Inkjet printing of oxide thin films and nanoparticles with potential use for anti-counterfeiting films and patterns

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RECINTO GRAN VIA
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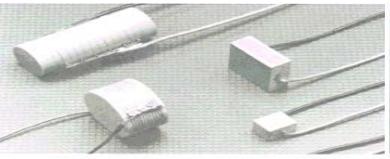
Motivation

Functional ceramic oxides

The unique and high value-added properties of **functional ceramic oxides** have enabled a significant number of scientific questions and applications

To fully exploit these developments, both the **search** for and the **implementation** of **low cost and scalable technologies** are crucial if they are to have an impact in fields such as **electronics, medicine and science, industrial processes, transport and power engineering**

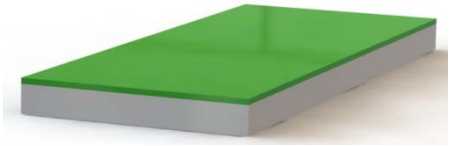




Functional ceramic oxides

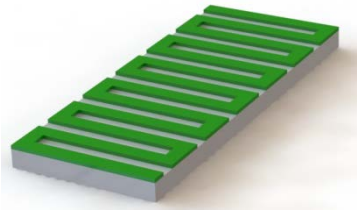
Functionalities: magnetoresistance, UV-upconversion, semiconductivity, piezoelectricity, thermocromicity, etc.

Applications → Functional devices



Films

Patterns



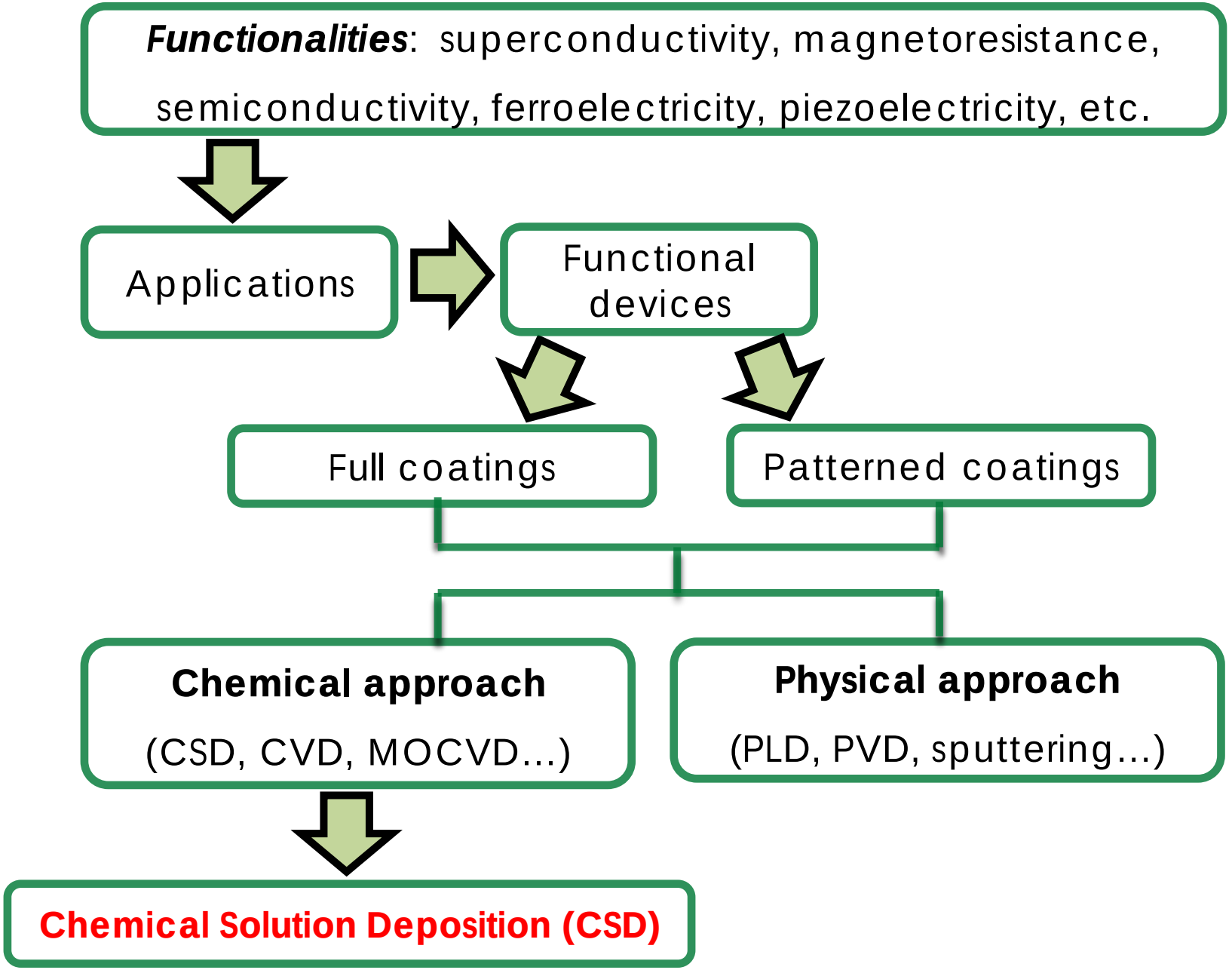
Chemical approach

(CSD, CVD, MOCVD…)

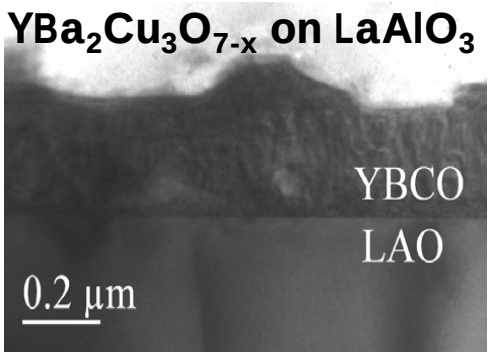
Physical approach

(PLD, PVD, sputtering…)

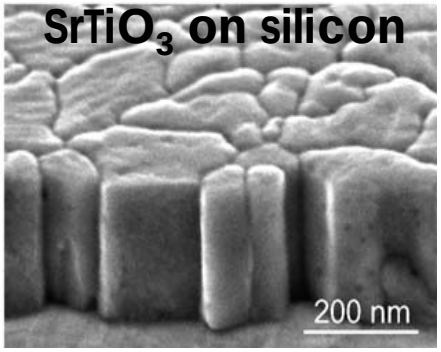
Functional ceramic oxides



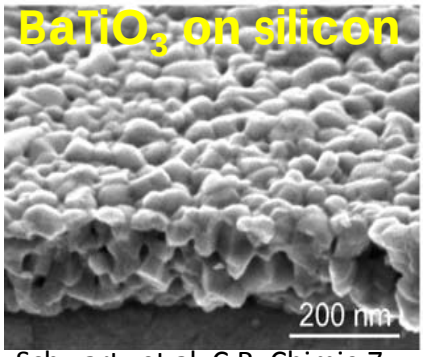
Chemical Solution Deposition (CSD) and functional ceramic oxides



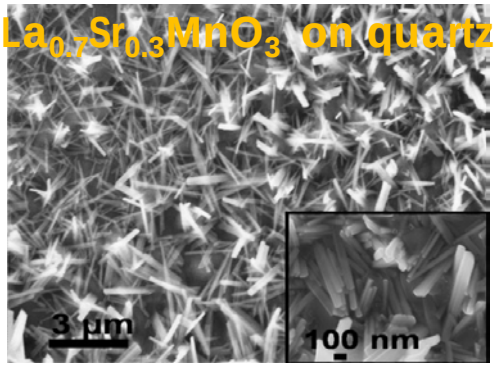
Obradors et al, (2006), Supercond. Sci. Technol., 19, S13 (2006)



