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

COST Action TD1105

WGs and MC Meeting at Cambridge, 18-20 December 2013

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EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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

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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, 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, and VOC's
  - Utilizing grain size and phase transition effects
  - Fabrication of sensors on flexible substrates PET/PEN substrates using printing techniques

STRUCTURAL CHARACTERIZATION AND GAS SENSING PROPERTIES OF VANADIUM OXIDE THIN FILMS

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4. Summary

1. Background

- Pulsed laser deposition (PLD) is a versatile deposition method for electroceramic thin films (e.g. PZT, WO_3).
- Vanadium oxides (VO_2, V_2O_5 etc.) is an interesting material group used in different types of applications.
- Nanostructures of V_2O_5 has been shown to be very sensitive material for ammonia (NH_3) sensing.[1]
- The metal-insulator transition of VO_2 has been studied for optical switching.[2]
- Vanadium oxide nanotubes (VO_x-NT) have been studied as a possible electrode material for Li^+ batteries.[3]
- Here we present some new structural and gas sensing studies of vanadium oxide thin films deposited by PLD

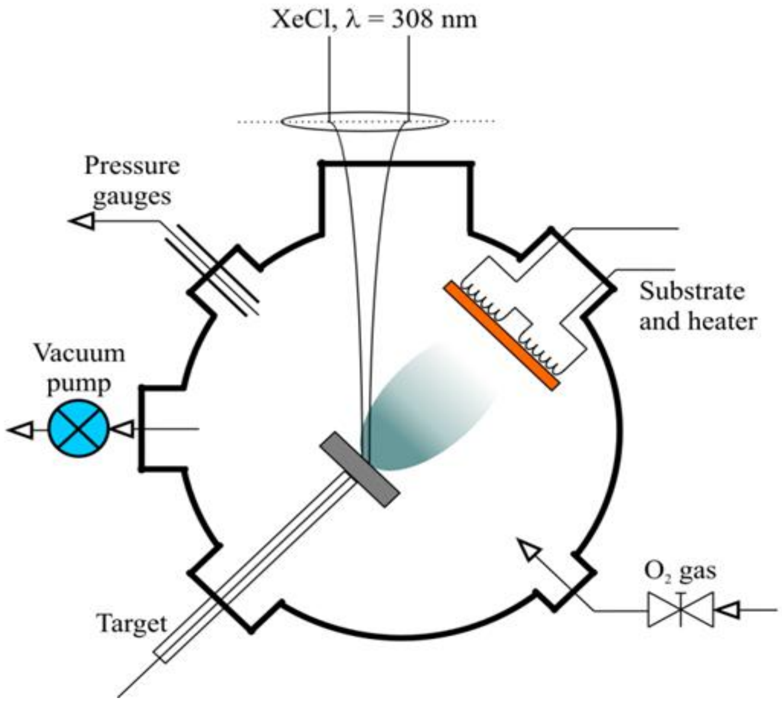
1) Modafferi et al., Sens. Act. B 163 (2012) 61-68.
2) Beteille et al., J. Sol-Gel. Sci. Technol. 13 (1998) 915-921.
3) Nordlinder et al., Chem. Mater. 15 (2003) 3227-3232.

2. Pulsed Laser Deposition of VO_x Thin Films

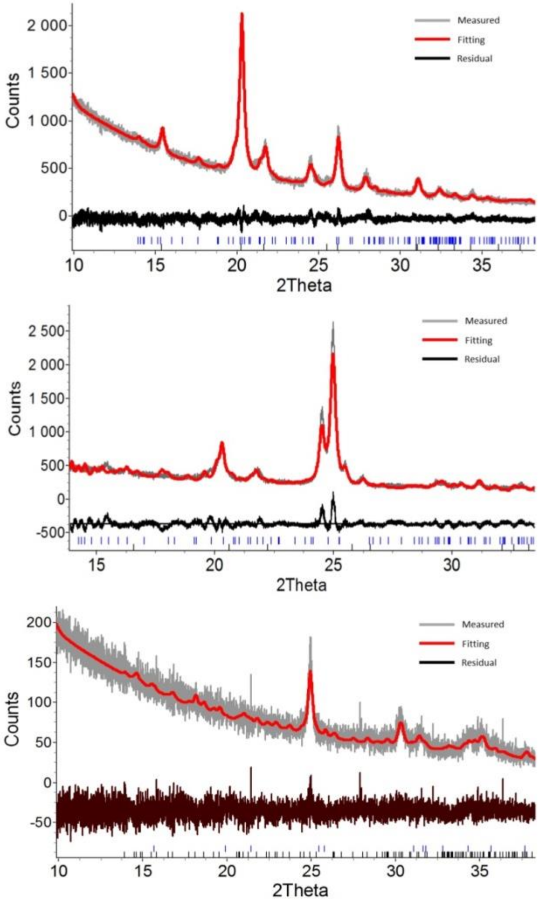
Pulsed laser deposition with different deposition parameters were used to manufacture vanadium oxide thin films on sapphire and silicon substrates from a pure ceramic V_2O_5 target:

