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

COST Action TD1105

WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

Action Start date: 01/07/2012 - Action End date: 30/04/2016 - Year 4: 1 July 2015 - 30 April 2016

STRUCTURAL MODIFCATIONS AND CHEMICAL SENSING PROPERTIES OF NANOSTRUCTURED METAL OXIDES

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cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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

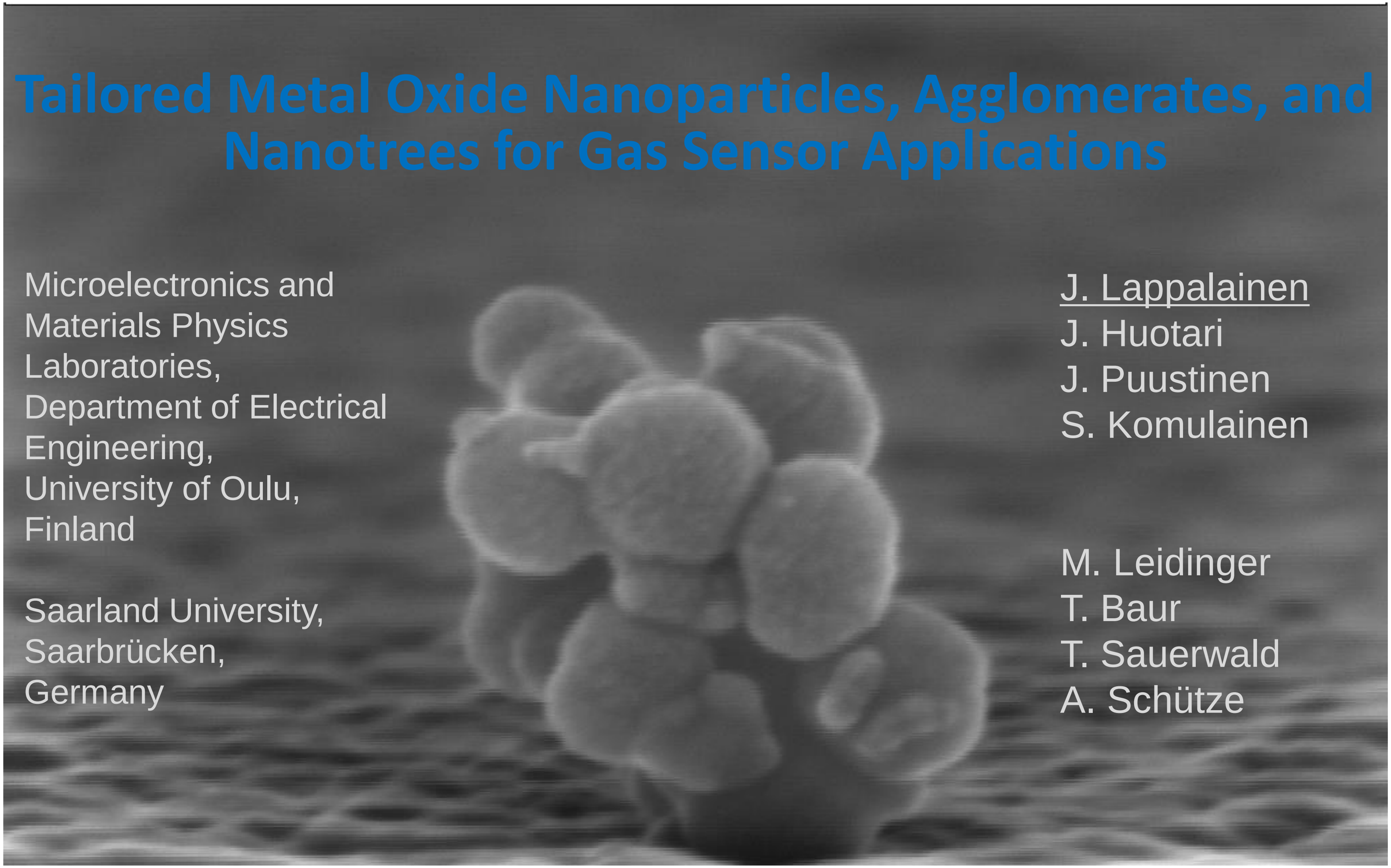
COST is supported by the EU Framework Programme

European Science Foundation ESF provides the COST Office through a European Commission contract

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, NO_2, H_2, NH_3, and VOC's
  - Utilizing grain size, phase transition, mixed phase, and *p-n* junction effects
  - Fabrication of sensors on various substrates including flexible substrates PET/PEN using printing techniques

Tailored Metal Oxide Nanoparticles, Agglomerates, and Nanotrees for Gas Sensor Applications



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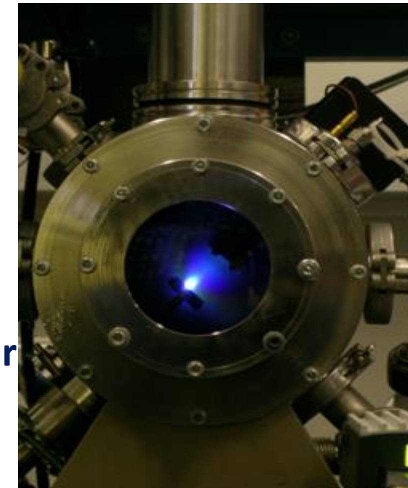
1. Introduction to Pulsed Laser Deposition (PLD) process
2. Some plasma physics of PLD

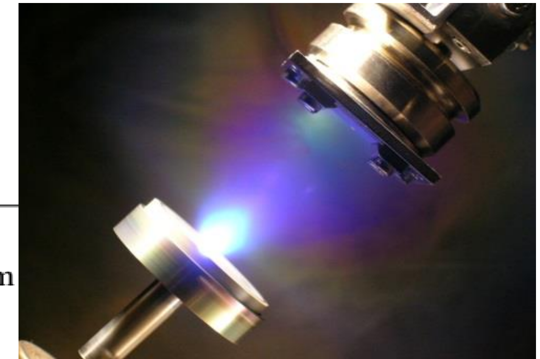
3. Nanoparticle (NP) generation in PLD
4. Agglomerates and nanotrees of NP's

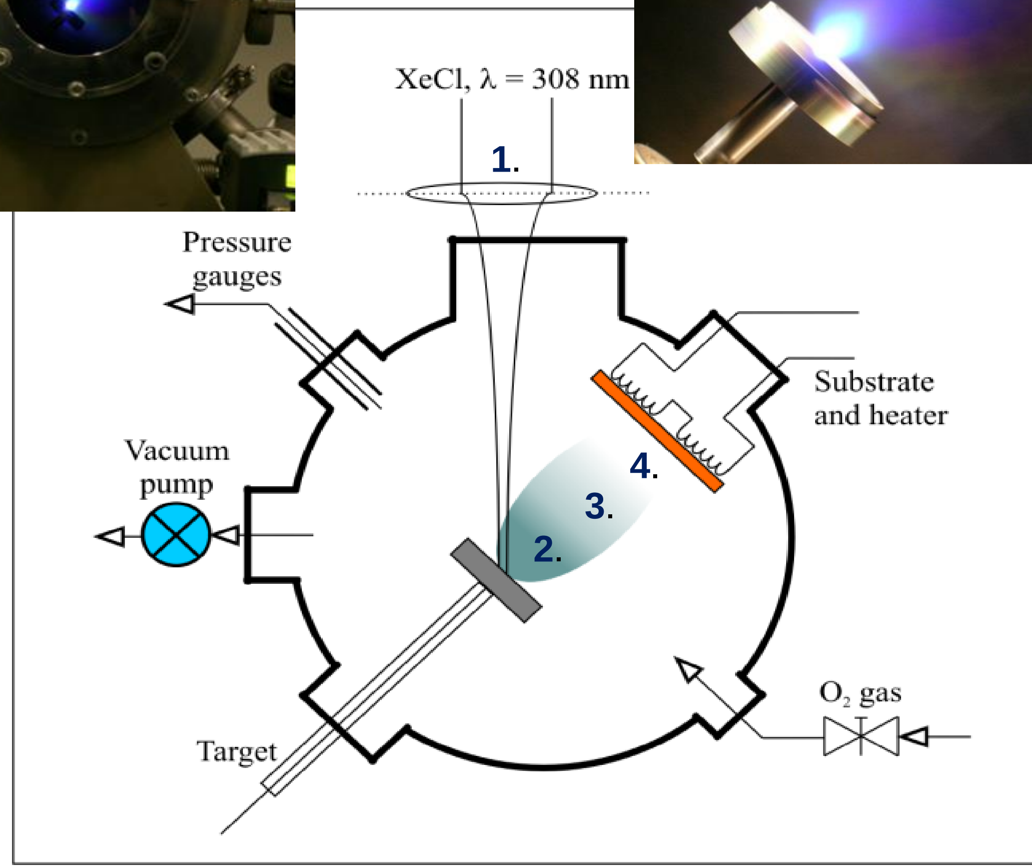
5. Examples of nanostructured metal oxide gas sensors:
   - Tungsten oxide WO_3
   - Tin Oxide SnO_2
   - Vanadium oxide V_2O_5

1. Introduction

Pulsed Laser Deposition (PLD):







1. **Focused laser pulse hits the target material surface placed in low-pressur conditions.**