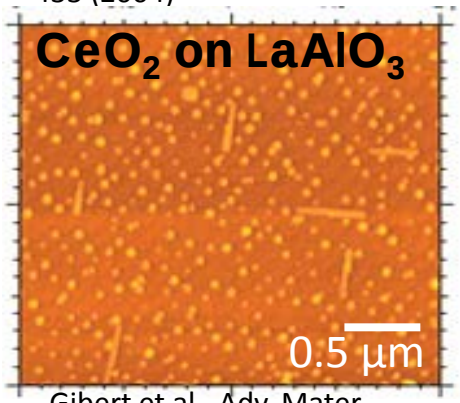
Schwartz et al, C.R. Chimie 7, 433 (2004)



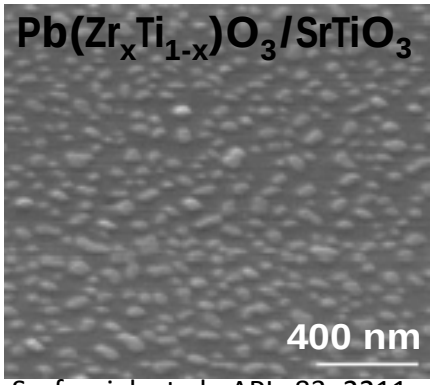
Schwartz et al, C.R. Chimie 7, 433 (2004)



Carretero-Genevrier et al, Adv, Mater., 20, 3672 (2008)



Gibert et al., Adv, Mater., 19, 3937(2007)



Szafraniak et al., APL, 83, 2211 (2003)

- **CSD…*versatile, low-cost processing and scalable to large areas***
- Deposition in standard room conditions
- High degree of control over the composition of the functional oxide

Chemical Solution Deposition (CSD)

1) Precursor solution synthesis

- Metalorganic precursors in appropriate solvents

2) Precursor solution deposition

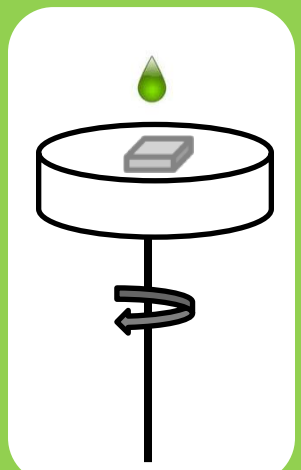
- Spin coating, dip coating, **inkjet printing**

3) Thermal treatment to obtain the ceramic oxide

- *Two-step process*: removal of the organic precursors at low temperatures (120-400ºC under special circumstances) (pyrolysis process), and crystallization into the desired ceramic phase in a second step at higher temperatures (~700ºC) (growth process).

Precursor solution deposition

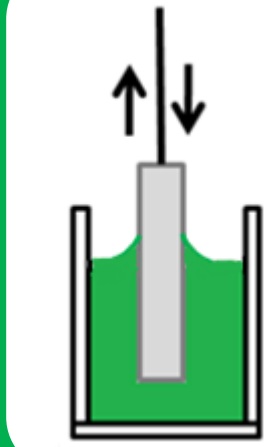
Full coatings



Spin coating

- Homogeneous thin films
- Lab scale
- Not available for long length samples

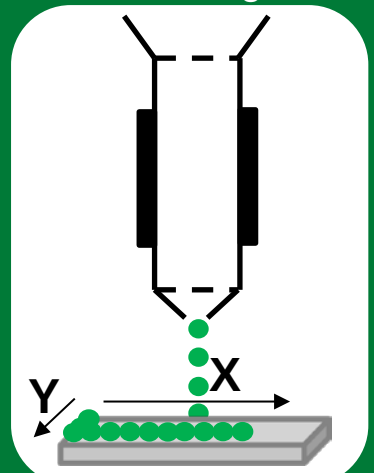
Full coatings



Dip coating

- Industrial scalability
- Deposition in two sides of the substrate
- Solution stored in an opened container:
  - Solvent loss due to the evaporation that may destabilizes the solution
  - Changes in concentration and rheological properties: variation in film thickness

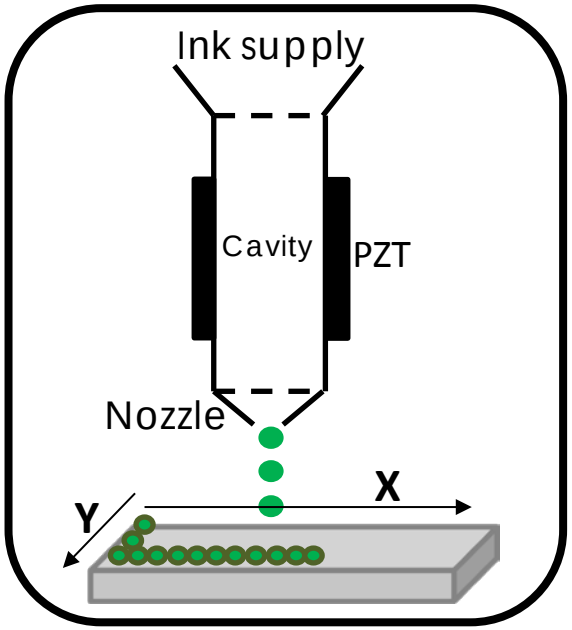
Full and patterned coatings



Inkjet printing

Precursor solution deposition

Why *inkjet printing* in functional oxide manufacturing?



Inkjet printing

- Industrial scalability in a continuous reel to reel system
- Solution stored in a closed vial → ink composition and rheological parameters control during deposition
- Possibility to control **film thickness** → high repeatability of drop ejection mechanism
- Possibility to **deposit according to patterns:** versatility to switch on the flight the deposited material and the pattern design for device manufacturing

Inkjet printing technology

Numerous printing processes

- Continuous mode
- **Drop on demand**
- Thermal inkjet printing
- Electromagnetic valve
- **Piezoelectric inkjet printing**

Broad gallery of printed materials

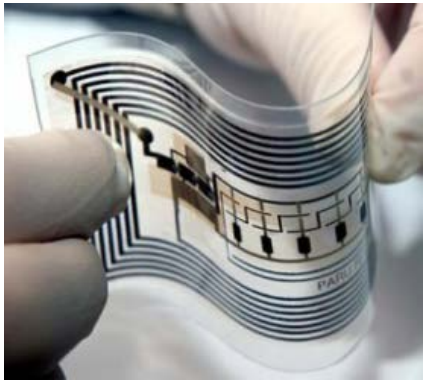
- **Functional ceramic oxides from inks**
- **Dispersion of nanoparticles**

