Totally water based synthesis routes to metal oxide nanostructures

with electronic applications

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Motivation

Water based synthesis of metal oxides

Fundamental aspects & chemistry
of water based synthesis methods

New materials

New applications

Development of new synthetic methods
without hazardous solvents

Overview

Water based solution-gel

general principles

precursor solutions

Water based chemical solution deposition of films

wetting

thin layers

'islands'

ultrathin layers

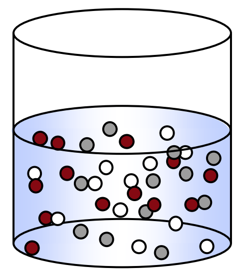
Water based synthesis of nanoparticles

solution-gel & hydrothermal synthesis

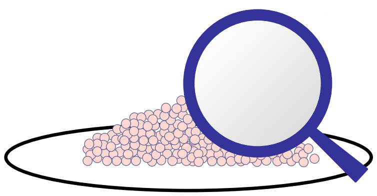
Nanostructured layers

packaging & green photovoltaïcs

Solution-gel
Introduction

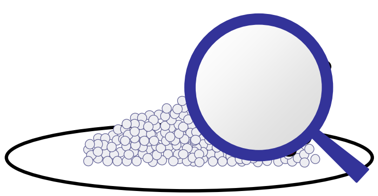


Preserve
Chemical homogeneity



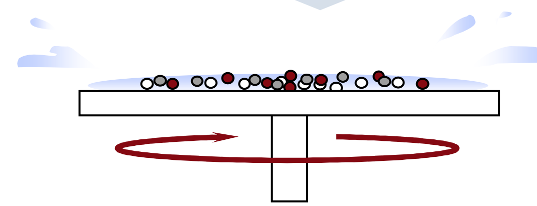
Gel powder

Thermal treatment

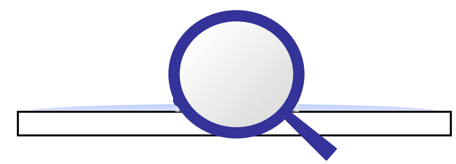


Oxide powder

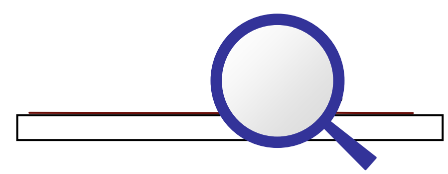
- ☺ Homogeneous mixture of metal ions
- ☺ Stoichiometry control
- ☺ Possibility for film deposition by CSD
- ☹ Expensive alkoxides
- ☹ Hazardous solvents
- ☹ Protection from moisture / air



Film deposition

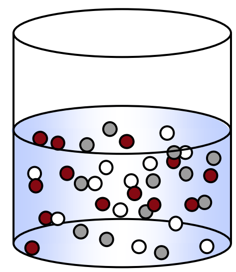


Thermal treatment



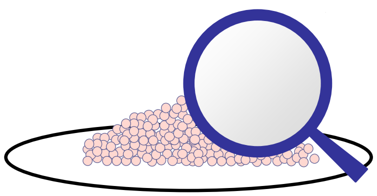
Oxide layer

Water based Solution-gel
Introduction



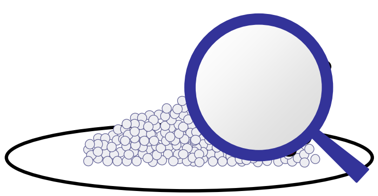
Preserve
Chemical homogeneity

- ☺ Homogeneous mixture of metal ions
- ☺ Stoichiometry control
- ☺ Possibility for film deposition by CSD
- ☺ Inexpensive metal sources (e.g. salts)
- ☺ Reduced risk for environment / health
- ☺ No protection from moisture / air

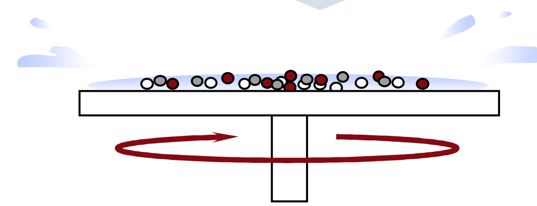


Gel powder

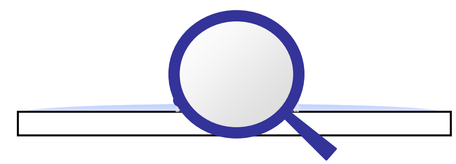
Thermal treatment



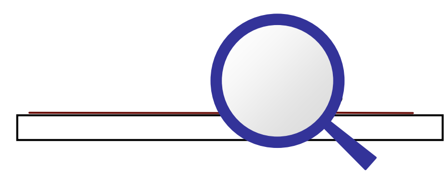
Oxide powder



Film deposition

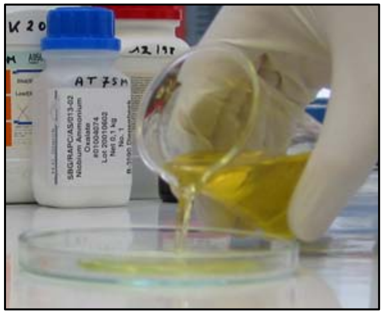


Thermal treatment

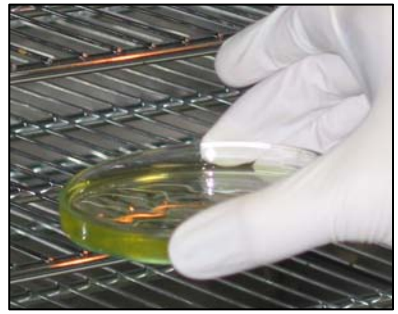


Oxide layer

Water based solution gel
General principles



Metal salts
in water



T ↑
→
evaporation of H_2O

Metal carboxylate
network

PROBLEM	Zr^{4+}, Nb^{5+}, Ta^{5+}, Ti^{4+}, ... are not stable in water
WE NEED	Ways to stabilize metal ions in aqueous solution in conditions suitable for gel formation (pH, concentration, other ions, additives, viscosity, ...)
APPROACH	Complexation with electron donating ligands e.g. citrate, acetate, peroxo

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Water based solution gel
Precursor solutions

Ta

Ta^{5+}-oxalate

↓ Hydrolysis

Ta^{5+}-hydroxide Precipitate

↓ H_2O_2 — Citric acid

Clear solution

↓ NH_3

Citrato peroxo Ta^{5+} precursor → Stable & clear gel

Nelis et al. (2001) J. Eur. Ceram. Soc.

