Functional thin films and surface nano-engineering (FUNSURF)

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Atmospheric chemical deposition of Functional materials

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Context

While deposition methods based on vacuum processing (such as ALD, PLD or sputtering) are of great interest for the fundamental study of materials, the possibility to process functional materials at atmospheric pressure is a key factor towards a future mass scale implementation.

Objectives

The research aims to develop efficient functional materials through the control and development of chemical vapor deposition techniques at atmospheric pressure suitable for large surfaces:
2 approaches are studied:
- Aerosol Assisted CVD (AACVD)
- Spatial Atomic Layer Deposition (SALD)

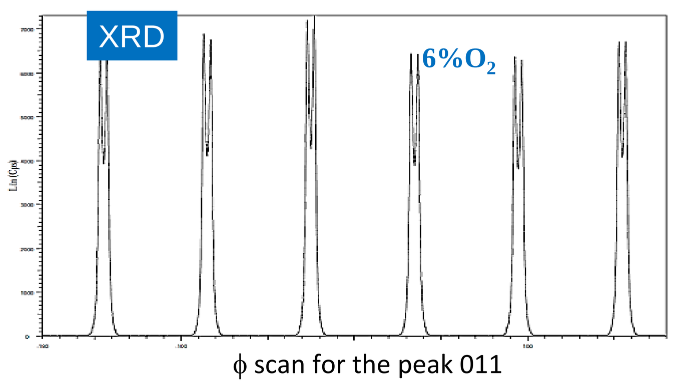
Skills & Competences

Among the liquid-source CVD techniques, **the AACVD** by the use of ultrasonic spraying allows an elaboration at atmospheric pressure under conditions leading to a very well controlled growth as illustrated by different **growth type** according to the experimental conditions:
- **epitaxial growth** [VO_2/Sapphire, SnO_2/TiO_2]
- **controlled texture** [Cu_2O]
- **3D nanostructure – nanoflowers** [TiO_2].

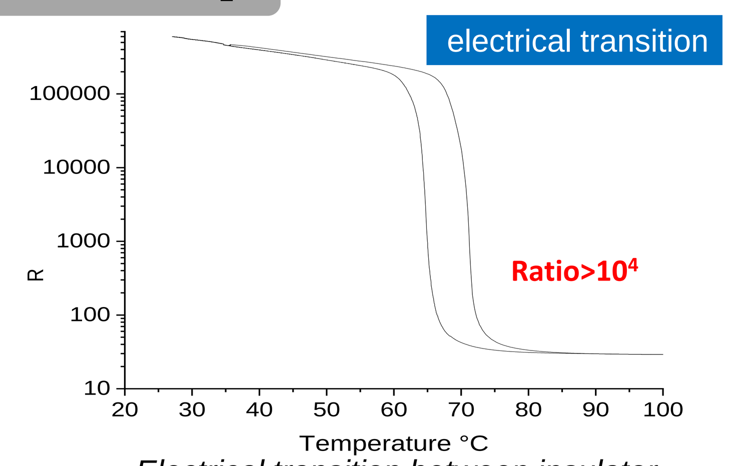
SALD:
1/ Design and fabrication of custom-made systems for different tye of substrates/materials/-applications (roll-to-roll. Hybrid materials, area selective deposition,…).
2/ Characteristics: deposition area from mm² to dm². Range of temperatures from RT to 350 ºC. Atmospheric plasma and laser activation. Substrates: syngle crystals, glass, silicon, plastic, tissue.
3/ Materials: **TiO_2, ZnO, ZnO:Al/Mg, Al_2O_3, Cu and Cu oxides, Ag and Ag oxides, MgO, MOFs, Ga_2O_3**

Aerosol assisted Chemical Vapour Deposition - AACVD

Epitaxial growth of Vanadium oxide - VO_2



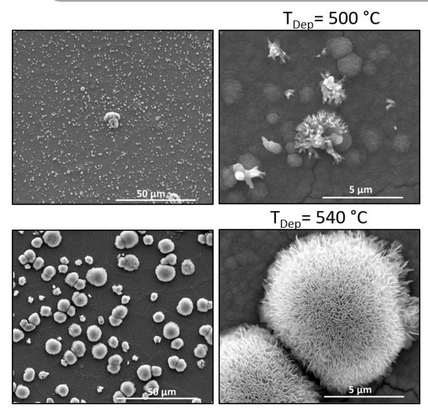
Analysis of the texture of the 011 plane demonstrating the epitaxial growth of the VO_2 film on the C Sapphire substrate deposited at 460°C



