La_2NiO_4 thin films on $NdGaO_3$ substrates: A possible oxygen diode

J.Roqueta[1], A.Apostolidis[1], J.Chaigneau[1], M.Burriel[2], J.Santiso[1]

1: Centro de Investigación en Nanociencia y Nanotecnología CIN2: Bellaterra, Spain

2:Department of Materials, Imperial College London , UK

INDEX

- La_2NiO_4 thin films.
  - Thin films and microstructure
  - Conductivity relaxation experiments
  - Thickness dependence and tracer diffusion
  - Effect of the substrate

- Mixed Ionic Electronic Semiconductors junctions.
  - Symmetric equations for electrons and ions.
  - Simulation and comparison to experiments.
  - Carrier concentration and Band diagrams.

- Discussion
  - Approximations and concepts
  - Analytical solutions for an Homojunction.
  - Perspectives and Devices.

THIN FILMS:

La_2NiO_4 Mixed ionic electronic conductor.
Interstitial oxygen and electron holes.

Epitaxial thin films→ High crystalinity

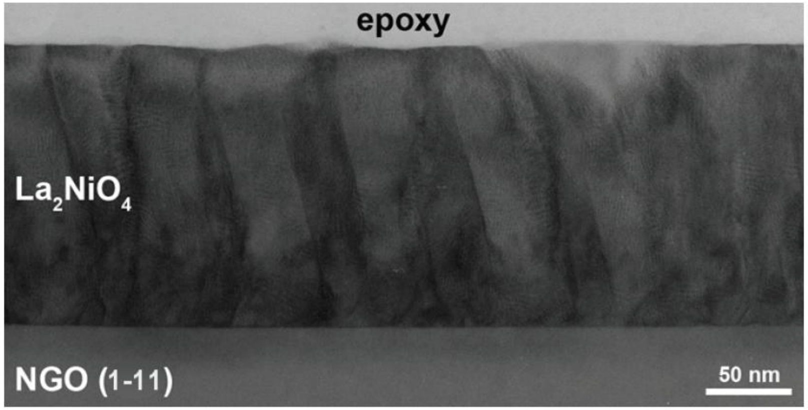
Direct access to intrinsic properties?

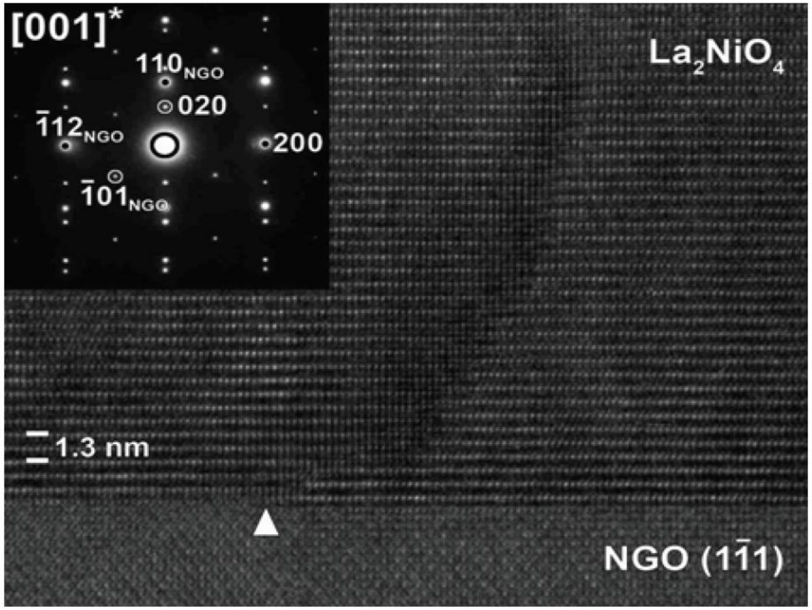
Electrochemical properties differs from bulk.

→Strain, Space charged layers, stoichiometry, interfaces, defects.

→Measurement geometry, Contacts.

Strange behaviour of La2NiO4 films





Enhanced High-Temperature Electronic Transport Properties in Nanostructured Epitaxial Thin Films of the Lan+1NinO3n+1 Ruddlesden-Popper Series (n), Burriel et al., Chem. Mater. 2007, 19, 4056-4062

