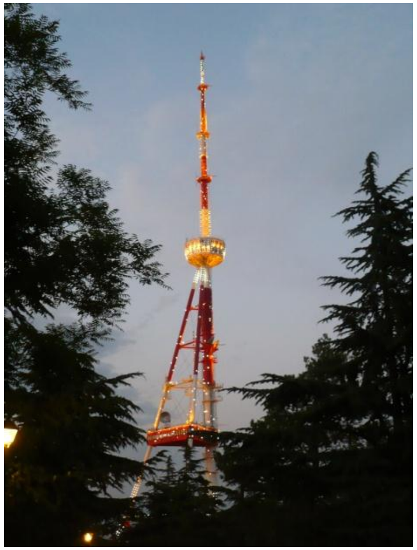
Transparent Oxides for Electronics: problem of electrical transport

Ekaterine Chikoidze

GEMaC, CNRS,Versailles University, France



cnrs
dépasser les frontières

UNIVERSITÉ DE VERSAILLES
ST-QUENTIN-EN-YVELINES

OXIDES: Transparent & Conducting

Heat reflecting windows, electrochromic windows, LCD panel, OLED, solar cells, touch panels ,….

Advantege of oxides:

- ✓ Higher voltage tolerances;
- ✓ More stability at high temperatures;
- ✓ Oxygen tolerance, opening up gas and air monitoring applications;
- ✓ The ability to make transparent electronics
- ✓ Magnetic sensors

Expect market value for TCOs in coming years will be more then 200 billions $

→ ***Goodbye silicon, hello oxides!!!***

cnrs dépasser les frontières

UNIVERSITÉ DE VERSAILLES ST-QUENTIN-EN-YVELINES

Figure of Merit for TCO

The first TCO by J.M.MOCHEL, *U.S. PATENT* NO.2,564, (1947) 706

$$\sigma / \alpha = -\{R_s \ln(T+R)\}^{-1}$$

Optical absorption

Electrical Conductivity

R.Gordon MRS Bull.2000

n type TCO

Important criteria for TCO:

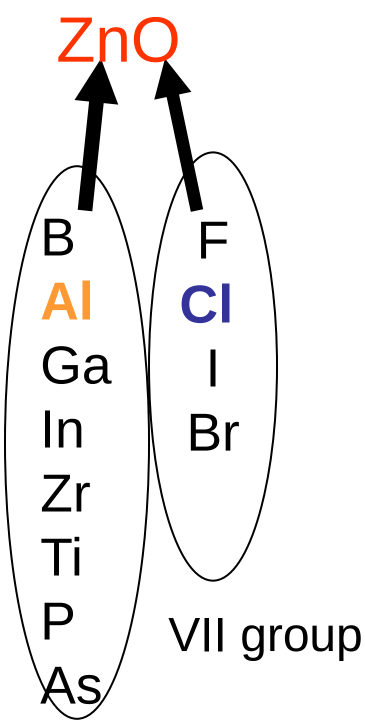
- The cost of the raw materials

Cd < **Zn** < Ti < Sn < Ag < ~~In~~

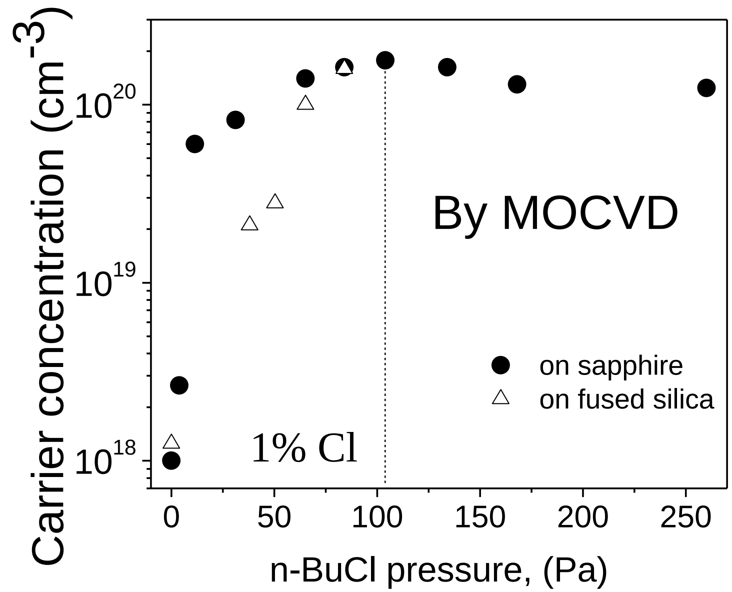
- Toxicity of the elements

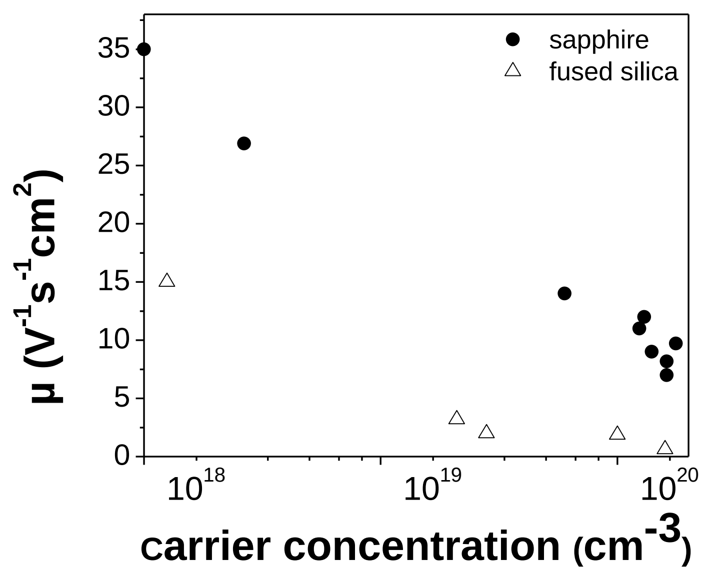
Zn < Sn < In < Ag < Cd

R.Gordon,MRS Bull.2000



ZnO:Cl





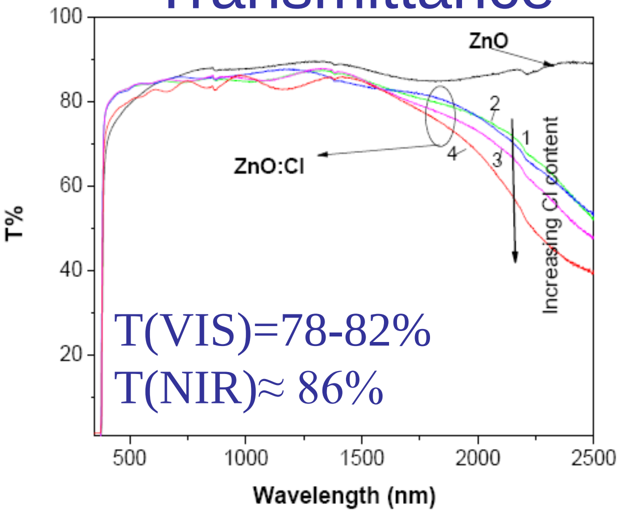
Phys. stat. sol. (a) **203**,2007

CNRS dépasser les frontières

UNIVERSITÉ DE VERSAILLES ST-QUENTIN-EN-YVELINES

n type TCO

Transmittance

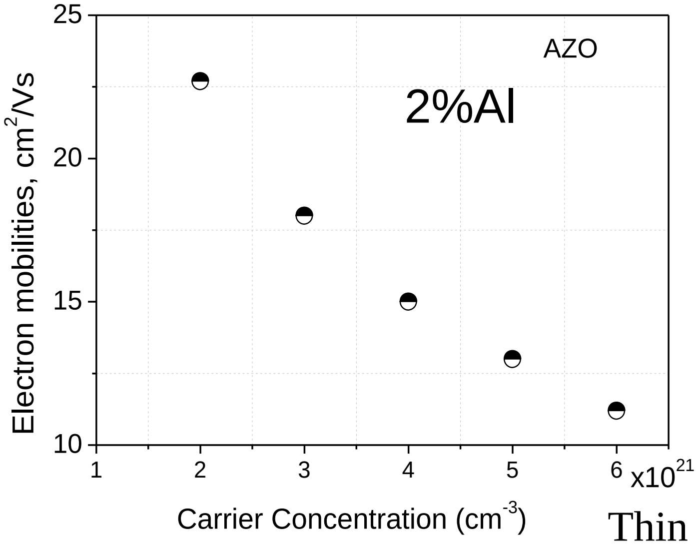


ZnO:Cl

ρ=1.3x10^{-3}Ohm cm

n=6.1x10^{20}cm^{-3}

μ=7 cm^2/Vs

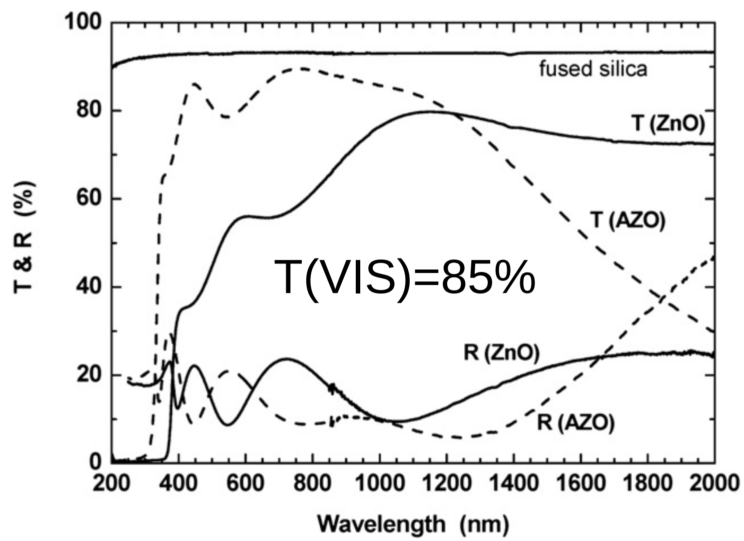


AZO by PLD

ρ=1.2x10^{-4}Ohm cm

n=1.2x10^{21}cm-3

μ=18 cm2/VS