Citratoperoxo **Ti^{4+}** from $Ti(O^iPr)_4$
Hardy et al. (2003) J. Eur. Ceram. Soc.

Citratoperoxo **Zr^{4+}** from $Zr(O^nPr)_4$
Van Werde et al (2007) J. Mater. Sci

Citratoperoxo **Ru** from $Ru(acac)_3$
Pagnaer et al. (2004) J. Eur. Ceram. Soc.

Citratoperoxo **Nb^{5+}** from Nb^{5+} oxalate
Van Werde et al (2001) J. Mater. Chem

Citratoperoxo **W^{6+}** from $(NH_4)_6W_{12}O_{39}$
Hardy et al (2007) Chem. Mater.

Citratoperoxo **Mo^{6+}** $(NH_4)_6Mo_7O_{24}.4H_2O$
ibidem

Nitrilotriacetatoperoxo **V^{5+}** from NH_4VO_3
ibidem

Suitable precursors for

$SrBi_2Ta_2O_9$	SBT
$(Bi,La)_4Ti_3O_{12}$	BLT
and variants with V, Mo, W	
$Pb(Zr,Ti)O_3$	PZT
$(Pb,Ca)TiO_3$	PCT
$SrRuO_3$, RuO_2, TiO_2	

Water based solution gel

Precursor solutions

Water soluble
Citrato peroxo complex

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									

Stabilized M^{n+} carboxylate solution
Acetate
Citrate
Lactate
...

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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precursor solutions for 'all' metal ions & combinations

Water based chemical solution deposition of films

wetting

examples thin layers

'islands'

screening & ultrathin layers

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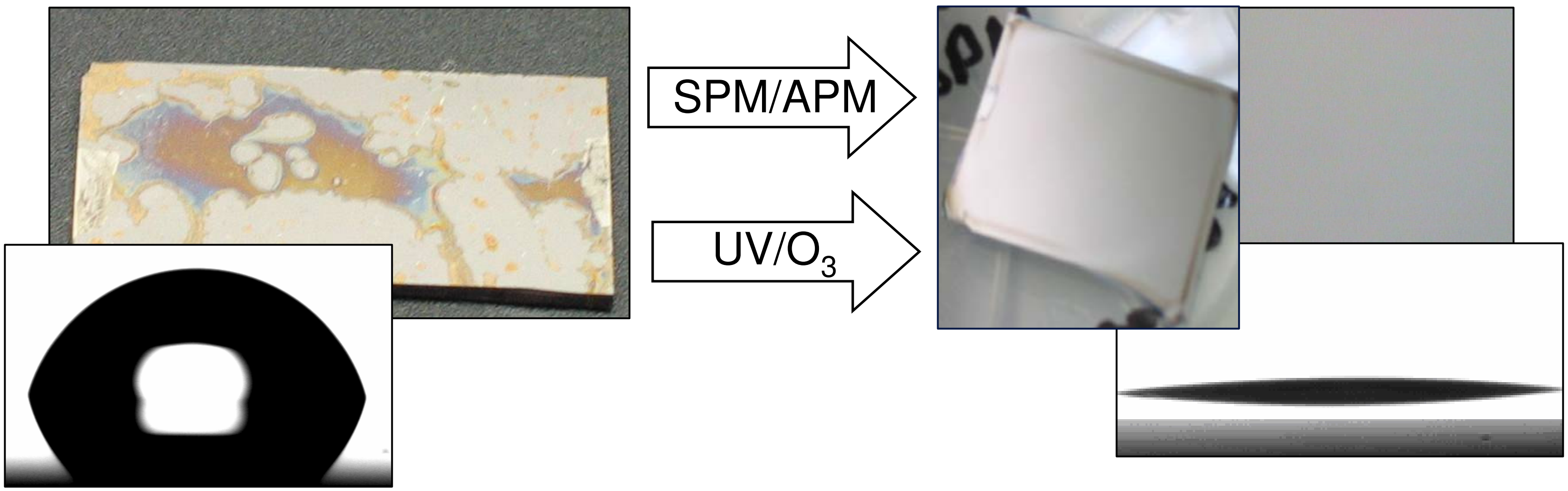
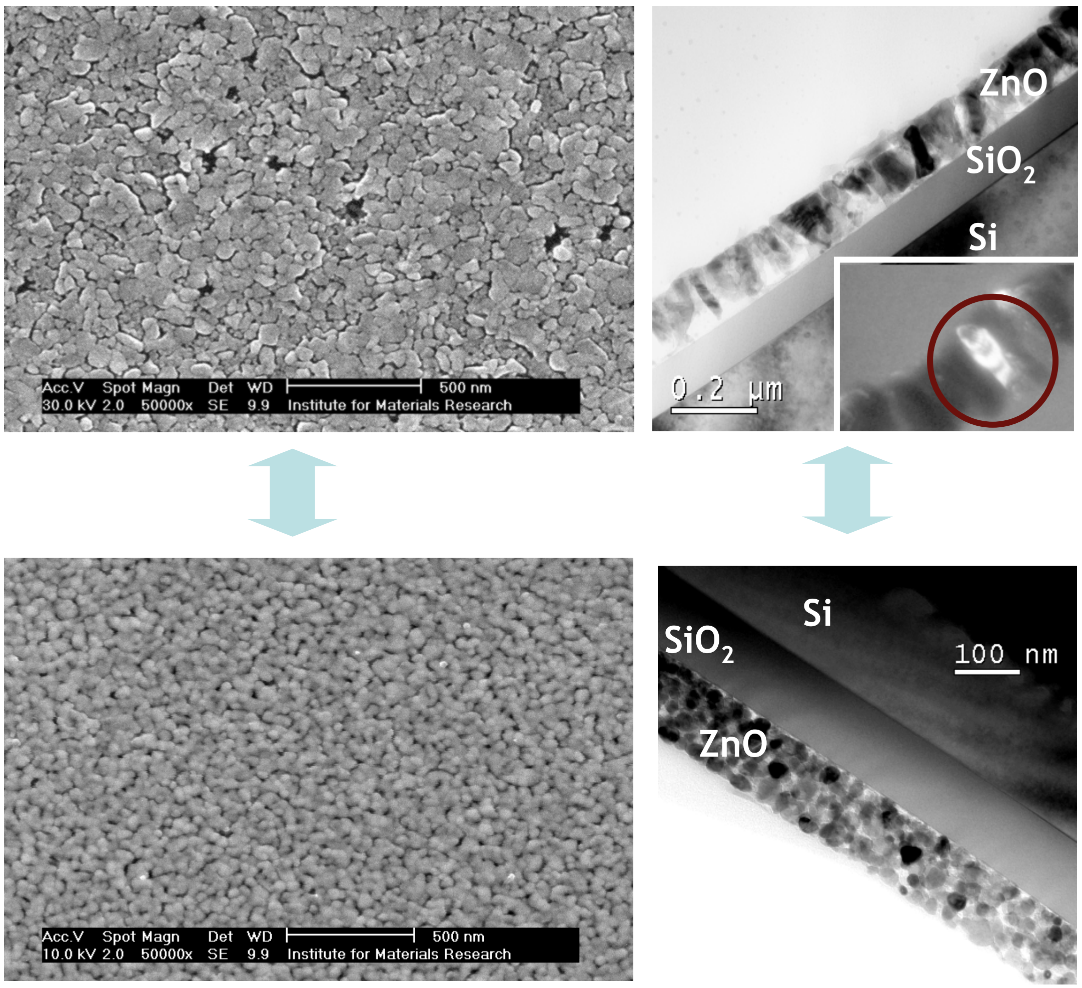
Aqueous Chemical Solution Deposition
Wetting



