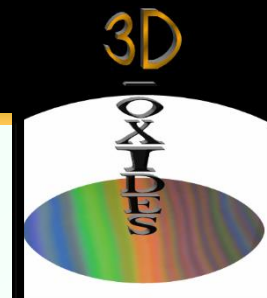


Workshop on Advanced Materials and Surfaces

G. Benvenuti, E. Wagner, C. Sandu, S. Harada

CERN 19-11-2013

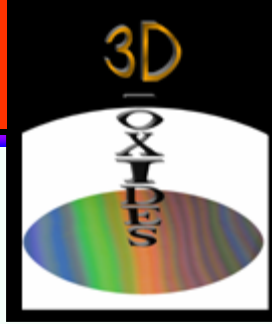


VERTICALLY
INTEGRATED

BIO
OPTICS
PHOTONICS
ELECTRONICS
DECORATIVE
SECURITY
ENERGY

SINGLE
Multi-Functional
CHIPS



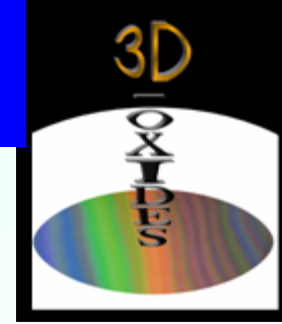


Company description

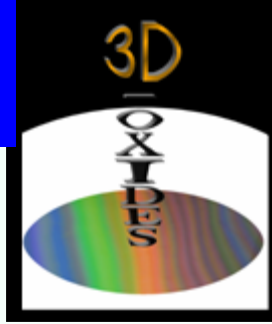
Short introduction to oxide thin films

3d-Oxides technology and assets: some result

Conclusions: from R&D to production



Company Information



Company activity start: 2010

Staff 2013: 6 persons

Turnover 2012: 0.65 M€ services + 0.2 M€ subsidies

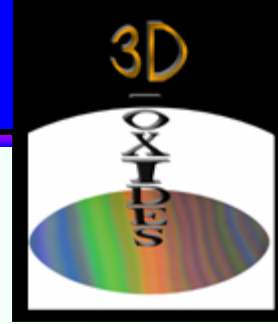
Locations:

St. Genis-Pouilly (F) (Headquarters + R&D lab thin films)

Tours (F) (R&D lab spectroscopy)

Le Bélieu (F) (R&D lab equipment testing)

Magurele (Ro) (Daughter company)

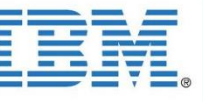
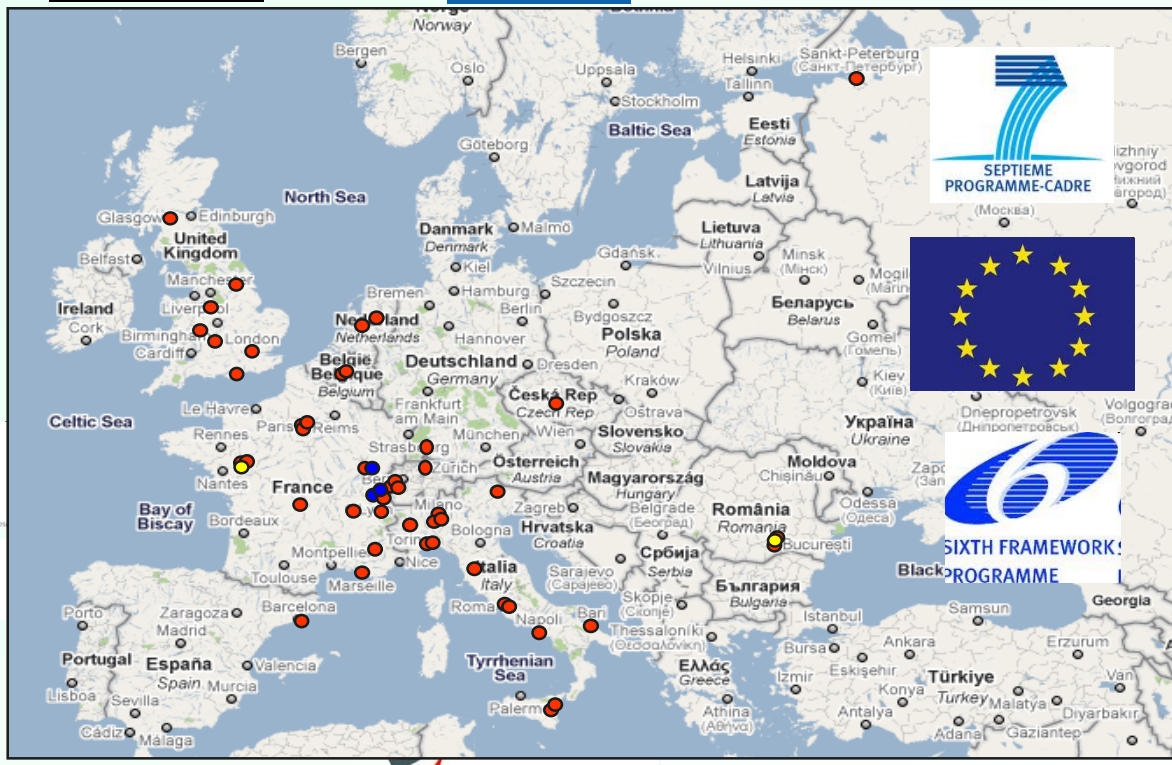
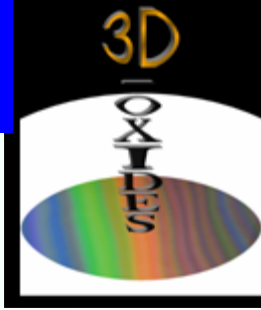


Develop complex multifunctional thin films

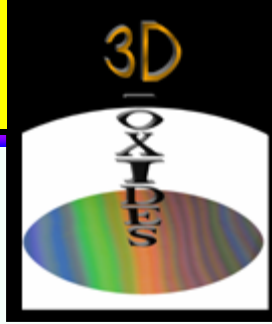
1. Multi-element oxide thin films
2. 3D-patterned thin films
3. New properties and architectures

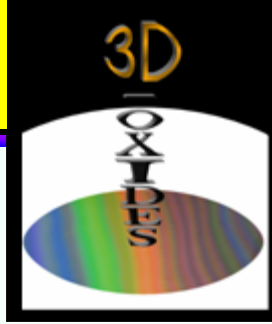
3D-Oxides targets and develops disruptive solutions

R&D Network



Thin films: a short introduction

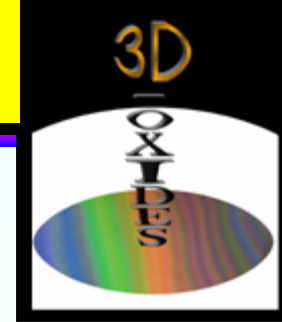




Improve sustainability, robustness, transportability

1. Miniaturization and integration of new functionalities
2. Optimize raw material use
3. Replace and/or minimize scarce and/or toxic elements

Markets & Applications



COST EFFECTIVE MASS PRODUCTION
Less Resources, Robust devices, Transportability

Micro-electronics

Clean-Tech

MEMS

Optics

Biotech

Memories

...

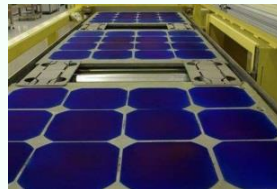
...

Chips



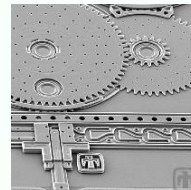
Photovoltaic
H₂ generation
Catalysis
Fuel cells

...



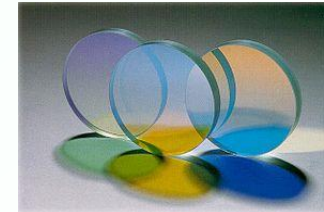
Inkjet heads
Actuators
Sensors

...