Printed configuration

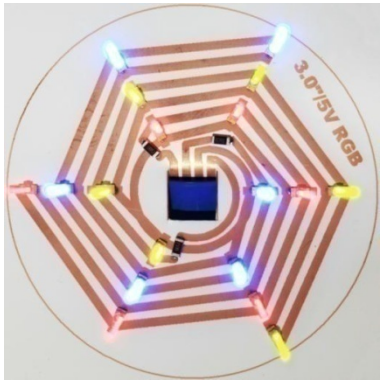
- Continuous films
- Patterns

Inkjet printing: applications

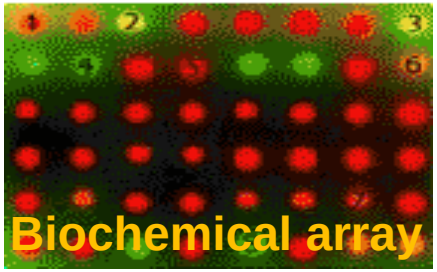
RFID



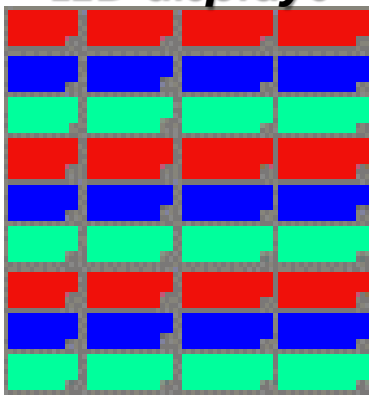
Printed boards



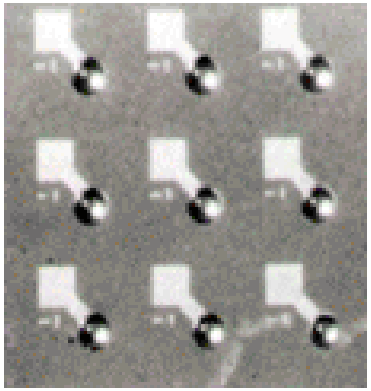
Biomedical *applications*



LED displays

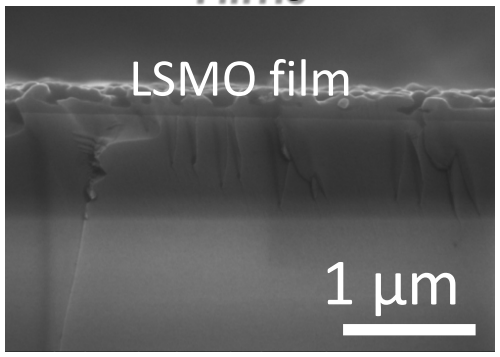


Microlenses



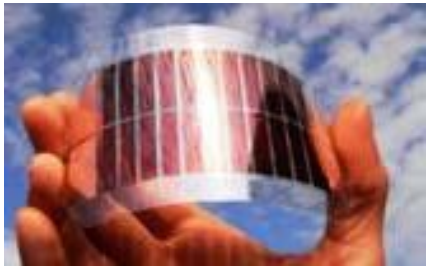
Sensors

Films



Antennas

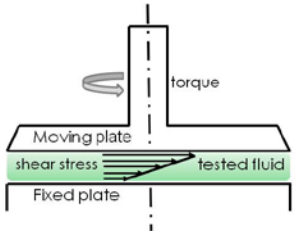
Photovoltaics



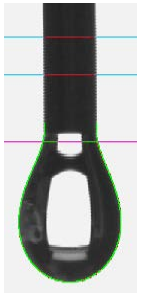
Actors involved in inkjet printing

ink

Ink properties influencing ink performances



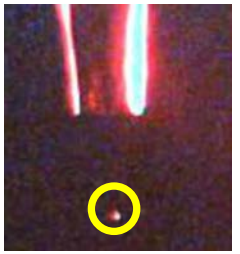
- viscosity (0.5-15mPa·s)
- Density
- Surface tension (20-30mN/m)
- Evaporation of solvent
- Stability



printhead

Drop formation process

- ink properties
- nozzle diameter
- Driving waveform

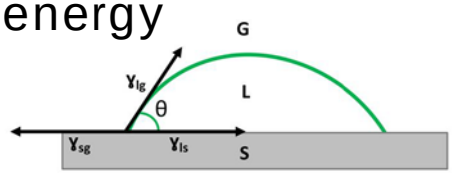


- **Drop volume**
- **Drop speed**
- **Drop aim**

substrate

Interaction ink-substrate: wettability

- contact angle
- surface energy



OXOLUTIA facilities related to inkjet printing

Laboratory tests:

Single nozzle piezoelectric printheads

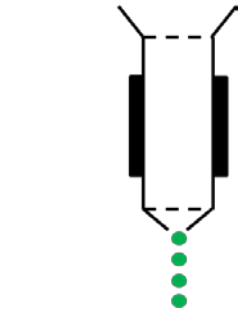
Manufacturing R+D:

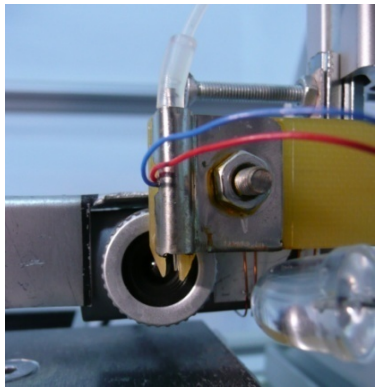
Multinozzle batch printer

Manufacturing:

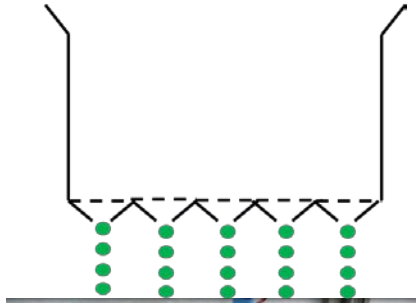
Reel to reel continuous system

Multinozzle piezoelectric printhead

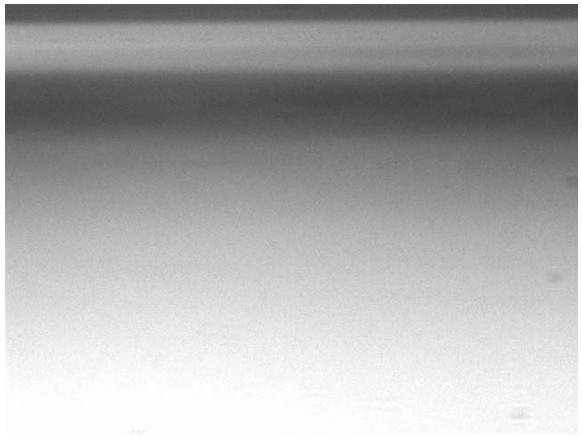




Single nozzle piezoelectric printhead ($Ø_{nozzle}$: 60µm)