Van Bael et al. Integr. Ferroelectr. 45 (2002) 113-122
Nelis et al. Integr. Ferroelectr. 45 (2002) 205-213

Aqueous Chemical Solution Deposition
Examples: ZnO

ZnO films from water based Zn-citrate precursor



21 layers **0,37 M**

dense

Column-like crystals

2 layers **1,0 M**

polycrystalline

No column-like crystals

Mondelaers et al. (2003) J. Sol-Gel Sci. Technol.

Aqueous Chemical Solution Deposition

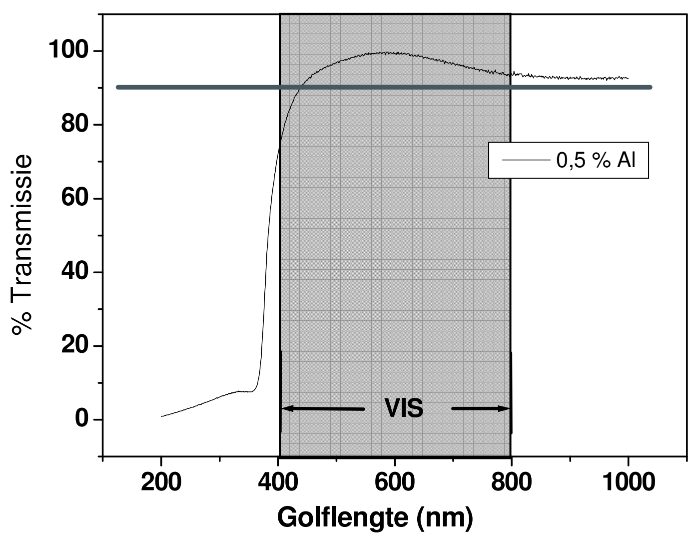
Examples: ZnO:Al

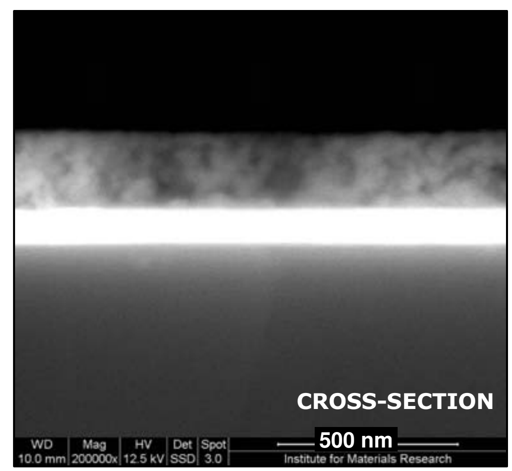
Transparent conducting oxides (ZnO:Al)

Good conductivity — Resistivity ↓ ~ 5 .10^{-3} Ω.cm

High transparency — Transparency ↑ > 90 %

ZnO + 0,5% Al^{3+}





ZnO

ITO

glass

Van den Rul, Mondelaers et al. (2006) J. Sol-Gel Sci. Technol. 39

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Aqueous Chemical Solution Deposition
Examples: ferroelectric films

Compositional flexibility

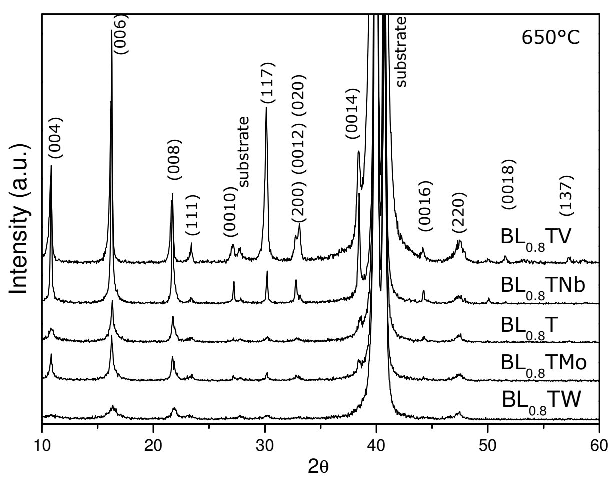
$(Bi,La)_4Ti_3O_{12}$

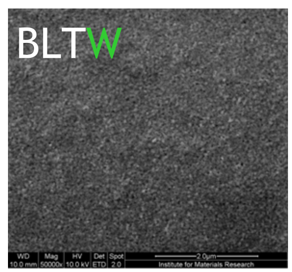
Co-substitution Ti^{4+} with Mo^{6+}, W^{6+}, Nb^{5+} or V^{5+}

