Oxide Films & Nanostructures on Silicon
for Thermal Energy Harvesting in Microelectronic Devices

R. Bachelet
R. Moalla, A. Carretero-Genevrier, L. Mazet, L. Louahadj, J. Penuelas, B. Vilquin, C. Dubourdieu, G. Saint-Girons

Outline

I. **Intro**: Context & INL presentation

II. **Thin films**: n-type doped $SrTiO_3$

III. **Nanowires**: Hollandites ($BaMn_8O_{16}$)

IV. **Pyroelectric** epitaxial thin films…

IV. **Conclusions**

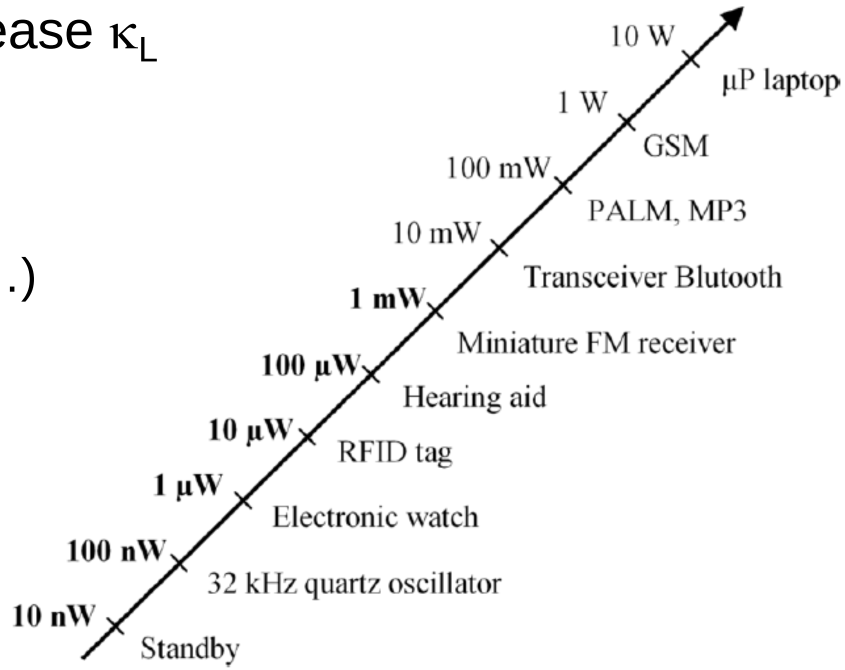
Context: nanostructured materials for TE

G.J. Snyder *et al.*, Nat. Mat. **7**, 105 (2008)
C.J. Vineis *et al.*, Adv. Mat. **22**, 3970 (2010)
K. Koumoto et al., J. Am. Ceram. Soc. **96**, 1 (2013)

Material challenges/requirements:

$ZT = \sigma S^2 T / (K_e + K_l)$ $ZT > 1$

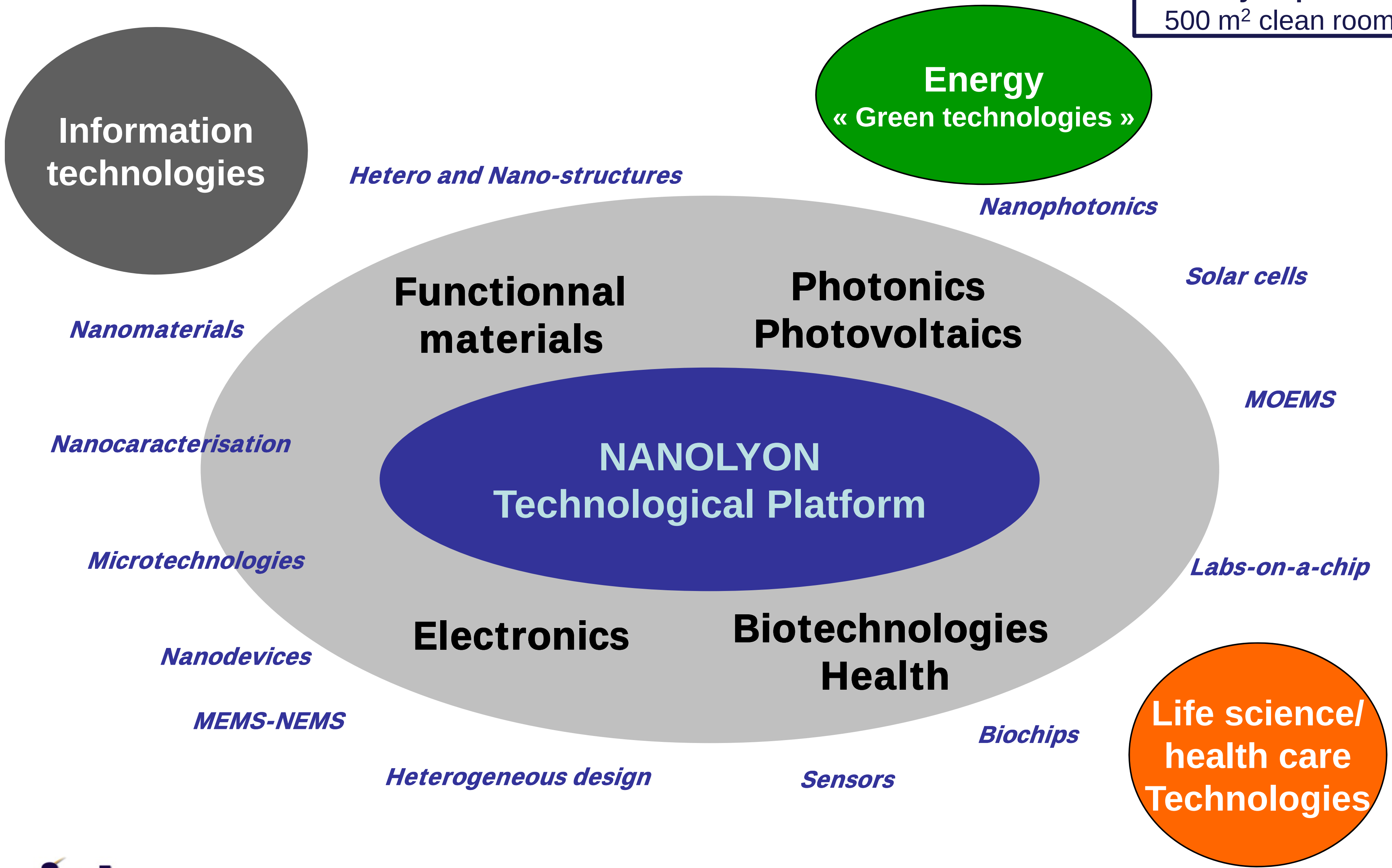
- Semi-conductor materials => large σ, S
- Nanostructured => Decrease κ_L