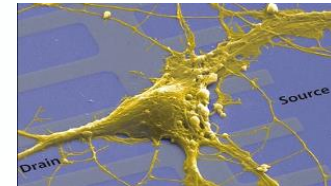
Integrated optics
Photonics
Sensors
Security

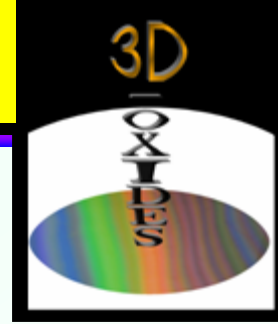
...



Bio-interfaces
Bio-photonics
Lab-on-chip

...





OPPORTUNITIES

- ✓ Eco-sustainable
- ✓ A wider number of possible functionalities
- ✓ Robust materials
- ✓ Multi-functional materials for monolithic integration



High added-value products

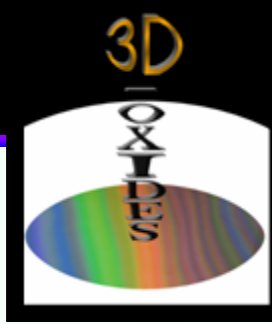
BOTTLENECKS

- ✓ Endless number of possible elemental compositions
- ✓ High process temperatures
- ✓ Properties strongly process-dependent
- ✓ Materials difficult to pattern after deposition

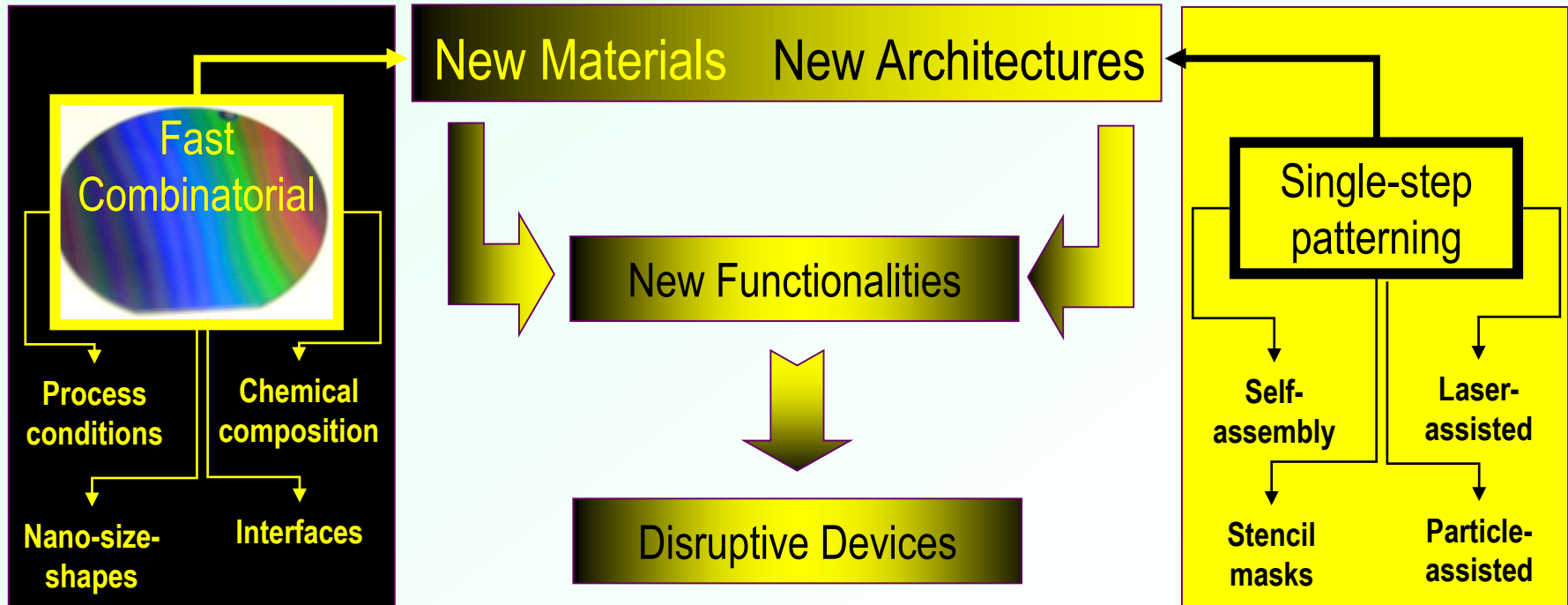
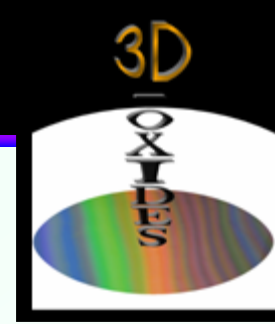


Complex materials and industrial up-scaling

3D-Oxides: Technology and Assets

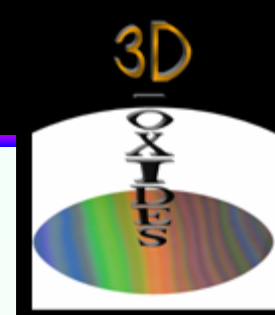


3D-Oxides disruptive solution



FAST TECHNOLOGICAL APPROACH SIMULTANEOUSLY ADDRESSING SEVERAL MATERIALS-PROPERTIES-MARKETS

Multi-element thin films

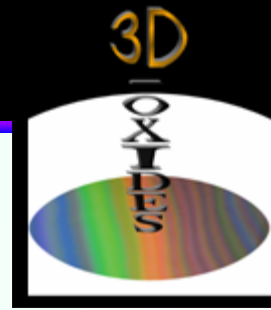


AVAILABLE ELEMENTS

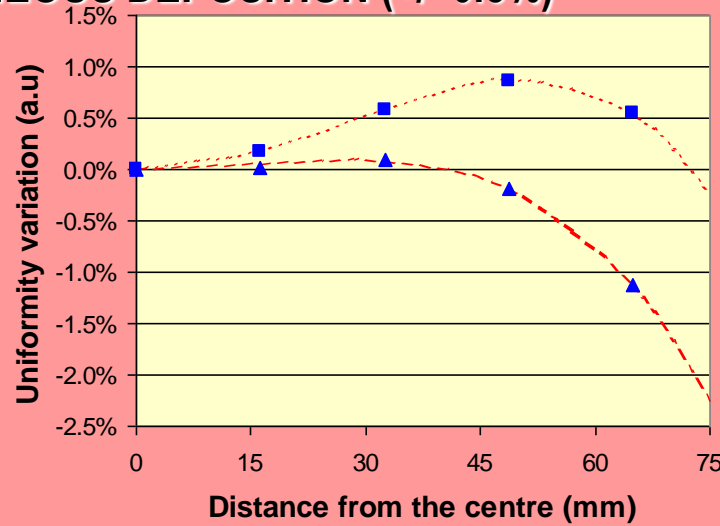
Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period																			
1	1 H																		2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo	
*Lanthanoids			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb			
**Actinoids			** 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No			

- 14 Known
- 7 Semiconductors
- 10 Under investigation
- Precursors available, not tested
- Radio-active, toxic, unstable