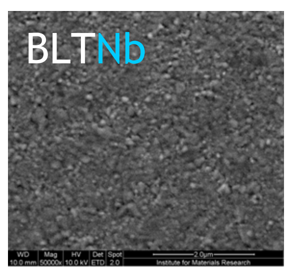
≠ P_r of BLT and BLTV ~ orientation

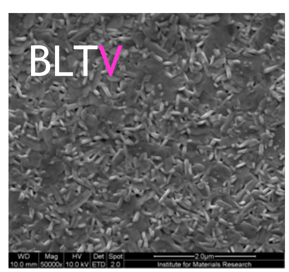
≠ P_r of BLT, BLTW, BLTMo and BLTNb ~ crystallinity:

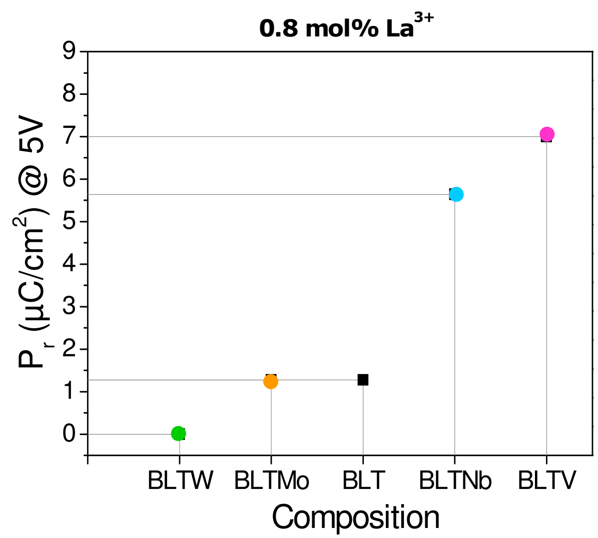
- W^{6+} prevents grain growth,
- Nb^{5+} stimulates grain growth,
- Mo^{6+} no effect / decrease XRD peak intensity





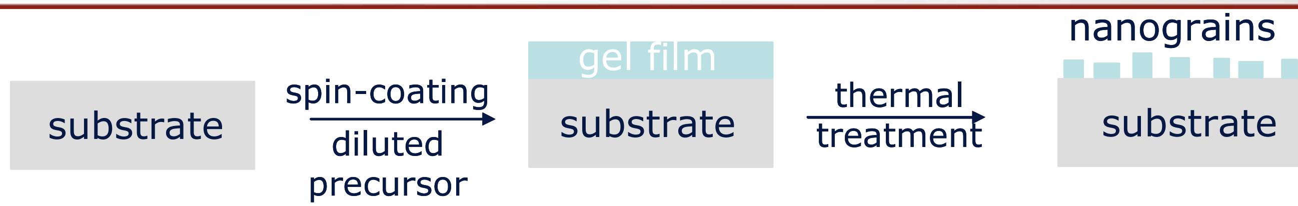


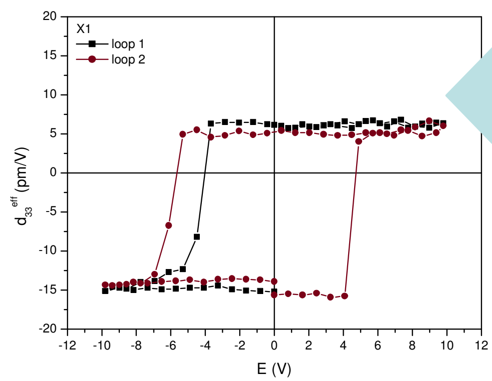


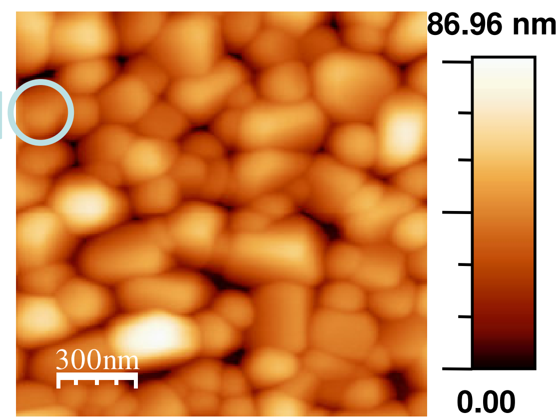


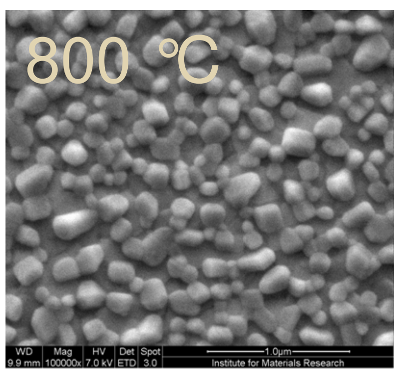
A. Hardy et al. Chemistry of Materials, 19 (2007)

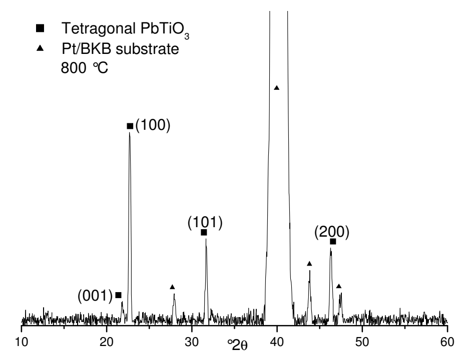
Aqueous Chemical Solution Deposition
‘nano’ islands







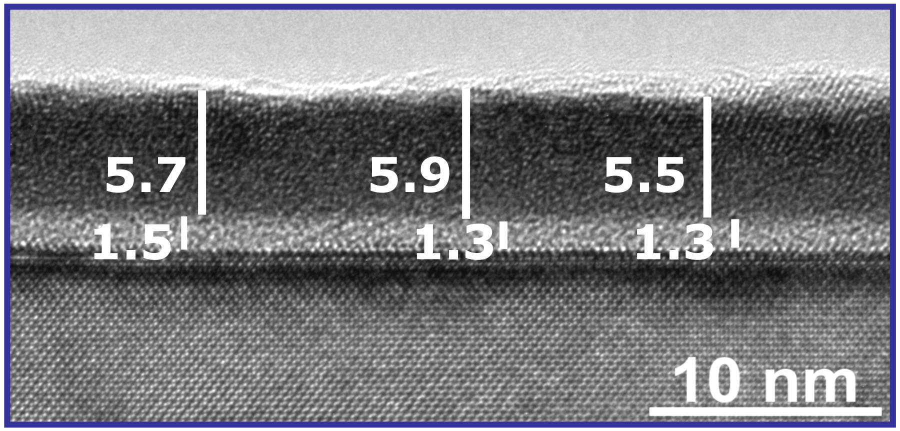




Collaboration with J. Ricote, M.L. Calzada, CSIC, Madrid in the frame of COST 539