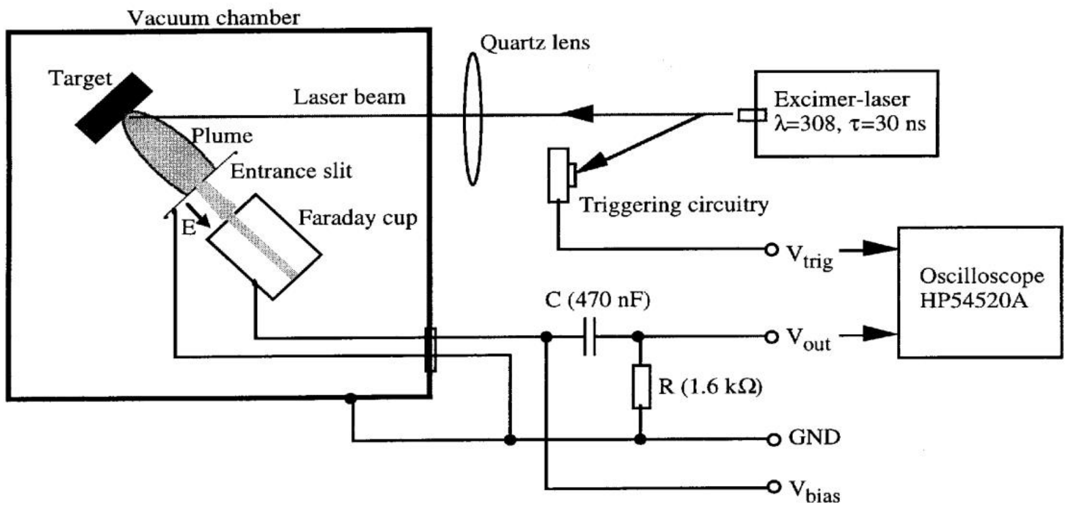
2. **Plasma is generated by ablation and/or evaporation processes.**

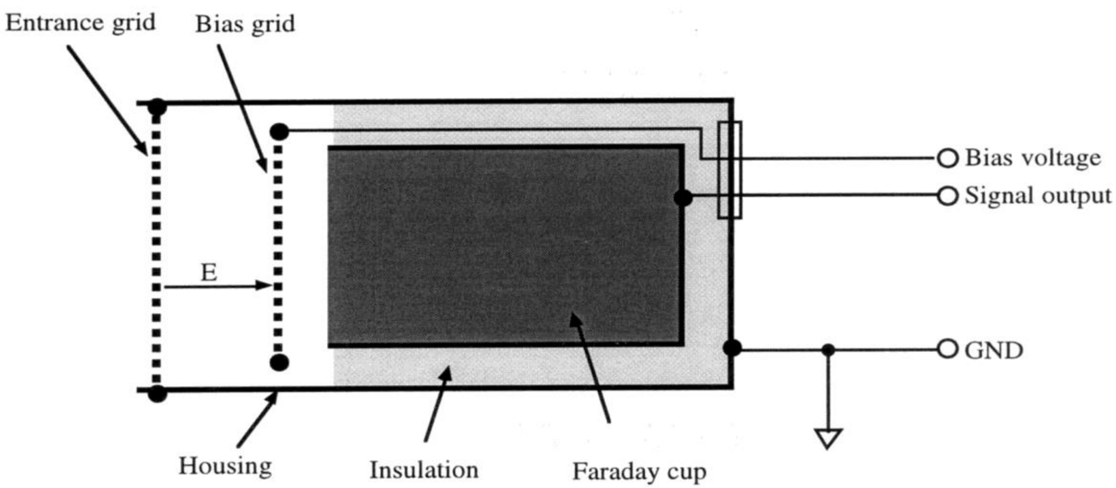
3. **Pressure gradient inside the plasma is very high, and thus the plasma expands extremely fast in the direction perpendicular to target surface.**

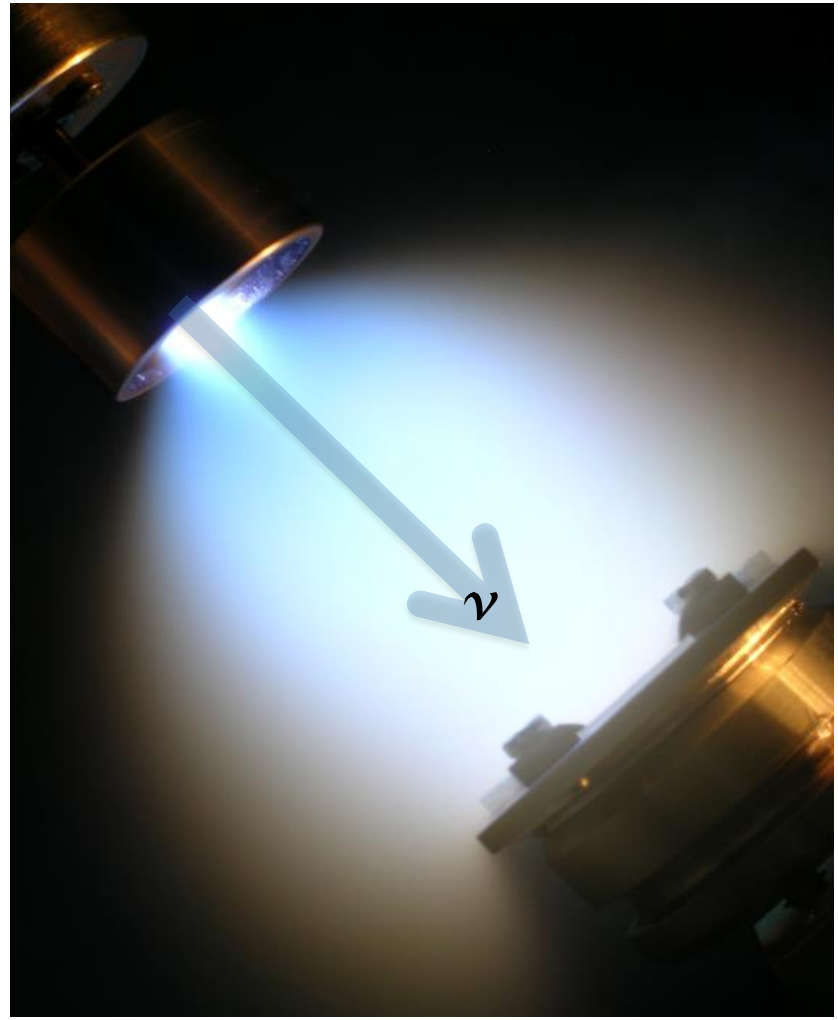
4. **Atomic (and other) species of the plasma are collected on substrate surface to form a thin film.**

2. Some plasma physics of PLD

Time of Flight (TOF) measurements with Faraday cup:







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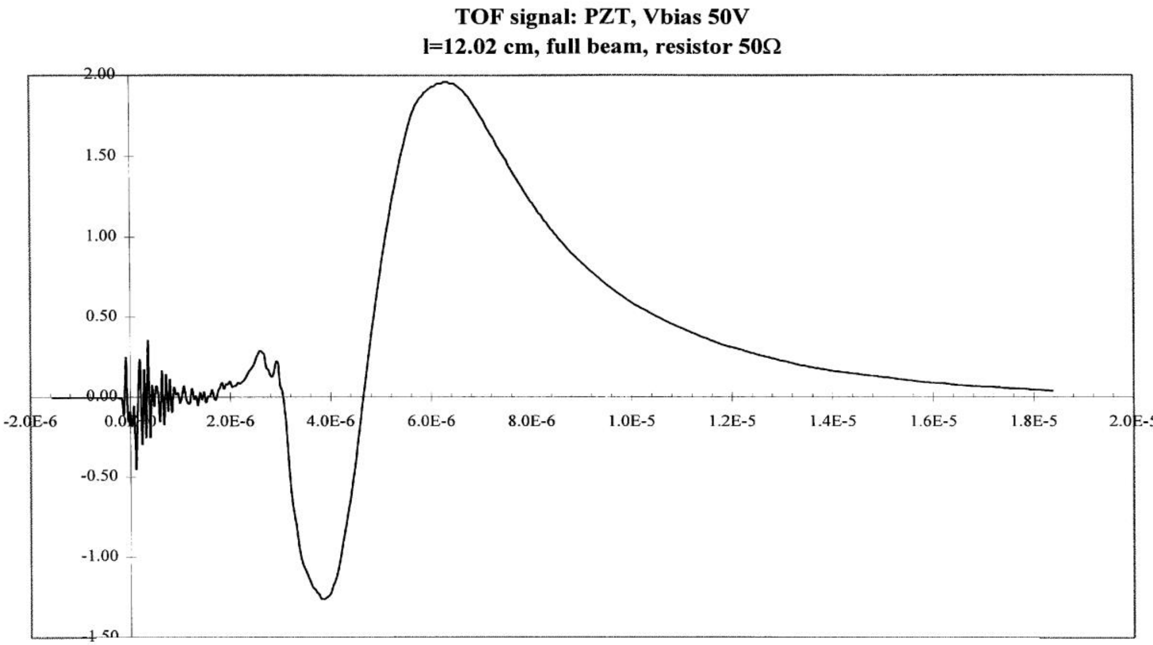
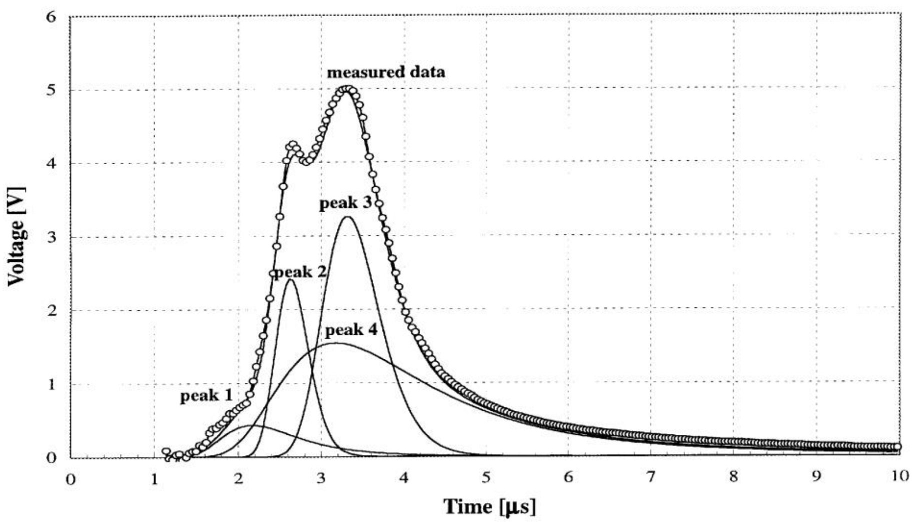
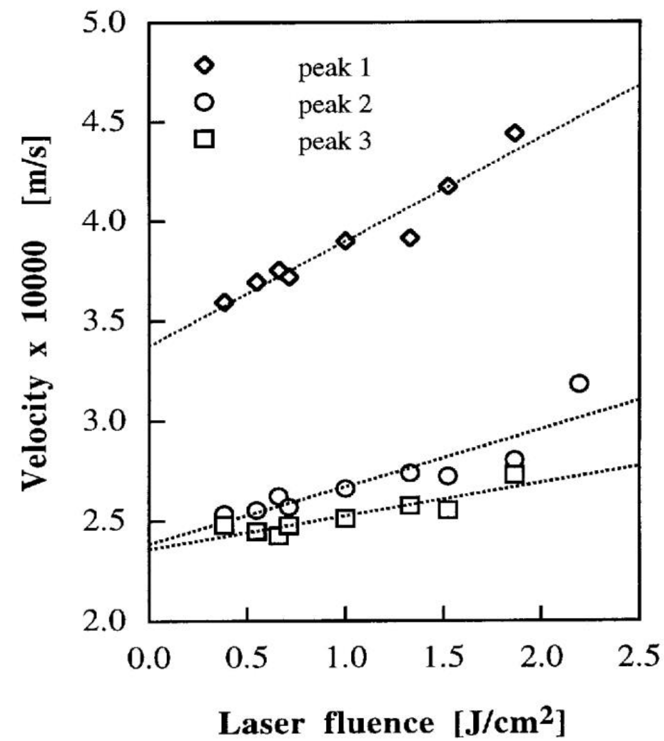