512 Konika-Minolta multinozzle piezohead



Inkjet printing technology

Reel-to-Reel UP setup: continuous deposition

Batch deposition printer

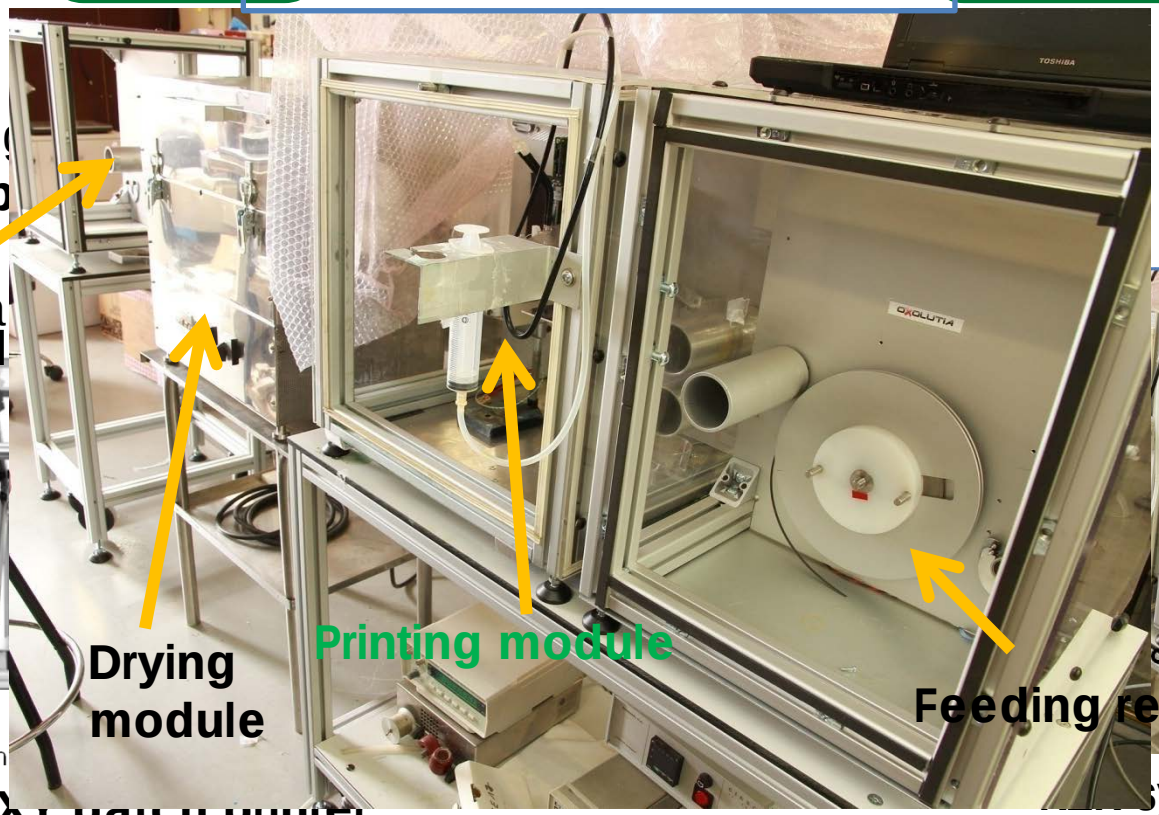
Reel to reel inkjet equipment

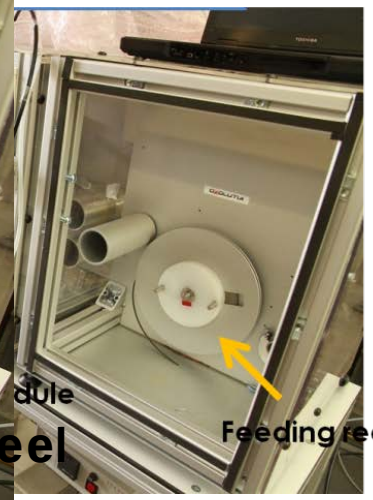
R2R deposition system

OXOLUTIA

- Screening and **drop**
- Optimiza

Take-up reel





XY batch printer

system

Potential applications: anti-counterfeiting

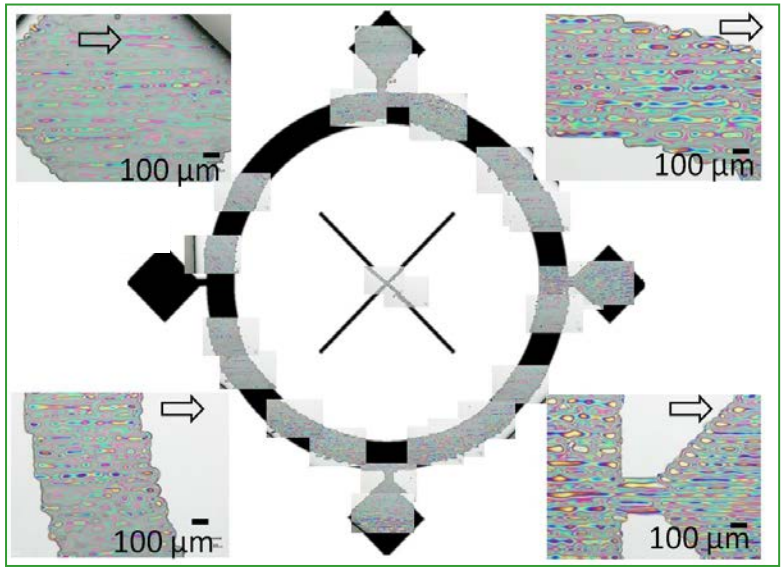
INKJET PRINTING

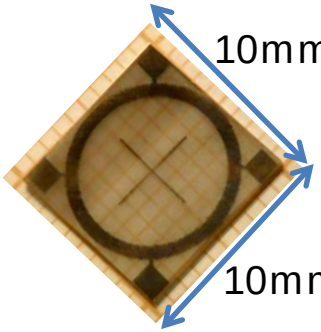
- Low cost
- Scalability
- Broad range of printed materials
- Versatility in printed materials and configurations

Anti-counterfeit printing applications with oxides?

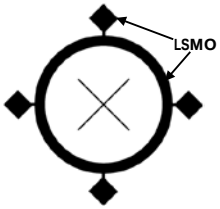
Patterning by inkjet printing: magnetoresistive patterns

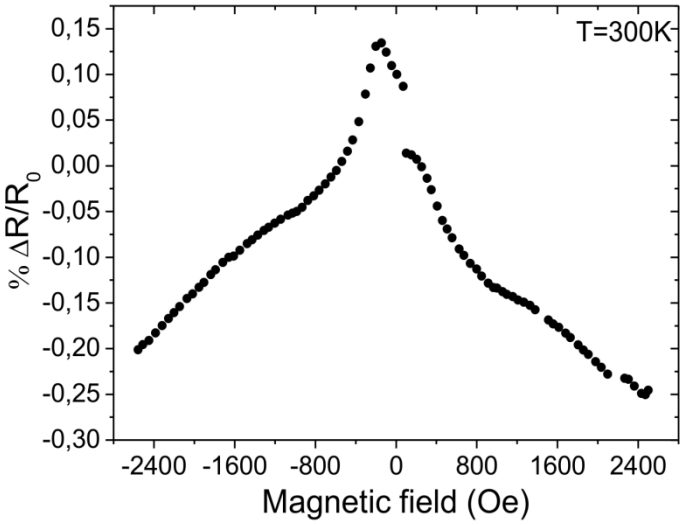
Contactless analog encoder based on Wheatstone bridge