Aqueous Chemical Solution Deposition
Ultrathin layers

Ultrathin layers
Suitable for screening
of alternative high-K oxides
Dielectric quality ≈ ALD

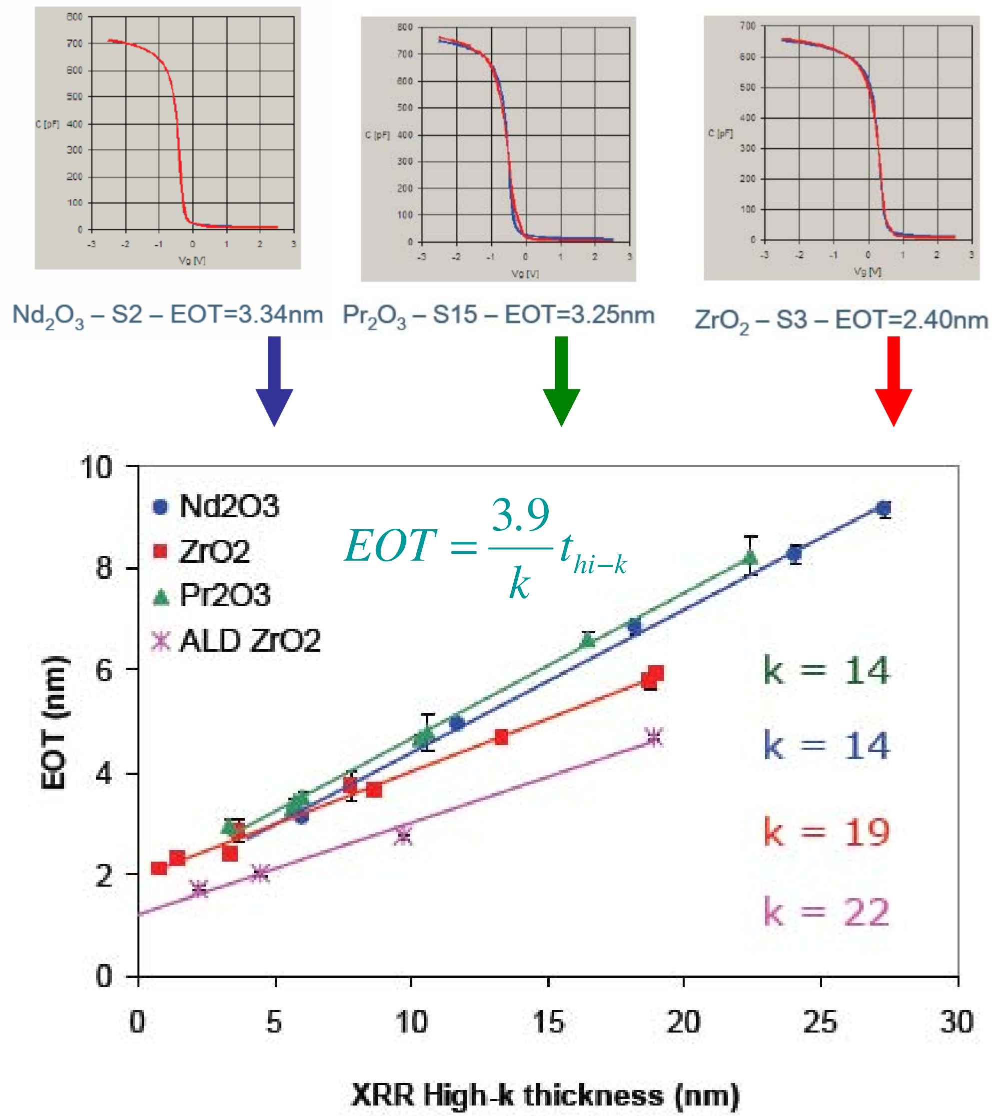


EOT down to 2.4 nm obtained

K-value

Pr_2O_3 and Nd_2O_3: *K* = 14

ZrO_2: *K* = 19



A. Hardy, S. Van Elshocht et al. J. Mater. Res.22 (2007)

Overview

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general principles

precursor solutions for 'all' metal ions & combinations

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examples thin layers

'islands'

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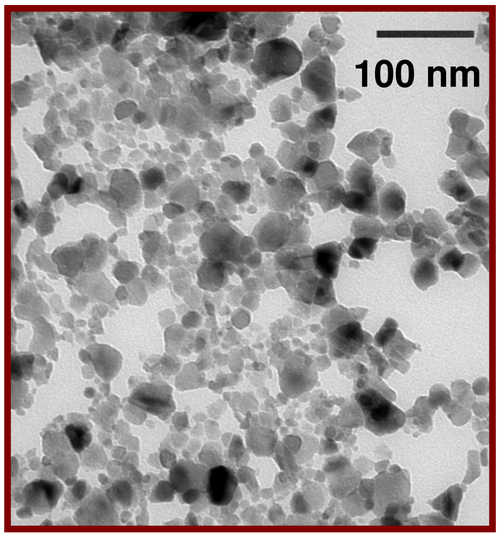
Nanostructured layers