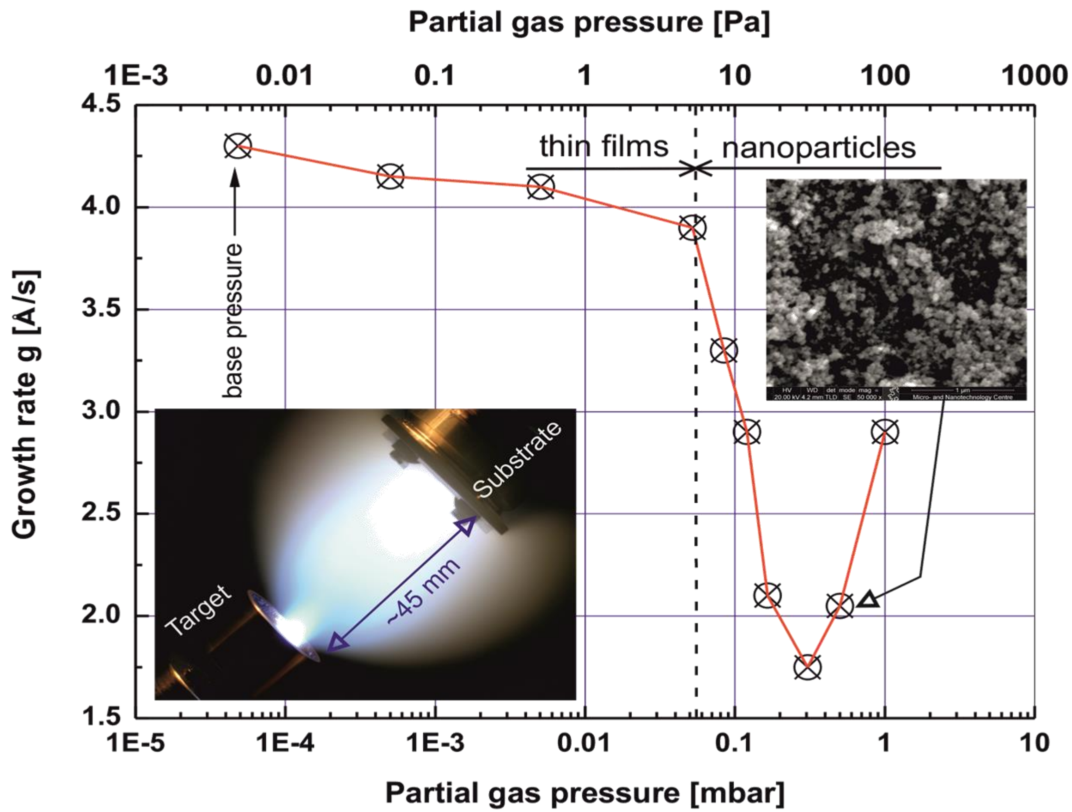
Maxwell – Boltzman distribution:

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left[\frac{-mv^2}{2kT}\right]$$

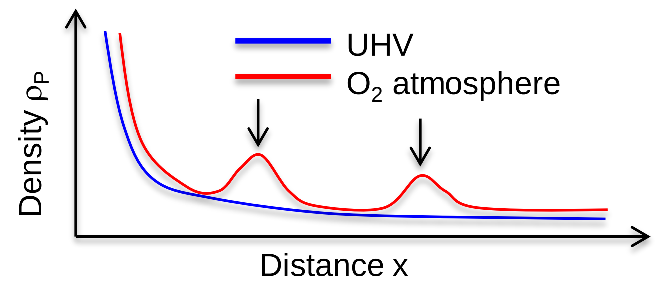


3. Nanoparticle generation in PLD

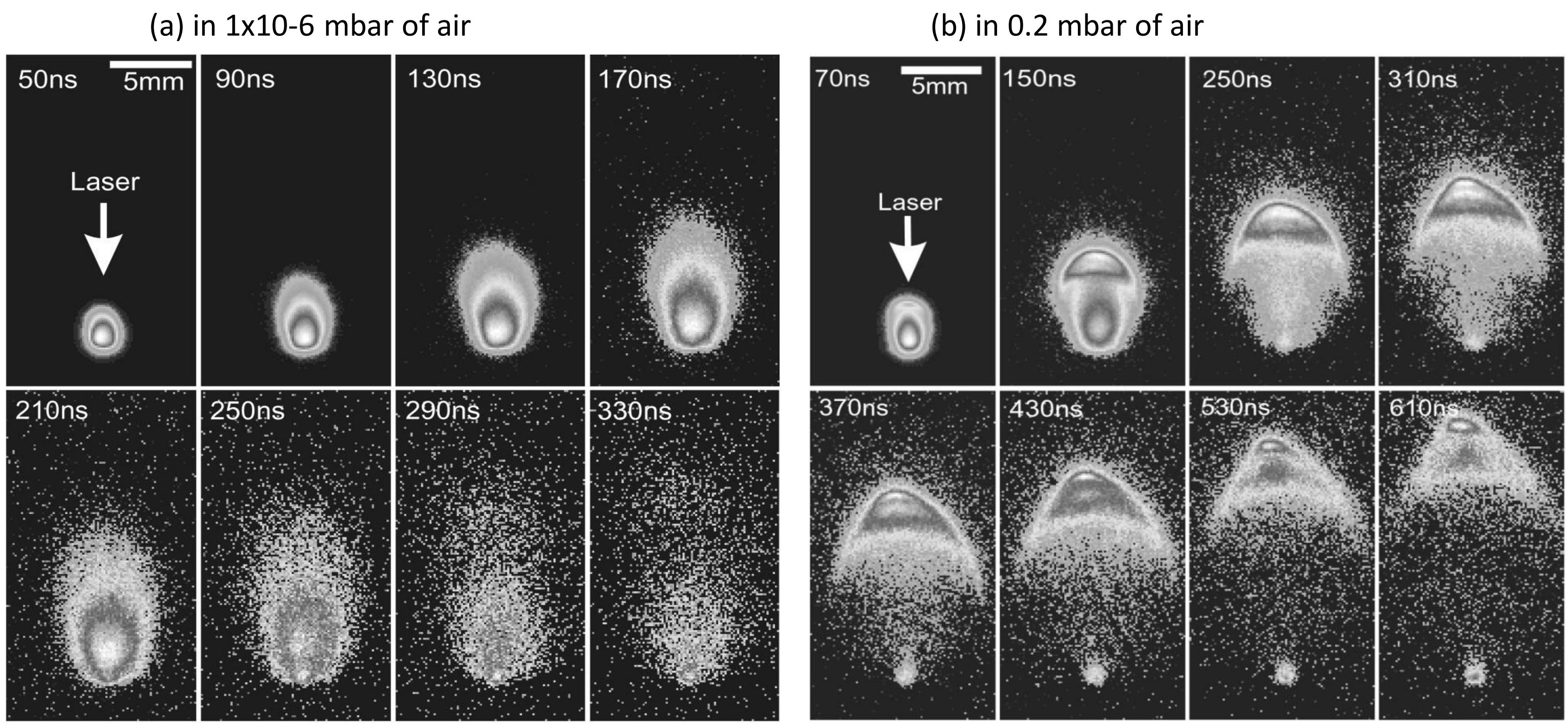
- **Two points of generation: (i) target surface, and (ii) high density plasma.**
- **Reactions in plasma can lead into: (i) dissosiation of particulates, or in (ii) nucleation of nanoparticles.**
- **Plasma can be controlled by deposition atmosphere, *i.e.* partial oxygen pressure $p(O_2)$, or by laser beam fluence (J/cm^2)**
- **Plasma can be controlled by deposition atmosphere, for example, by liquids – LAPLD.**
- **Extremely small particles, $\phi < 5$ nm, can be grown.**