THIN FILMS: Conductivity Relaxation Experiments

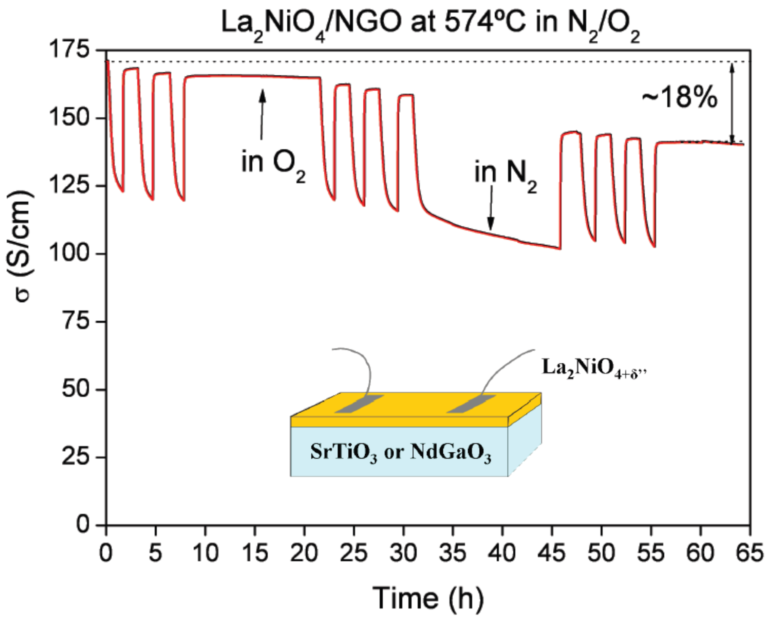
Switching from pure Oxygen to Nitrogen

→Conductivity of the film changes.

There is a very slow and irreversible drift.

PO2 dependence very low $\sigma \sim {P_{O2}}^{1/20}$

→ Attributed to degradation of the sample

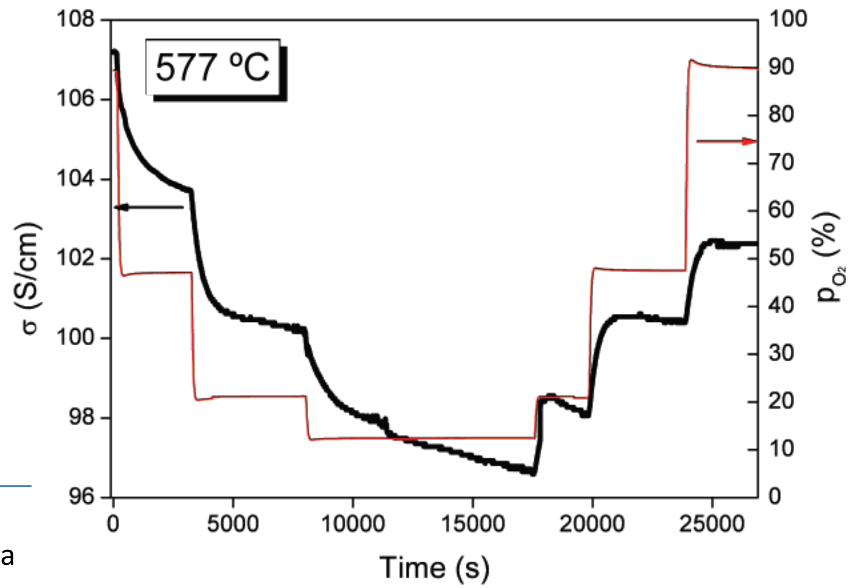


In this Work :

Take into account the effect of the substrate.

→Conditions not really severe for degradation

→Unstable measurements around 500°C is typical of thin films.



Electrical Conductivity and Oxygen Exchange Kinetics of La2NiO4+ Thin Films Grown by Chemical Vapor Deposition, Garcia et al, Journal of The Electrochemical Society, 155 28 2008

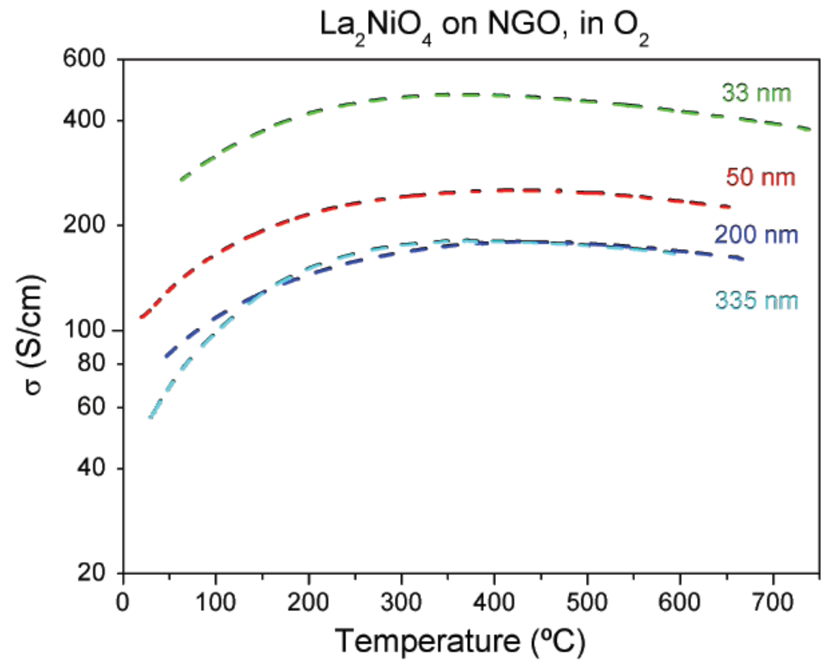
THIN FILMS: Thickness dependence and tracer diffusion

Enhanced conductivity on thinner films

Isotope exchange experiments:

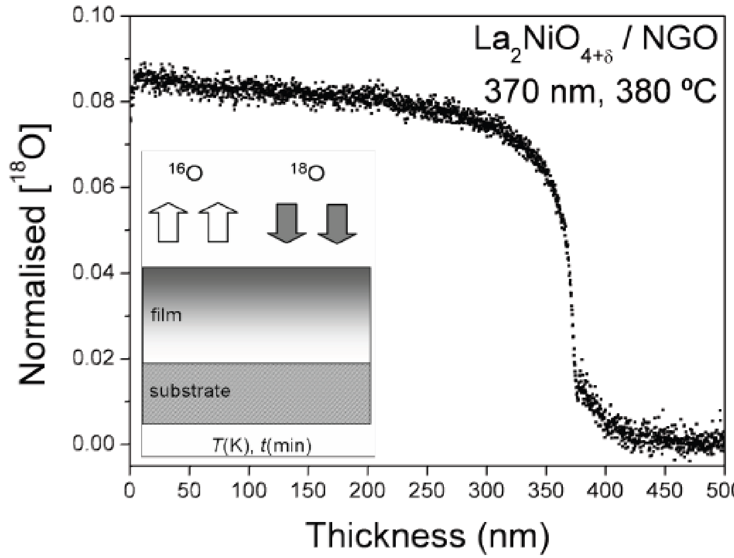
→Diffusion of oxygen from the film to the substrate

→Apparently a depletion layer of oxygen 50nm thick.



Presence of a space charged layer

→ Depletion of intersticials and accumulation of holes.

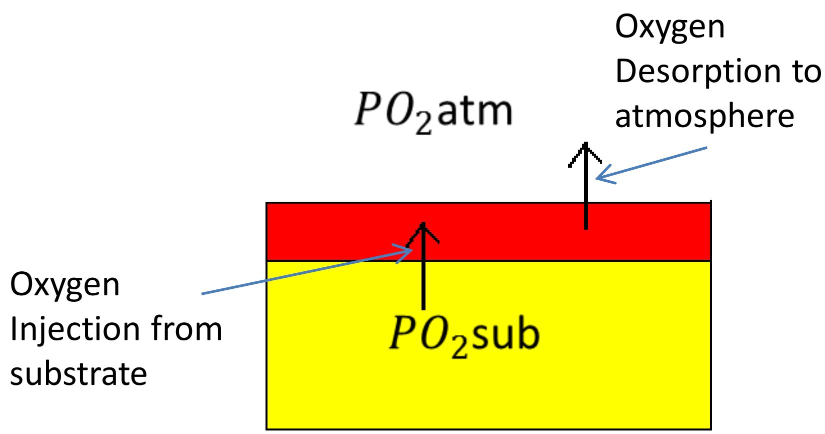


Anisotropic oxygen diffusion properties in epitaxial thin films of La2NiO4+d, Burriel et al., J. Mater. Chem., 2008, 18, 416–422

THIN FILMS: Effect of the substrate

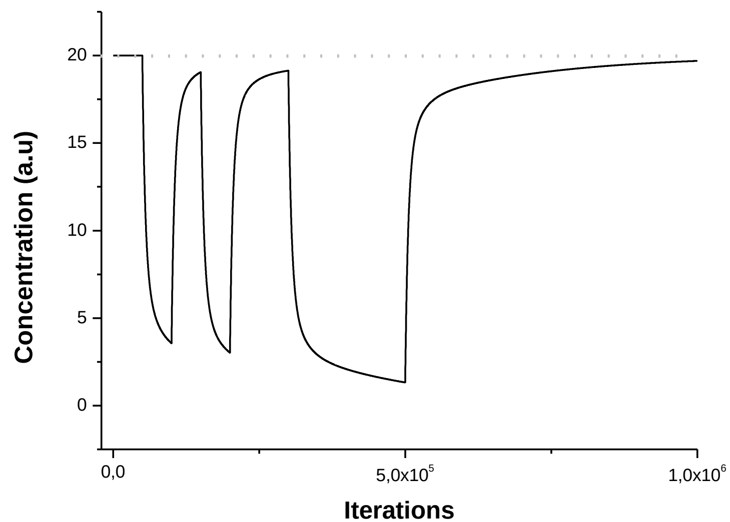
The substrate is electrochemically active.
It also changes the defect equilibrium.

$$\frac{dC}{dt} \cong -k_{atm}(C - C_0) - k_{sub}(C - C_1)$$



C_1 Drifts very slowly as the substrate gets reduced.

Simulation of Fick's equations taking into account reduction of the substrate.

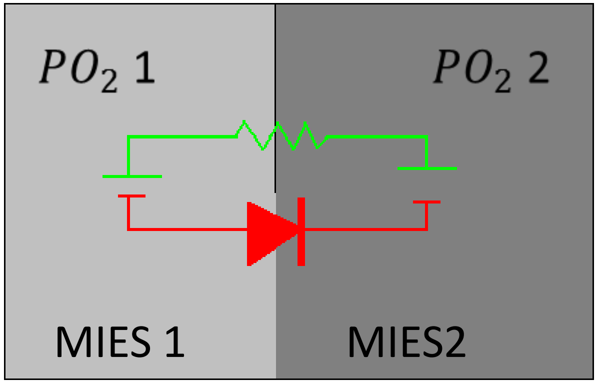


Simulation of the oxygen transport of the whole system

Modelling the film as a permeation membrane between the atmosphere and substrate reproduces the decay on conductivity relaxation experiments under N2, but is not able to reproduce the reoxidation step on O2.

