Nanocomposite oxide thin films grown by pulsed energy deposition

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Introduction

Oxide thin films:

oxygen composition !!!!!

...YBaCuO

Wu M.K., Ashburn J.R., Torng C.J, Phys. Rev. Lett.(1987) **58** 908

...SrTiOx,...

Perez-Casero R., Perriere J., Gutierrez-Llorente A, et al. Phys. Rev. B (2007) **75** 165317

What is the nature of oxygen defficient oxide films whose sub-oxides are not thermodynamically stable ??

...Ga_2O_3...

L. Nagarajan, R.A. De Souza, D. Samuelis et al. Nature Materials **7**, 391 (2008)

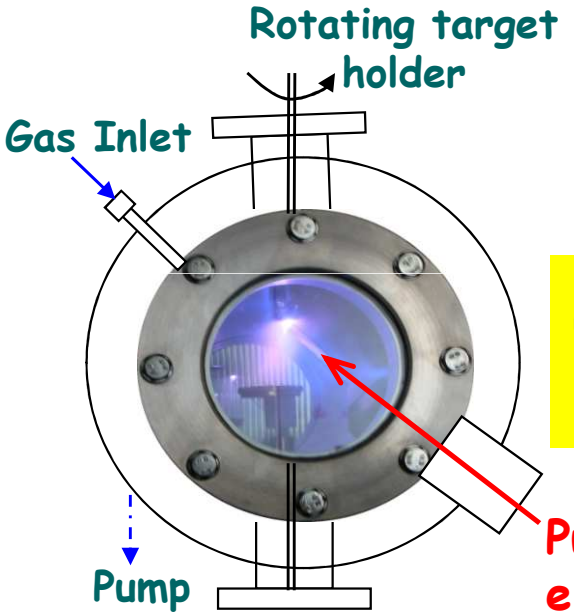
...**ITO**....

M. Nistor, J. Perriere, C. Hebert, W. Seiler, J.Phys.Cond. Matt. 22, 045006 (2010).

...Nanocomposite films are formed through a *phase separation* of metastable sub-oxides...

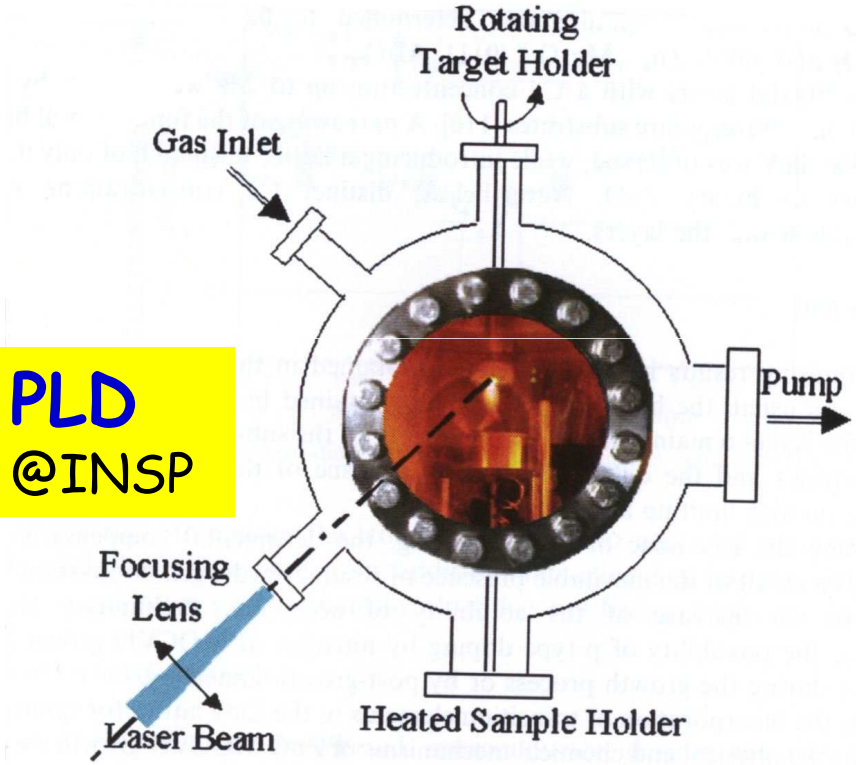
... potential applications ???

