European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

WGs and MC Meeting at ISTANBUL, 3-5 December 2014

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Year 3: 1 July 2014 - 30 June 2015 (Ongoing Action)

Pulsed Laser Deposition of Nanostructured Metal Oxides For Gas Sensors





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Scientific context and objectives in the Action:

- Background / Problem statement:
 - Development of new sensitive and selective gas sensor materials for environmental quality control, public safety issues, medical, automotive applications such as Selectice Catalytic Reaction (SCR), air conditioning system setups in aircrafts, spacecrafts, vehicles, houses, etc.
- Brief reminder of MoU objectives:
 - Study the sensitivity of nanostructured MO films to harmful gases, e.g. NO_x, NO₂, H₂, NH₃, and VOC's
 - Utilizing grain size, phase transition, mixed phase, and p-n jubction effects
 - Fabrication of sensors on various substrates including flexible substrates PET/PEN using printing techniques





Pulsed Laser Deposition of Nanostructured Metal Oxides For Gas Sensors

Contents:

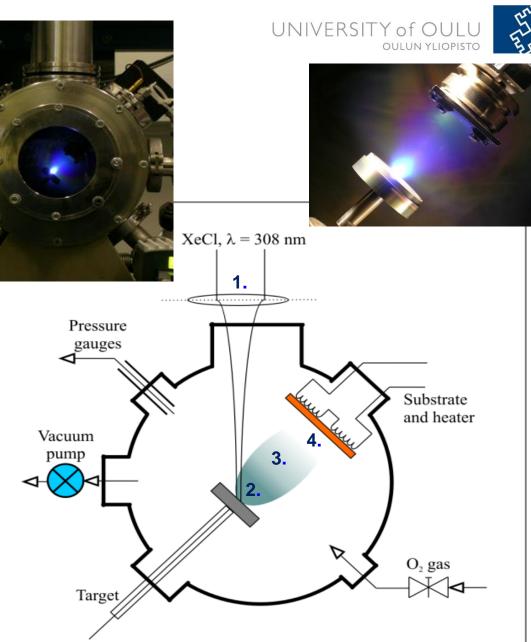
- 1. Pulsed laser deposition (PLD) technique
- 2. Partcle generation in PLD
- 3. Examples:
 - WO₃ nanoparticle films
 - V₂O₅ nanoparticle films
- 4. Gas sensing examples of the nanoparticle films





1. Pulsed Laser Deposition (PLD):

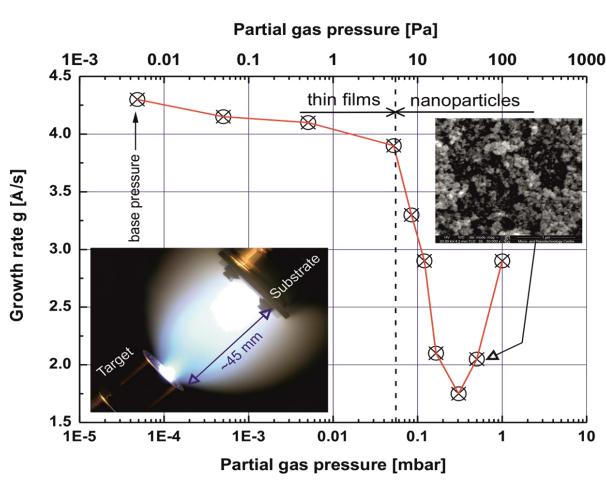
- **1.** Focused laser pulse hits the target material surface placed in lowpressure conditions.
- 2. Plasma is generated by ablation and/or evaporation processes.
- 3. Pressure gradient inside the plasma is very high, and thus the plasma expands extremely fast in the direction perpendicular to target surface.
- 4. Atomic (and other) species of the plasma are collected on substrate surface to form a thin film.





2. Particle Generation in PLD:

- Two points of generation: (i) target surface, and (ii) high density plasma.
- Reactions in plasma can lead into:
 (i) dissosiation of particulates, or in
 (ii) nucleation of nanoparticles.
- Plasma can be controlled by deposition atmosphere, *i.e.* partial oxygen pressure p(O₂), or by laser beam fluence (J/cm²)
- Plasma can be controlled by deposition atmosphere, for example, by liquids – LAPLD.
- Extremely small particles, $\phi < 5$ nm, can be grown.