packaging & green photovoltaïcs

Nanoparticles
Water based synthesis: examples

ZnO:Al

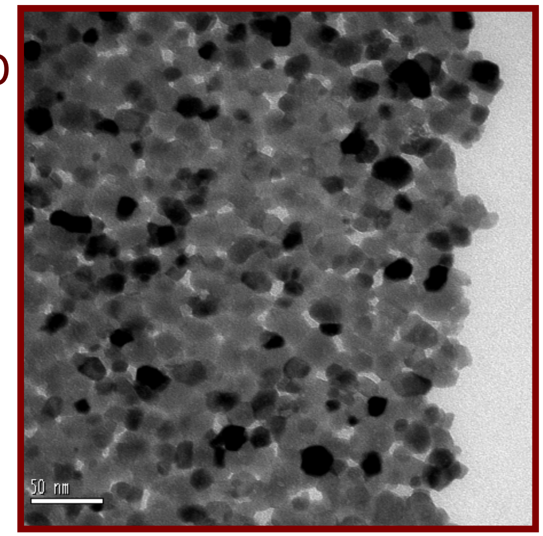


Water based solution-gel

Multi metal oxides

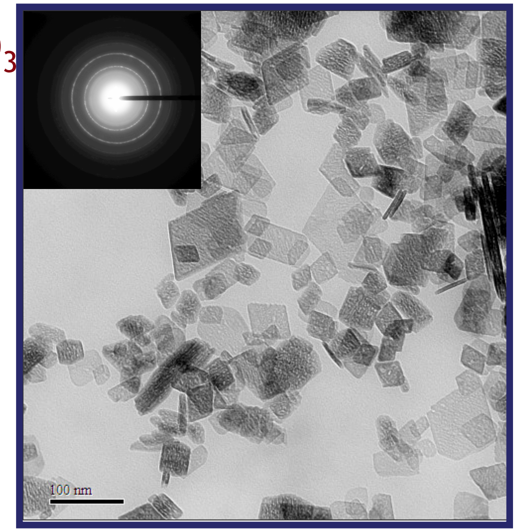
Agglomeration issues

ITO



Nanoparticles
Water based synthesis: examples

Al_2O_3



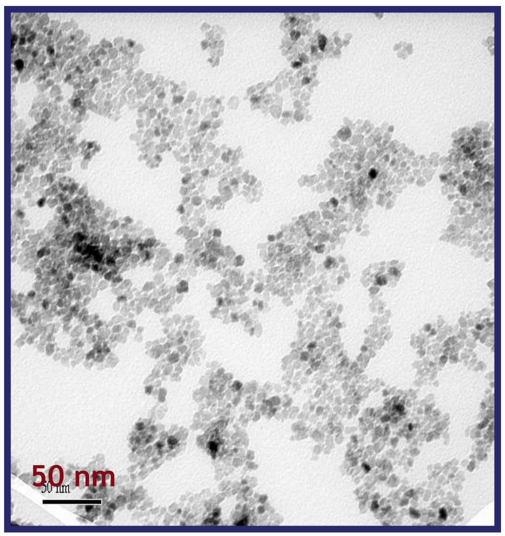
Hydrothermal methods

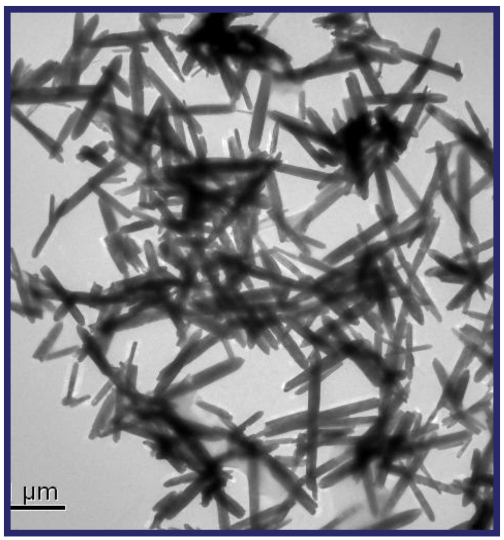
Less agglomeration

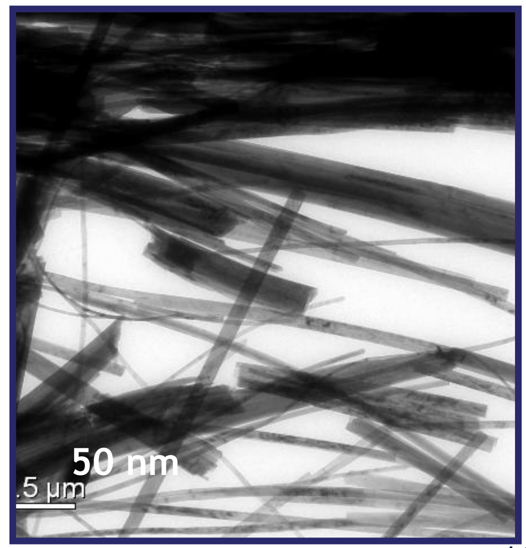
Different morphologies

depending on conditions

TiO_2

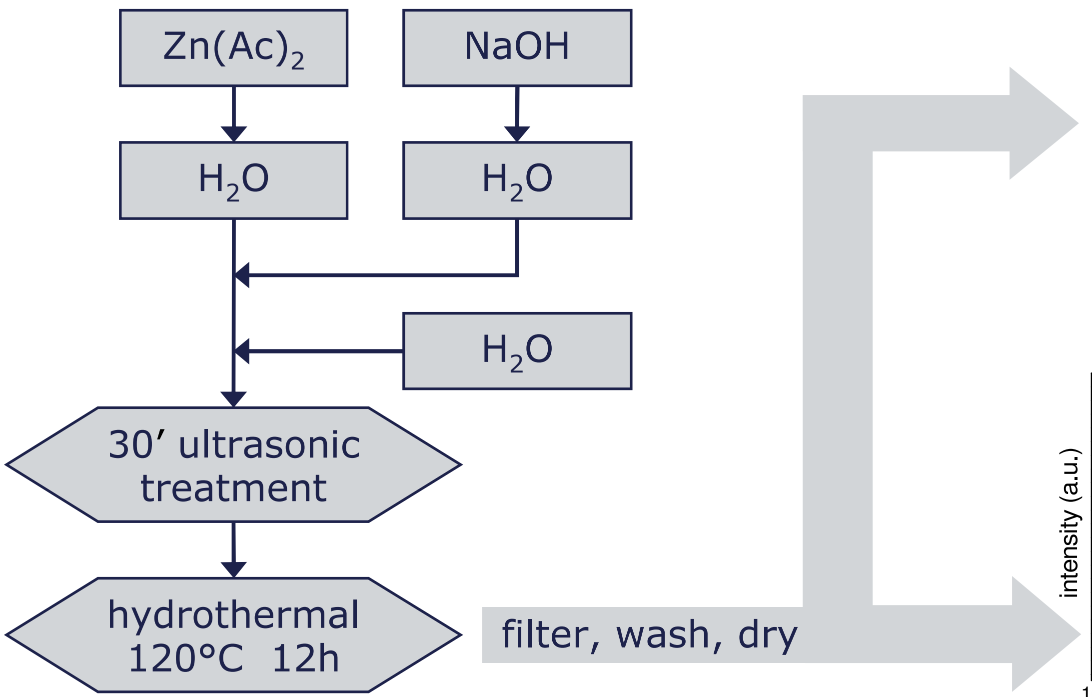




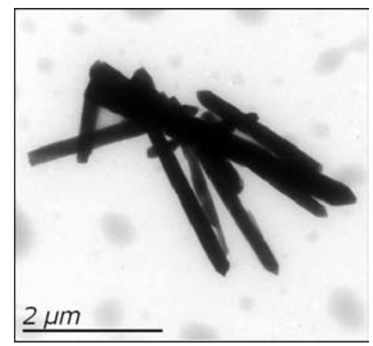


Nanoparticles
Water based synthesis: examples

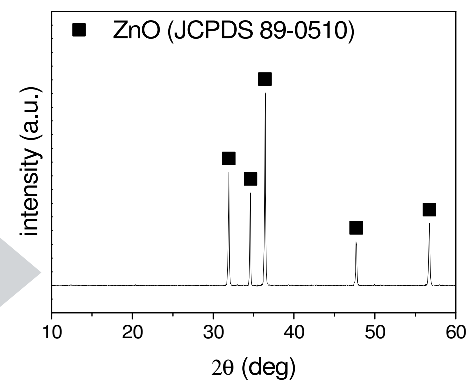
ZnO nanorods
Precipitation in hydrothermal conditions
Without (organic) additives



TEM



XRD



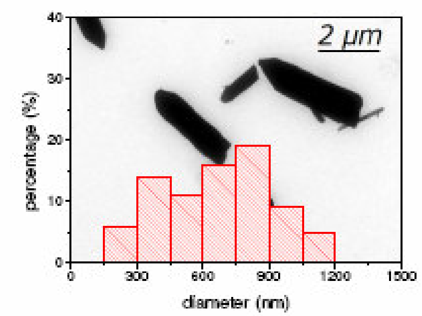
K. Elen, H. Van den Rul, A. Hardy, M. K. Van Bael, J. D'Haen, R. Peeters, D. Franco, J. Mullens (2008) submitted
K. Elen, M. K. Van Bael, H. Van den Rul, J. D'Haen, R. Peeters, D. Franco and J. Mullens: Chem. Lett. 35 (2006) 1420.

