PAUL SCHERRER INSTITUT

Paul Scherrer Institut
Daniele Pergolesi

The Search for Low Temperature Super-Ionic Conductivity along Oxide Interfaces

Tuning the Strain by Thin Film Pulsed Laser Deposition

Scientific background and working experiences

PhD in Materials Science

(February 2004)

1999 – 2000 Max Plank Institute for Physics,
Werner-Heisenberg Institute, Munich, Germany

2000 – 2003 Department of Physics and Chemistry, University of Genoa, Italy

2004 – 2006 Post-Doctoral Research Fellow,
Italian National Institute for Nuclear Physics (INFN), Genoa, Italy

2006 – 2008 Post-Doctoral Research Fellow, University of Florida (Gainesville, FL, USA)

2008 – 2009 Scientist, Italian National Institute for Nuclear Physics (INFN),
Technology Department, Genoa, Italy

2009 – 2011 MANA Scientist
(Fuel Cells nano-Materials Group)

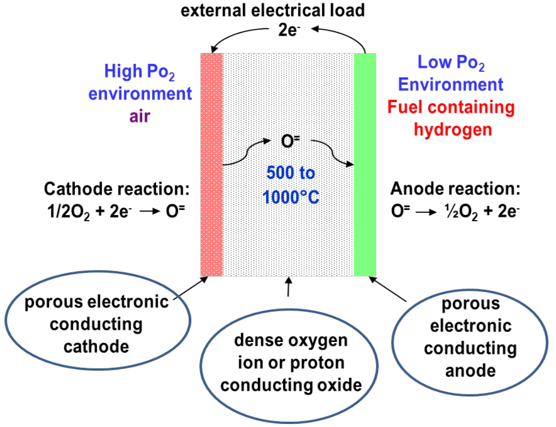
2011 – 2012 MANA Independent Scientist

Permanent staff member
Department of Materials Nano-Architectonics (MANA)
National Institute for Materials Science (NIMS)
Tsukuba, Japan

January 2013 to present, PSI-Fellow, Materials Group,
Paul Scherrer Institute, Villigen, Switzerland

Scientific Background of PSI-Fellow Project

Solid Oxide Fuel Cells, highly efficient electrochemical energy conversion systems based on oxygen ion conducting oxides as electrolyte membranes



Current SOFC technology requires very high operating temperatures (≈ 1000°C)

- ✓ Materials instability and interfacial reactions (durability)
- ✓ Expensive high temperature materials
- ✓ Long start-up time

Lower operating temperatures are required for a full exploitation of this technology

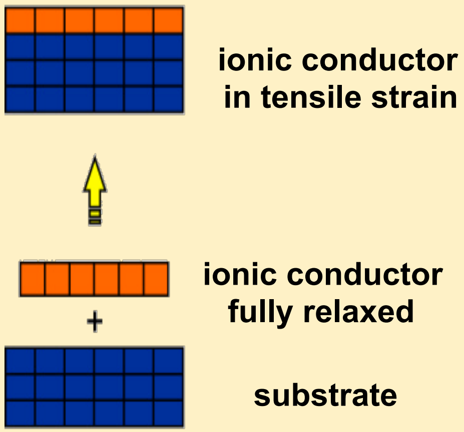
According to recent literature:

Tensile lattice distortions in thin films seem to create faster oxygen ion conduction pathways with larger conductivity at lower temperatures

This effect, if confirmed, might have very important scientific implications and technological applications

Experimental approach:

Fabrication of highly ordered thin films of the ionic conductor with different strain-state and compare their ionic conductivity

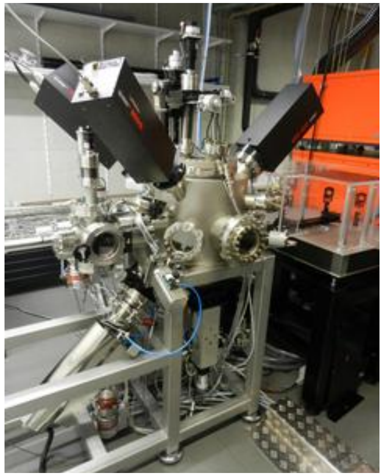


What's new?