- Efficiency / Reliability (oxidation/intermixing…)
- Non toxic / Abundant elements
- Integration…

Scientific and application fields

250 people
(130 permanent)
~7 900 m²
NanoLyon platform
500 m² clean room



NANOLYON technological platform

A « proximity » platform for Micro- & Nano-Technologies

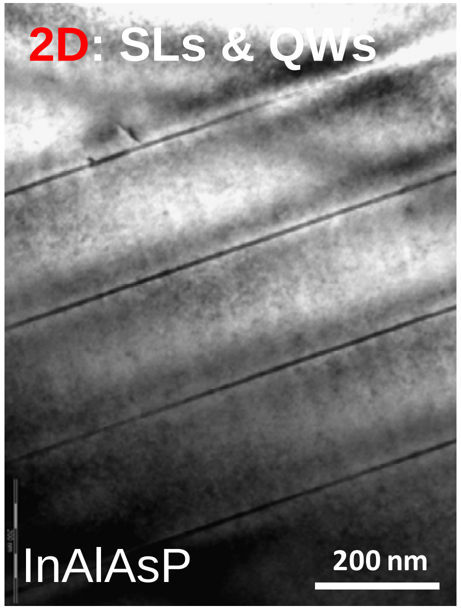
To develop novel (nano)materials
& novel concepts of devices
& characterizations

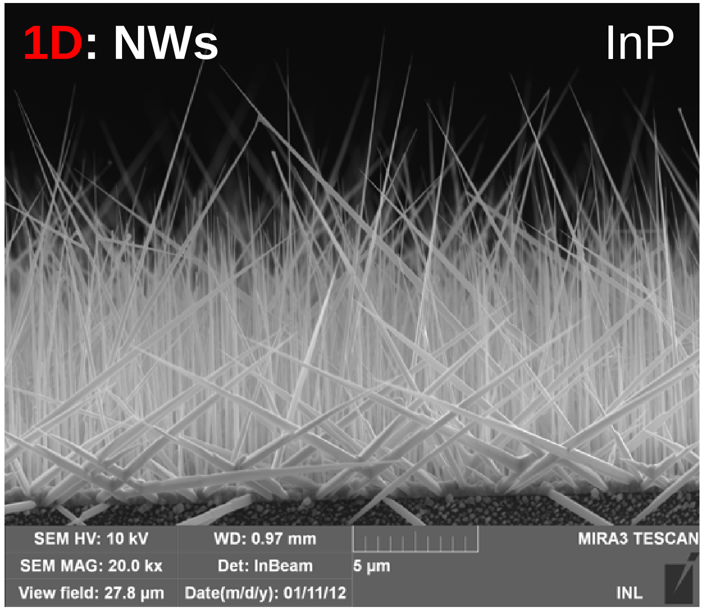
New clean rooms in 2013
(500 m²)

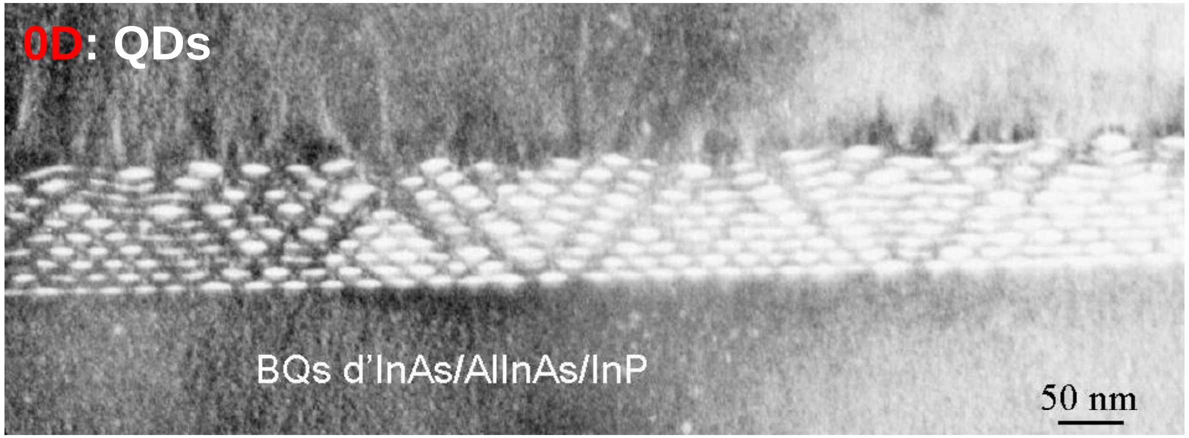
MBE
Sputtering
Sol-gel
Lithography
…

III-V Nanostructures

Semiconductor nanostructures: reducing dimensions at the nanoscale…



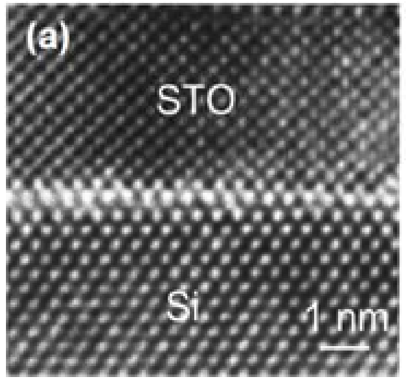




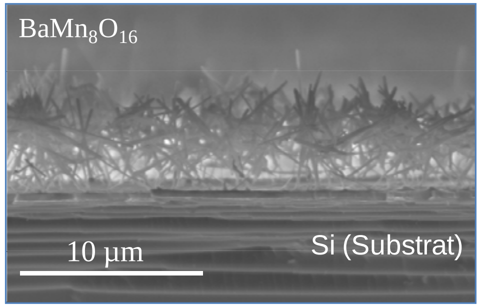
Works led by P. Regreny and Michel Gendry, H&N team, INL