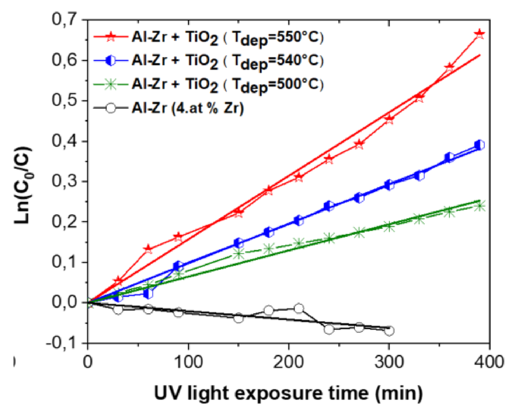
Electrical transition between insulator monoclinic phase and metallic rutile phase.

The large variation of the electrical and optical properties of VO_2 thin films can be exploited for RF commutation switch, in Mott FET transistor and in thermochromic devices.

TiO_2 coatings combining anticorrosion and antifouling Properties : 3D nanoflowers



Growth of TiO_2 nanoflowers by adjusting the deposition temperature.



Kinetic of orange G degradation by the AlZr/TiO_2 thin films under UV light vs irradiation time.

Photocatalysis enhacement thanks to the high specific surface area of the microflowers

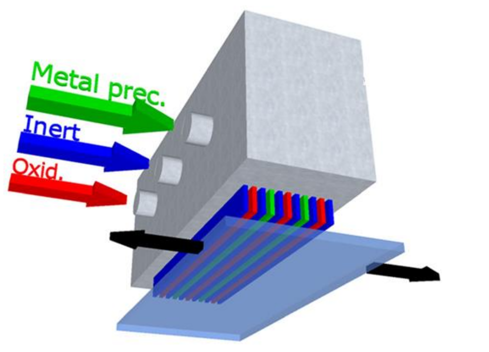
C. Villardie, Coatings 9 (9), 2019, 564

Spatial Atomic Layer Deposition - SALD

SALD is an alternative approach to ALD in which **precursors are continuously injected in different locations** of the reactor while being kept apart by an inert gas region. By alternatively exposing a substrate to the different regions, the ALD cycle is reproduced, but without the need of a purging step. As a result SALD can be up to **tow orders of magnitude faster than ALD** and is easily done at **atmospheric pressure and even in the open air (no deposition chamber)**. The research is organized in three different axes:

Design and optimization of SALD reactors

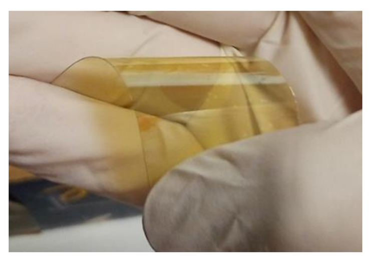
Systems based on close-proximity manifold heads & Conceived to be versatile (samples, materials, applications and reaction activation).



Scheme of a typical close-proximity head & SALD system.

Fundamental studies

Reaction mechanisms (*in situ*)
Effect of open-air processing.
New materials (oxides, metals and hybrid materials).

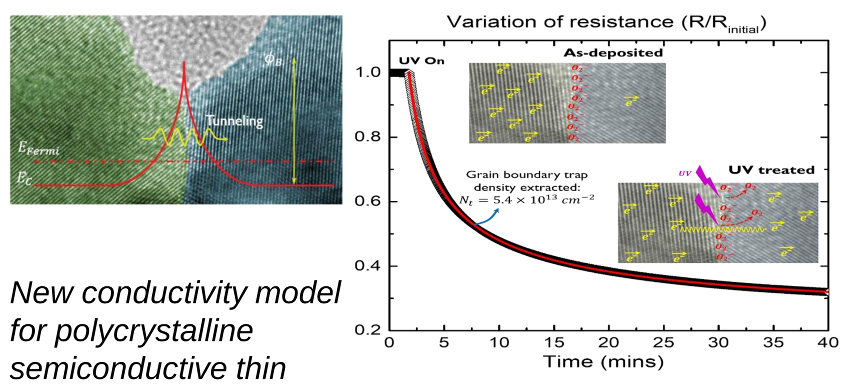


Cu_2O film deposited on a flexible substrate.

Comptes Rendus Physique, 2017, 18, 391.
Nanotechnology, 2018, 29, 085701.
ACS AM&I, 2018, 10, 19208.
Adv. Func. Mater. 2019, 29, 1805533.
Mat. Today Chem, 2019, 12, 96.

