NCCAVS Joint Users Group Technical Symposium
“Nanomaterials for Energy, Biomedical, and Electronic Devices”
In Conjunction with the NCCAVS 35th Annual Equipment Exhibition

Nanoparticle generation using sputtering plasmas

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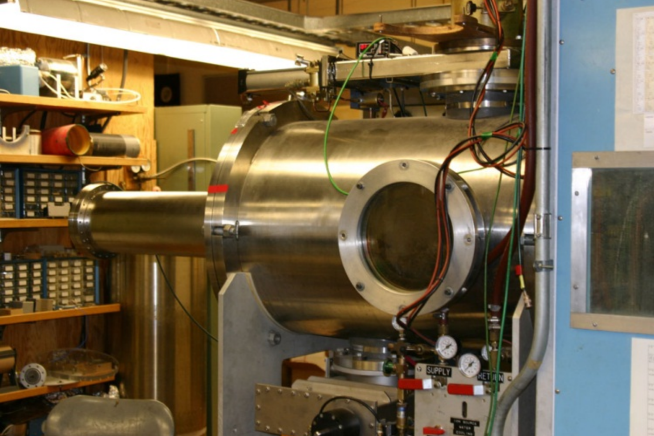
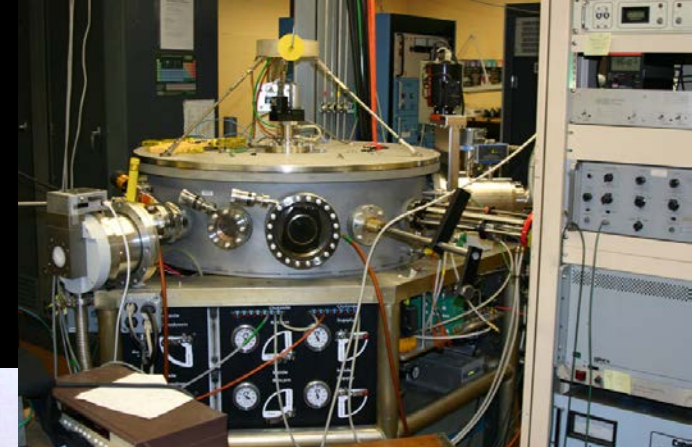
Northern California Chapter



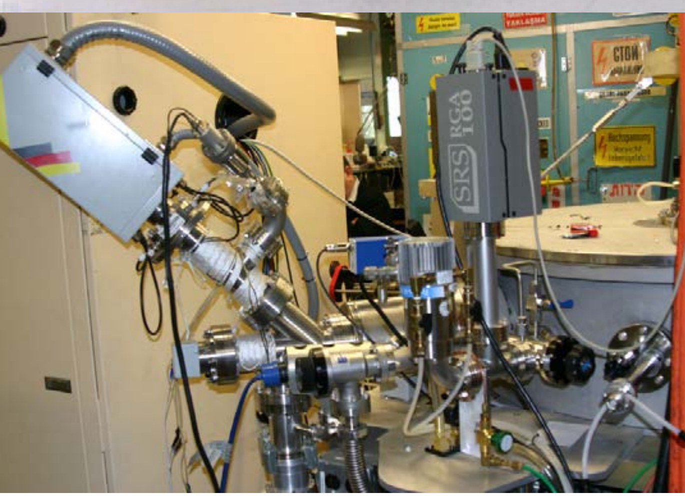
synthesis

&

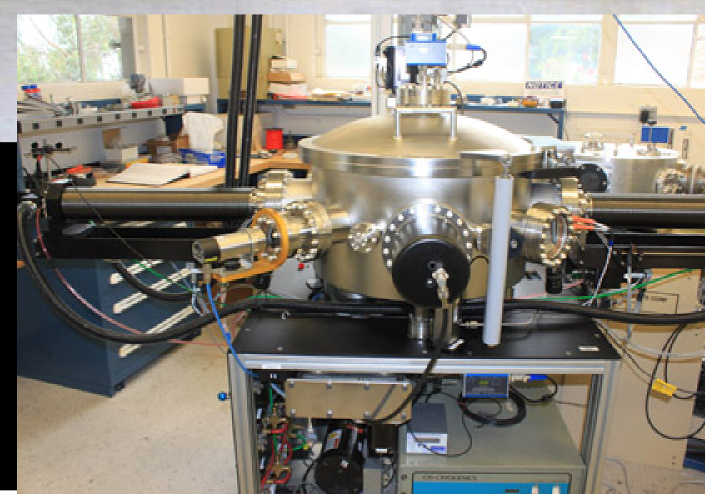


materials

plasmas

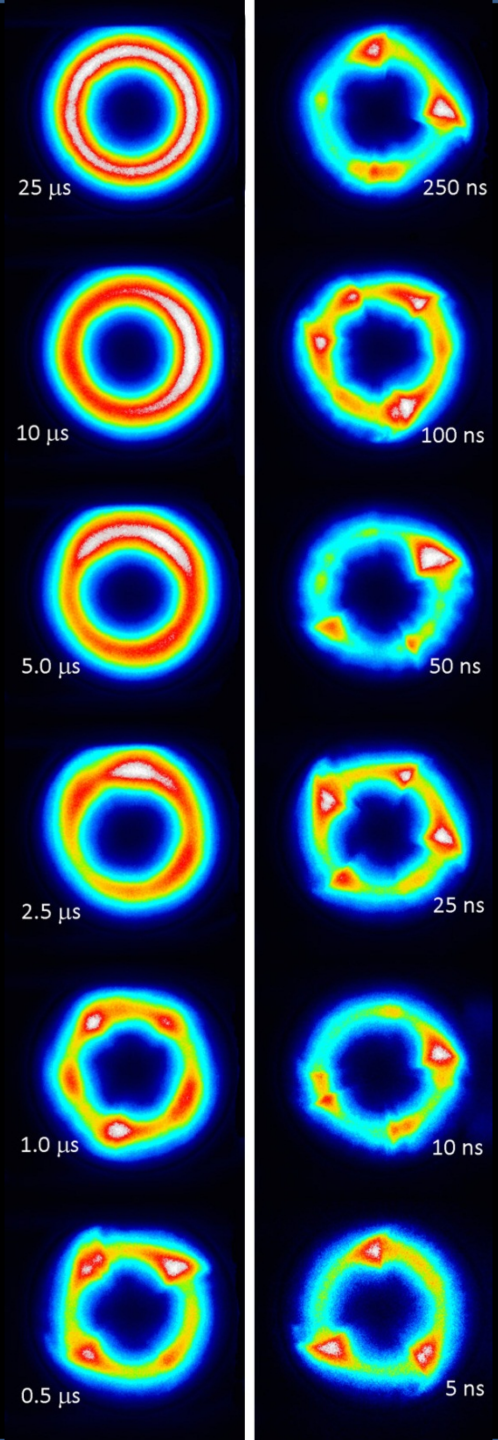


characterization



HiPIMS – an important theme for some years. Moving Ionization Zones

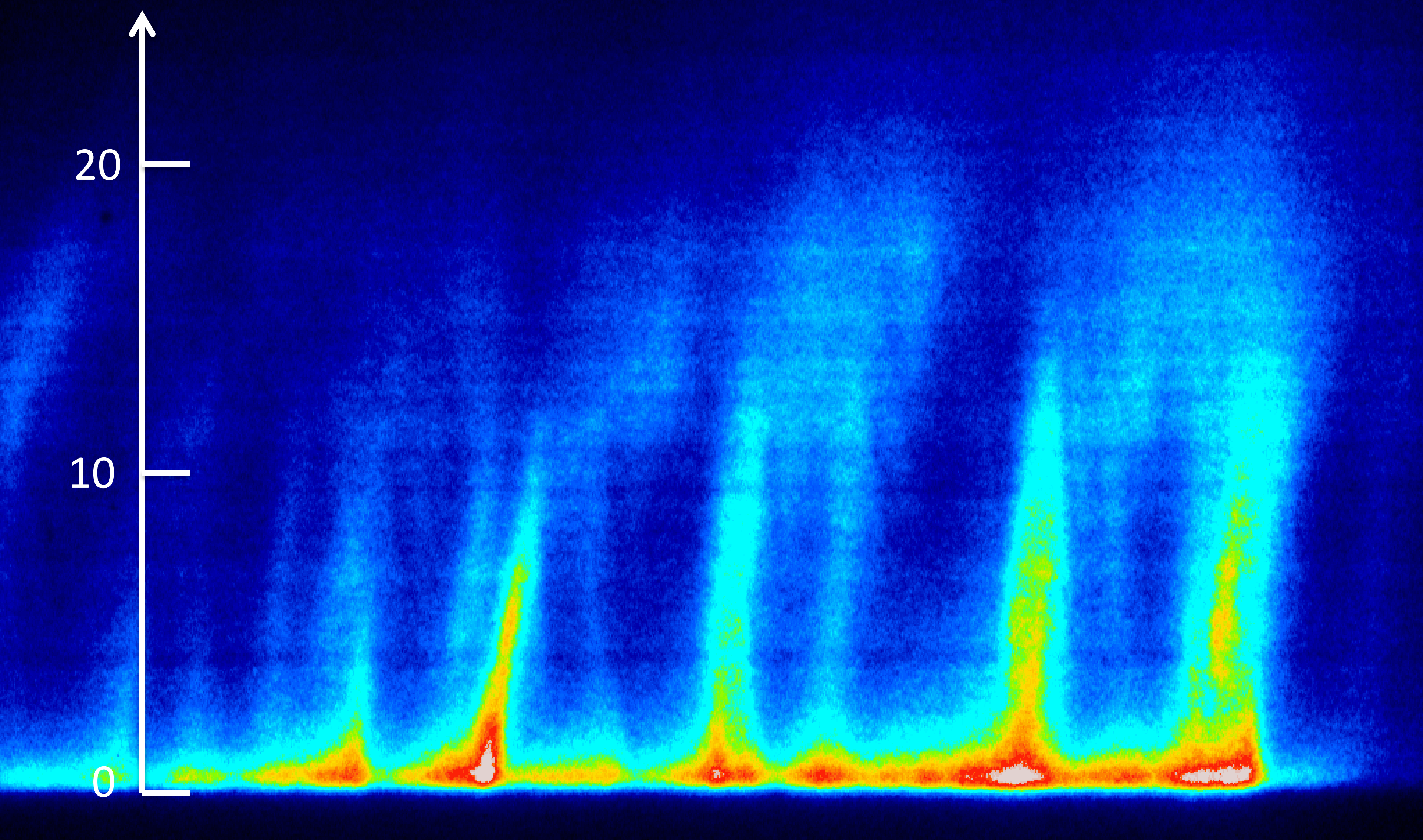
- Nb discharge, peak ~ 200 A
- reduction of image exposure time gives immediate clues on rotational speed → ~ 10^4 m/s



