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

COST Action TD1105

WGs and MC Meeting at LINKÖPING, 3 - 5 June 2015

Action Start date: 01/07/2012 - Action End date: 30/06/2016

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

Pulsed Laser Deposition of Metal Oxide Nanoparticles, Agglomerates, and Nanotrees

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COST EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

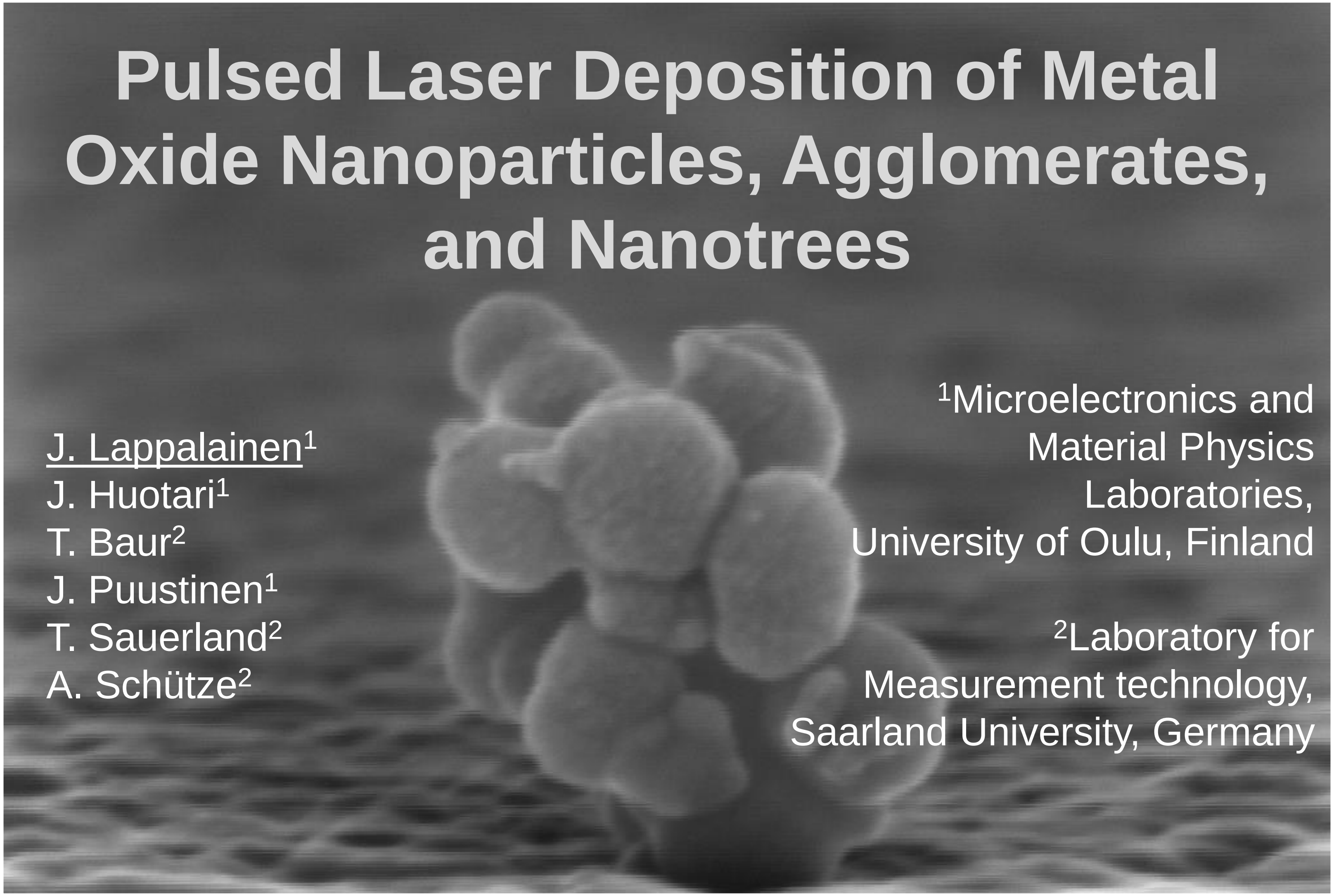
EuNetAir
European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

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



Pulsed Laser Deposition of Metal Oxide Nanoparticles, Agglomerates, and Nanotrees

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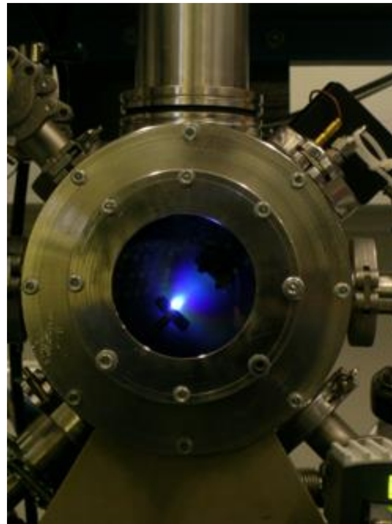
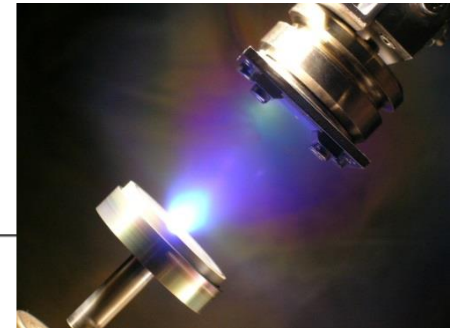
Introduction:





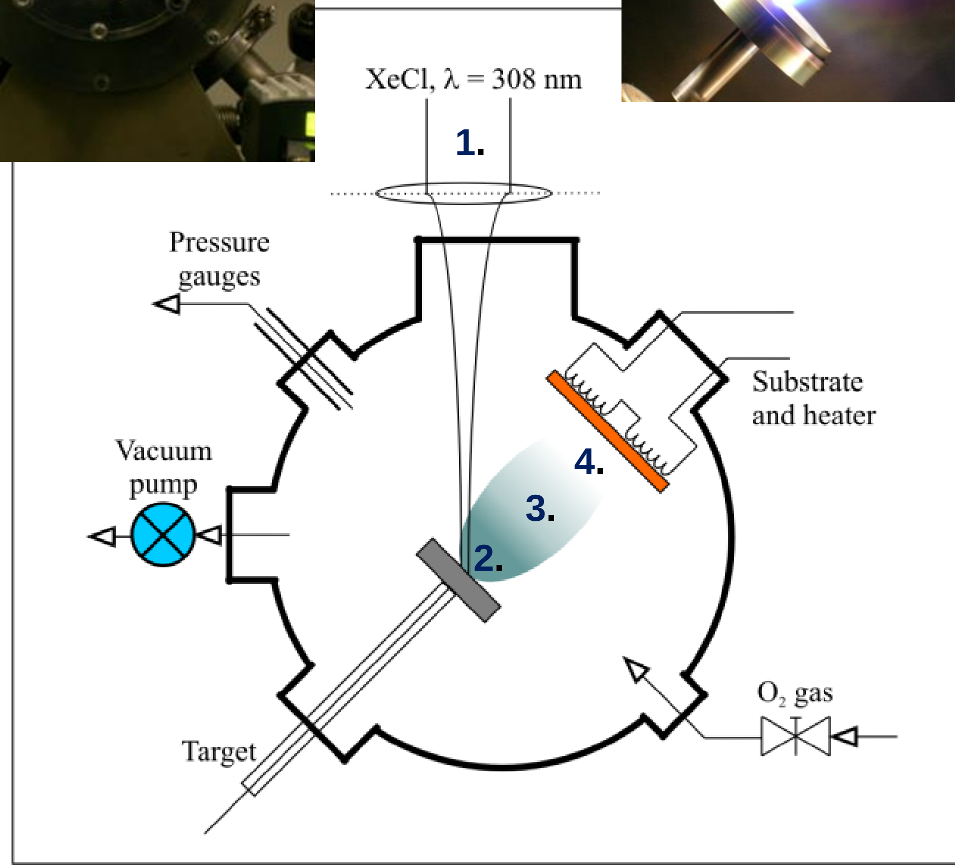
***1. Pulsed Laser Deposition* (PLD):**

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

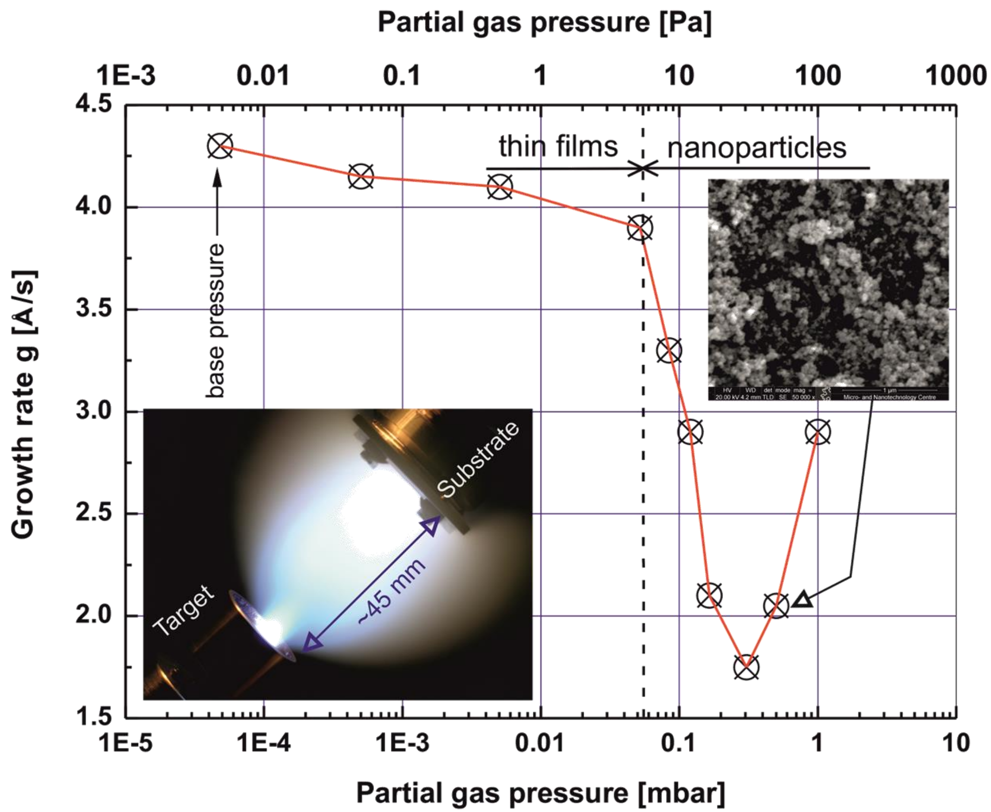
4. **Atomic (and other) species of the plasma are collected on substrate surface to form a thin film.**



Introduction:

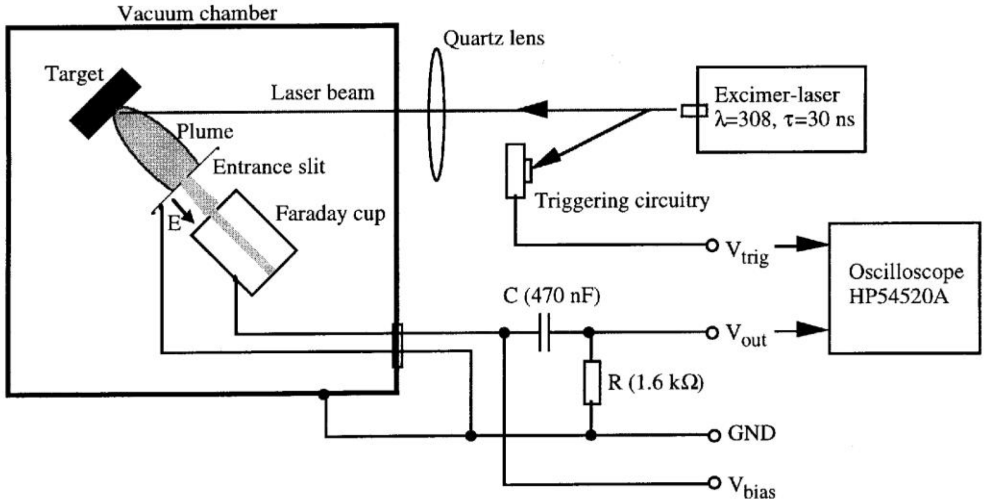
***2. Particle Generation in* PLD:**

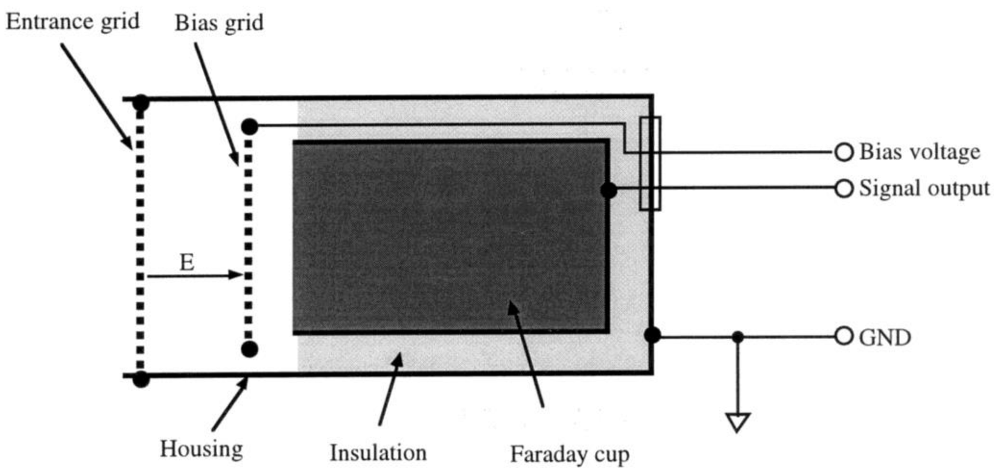
- **Two points of generation: (i) target surface, and (ii) high density plasma.**
- **Reactions in plasma can lead into: (i) dissosiation of particulates, or in (ii) nucleation of nanoparticles.**
- **Plasma can be controlled by deposition atmosphere, *i.e.* partial oxygen pressure p(O_2), or by laser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

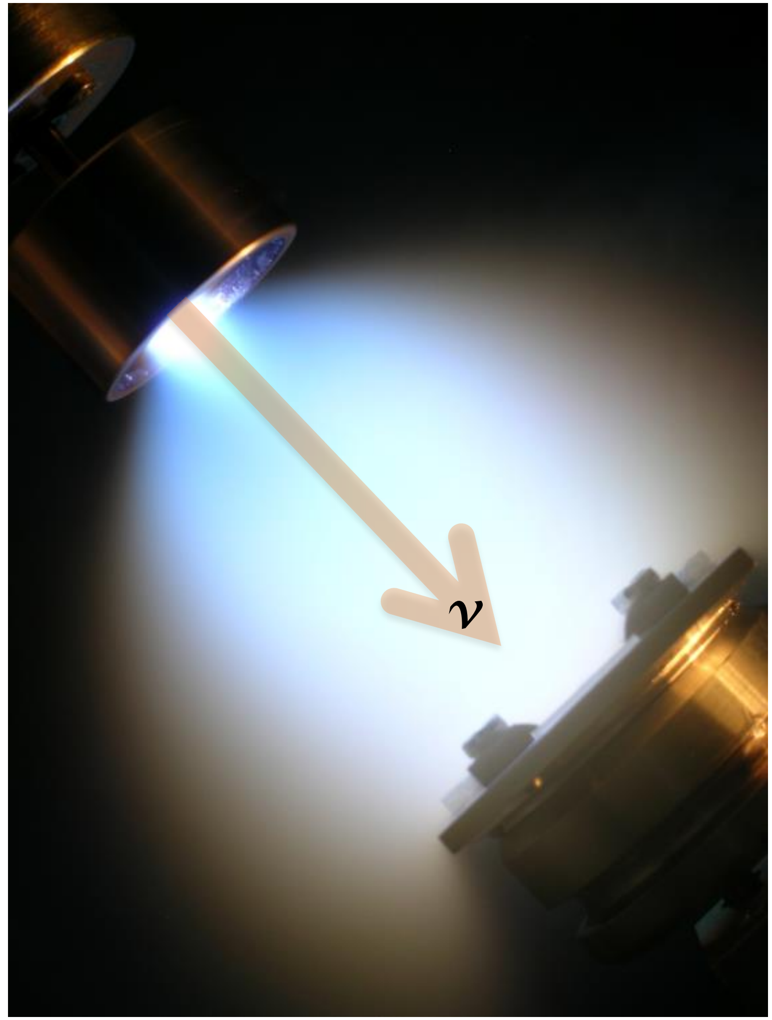


Introduction:

Time of Flight (TOF) measurements with Faraday cup:







Introduction:

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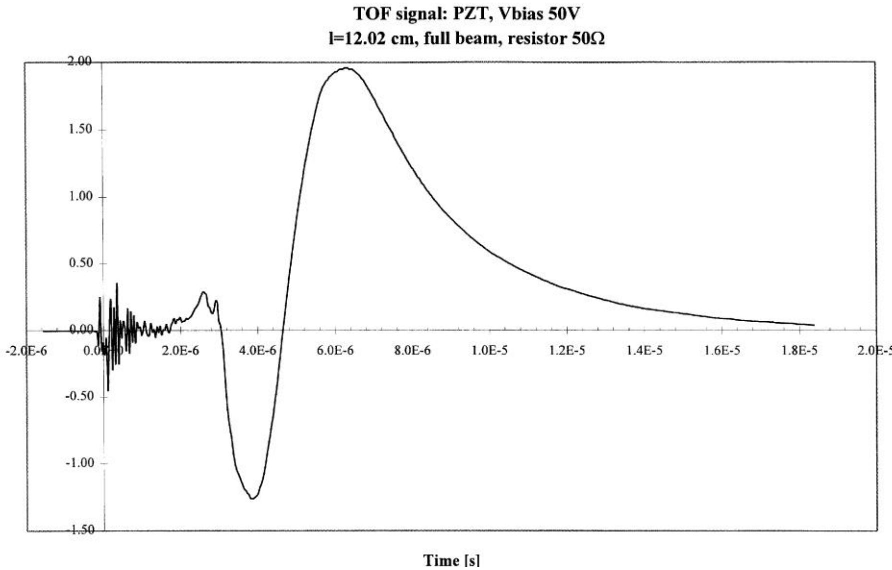
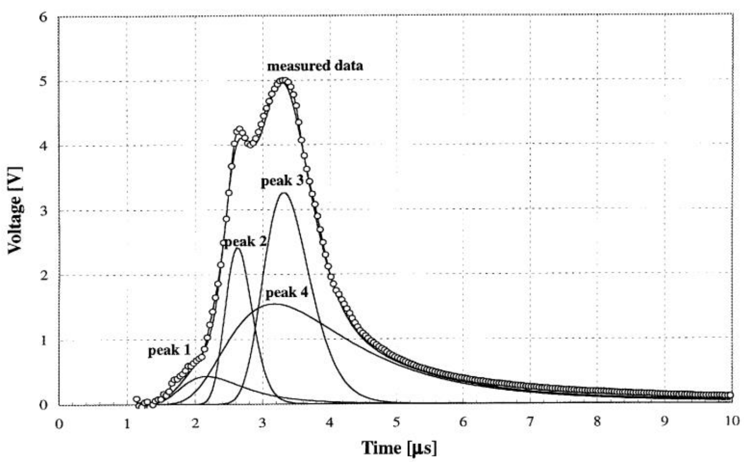
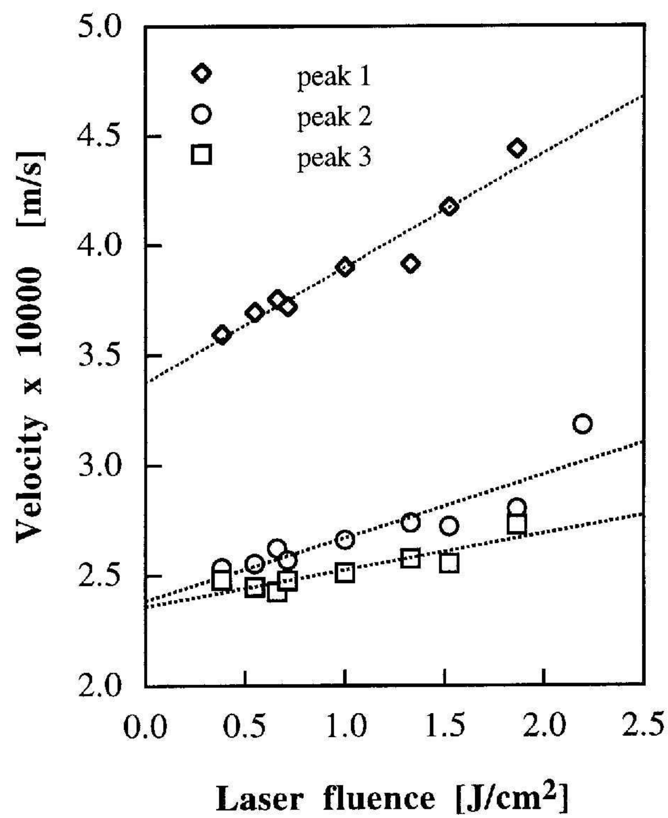




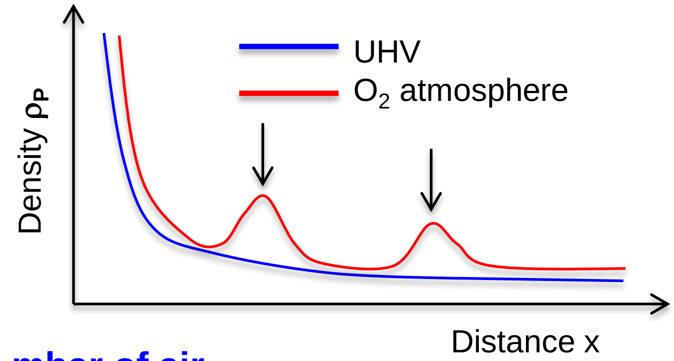
Maxwell – Boltzman distribution:

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

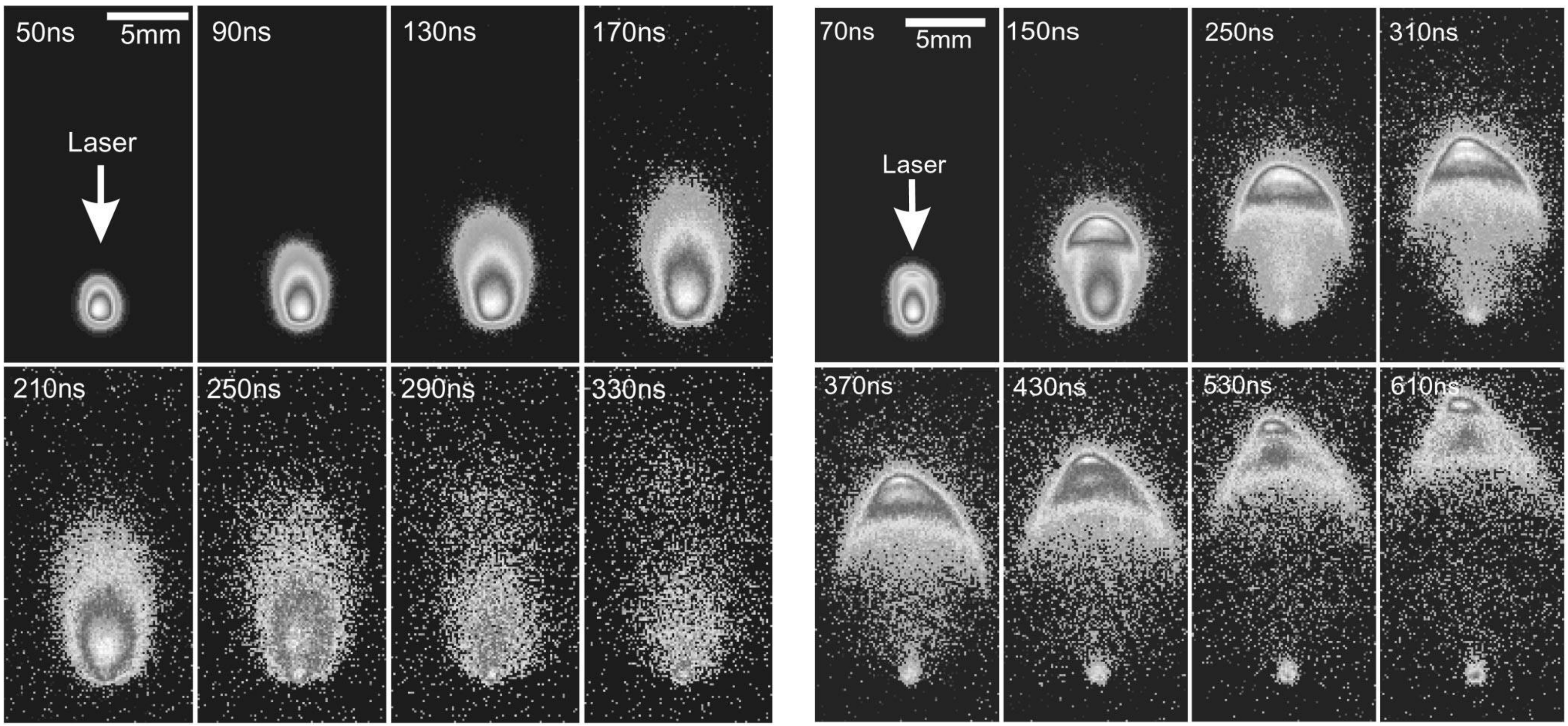


Introduction:

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

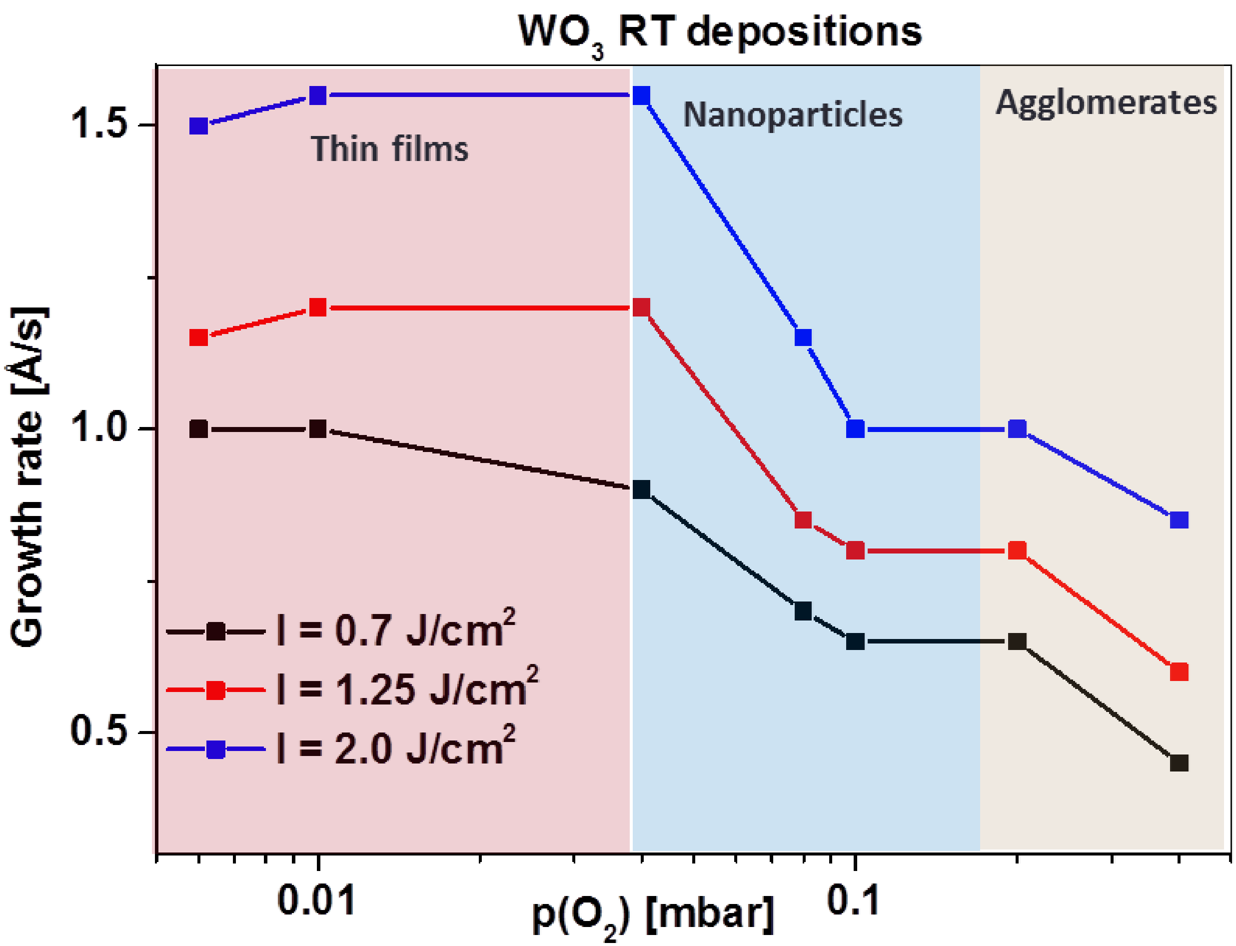


(a) in 1x10^{-6} mbar of air **(b) in 0.2 mbar of air**



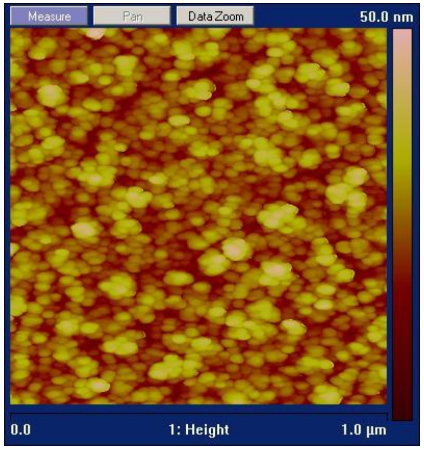
Manufacturing of WO_3 nanostructures

- **Ceramic target of pure WO_3 was used in PLD process**
- **In QCM measurements, change in the growth modes from thin films to nanoparticle agglomerates was seen**

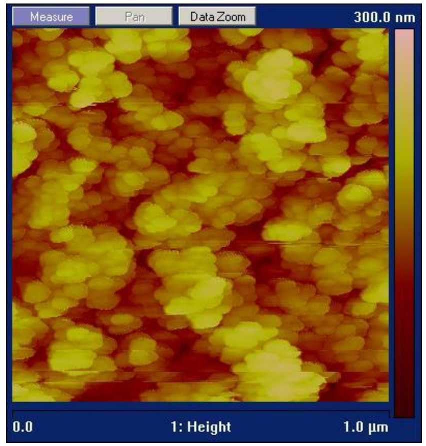


Manufacturing of WO_3 nanostructures

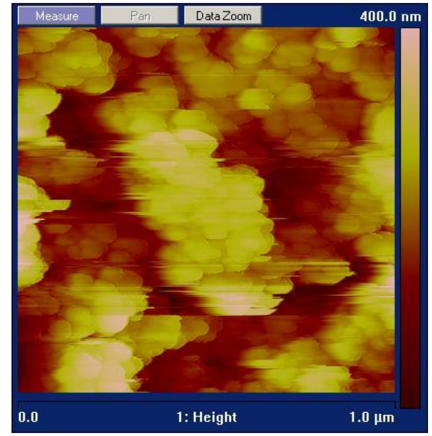
$p(O_2)$ = 0.08 mbar



$p(O_2)$ = 0.2 mbar

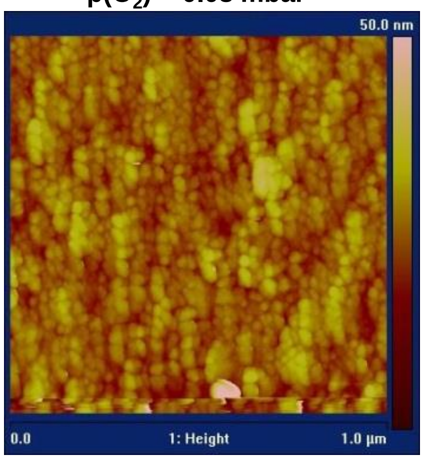


$p(O_2)$ = 0.5 mbar

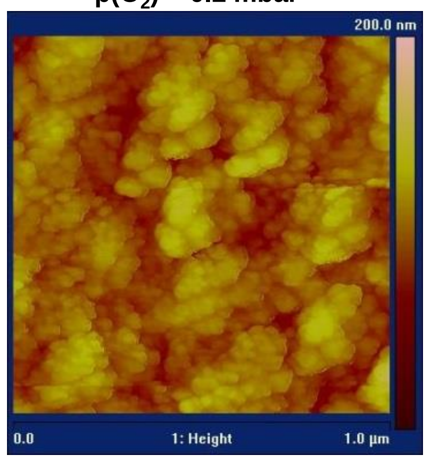


Effects of post-annealing at 400 ºC for 1 h period:

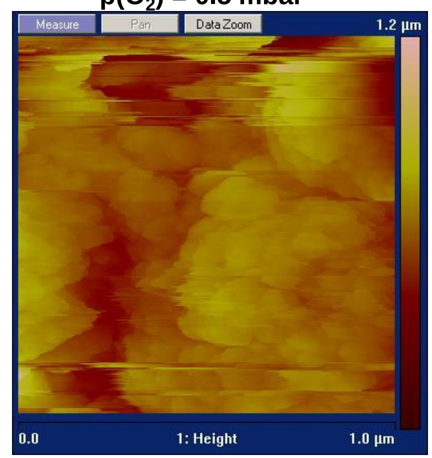
$p(O_2)$ = 0.08 mbar



$p(O_2)$ = 0.2 mbar



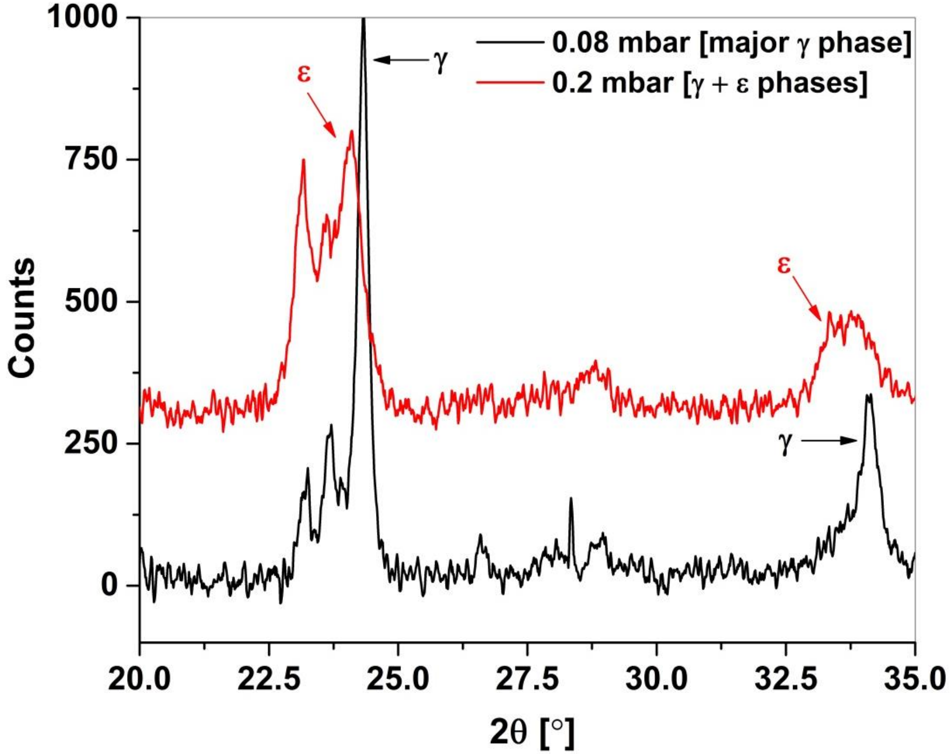
$p(O_2)$ = 0.5 mbar

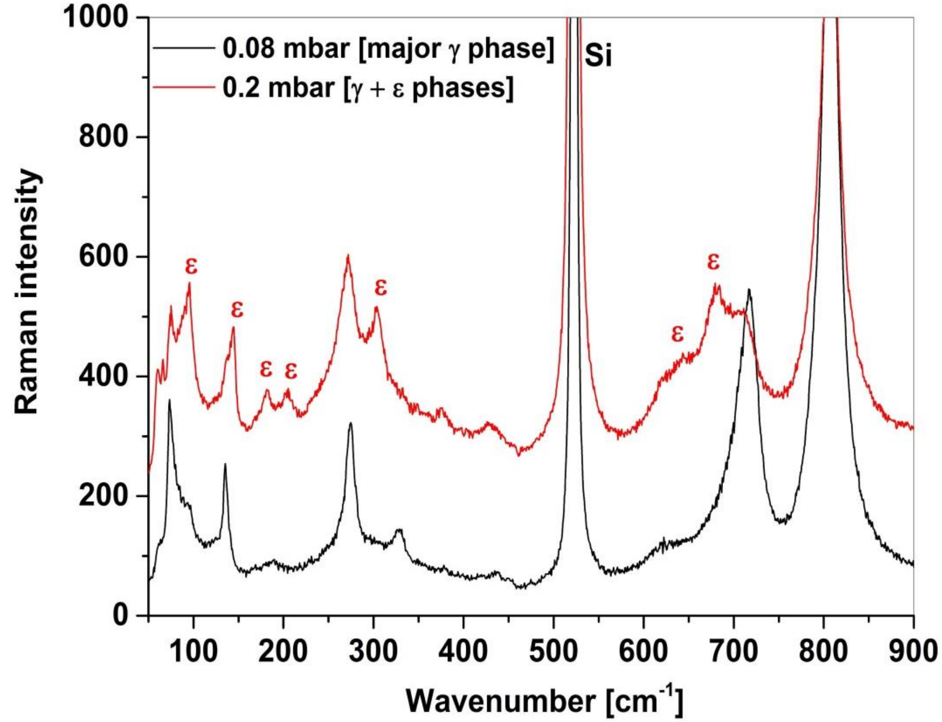


Manufacturing of WO_3 nanostructures

XRD and Raman Spectroscopy: layers are composed of γ-phase and ε-phase of WO_3 :

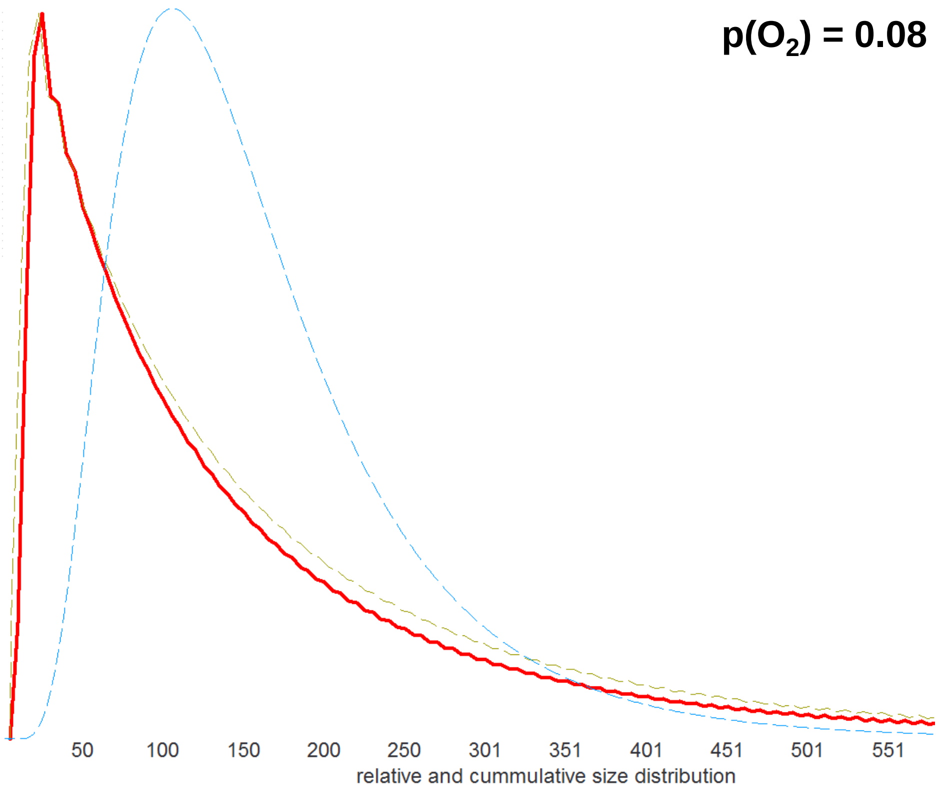
T_{ann} = 400 ˚C:

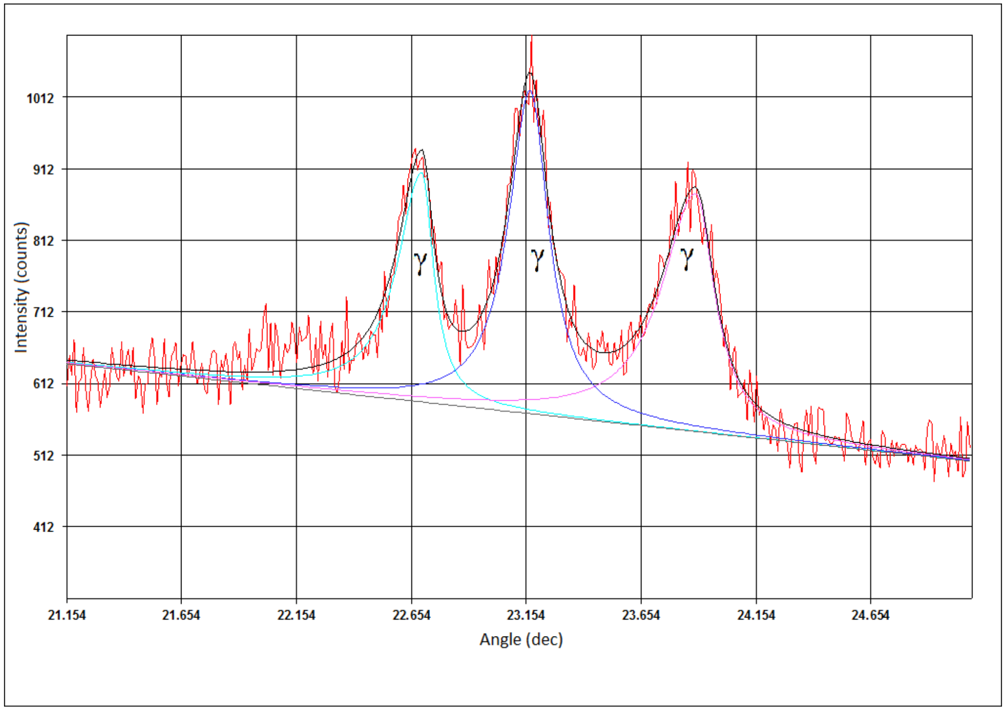




Manufacturing of WO_3 nanostructures

$p(O_2)$ = 0.08 mbar, T_{ann} = 500 ˚C:

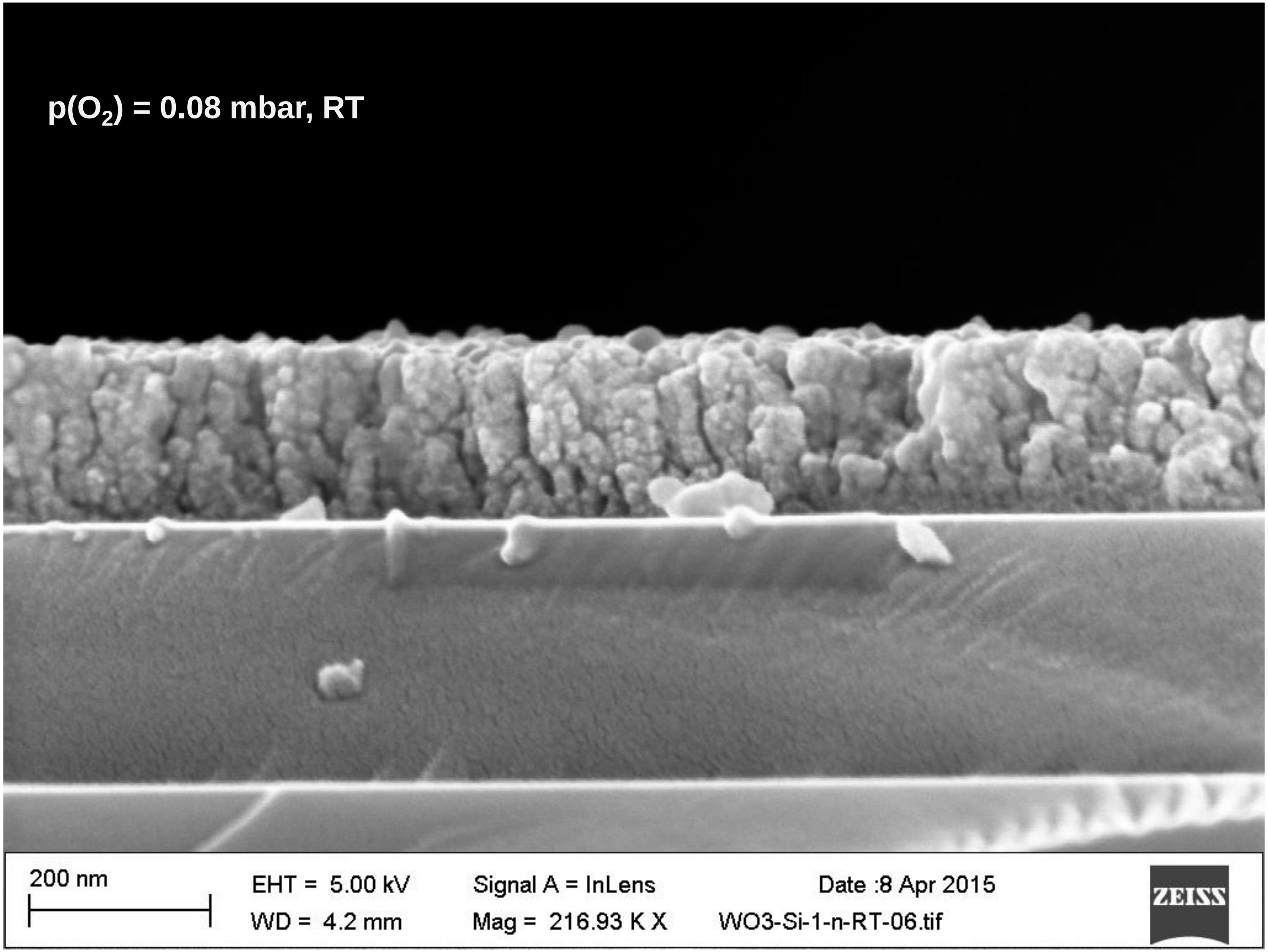




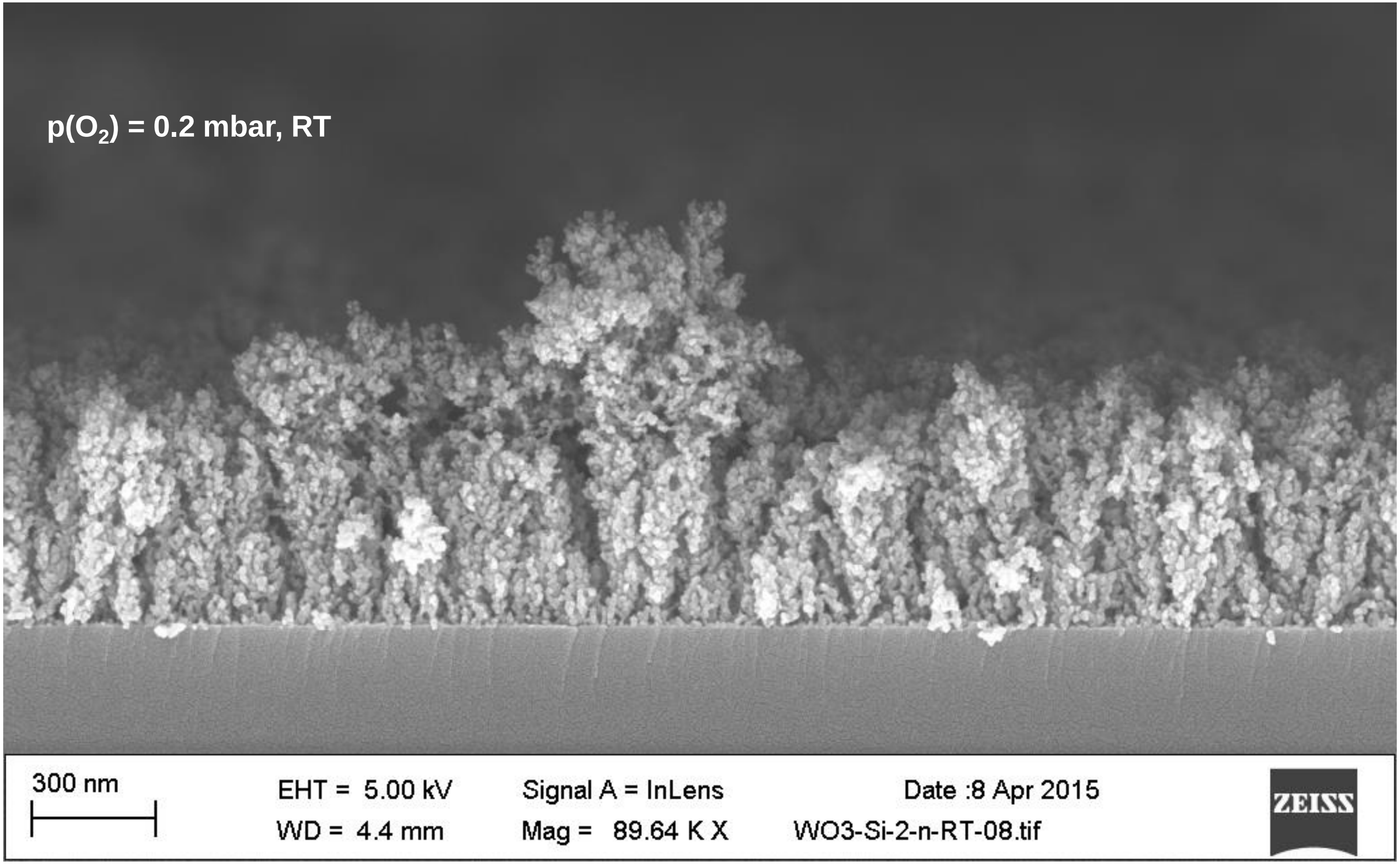
Warren-Averbach, <D> from distr.: 143 Å (may be too low due to truncation)

