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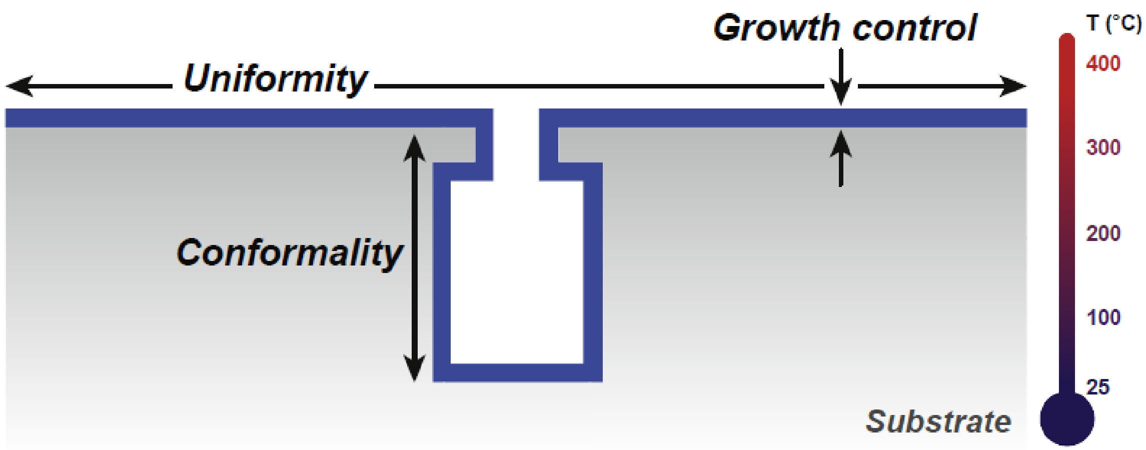
Atomic Layer Deposition (ALD)
(Thin Film Deposition Technique)



Conformality: ALD´s core benefit

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Outline

- Part 1
  - Thin film by thermal Atomic Layer Deposition (ALD)
    - *From fundamentals to applications; examples*

- Part 2
  - ALD of nanostructured materials
    - *Exemples (made in our lab's)*

Vapour phase depositon techniques: <u>ALD</u>

- ***<u>Atomic layer deposition (ALD)</u>***

Inorganic materials (e.g., metal oxides, nitrides,…)

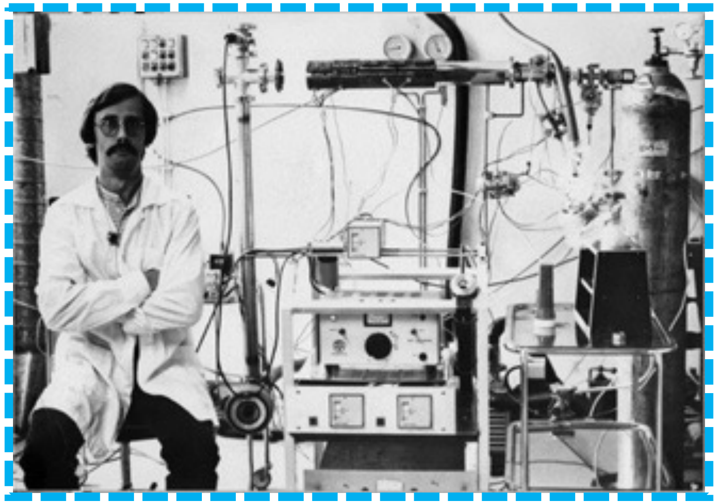
ALD is a special variant of the CVD

Chemical vapour deposition (CVD)
(chemisorption)

- ***Thermal ALD; uses the thermal energy to activate the chemical reactions***
- ***Gaseous reactants (precursors) → <u>Deposited solid</u> gaseous products***

History of Atomic Layer Deposition (ALD)

- Developed in 1974 by T. Suntola in Finland
- *ALD was primarily designed for deposition of inorganic compounds*
- ***$ZnCl_2 + H_2S \rightarrow ZnS$ (electroluminescent flat panel display - TFEL)***