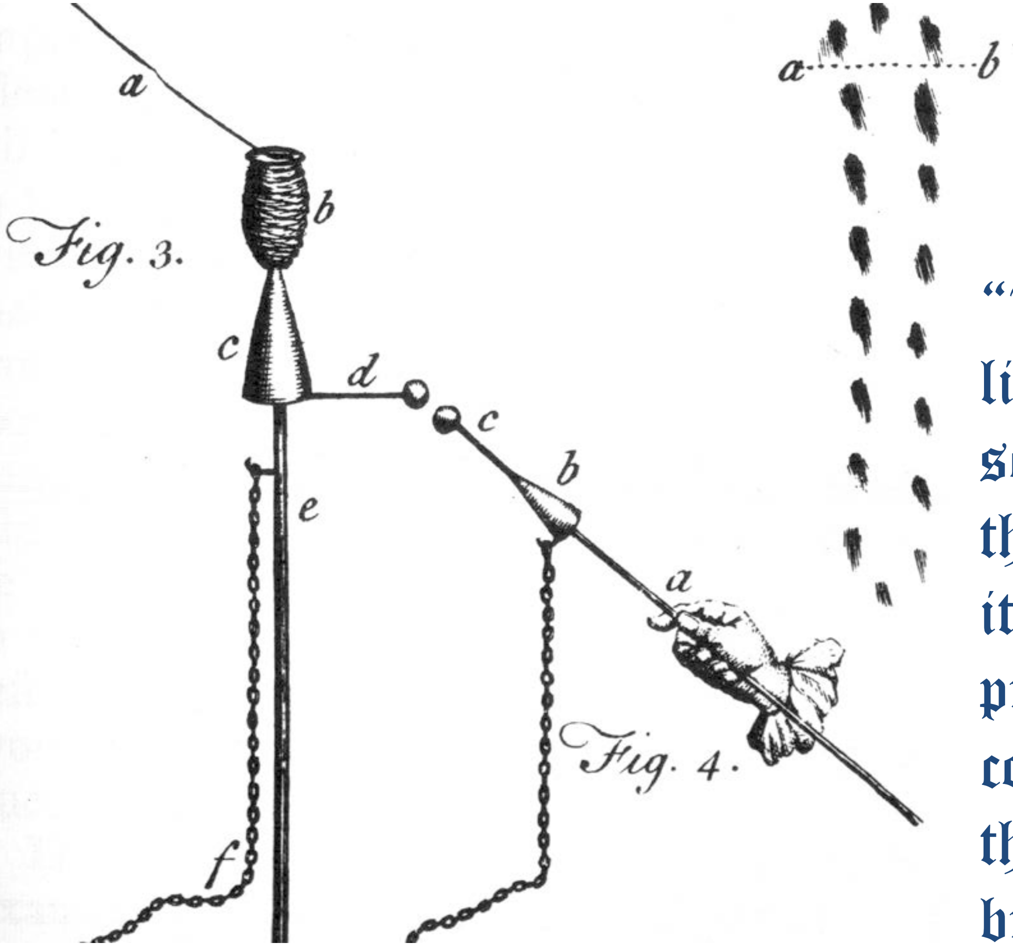
A. Anders et al., *J. Appl. Phys*. **111** (2012) 053304

Streak image sequence, 20 μs sweep time

A. Anders et al., *J. Appl. Phys*. **111** (2012) 053304



Perhaps the first observation of nanoparticles

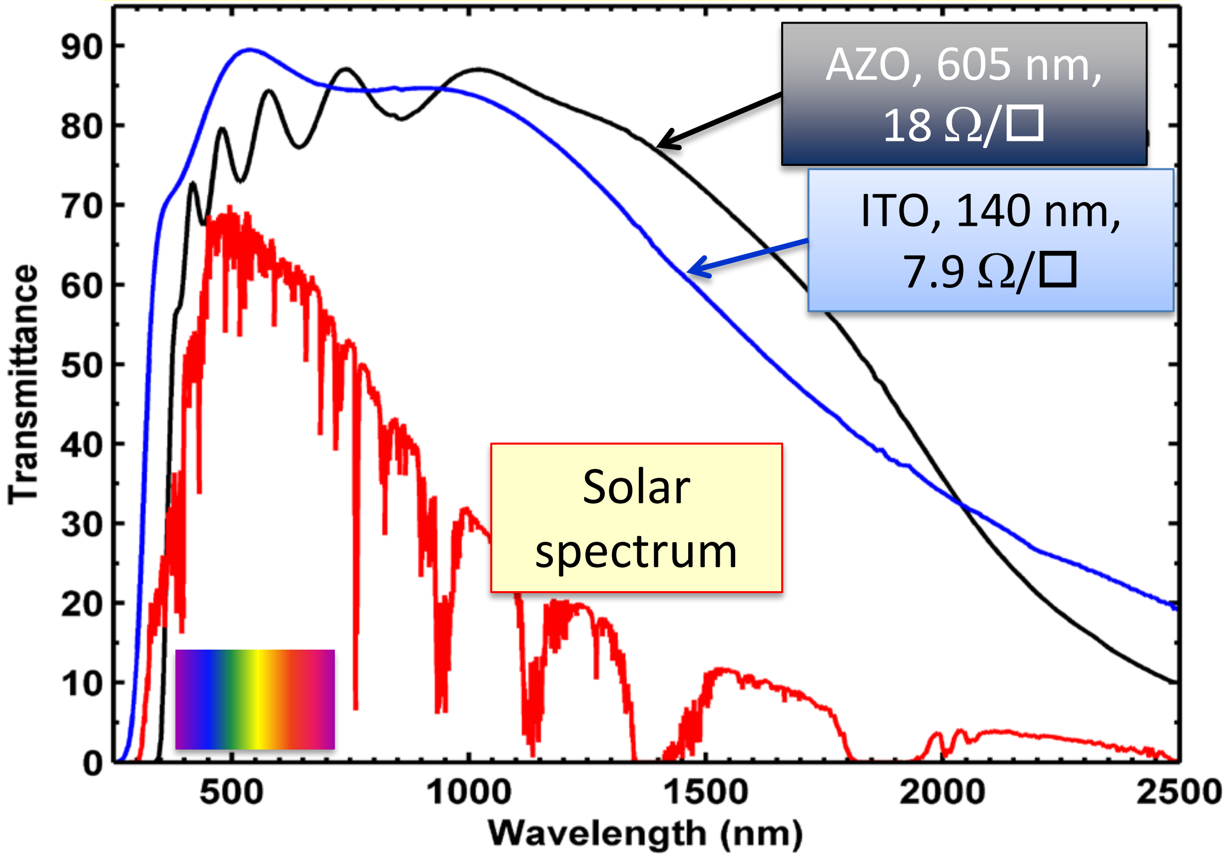


"The black dust was so extremely light as to rise like a cloud in the air, so as sometimes to be visible near the top of the room; I concluded that it could not be the metal itself, but probably the calx [oxide], ….I was confirmed in this opinion by finding that this black dust collected from a brass chain would not conduct electricity…" (J. Priestley, 1775)

J. Priestley, The History and Present State of Electricity, 3rd ed., London, 1775;
A. Anders, IEEE Trans. Plasma Sci. **31** (2003) 1052.

Starting Point:
Plasma-Assisted Deposition of Oxide Films

R. J. Mendelsberg, *et al*., J. Physics D **44** (2011) 232003.



Interesting for energy related applications:

- Transparent in visible and near infrared ranges
- High electrical conductivity

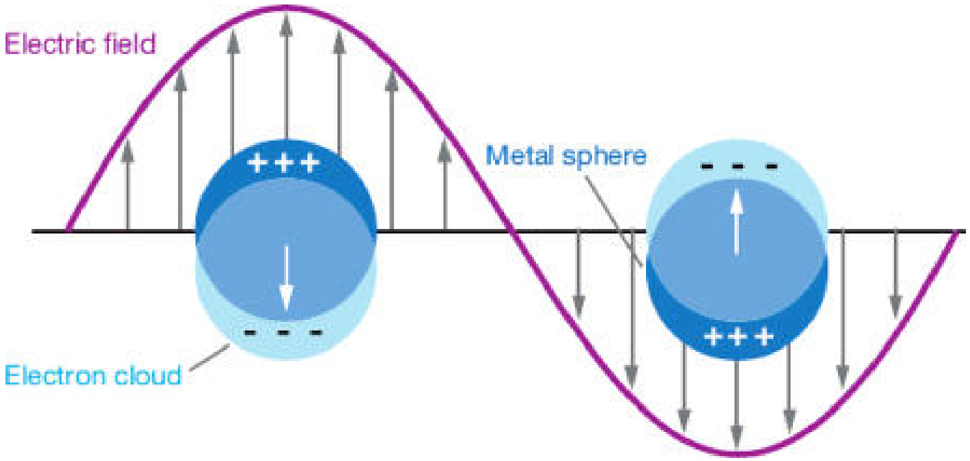
- $In_2O_3:SnO_2$ (ITO)
- ZnO:Al (AZO)
- SnO_2:F (FTO)
- ZnO:Ga (GZO)

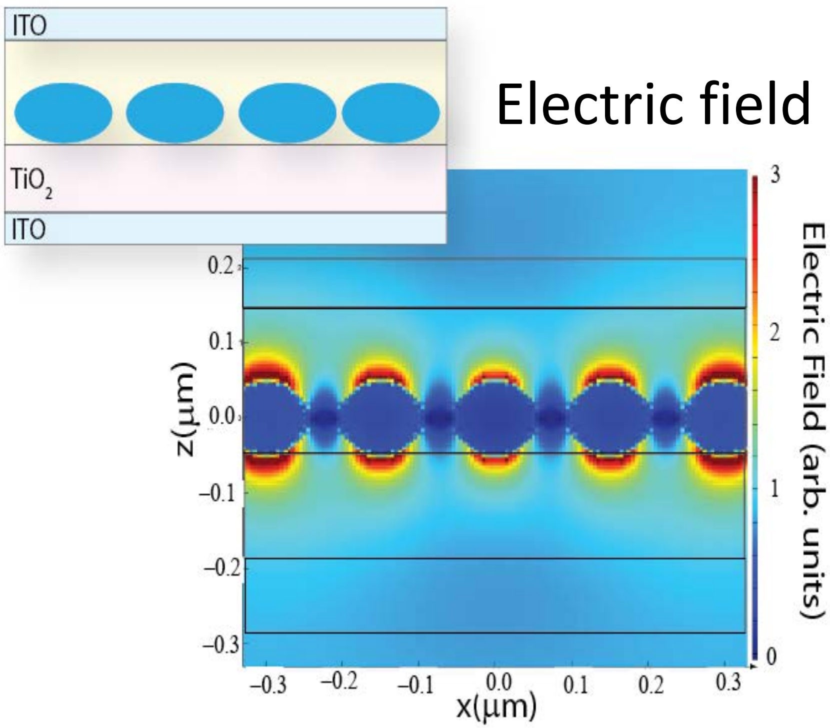
<u>Other metal oxides of interest:</u>

- VO_2 : thermochromic material: Metal-to-insulator transition (MIT) at 68 °C
- TiO_2 : Wide band-gap semiconductor, catalysis applications
- WO_3 : electrochromic material

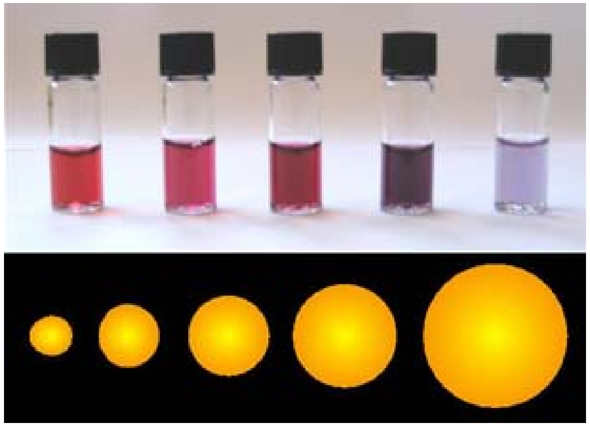
From Films to Nanoparticles and Nanocomposites