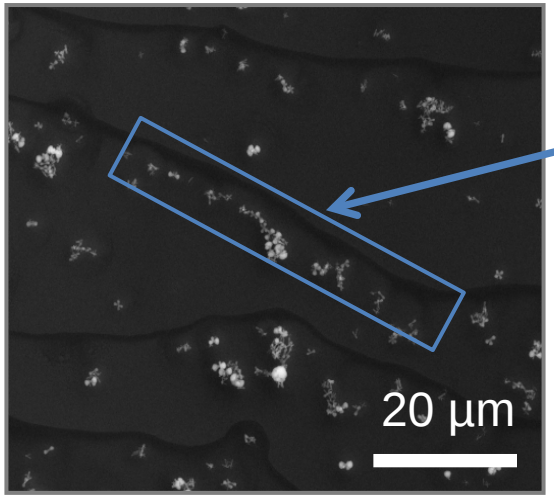


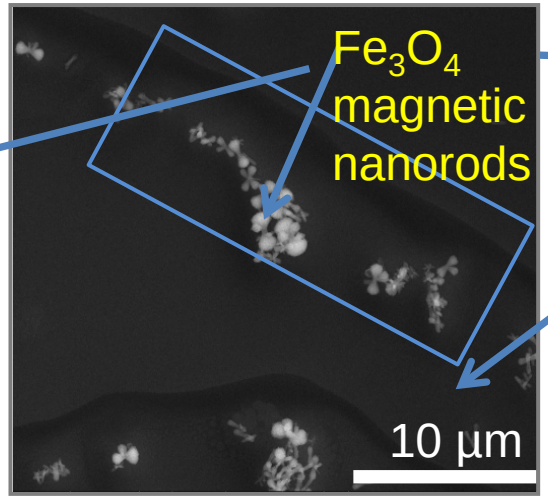


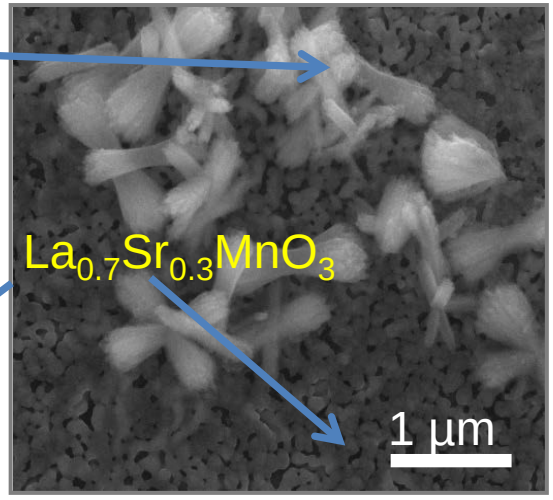
Resistance of each branch is in the range of 10KΩ with <20% dispersion between branches





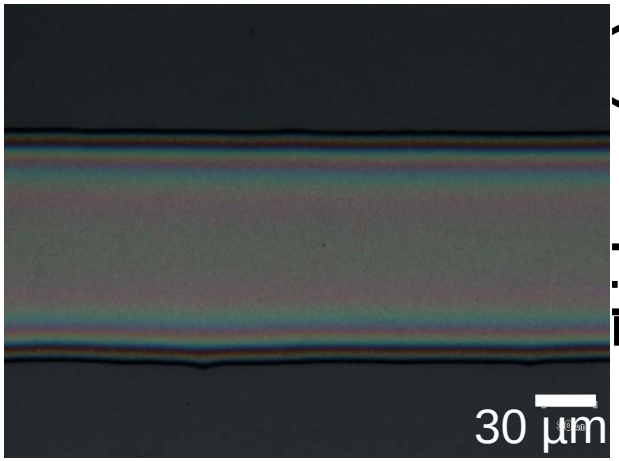






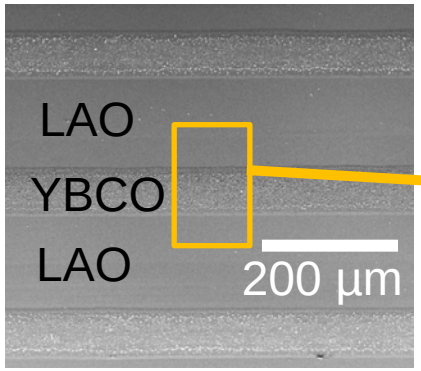
Patterning by inkjet printing: multifilamentary patterns