Oxide Films and Nanostructures /Si

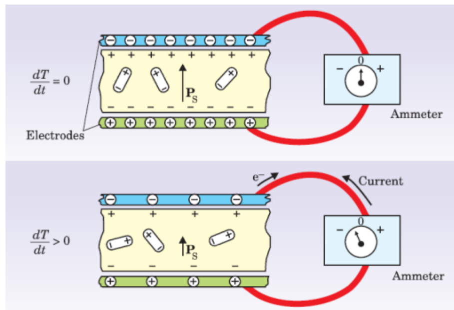
1. Thin films: n-type doped $SrTiO_3$



2. Nanowires: Hollandites ($BaMn_8O_{16}$)



3. Pyroelectric epitaxial thin films…



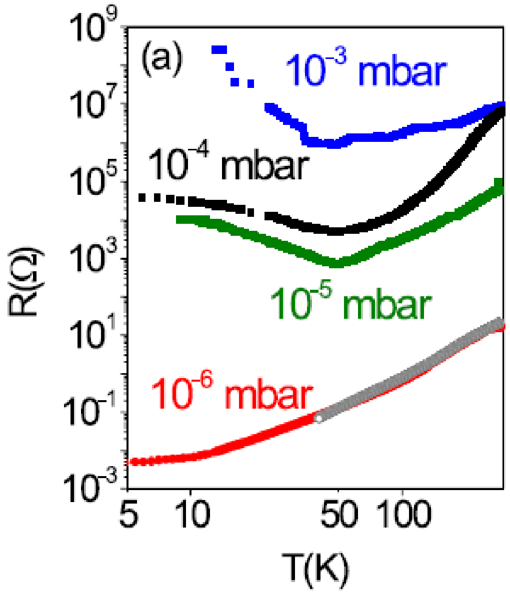
1. n-type doped $SrTiO_3$ /Si

$SrTiO_3$: a model for oxide electronics

Tuning σ (& S)

By doping

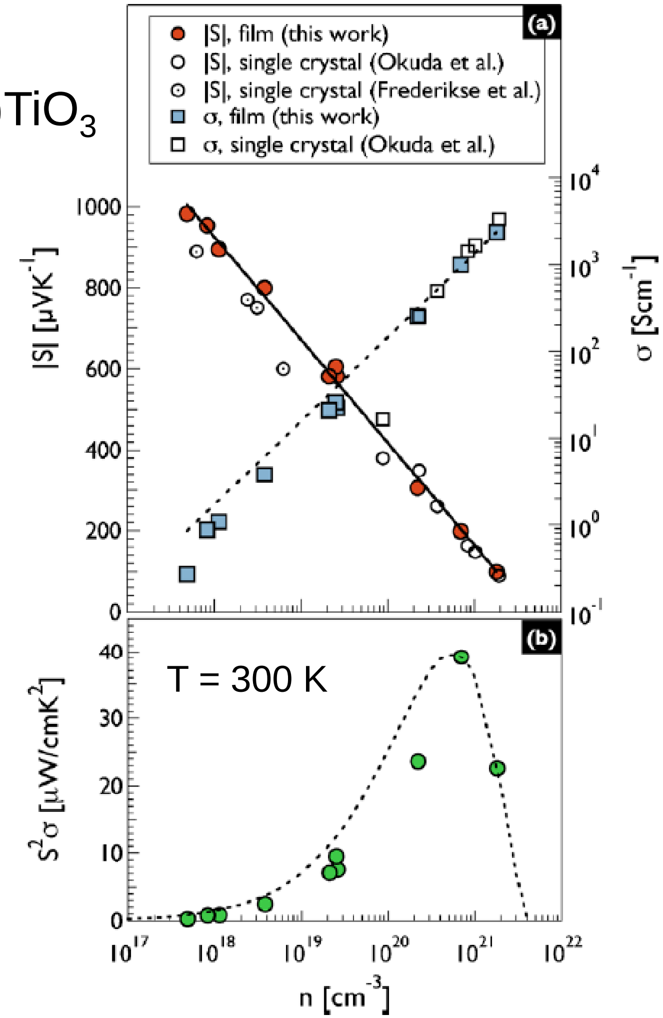
- Doped by *oxygen vacancies:*



G. Herranz *et al*. PRL **98**, 216803 (2007)

- Doped by *aliovalent cations*

La-STO:
$(La^{[3+]},Sr^{[2+]})TiO_3$



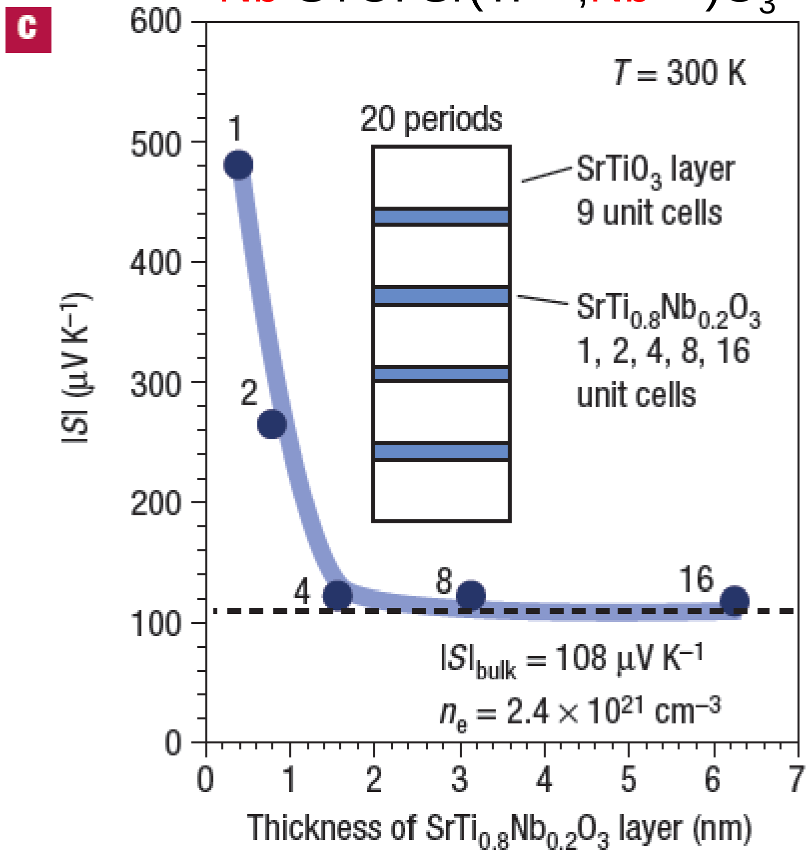
B. Jalan & S. Stemmer, APL **97**, 042106 (2010)