Pulsed Energy Beam Deposition



PED
@INFLPR

HV ≤ 15 kV; C = 16 nF; 1 Hz;
Fluence ≤ 3 J/cm^2; Ar pressure:
10^{-2} mbar



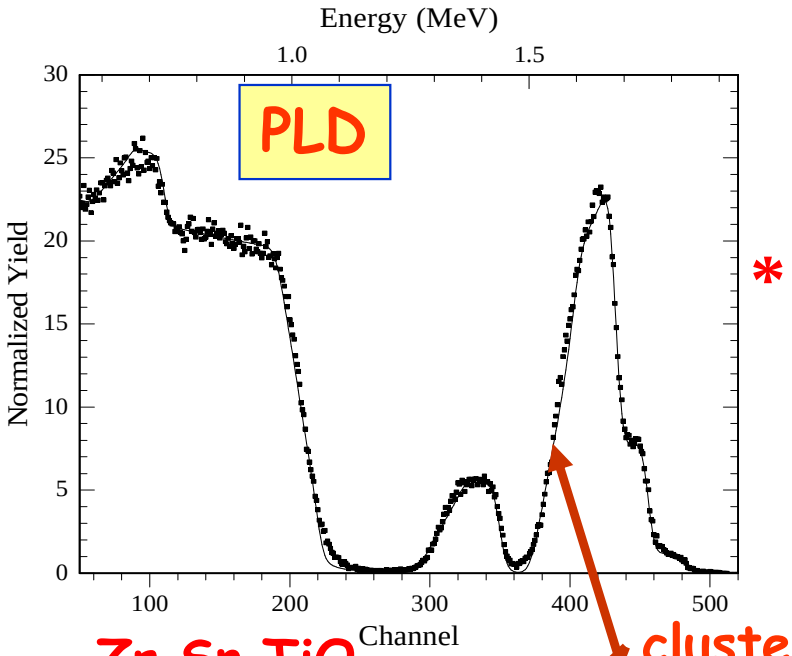
PLD
@INSP

Nd:YAG 266 nm, 7 ns, 5 Hz,
50-500 MW/cm^2

Substrate temperature: RT → 700°C
Substrate: sapphire c-cut

… 10^{-6} mbar 10^{-5} mbar 10^{-4} mbar 10^{-3} mbar 10^{-2} mbar 10^{-1} mbar 1 mbar …