3. Nanoparticle generation in PLD



- Fast ICCD camera images of expanding laser ablation plume of aluminum
- [S.S. Harilal *et al*., Journal of Applied Physics 93(2003)2380]



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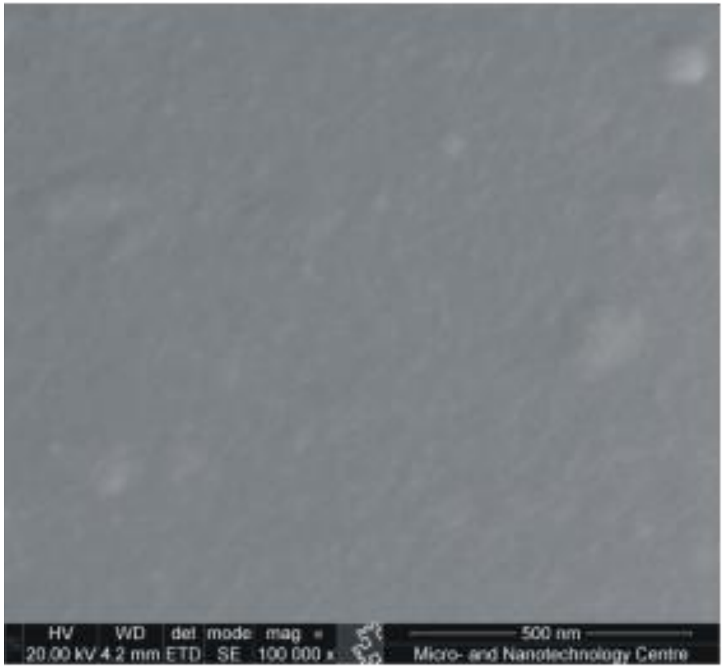