MIES JUNCTIONS: Symmetric formalism

Presence of rectification in one of both species at the junction may be the reason for the observed phenomena.



SrTiO3 or NdGaO3:

High band gap electronic semiconductor.
Acceptor doped
Slightly p type electronic conductor.
High band gap ionic semiconductor, V type.

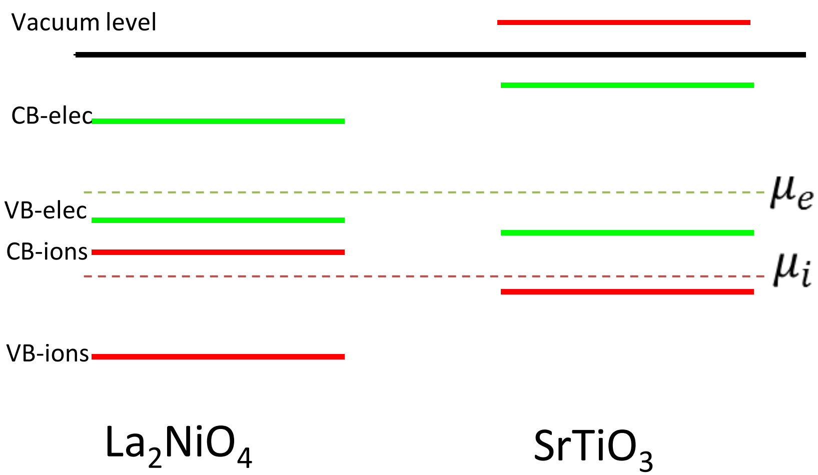
$$V_o \gg h \gg n \gg I_o$$

La2NiO4:

Small band gap electronic semiconductor
Intrinsic.
p type.
Small band gap ionic semiconductor I type.

$$I_o \cong h \gg n \cong V_o$$

Flat Band diagramm (proposed)



Nanoionics: ion transport and electrochemical storage in confined systems
J. Maier Nature Materials 4, 805 - 815 (2005)

MIES JUNCTIONS: Symmetric formalism

Charge ion = -1 for simplicity

$$n = N_{ec} e^{\frac{E_{ec}-\mu_e}{kT}}$$

$$p = N_{ev} e^{\frac{-E_{ev}+\mu_e}{kT}}$$

$$I = N_{ic} e^{\frac{E_{ic}-\mu_i}{kT}}$$

$$V = N_{iv} e^{\frac{-E_{iv}+\mu_i}{kT}}$$

Carrier concentration in terms of band energies, density of states and chemical potentials

$$\mu_X = \mu_i - \mu_e$$

$$\mu_Q = \mu_i + \mu_e$$

Gas phase chemical potential

Charged potential (as in spintronics)

Electroneutrality condition

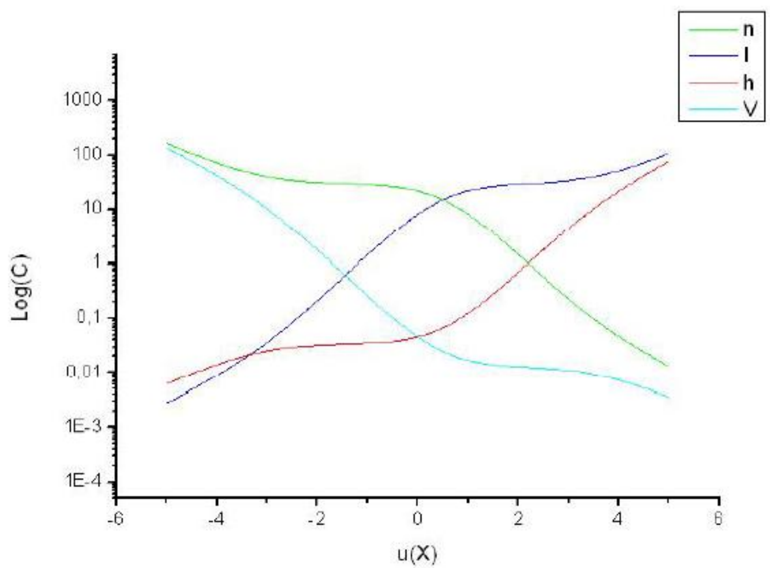
$$Q = V + h - n - I + D - A = 0$$

-Solve the electroneutrality equation and find the electrochemical potentials (hard)

-Fix the electrochemical potentials and find the Doping concentration (easy)

The model reproduces simple defect chemistry diagrams.