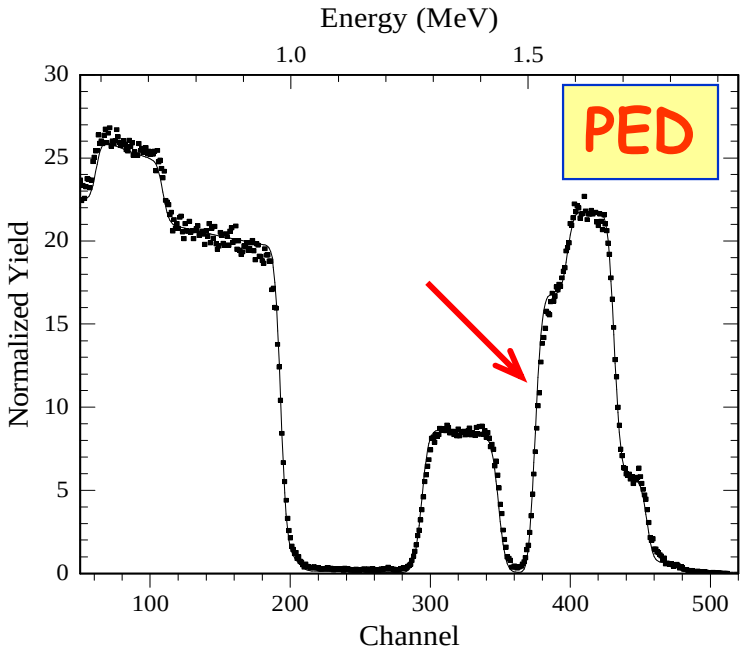
PED vs. PLD



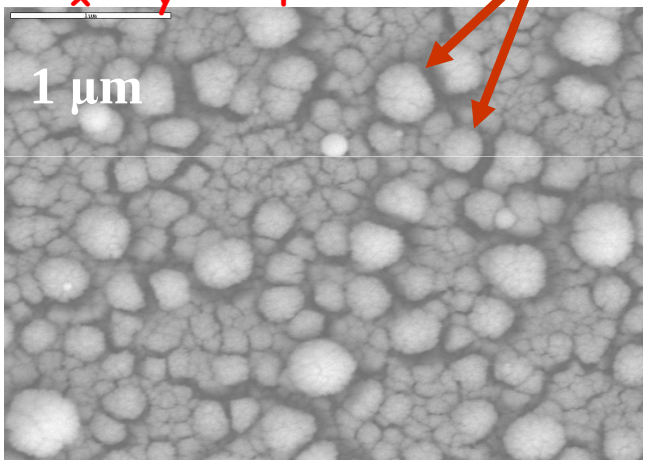
RBS

$Zr_{0.8}Sn_{0.2}TiO_4$ /Si

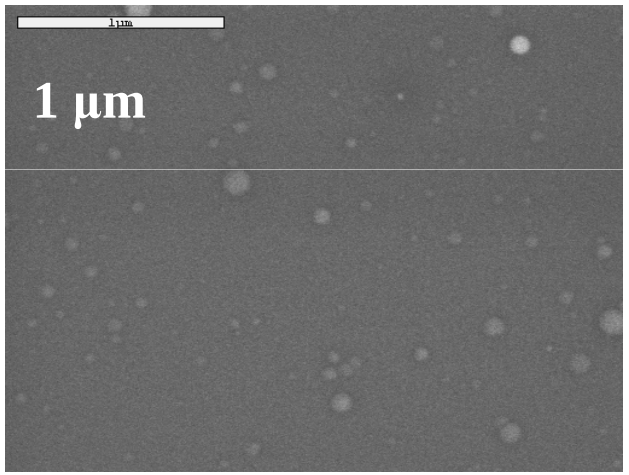
room T



$Zr_xSn_yTiO_4$ clusters



SEM

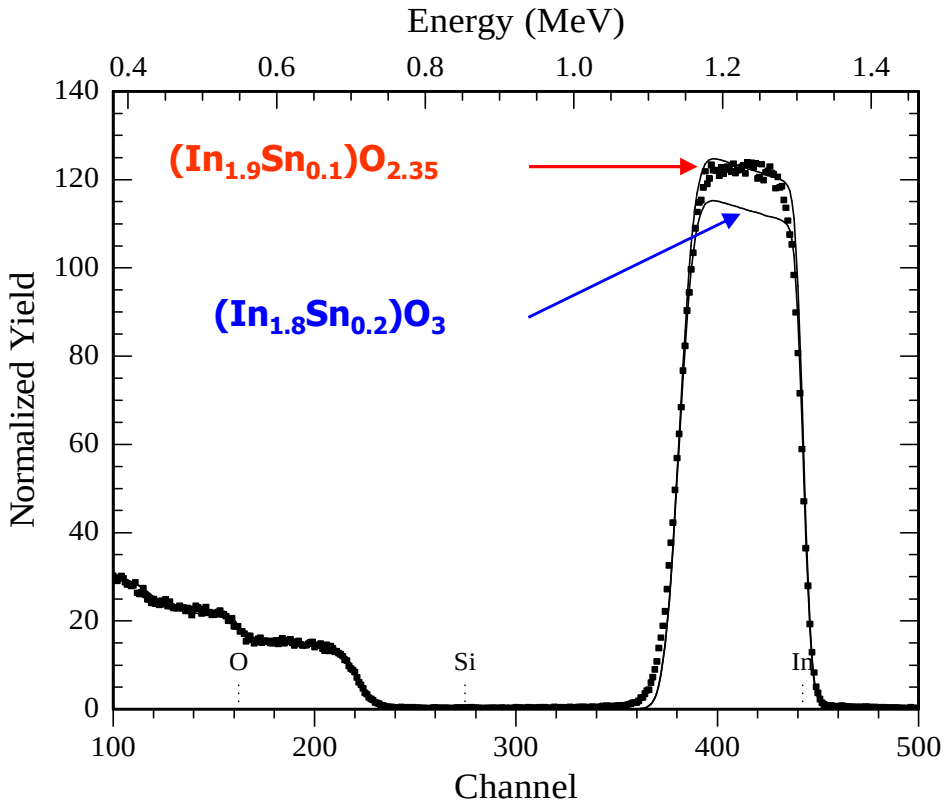


M.Nistor, A.Ioachim, B.Gallas, D.Defourneau, J.Perrière, W.Seiler, J. Phys.:Condens.Matter 19 (2007) 096006