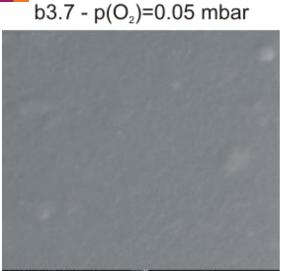


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Microstructure studies of WO₃ -nanoparticle thin films: UNIVERSITY of OULU

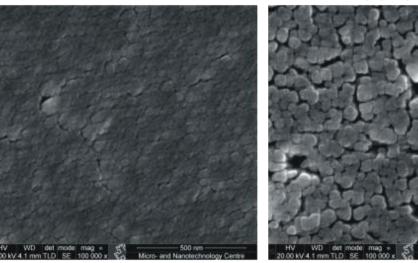






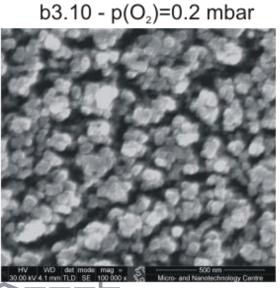
b3.8 - p(O₂)=0.08 mbar

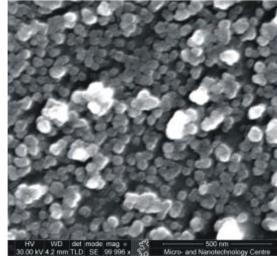
b3.9 - p(O₂)=0.1 mbar

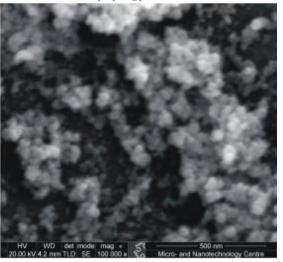


b3.5 - p(O₂)=0.3 mbar

b3.5 - p(O₂)=0.5 mbar



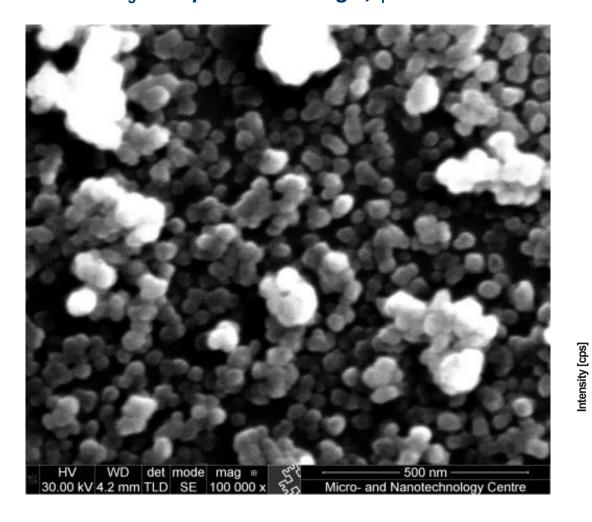


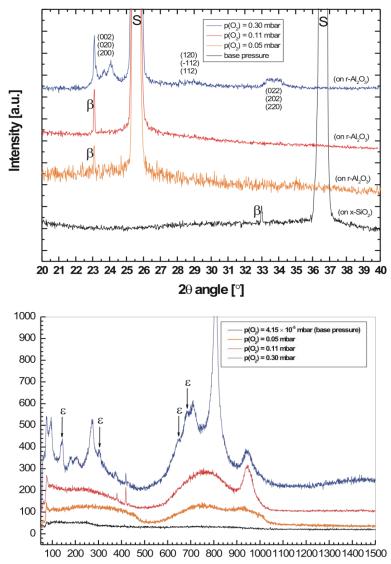




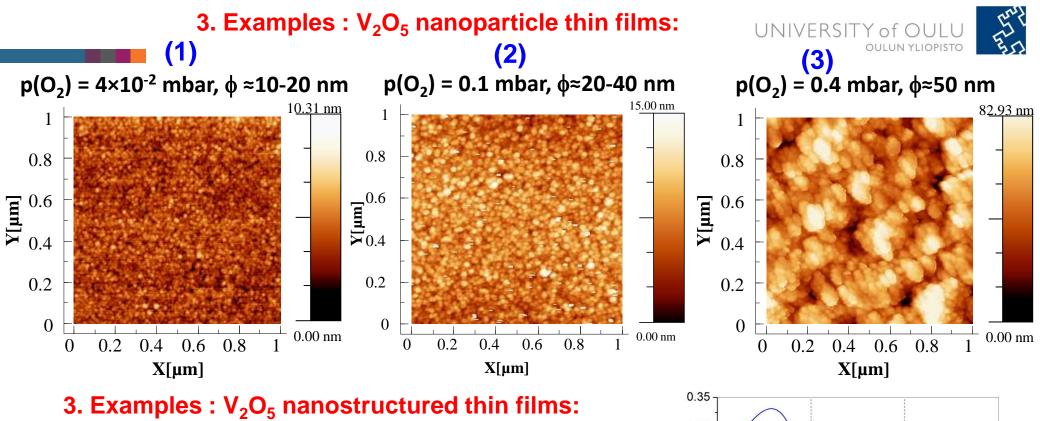
3. Examples : WO₃ nanoparticle thin films:

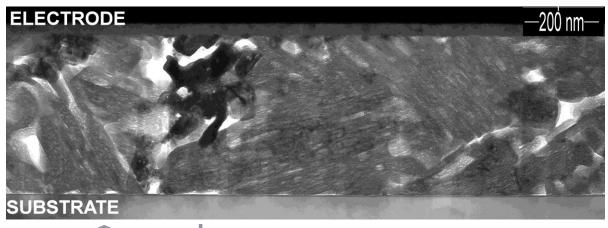
 WO_3 nanoparticles on MgO, $\phi \approx 50$ nm:

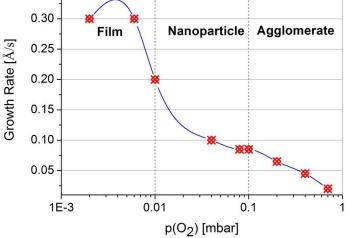




Raman shift [cm⁻¹]







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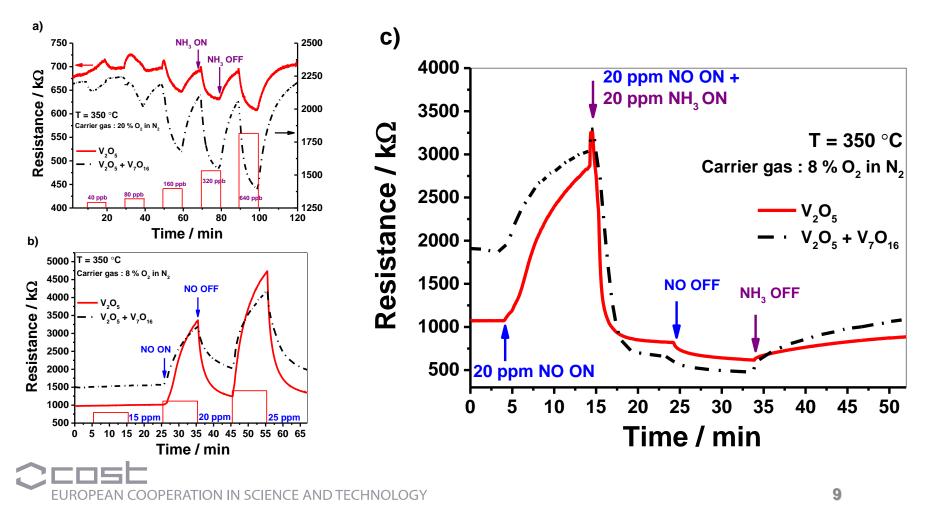
4. Gas sensing examples of the nanoparticle films: UNIVERSITY of OL



Gas sensing examples of vanadium oxide thin films:

-The thin films have proven to be highly sensitive to ammonia gas (NH_3) - a reducing response was seen already at ppb level!

-Also clear selectivity to NH_3 has been seen in presence of NO - utilization in Selectice Catalytic Reaction (SCR) applications!



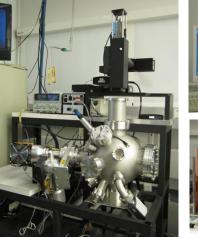


Research Facilities available for the Partner:

PLD laboratory in UO-FETF:

- XeCI-excimer laser (LamdaPhysik 201)
- I = 308 nm (248 nm optional)
- $\tau = 25 \text{ ns}, \text{ E}_{\text{max}} = 400 \text{ mJ}, \text{ f}_{\text{max}} = 10 \text{ Hz}$
- Optics with continuos energy adjustment
- Computer controlled micromovement stage for laser beam guiding and scanning
- Custom modified PLD chamber (K.J. Lesker)
- UHV capability (~10⁻⁷ mbar)
- Computer controlled rotating two-target system
- Sample holder $\phi = 1$ inch, $T_{max} = 900$ °C
- Gas atmosphere control from ~0.0005 mbar
- QCM rate/thickness monitor
- Fully computerized target motion,
- Gas atmosphere and profile, temperature profile, and laser controllers in order to perform automatized PLD procedures.











Suggested R&I Needs for future research

- Research directions as PRIORITIES:
- <u>Development of mixed-phase structures of MO's for gas</u> <u>sensing applications</u>!
- Development of fabrication methods of WO₃, V₂O₅, VO₂, etc. nanostructures and nanoparticles in various conditions: hightemperature - RT, fabrication in liquids, etc.
- Detailed structural characterization and physics of gas sensing mechanism.
- <u>Utilization of phase transition and p-n junction effects in gas</u> <u>sensing process</u>.
- Integration into low-cost mass-production processes.