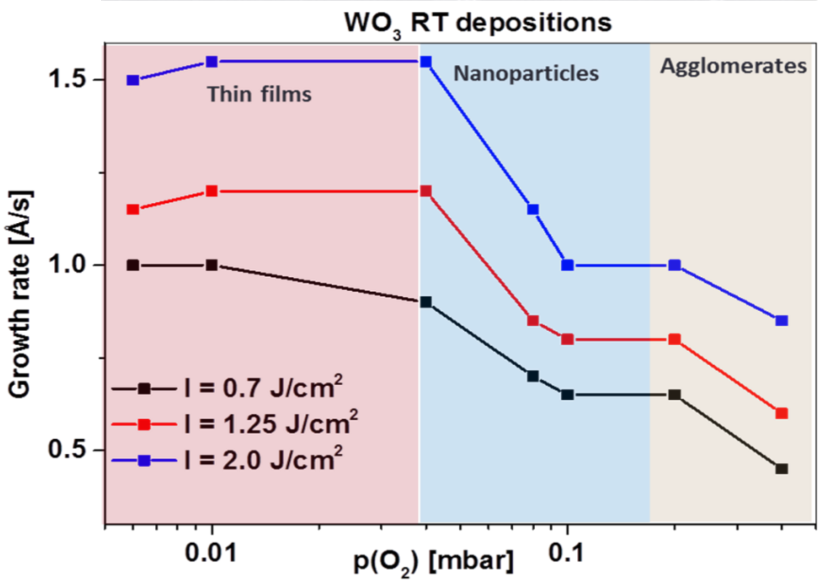

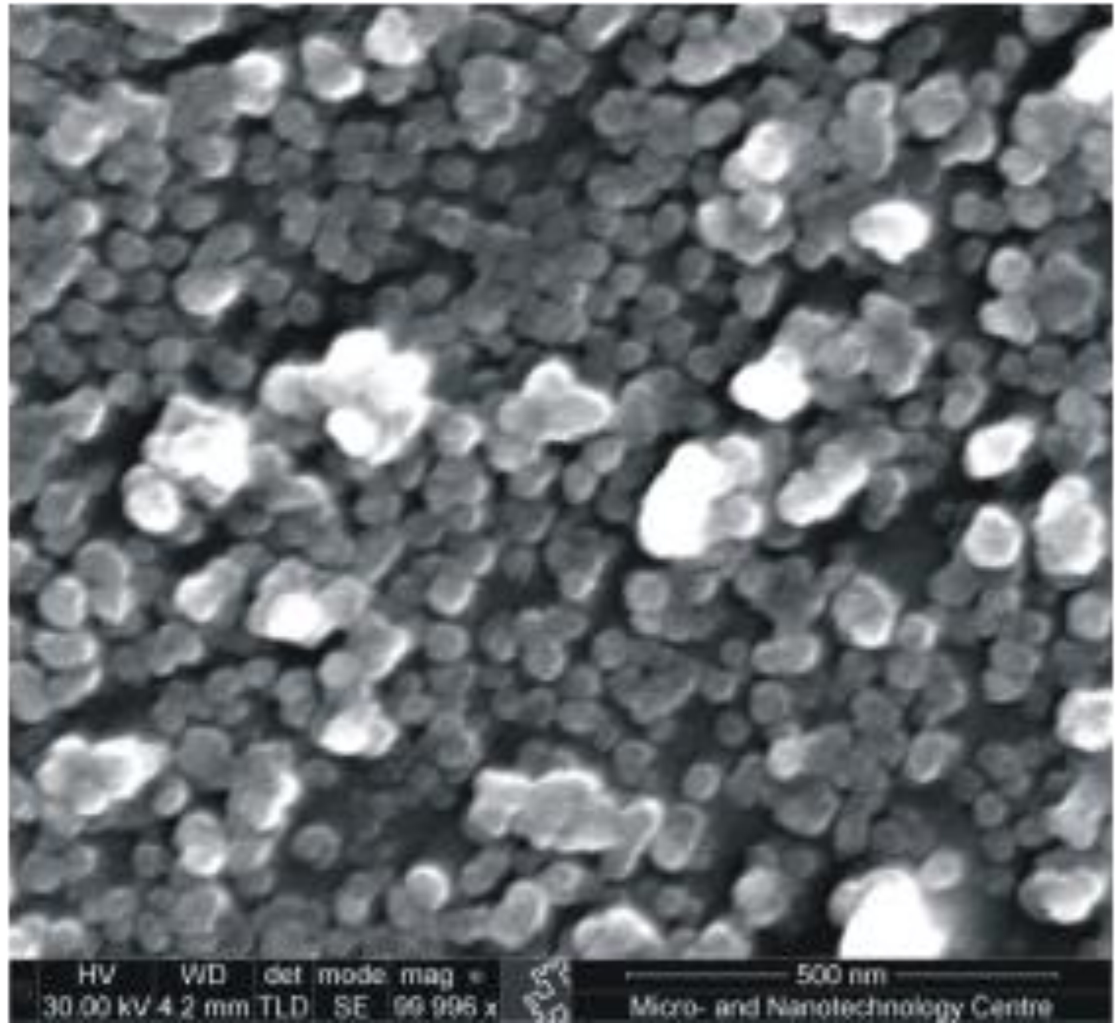

$g_{av} \approx 50$ nm

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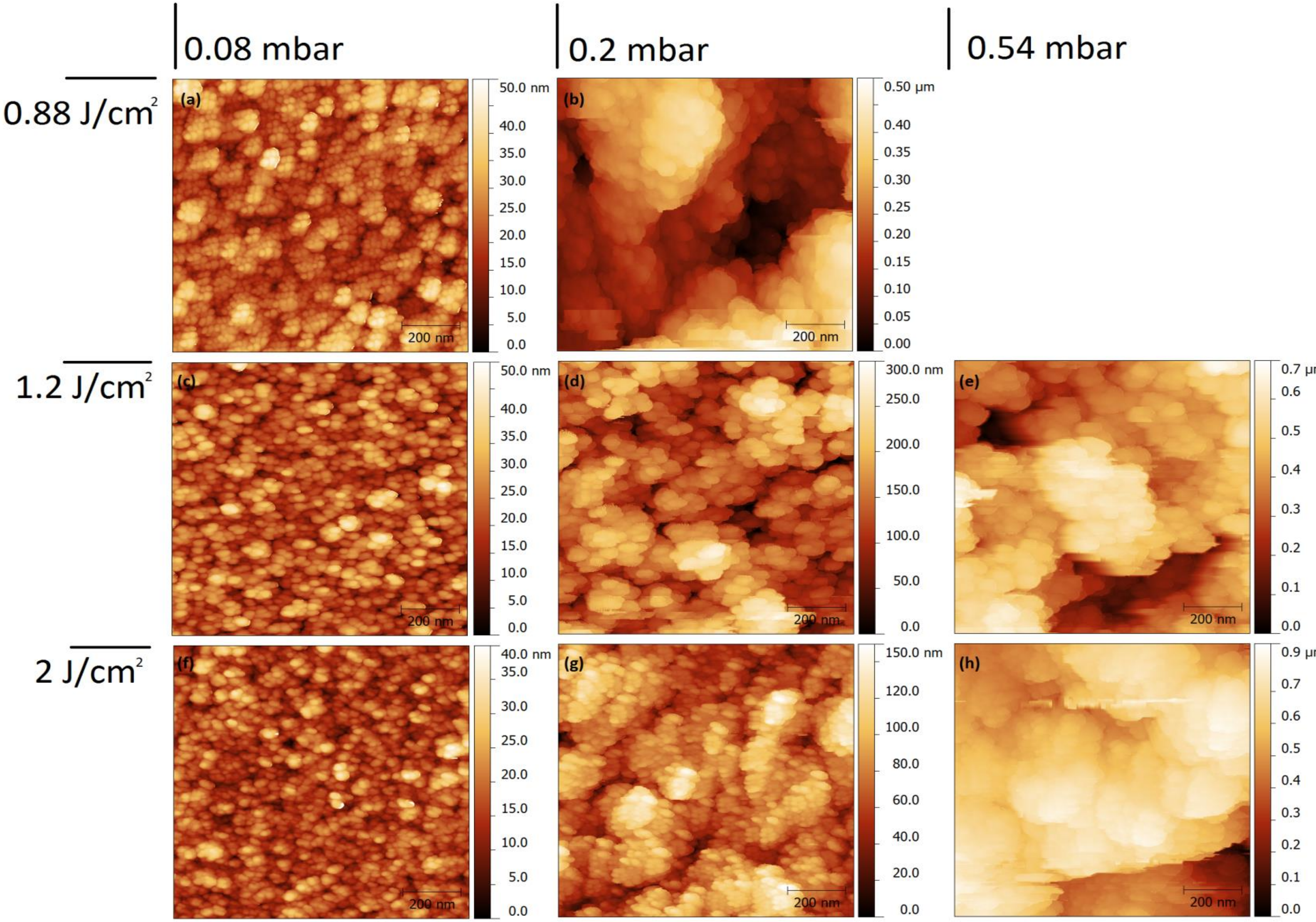
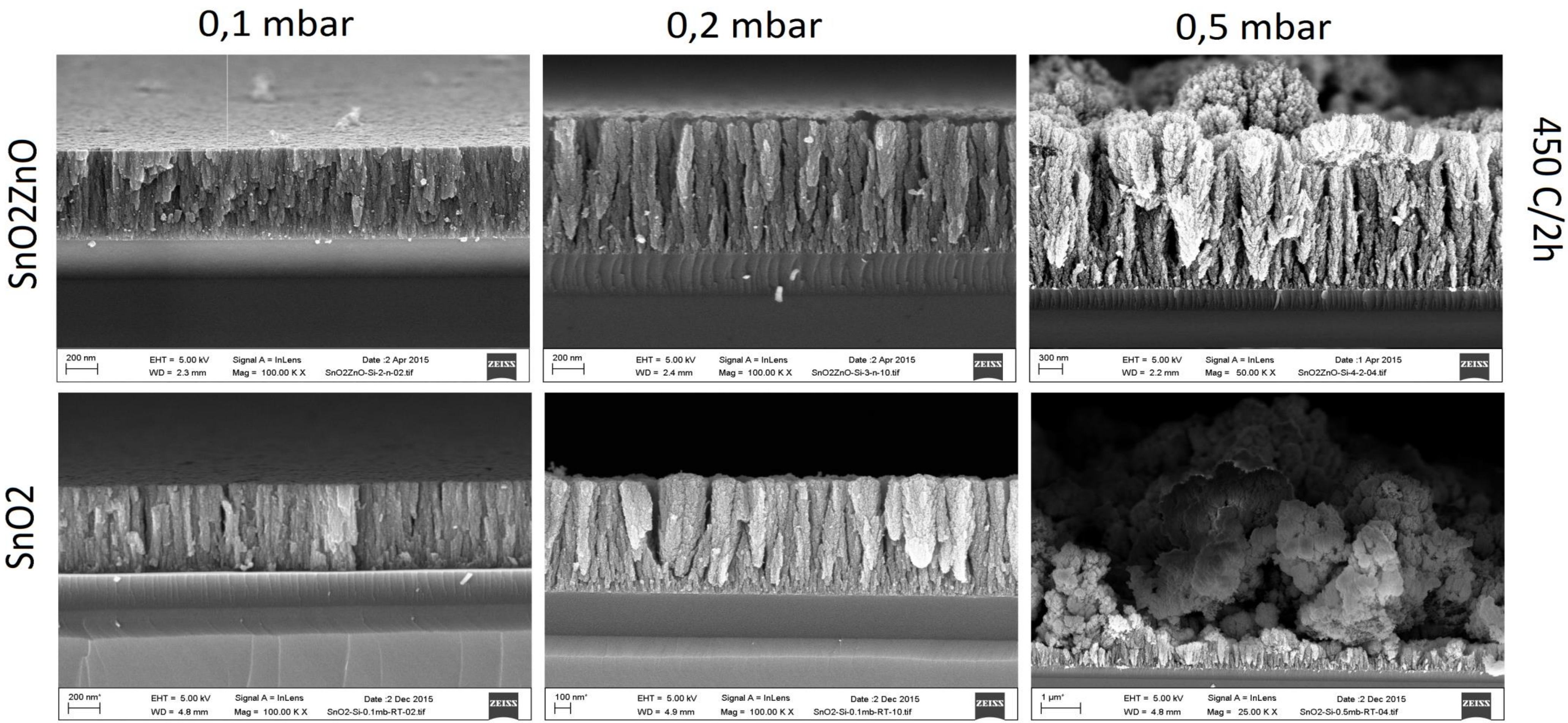
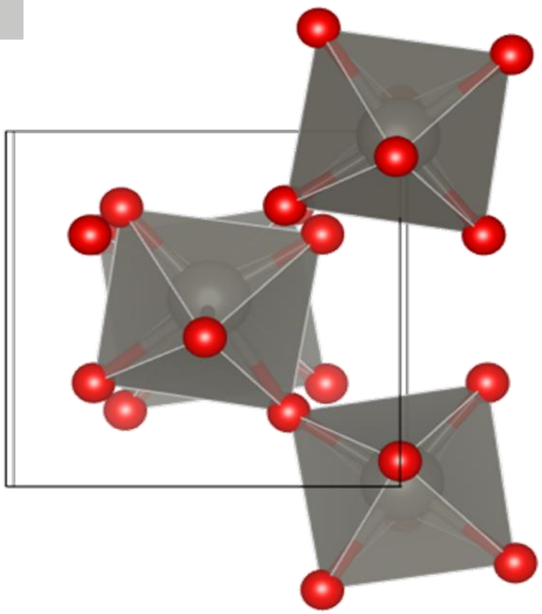
4. Agglomerates and nanotrees



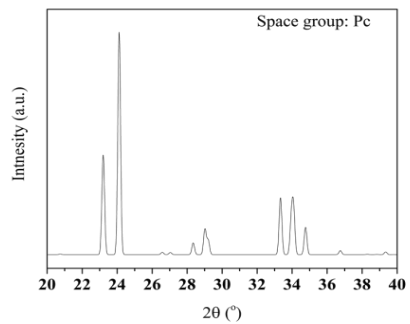
4. Agglomerates and nanotrees



5. Examples - Tungsten oxide WO_3



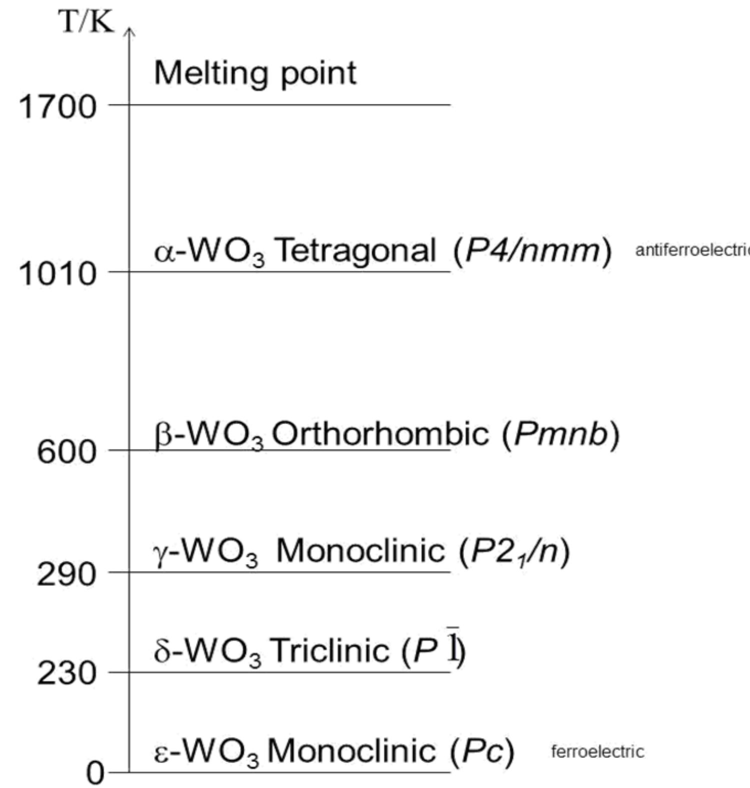
Phase: ε-WO_3
Space Group: Pc
Lattice constants:
a = 5.27793 Å
b = 5.15594 Å
c = 7.66392 Å
Cell Angles:
α = 90
β = 91.762
γ = 90



Properties of WO_3

- Physical properties of the strcuture depends crucially on the details of the distortions and tilting of oxygen octahedra in the structure
- Electrical characteristics:
  - electrochromic (smart windows, etc.)
  - n-type semiconductor (gas sensing)
  - ferroelectric in ε-WO_3 phase

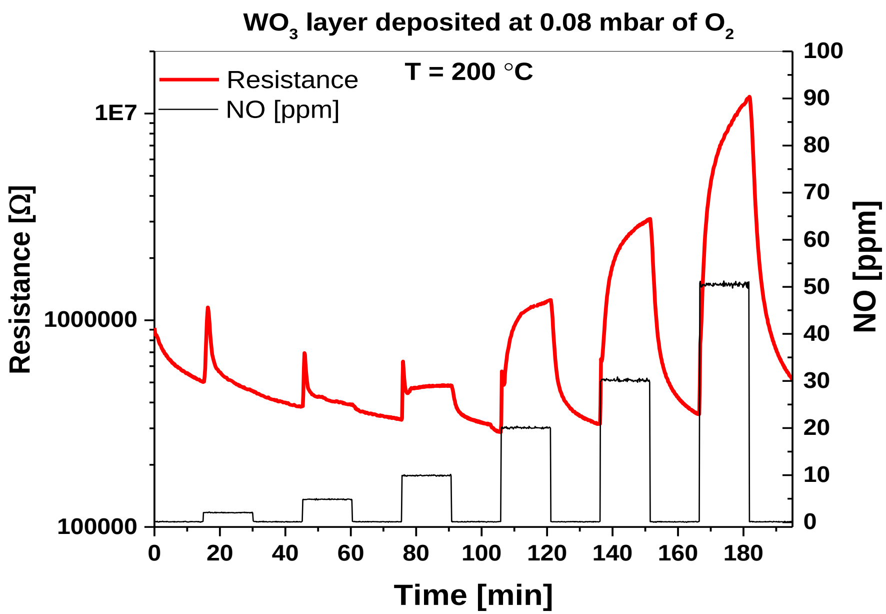
Different phases of WO_3 (crystal structures)*