Application to devices

Application of our materials in **photovoltaics, resistive switching, sensors, microelectronics, photo-splitting, etc.**



New conductivity model for polycrystalline semiconductive thin films.

Mat. Horizons, 2018, 5, 715.
ACS App. Nano Mater. 2018, 1, 6922

Transparent conductive materials

D Bellet , D Muñoz-Rojas, JL Deschanvres

Context

Transparent conducting materials (TCMs) constitute a research topic that has been extensively studied in recent decades since they are of great interest for applications or devices such as electrodes for solar cells or for OLEDs, gas sensors, transparent heaters or for transparent electronics.

Objectives

Our goal is the design, understanding and optimization of TCMs of two different types:
- Silver nanowire networks (AgNWs),
- Transparent conductive oxides (TCOs) n- or p-type, with a particular interest in fluorine-doped tin oxide (FTO) and thin layers of Cu(I)-based oxides.

Our approach is not only experimental but also supplemented by modeling.

Skills & Competences

AgNWs: Good understanding of the influence of the main parameters (AgNW sizes, network density, post-deposition treatments etc.) on the physical properties of AgNW networks; Physical modelling and Monte Carlo simulations of AgNW networks

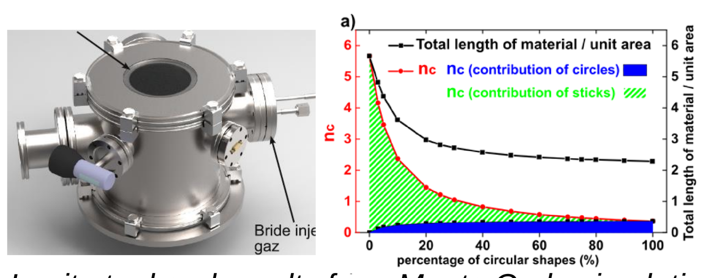
N-type TCO: Better understanding of the physical properties (scattering of carriers); Control of the n-type TCO haziness and integration into devices (solar cells).

P-type TCO: improving the properties of the films by optimizing microstructues, compositions and doping and integration of the p-type layers into devices (transparent pn junctions in sensors, Hole transport layer in solar cells, …)

Silver nanowire (AgNW) networks

Understanding of AgNW networks

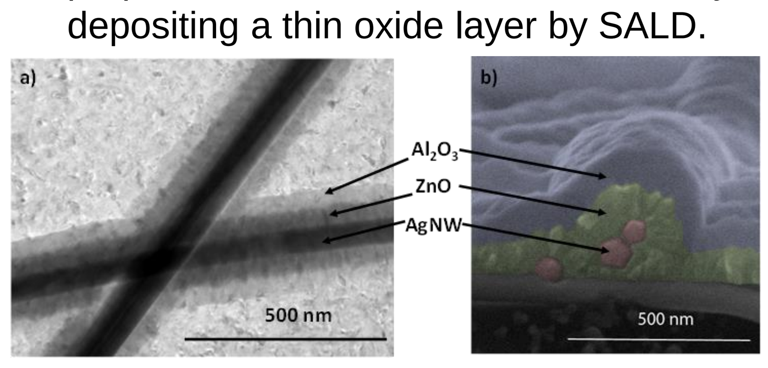
Innovative characterization tools combined with Monte Carlo modelling led to a better understanding and optimization of their physical properties.



In-situ tool and results from Monte Carlo simulations

Stability enhancement

Their excellent optical and electrical properties can be stabilised by depositing a thin oxide layer by SALD.



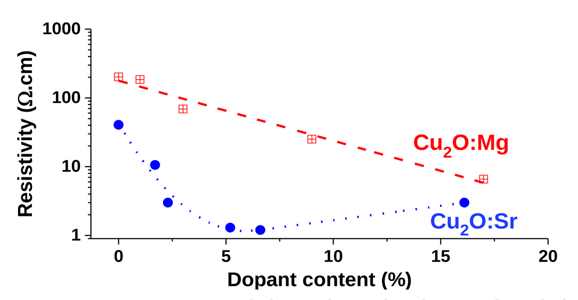
Al_2O_3/ZnO coating on AgNWs enhances stability

Integration of AgNW in devices

- Cold electrons emission from AgNW networks: ANR Panassé (2019-2021) with Thalès RT and IEMN
- Replacing ITO in OPV by stable AgNW network based electrode in Organic solar cells (OPV): ANR Meaning (2019-2022) with Armor and ICMCB.
- Local heating in microfluidic devices: in collaboration with the IMBM team, we develop a light set-up to control the temperature with AgNW based transparent heater device.