Warren-Averbach, <D> from slope: 176 Å

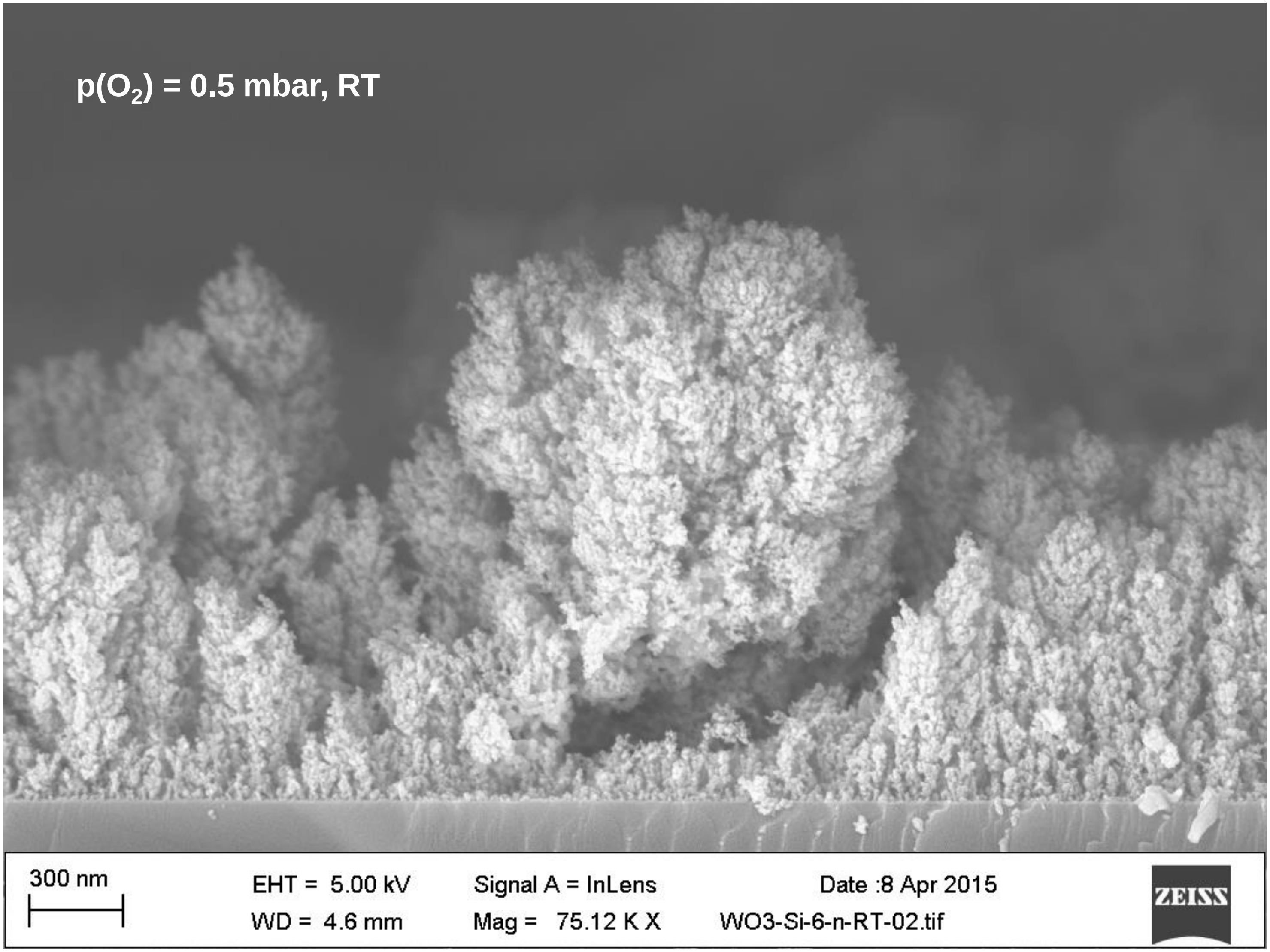
Manufacturing of WO_3 nanostructures



Manufacturing of WO_3 nanostructures

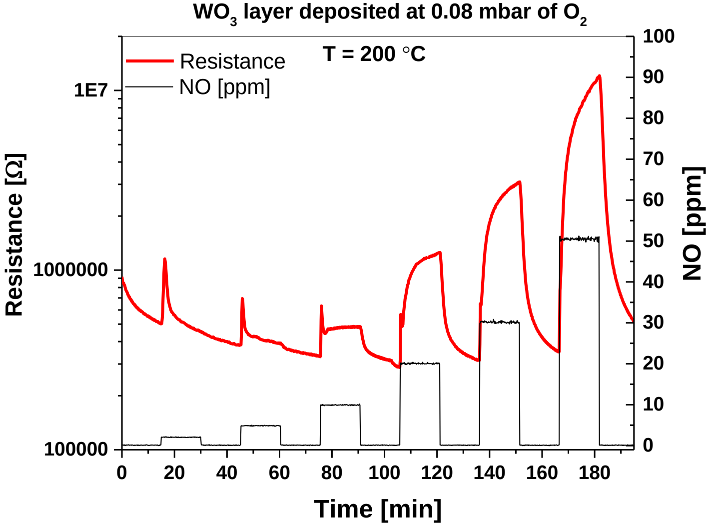


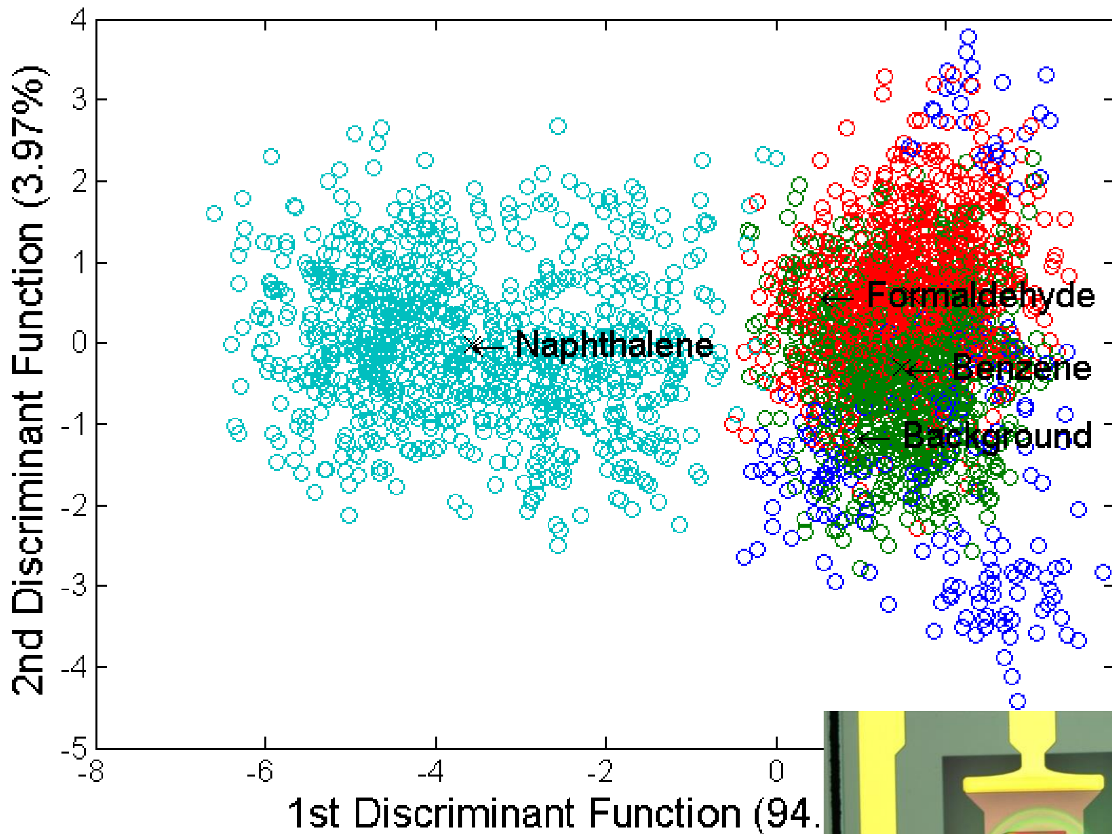
Manufacturing of WO_3 nanostructures

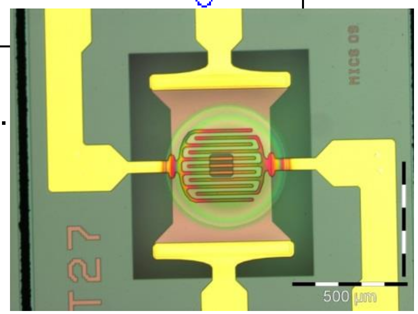


Manufacturing of WO_3 nanostructures

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



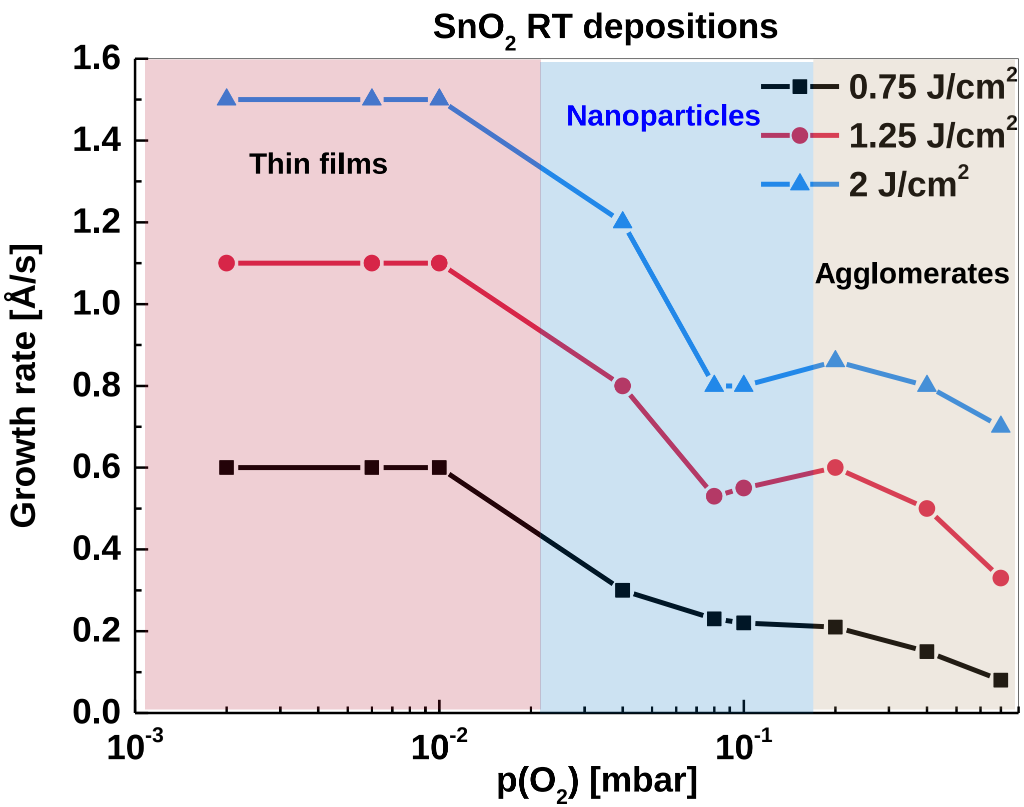


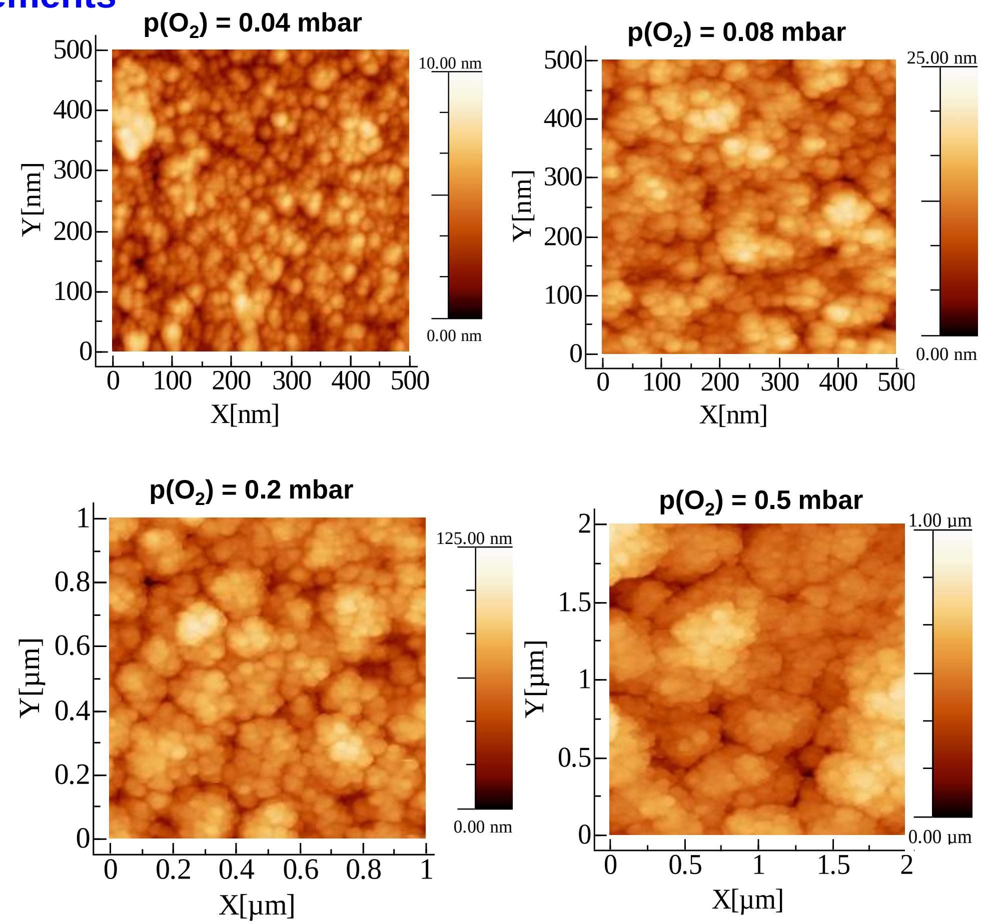