1. n-type doped $SrTiO_3$ /Si

Increasing interfaces at the nanoscale

- *Superlattices*

Nb-STO: Sr(Ti[4+],Nb[5+])O$_3$



H. Ohta *et al*., Nat. Mat. **6**, 129 (2007)
S. Ohta *et al*., APL **87**, 092108 (2005)

- *(Nano)Polycrystalline*

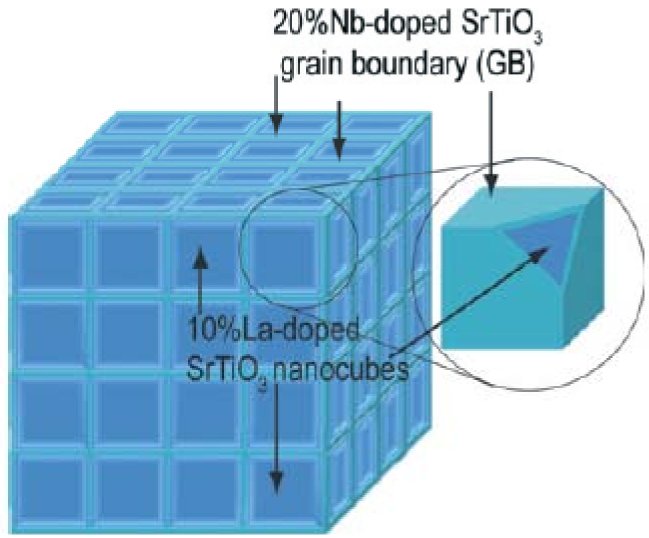


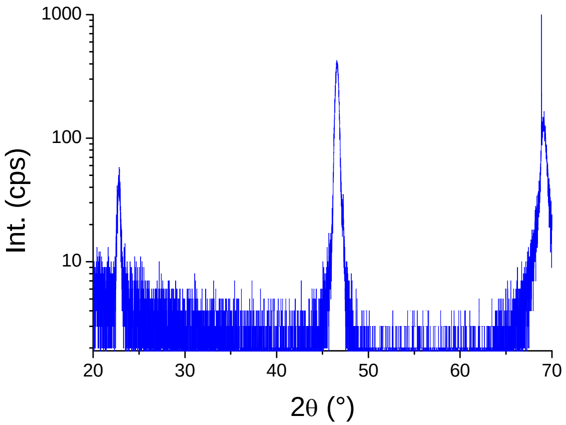
Fig. 21. 3D superlattice STO ceramics.

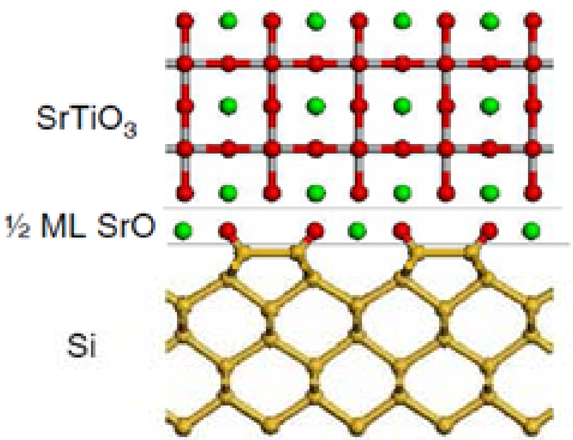
ZT_{300K} > 1 with
$K_{min} \sim 1.4$ W.m^{-1}.K^{-1}
$S_{bulk} = 61$ μV.K^{-1};
n = 2-4 10^{21} cm^{-3} ; $n_{undoped} < 10^{15}$ cm^{-3}