homogeneous, uniform and stoichiometric film

M.Nistor, N.Mandache, J. Perriere, *J. Phys.:D.Appl.Phys.* ***41*** *(2008) 165205*

Control of oxygen incorporation



RBS – large oxygen deficiency !!!

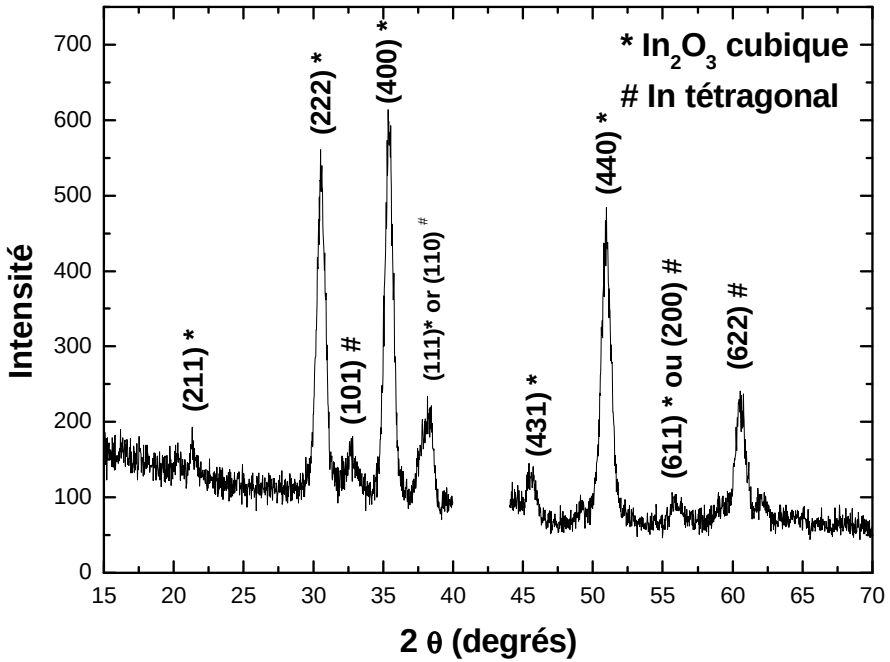
M. Nistor, J. Perriere, C. Hebert, W. Seiler, J.Phys.Cond. Matt. 22, 045006 (2010).

What is the exact nature of such oxygen deficient oxide films ?