Nanoparticles
Influence of synthesis conditions

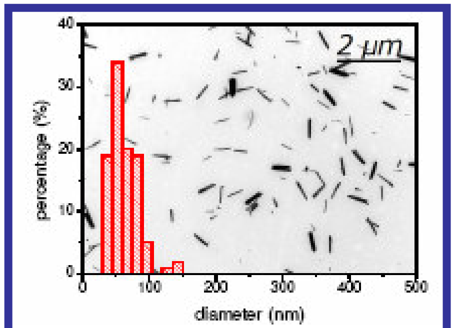
Design of experiments
"An efficient procedure for planning experiments so that the data obtained can be analyzed to yield valid and objective conclusions."

2^{8-4} fractional factorial design of resolution IV

	variable	low level (-)	high level (+)
1	temperature (°C)	80	200
2	time (h)	4	48
3	heating rate (°C/min)	1	4
4	$[Zn^{2+}]$ (mmol)	5	20
5	$[Zn^{2+}] : [OH^-]$	1 : 8	1 : 12
6	zinc source	$Zn(Ac)_2.2H_2O$	$ZnCl_2$
7	stirring	no	yes
8	ultrasonic treatment	no	yes



d_{mean} = 660 nm

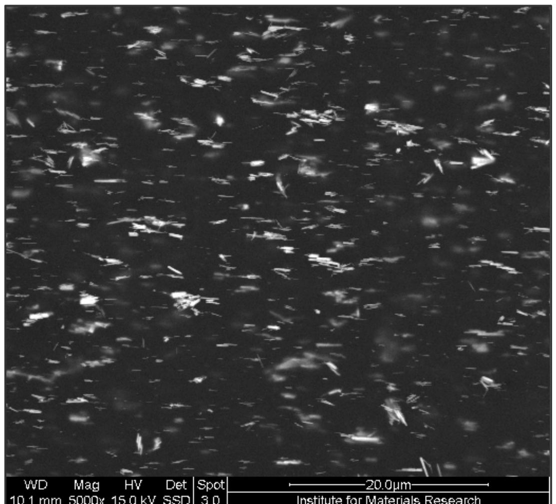


d_{mean} = 60 nm

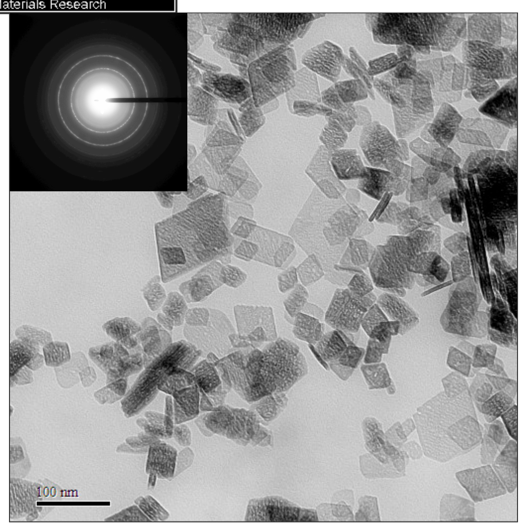
G. Box et al.: Statistics for Experimenters (1978)
K. Elen, H. Van den Rul, A. Hardy, M. K. Van Bael, J. D'Haen, R. Peeters, D. Franco, J. Mullens (2008) submitted
K. Elen, M. K. Van Bael, H. Van den Rul, J. D'Haen, R. Peeters, D. Franco and J. Mullens: Chem. Lett. 35 (2006) 1420.

