2234-1

Meeting of Modern Science and School Physics: College for School Teachers of Physics in ICTP

27 April - 3 May, 2011

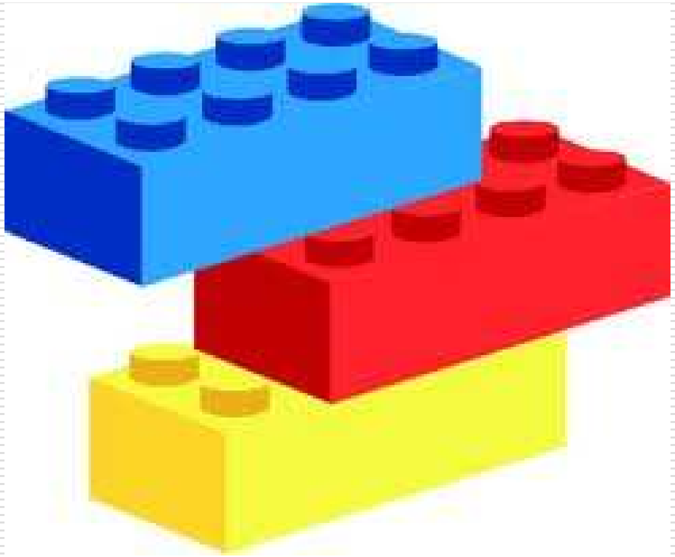
Materials engineered by layer-by-layer deposition

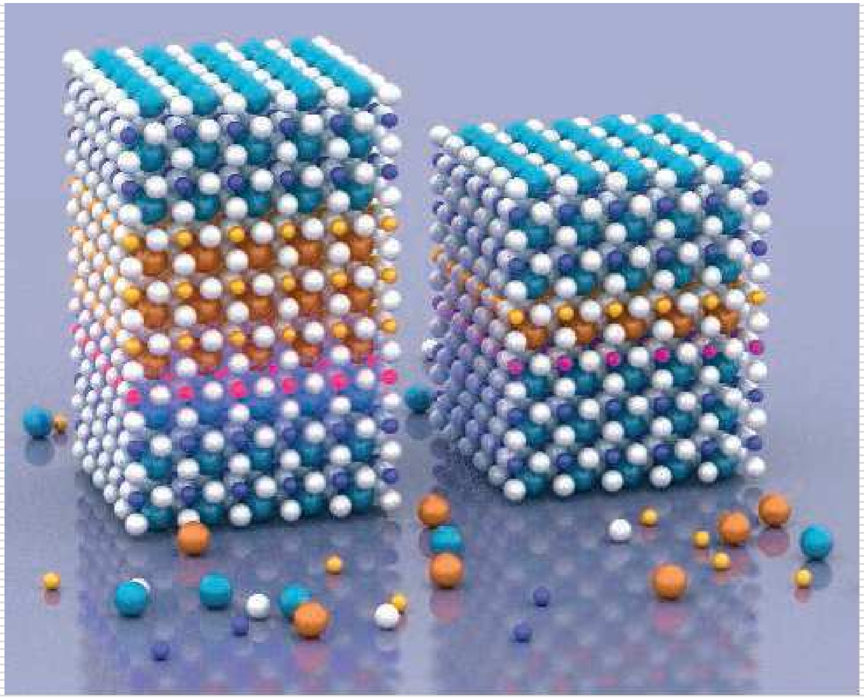
Giuseppe Balestrino
CNR SPIN & University of Rome "Tor Vergata"
Rome
ITALY

Materials engineering by layer-by-layer deposition

Thin oxide films with novel or enhanced physical properties obtained by design

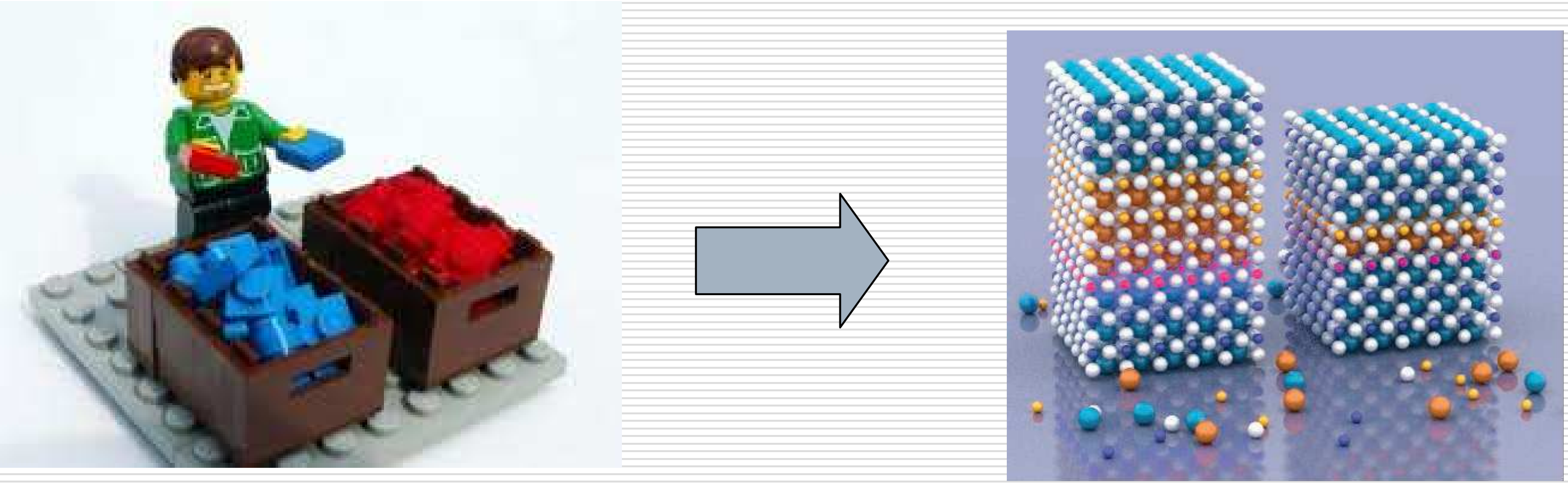
G. Balestrino
CNR SPIN & University of Roma “Tor Vergata”





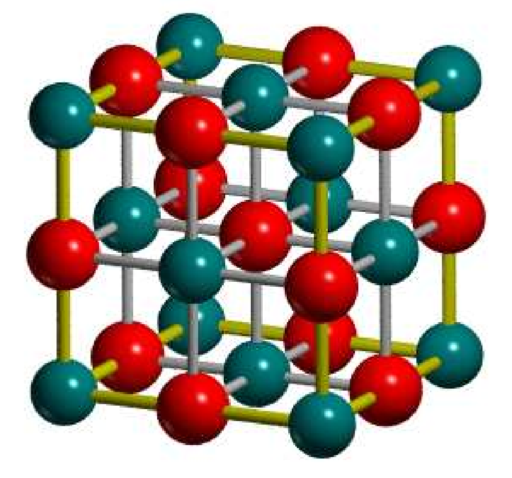
Choosing the right bricks

- Chemical compatibility
- Structural compatibilty

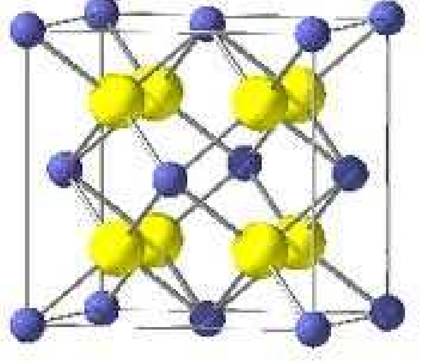


Oxide structures may be quite complex

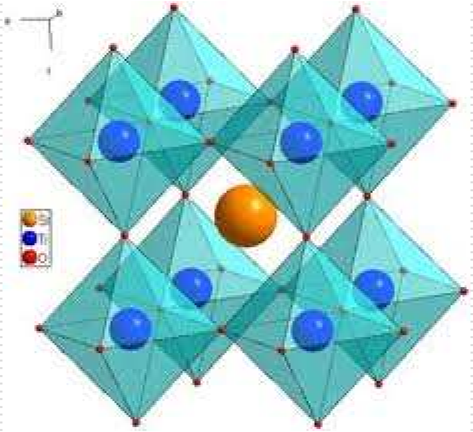
MgO structure



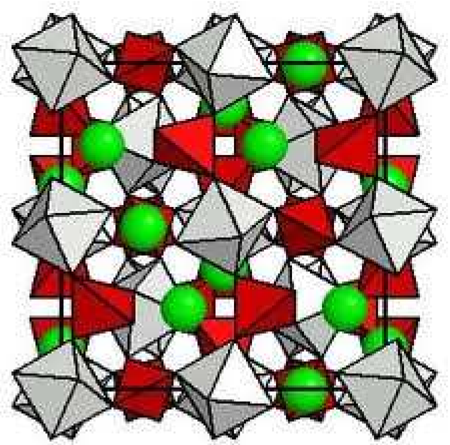
Fluorite structure
CeO_2



Perovskite structure
$SrTiO_3$

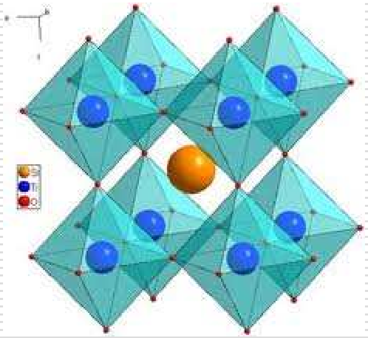


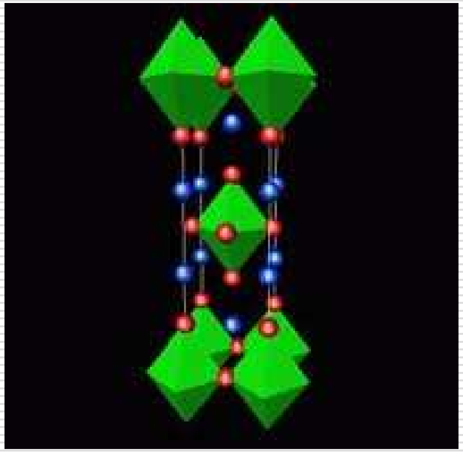
and much more !