Structure of the oxygen deficient oxide films

PLD

T=150°C

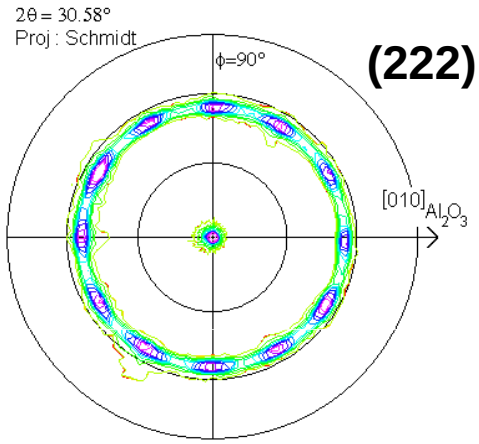


Multiphase materials are formed in oxygen deficient ITO films…

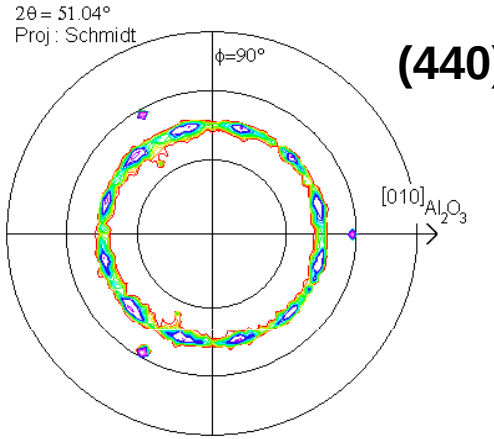
Epitaxy…

T=500°C **PED**

poles are observed...



(222)

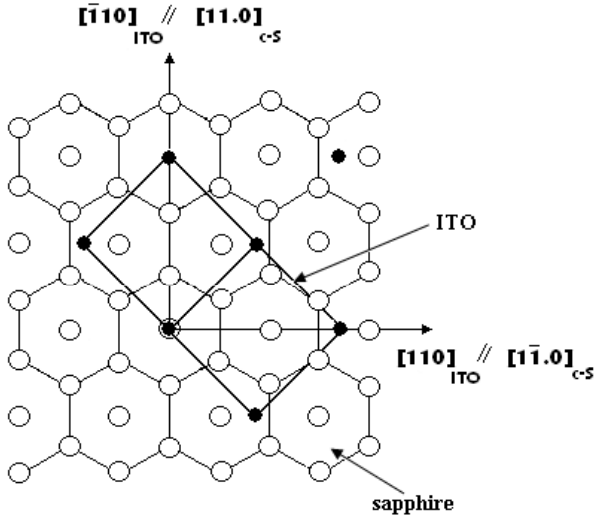


(440)

Epitaxial relationships

$[-110]_{ITO}$ // $[11.0]_{c-S}$

$[110]_{ITO}$ // $[1\text{-}1.0]_{c-S}$



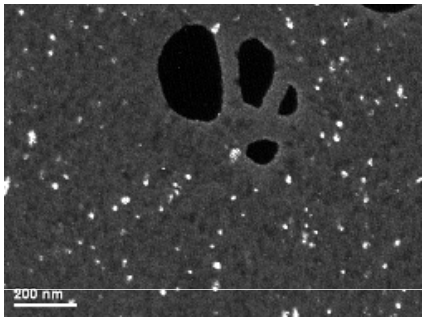
+ lattice mismatch 0.77% and 0.2%

The **ITO stoichiometric phase** is textured : (222) et (400) with a reasonable mosaic spread.