P-type TCO

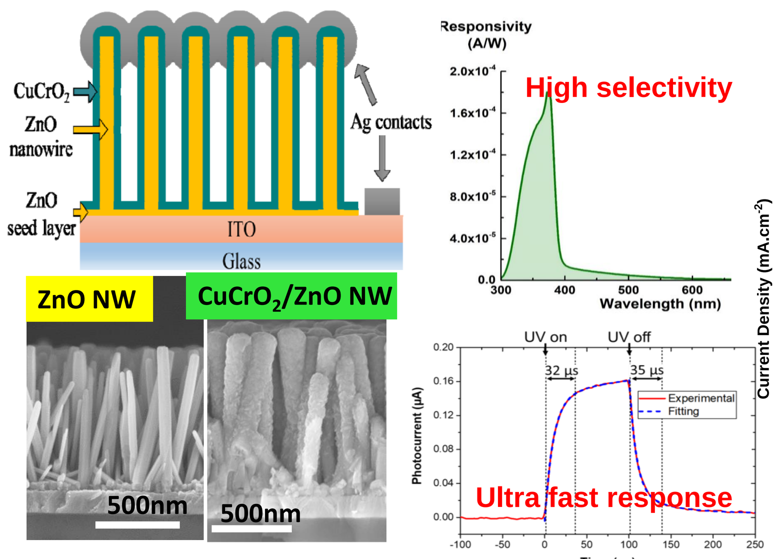
3 families of compound with different transport mechanisms are studied:
1. Cu(I) based oxide films - Cu_2O with Mg, Sr, Y substitutions, and N doping
2. Strongly correlated material - $LaSrVO_3$
3. Small polaron hoping $CuCrO_2$, $LaCrO_3$



Improvement of the electrical conductivity of Cu_2O films by substitution with Mg or Sr

Integration of p type TCO: $CuCrO_2$

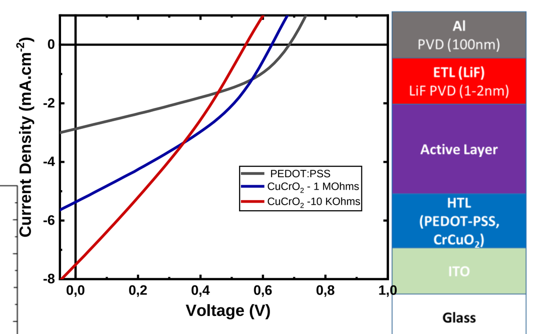
In UV sensor 3D configuration



Advanced Functional Material 28(2018)1803142

In Solar cell : Hole transport layer

$CuCrO_2$ as HTL and blocking layer on OPV

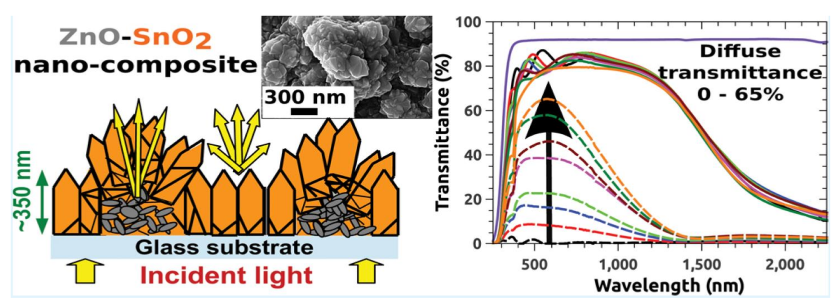


Lower Voc and FF than PEDOT:PSS but larger Jsc leading to a higher efficiency up to 1.31%

N-type TCO

Diffuse FTO layers: developing fluorine-doped tin oxide (FTO) thin layers with controlled haziness for integration in thin Si solar cells.

Other In-free transparent electrodes are being studied by SALD or AACVD: Al doped ZnO, Ga doped ZnO, $SrVO_3$…

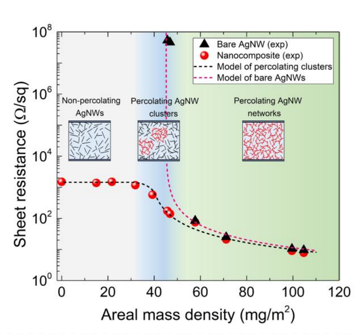


ZnO NPs/FTO nanocomposites lead to TCO layers of controlled haziness

Composite TCM

TCM based on oxides and metallic nanostructures

Composite electrodes based on AZO and AgNWs.
Nanoscale, 2019, 11, 12097.



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