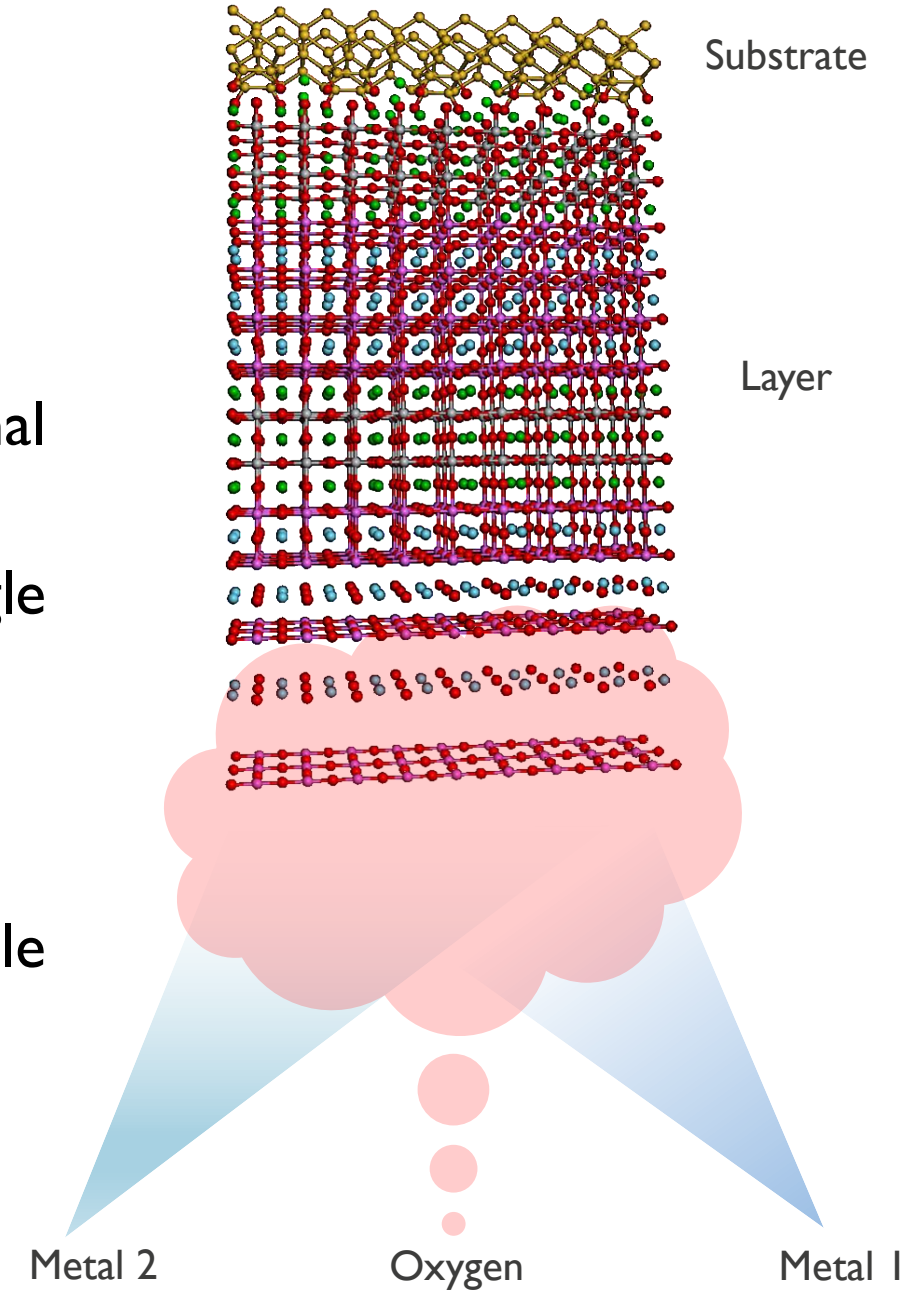
Wrap up

Wrap up

- Large field of potential applications for functional perovskites / oxides
- Molecular Beam Epitaxy: the only solution to enable single crystal oxide growth on Si(001)
- The $SrTiO_3$ buffer quality on Silicon is crucial
- $BaTiO_3$ is of strong interest for optical applications
- Novel materials with topological protection could enable stable quantum applications