*Sven Lindfors and a flow-reactor ALD reactor

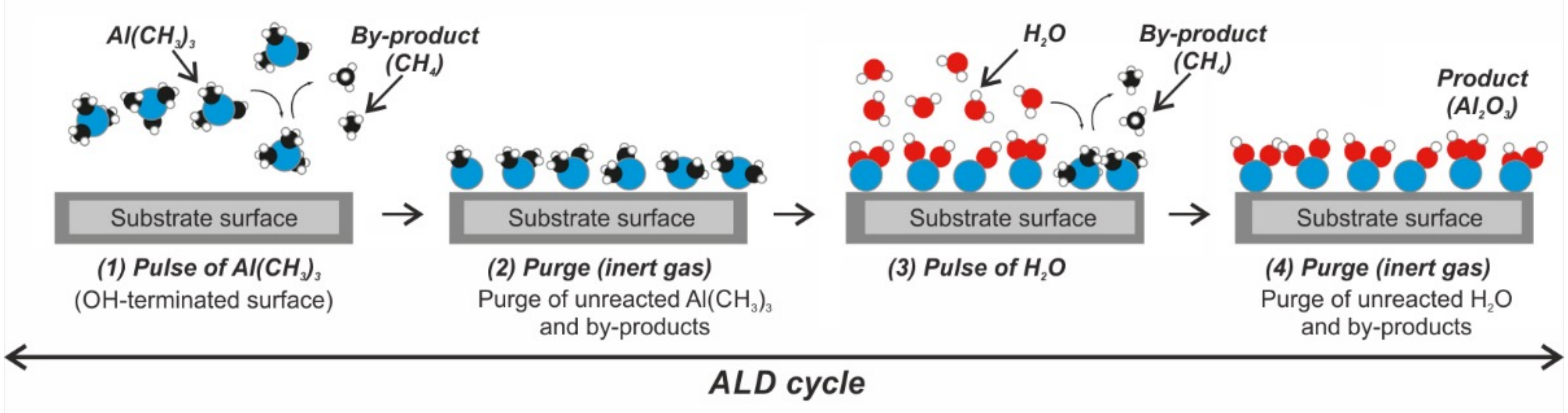
The beginning → Nowadays

- The motivation behind developing ALD was the desire to achieve a technique for creating thin films electroluminescent *(TFEL)* flat panel displays

How is Atomic Layer Deposition (ALD) defined?

- ALD can be defined as a film deposition technique that is based on the sequential use of **self-terminating** gas-solid reactions of two precursor chemicals, each one being **separated by purge step** (inert gas)

- *ALD of Al_2O_3:* $Al(CH_3)_3 + H_2O \rightarrow Al_2O_3 + CH_4$



Principle of technique: schematic illustration for a standard ALD cycle for Al_2O_3

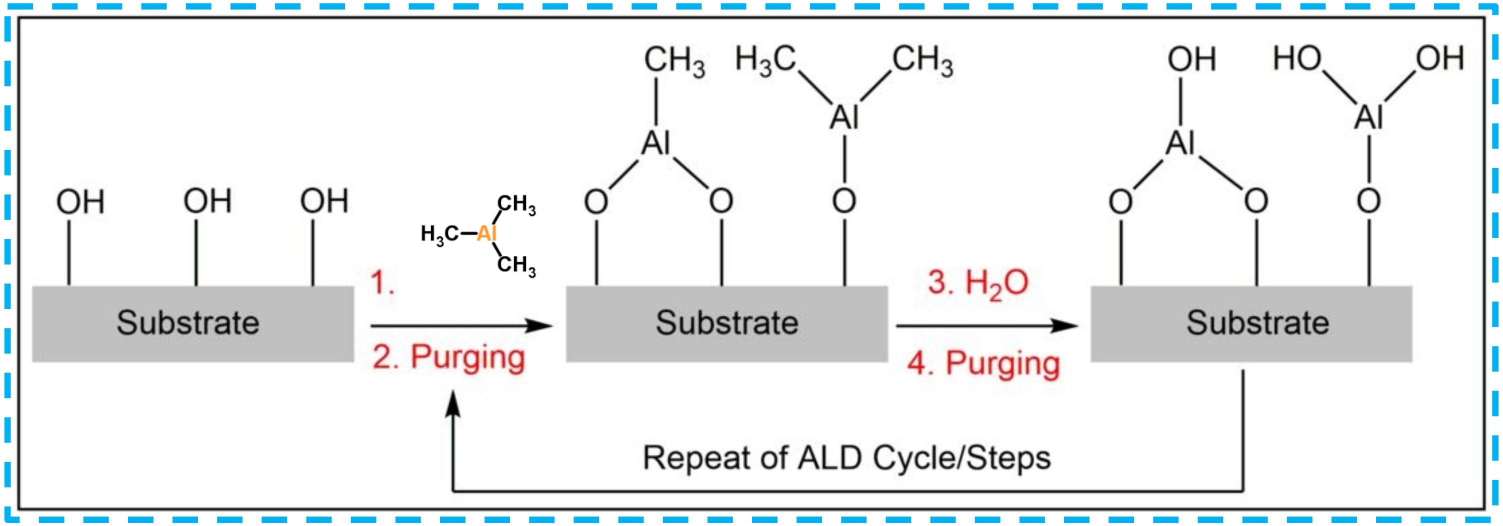
- Whole process consists in 4 steps which is called a cycle