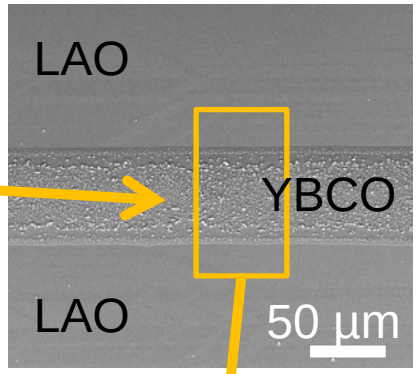
Optical microscopy after pyrolysis

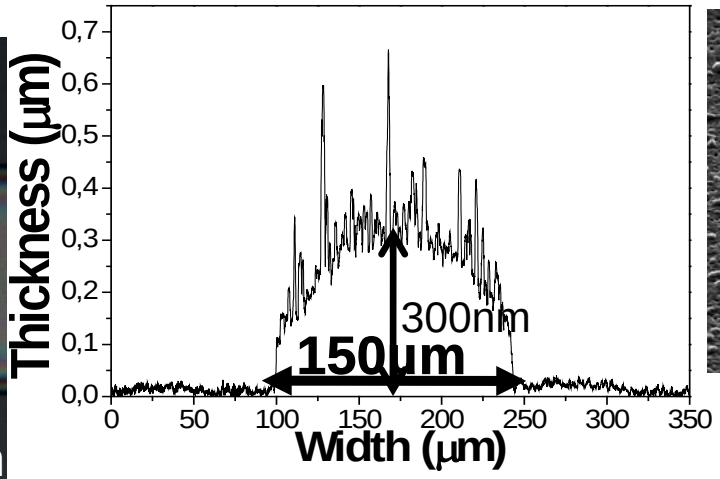


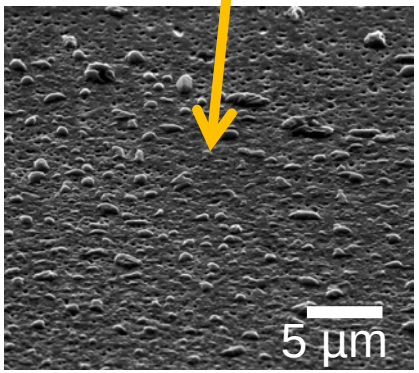
Triple perovskite

SEM after $YBa_2Cu_3O_{7-x}$ (YBCO) growth







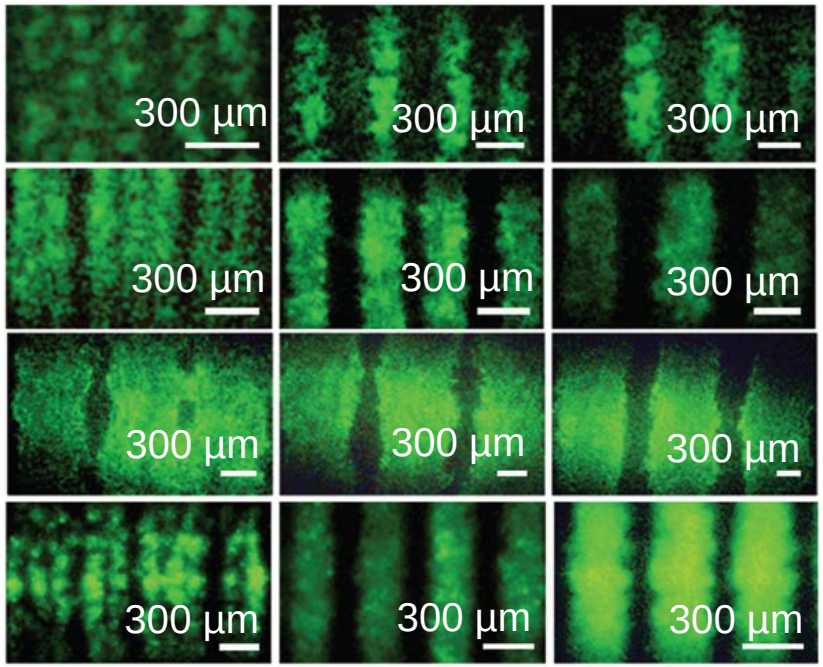


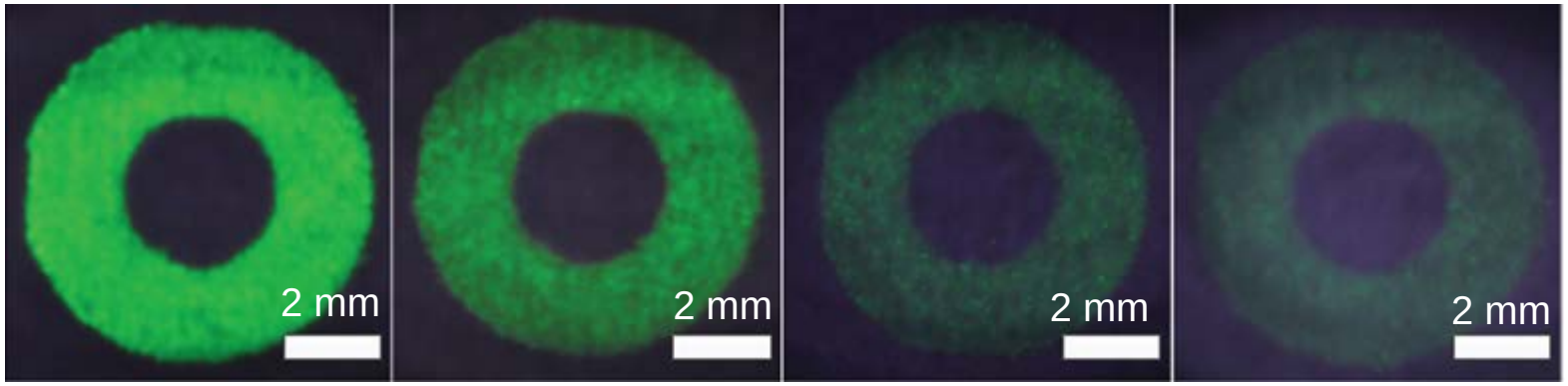
Homogeneous epitaxial tracks are obtained

Thin Solid Films 548 (2013) 489-497

Nanoparticle deposition by inkjet printing

Fluorescent nanoparticles: Eu, Yb based nanoparticles for anti-counterfeiting applications





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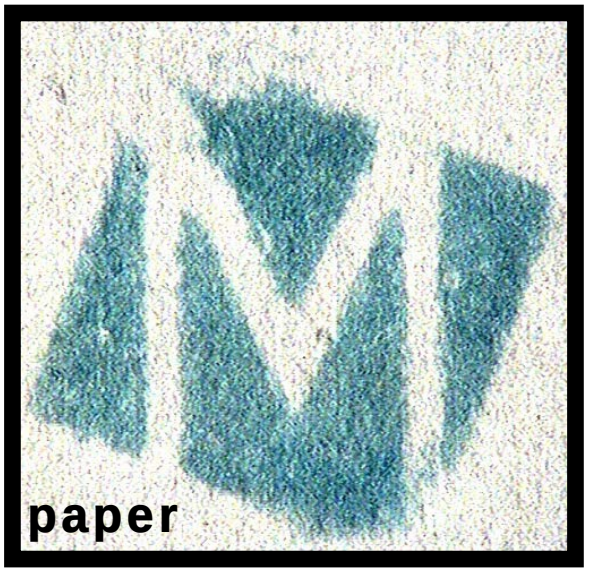
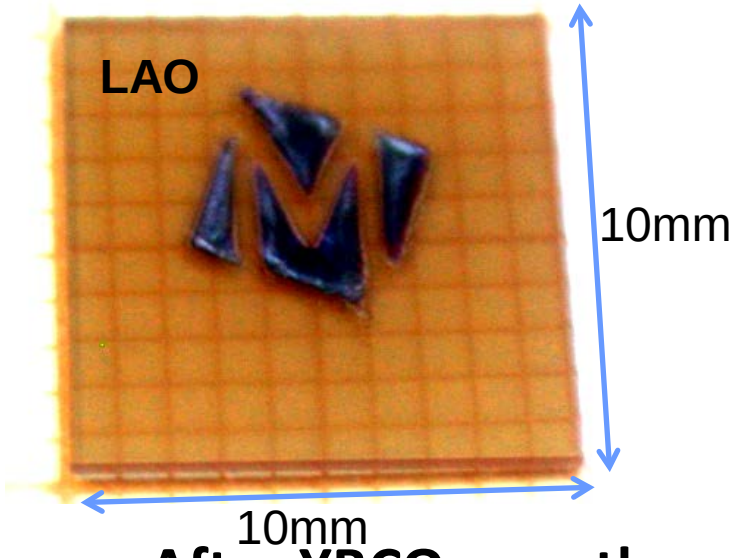
Patterning by inkjet printing: images

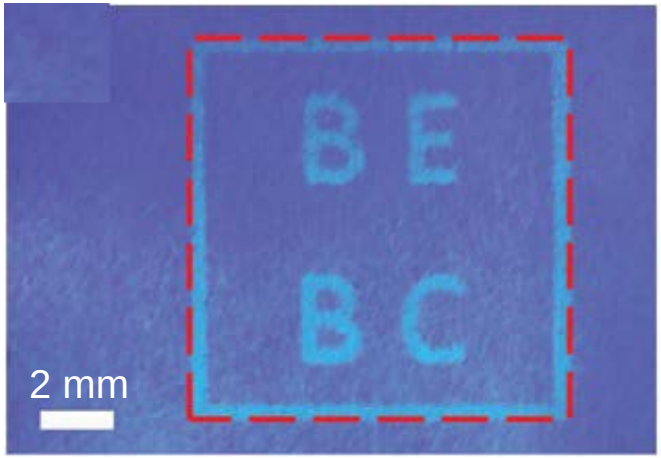
ICMAB logo



ICMAB logo by inkjet



After YBCO growth



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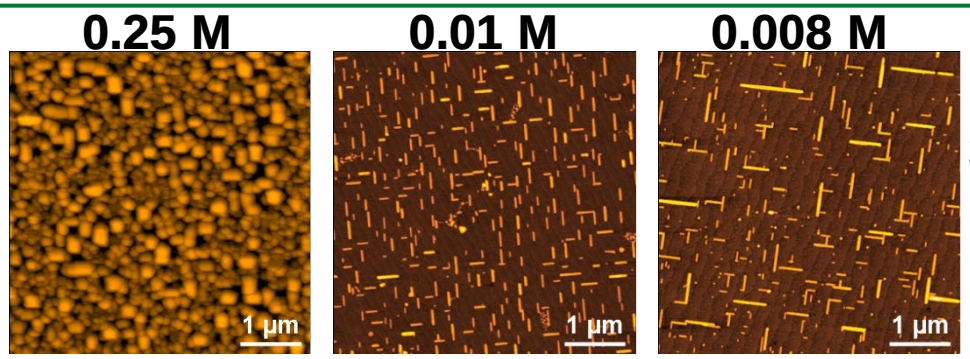
Journal of Imaging Science and Technology 55 (2011) 040304

Nanorelief patterns by CSD

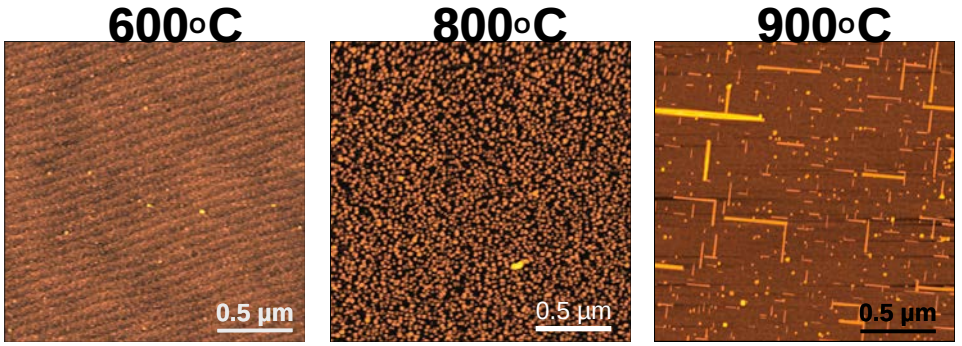
Cerium oxide nanoislands: tuning by growth conditions