WO_3 gas sensing properties: the WO_3 layers are extremely selective to ppb-levels of naphthalene!

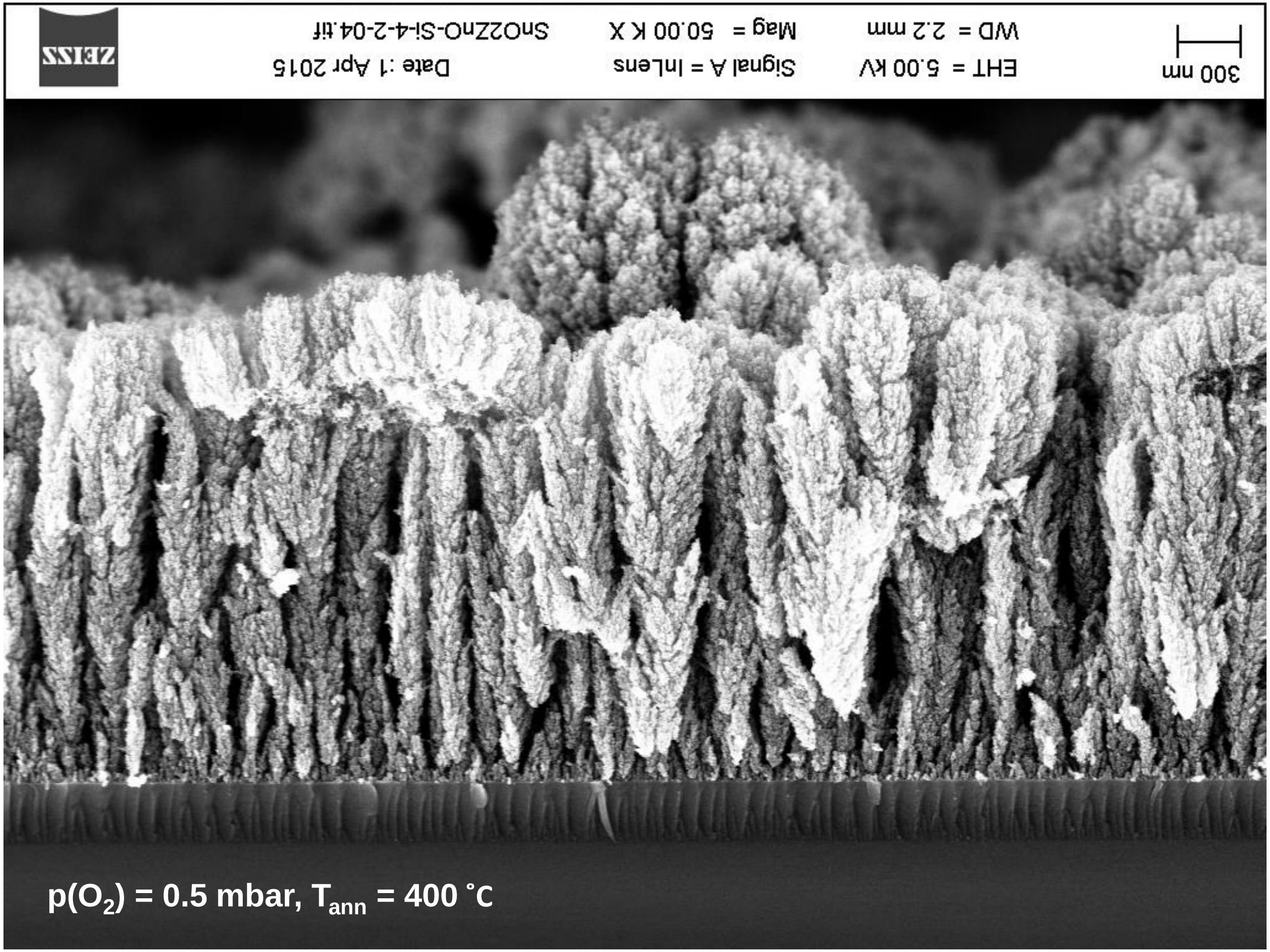
Manufacturing of SnO_2 nanostructures

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





Manufacturing of SnO_2 nanostructures



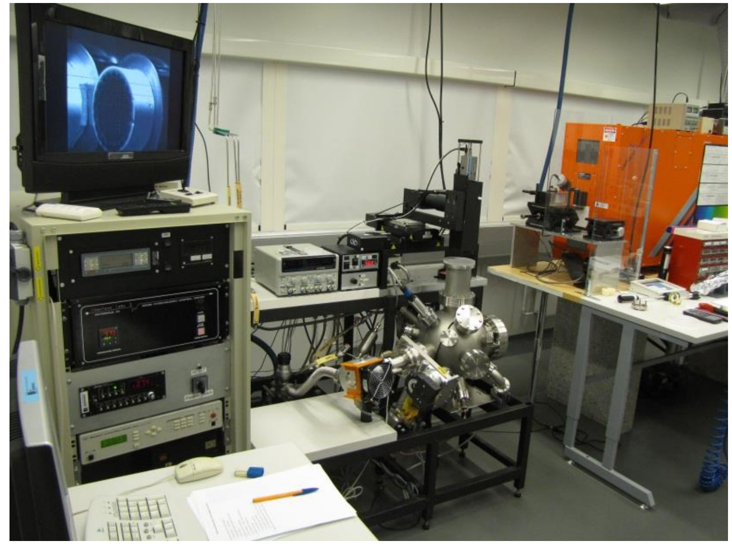
Research Facilities available for the Partner:

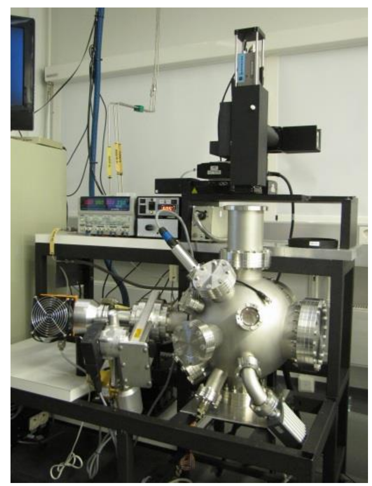
PLD laboratory in UO-FETF:

- **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.