Macroscopic homogeneous or graded flows



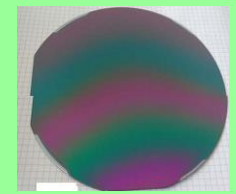
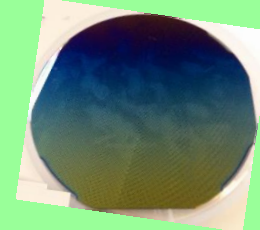
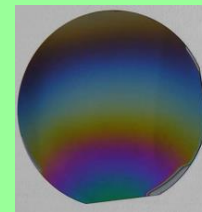
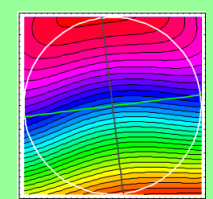
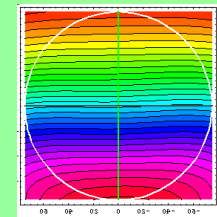
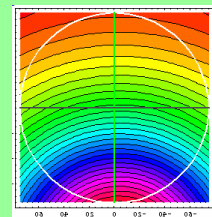
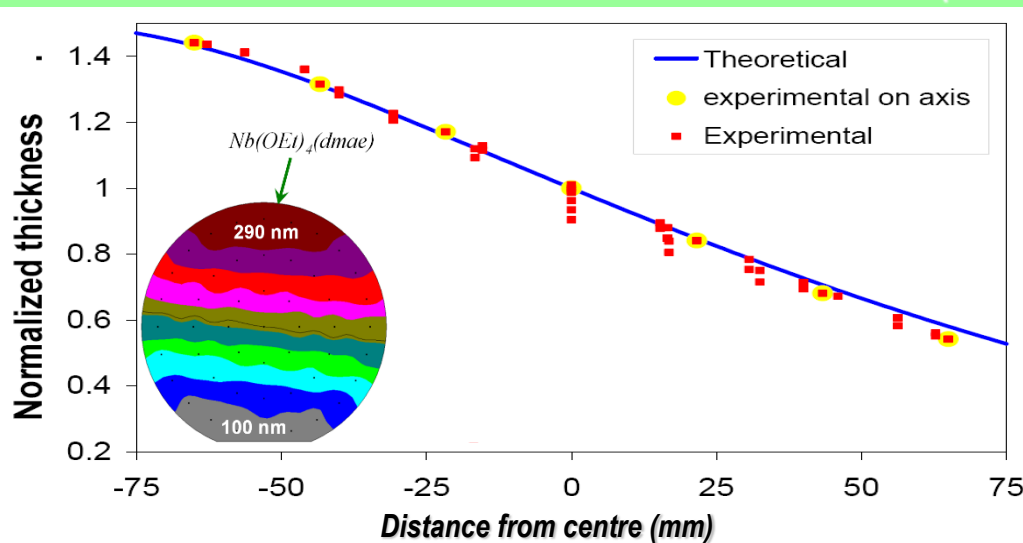
HOMOGENEOUS DEPOSITION (+/- 0.5%)



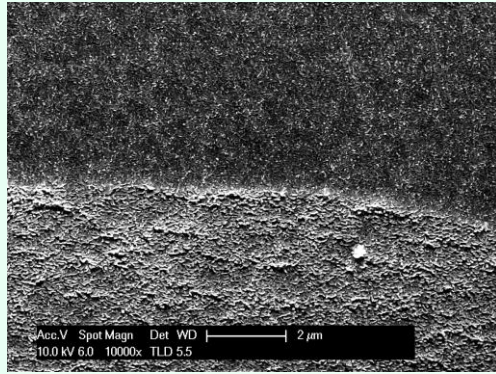
- Experimental data d=148.6 mm
- Model
- ▲ Experimental data d=158.3 mm
- Model

TiO₂ on 6" Si substrates

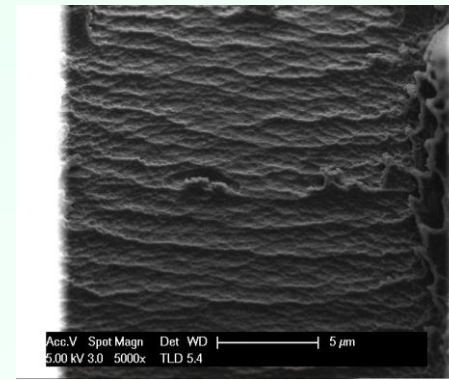
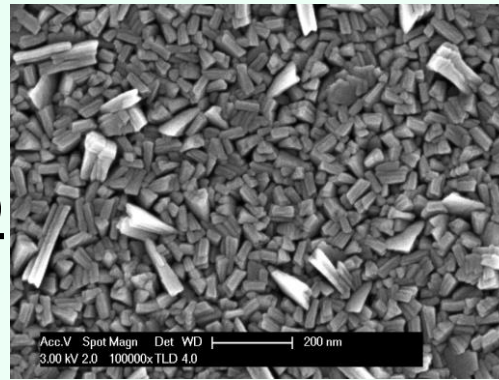
CONTROLLED GRADIENTS (variation x6)



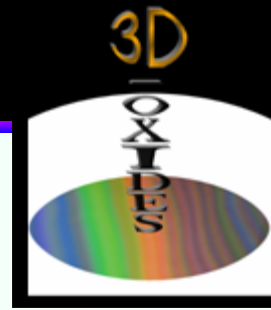
Process optimization (morphology)



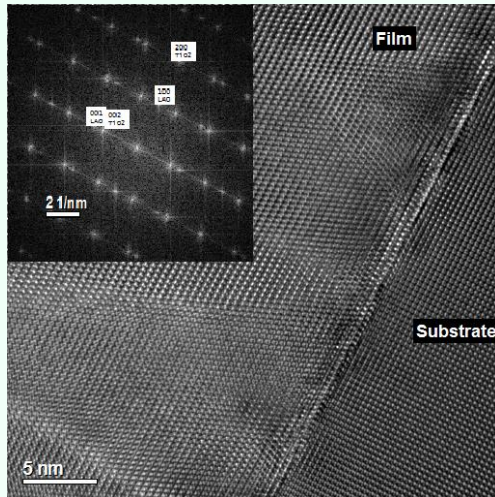
a)



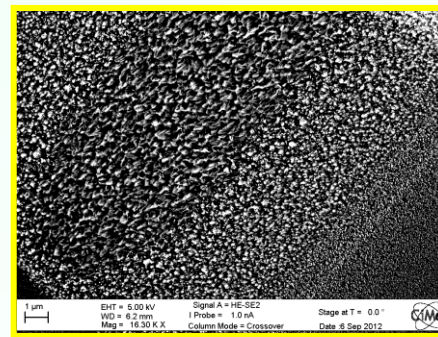
b)



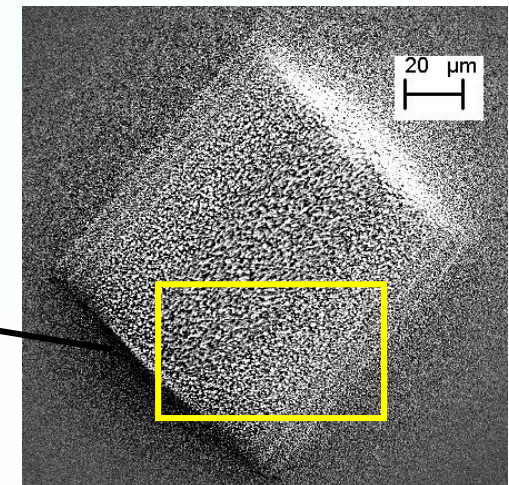
Growth rates influence on TiO₂ layers morphology

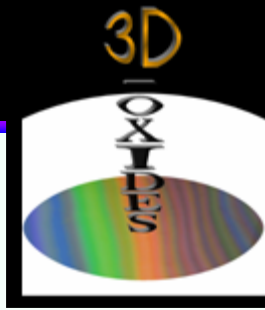


c)