- **Solutions' concentration**



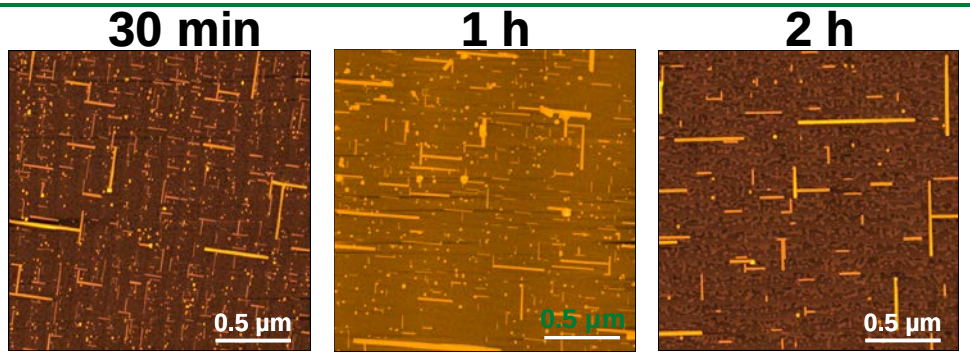
30 min-8 h
1000ºC
Ar-H_2

- **Temperature**



0.008 M
1 h
Ar-H_2

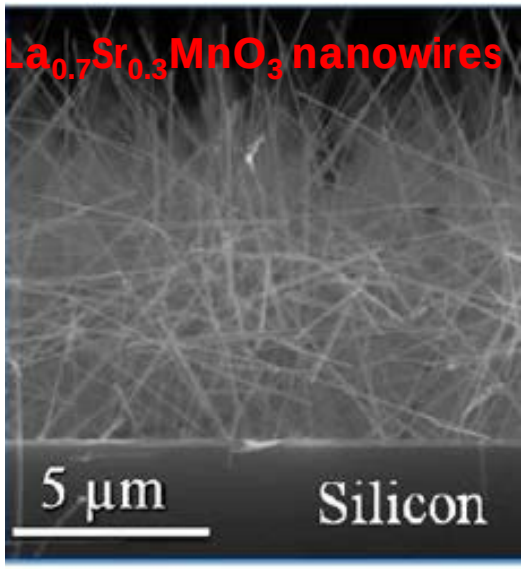
- **Time**

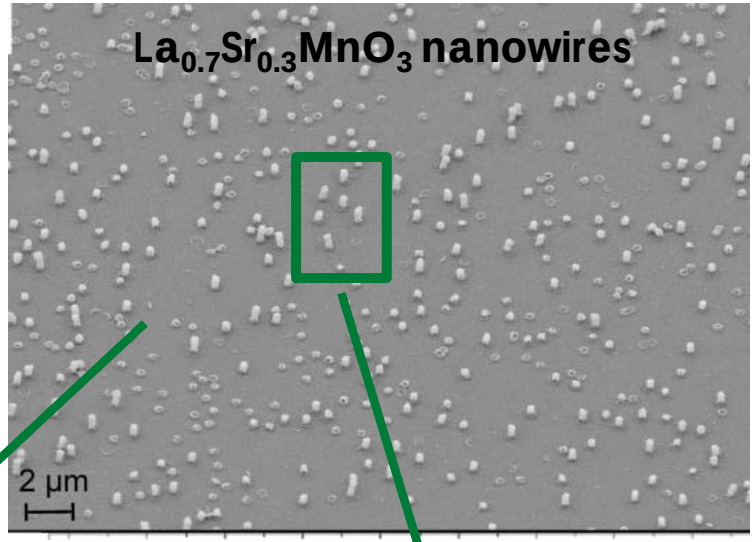


0.008 M
900ºC
Ar-H_2

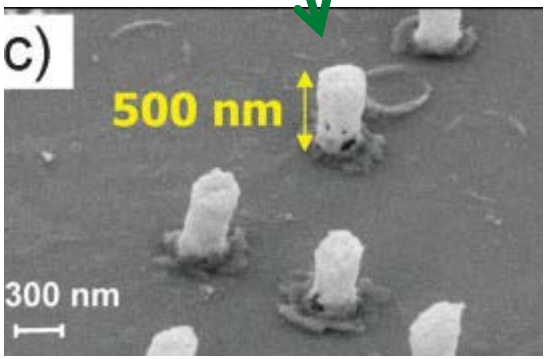
Nanorelief patterns by CSD

Manganite ($La_{0.7}Sr_{0.3}MnO_3$) nanowires





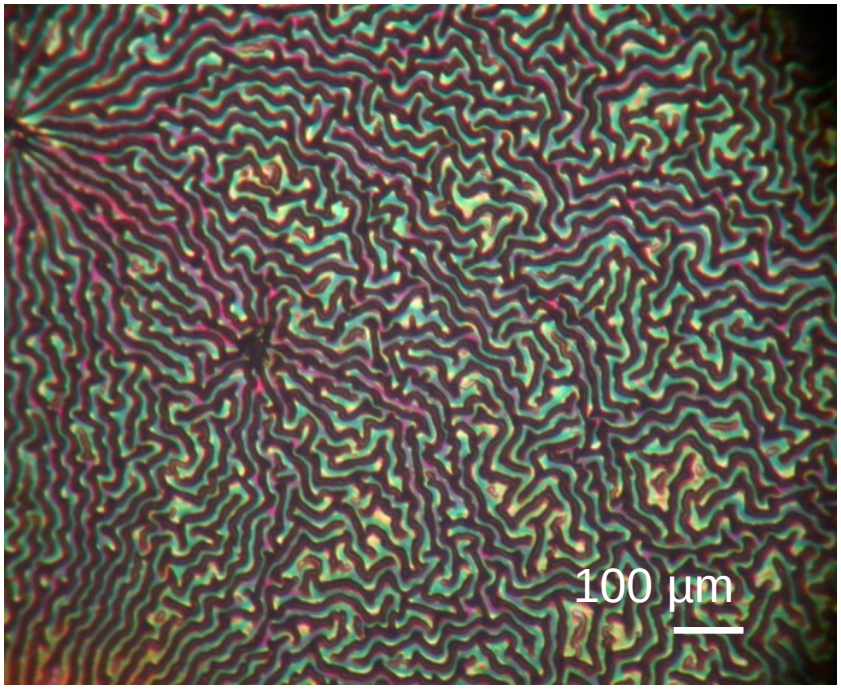
$LaAlO_3$ single crystal substrate

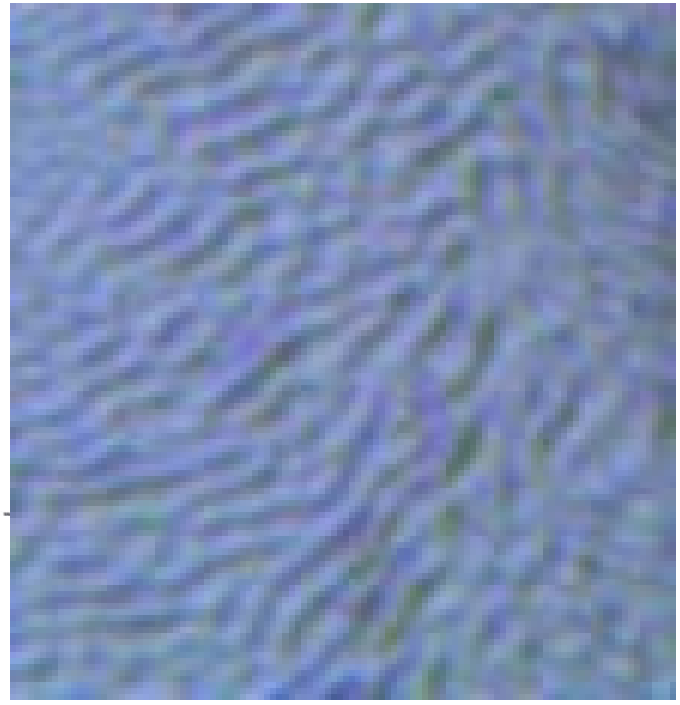


Chem Mater. 26 (2014) 1019-1028
Adv. Funct. Mater. 20 (2010) 892-897

Microrelief patterns by CSD

Stress relaxation: film inhomogeneities as identity signs





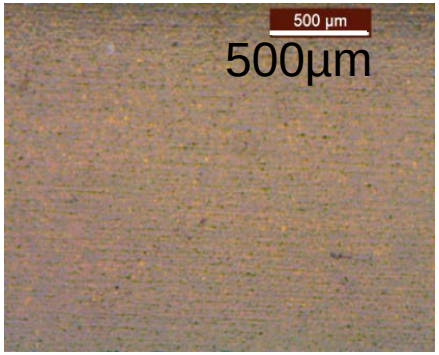
Buckling effect: stress relaxation way during thermal decomposition

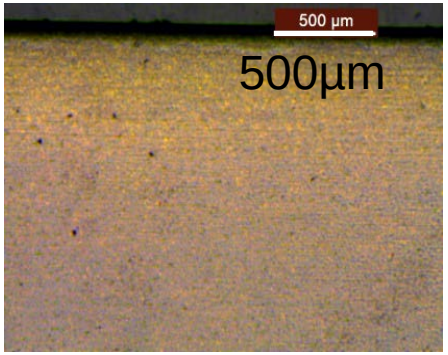
Layering by inkjet printing: functional oxide films

R2R inkjet deposition

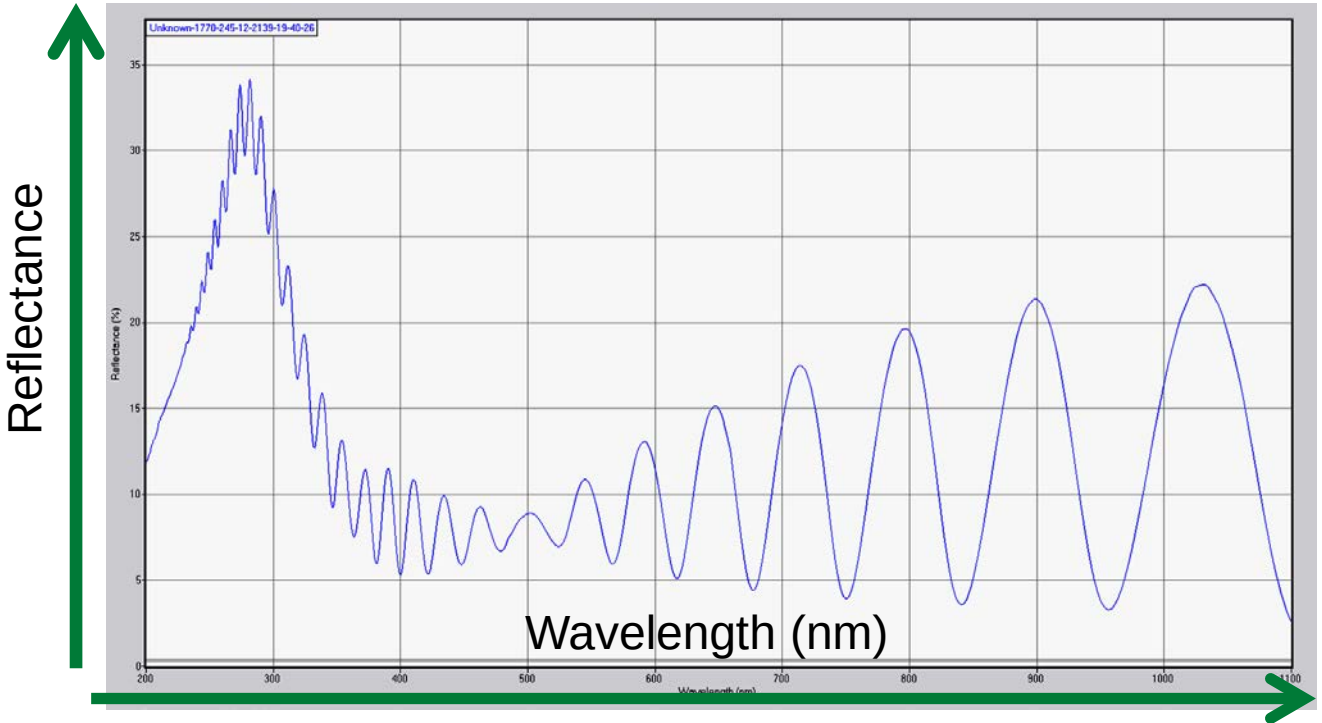
20 nm in a continuous mode

OM after $Ce_{0.9}Zr_{0.1}O_2$ growth