Thin Solid Films 516 (2008) 8141–8145

p type TCO

WBG metal-oxydes

Most are Insulators ;Few are naturally n-type; rarely naturally p-type

The monopolarity in existing TCOs results from strong localization of positive holes at oxygen 2p levels or an upper edge of the valence band due to the strong electronegative nature of oxygen.

- **Conductivity type inversion in n-type TCO by cation doping**

  SnO_2, CdO, ZnO,In_2O_3....

Difficulty *(solubility limit, killer defects, deep levels)*

- « **Chemical modulation of VB** »

Delocalize holes by reduction of Columb interaction

delafossites : *$CuAlO_2$, (Kawazoe et al, 1997)*

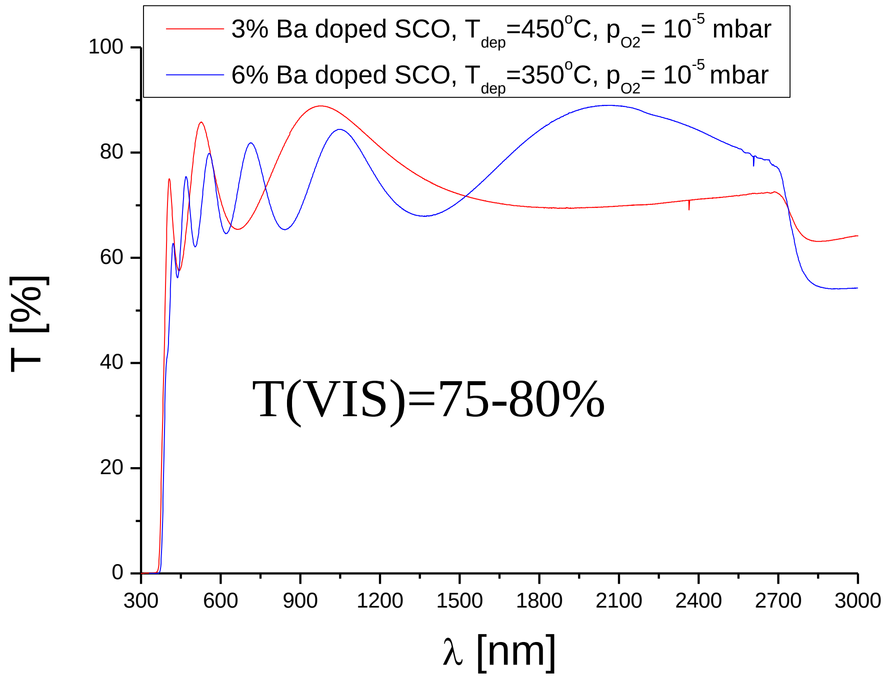
$CuGaO_2$;$CuInO_2$;$CuCrO_2$;$CuBO_2$;