Localized Surface Plasmon Resonance



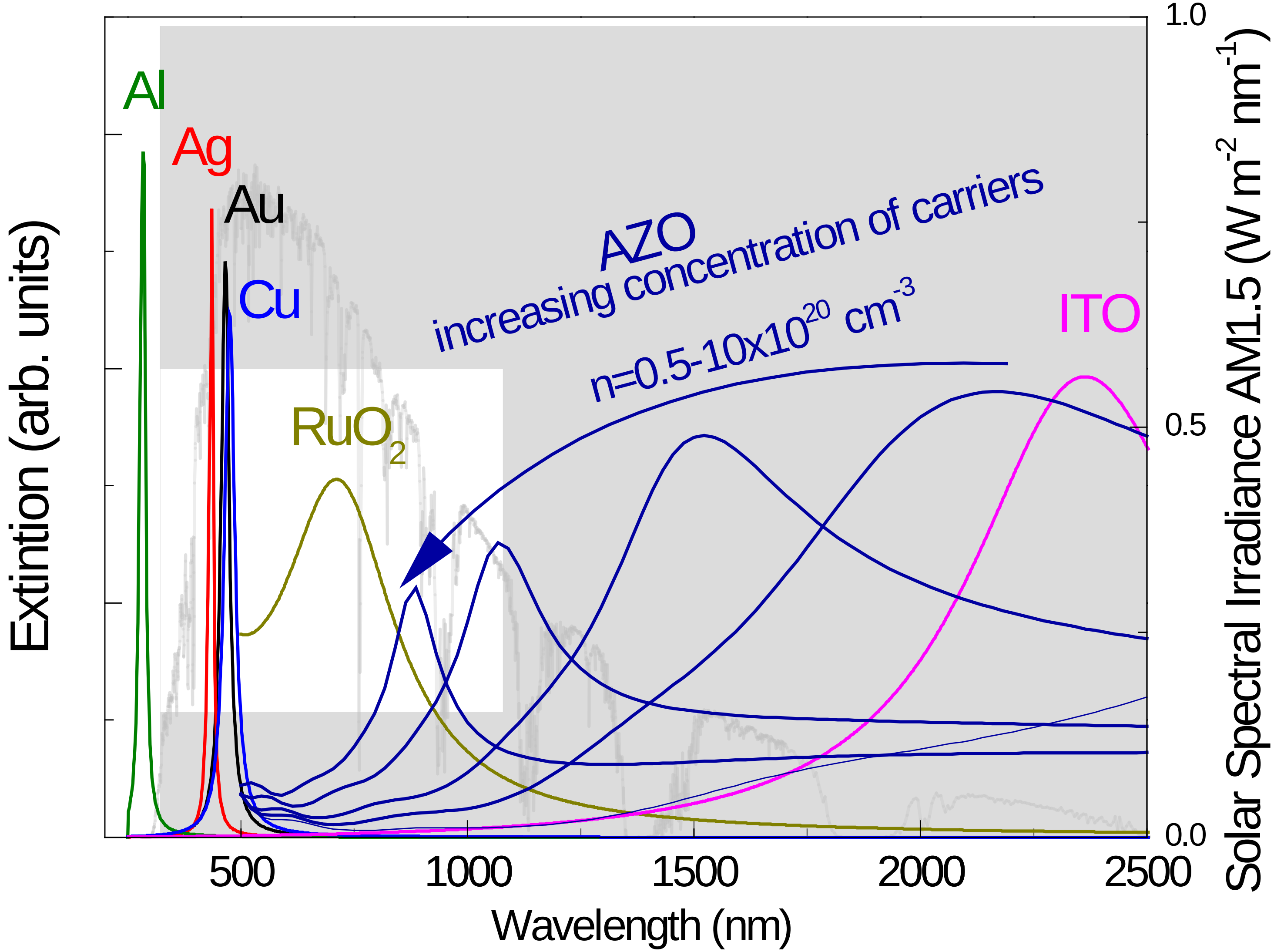


Resonance: frequency of field is equal to plasma frequency of free electrons



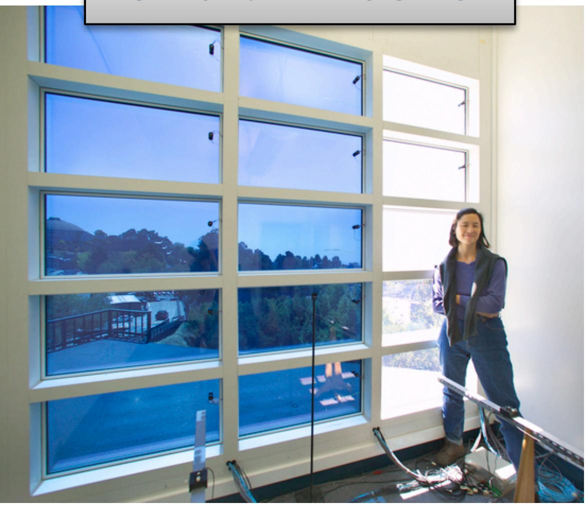
Resonance is size-dependent

Metal vs. TCO Nanoparticles as Plasmonic Materials



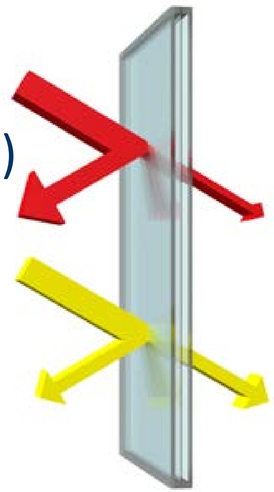
Some Applications of Nanostructured Oxides

Smart Windows



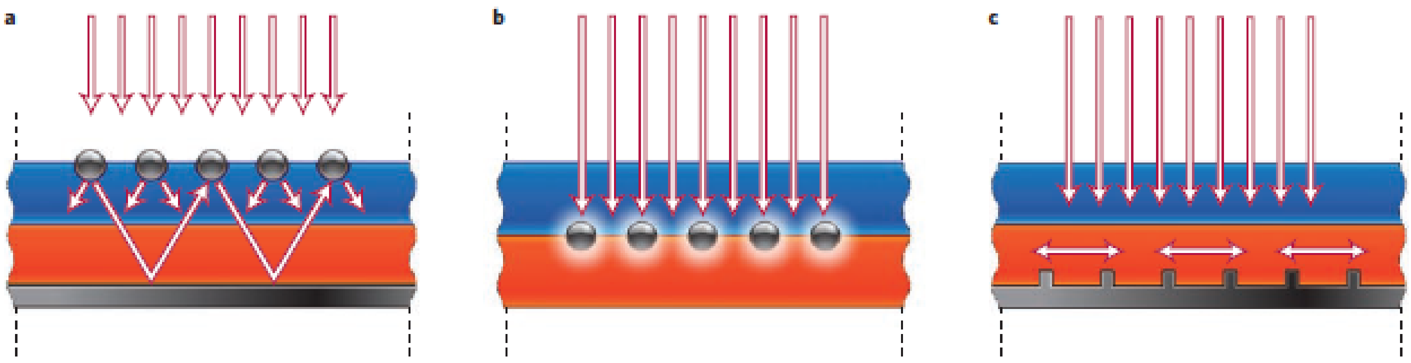
Solar heat
(infrared radiation)

Visible light



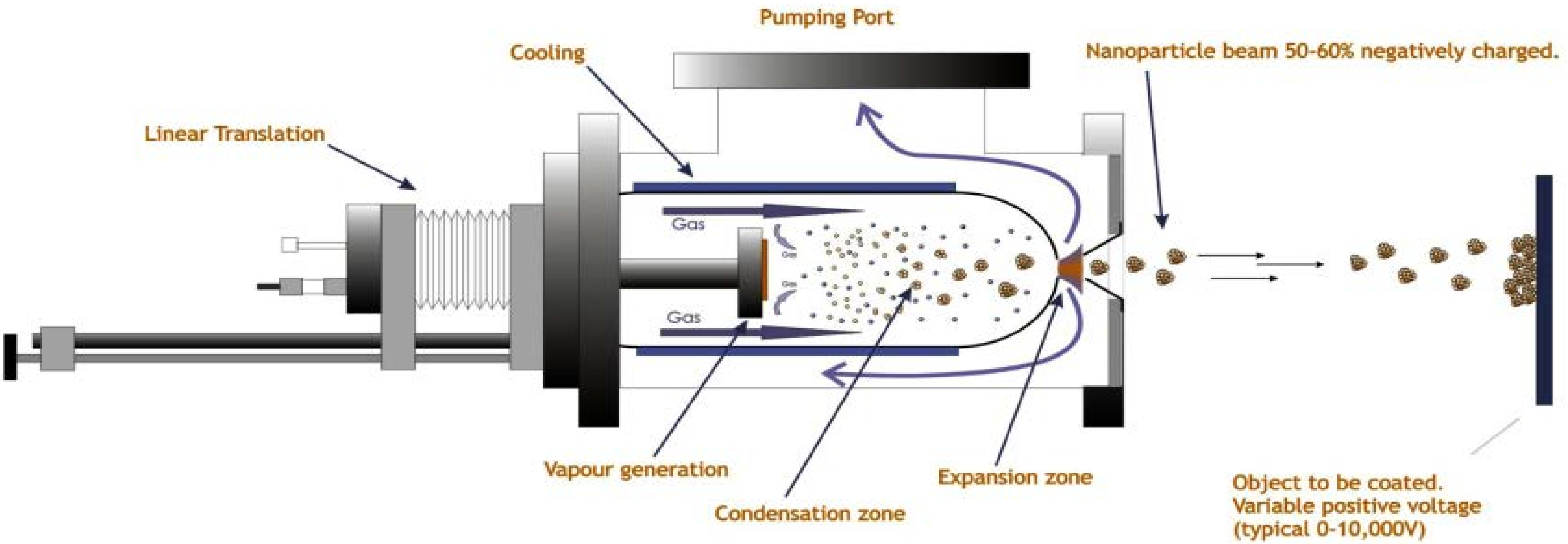
<u>Ultimate Goal:</u>
independent switching in the visible and infrared ranges