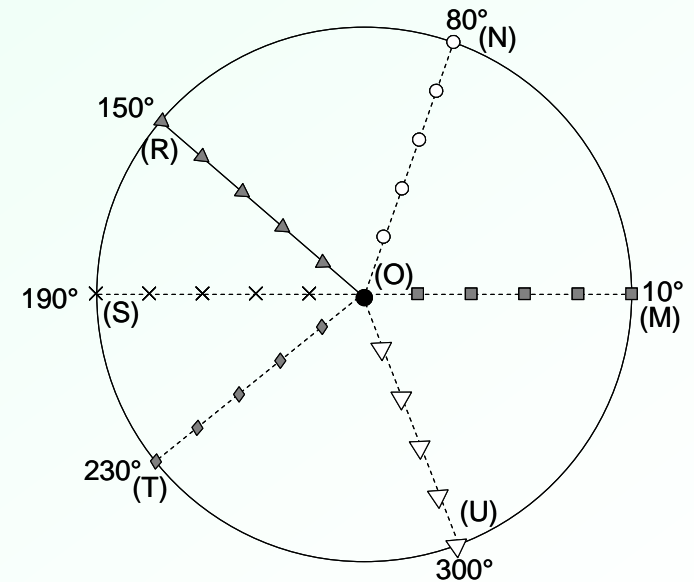
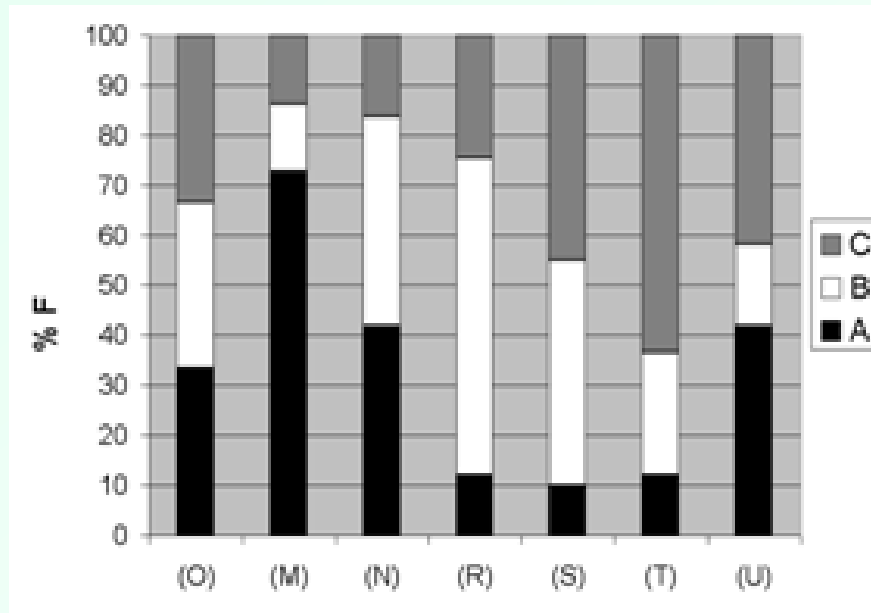


d)



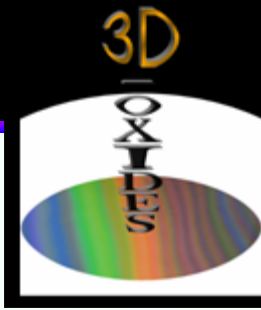


3 element combinatorial deposition : phase diagrams

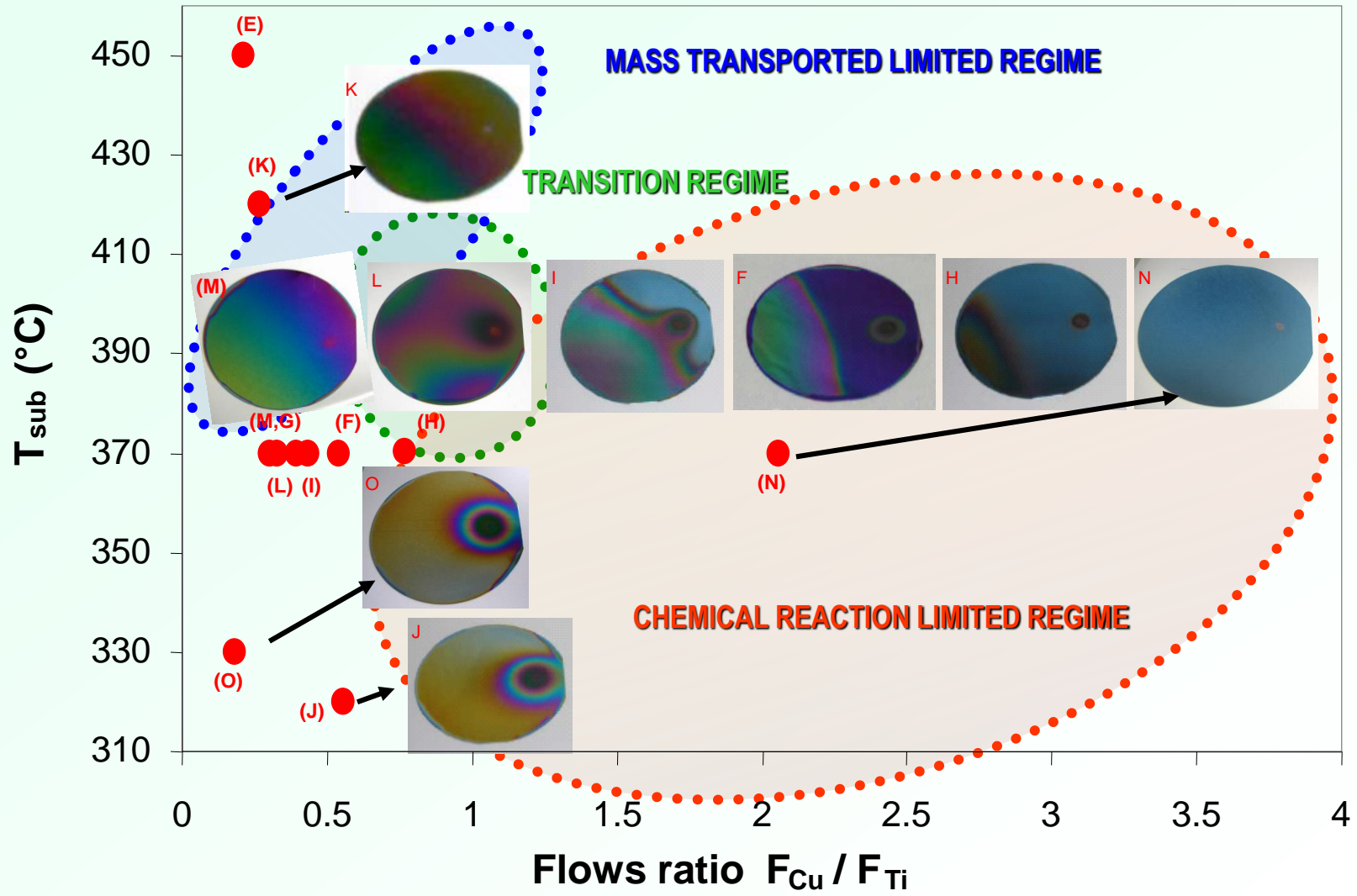


Elemental composition ratios on a 150 mm wafer substrate @ different positions for a ternary oxide thin film of the form $A_xB_yC_zO_n$

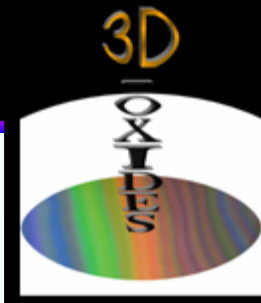
Process optimization (chemistry)



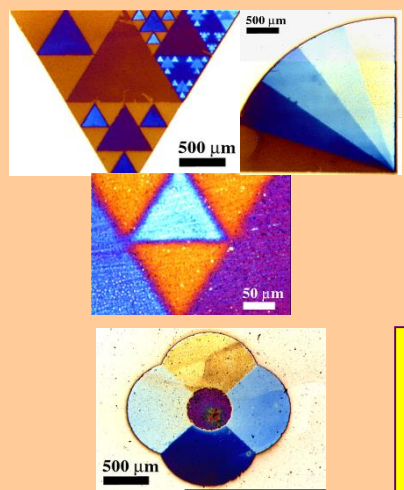
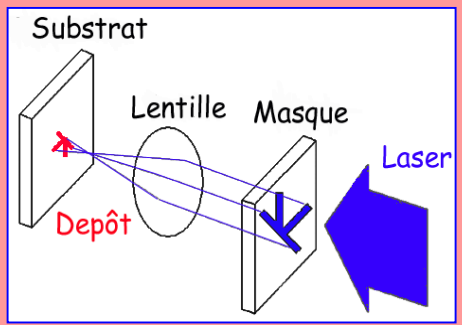
Process diagram (substrate temperature vs precursors flow ratios)



Single step patterning by laser



Deposition/ablation/etching is limited to the irradiated area:

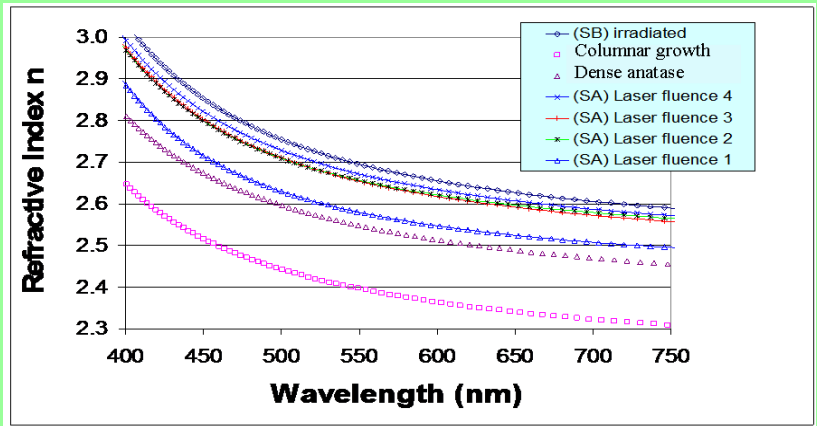


Selective deposition for real 3D patterned films

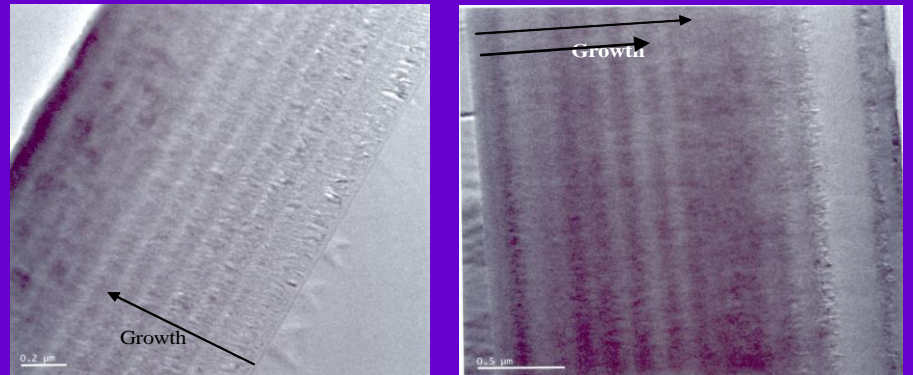
Deposition at lower temperature even on polymers

TiO₂ on various substrates

Film densification and refractive index fine tuning

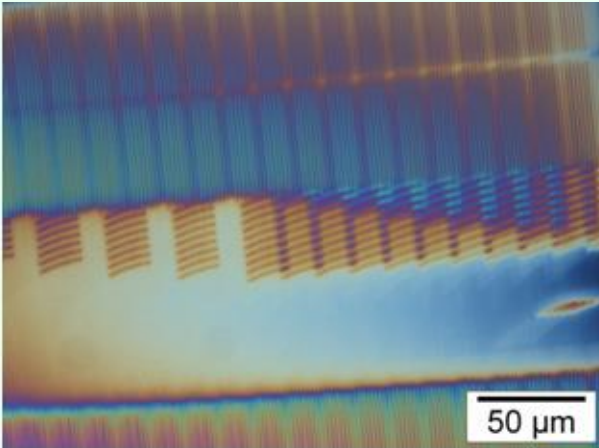
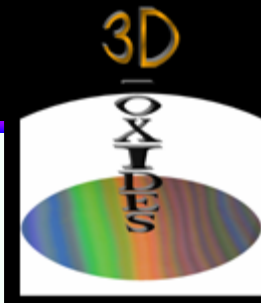


Selective doping during the growth

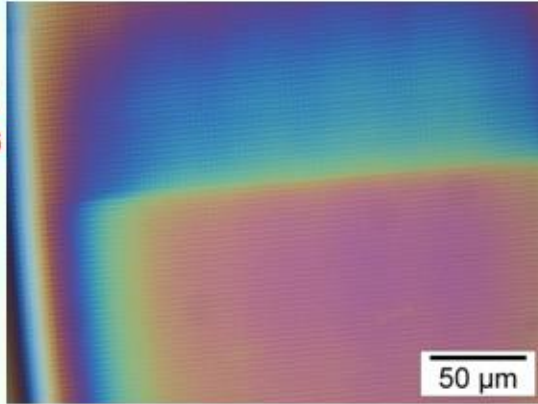


Thermal and laser assisted deposition of same sample Ti-(Ti_(1-x)Si_xO₂) multi-layers

Stencil mask thin film patterning

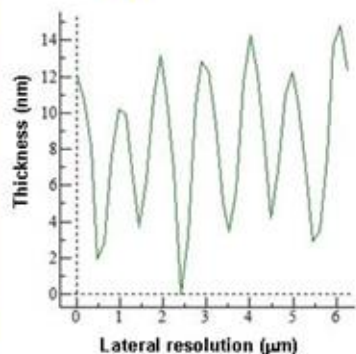
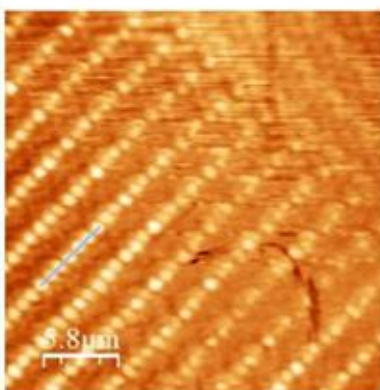


Real colors
Optical microcopy images
showing interference colors
due to TiO₂ different
thickness

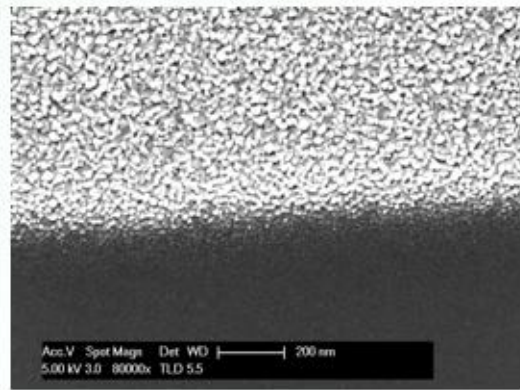


Complex materials with graded composition and thickness can be achieved by superposition of 2 or more elemental patterns