Problem: very high deposition T, indirect band gap

Transparent p-n junction: oxide with direct band gap, low deposition T, high quality epi-layers

Cu based p type TCO

$SrCu_2O_2$



<u>Cu_2O (archetype of Cu based TCO)</u>

V.B.Hybrydised Cu 3d & O2p

→

---

localized holes

↓

Polaronic-hopping conduction

(R.S.Toth, Phys.Rev. 122,482, 1961;
L.C.Bourne,PRB 40,10973,1989)

Delocalization of holes

V_{Cu} 3d10Cu(I) 3d9Cu(II)

Coll: Tyndall National Institute University College Cork, Ireland;
Thales TRT, France

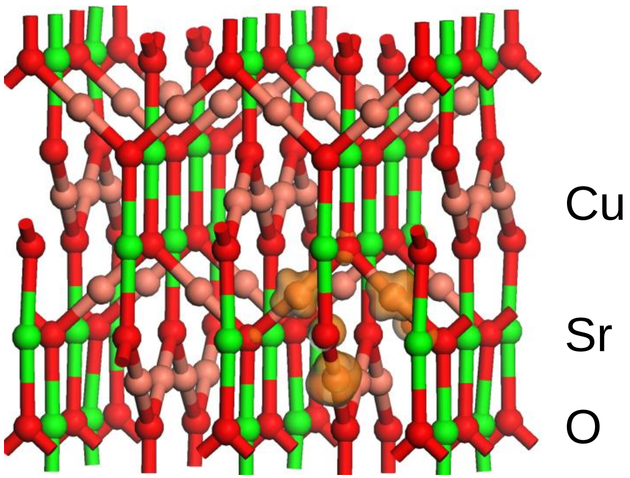
D.O.Scanlon, PRL, 103,096405, 2009
K.G.Godhino, J.Matt.Chem.20,1086,2010

cnrs
dépasser les frontières

UNIVERSITÉ DE VERSAILLES ST-QUENTIN-EN-YVELINES

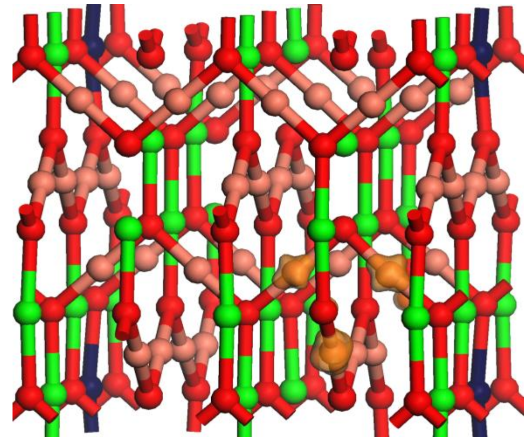
Introducing holes in $SrCu_2O_2$ *by Ba doping*