K. Koumoto *et al*.,
J. Am. Ceram. Soc. **96**, 1 (2013)

1. n-type doped $SrTiO_3$ /Si

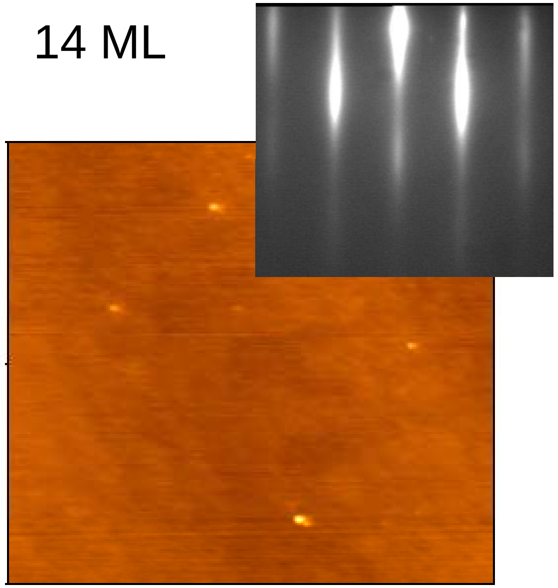
Epitaxial $SrTiO_3$/Si…

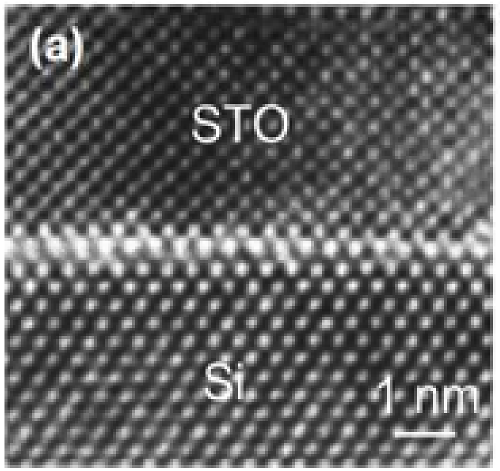




G. Niu *et al.* APL 2009

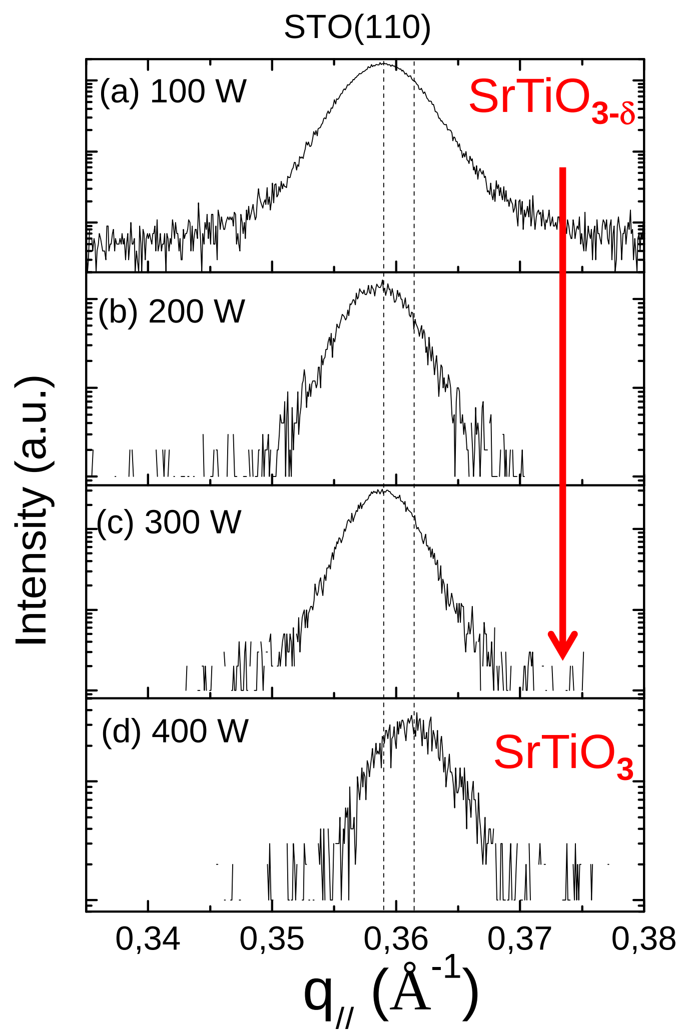
14 ML





L. Louahadj *et al.*

Doped by oxygen vacancies



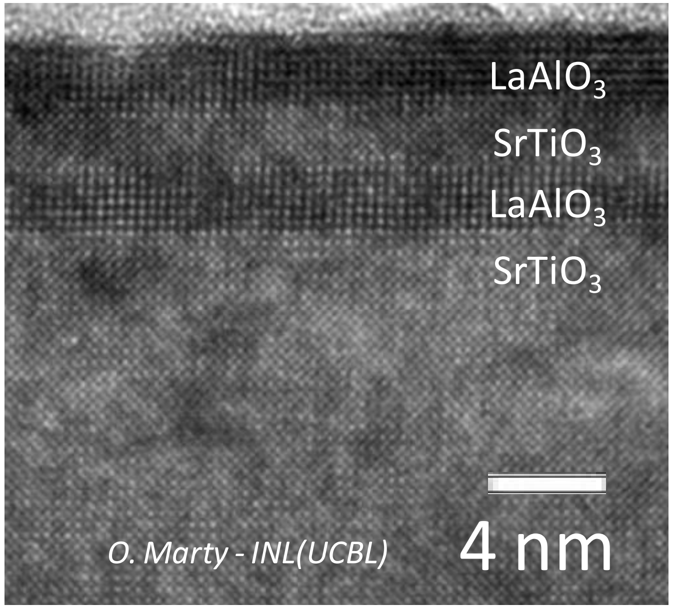
1. n-type doped $SrTiO_3$ /Si

Electrical measurements (I-V) on p-type Si(001):
=> p-n junction

TE measurements: *in progress*
(σ, S, K)
Collab: Fransisco Rivadulla (CIQUS, Spain)
(Univ. Santiago de Compostela)

Perspectives:
- Full TE measures
- SL polycristalline - doped / undoped…
- p-type thin films