$$\frac{d\mu_Q}{d\mu_X} = -\frac{V - p - n + I}{V + p + n + I}$$



Trick : No need to solve electroneutrality equation

Theory of spin-polarized bipolar transport in magnetic *p-n* junctions
J. Fabian I. Žutić and S. D. Sarma Phys. Rev. B 66, 165301 (2002)

Física de los *Semiconductores*. *Shalimova*, K.V. Editorial Mir

MIES JUNCTIONS: Symmetric formalism

Transport equations

$$j_i = \nu_i kT \frac{dC_i}{dx} + \nu_i C_i * E$$

Drift and diffusion currents

$$\frac{dC_i}{dt} = \nabla j_i - r(C_i C_j - C_{io} C_{jo})$$

Mass conservation and recombination.

$$E(x) = E_0 + \int_0^x Q(x')dx'$$

← The electric field is calculated with this numerical integral. Eo = 0

Iteration loop

Boundary Conditions

Chemical reaction at surface of the first material.

$$X_g \rightarrow I + h$$

$$\frac{dC_i}{dt} = K_+ PX - K_- C_i Cj$$

At the bottom of the substrate

J=0;

Current at the heterojunction. Taking into account the band offset.

$$J+ = D * C_i$$

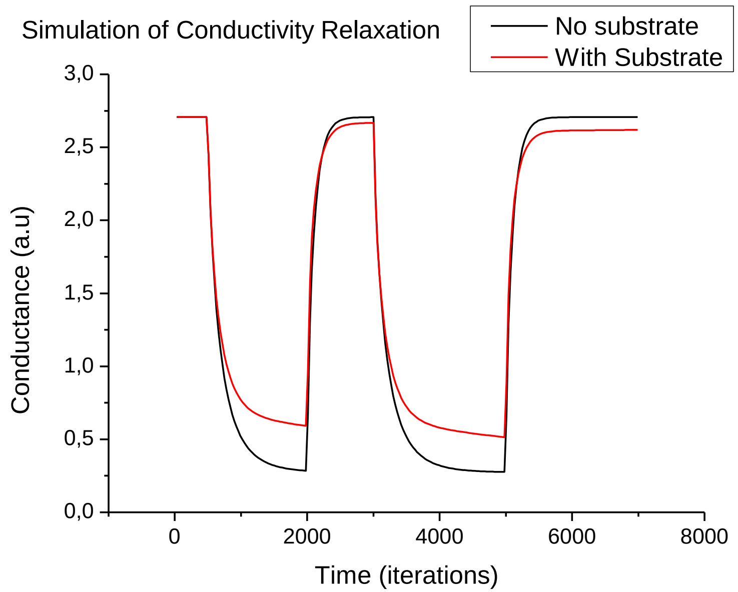
$$J- = D * C_i e^{-\Delta\phi/kT}$$

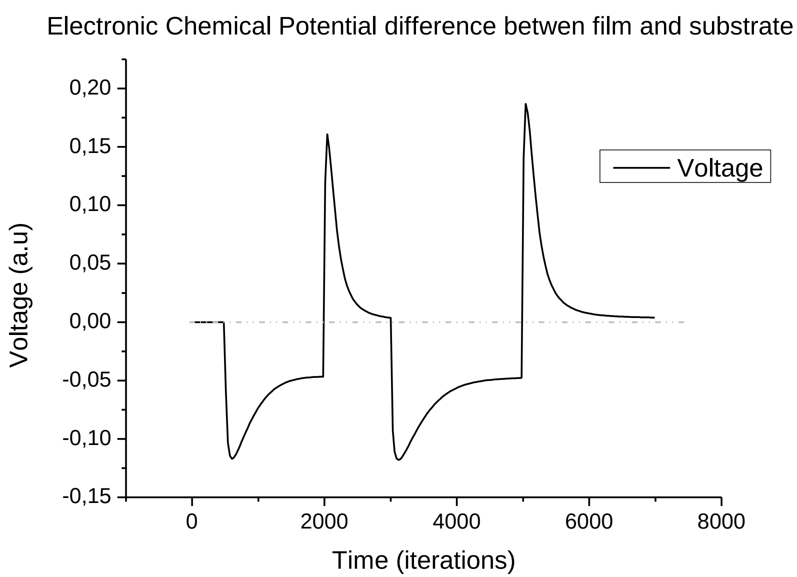
Where the band offset is

$$\Delta\phi = E_{i1} - E_{i2}$$

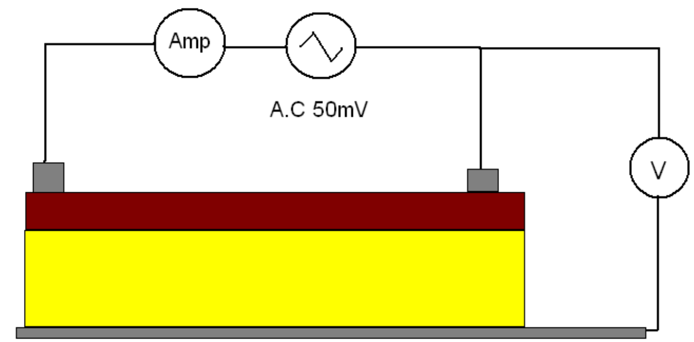
J+ = J- in equilibrium

MIES JUNCTIONS: Simulation and comparison

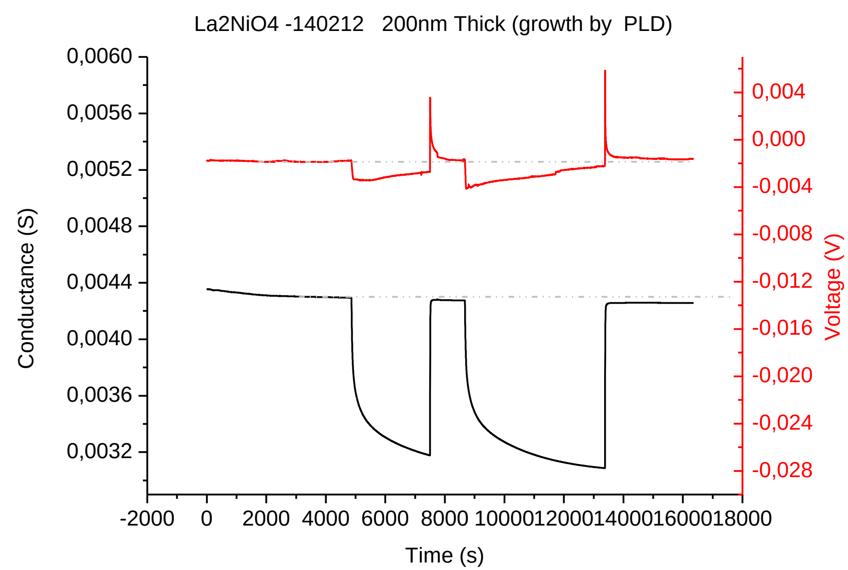




Experiments performed on PLD grown samples



Schematics of measurement set-up

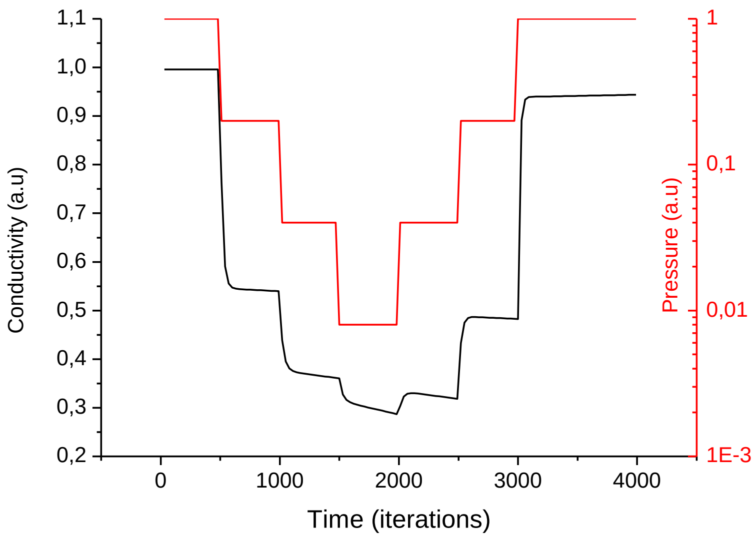


Measurements on PLD grown samples

MIES JUNCTIONS: Simulation and comparison

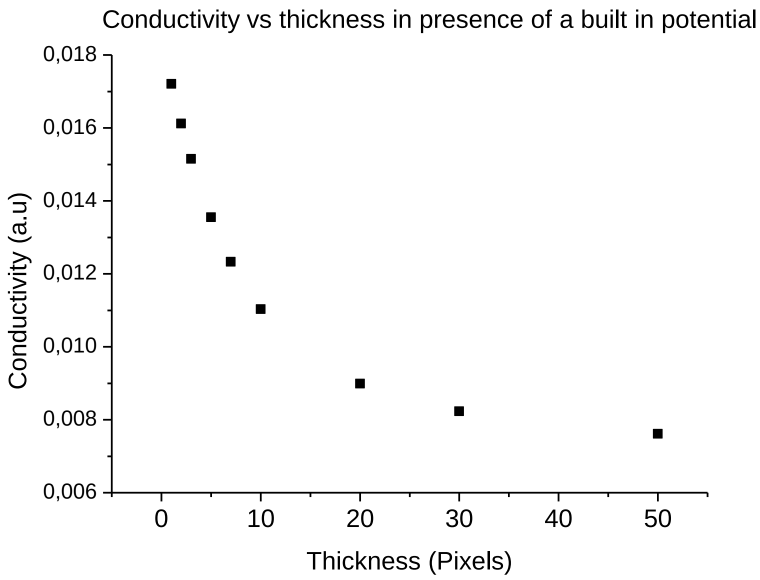
Reproduces also small changes in pO_2 observed by M.Burriel

The drift is observed when the atmospheric pressure is lower than the substrate oxygen pressure.