$SrCu_2O_2$



Hybrid DFT

Ba:$SrCu_2O_2$



Holes Predominantly localised on Oxygen atoms near vacancy site – **Polaron**

New localized state in band gap 1.1 eV above VB

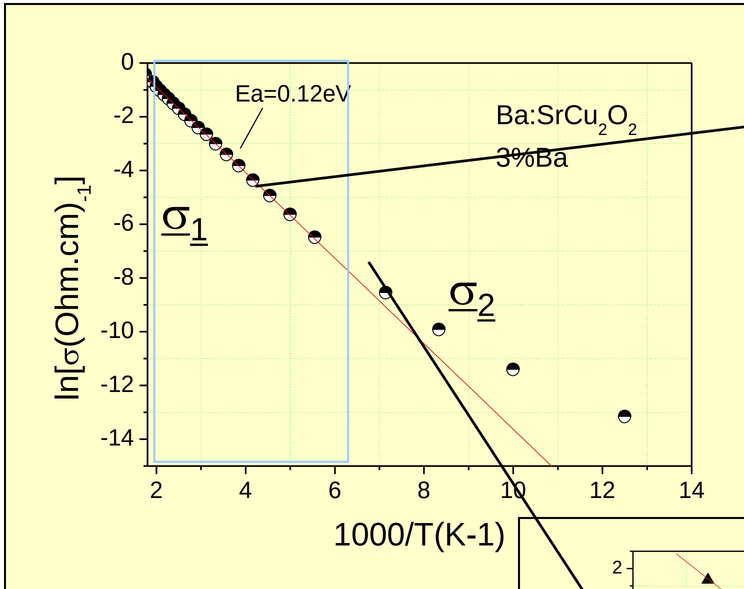
Structure	**Eg / HSE06**
$SrCu_2$O2	**3.20 eV**
Ba-$SrCu_2$O2	**3.24 eV**

Ba changes band gap but not the polaronic nature of the material

M.Nolan
Tyndall National Institute ,University College Cork, Ireland

dépasser les frontières

Conduction Mechanism of Ba:SCO



$\underline{\sigma = \sigma_1 + \sigma_2}$

NNH

$\sigma_1 = \sigma_0 \exp(-W_H/k_BT)$

Constant Activation energy

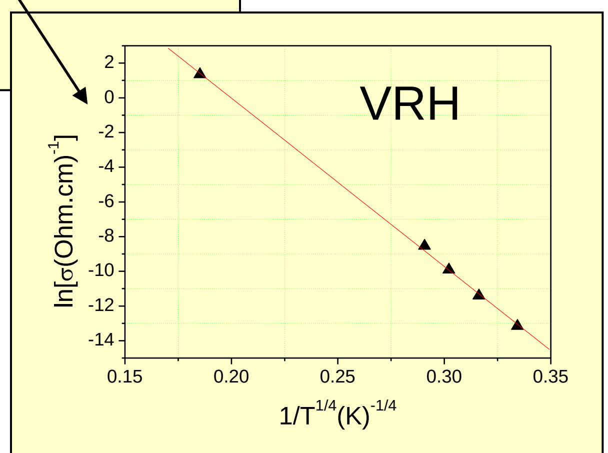
$E_a = [E_a(p(T)); E_a(\mu(T))]$

$E_a = E_a(\mu(T)) = W_H$ polaron hopping energy

$W_H = 120$ meV

polaron binding energy $E_p = 240$eV

Polaron conductivity



$\sigma_2 = \sigma_0 \exp(T_0/T)^{-1/4}$

Activation energy

$T_0 \sim \beta / k_{NEf}\, r\, p$

$\mathbf{T_0 = 9x10^4 K}$

Mobility is thermally activated

@300K $\rho = 79\ \Omega$.cm

$\sigma = 1.2x10^{-2} Scm^{-1}$

$p = \sim 10^{17} cm^{-3}$

$\mu < 1\ V^{-1}s^{-1}cm^2$

Influence of Ba doping on Conductivity of SCO

%Ba 0	σ(Scm^{-1}) 1x10-3	μ_H(cm^{2}/VS)	E_p eV **Polaron binding energy**
3	$3x10^{-2}$	<1	240
6	$1.2x10^{-2}$	<1	180

- Ba:SCO keeps good transparancy in VIS (with small open of Gap)
- Ba doping induces less localised holes

Problem remains: low mobility of carriers

Delocalization of carriers by doping another dopant?