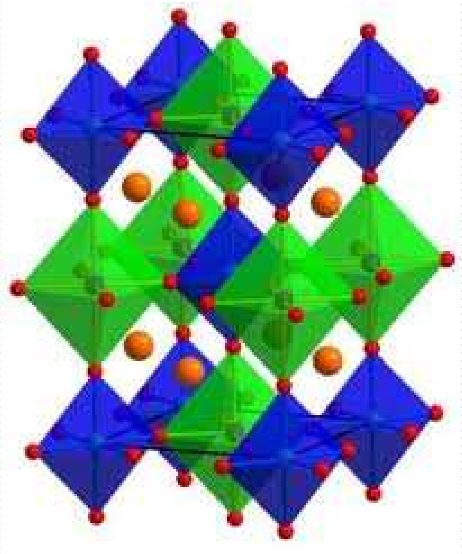
Garnet structure

Perovskite-like structures: a good compromise





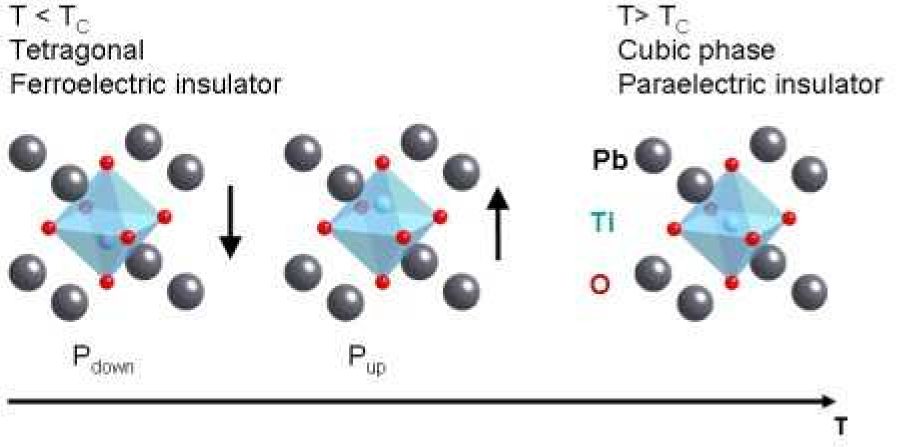
Layered perovskites

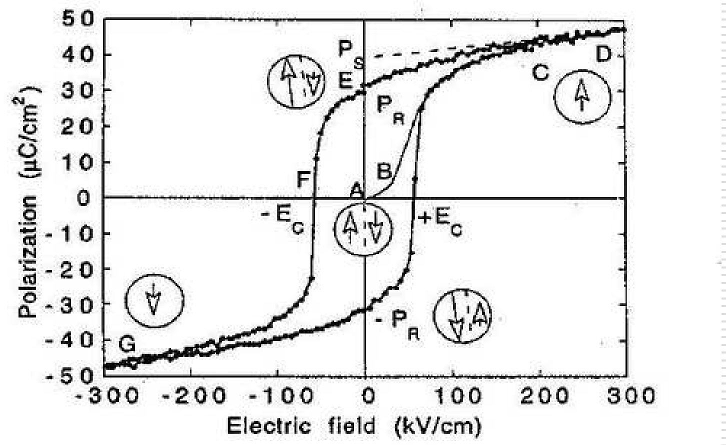


Double perovskites

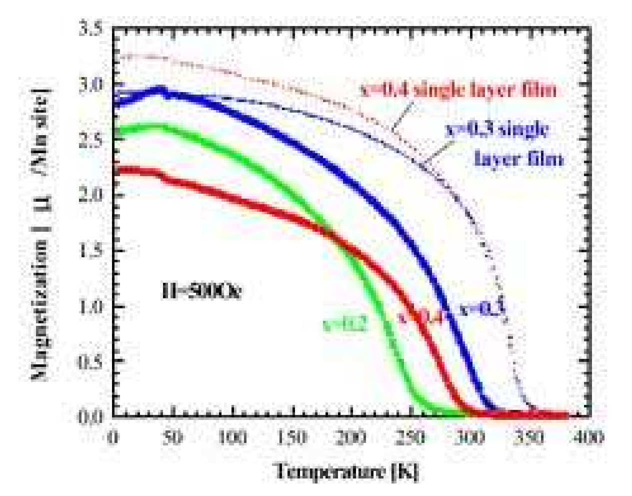
Functional properties of perovskites

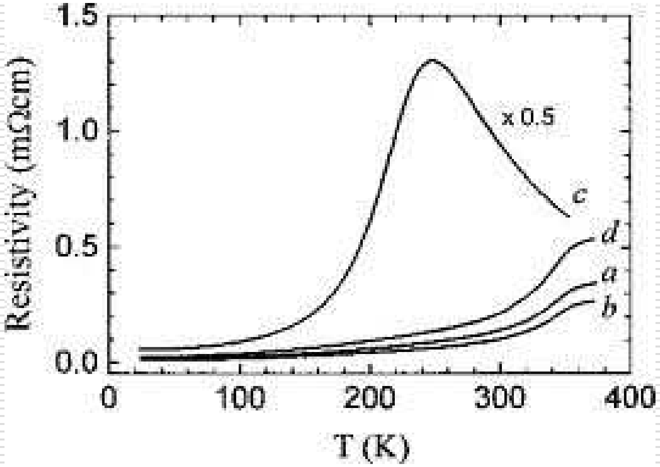
Ferroelectricity



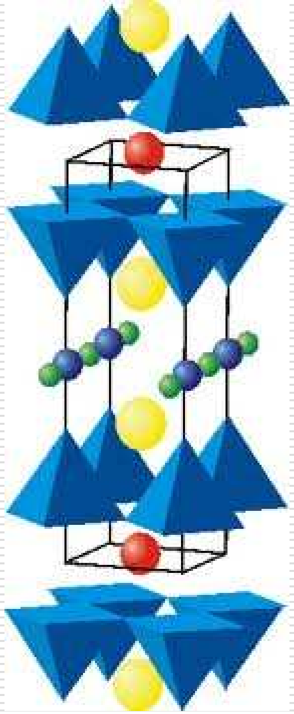


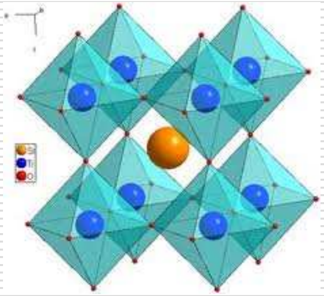
Half metallic, ferromagnetic

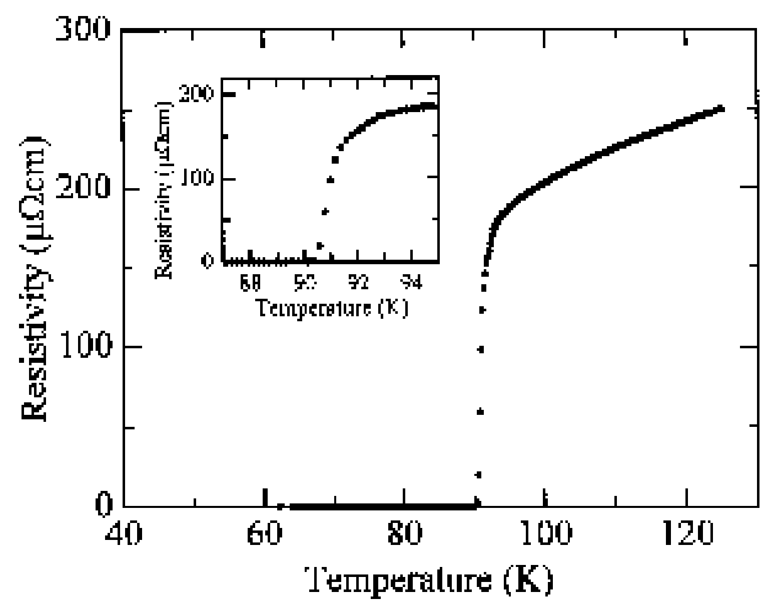




HTS layered superconductors

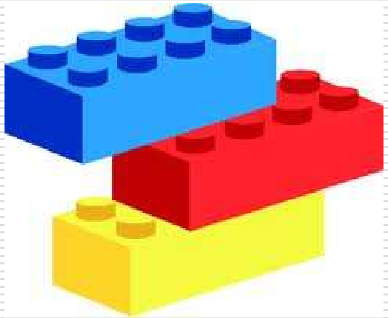






YBCO

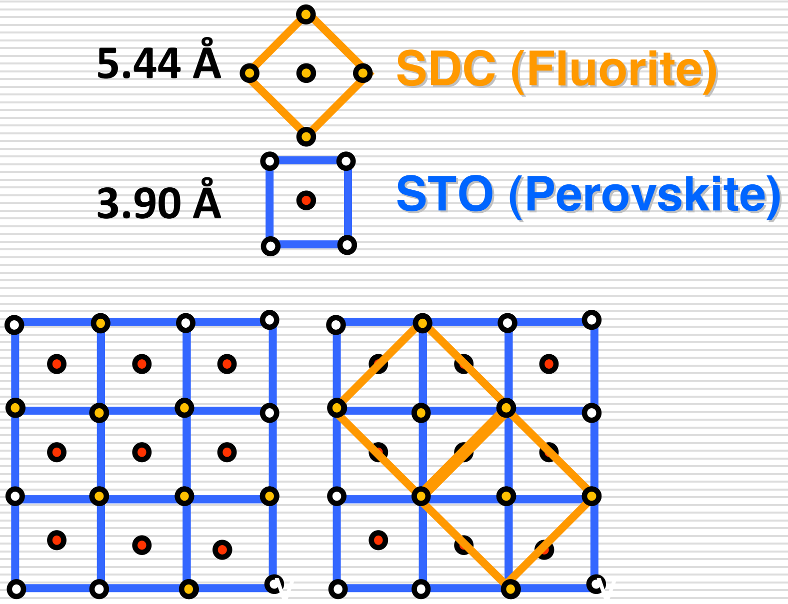
Choice of the right substrate



A large variety of commercial substrates available with the perovskite structure

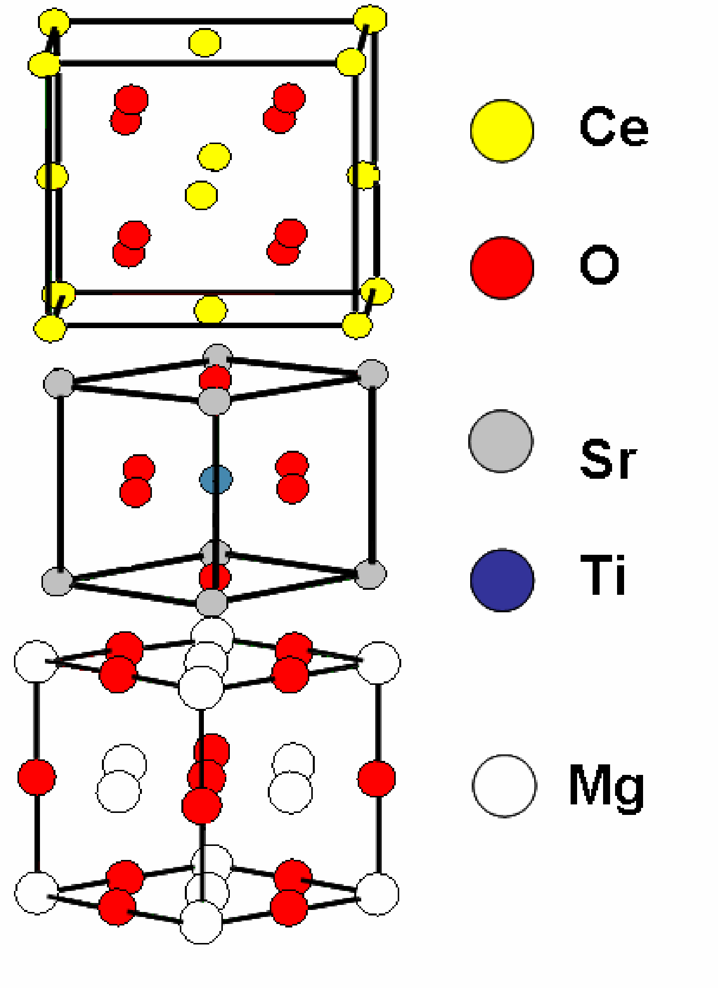
$SrTiO_3$	cubic	a=3.905 Å
$LaAlO_3$	cubic	a=3.76 Å
$NdGaO_3$	pseudocubic	a=3.86 Å

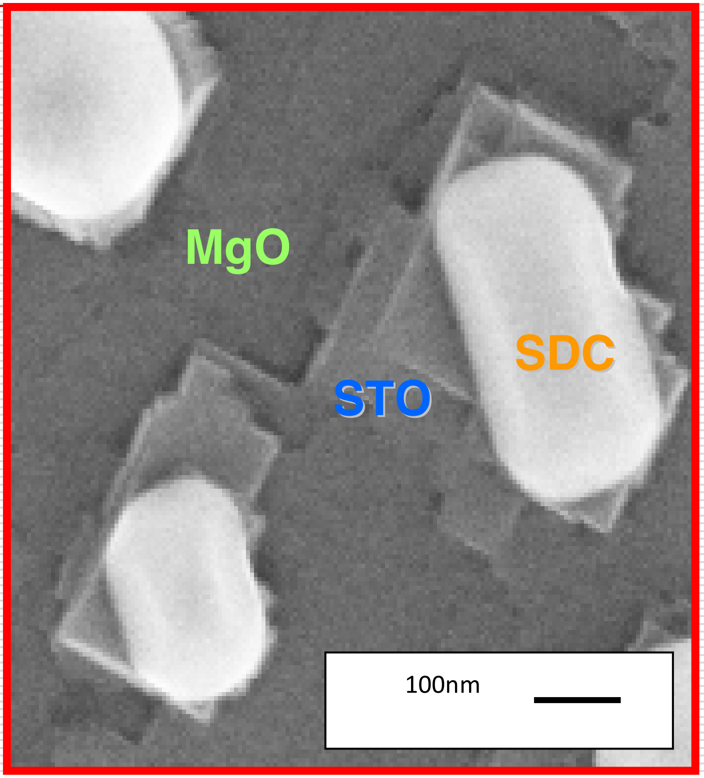
$Sm_{0.2}Ce_{0.8}O_2$ (SDC) on STO

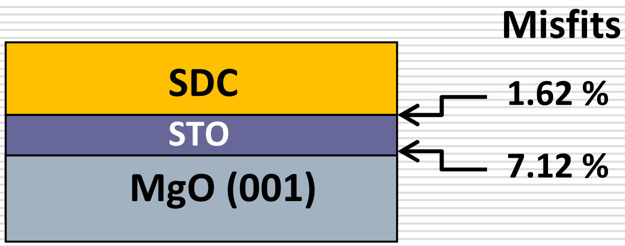


$$d_{110}^{SDC} = \left. 5.44\text{Å} \middle/ \sqrt{2} \right. = 3.85\text{Å} \quad \Rightarrow \quad \frac{d_{100}^{STO} - d_{110}^{SDC}}{d_{100}^{STO}} \cong 1.3\%$$

SDC/STO/MgO(001)

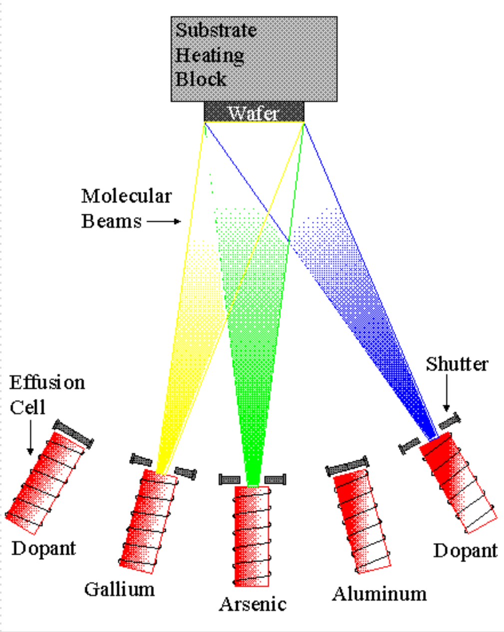


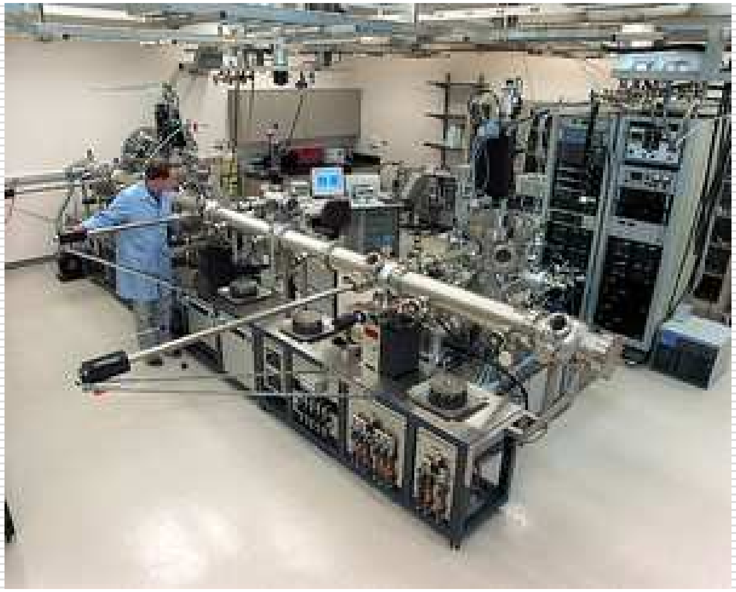


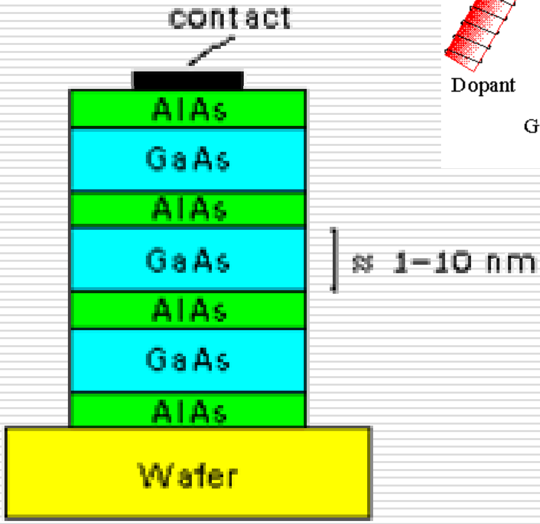


Schematic sketch of the correlation between the cubic cells of SDC, STO, and MgO.