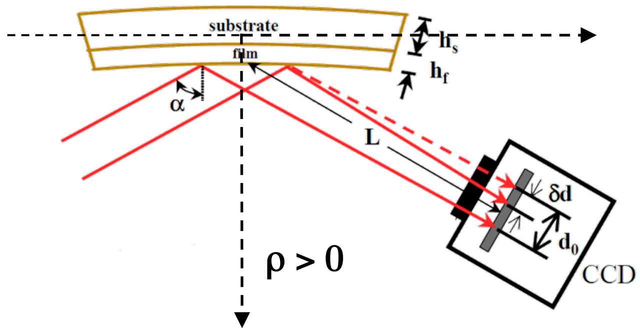
Two independent ***in situ* diagnostic methods** during pulsed laser deposition were **coupled together** for the first time in order to probe simultaneously the film growth mechanism by reflection high energy electron diffraction (**RHEED**) and the film stress by multi-beam optical stress sensor (**MOSS**)

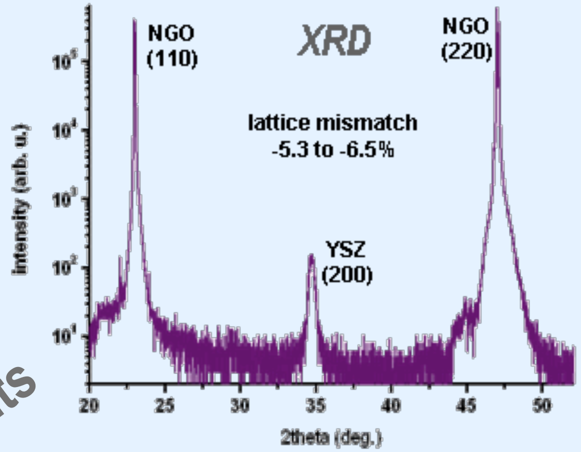
First Results: *In situ* diagnostic of growth mechanism and stress evolution

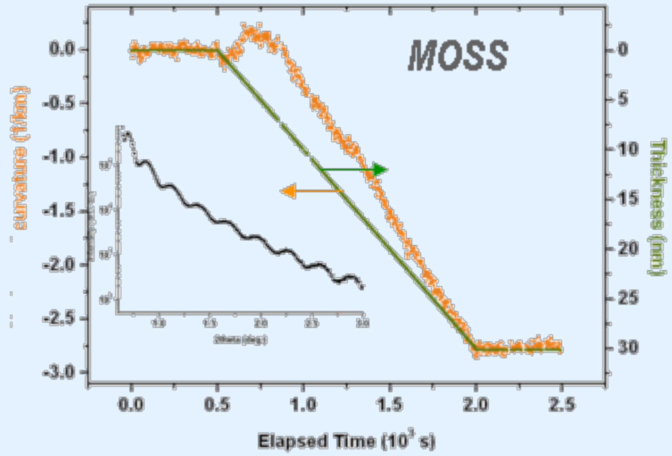
Setup of the new deposition chamber



Optical measurement of the wafer curvature to probe the stress state of the growing film







First Results

It has been proved that it is possible to monitor in-situ the growth mechanism and the stress generation and evolution during pulsed laser deposition

Scientific productivity

National and international collaborations

Imperial College London (UK), (La, Li)TiO_3 thin films for solid state Li-ion batteries

Chalmers University, Göteborg (S). $Ba_2In_2O_5$ thin films for neutron reflectivity measurements of proton concentration

EPFL, Lausanne (CH). Influence of the lattice distortions on the protonic conductivity

International Conferences and Workshops

Conference on Laser Ablation 2013
October 6-11, 2013, Ischia, Italy

European Materials Research Society 2014 SPRING MEETING
May 26-30, 2014, Lille, France

MANA International Symposium 2014
March 5-7, 2014, Tsukuba, Japan

Publications:

2 publications (1 full article and 1 communication) will be submitted within the end of this year

3 full articles were planned for this year concerning the MOSS and RHEED measurements during the growth of two oxygen-ion conductors (Sm-doped CeO_2 and yttria stabilized zirconia) and one proton conductor (Y-doped $BaZrO_3$).