- H_2O or O_3 are commonly used as one of the reactant for oxide materials

How is Atomic Layer Deposition (ALD) defined?

- *ALD of Al_2O_3:* $Al(CH_3)_3 + H_2O \rightarrow Al_2O_3 + CH_4$ (CH_4 by-product)

- *The reaction mechanism for ALD of Al_2O_3 process*

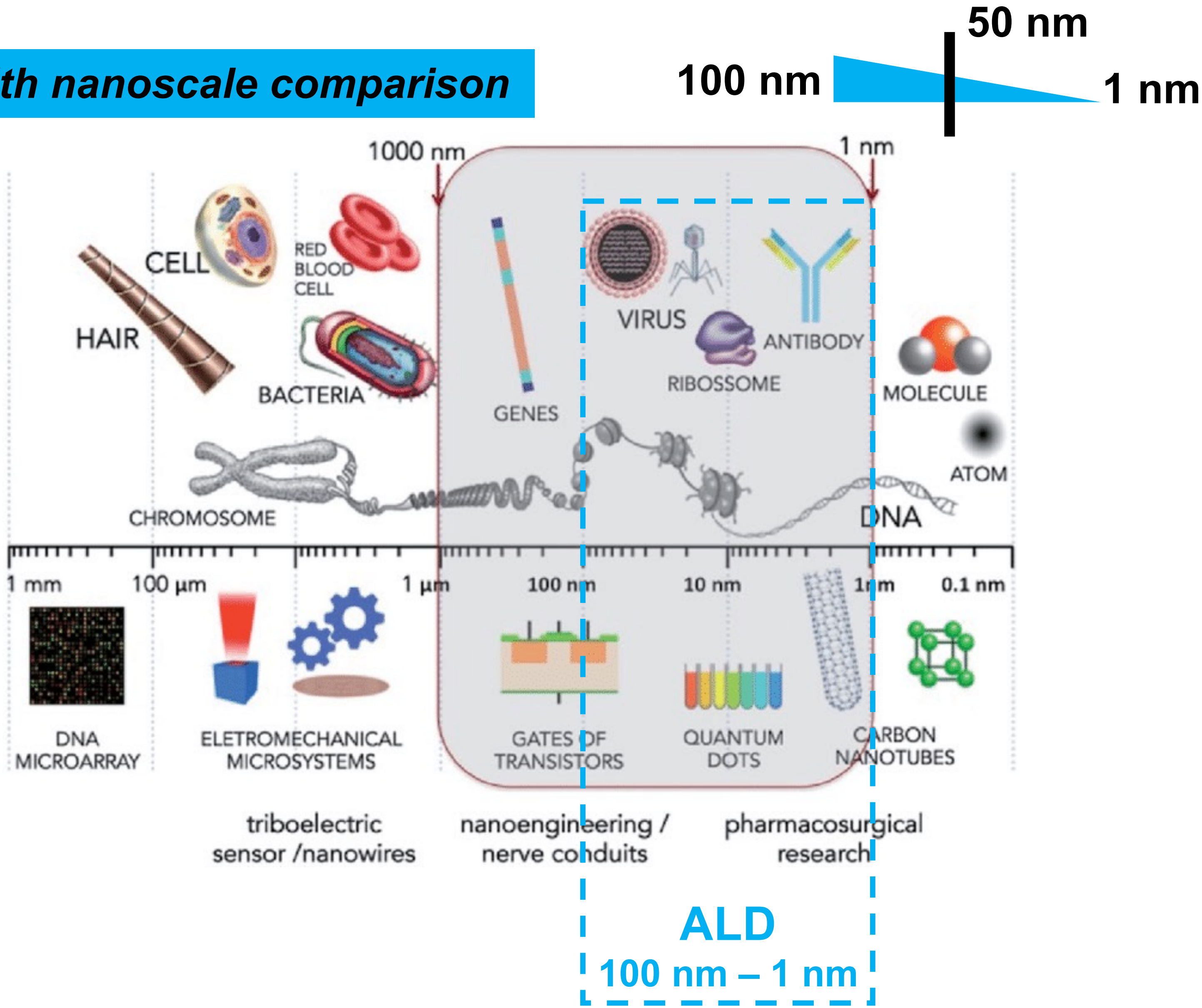