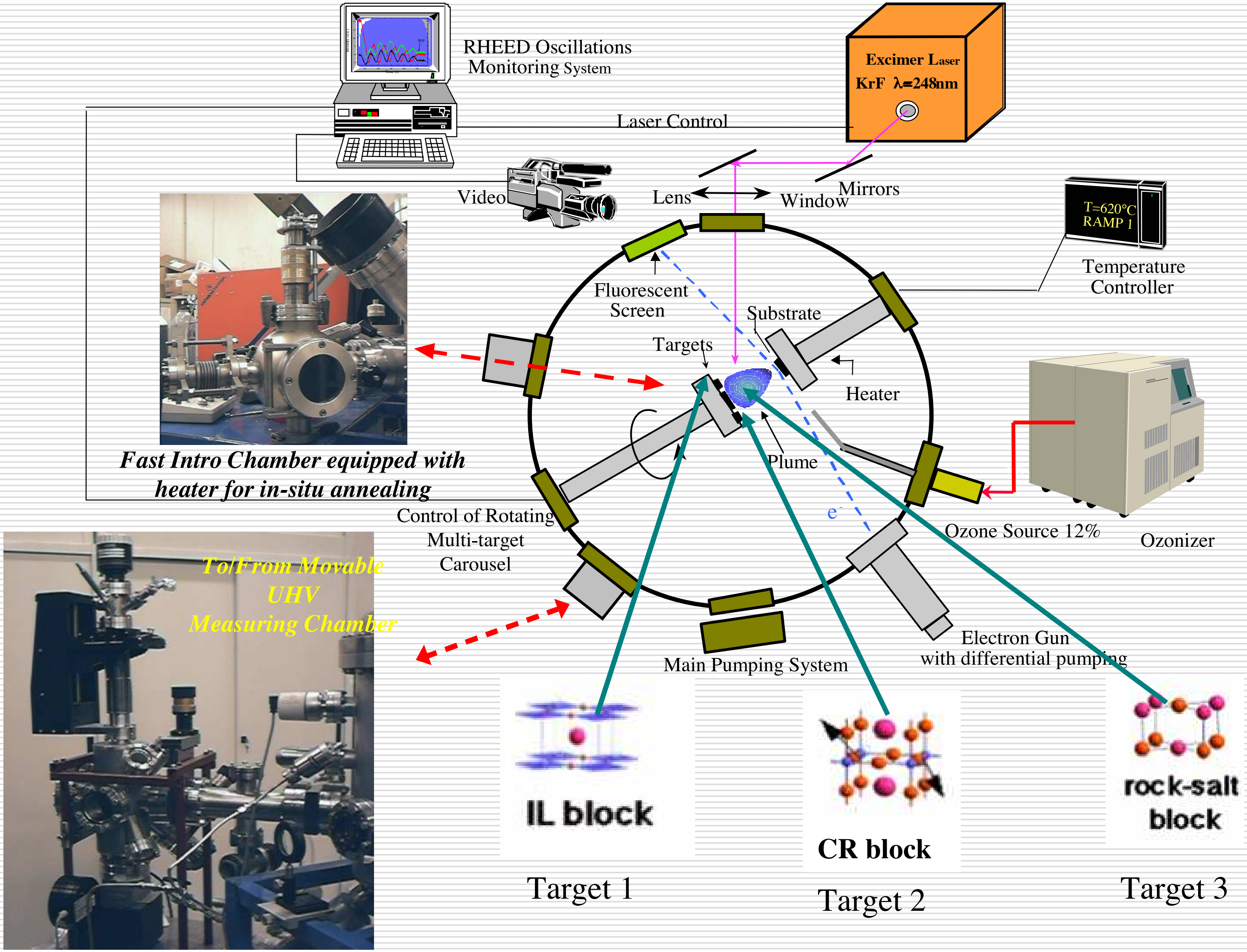
Deposition techniques: MBE







Pulsed Laser Deposition (PLD)



RHEED Oscillations
Monitoring System

Excimer Laser
KrF λ=248nm

Laser Control

Video

Lens

Window

Mirrors

T=620°C
RAMP 1

Temperature
Controller

Fluorescent
Screen

Substrate

Targets

Heater

Plume

e^-

Ozone Source 12%

Ozonizer

Fast Intro Chamber equipped with
heater for in-situ annealing

Control of Rotating
Multi-target
Carousel

To/From Movable
UHV
Measuring Chamber

Main Pumping System

Electron Gun
with differential pumping

IL block

Target 1

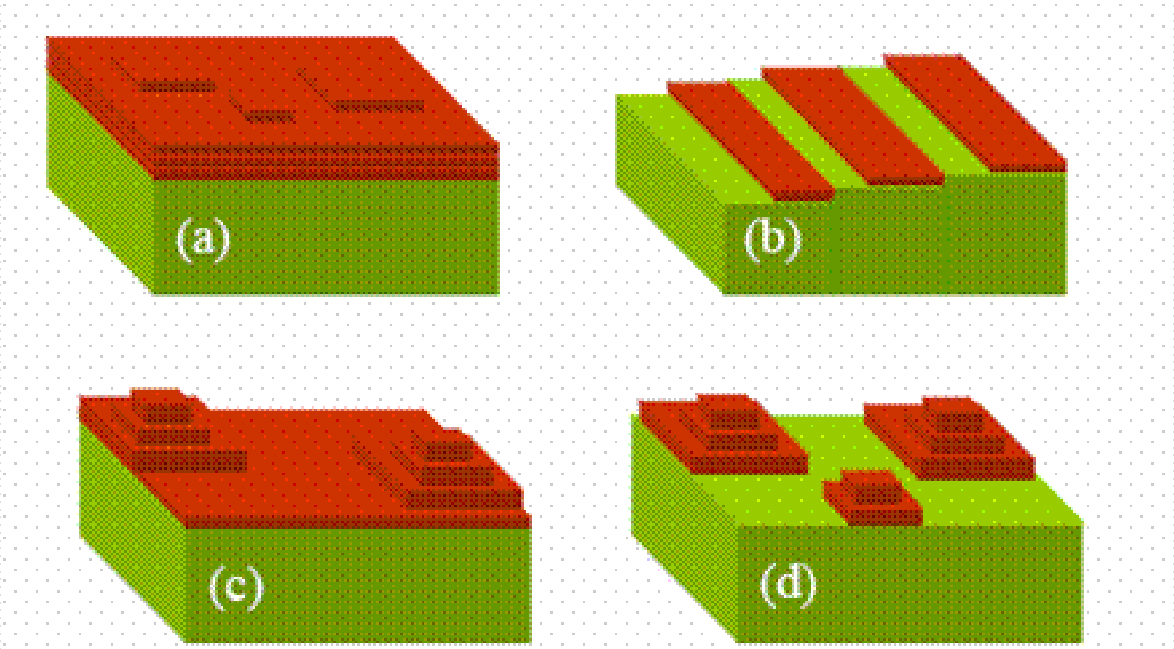
CR block

Target 2

rock-salt
block

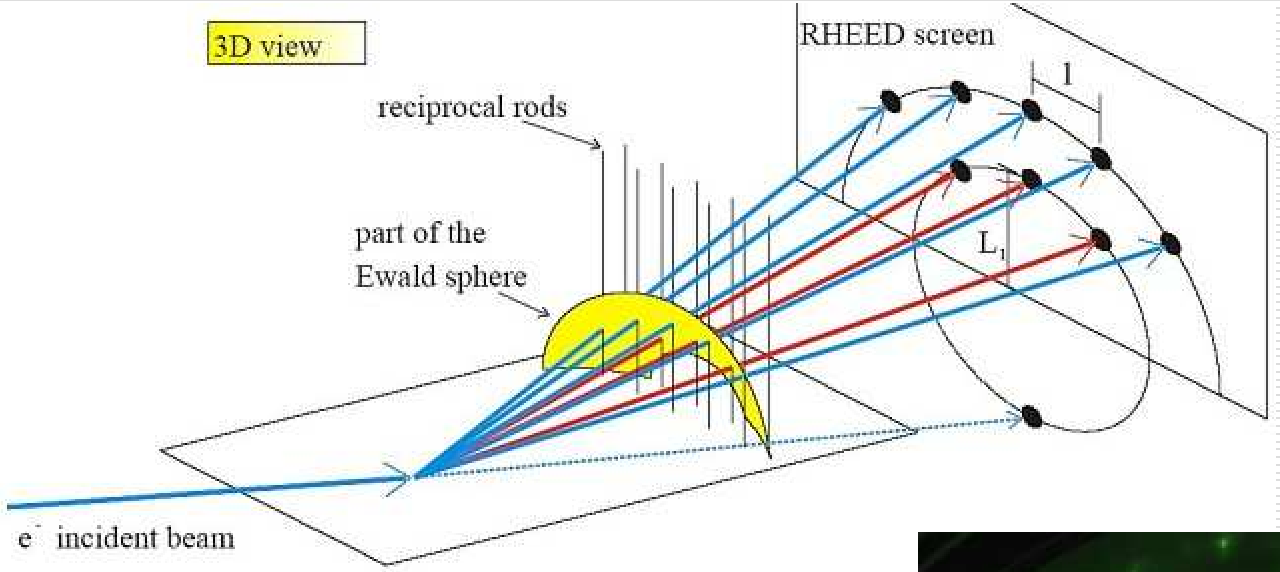
Target 3

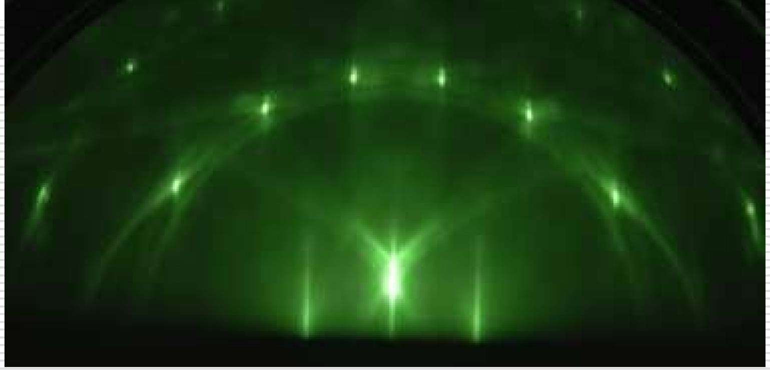
Growth mechanisms



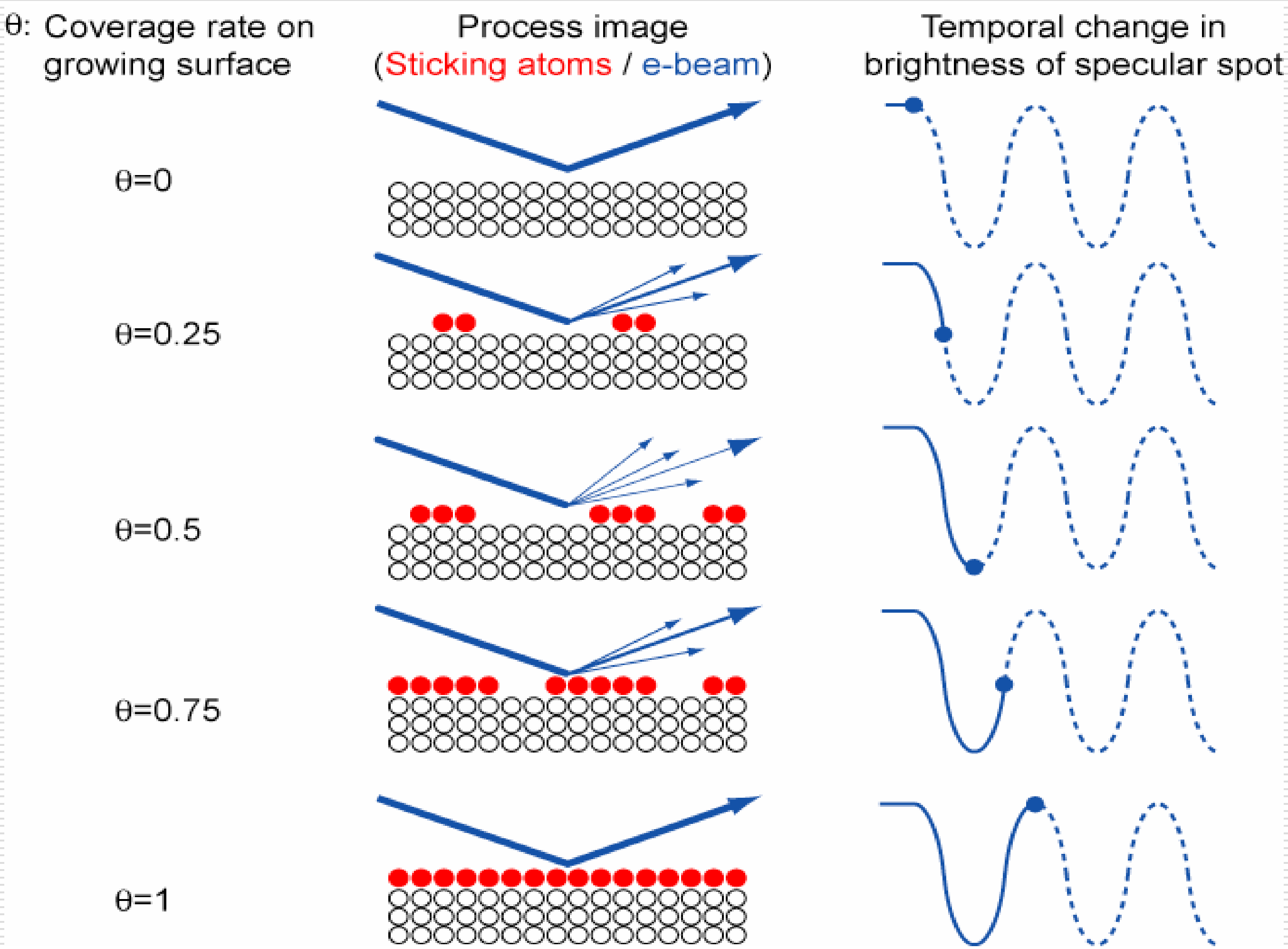
(a) Frank-Van der Merwe or layer-by-layer growth,
(b) step-flow growth,
(c) Stranski-Krastanov growth,
(d) Volmer-Weber growth.