Nanoparticles
In food packaging

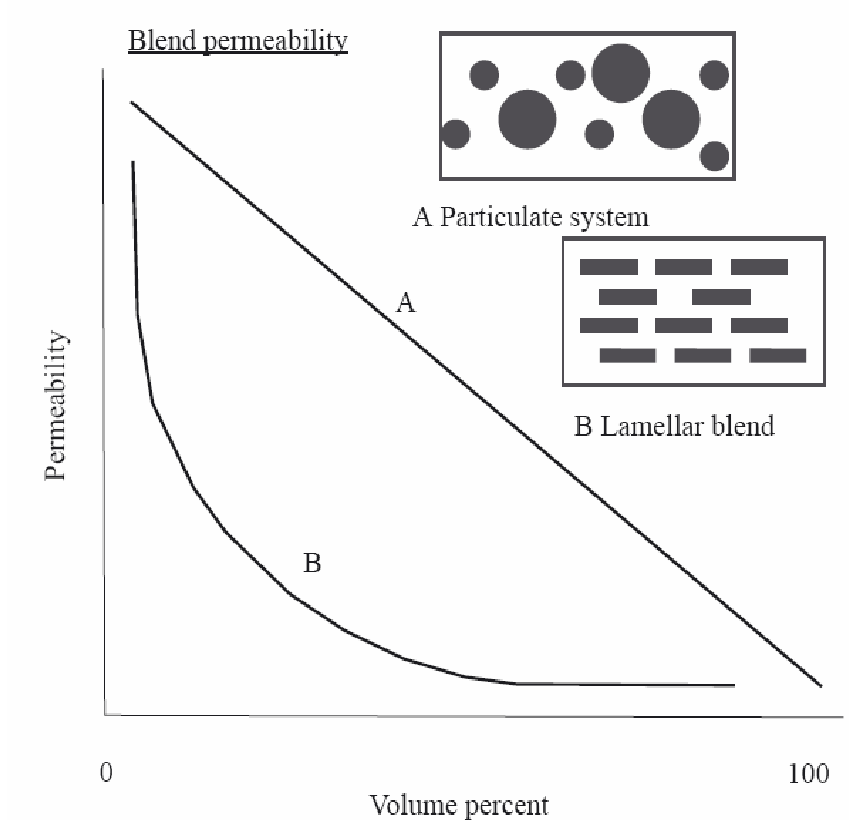
Nanoparticles dispersed in packaging foils → reduce gas permeability



ZnO rods dispersed in PP



Al_2O_3 platelets



N. Lepot, M. K. Van Bael et al. Polimery, 51, 9 (2006)
N. Lepot, M. K. Van Bael et al. Materials Letters 61, 13 (2007)
N. Lepot, M. K. Van Bael et al. Ceramics International (2007)

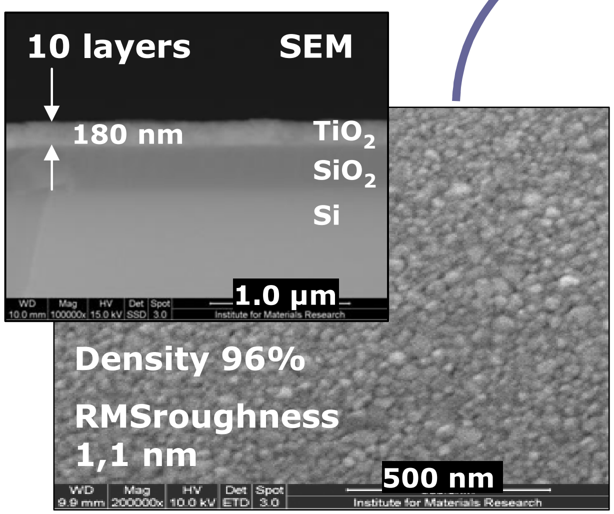
Nanostructured layers
In ‘green’ photovoltaïcs

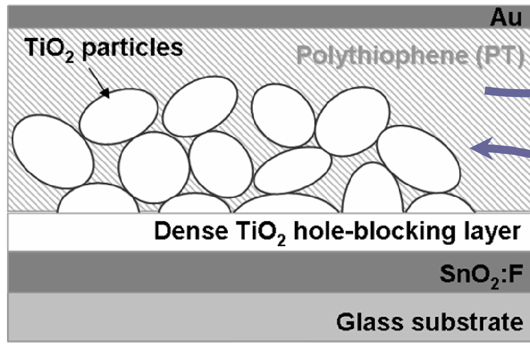
TiO_2 films from water based citrato-peroxo-Ti precursor solution

In ‘green’ solid state photovoltaic cell with water soluble polythiophene

Thin - dens

600°- 650°C
Pure anatase



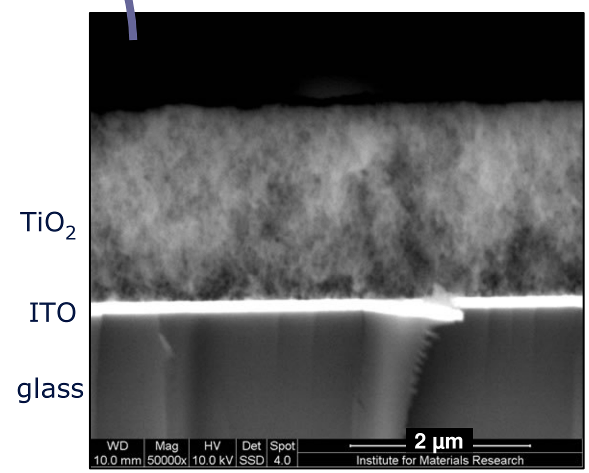


Promising results

Haeldermans et al.
Thin solid films (2007)

Thick - porous

pore former PVA / HPC
Or dispersion nanoparticles
450°C
Pure anatase



Truijen, Van Bael et al. (2007) J. Sol-Gel Sci. Technol. 41(1)
Truijen, Van Bael et al. (2007) J. Sol-Gel Sci. Technol. 43(3)

Beusen, Van Bael et al. (2007) J. Eur. Ceram. Soc.
Truijen, Haeldermans et al. (2007) J. Eur. Ceram Soc.

Conclusions

Water based routes are versatile synthesis methods

Ecologic, economic and practical advantages

Suitable for the fabrication of complex oxide materials
in different morphologies
(ultra)thin films & islands

Future :
extension of materials – nanostructures
Assessment of technological possibilities

Acknowledgements

CSIC, Madrid
dr. ML Calzada, dr. J. Ricote, dr. R. Jimenez

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