The publication of these data has been postponed since the measures suggest the existence of a common mechanism of stress evolution for different oxide materials. We are now trying to verify this hypothesis.

Next steps

Verify the new hypothesis:

Extending the MOSS + RHEED analysis of the PLD process over other classes of materials (different crystalline structures and compositions) searching for a generalization of the phenomena observed up to now with fluorite (doped CeO_2, yttria stabilized zirconia) and perovskite (doped $BaZrO_3$, $SrRuO_3$) thin films.

investigation of the mechanism of stress generation and evolution in thin oxide films grown by PLD

High Resolution Transmission Electron Microscopy (HR-TEM) analysis of Sm-doped CeO_2 and yttria stabilized zirconia thin films aiming to correlate the stress state (MOSS) and the growth mechanism (RHEED) with the local microstructural properties and morphological features.

Electrochemical Impedance Spectroscopy analysis of the oxygen-ion conductivity along thin films with different stress states and well characterized microstructures, as revealed by MOSS and HR-TEM, respectively.

Results publication

Progress of work: critical paths and the “contingency plan”

original experimental road map

2013

2014

Set up of the experimental apparatus

Thin film growth with different stress-state (RHEED and MOSS)

Ionic conductors: SDC and YSZ

Proton conductor: BZY

Electrical characterization

highly textured stress-free films of SDC and YSZ

SDC and YSZ films in tensile and compressive stress

Literature report

The data currently available suggest the existence of a mechanism of stress generation and evolution common to thin films of various oxide materials grown by PLD. *This hypothesis*, if confirmed, *would be a matter of absolute novelty with important implications for many areas of research*

The research program has been temporarily redirected to test this thesis

Critical point: we are ahead to the original road map but a long experimental work (longer than the duration of the PSI-Fellow programme) may be necessary to verify this new theory

Contingency plan: the electrical characterization will proceed as planned and the experimental results obtained with different materials will be reported separately

Outlook to future career

Application for research funds: ***Lattice Distortions and Protonic Conductivity in Oxide Materials***

3 years research plan submitted on October 1st 2013 to the Swiss National Science Foundation

Application for **Consolidator Grant, European Research Council, Horizon 2020**

Development of an independent research programme at PSI (host institution)

The research programme will focus the study of proton conducting oxides and their applications:

- **Effect of lattice distortion on the protonic conductivity**
- **Search for low temperature super protonic conductivity**
- **Development of micro-SOFCs based on proton conducting electrolyte materials**
- **Hydration mechanism in oxide material: neutron reflectivity study of proton concentration profile**
- **Application of proton conducting oxides in micro-electronics**
- **First exploitation of the Beta Environmental Fine Structure for local microstructural investigation**

SwissFEL collaboration in the field of catalysis:

Fabrication of highly textured thin films as *model samples* for the investigation of the catalytic activity of surface and interfaces

PSI-Fellow programme: expectations, pros and cons

Within the frame of the PSI-Fellow Programme, my expectations were fully met if not exceeded in terms of resources available, independency, competences, working conditions

My personal suggestion for future programmes

From the PSI-Fellow web page:

"The PSI-FELLOW Postdoctoral programme aims at increasing the European-wide mobility … of experienced researchers ...
The beneficiary aims to broaden and deepen researchers individual competence shortly after having obtained a doctorate …"

After the PSI-Fellow Kick-off Meeting (27th of March, 2013) it seems to me that most of the PSI-Fellows have already several years of experience after the doctorate.

In this case, a two years research project is a very short time-frame for more ambitious projects requiring experienced researchers, for research proposal submission, and supervision of PhD students.

It would be very good to find in the near future a PSI-Fellow Programme specifically designed to support experienced researchers at the stage at which they are consolidating their own independent research

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Thank you very much for your kind attention