RHEED geometry

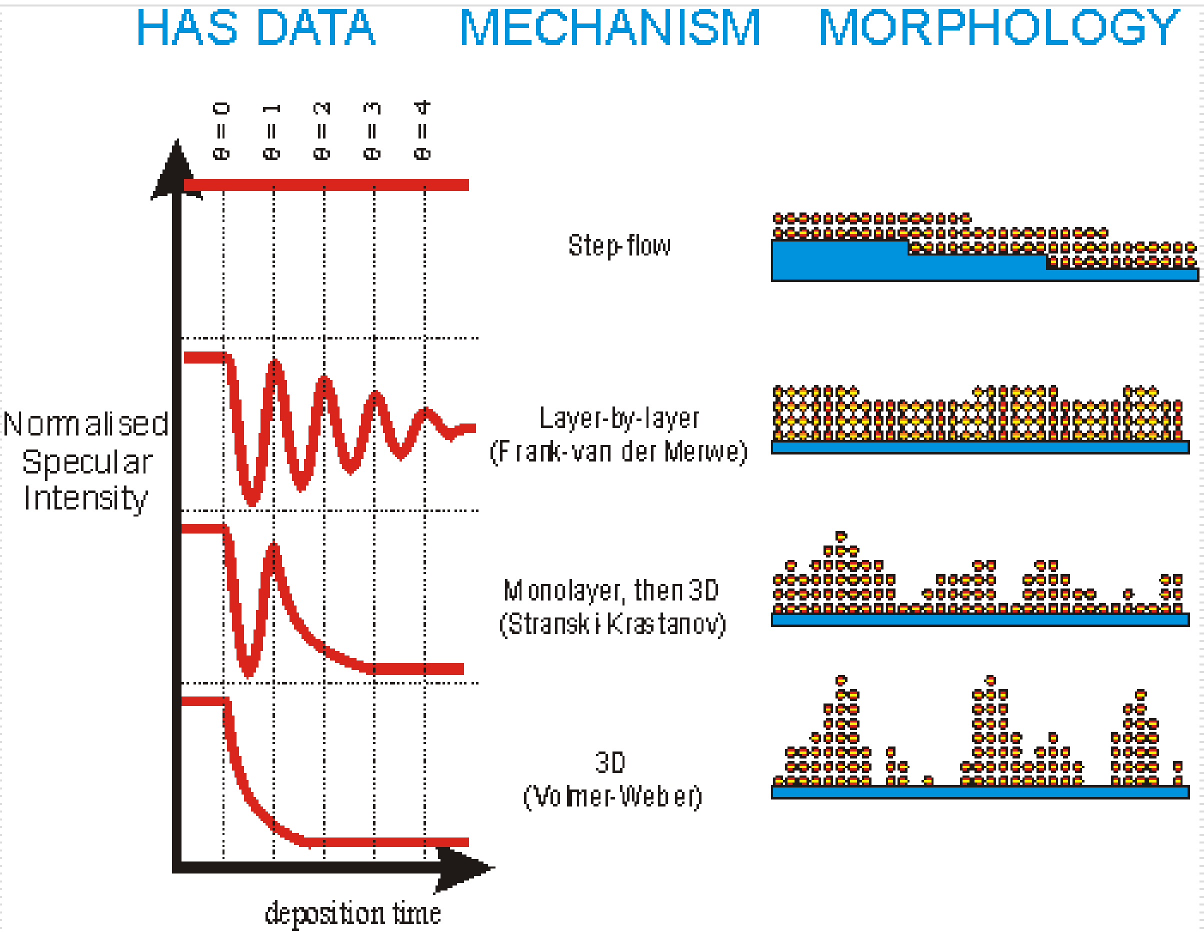




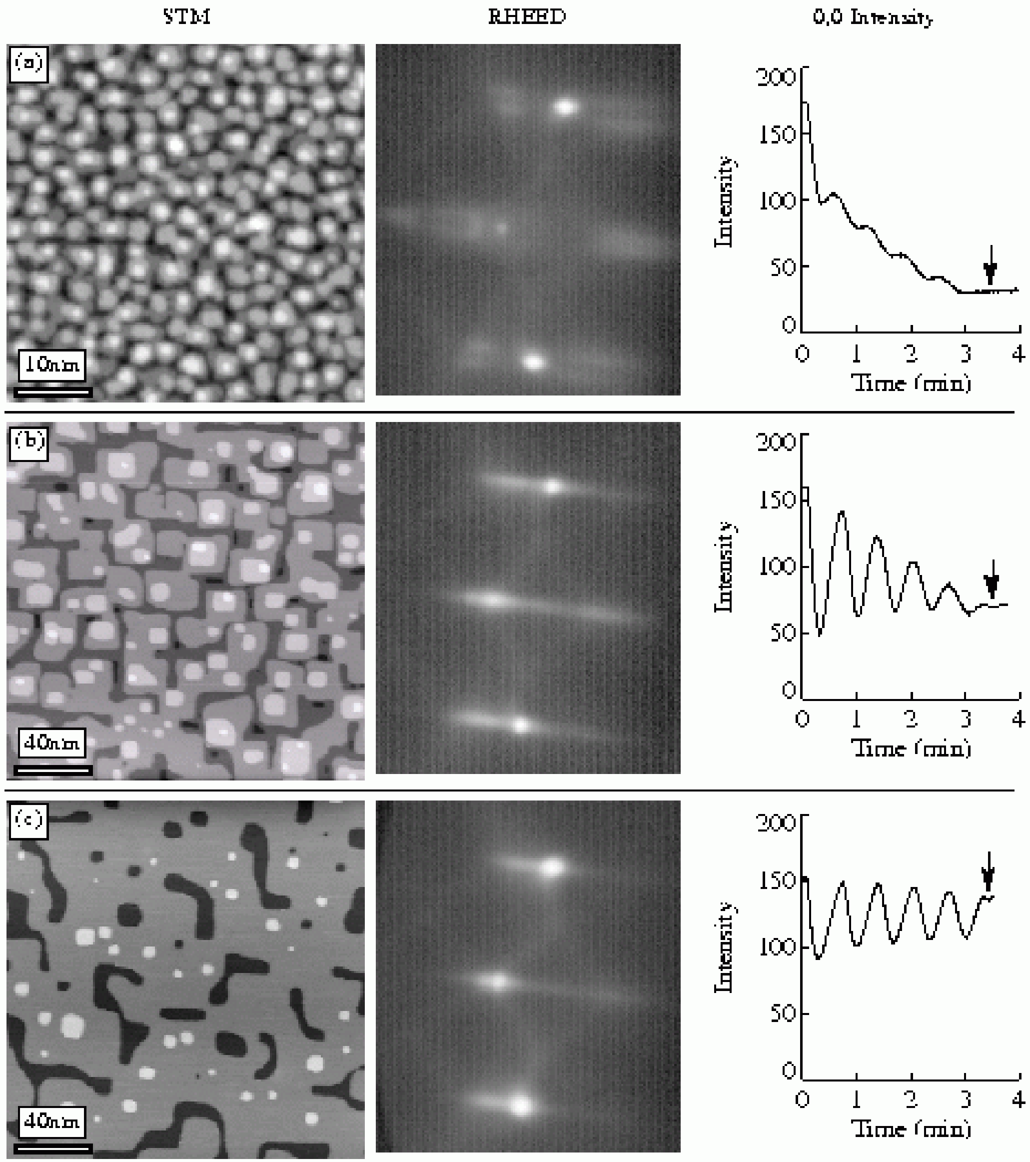
RHEED intensity oscillations



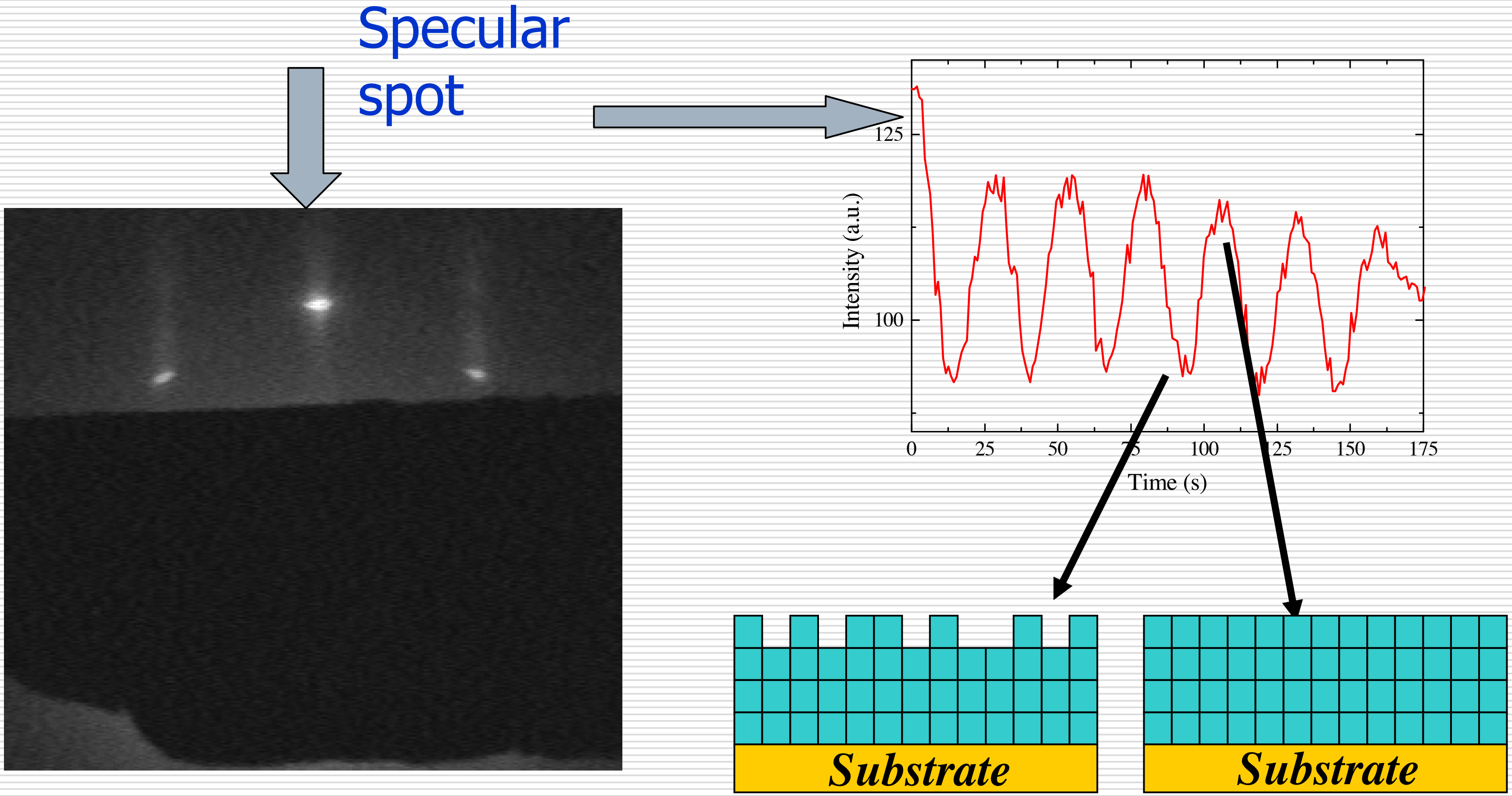
RHEED oscillations vs. surface morphology