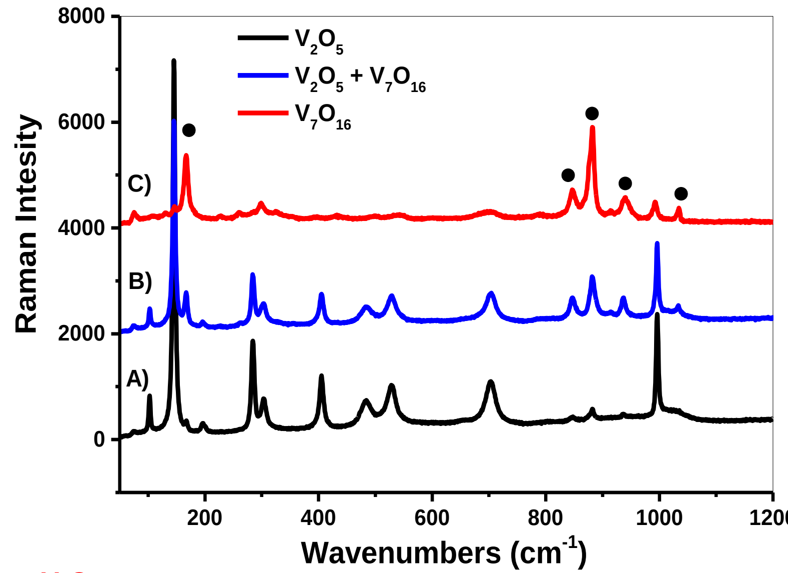
In PLD deposition many different deposition parameters can be altered to control the film structure, for example:

- The substrate T
- Gas partial pressure in the chamber
- Laser pulse density

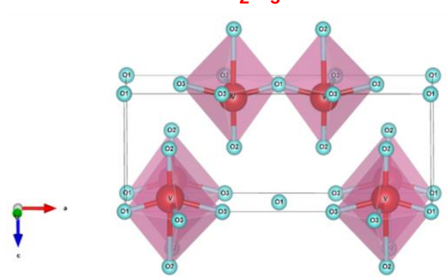


3. Characterization of the thin films (1/6)

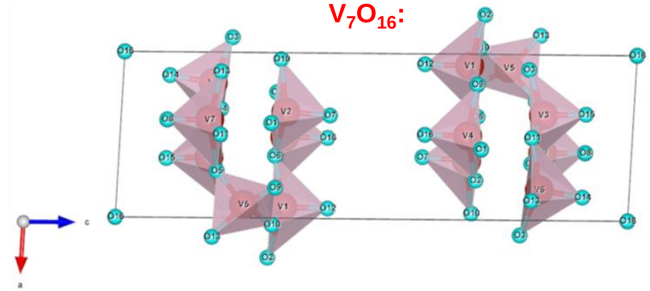




V_2O_5:



V_7O_{16}:



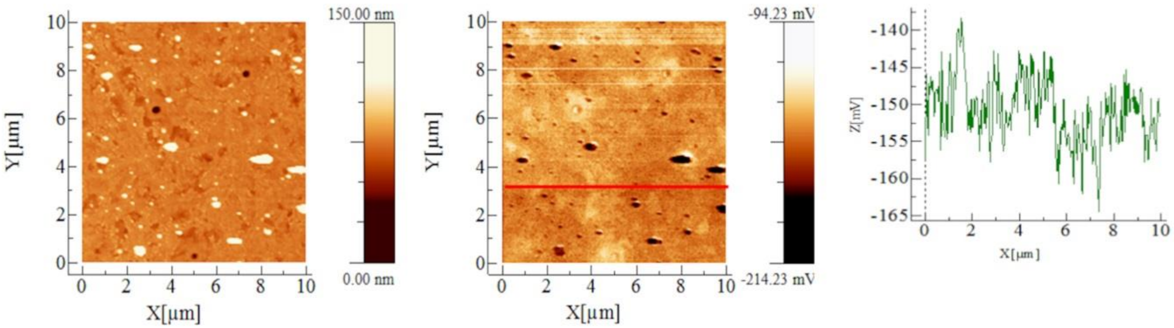
XRD and Raman spectroscopy results:

– Raman spectroscopy and X-ray diffraction together with Rietveld refinement showed the existence of two phases in the thin films: orthorombic V_2O_5 phase and triclinic V_7O_{16} phase

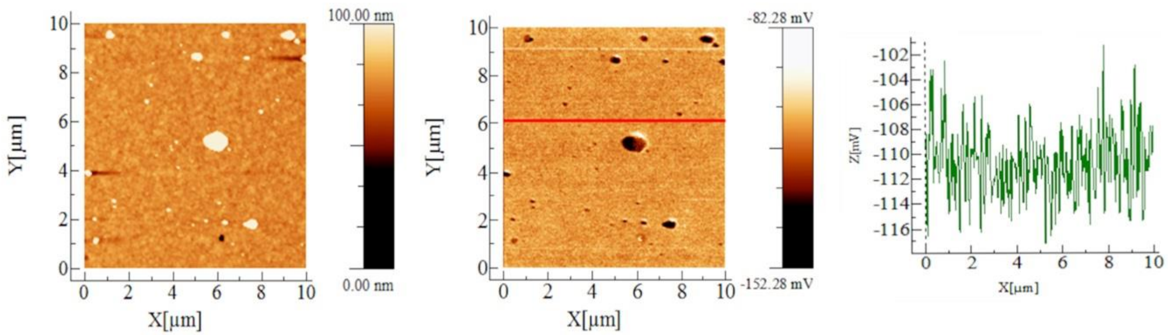
– To our knowledge, this is the first time V_7O_{16} phase has been shown to exist in solid-state thin-film form

3. Characterization of the thin films (2/6)

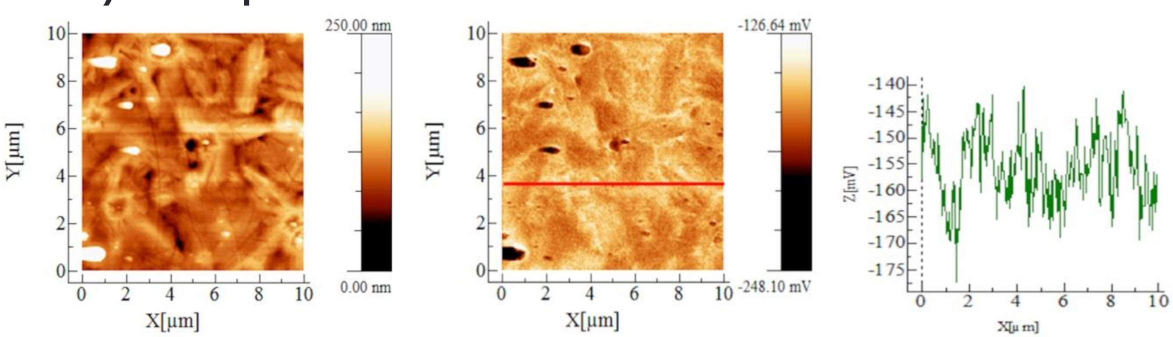
a) V_2O_5:



b) V_7O_{16}:



c) Mixed phase:



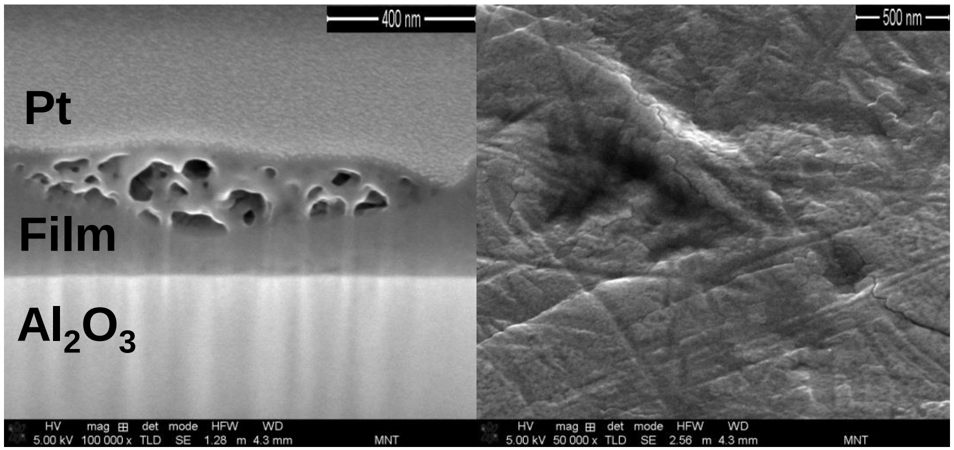
AFM results:

- Films **a)** and **c)** showed a quite smooth surface morphology
- Film **b)** had an interesting tubular like surface and the roughest surface morphology
- All the sample surfaces had particulate droplets from the PLD on them (white spots)
- The surface potential (ΔΦ of tip and film surface) proved to be different in the two phases by ΔΦ ~40 meV
- In films **a)** and **c)** (major V_2O_5 and major V_7O_{16}) the surface potential value was relatively flat over the whole surface area
- In mixed-phase film **b)**, the surface potential value varied strongly with surface morphology and phase structures with different work functions

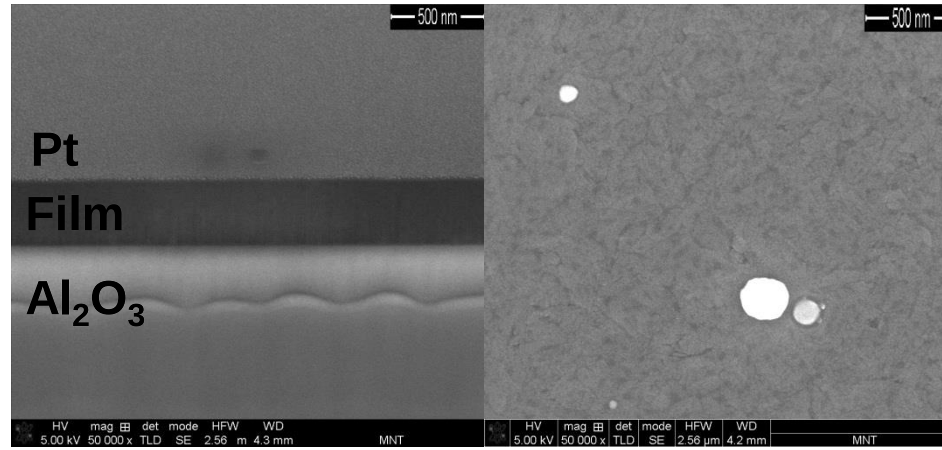
3. Characterization of the thin films (3/6)

Scanning electron microscopy (SEM) results:

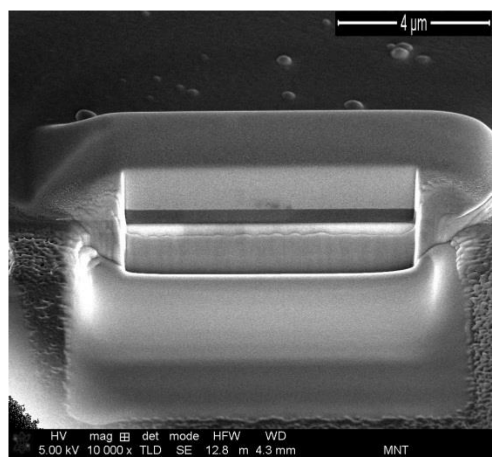
Mixed phase:



V_7O_{16}:



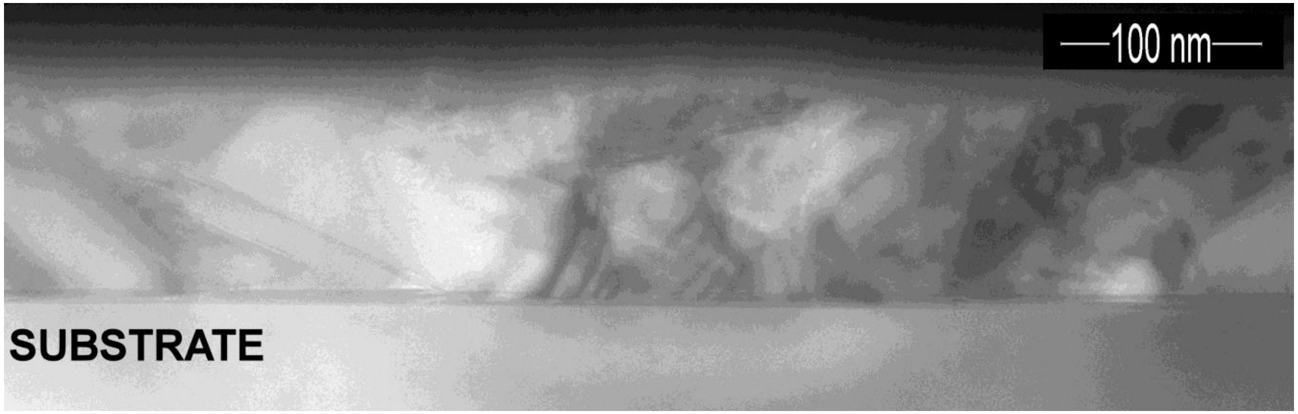
The SEM of focused ion beam etching (FIB) device was used to make the measurements



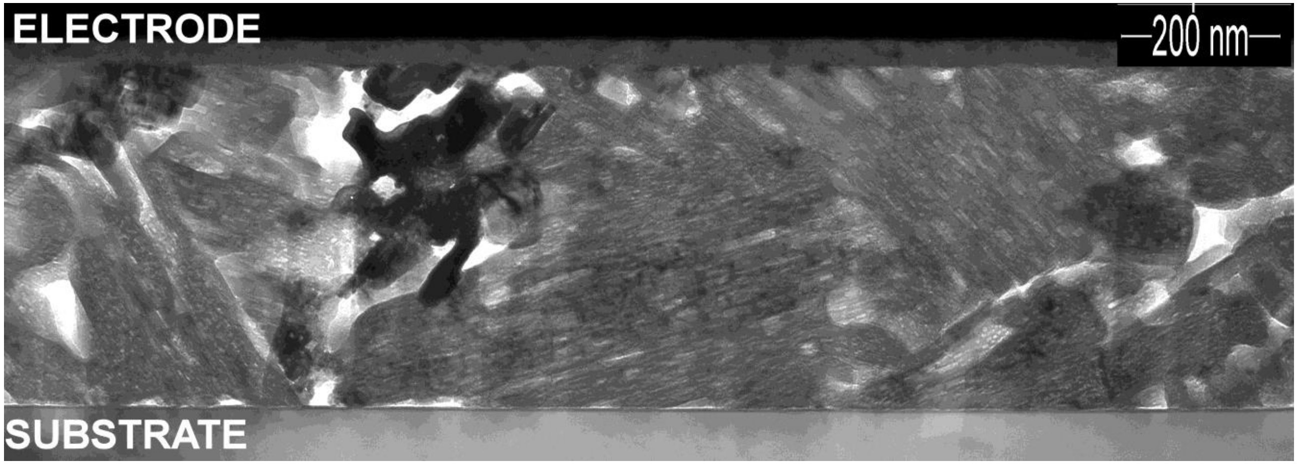
3. Characterization of the thin films (4/6)

Transmission electron microscopy (TEM) results:

V_2O_5:



Mixed phase:



- Both films showed polycrystalline microstructure
- Film with a pure V_2O_5 phase had a more dense structure, film with mixed phases showed more porous structure, confirming the results already seen in SEM
- Especially mixed phase samples showed tubular-like structures in the films

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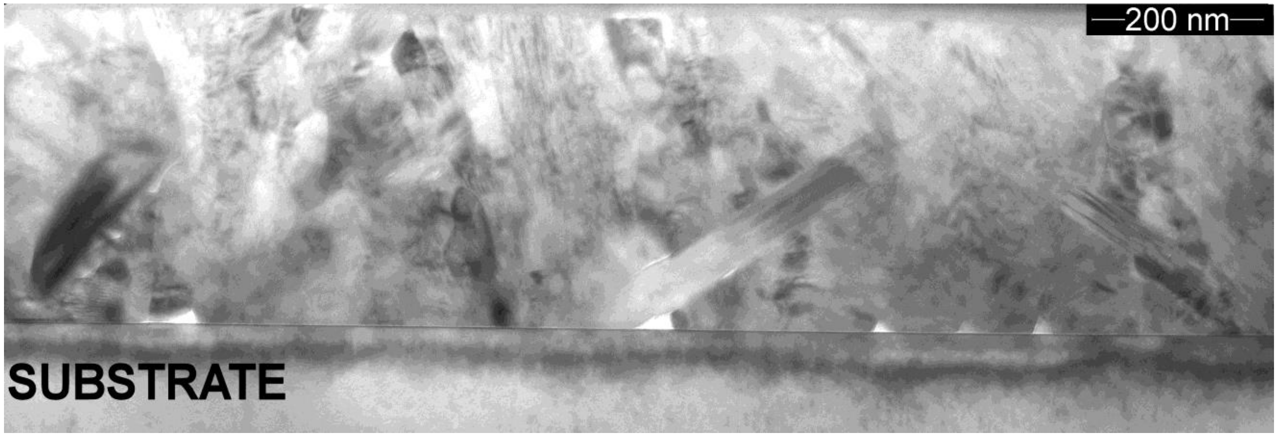
3. Characterization of the thin films (5/6)