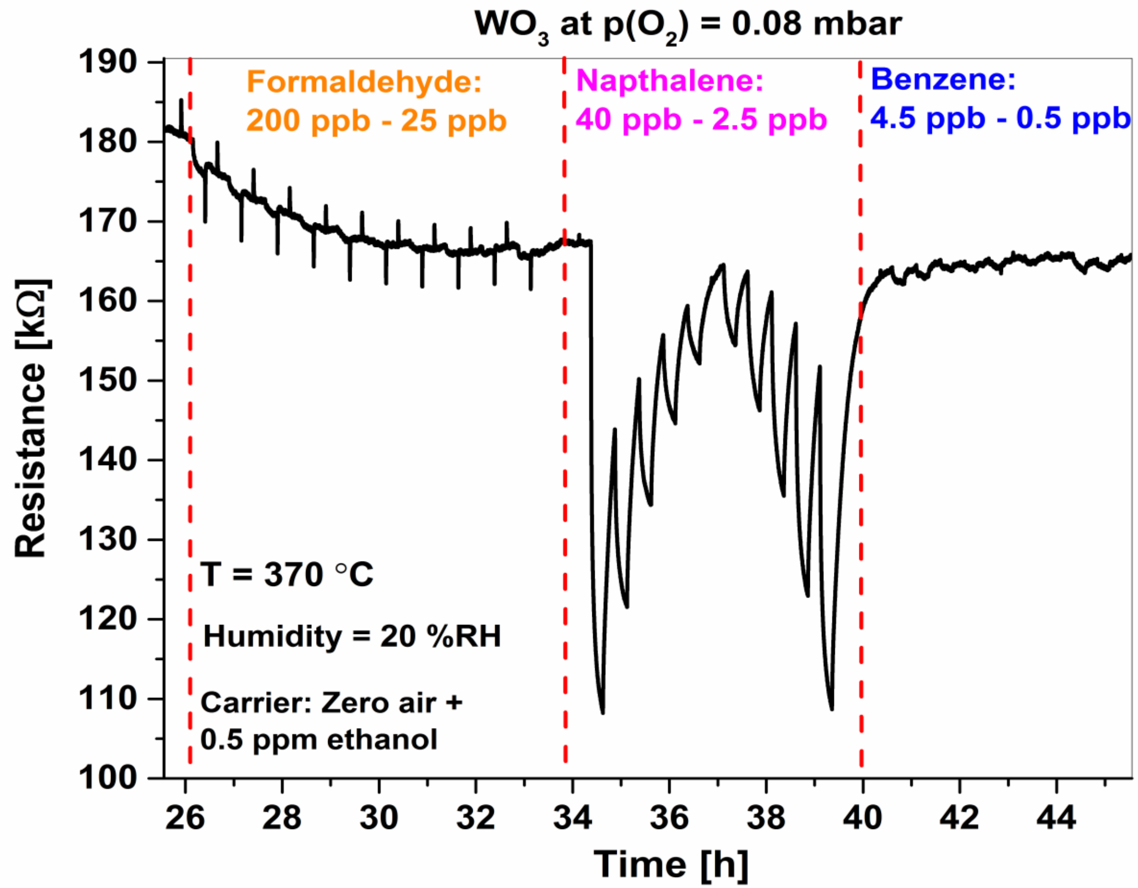


*P. M. Woodward, A. W. Sleight, and T. Vogt. Ferroelectric tungsten trioxide. *Journal of Solid State Chemistry*, 131(1):9-17, 1997.

5. Examples - Tungsten oxide WO_3

$p(O_2)$ = 0.2 mbar, T_{ann} = 400 ˚C: Gas responses for NO_x and volatile organic compounds (VOC):

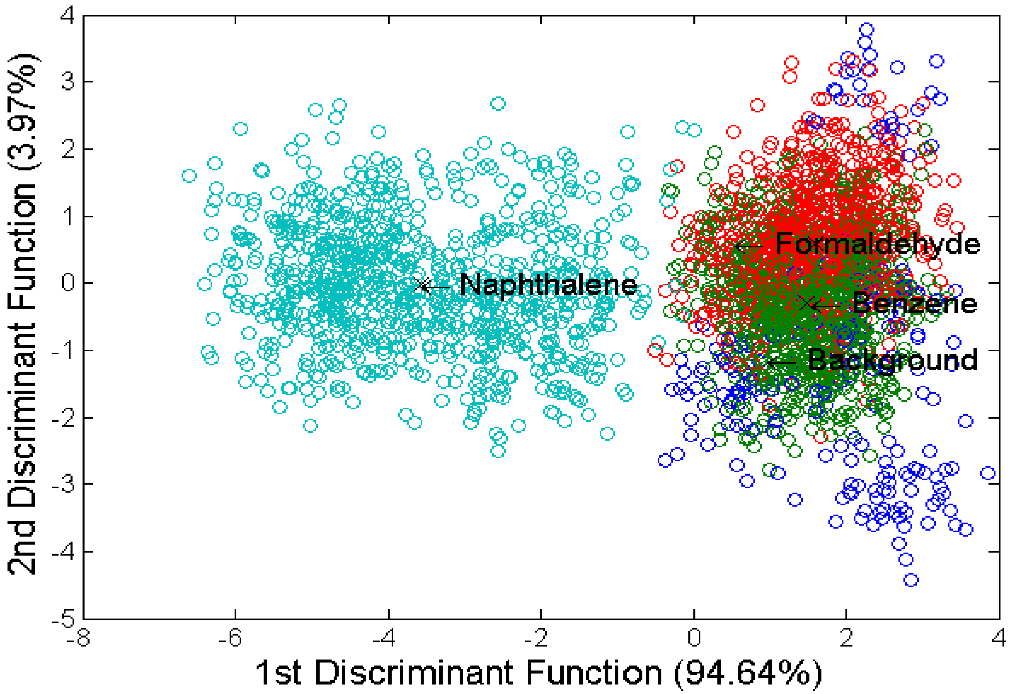


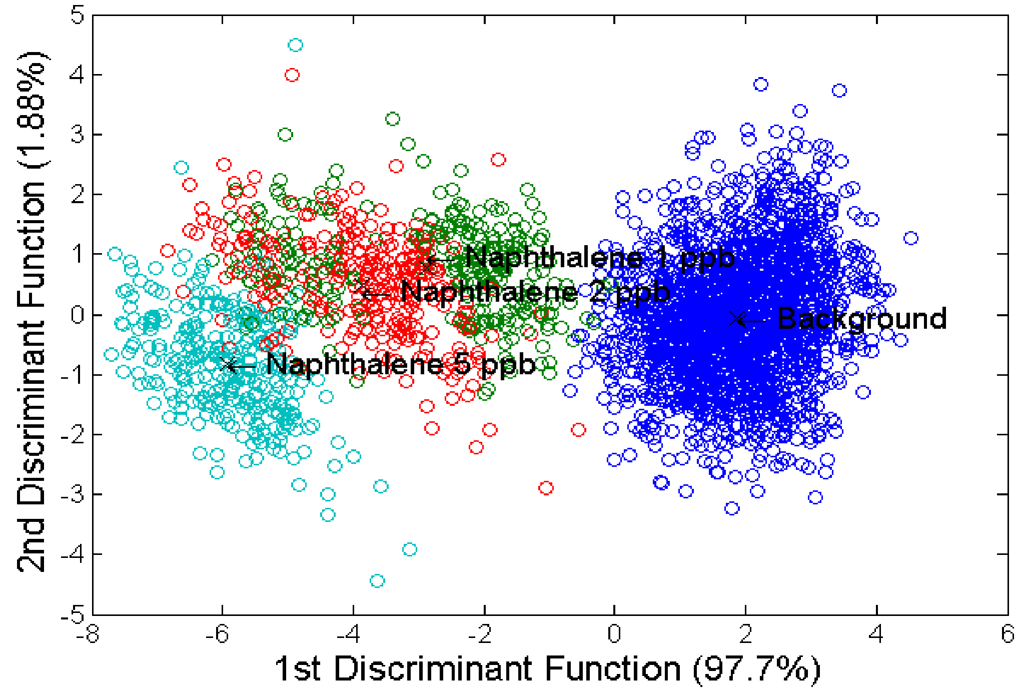


WO_3 gas sensing properties: It is clear from the measurement results that the WO_3 layers are extremely selective to ppb-levels of naphthalene!

5. Examples - Tungsten oxide WO_3

$p(O_2)$ = 0.2 mbar, T_{ann} = 400 ˚C: Linear Discriminant Analysis (LDA) at naphthalene concentrations below 5 ppb-level.