Superlattices and 2DEGs
LAO/STO SLs



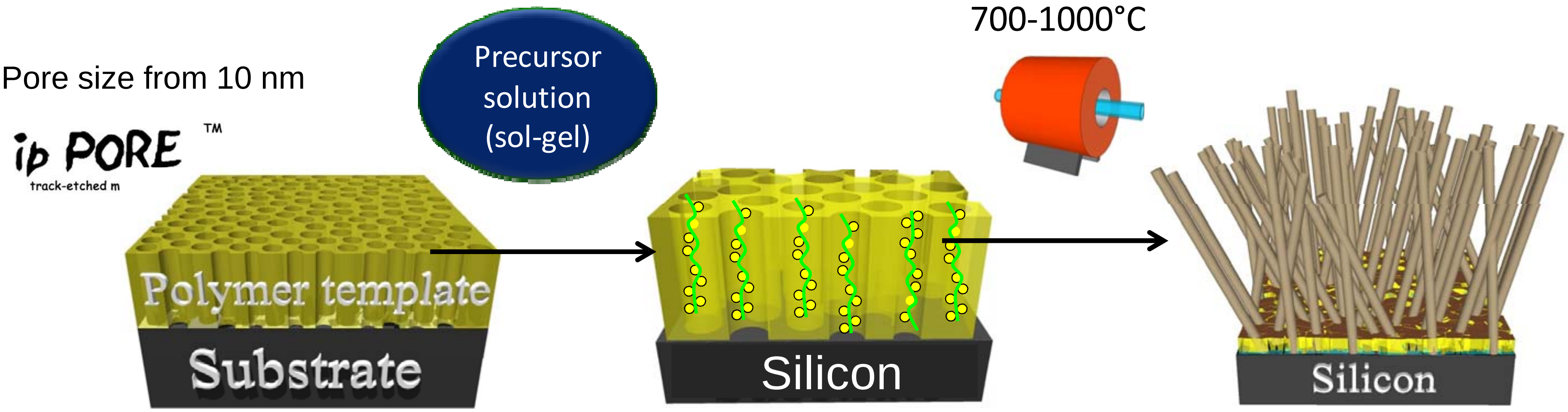
C. Merckling *et al.*

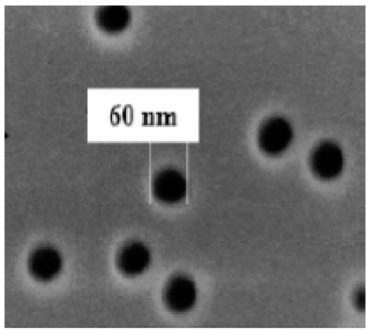
2. Oxide Nanowires of Hollandites

Integration of 1D oxide nanowires in confined geometries (CSD)

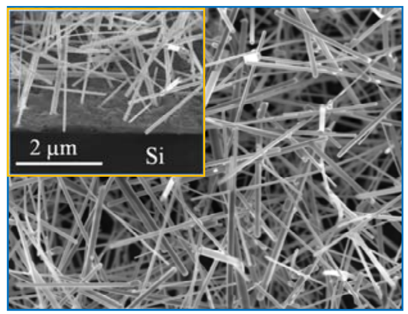
1. Synthesis: track-etched polymer template assisted elaboration

Pore size from 10 nm

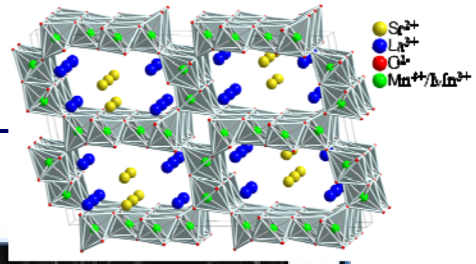




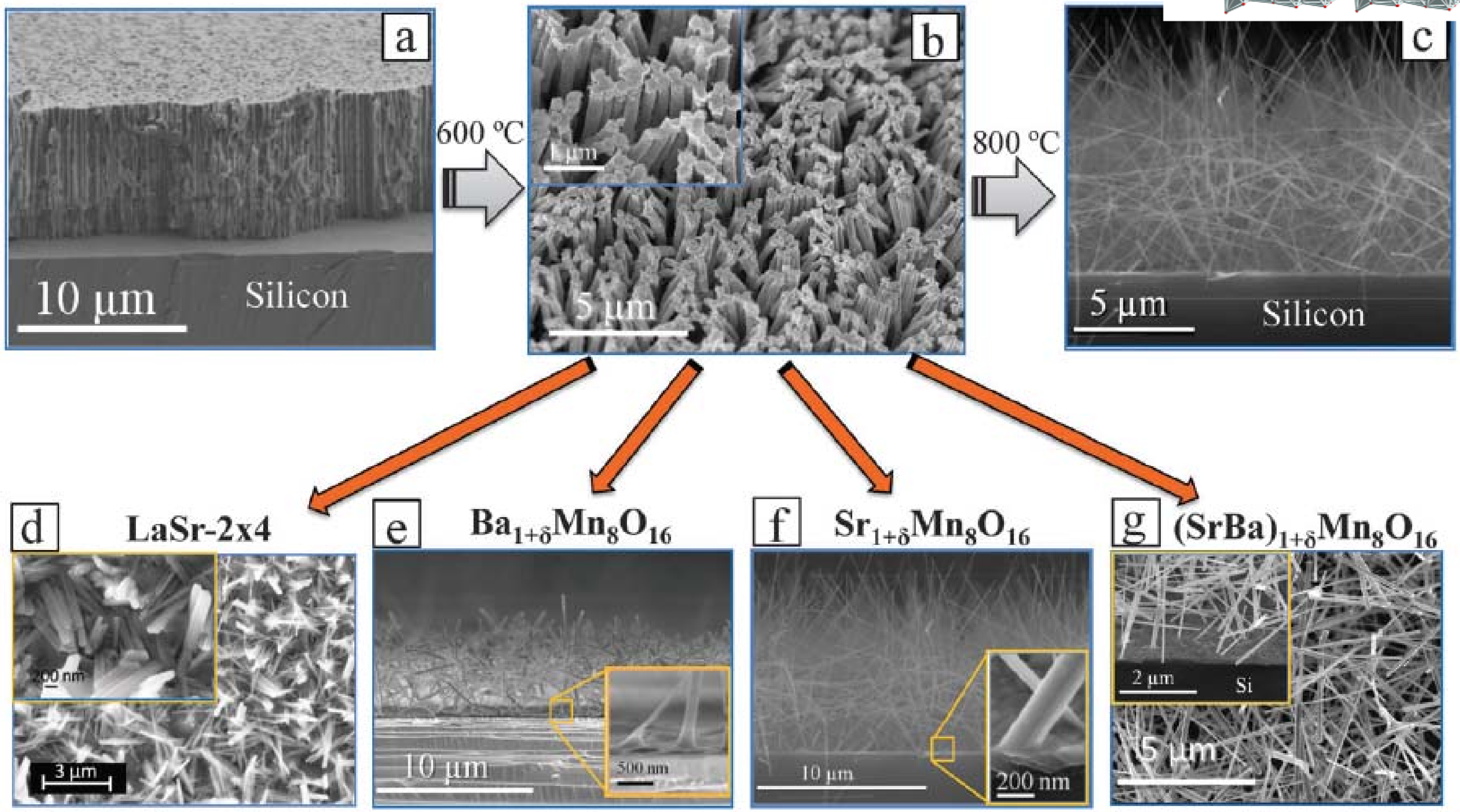
A. Carretero-Genevrier *et al.*, Chem. Soc. Rev. (2013)