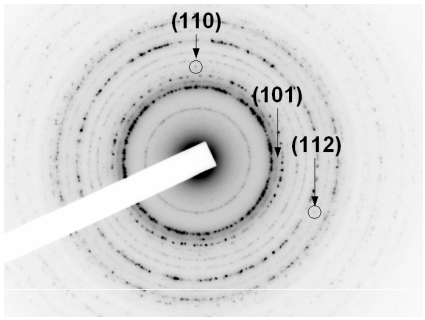
→ **the epitaxy on c-cut sapphire substrate is possible…..**

M. Nistor, J. Perriere, C. Hebert, W. Seiler, J.Phys.Cond. Matt. 22, 045006 (2010).

Microstructure of the oxygen deficient oxide films

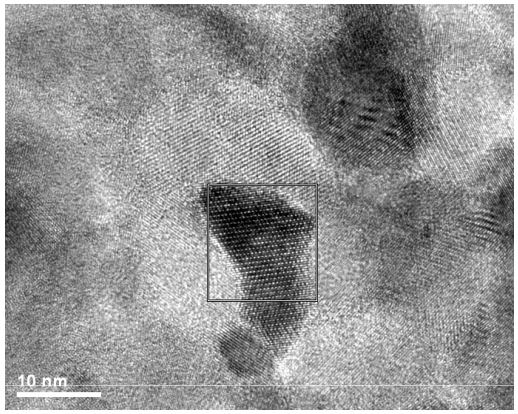


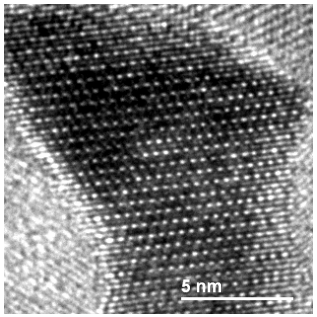
TEM

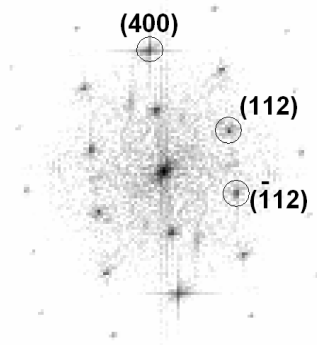


SAED

T=150°C







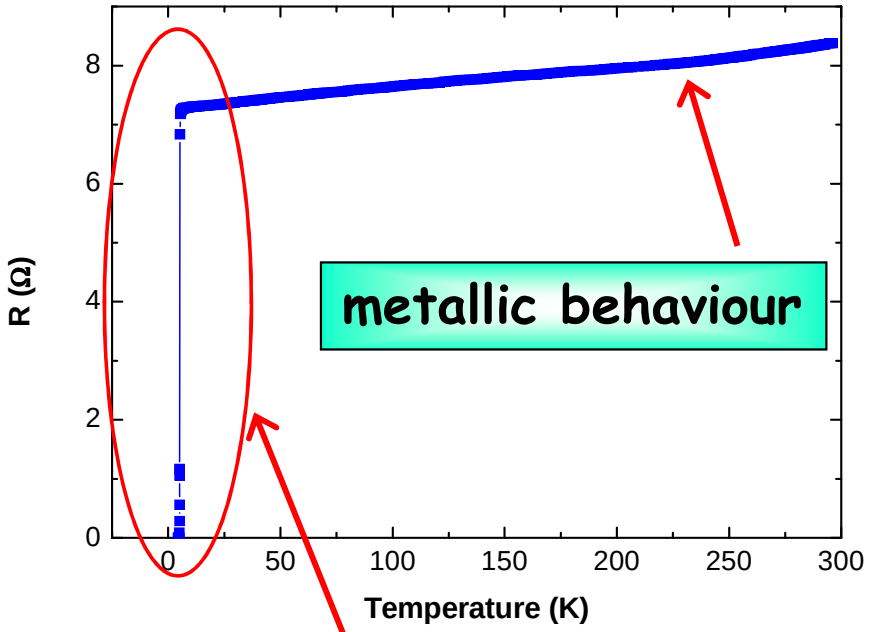
HRTEM+FFT

By courtesy of X.Portier, CIMAP, ENSICAEN/UCBN, Caen

What are the properties of such multiphase materials ??