Photovoltaic and Photocatalytic devices



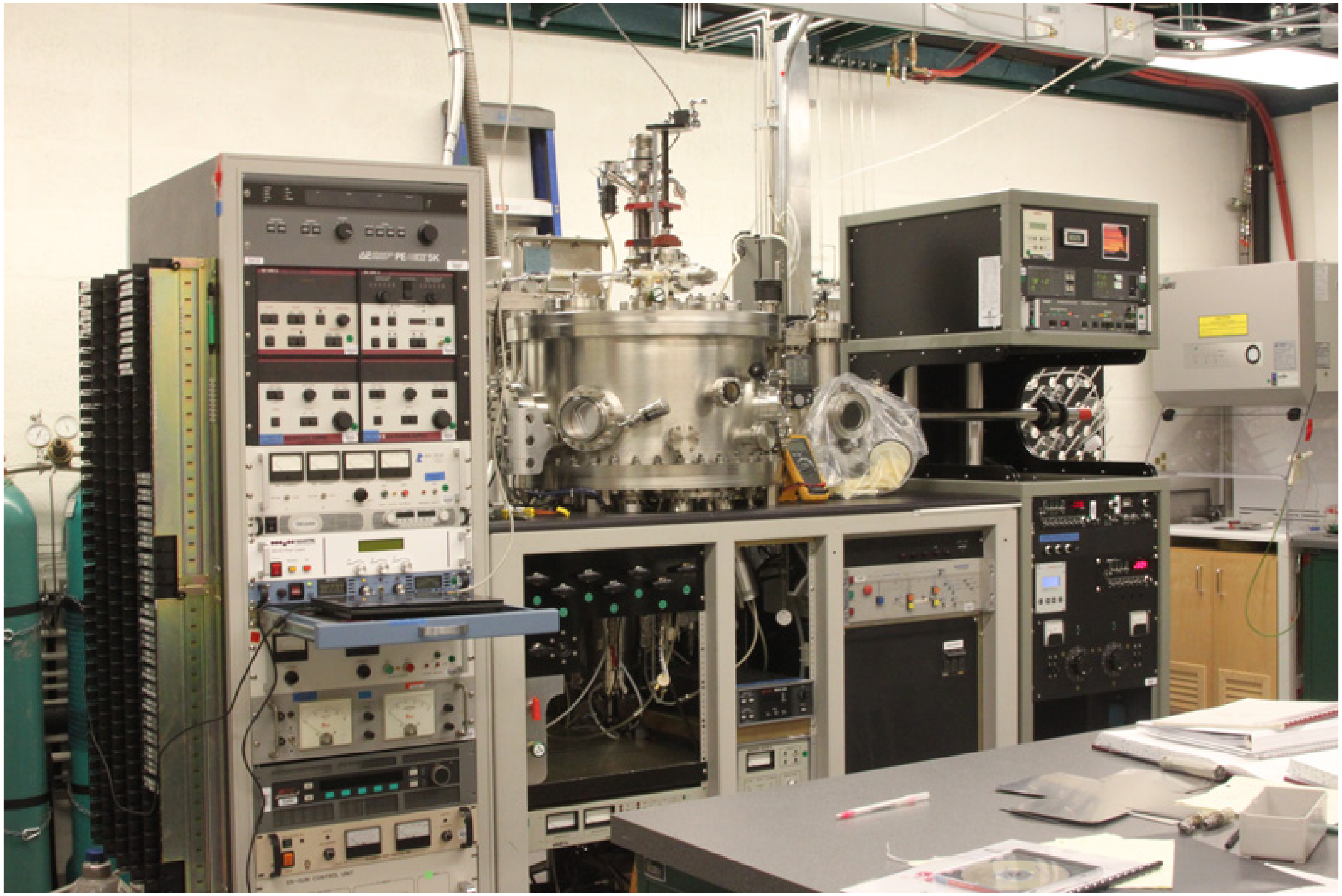
H. A. Atwater and A. Polman, Nat. Mater. **9** (2010) 205.

Approach: Terminated Cluster Growth



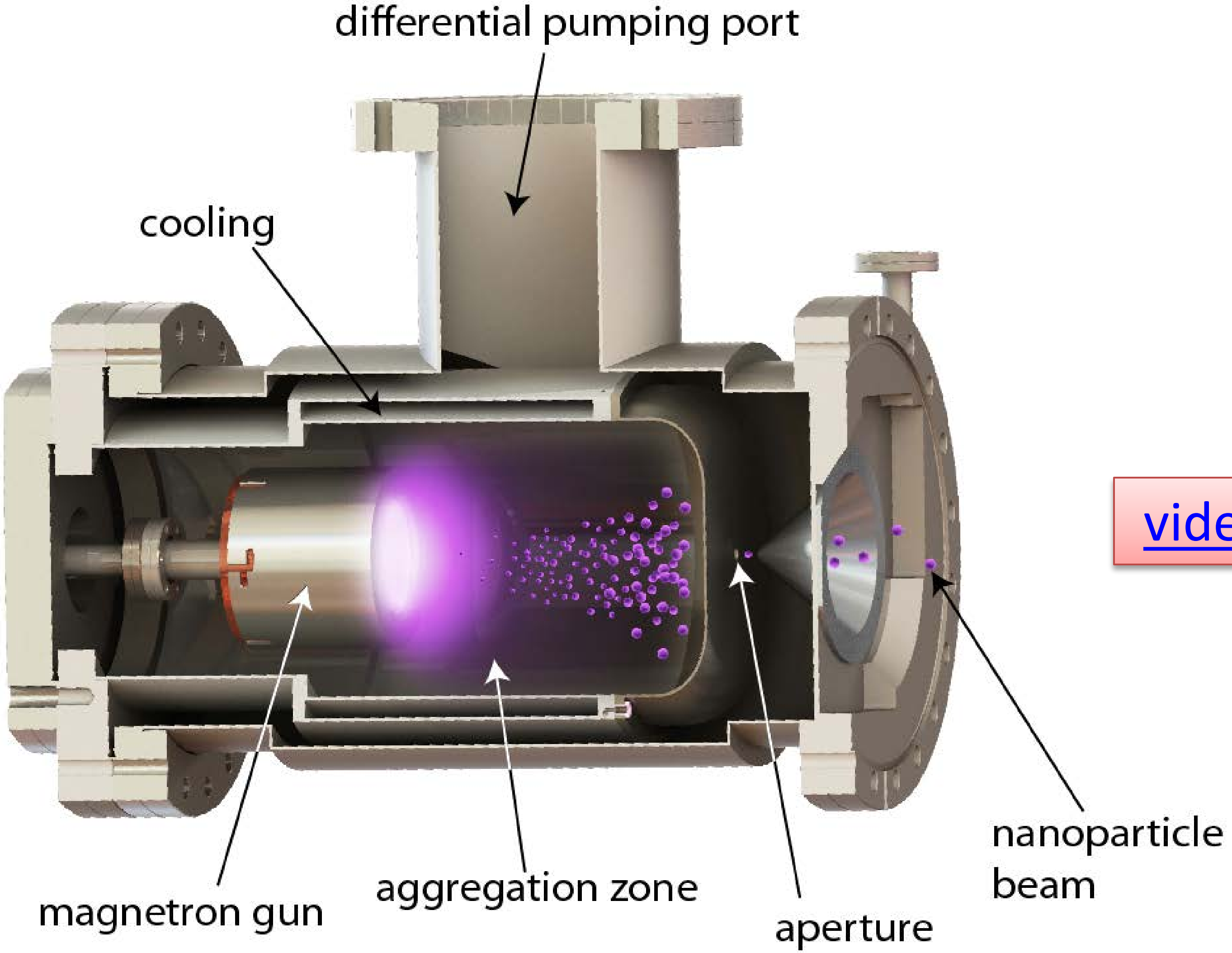
Source: Mantis Deposition LTD

Terminated Cluster Growth Setup



Nanoparticle generator integrated in a sputtering process chamber: option to combine nanoparticles and thin film in devices

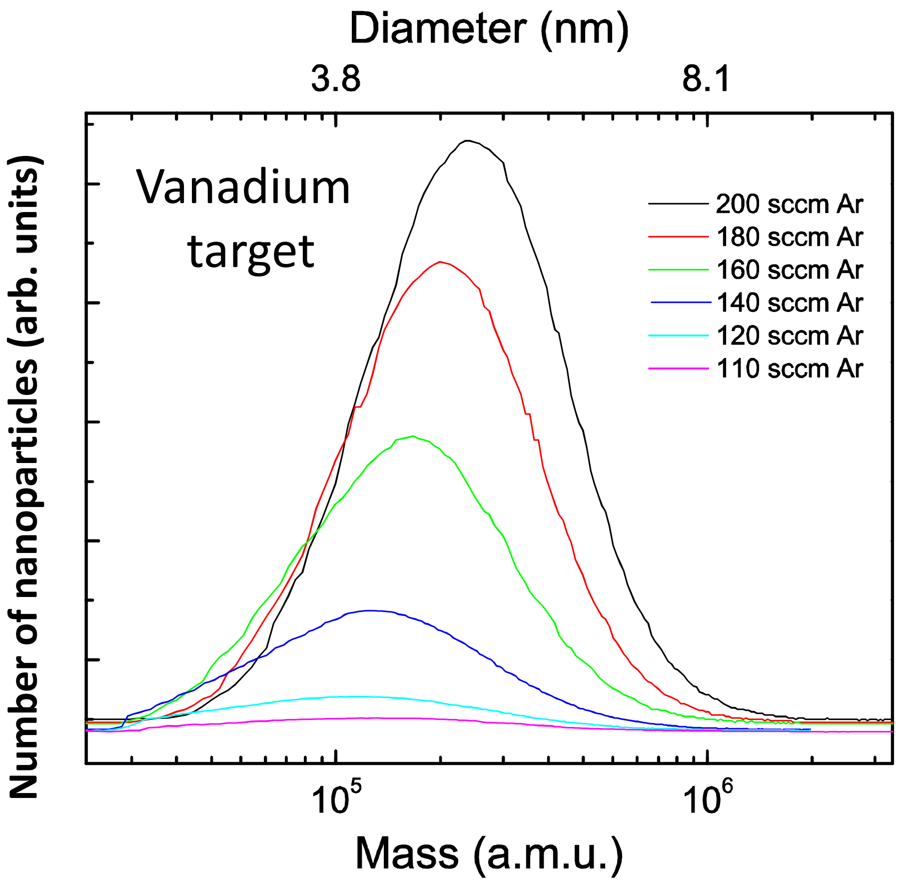
Nanoparticle Generator



video

Source: Mantis Deposition LTD

Effect of Density of Nucleation and Growth



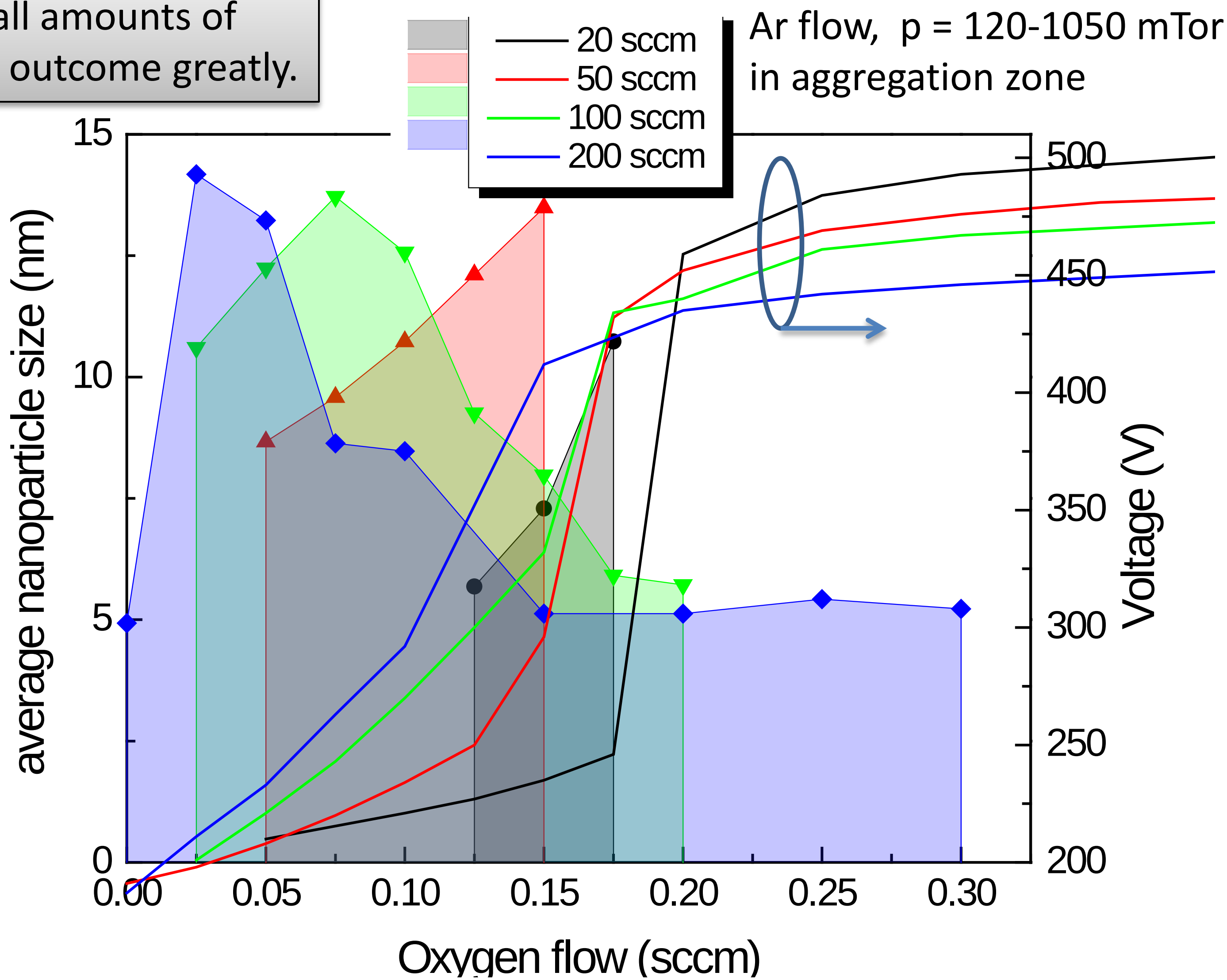
The nanocrystals size and production rate can be varied by controlling a number of parameters including:

- Sputtering gas flow rate
- Aggregation zone pressure
- Position of the target in the aggregation zone
- Sputtering power

Increased collision rate increases number and size and nanoparticles.