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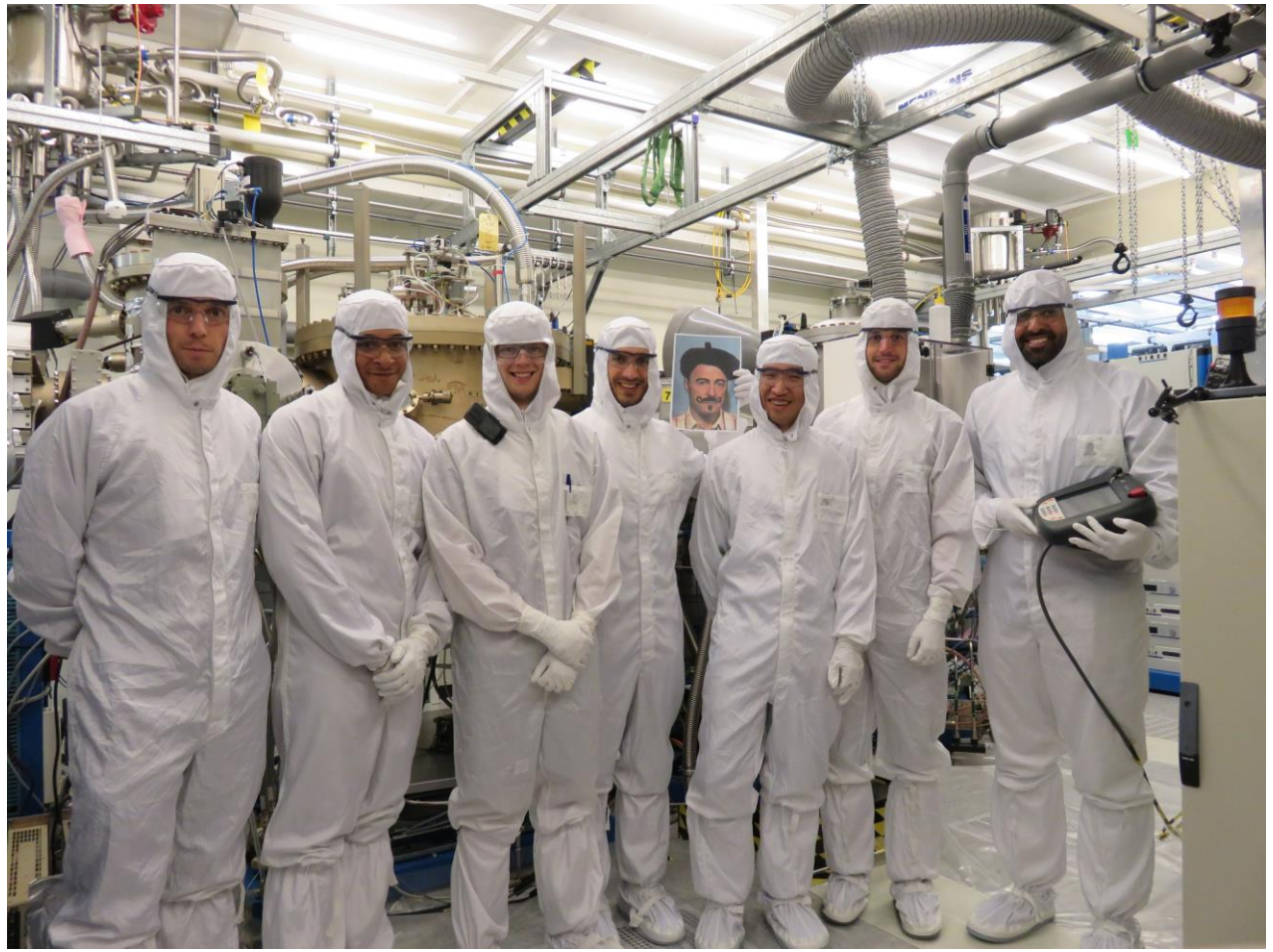

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