RHEED vs. surface morphology

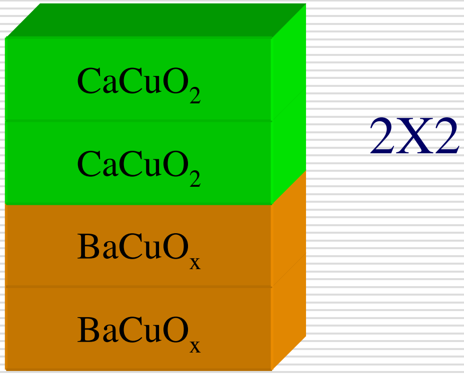


$La_{0.7}$ $Sr_{0.3}$ MnO_3|film on $NdGaO_3$: RHEED oscillations

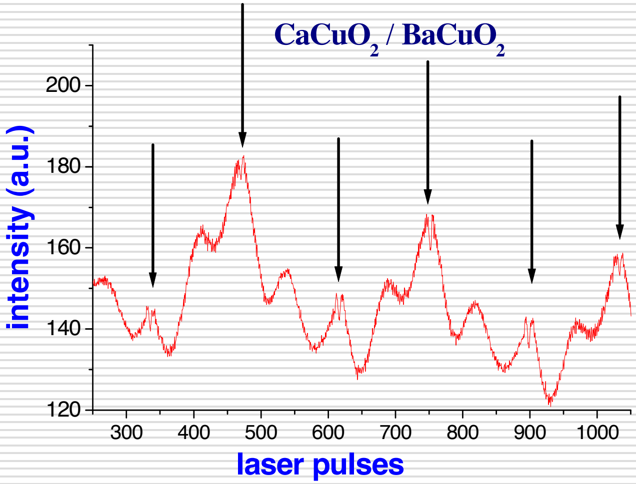


Specular spot

$(BaCuO_2)_2/(CaCuO_2)_2$ SL by Laser MBE technique

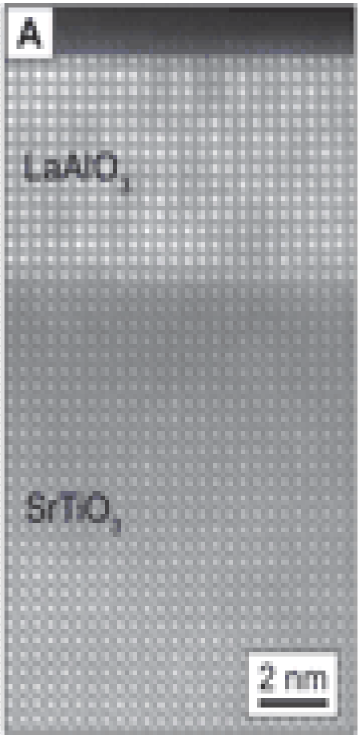


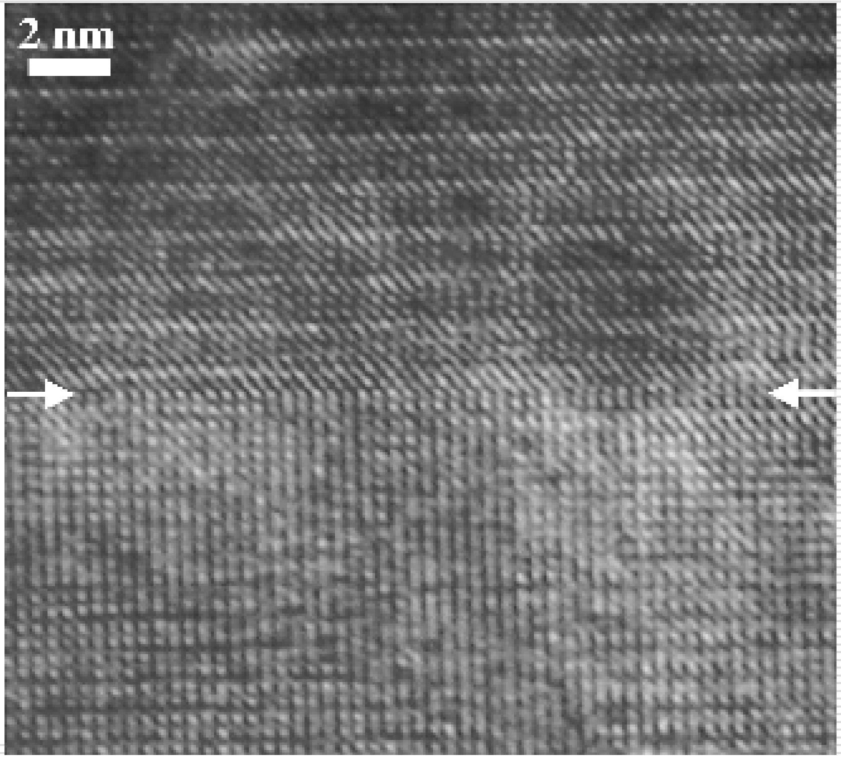
Multitarget Pulsed Laser Deposition



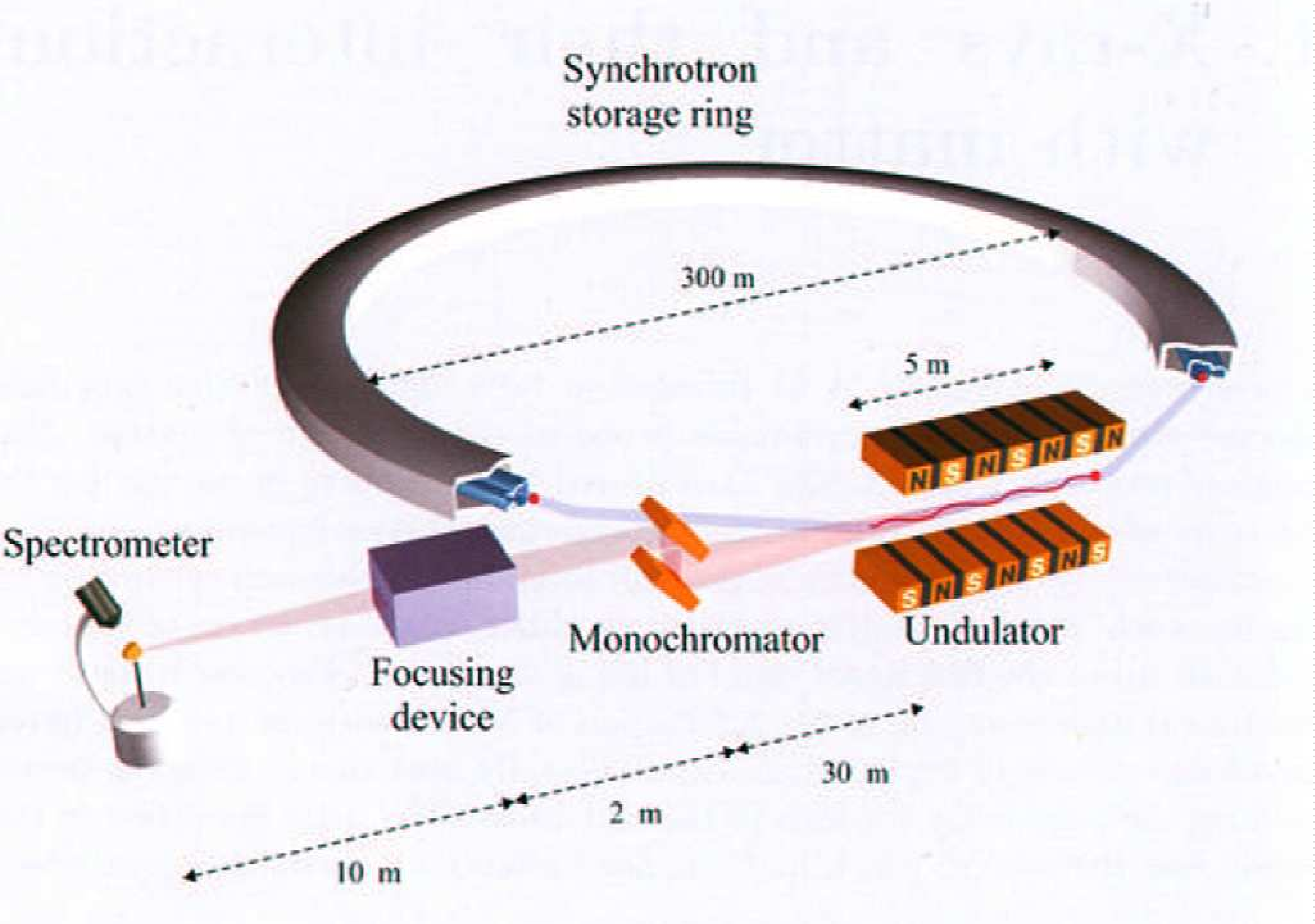
RHEED Oscillations

HRTEM of oxide interfaces and superlattices





Synchotron characterization



Characteristics of synchrotron radiation

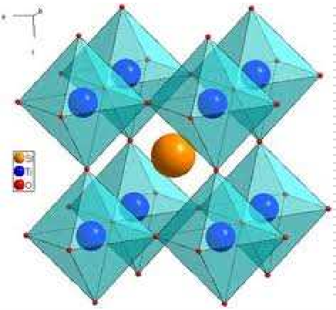
- High brilliance, exceeding other natural and artificial light sources by many orders of magnitude: 3rd generation sources typically have a brilliance larger than 10^{18} photons/s/mm^2/mrad^2/0.1%BW, where 0.1%BW denotes a bandwidth 10^{-3} ν centered around the frequency ν.
- High collimation, i.e. small angular divergence of the beam
- Widely tunable in energy/wavelength by monochromatization (sub eV up to the MeV range)
- High level of polarization (linear or elliptical)
- Pulsed light emission (pulse durations at or below one nanosecond),

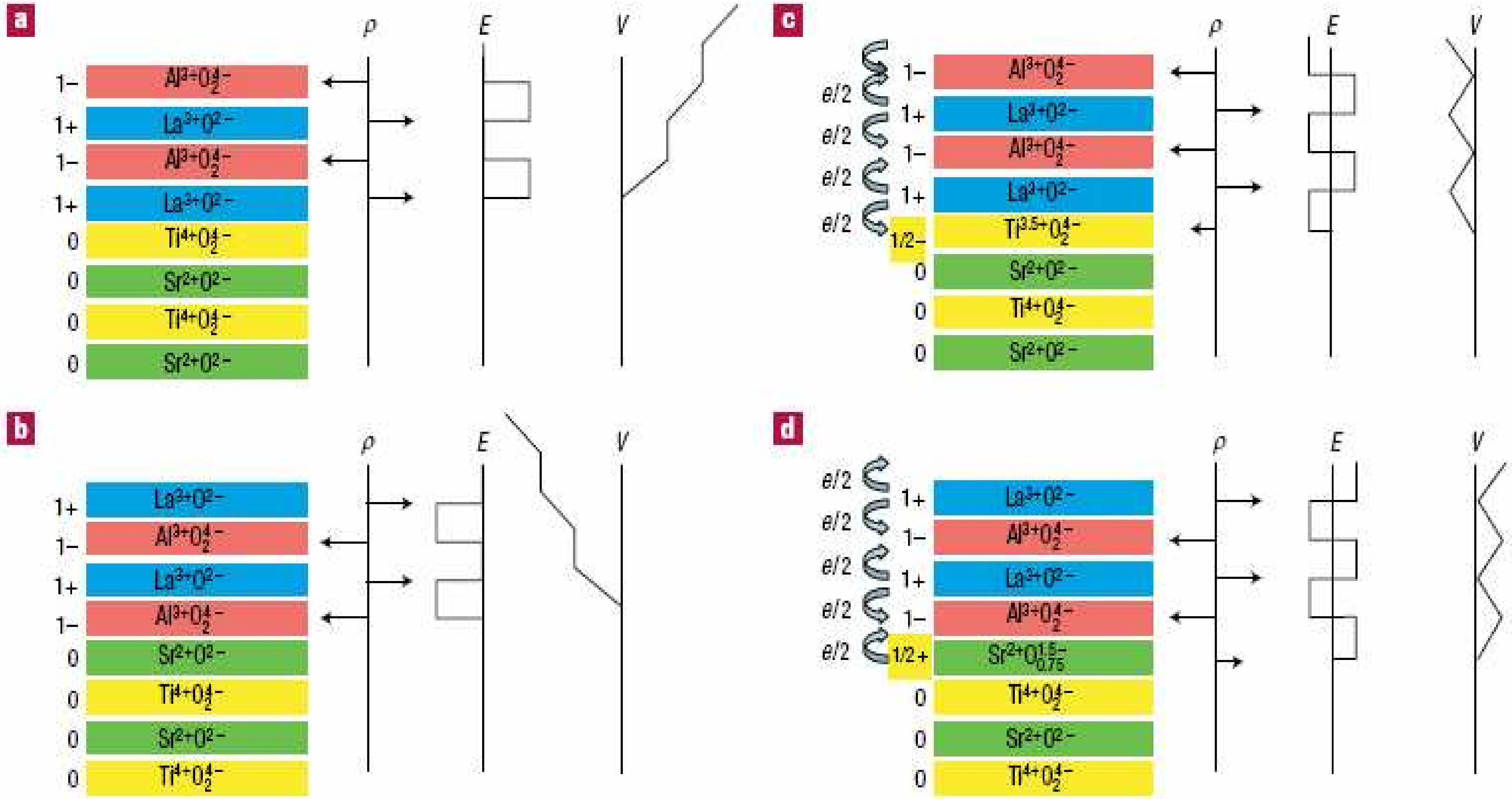
An ideal tool for ultrathin layers (few u.c.) and interfaces

Interface effects

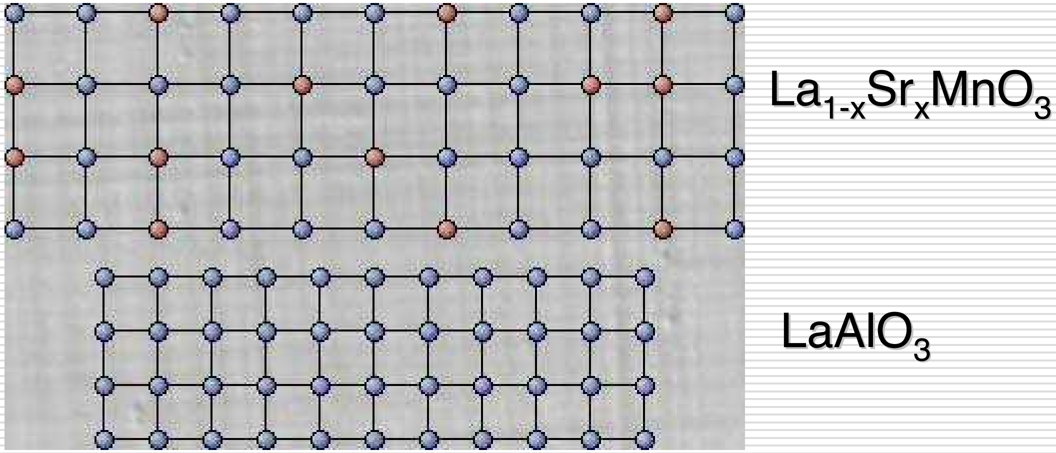
- Epitaxial strain as a consequence of lattice misfit
- Non equilibrium distribution of ions and vacancies (space charge region)
- Polarity discontinuity
- Electrical charge transfer

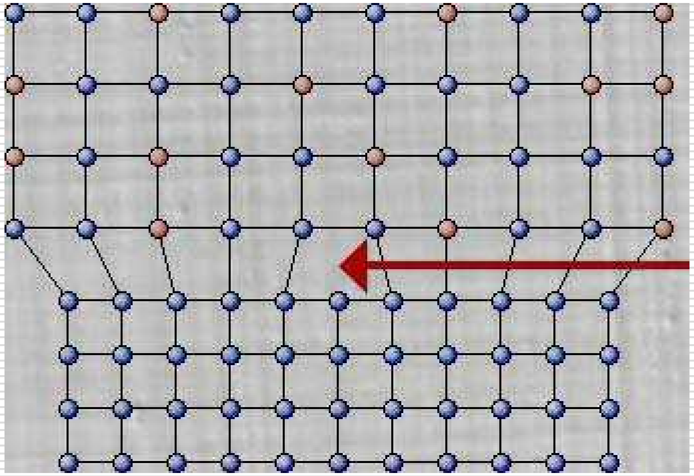
Interface effects: polar discontinuity LaAlO$_3$|SrTiO3