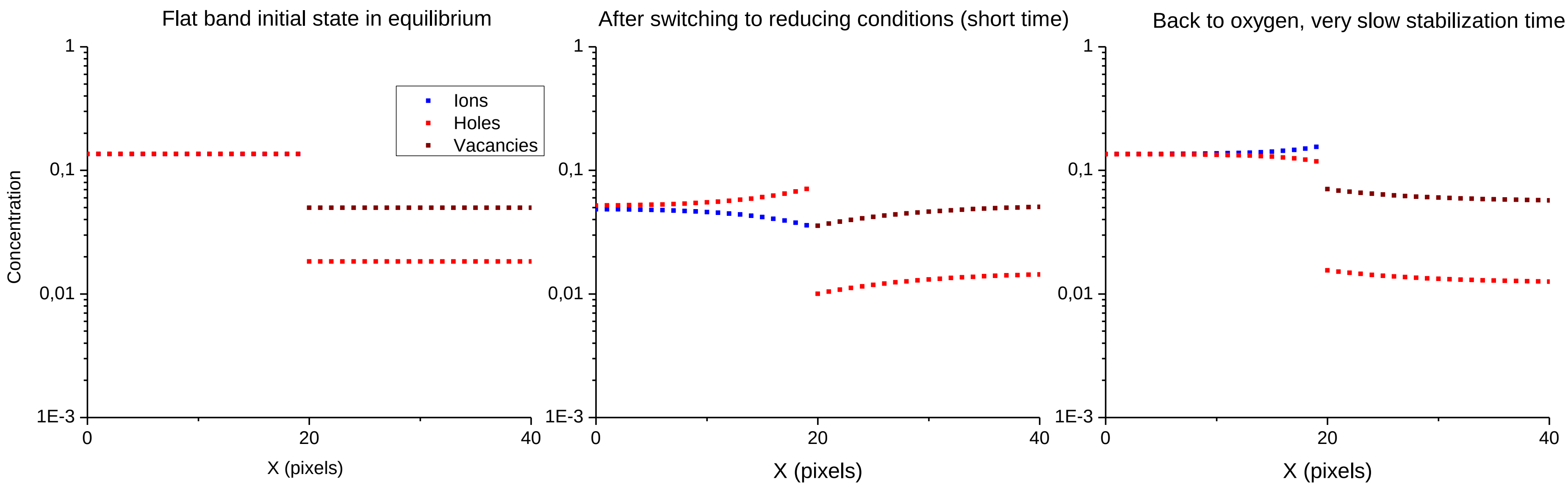


Thickness dependence of the conductivity

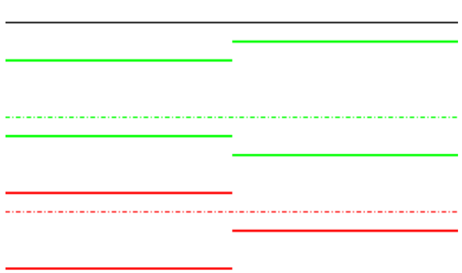
→ Presence of a built in potential



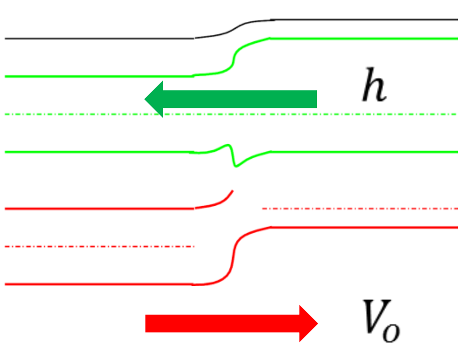
MIES JUNCTIONS: Carrier distribution and band diagrams



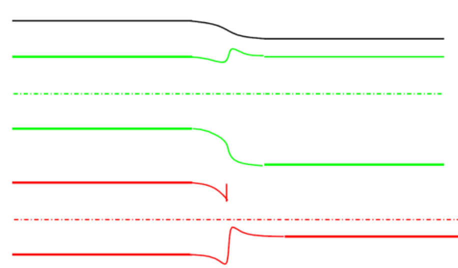
Initial State:
Flat band in equilibrium



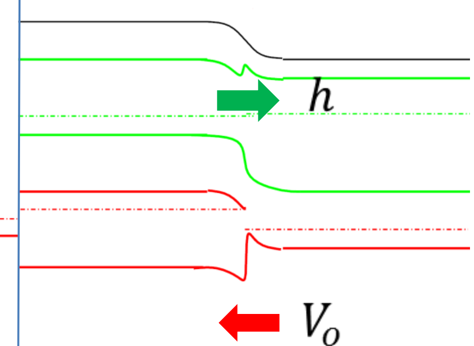
Reducing conditions:
Quasi equilibrium of
electron Fermy level
Large oxygen flow.



Reduced in equilibrium
No flat band.



Oxidizing: Quasi
equilibrium for holes.
Very low oxygen leakage



Discussion: Symmetric equations for MIES

→ The approximation of treating electrons and ions equally is crude but likely useful

Too many parameters, scarce data.