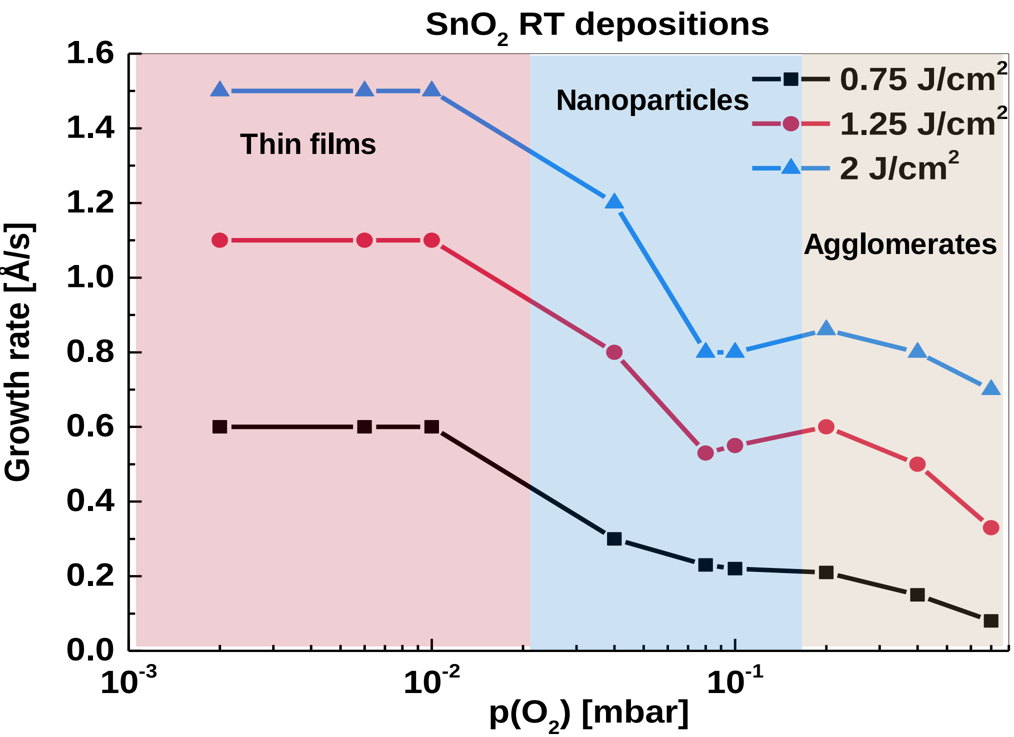


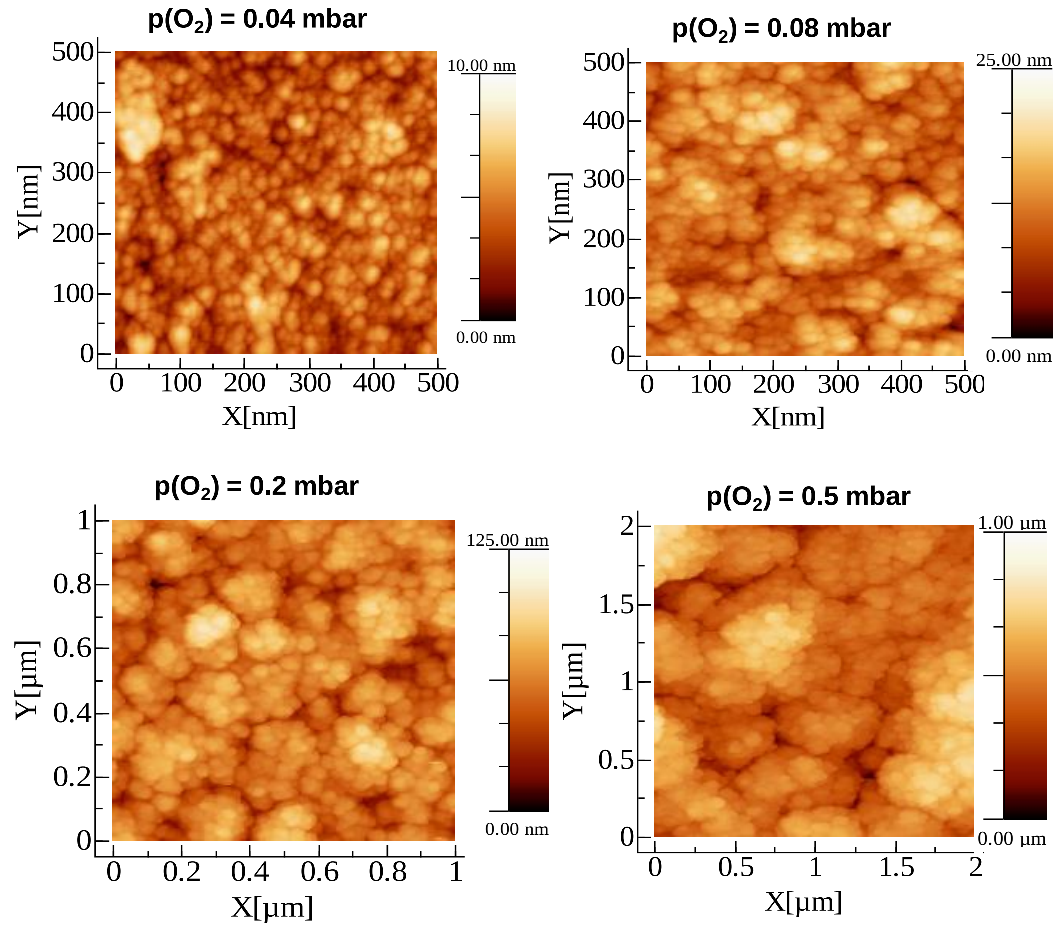


WO_3 gas sensing properties: It is clear from the measurement results that the WO_3 layers can distinguish different ppb-concentrations of naphthalene!

5. Examples - Tin Oxide SnO_2

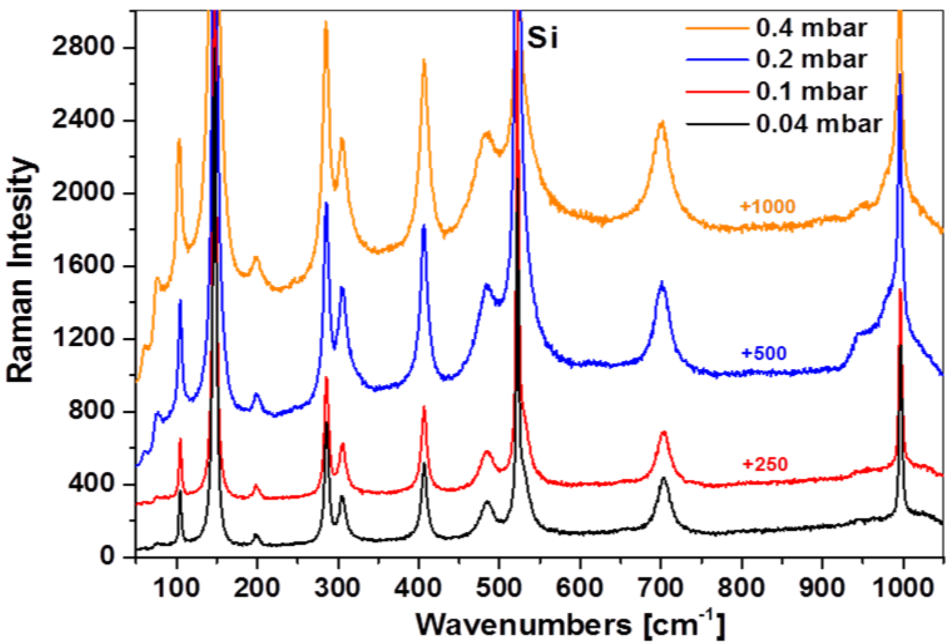
- Ceramic target of 99.7 % of SnO_2 + 0.3 % of ZnO as sintering aid was used in PLD process
- In the QCM measurements change in the growth modes from thin films to nanoparticle agglomerates was seen
- The QCM result was confirmed by AFM measurements



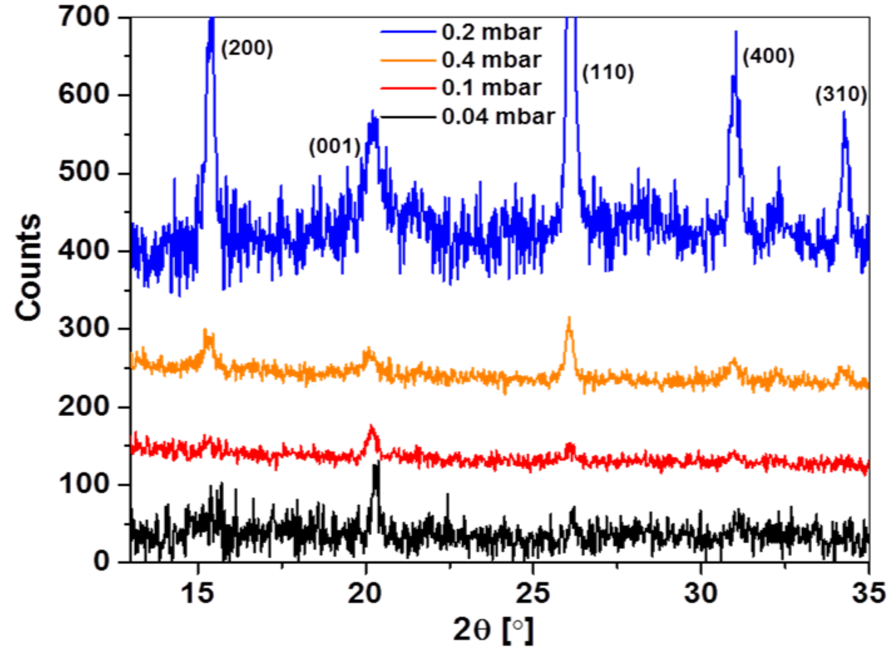


5. Examples - Vanadium oxide V_2O_5

XRD and Raman Spectroscopy results confirmed that all layers are composed of pure orthromibic V_2O_5 phase:



T_{ann} = 400 ˚C:

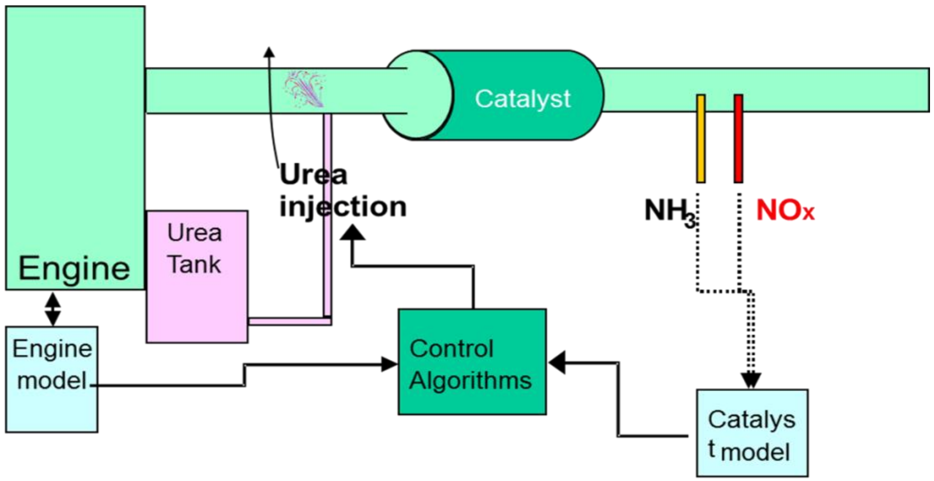


T_{ann} = 400 ˚C:

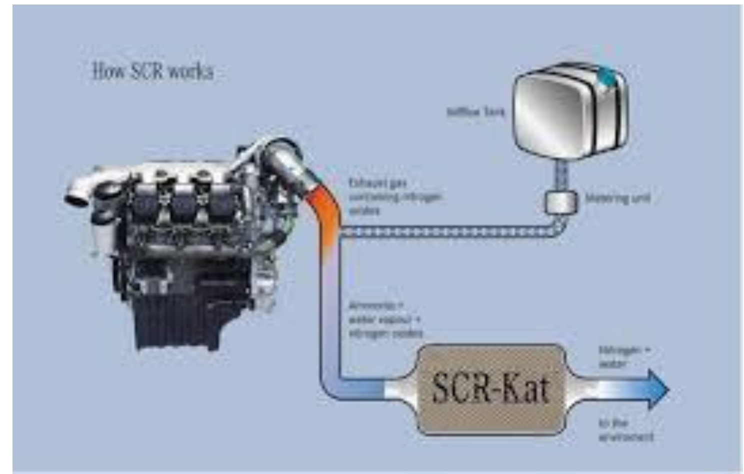
5. Examples - Vanadium oxide V_2O_5

The layers are being tested as sensors to control selective catalytic reduction (SCR) :

$$NH_2CONH_2 + H_2O \rightarrow 2\ NH_3 + CO_2$$



$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$



Selective Catalytic Reduction: Ammonia, mostly introduced in liquid phase as urea, is used to reduce the nitrogen oxide content in, for example, diesel exhausts. A sensitive and selective NH_3 or NO_x sensor can be used to control this complex process.

Conclusions:

1. Pulsed laser deposition (PLD) technique is a very versatile method for fabrication of thin films, nanoparticles, nanotrees with fractal geometry, and even nanofoams in the scale of tenths of nanometers.
2. These nanostructures have shown exceptional chemical sensing properties, for example for VOC like naphthalene and formaldehyde, as well as for CO, in ppb range.

Acknowledgements:

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SENSIndoor

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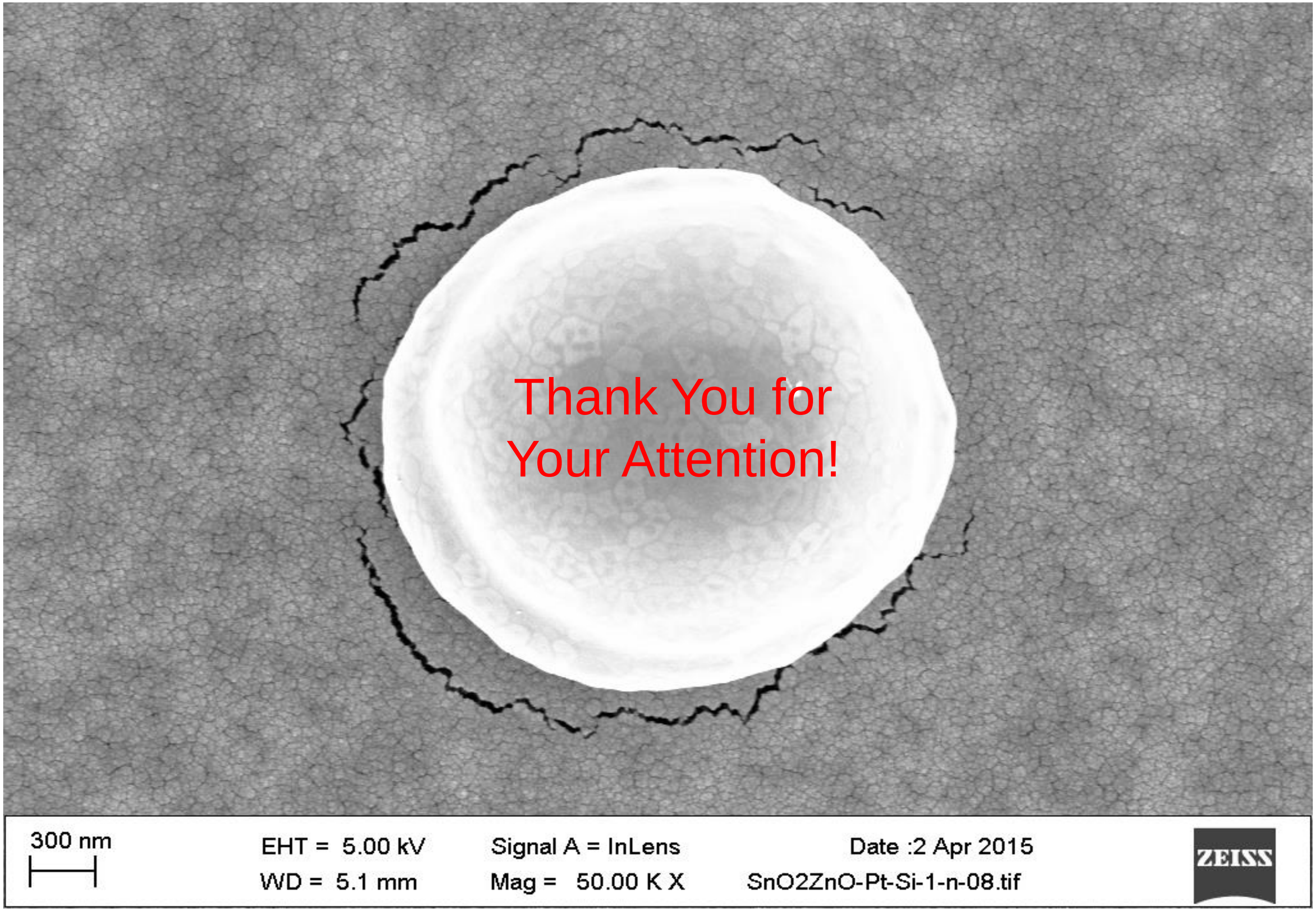

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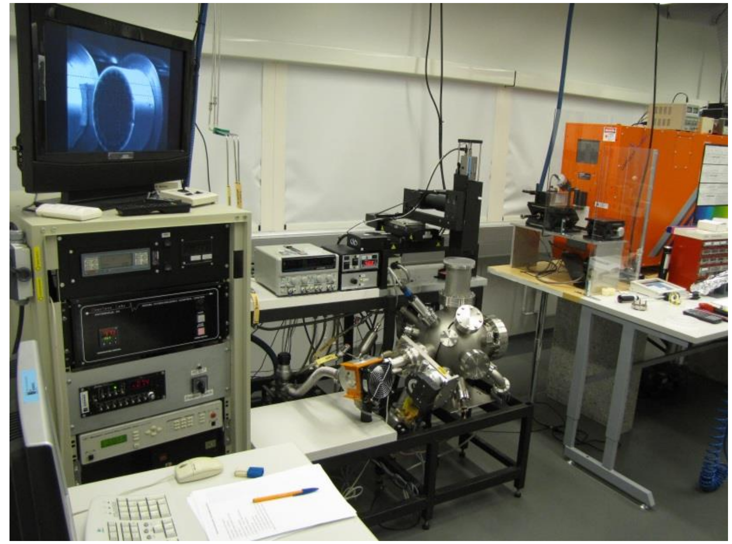
Research Facilities available for the Partners:

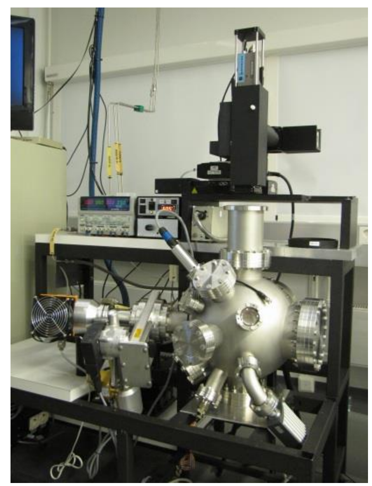
PLD laboratory in UO-FETF:

- XeCl-excimer laser (LamdaPhysik 201)
- λ = 308 nm (248 nm optional)
- τ = 25 ns, E_{max} = 400 mJ, f_{max} = 10 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 ϕ = 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:**
- Development of mixed-phase structures of MO's for gas sensing applications!
- *Development of fabrication methods of WO_3, V_2O_5, SnO_2, etc. nanostructures in various morphologies and geometries*!
- Detailed structural characterization and physics of gas sensing mechanism.
- *Utilization of phase transitions and p-n junction effects in gas sensing processes*!
- Integration into low-cost mass-production processes.