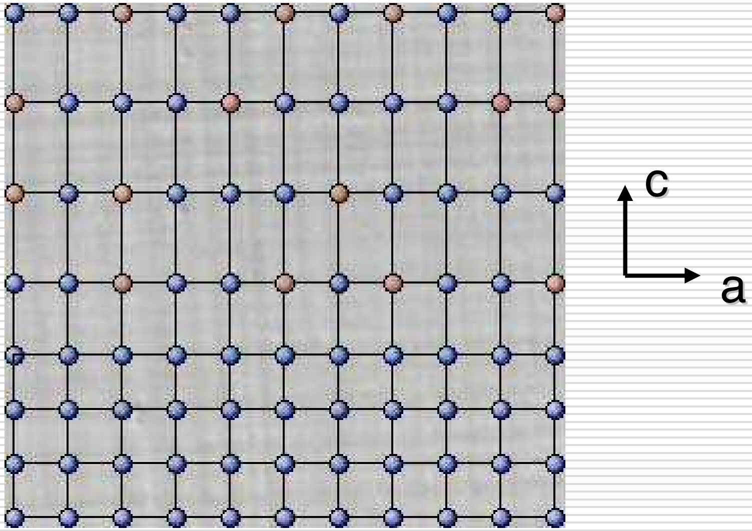




Interface effects: epitaxial strain







$$\frac{\Delta c}{c} = -\frac{2\nu}{1-\nu}\frac{\Delta a}{a}$$

$$\nu \cong 0.3 - 0.5$$

Three examples

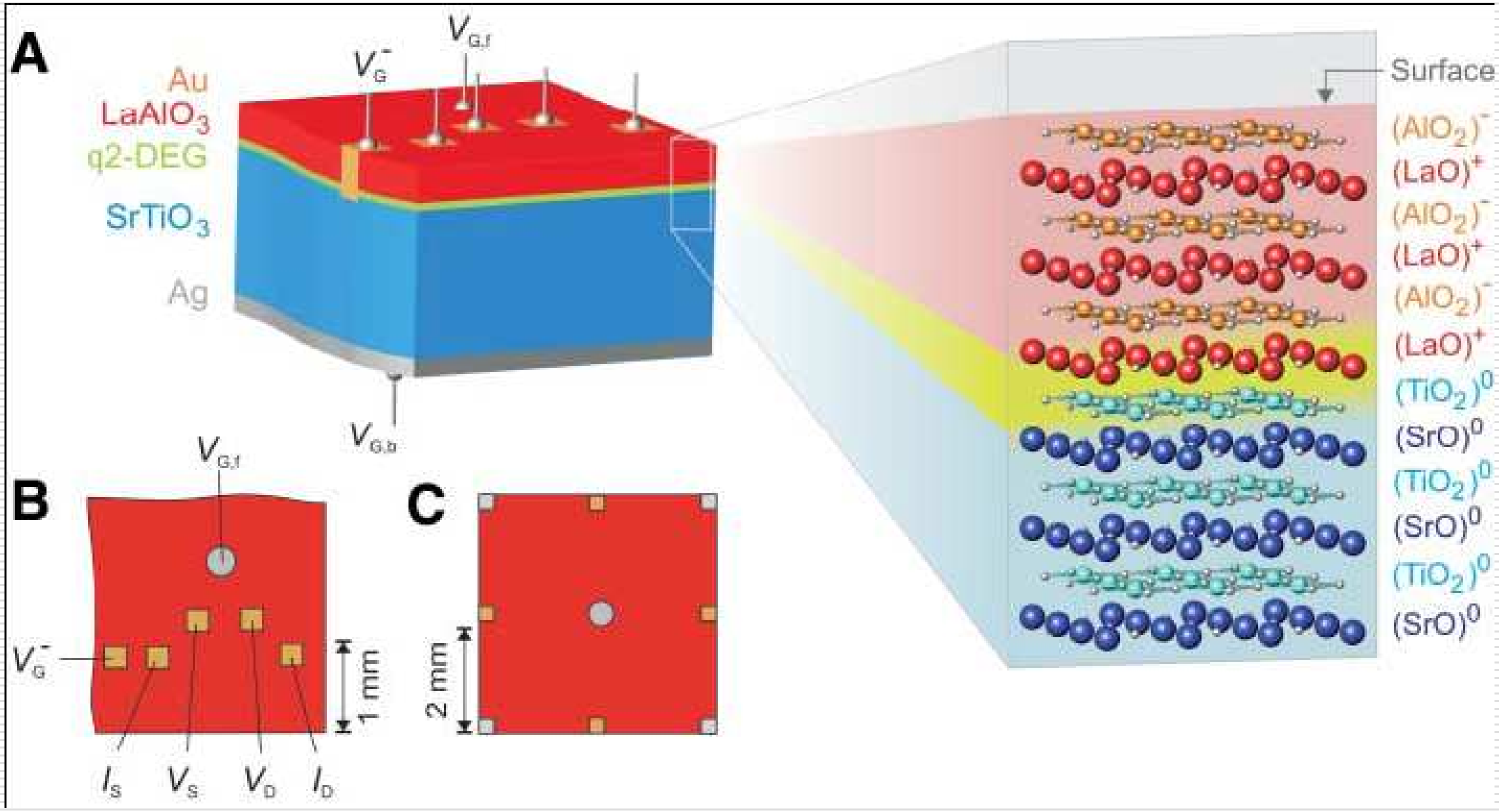
- 2D electron gas in oxide heterostructures
- Induced superconductivity in oxide heterostructures
- Enhanced ionic conductivity in oxide heterostructures

Engineering complex oxide heterostructures

Tunable Quasi–Two-Dimensional Electron Gases in Oxide Heterostructures

S. Thiel,[1] G. Hammerl,[1] A. Schmehl,[2] C. W. Schneider,[1] J. Mannhart[1]*

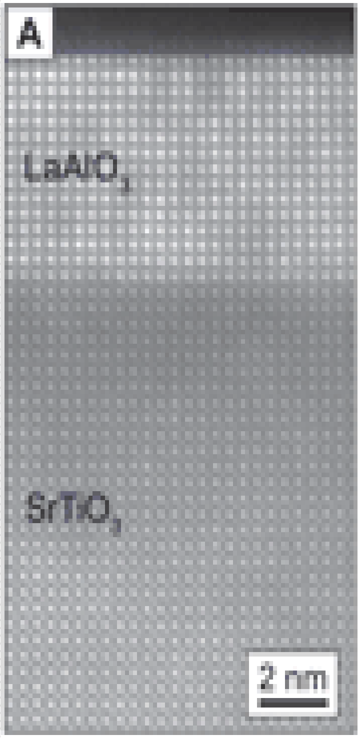
Science 313, 1942 (2006)

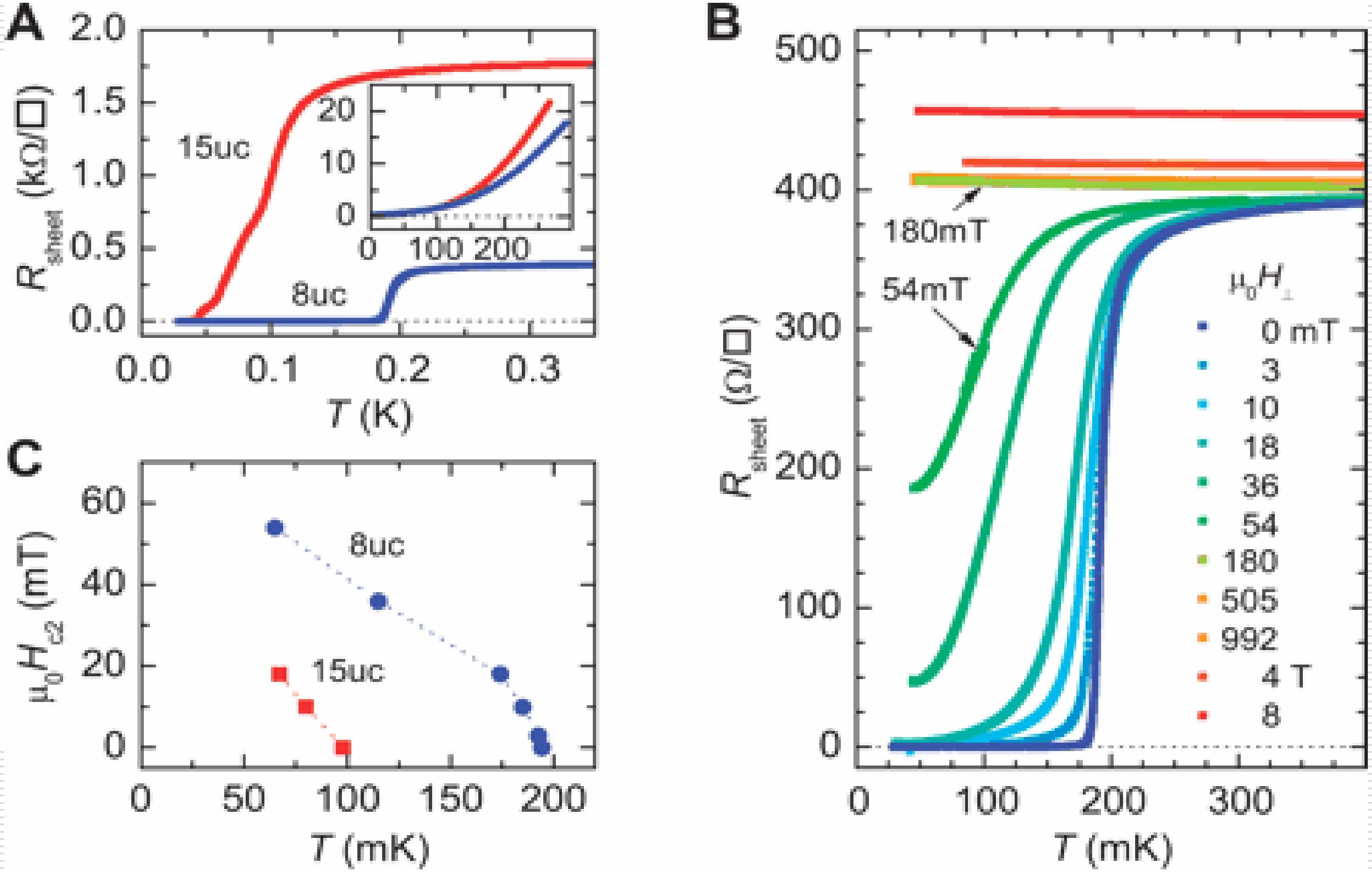


Superconductivity at the interface LAO/STO

Superconducting Interfaces Between Insulating Oxides

N. Reyren et al., *Science* 31 August 2007: Vol. 317. no. 5842, pp. 1196 - 1199



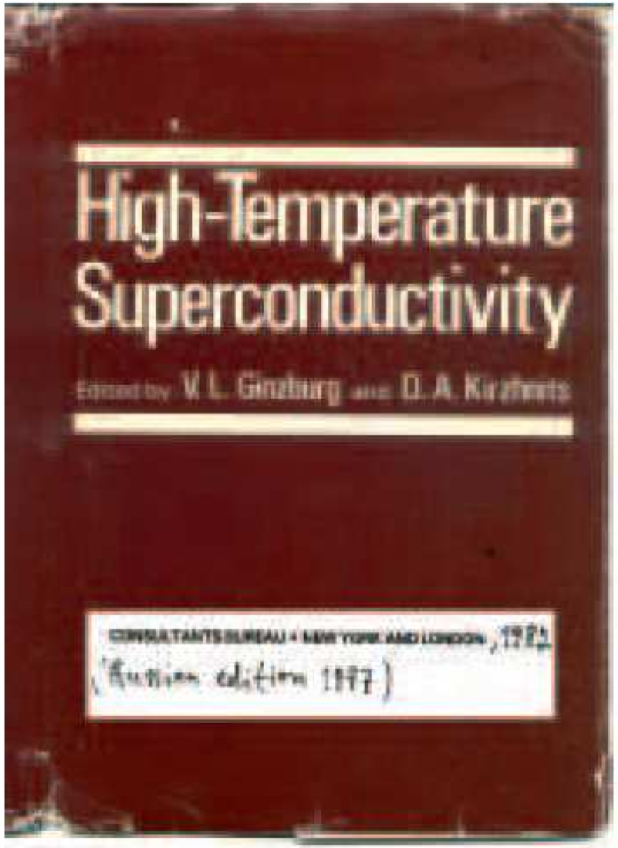


Induced superconductivity in oxide based heterostructures

Nobel Lecture, December 8, 2003

by

Vitaly L. Ginzburg



High-Temperature Superconductivity

(Moscow: Nauka, 1977)

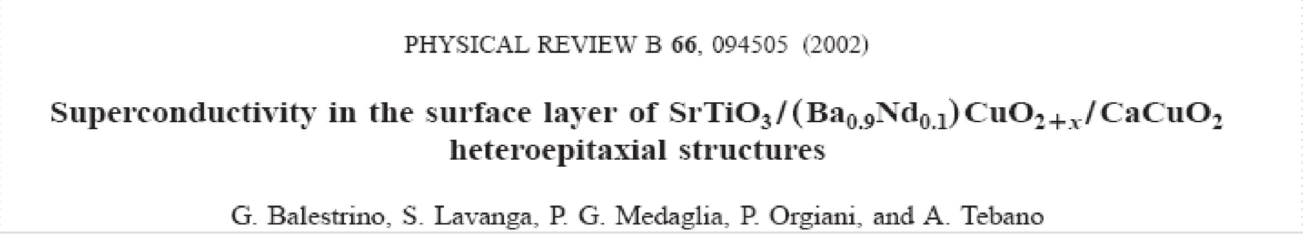
From the Nobel Lecture (citing his book)

“On the basis of general theoretical considerations, I believe at present that the most reasonable estimate is Tc 300 K. …omissis… In this scheme, the most promising materials – from the point of view of the possibility of raising Tc – are, apparently, layered compounds and dielectric–metal–dielectric sandwiches…

And now oxide heterostructures come!

Ginzburg V L *Phys. Lett.* **13** 101 (1964)

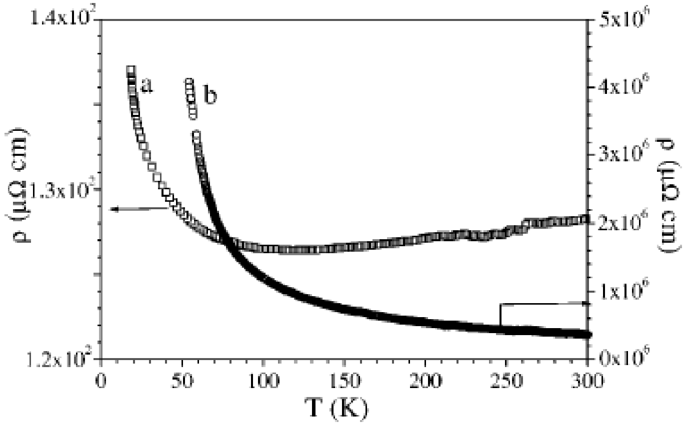
Recent experimental evidence

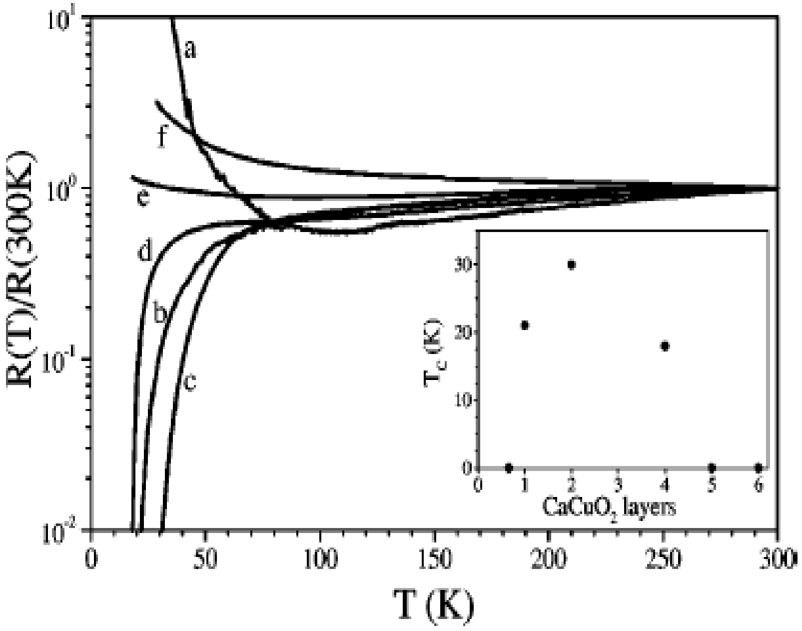


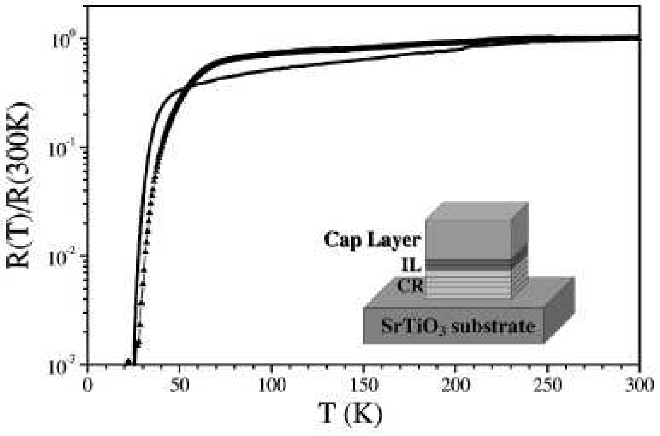
PHYSICAL REVIEW B **66**, 094505 (2002)