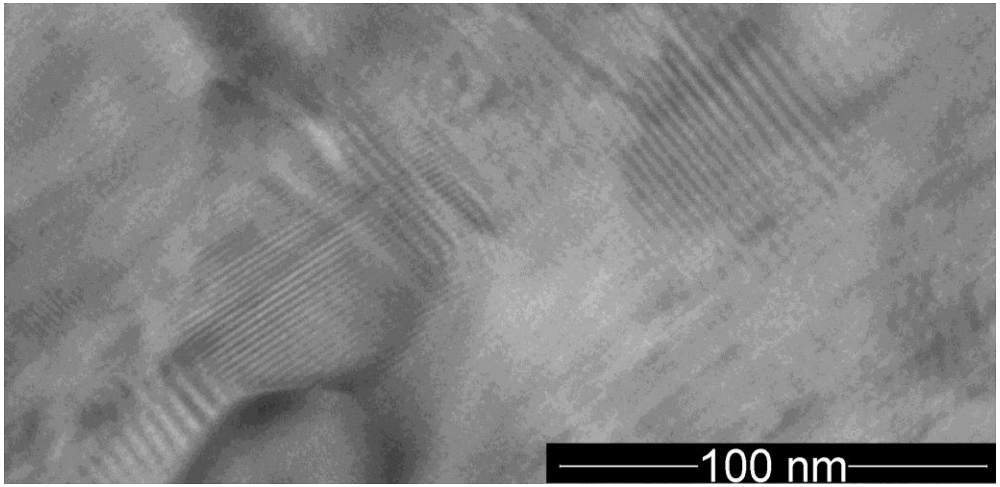
Transmission electron microscopy (TEM) results:

V_7O_{16}:



- Film with major V_7O_{16} phase showed also a dense structure, as seen in SEM studies, aswell
- The existence of a tubular-like structure is more clear in this films, hence the tubular-like structures are believed to be a result of the existence of V_7O_{16} phase in the film crystal structure!!

Close-up:



- Also, the two phases with different crystal structures could be clearly distuingshed from the TEM images of film with a major V_7O_{16} phase

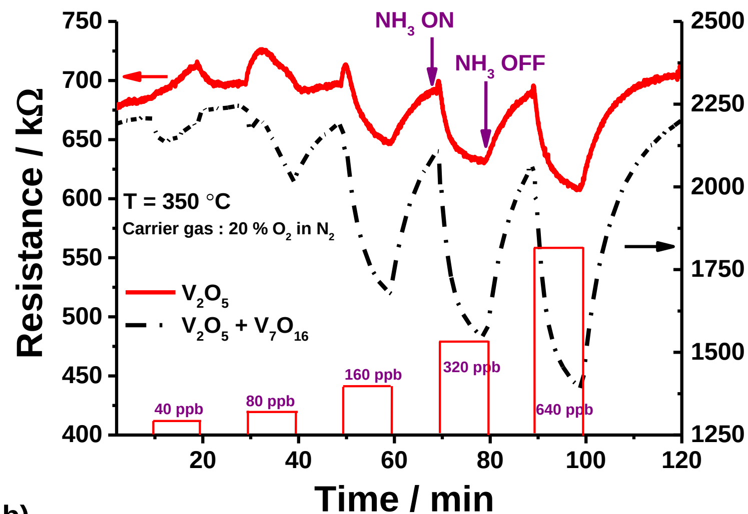
3. Characterization of the thin films (6/6)

Gas sensing examples of vanadium oxide thin films:

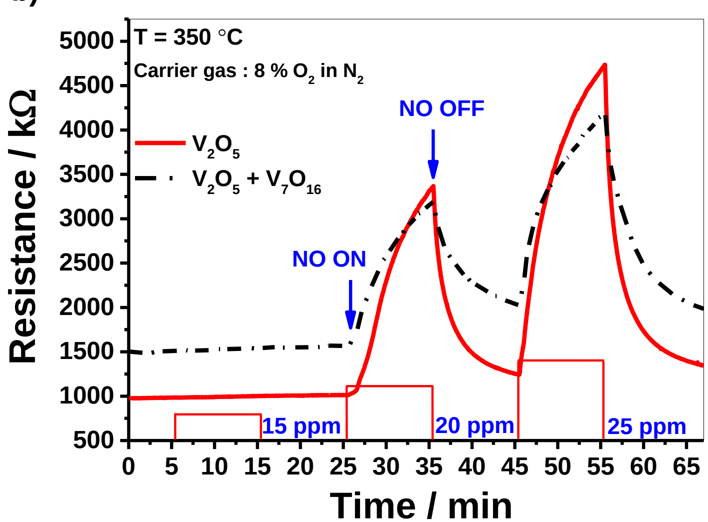
–The thin films have proven to be highly sensitive to ammonia gas (NH_3); a reducing response was seen already at ppb level!

–Also clear selectivity to NH_3 has been seen in presence of NO

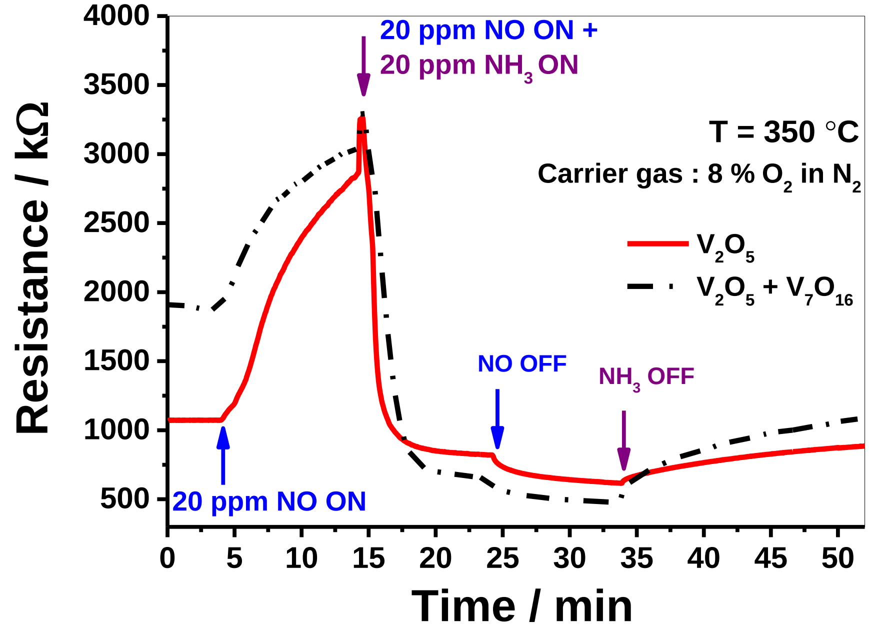
a)



b)



c)



4. Summary

- PLD fabricated vanadium oxide thin films were studied
- Raman spectroscopy and XRD studies together with Rietveld refinement showed existence of two phases in the films; orthorombic V_2O_5 and triclinic V_7O_{16}
- AFM surface morphology studies showed that films with either a strong V_2O_5 or V_7O_{16} phase had smoother surface than the film with a more mixed phase structure
- The surface potential studies proved the existence of two different work functions of the two different phases in the film surfaces
- SEM and TEM studies showed that the mixed phase film had much more porous microstructure than the films with more uniform phase structure
- In TEM studies interesting tubular-like structures were noticed in the films
- The films were shown to be sensitive to NH_3 already at ppb level

Suggested R&I Needs for future research to Action WGs/SIGs General Assembly

- **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, VO_2, etc. nanostructures and nanoparticles in various conditions: high-temperature - RT, fabrication in liquids, etc.
- Detailed structural characterization and physics of gas sensing mechanism.
- *Utilization of phase transition effects in gas sensing process*.
- Integration into low-cost mass-production processes, *e.g.* ink-jet printing, GASFET's etc.