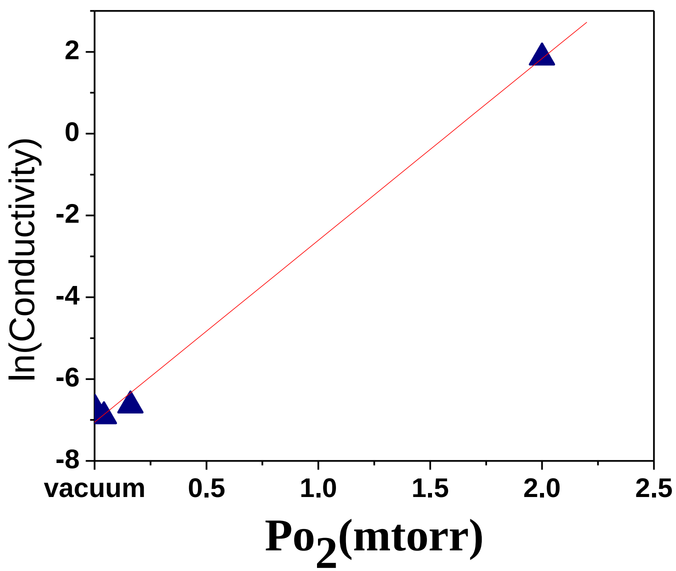
cnrs dépasser les frontières

UNIVERSITÉ DE VERSAILLES ST-QUENTIN-EN-YVELINES

FTO- IR transparent conducting magnetic Oxide

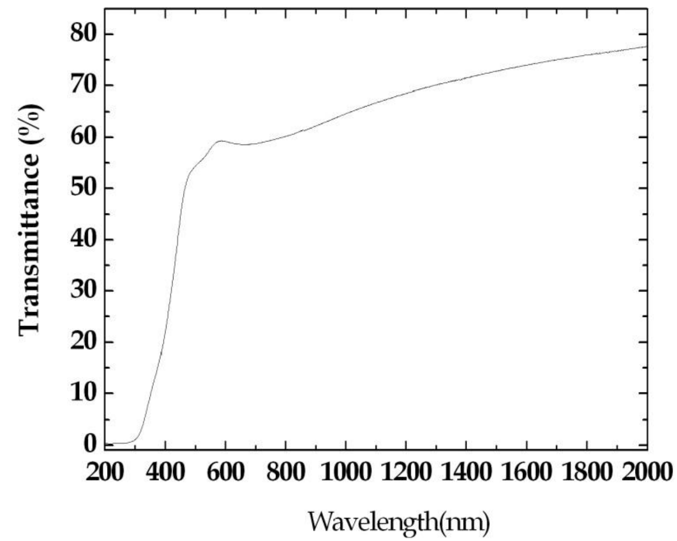
Ilmenite $FeTiO_3$
E_g=3.5 eV
Antiferromagnet T_N =55K

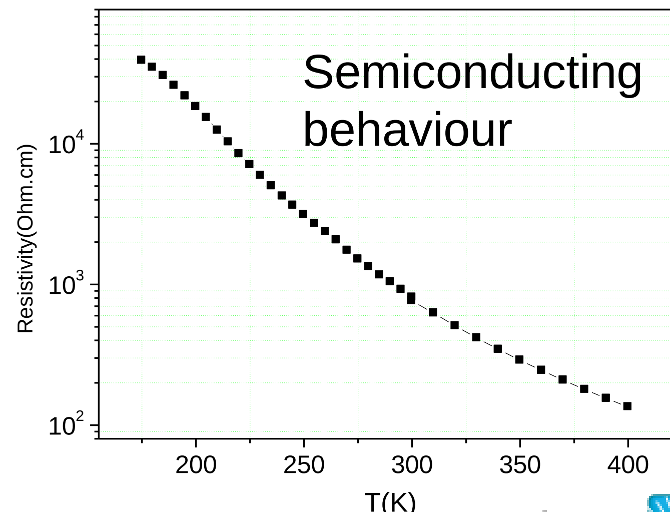
By PLD
Growth $P_{O2}=10^{-7}$ – 2 mTorr