→ 4 kinds of carriers

Majority: Neutralize doping. Capacitance and Voltage.
Secondary: Changes when chemical potential is varied.
Minorities: Minority injection, leakage currents

$$FeO_2 \rightleftharpoons FeO_2^- + h$$

→ 4 kinds of impurity states

Impurities may act as:
electron Acceptors or Donors
ionic Acceptors or Donors.

$$FeO_2 + \frac{1}{2}V_o^{++} \rightleftharpoons \frac{1}{2}Fe_2O_3^+$$

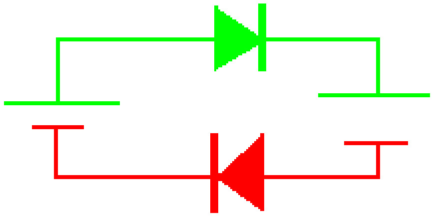
$$\frac{1}{2}Fe_2O_3 + h \rightleftharpoons \frac{1}{2}Fe_2O_3^+$$

$$\frac{1}{2}Fe_2O_3 \rightleftharpoons FeO_2^- + \frac{1}{2}V_o^{++}$$

→ Many kinds of junctions

Rectification of electrons or ions only.

Rectification of both species : Charge rectifier
Chemical rectifier



Discussion: Analytical solution homojunction

I.Riess solutions (Type I and II) for the bulk part.

If total depletion → Shockley approximation. (Pseudo potentials)

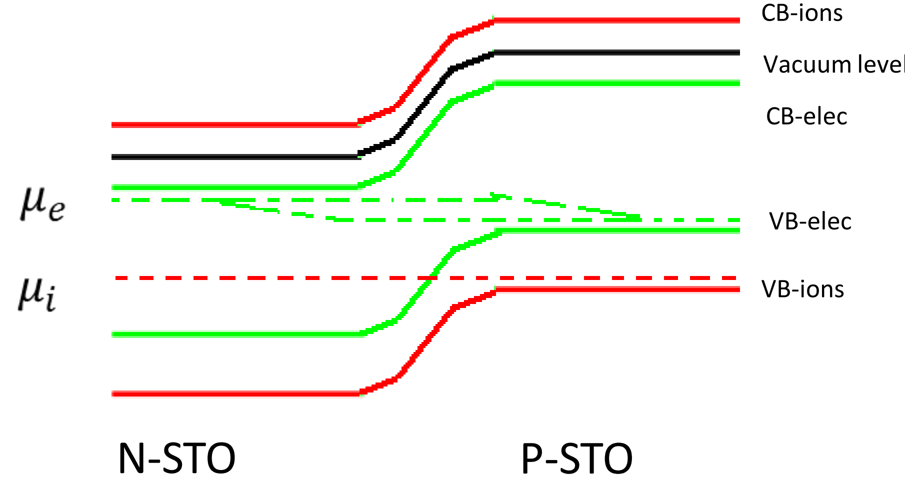
If no total depletion → Continuity of the electrochemical potential. (no significant resistance at the junction)

At the bulk region, the electrochemical potentials can be considered flat if:

$$\frac{D_V V_0}{L_{sample}} \ll j_{0e} = \frac{D_n n_{op}}{L_{np}} + \frac{D_p p_{on}}{L_{pn}}$$

The permeation current under a chemical gradient

$$j_e = \frac{D_n n_{0p}}{L_{np}} \left(e^{\frac{\mu_{e1} - \mu_{e2}}{kT}} - 1 \right) + \frac{D_p p_{0n}}{L_{pn}} \left(1 - e^{\frac{\mu_{e1} - \mu_{e2}}{kT}} \right)$$



Theoretical Treatment of the Transport Equations for Electrons and Ions in a Mixed Conductor. I. Riess . Electrochem. Soc., Volume 128, 2077(1981)

Defect chemistry of *pn* junctions in complex oxides Shimon Saraf, Miri Markovich, and Avner Rothschild* Phys. Rev. B 82, 245208 (2010)

Discussion: Prespectives and Devices

MIES junctions: new functionalities

Semiconductor Devices → Electrochemical Devices

Semiconductor Devices	Electrochemical Devices
Ohmic contacts	Engineered cathodes
Low leakage p-n junction	p-n junction as electrolyte (Single material fuel cell)
Photovoltaic effect	Photochemical cells, photoreduction.
Population Inversion (LASERS)	¿¿¿ ???

Concluding remarks (If these models are true):

- Finding new measurement setups and devices.
- Explain other results on thin films. ANNEALING has no effect on oxygen vacancies in space charged layers
- The charging potential is crucial at high temperatures. Segregation
- Applicable at liquid or polymeric membranes?

Madrid 15th of May 2011, Spain
A beautiful social movement   (self assembly)

The revolution won’t be televised!

Collaborations and discussions:

- M. Markovich. A.Rothschild (Technion, Haifa)

- A. Cavallaro. J. A. Kilner (Imperial College, London)

- P. García, R. Moreno, J. Zapata, G. Catalan (CIN2, Barcelona)

- G. Herranz, I.Fina (ICMAB, Barcelona)

Thank you for giving me the opportunity to present this work

Thank you very much for listening!