Superconductivity in the surface layer of $SrTiO_3/(Ba_{0.9}Nd_{0.1})CuO_{2+x}/CaCuO_2$ heteroepitaxial structures

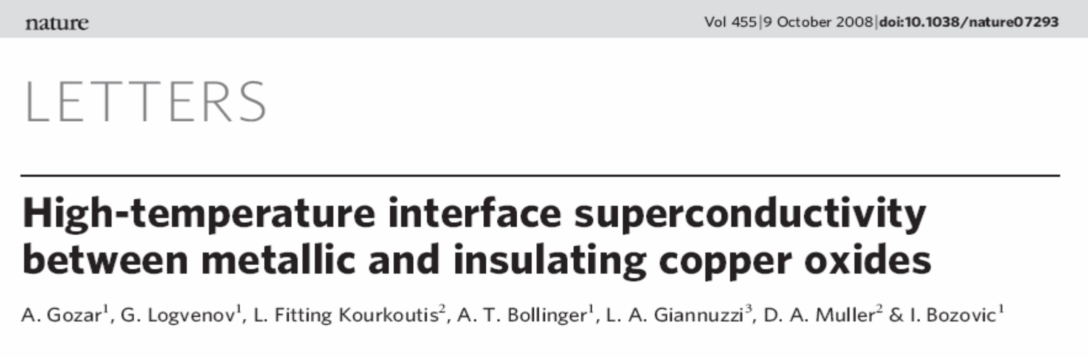
G. Balestrino, S. Lavanga, P. G. Medaglia, P. Orgiani, and A. Tebano







Further evidence



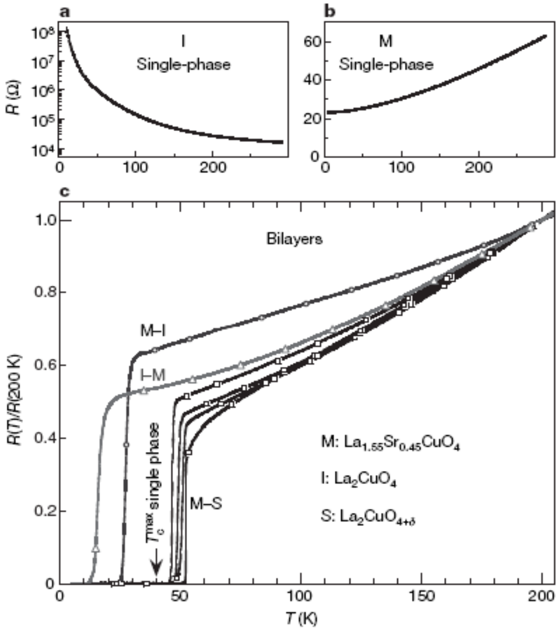
nature

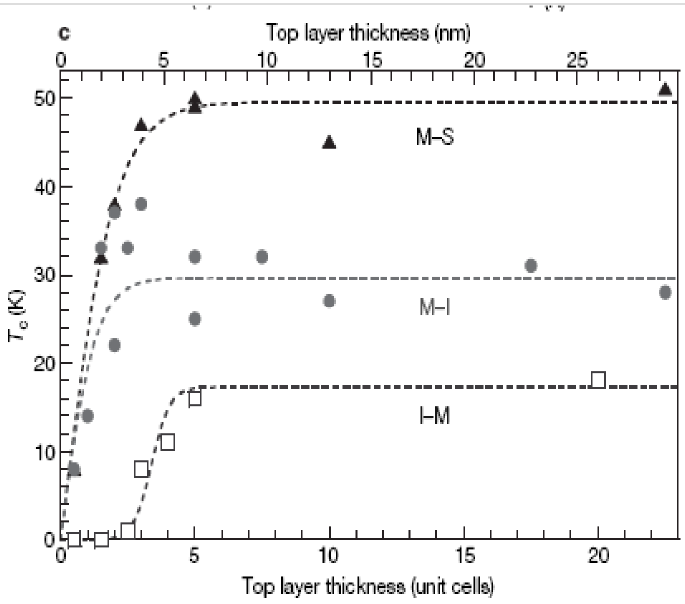
Vol 455|9 October 2008|doi:10.1038/nature07293

LETTERS

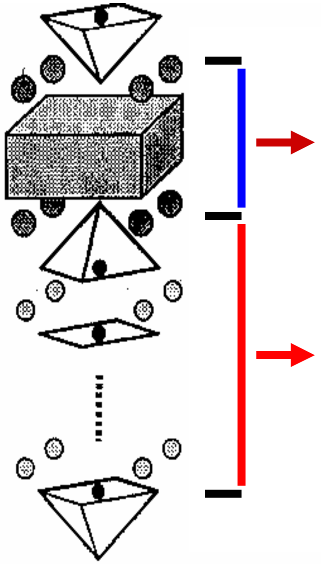
High-temperature interface superconductivity between metallic and insulating copper oxides

A. Gozar[1], G. Logvenov[1], L. Fitting Kourkoutis[2], A. T. Bollinger[1], L. A. Giannuzzi[3], D. A. Muller[2] & I. Bozovic[1]





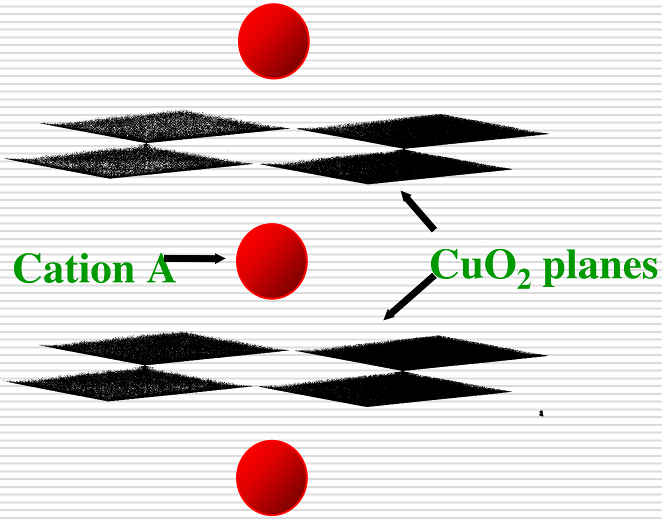
Engineering superconducting superlattices



Charge Reservoir (CR) Block

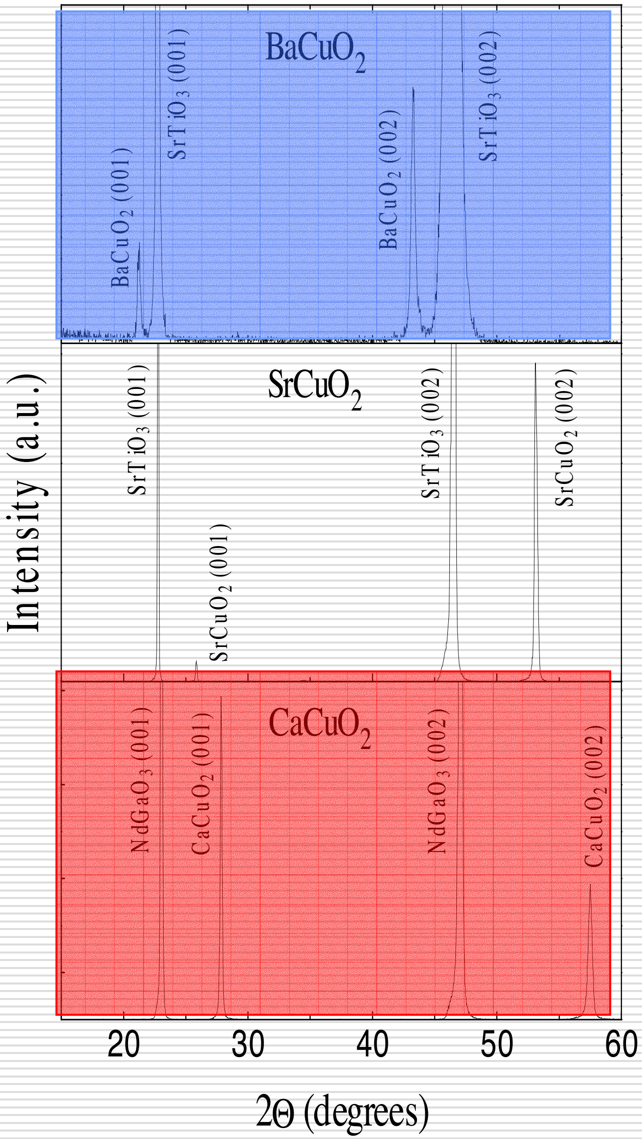
“Infinite Layer” (IL) Active Block

(CuO_2 superconducting planes)