Effect of Argon and Oxygen Flows on Nanoparticle Formation

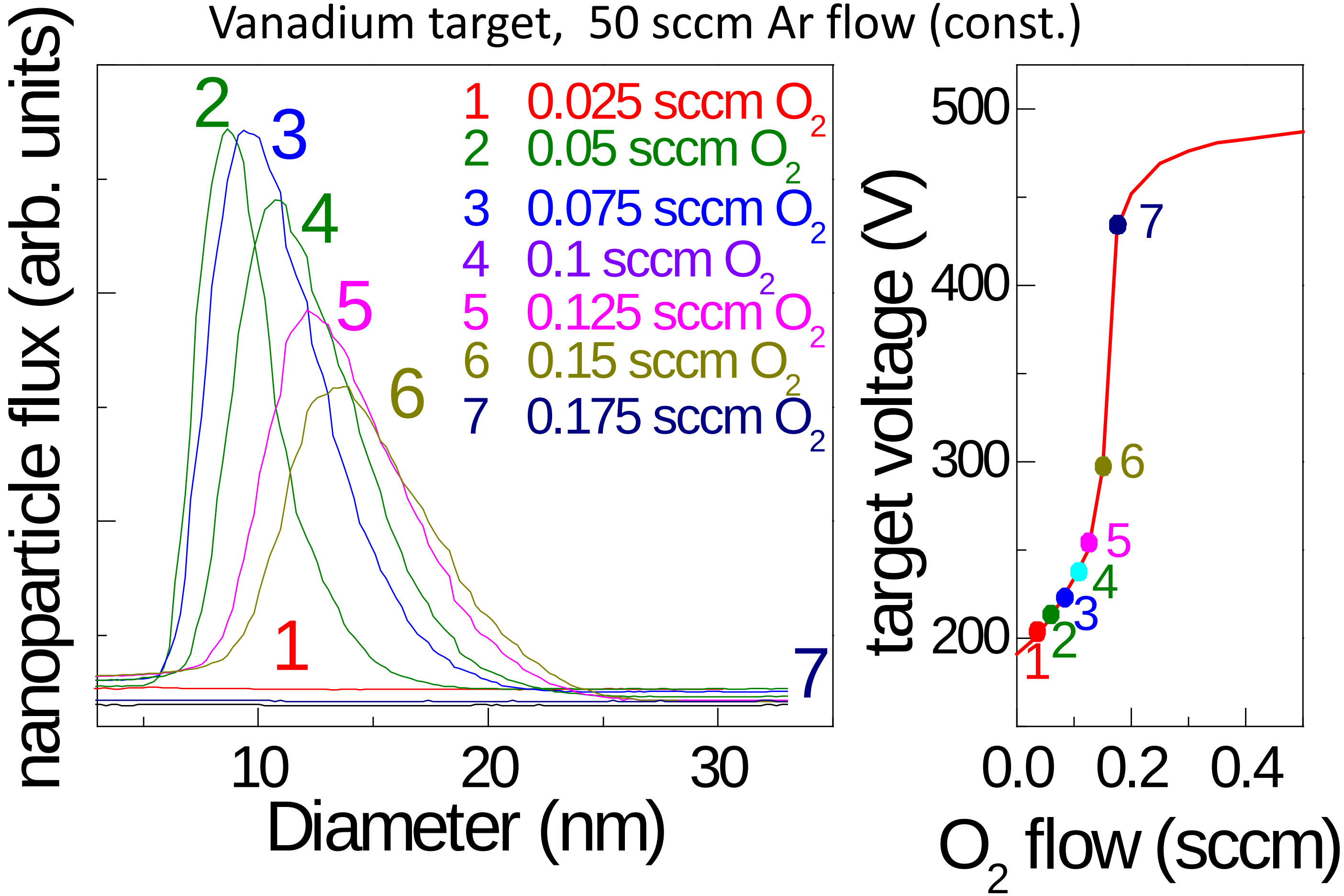
Even very small amounts of oxygen affect the outcome greatly.



C. Clavero, *et al.*, J. Phys. D: Appl. Phys. **46** (2013) 362001.

Effect of Oxygen on Nanoparticle Size and Rate

Vanadium target, 50 sccm Ar flow (const.)



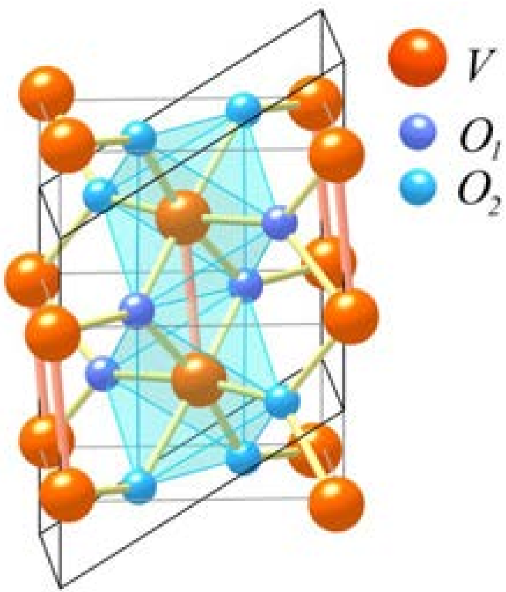
→ heterogeneous nucleation is much more effective than homogenous nucleation
→ there is a very pronounced parameter window of effective oxide nanoparticle formation

C. Clavero, *et al.*, J. Phys. D: Appl. Phys. **46** (2013) 362001.

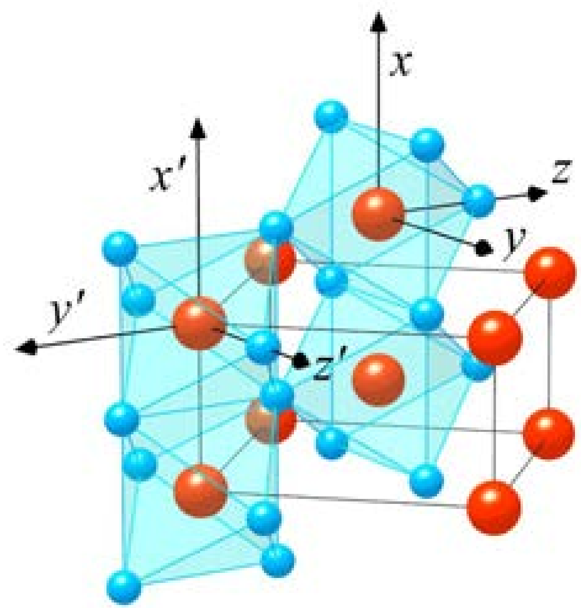
Why Vanadium Oxide?

Low temperature
monoclinic phase
(insulating)

High temperature
rutile phase
(metallic)