2. Oxide Nanowires of Hollandites



2. Some results



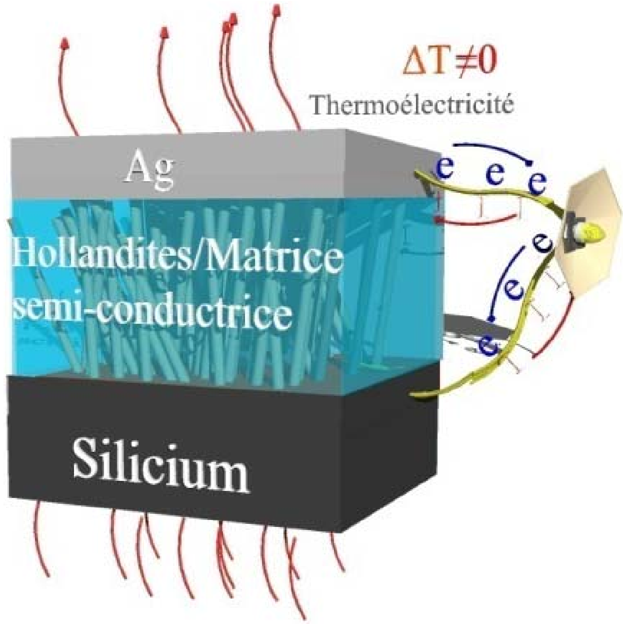
A. Carretero-Genevrier *et al*., Chem. Soc. Rev. (2013)
Chem. Mater (2013)

S_{300K} = 20 µV/K
PF_{75K}= 30 µW/cm.K^2
n=10^{22} cm^{-3}
Phys.Rev. B 79 085207 (2009

2. Oxide Nanowires of Hollandites

3. Perspectives

- Measuring TE parameters
- Composite materials (NWs + SC Matrix)
- n- & p-type materials…
- Integration in modules (structuring, contacts,…)

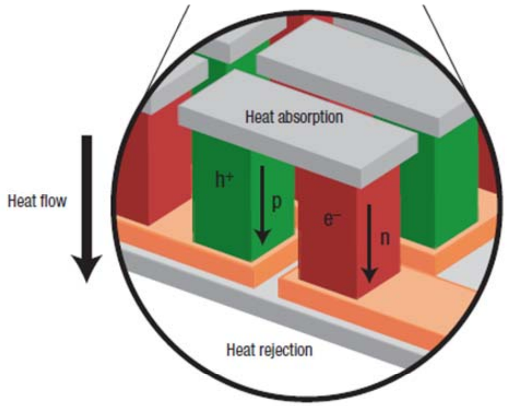


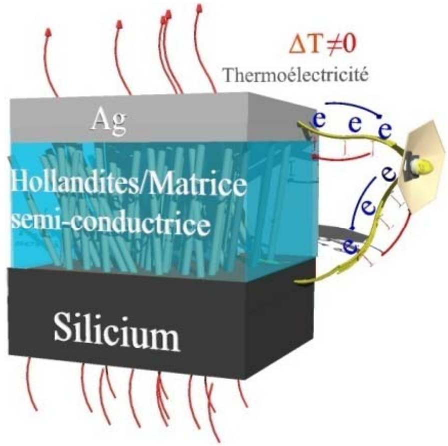
3. Pyroelectric epitaxial thin films

• ***Thermal* energy harvesting for electrical conversion**

With *Thermoelectrics*

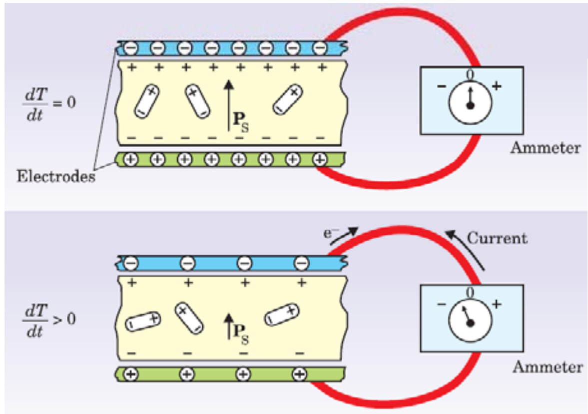
I = f (ΔT)



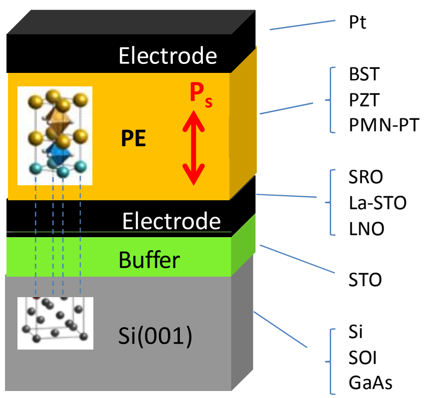


With *Pyroelectrics*

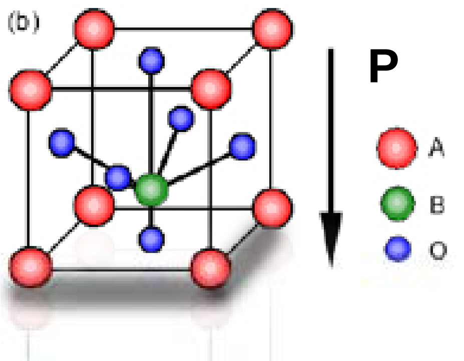
I = f (dT/dt)