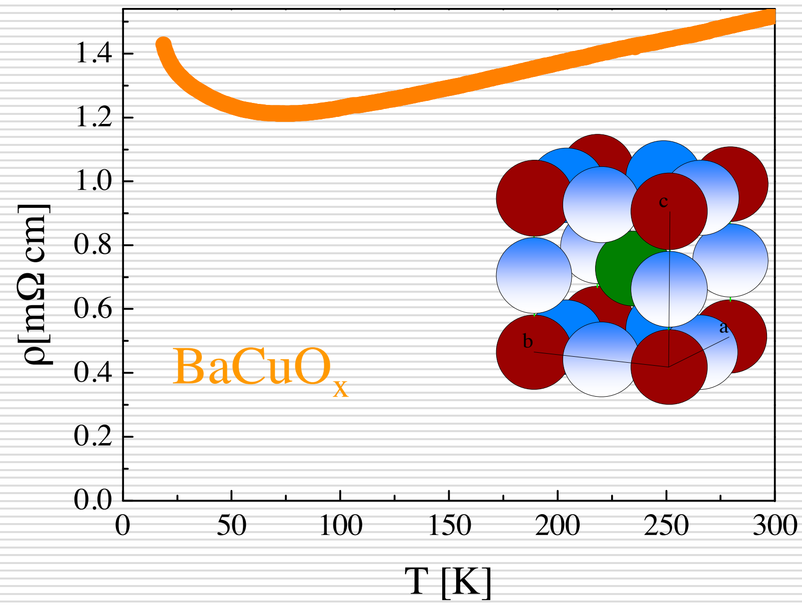


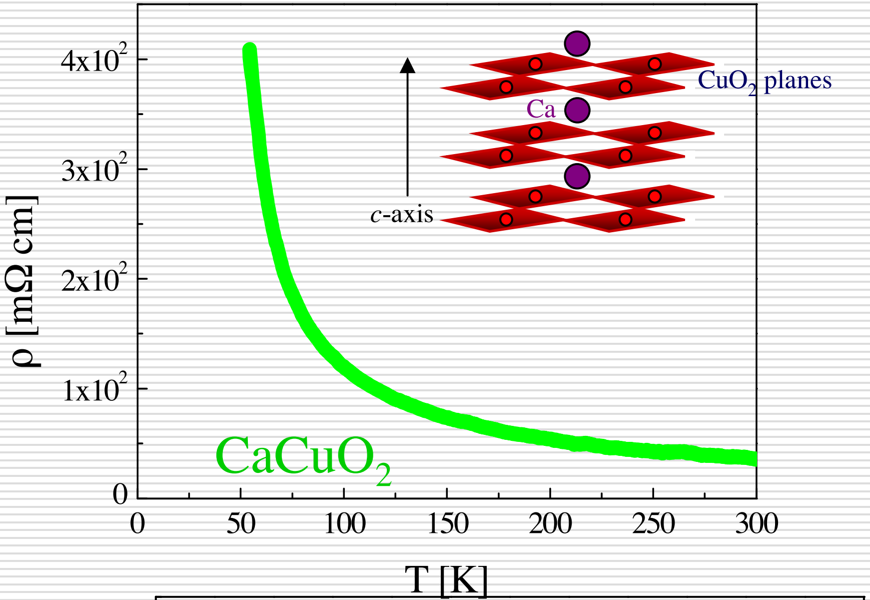
Cation A

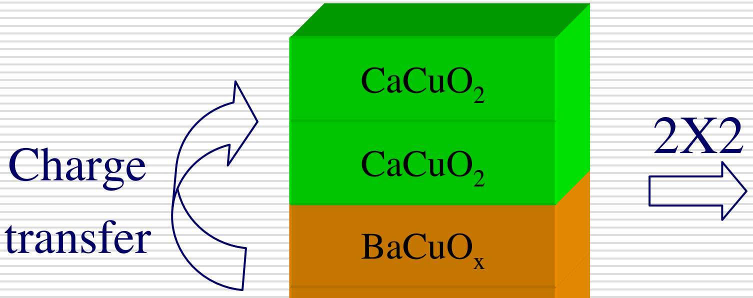
CuO_2 planes



Superconducting superlattices on atomic dimensions







Charge transfer

$CaCuO_2$

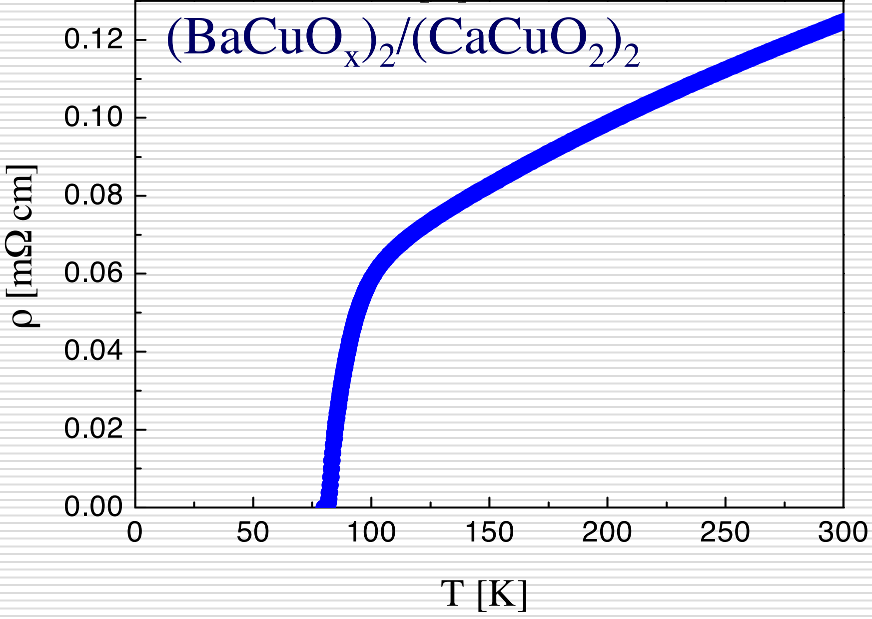
$CaCuO_2$

$BaCuO_x$

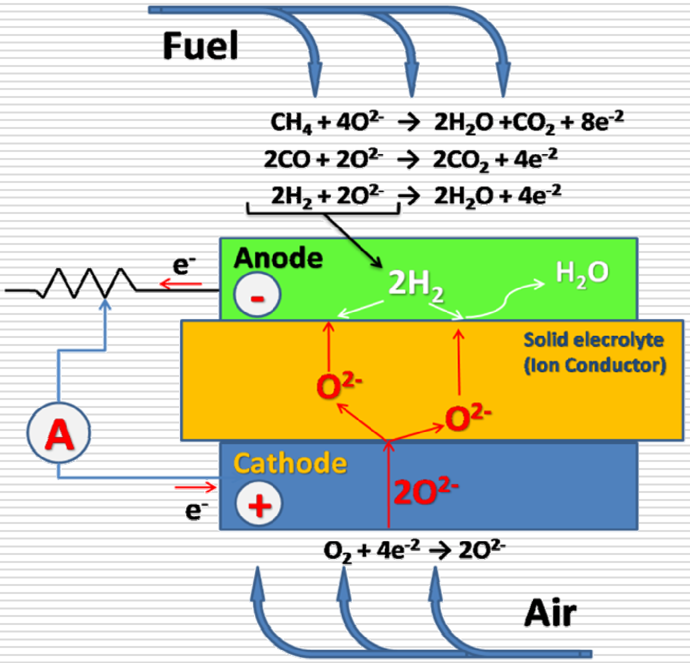
$BaCuO_x$

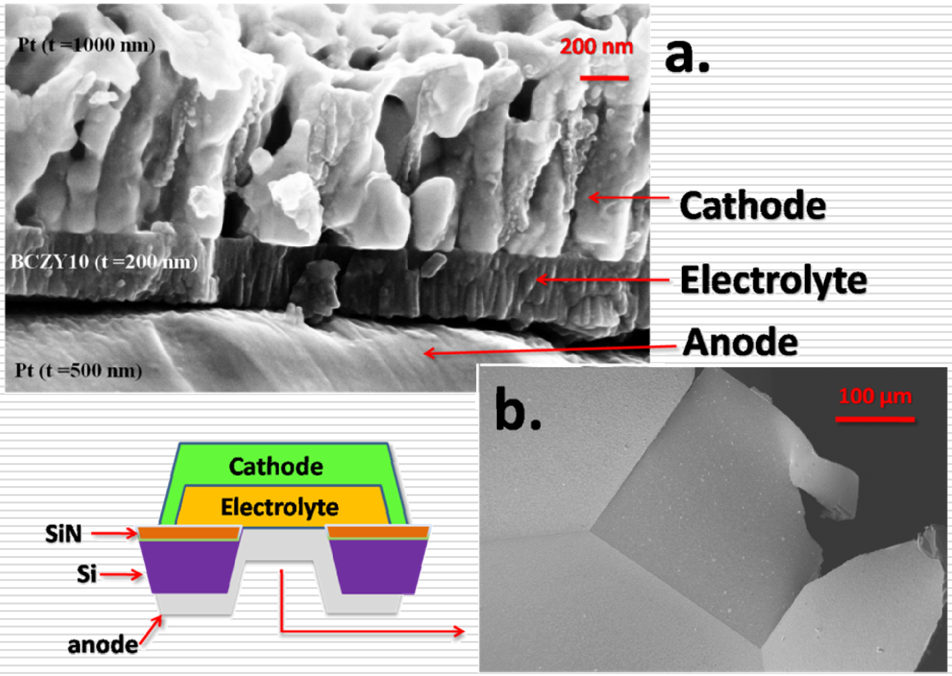
2X2

Multitarget Pulsed Laser Deposition

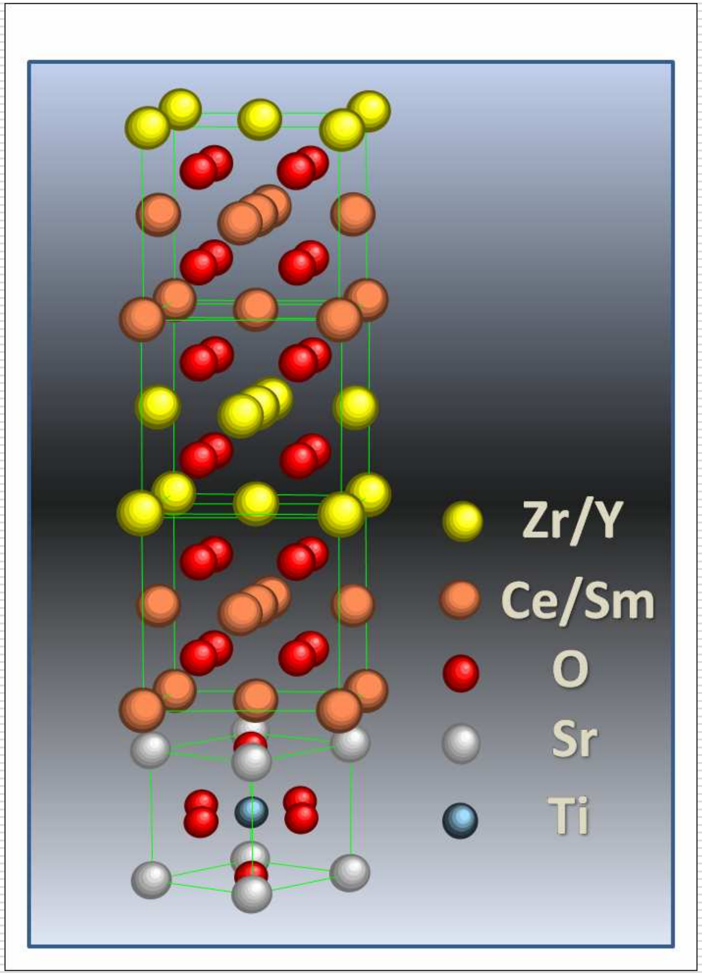


μ SOFCs based on thin film technology





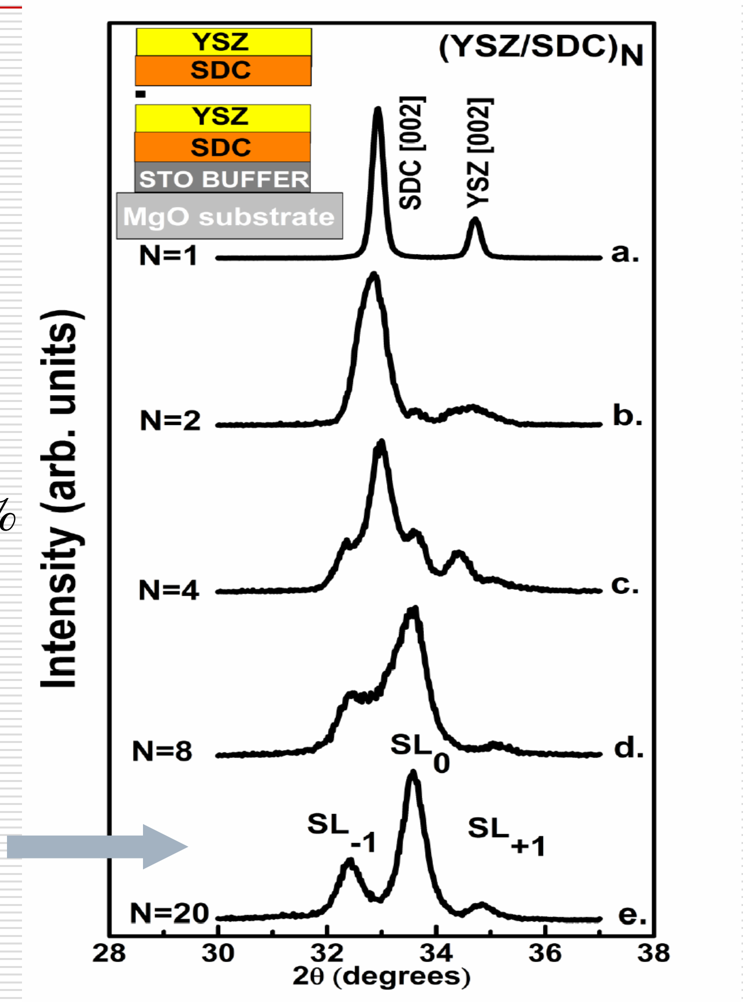
$Y_{0.08}Zr_{0.92}O_2$ (YSZ)/SDC superlattices on STO buffered MgO



Epitaxial relationship among the different constituent blocks of the $(YSZ/SDC)_N$/STO/MgO heterostructure.

$$\frac{d_{100}^{SDC} - d_{100}^{YSZ}}{d_{100}^{SDC}} \cong 5\%$$

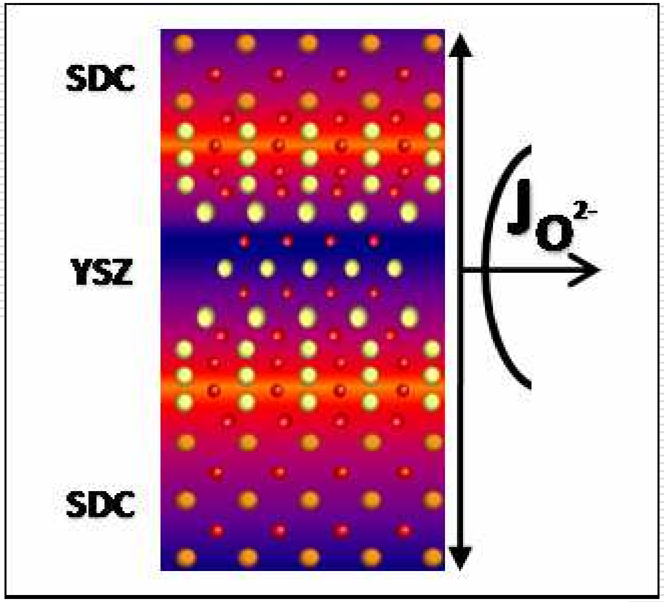
7x7



XRD θ -2 θ patterns of several $(YSZ/SDC)_N$/STO/MgO heterostructures with approximately the same overall thickness but N ranging from 1 to 20 (fig.a. to fig.e.). A sketch of the heterostructure is shown at the top.

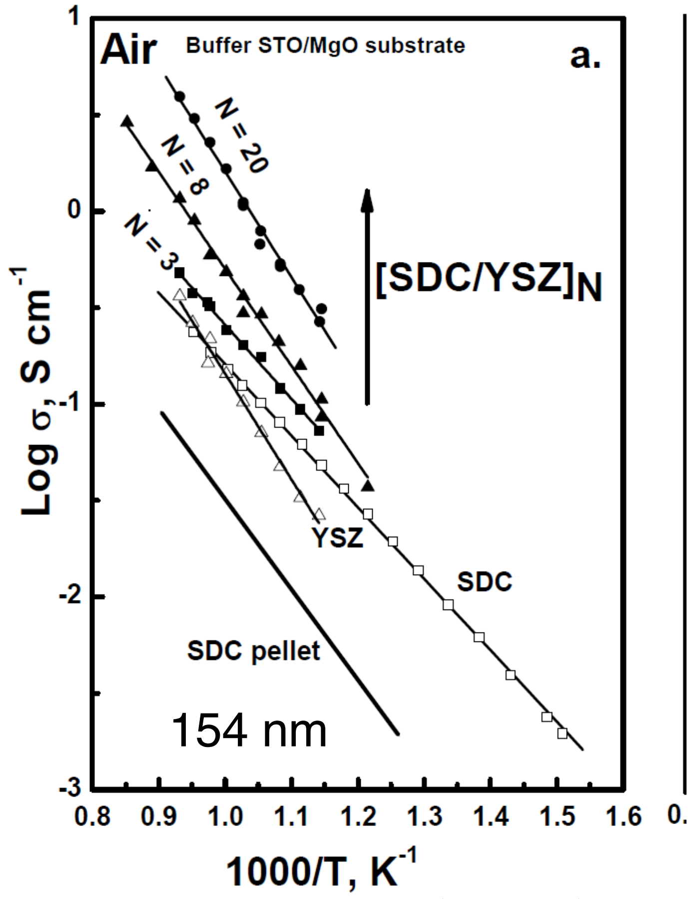
Electrochemical characterization of

$[SDC/YSZ]_N/STO/MgO$



$$\ln\left(\frac{\sigma_{\text{int}}}{\sigma_{bulk}}\right) \cong \frac{2}{3}\frac{\Delta V^M}{RT}\frac{Y}{1-\nu}\frac{\Delta a}{a}$$

N. Schichtel et al.Phys. Chem Chem Phys, 2009, vol 11, p 3043



$$\ln\left(\frac{\sigma_{\text{int}}}{\sigma_{bulk}}\right) \cong 2.8$$

Th

$$\ln\left(\frac{\sigma_{N=20}}{\sigma_{YSZ}}\right) \cong 2.4$$

Ex

Conclusions

Recent developments in thin film growth techniques have opened new perspective for the deposition of heterostructures based on complex oxides.

This has made possible to engineer oxide heterostructures with novel and interesting physical properties.

Few examples were given

Chances are good that the field of "oxide electronics", boosted by the large variety of oxide functional properties, will experience a fast development in the near future.