68 °C

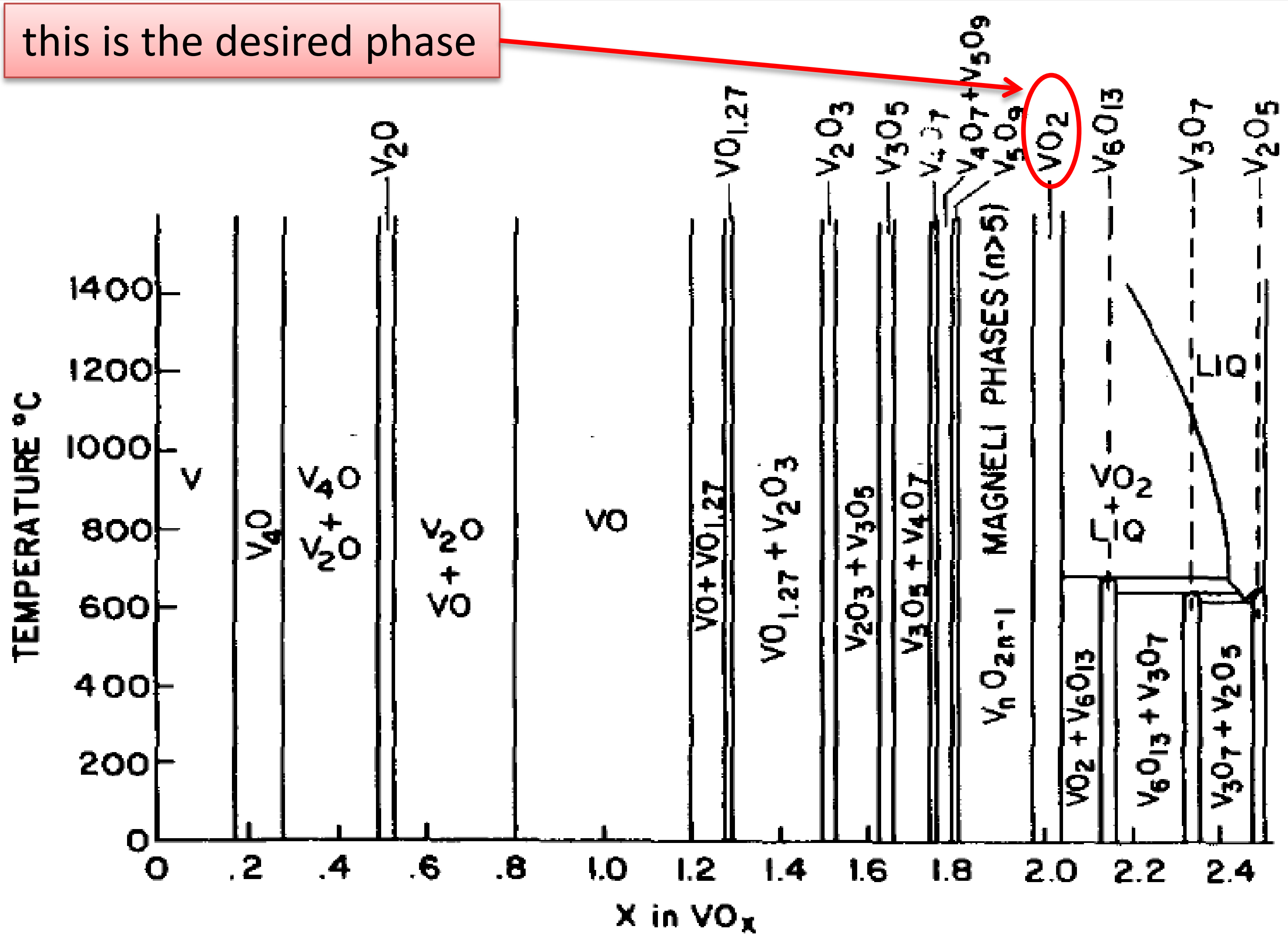


VO_2 is a thermochromic material

VO_2 nanocrystals are difficult to synthesize by solution chemistry

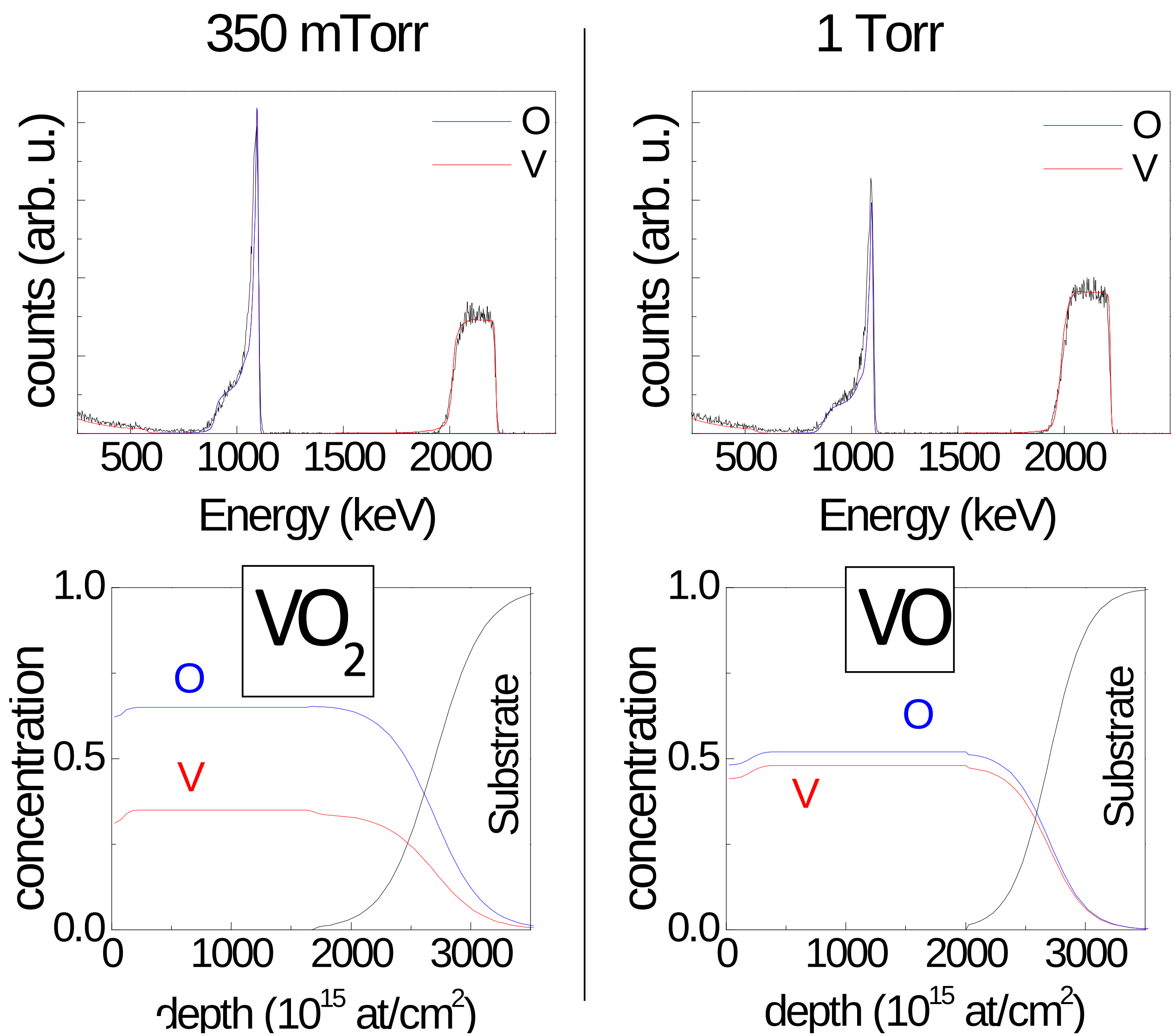
Vanadium Oxide: Very Complicated Phase Diagram

this is the desired phase



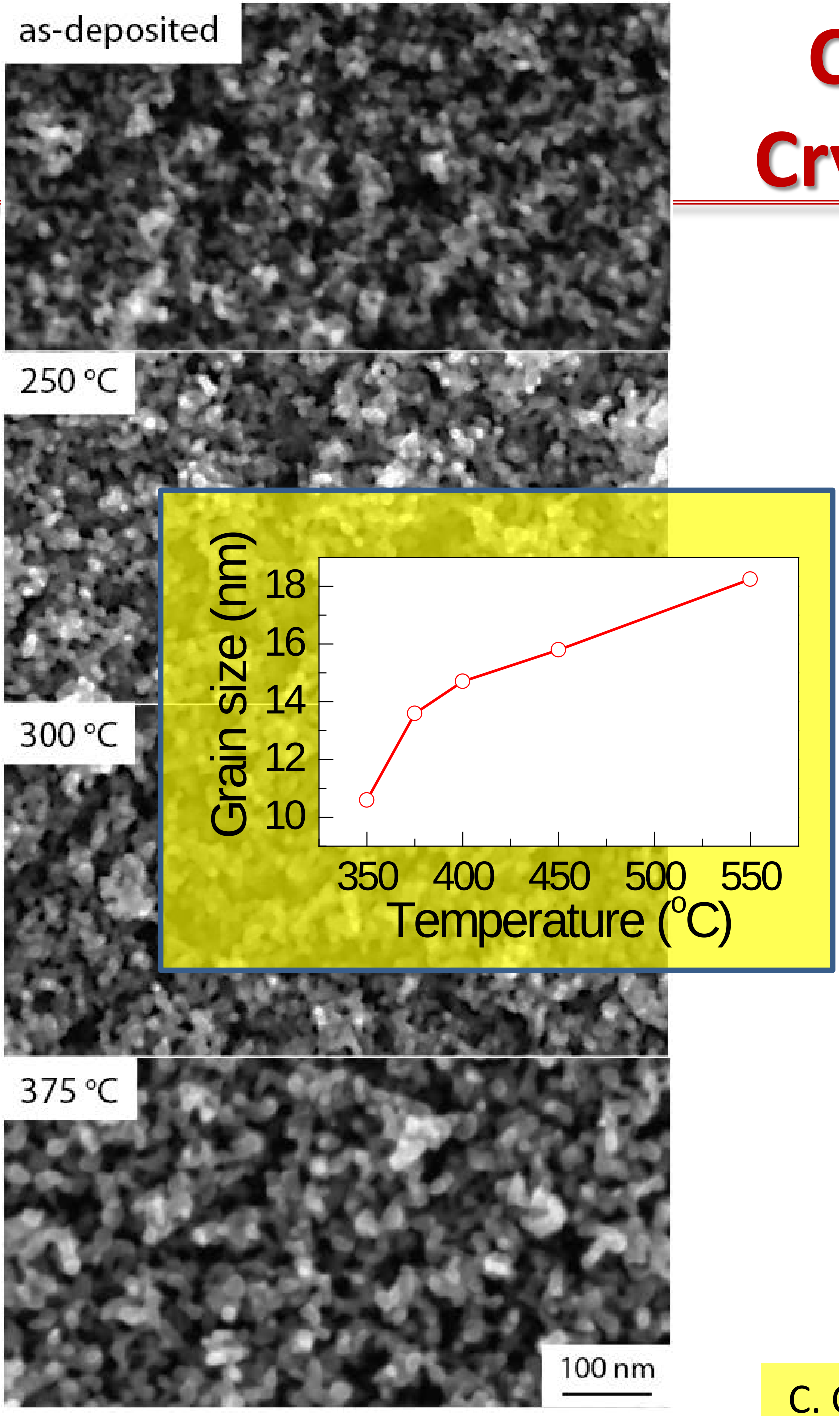
C. H. Griffiths and H. K. Eastwood, J. Appl. Phys. **45**, (1974) 2201.

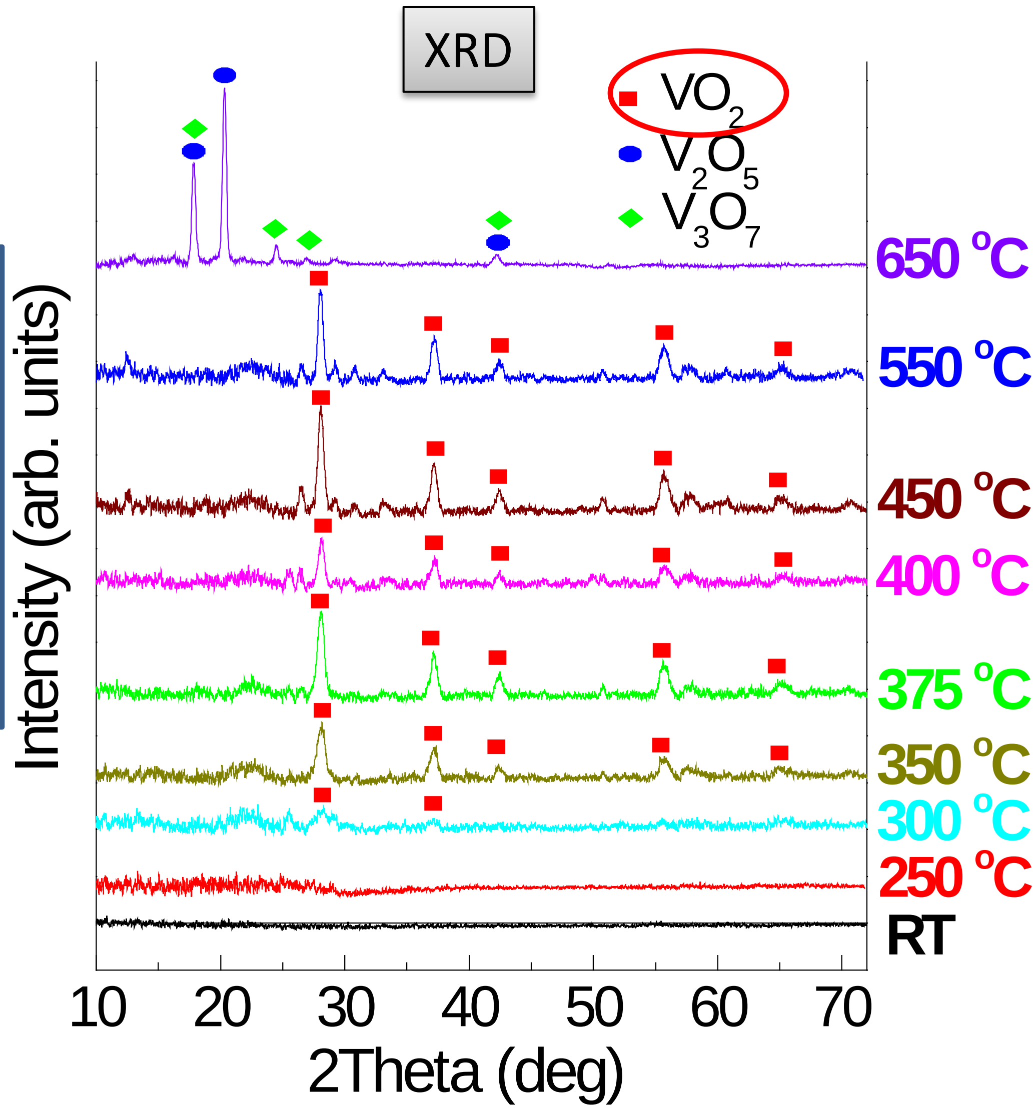
RBS: Checking the Nanoparticle Composition