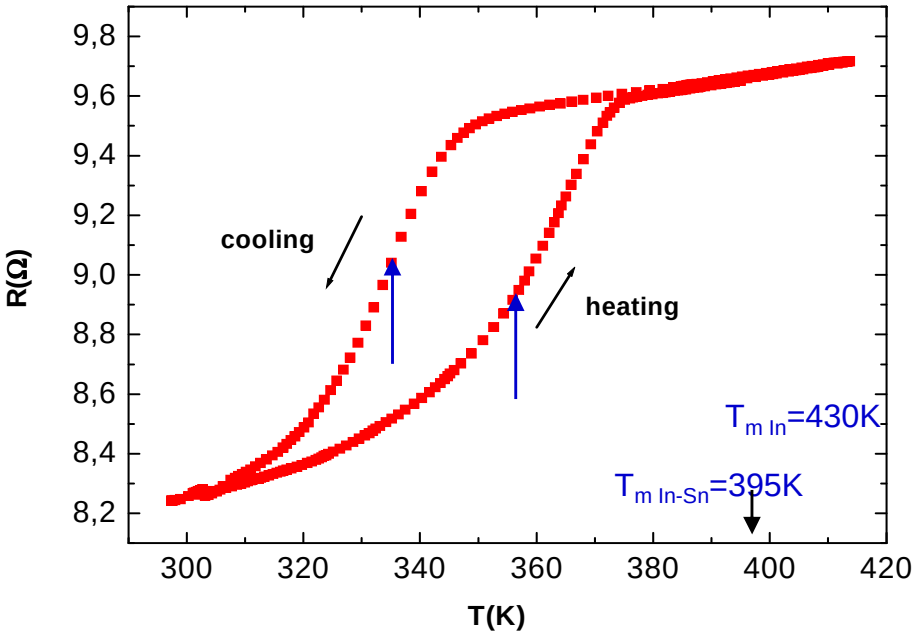
A.Petitmangin, PhD Thesis, University Paris 6, Paris, September 2010

Resistivity measurements



metallic behaviour

superconducting transition at
T_c = 6K > Tc (In) or Tc (Sn)
≈ Tc (In-Sn)



metallic In-Sn clusters:
ρ liq. > ρ sol. → R(T)