Conductivity increases
with oxygen partial pressure

p type conductivity



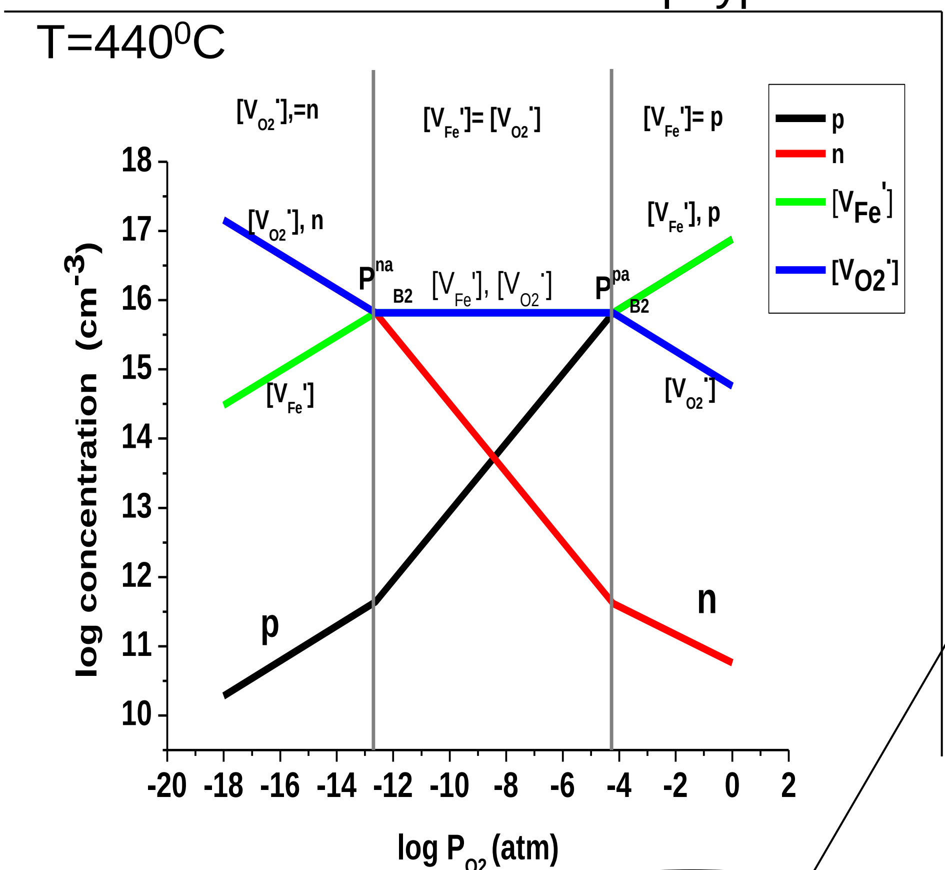


Conductivity type inversion in FTO

Coll: T.Tchelidze, TSU, Georgia

Thermodynamical analyses

n type insulator p type



Hole conductivity $P_{O2}>6x10^{-5}$atm

Electron conductivity $P_{O2}<3x10^{-13}$atm

Experiment:

Treatment in oxygen atmosphere

$P_{O2}=5.6x10^{-4}$atm	***p***
$P_{O2}=2x10\text{-}^{13}$atm	***n***

Conductivity type inversion

dépasser les frontières

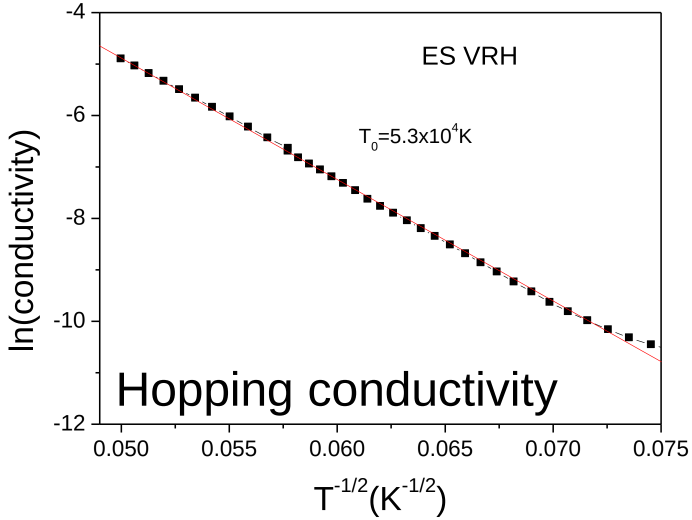
UNIVERSITÉ DE VERSAILLES ST-QUENTIN-EN-YVELINES

Conclusion:

Present challenge is to get low temperature deposition of high quality p type type TCO…..

Future belongs to

"Invisible Electronics"


ES VRH
T0=5.3x10^4K
Hopping conductivity
ln(conductivity)
T^-1/2(K^-1/2)
-4
-6
-8
-10
-12
0.050
0.055
0.060
0.065
0.070
0.075