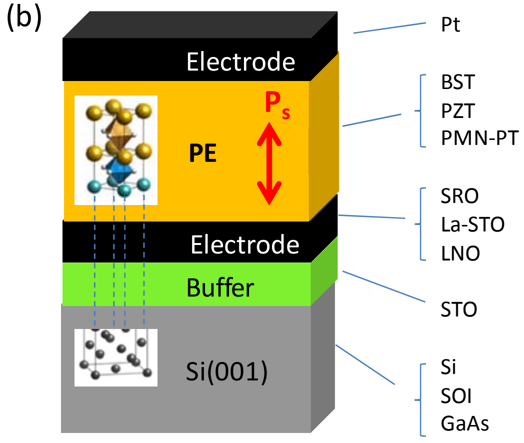


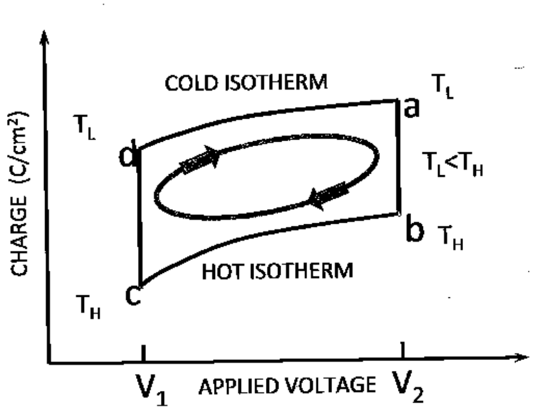
(b)



3. Pyroelectric epitaxial thin films







	Polycristalline	Single-crystalline
Bulk materials	ref	+
Thin films	+	++?

⇒ >1 mW/cm³ for temperature variations of 10°C

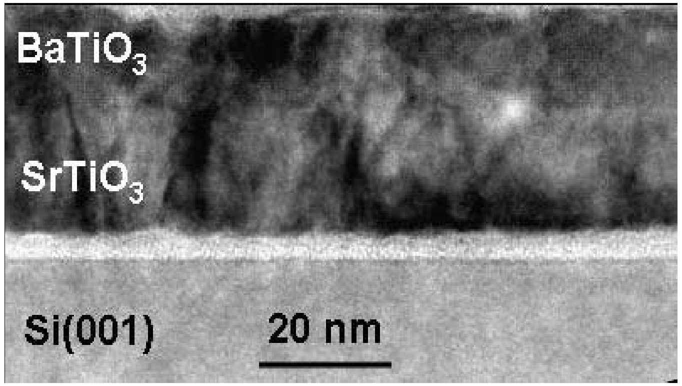
⇒ PhD thesis starting (R. Moalla): Collab. with LGEF-INSA (G. Sebald, D. Guyomar)

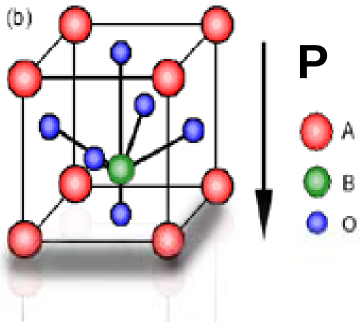
S.B. Lang, Phys. Today **58**, 31 (2005)

G. Sebald *et al*., Smart Mater. Struct. **18**, 125006 (2009)

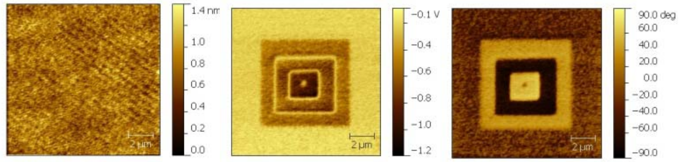
3. Pyroelectric epitaxial thin films

Ferroelectric ABO$_3$/SrTiO$_3$/Si…

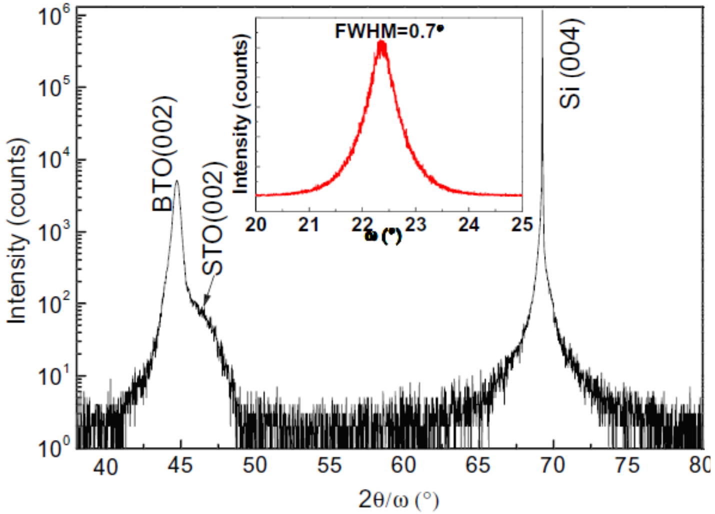


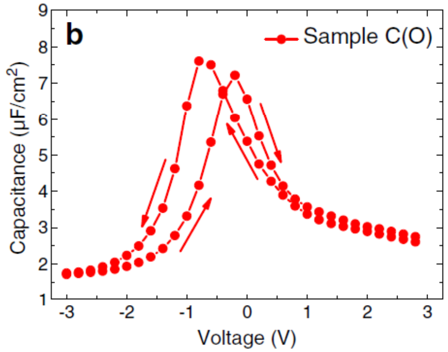


PFM (Collab. B. Gautier, INL):



In progress:
L. Mazet *et al.*
R. Moalla *et al.*





S. Yin *et al.*, Thin Solid Films **520**, 4572 (2012)
G. Niu *et al.*, Thin Sol. Films **520**, 4595 (2012)
G. Niu *et al.*, Microelec. Eng. **88**, 1232 (2011)

Material challenge:
- High Pyroelectric coef.
- High P
- Out-of-plane P
- Low leakage currents

=> BST, PZT, PMN-PT

BST/SRO/STO/Si

Conclusions

• $SrTiO_3$-based TE thin films by *physical method*

control of σ, S by doping & reducing K_L by nanostructuring

• Hollandites Nanowires by original *chemical method*

control of density, diameter, chemical composition..

• Need of full TE characterizations…

• Alternatively, promising single-crystalline *Pyroelectric* films