C. Clavero, *et al.*, J. Phys. D: Appl. Phys. **46** (2013) 362001.

Control of Morphology and Crystal Structure by Annealing

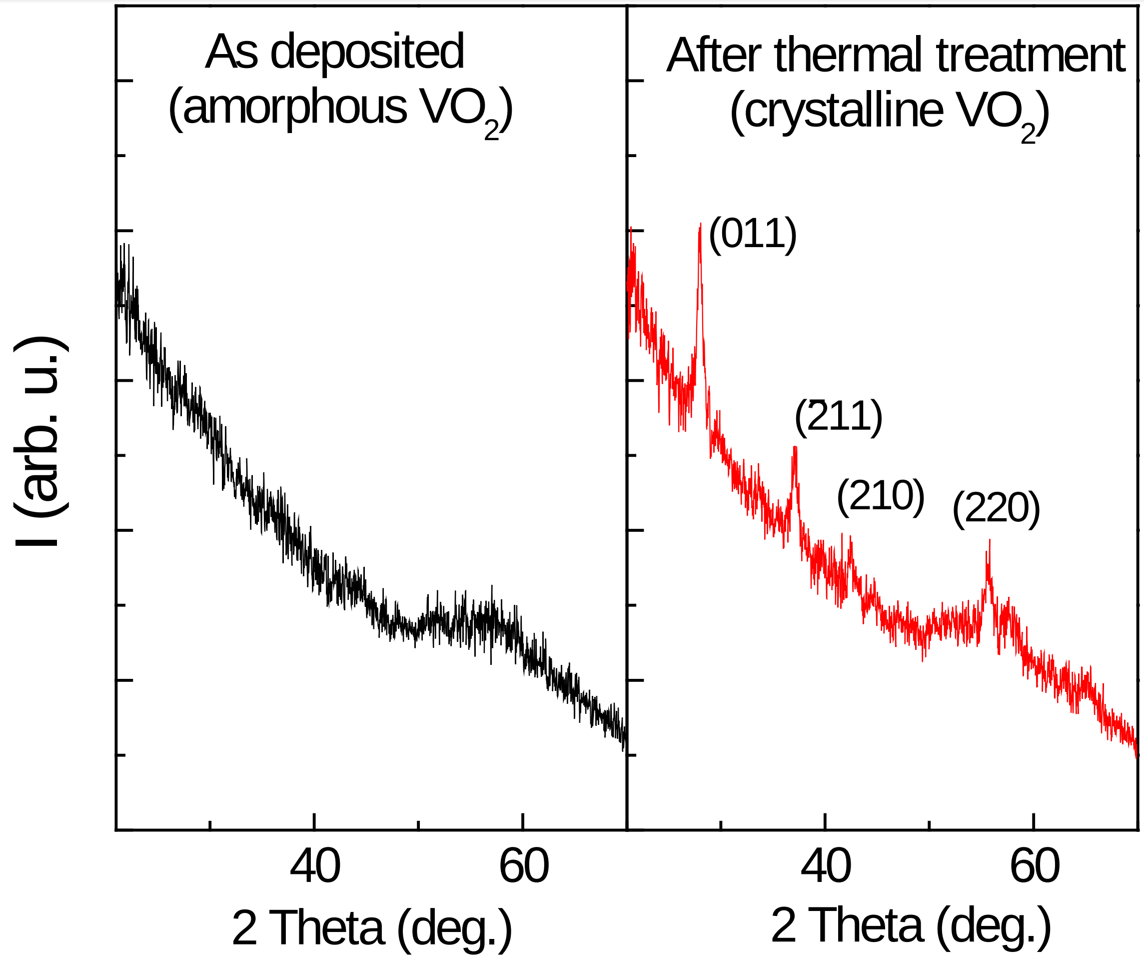




C. Clavero, *et al.*, J. Phys. D: Appl. Phys. **46** (2013) 362001.

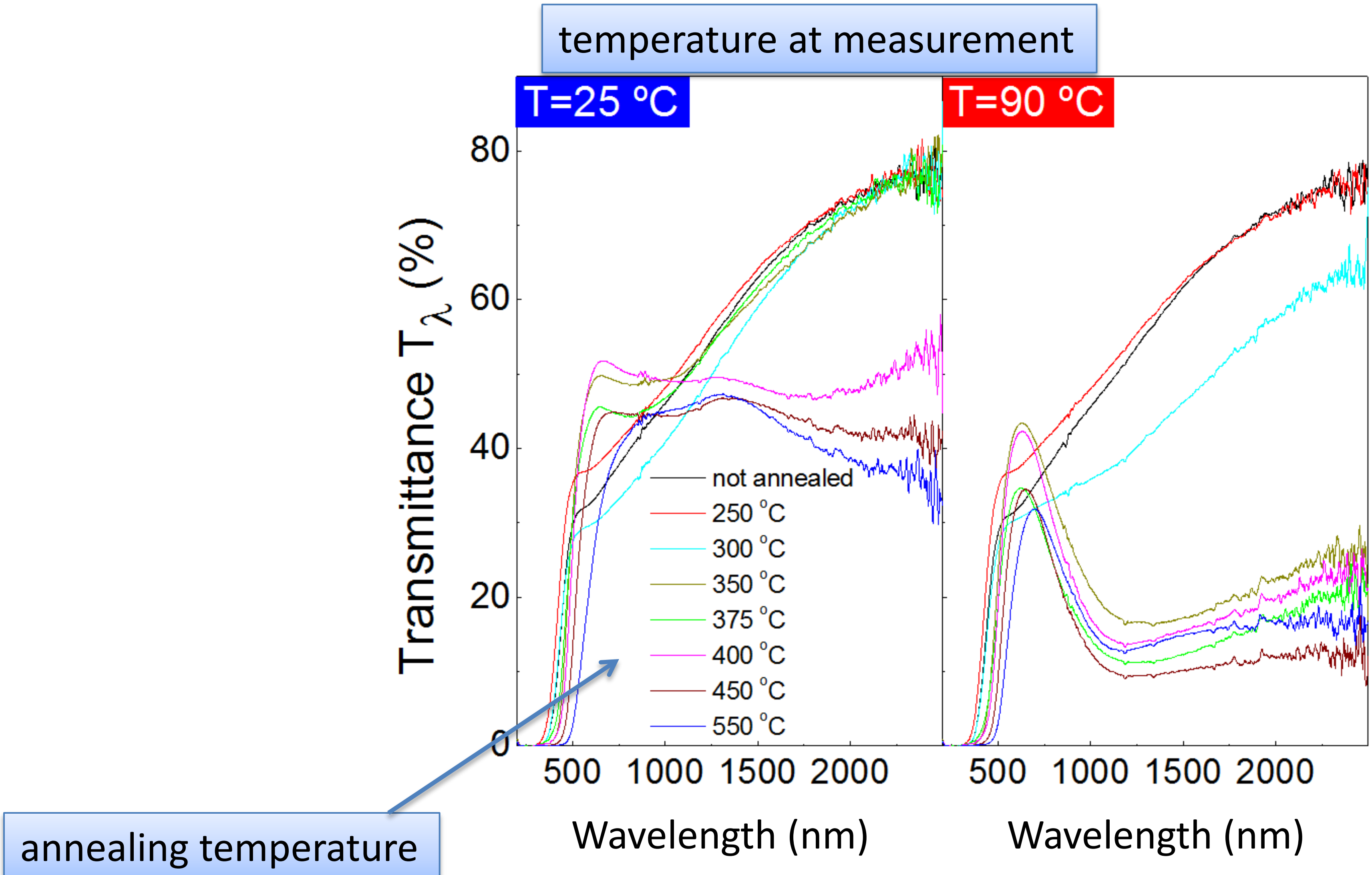
From Nanoparticles to Nanocrystals

Optimum thermal treatment (375°C < T < 500°C)
→ VO_2 nanoCRYSTALS



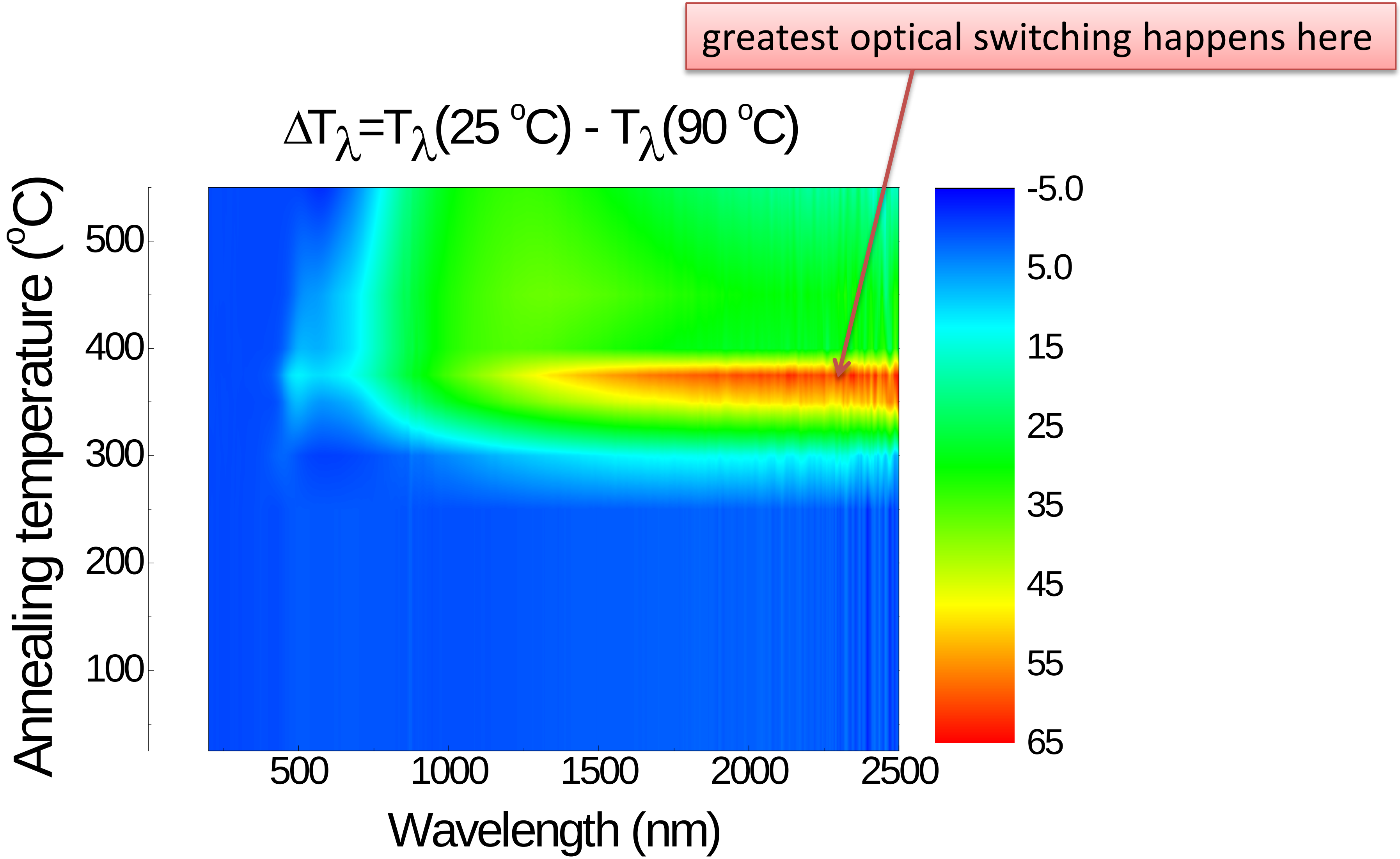
C. Clavero, *et al.*, J. Phys. D: Appl. Phys. **46** (2013) 362001.