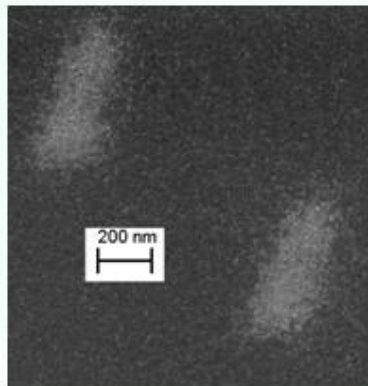
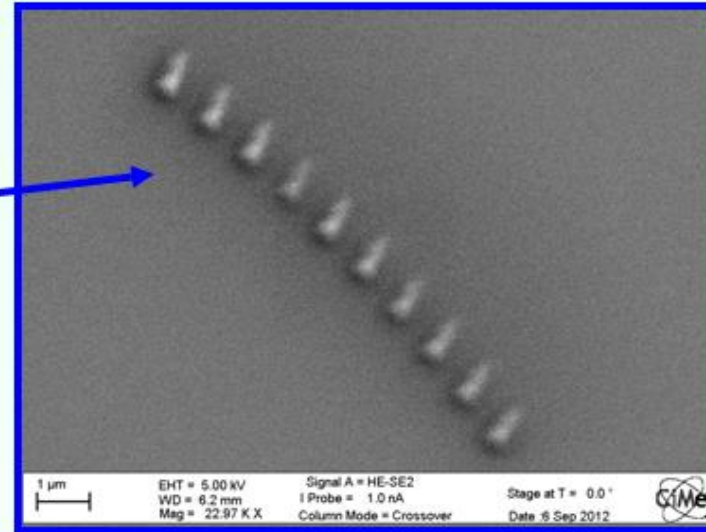
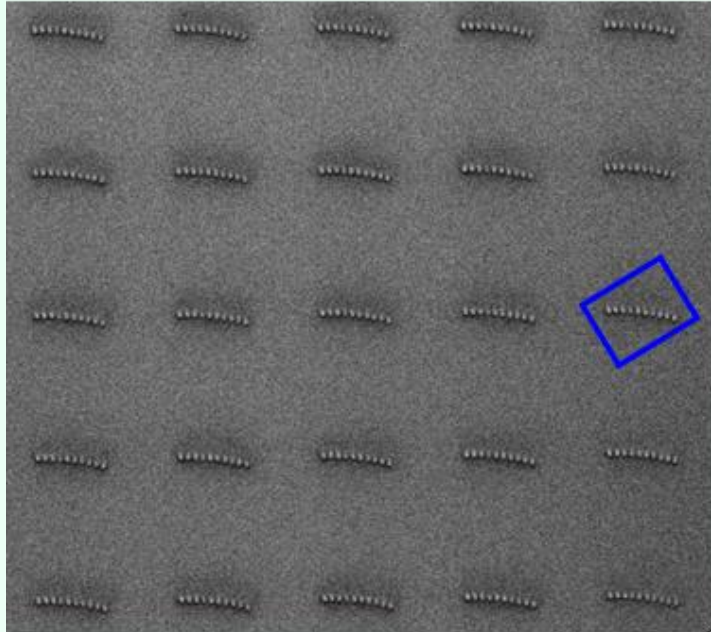
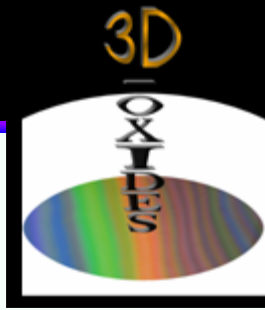
AFM Measurements
showing dots with 500 nm
resolution



SEM measurements
showing very high border
resolution (<100 nm)