Sample length: 30cm



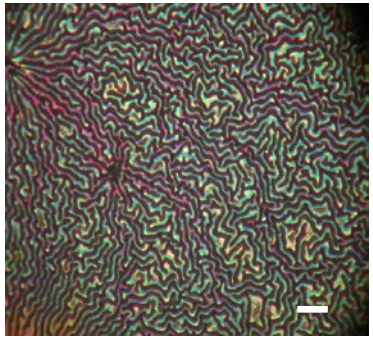
CZO films give a particular reflectometric pattern which may be used as an anti-counterfeiting system

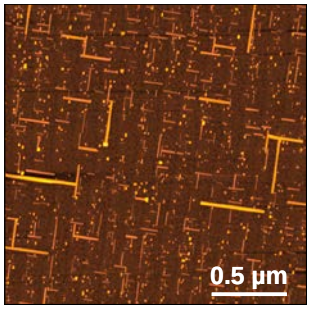
Conclusions

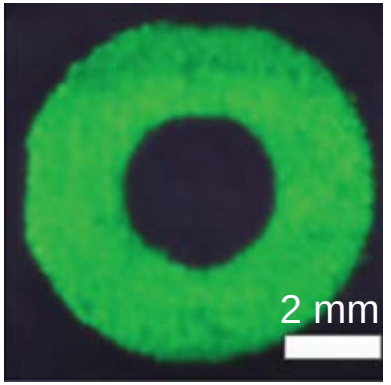
✓ Combination of the **inkjet printing technology** with the **Chemical Solution Deposition (CSD)** methodology has been demonstrated.

✓ **Long length functional oxides films and patterns can be manufactured** with a tape speed of about 36 m/h and 30 mm wide.

✓ This technology opens a broad gallery for anti-counterfeiting applications.







ICMAB CSIC Clúster MAV Clúster de Materials Avançats de Catalunya

OXOLUTIA

eurotapes EUROPEAN DEVELOPMENT OF SUPERCONDUCTING TAPES

Inkjet printing of oxide thin films and nanoparticles with potential use for anti-counterfeiting films and patterns

Thank you for your attention!!!!

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Hispack 2015

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