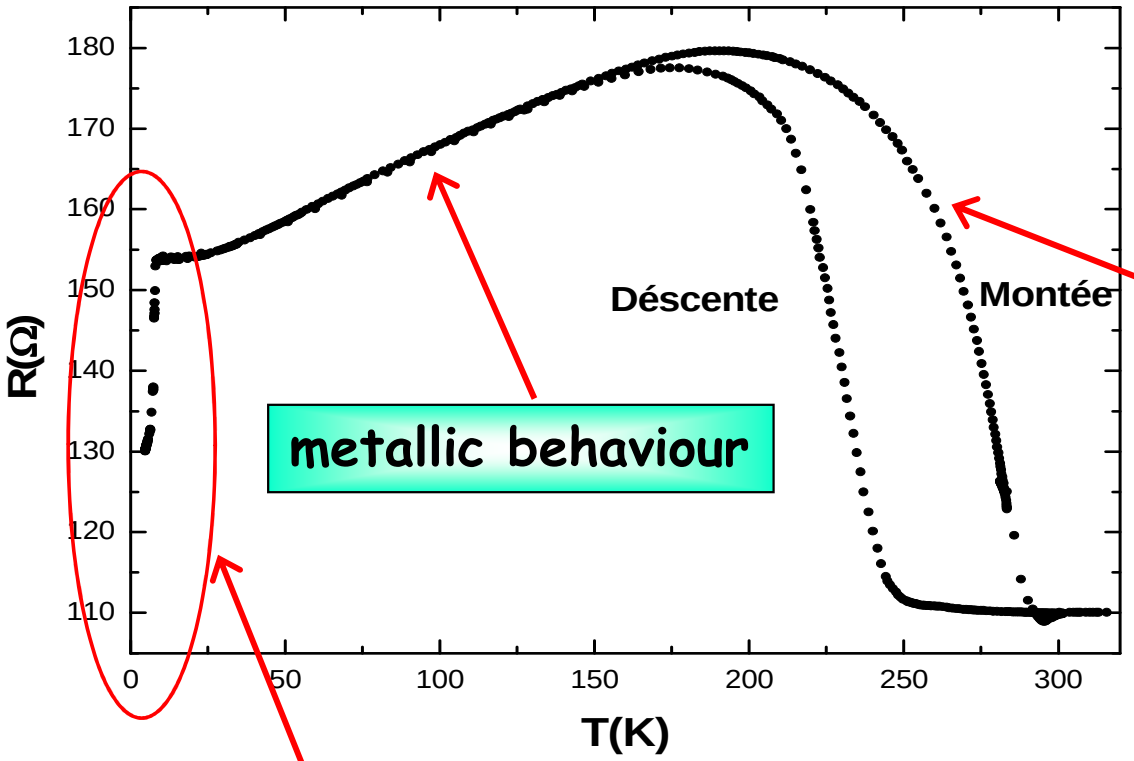
In-Sn clusters in stoichiometric matrix

- solid to liquid transition at T_m= 360K
- cooling down: freezing at T_s= 335K

(i) T_m (clusters) < T_m (bulk)
(ii) Hysteresis between heating and cooling curves : $T_m \neq T_f$
→ characteristics of thermal properties of metallic clusters (In-Sn) embedded in an oxide matrix…= Nanocomposite ITO thin films

M. Nistor, J. Perriere, C. Hebert, W. Seiler, J.Phys.Cond. Matt. 22, 045006 (2010).

General phenomenon…Ga_2O_x…



metallic behaviour

liquid to solid transition in Ga clusters

superconducting transition at T_c = 8 K > Tc (Ga bulk) 1.5 K

A.Petitmangin, PhD Thesis, University Paris 6, Paris, September 2010

Nanocomposite films formation is a general phenomenon occurring in oxygen deficient oxide films

NAGARAJAN L., DE SOUZA R.A., SAMUELIS D. et *al*, Nature Materials (2008) **7** 391
A chemically driven insulator–metal transition in non-stoichiometric and amorphous gallium oxide

How such nanocomposite films can be formed ?

oxygen deficiency & growth temperature

ITO : oxide compound with metastable sub-oxides !!!!

.... Crystallisation starts with stable oxide growth at the expense of sub-oxide... **phase separation** starts :

$$In_{1.8}Sn_{0.2}O_{2.5} \rightarrow a\ (In_{1.8}Sn_{0.2}O_3) + b\ (In_{1.8}Sn_{0.2}O_{2.5-x})$$

.... The **disproportionnation reaction** is complete:

$$In_{1.8}Sn_{0.2}O_{2.5} \rightarrow a(In_{1.8}Sn_{0.2}O_3) + b(In\text{-}Sn)$$

and **phase separation**...
...a **nanocomposite film** (metallic nanoclusters embedded in a stoichiometric matrix) is formed... with very specific transport properties....

Conclusions - Perspectives

By the precise control of the oxygen deficiency and temperature (growth and/or annealing) it is possible to control the nanocomposite film formation and nanocluster size and density…

→ the optical properties of the films could be tuned from purely transparent and insulating to absorbing and metallic like films.

→ a local and possibly periodic modulation of the optical and/or electrical properties of such films appears possible via a local heating (laser beam) under control atmosphere … **new materials for photonic applications.**

Other oxide compounds with metastable sub-oxides, like In_2O_3, Ga_2O_3 or SnO_2 (and their combination)… could give similar nanocomposite films with interesting optical and transport properties.

Such nanocomposite films appear as « model systems » to carry on more investigations on thermal properties of metallic nanometric clusters embedded in an insulating matrix.

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