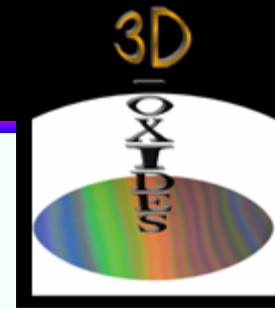


3D submicron structures



Best resolution achieved
around 200 nm

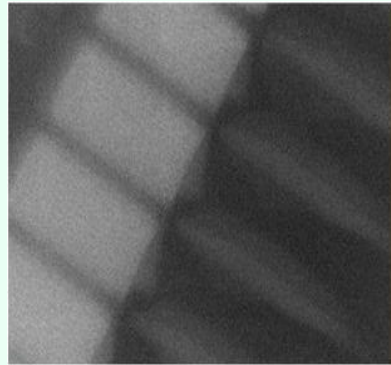
Chemical patterning: separated elements



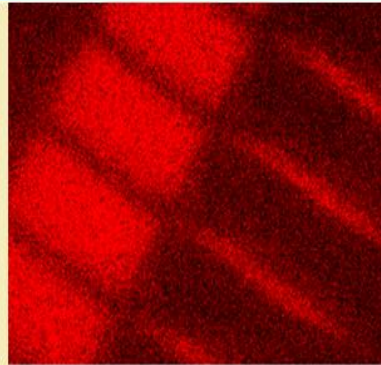
SEM image

50 μm

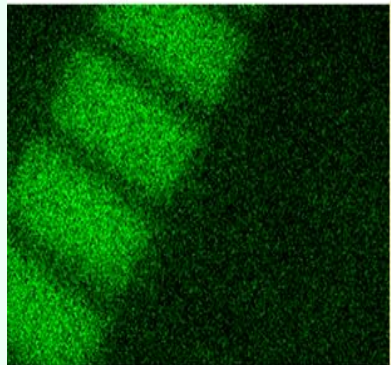
Oxygen mapping



Electron Image 1

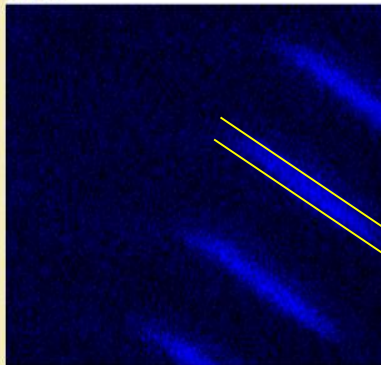


O Ka1



Ti Ka1

Titanium mapping



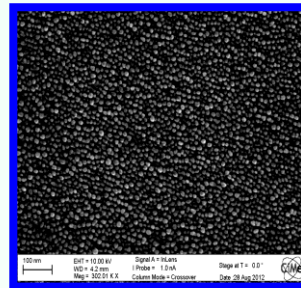
Nb La1

Niobium mapping

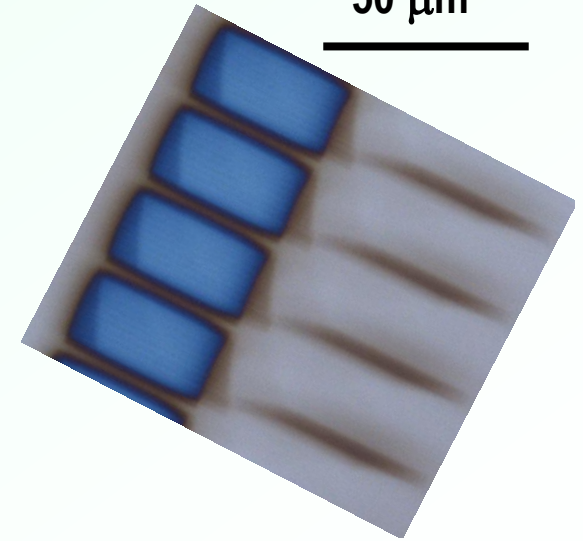
5 μm

SEM top-view

500 nm



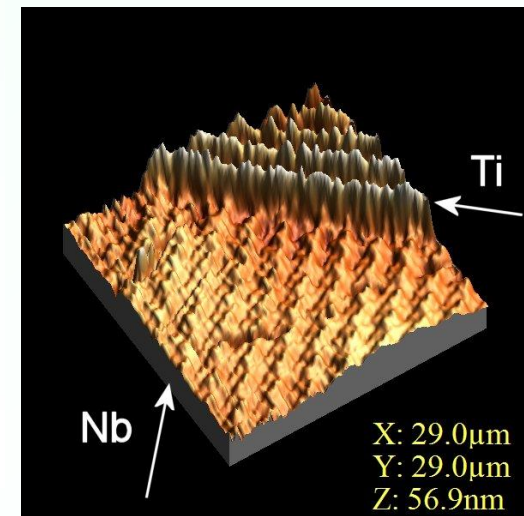
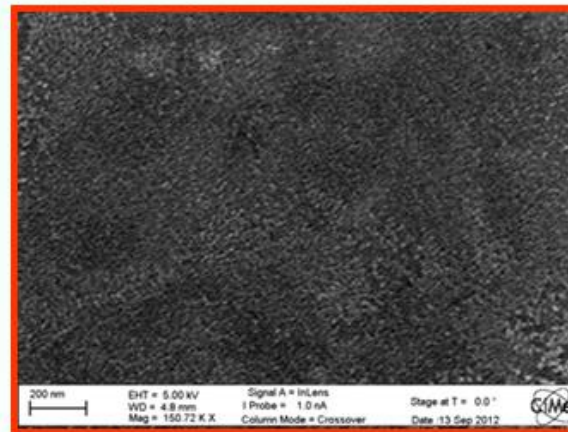
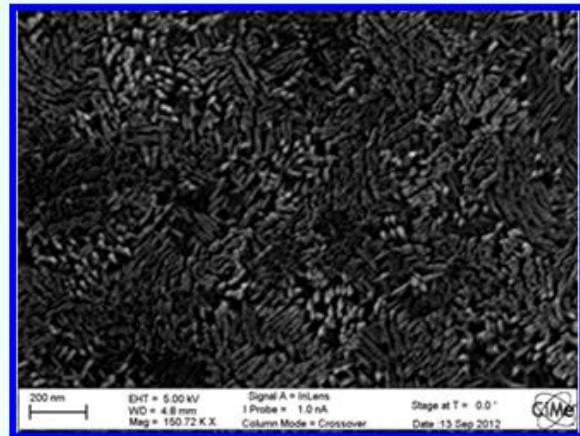
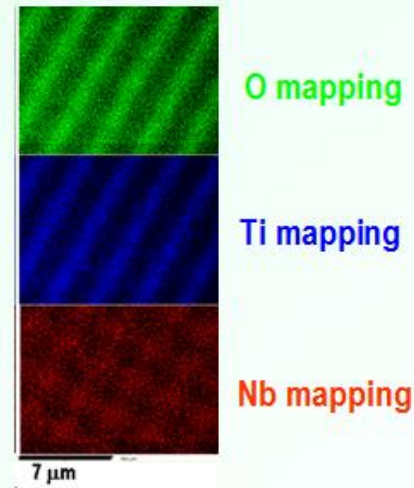
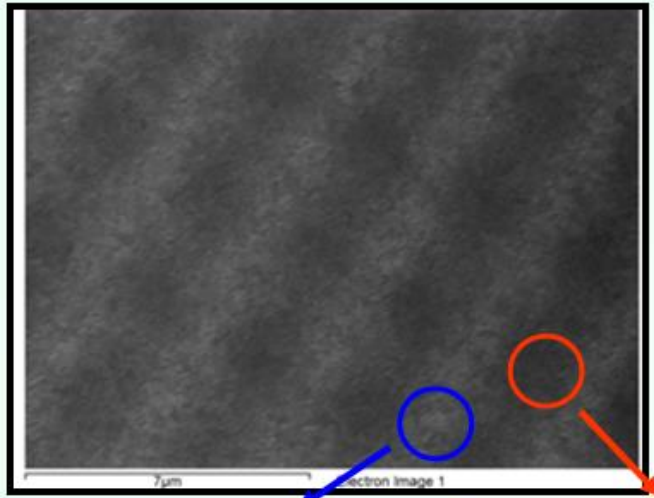
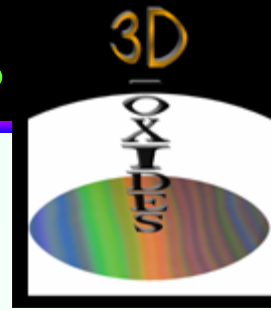
50 μm



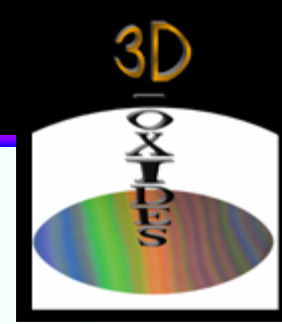
Variable chemical composition from 95-5% to 5-95% Ti/Nb ratio by EDX

Optical microscope picture of the layer thickness 80 nm for TiO_2 , 40 nm for Nb_2O_5

Chemical patterning: superposed elements

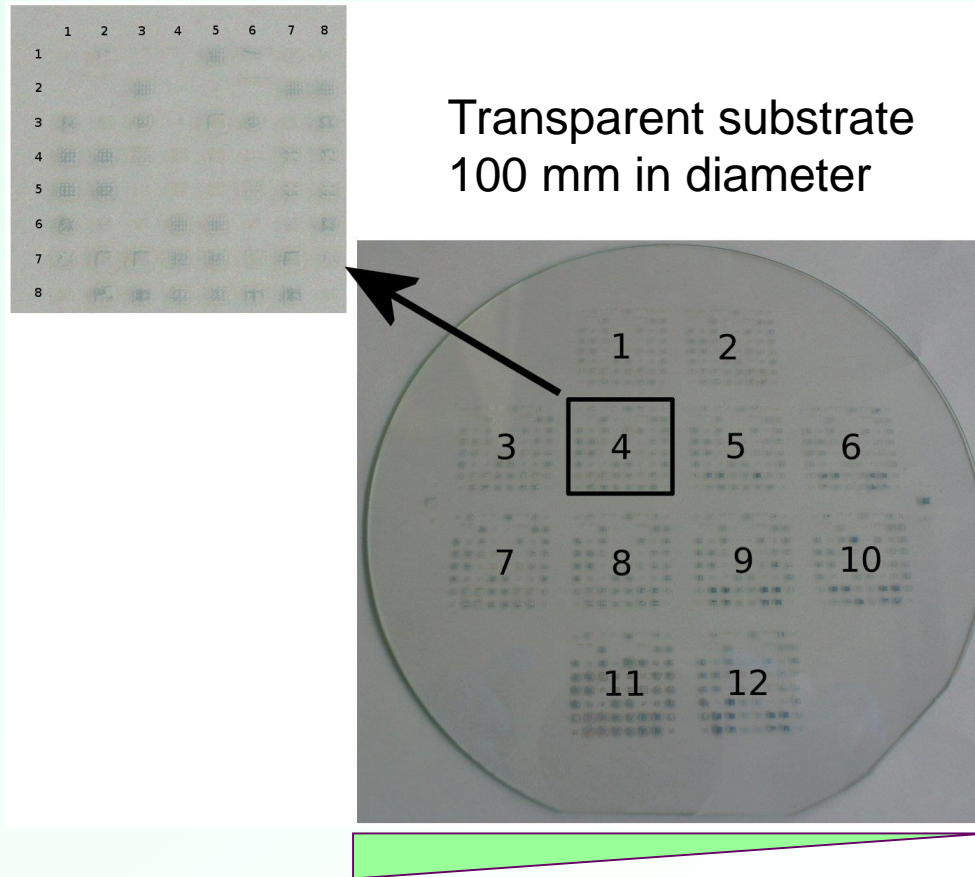


Disruptive nano-combinatorial



Nanostructure
shape variation

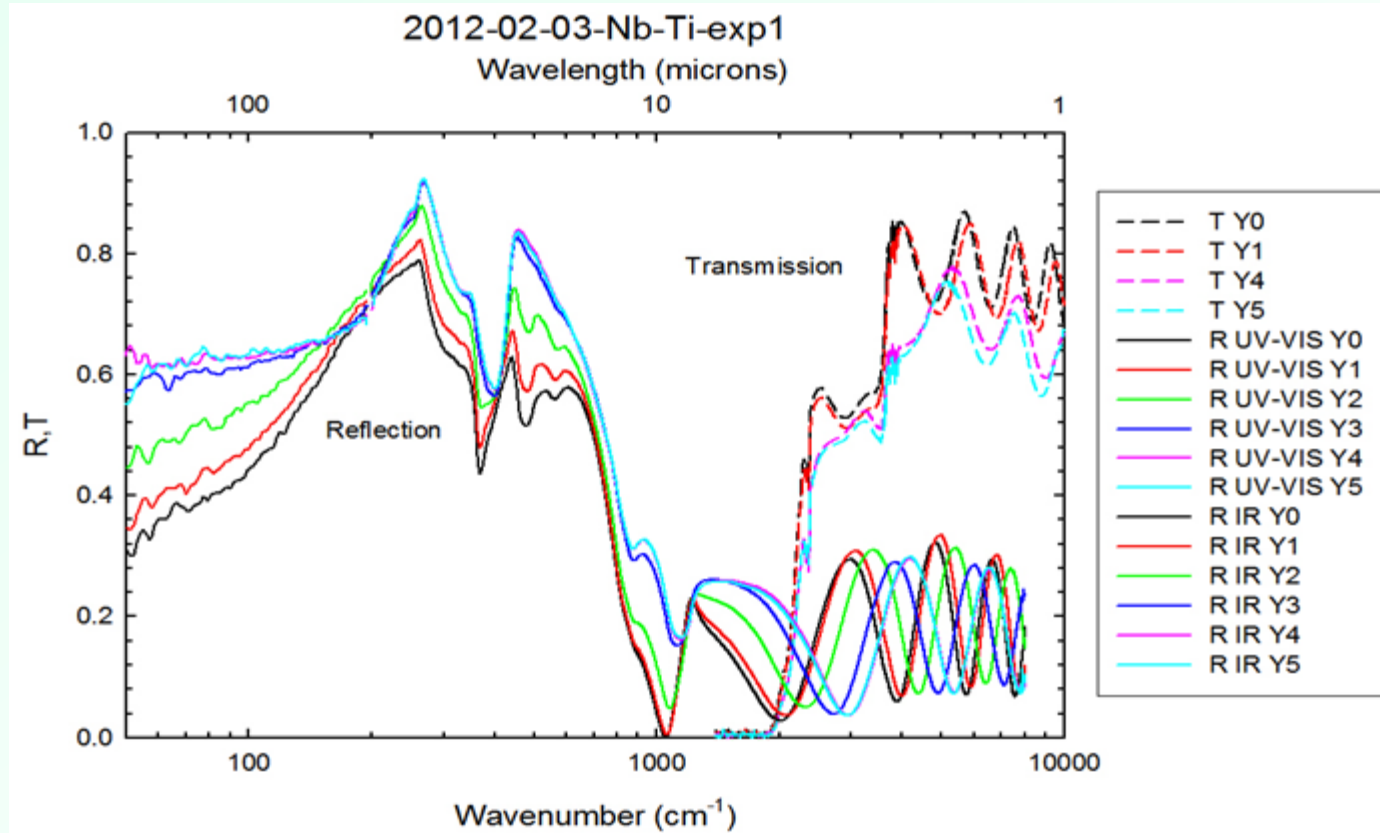
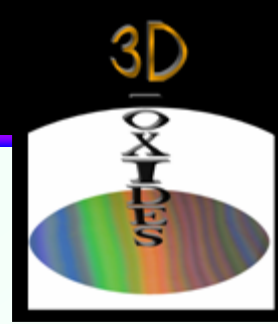
Nano-structures
size variation