Spectral Response: Demonstrate Switching

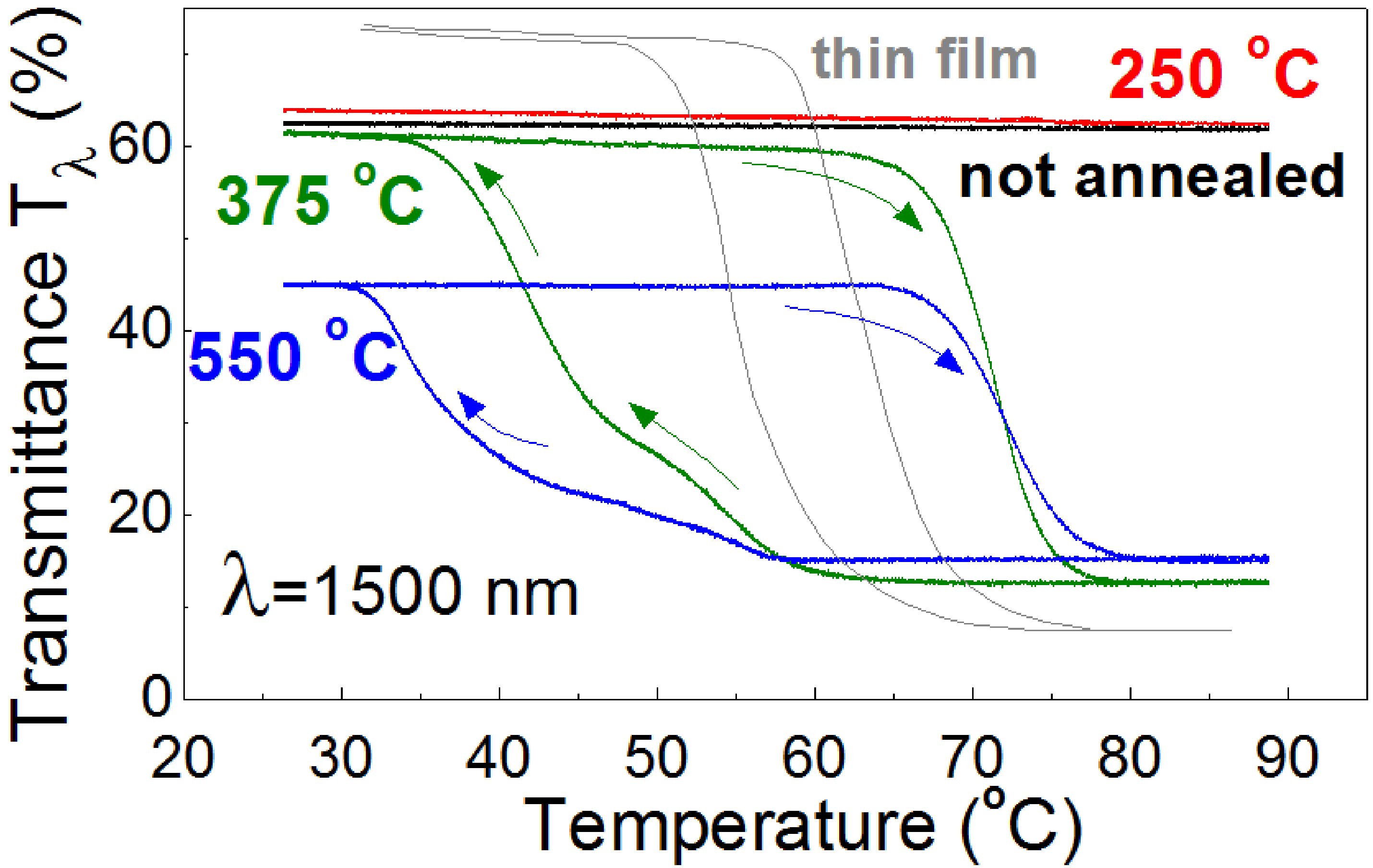


C. Clavero, *et al.*, J. Phys. D: Appl. Phys. **46** (2013) 362001.

Spectral Response: Checking Change in Transmission



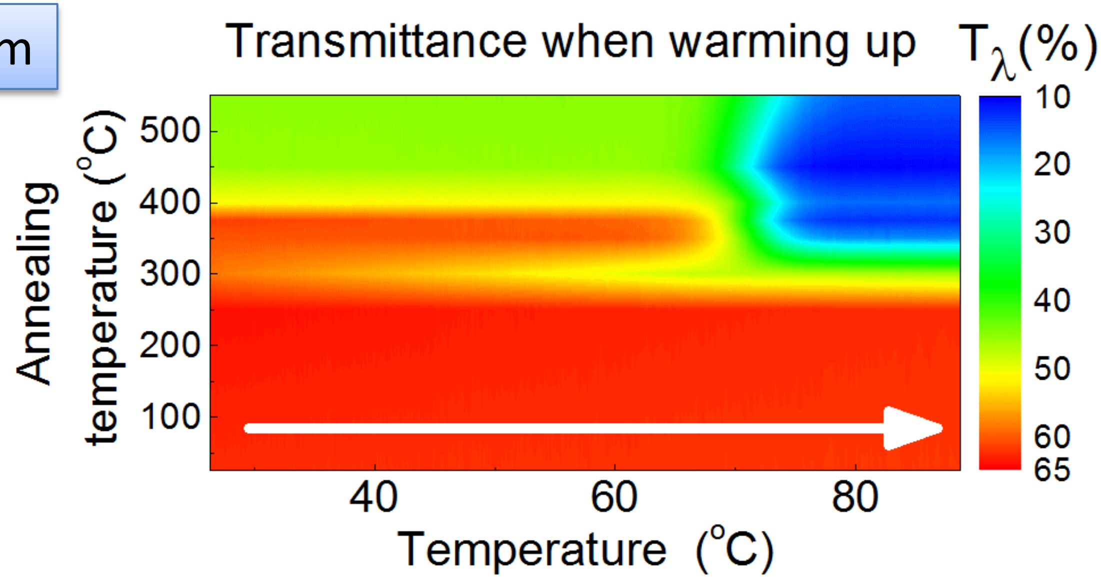
Hysteresis of the Transition Temperature as a Function of Annealing

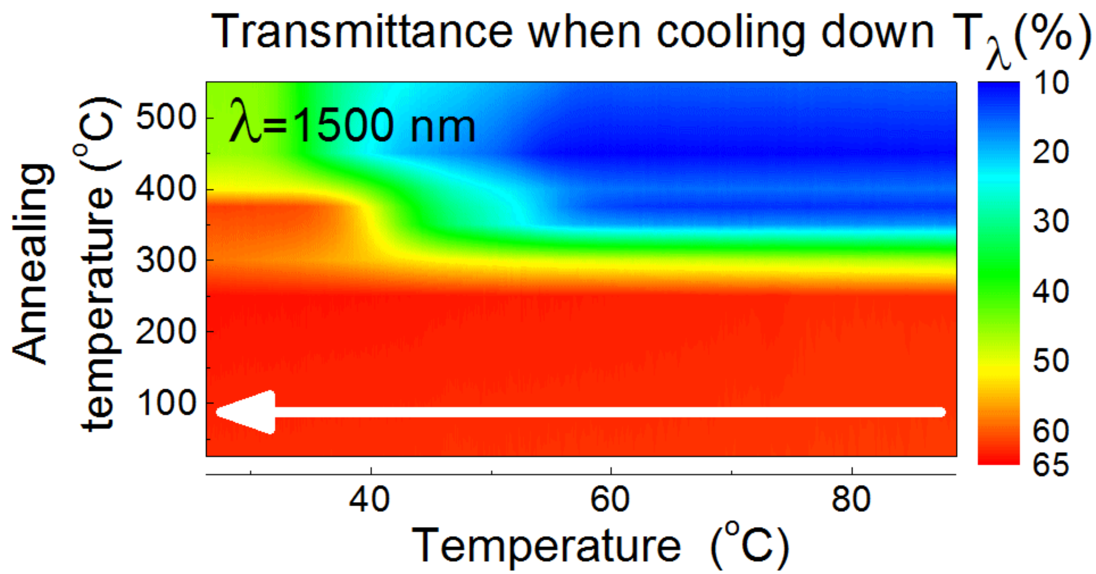


C. Clavero, *et al.*, J. Phys. D: Appl. Phys. **46** (2013) 362001.

Hysteresis of Phase Transition

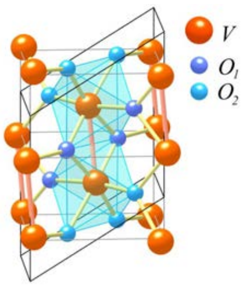
at λ= 1500 nm

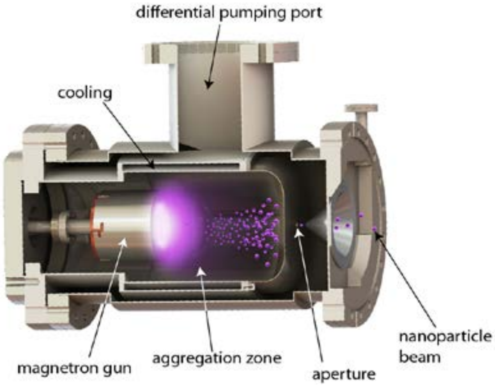


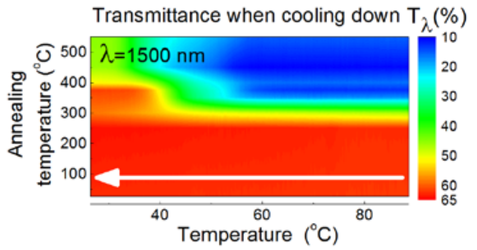


Summary & Conclusions

1. Oxide nanocrystals can have plasmonic properties; depend on free carrier concentration and size
2. Especially interesting are those that show insulator-to-metal transition, such as thermochromic VO_2
3. Demonstrated Terminated Cluster Growth as a synthesis method for VO_2 nanoparticles
4. There is a pronounced optimum of oxygen partial pressure (flow) for oxide nanoparticle synthesis
    1. even little oxygen promotes heterogeneous nucleation
    2. too much oxygen poisons the target and reduces rate
5. Demonstrated transition from nanoparticles to nano**<u>crystals</u>** with optimum annealing temperature ~ 400°C as judged by maximum switching in the infrared (1500 nm)







Outlook

1. Use pulse sputtering → we have seen significant rate increases
2. Use in-situ annealing to obtain nanocrystals
3. Use multi-element targets and gases
4. Embed nanoparticles/crystals in a matrix and make devices
5. Scale to a linear system for large area
6. ....