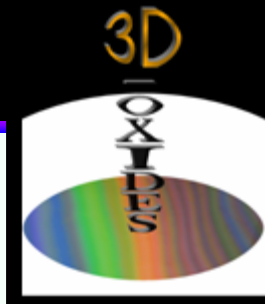
Thickness gradient

Doping gradients

UV-Vis-IR Spectroscopy



Disruptive combinatorial approach



Main Application

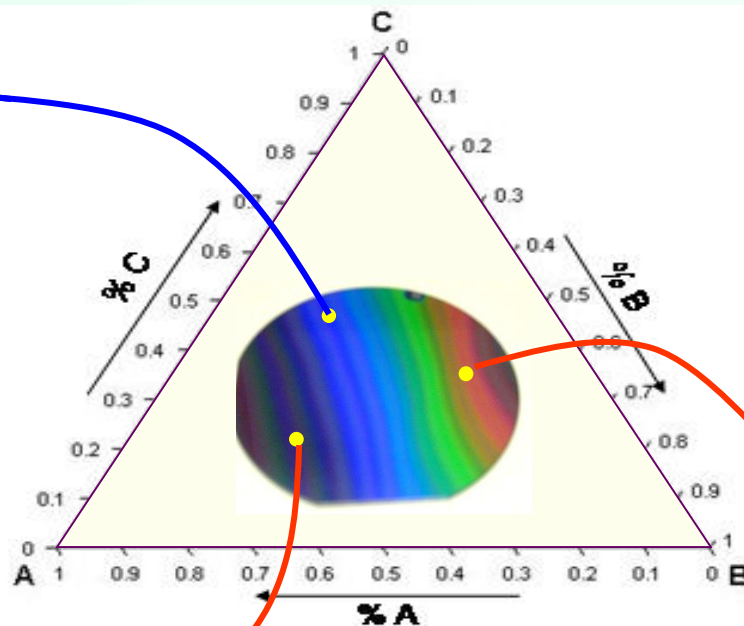


Patterning-
Architecture

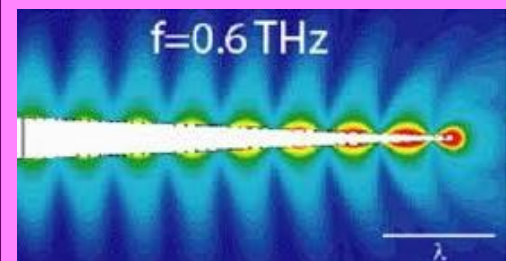


Photovoltaic
panels

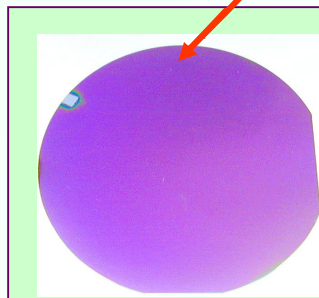
COMPLEX PHASE DIAGRAM
Chemical composition, size, shape, phase



Secondary Applications

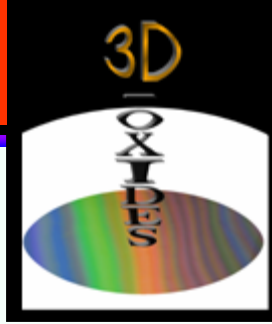


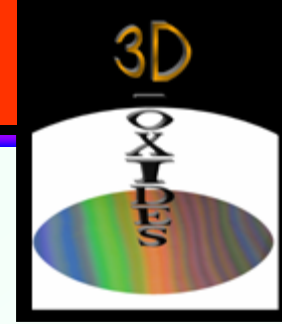
Lasers and
light sources



Memories
CPUs

Conclusions

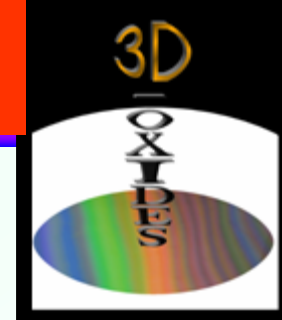




Flexibility, reliability and cost efficient

<u>Growth rates:</u>	5 nm h ⁻¹ up to 20 μm h ⁻¹
<u>Layer Quality:</u>	Epitaxy to highly porous thin films
<u>Substrate size:</u>	Scalable to any size
<u>Number of elements:</u>	Actually 3-5, but scalable to 6 or even more
<u>R&D results uptake:</u>	Very fast as the same equipment is used
<u>Process modification:</u>	Very fast: process is not geometry dependent
<u>Precursors use:</u>	Even a high as 65%
<u>Equipment life-time:</u>	Extensive (different materials/applications)
<u>Costs of ownership:</u>	Possibly down to a few 10's € / m ²
<u>Combinatorial production:</u>	Possibility to produce ≠ pieces in the same run

Enabling disruptive thin films...



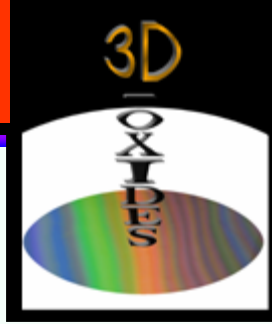
SYBILLA EQUIPMENT

Multi-element oxide thin films
even on large substrates

Complex material stacks with modified
properties via beam assistance

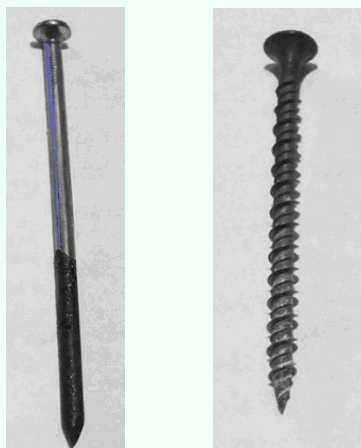
Single step 3D-patterned thin films
with complex shapes and gradients

Unique combinatorial facility for fast and
massive development of new materials



Prof Paul Muralt & Dr Veronica Savu @ EPFL

Thank you for your attention!



**SIMILAR SHAPES, SIMILAR APPLICATIONS, SIMILAR BUSINESS,
BUT A TOTALLY DIFFERENT WAY TO BUILD...**

We await you at our stand for further discussion