Hydroxyl-terminated starting surface

- The ***nature and surface density of functional groups*** on the substrate surface are among the key factos that determine the first steps of the film growth

ALD – Size and scale

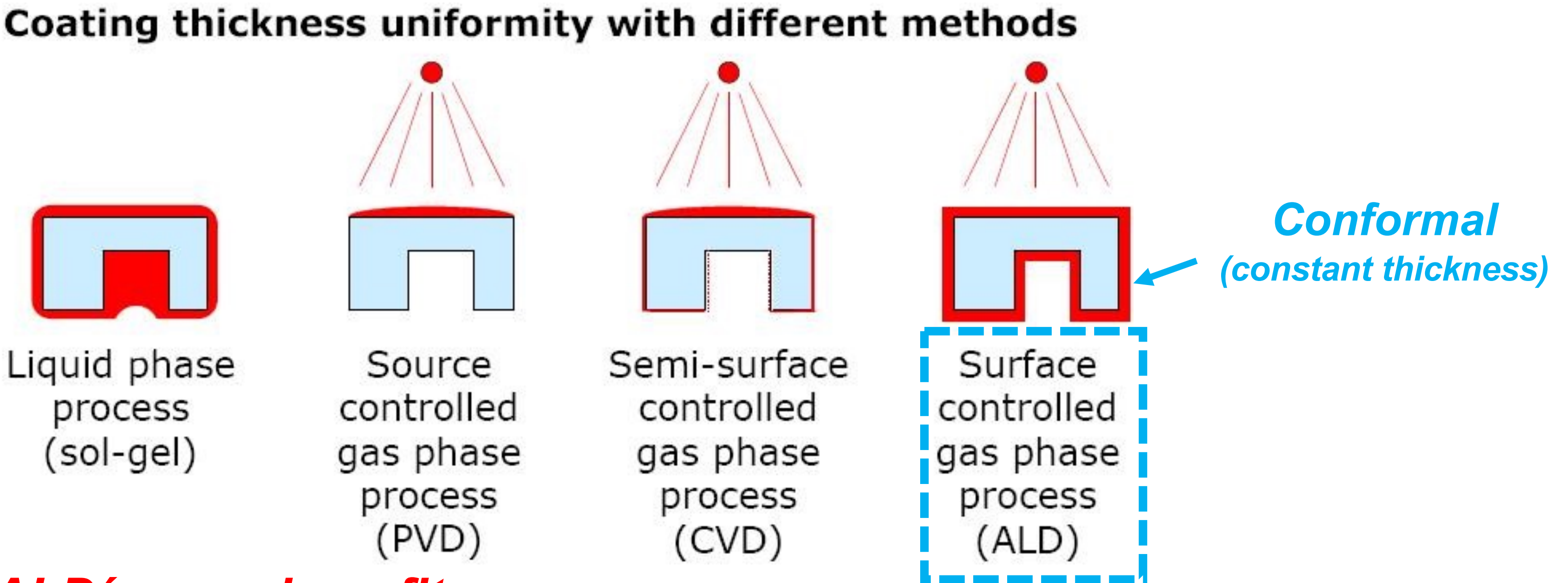
- ***Scheme with nanoscale comparison***



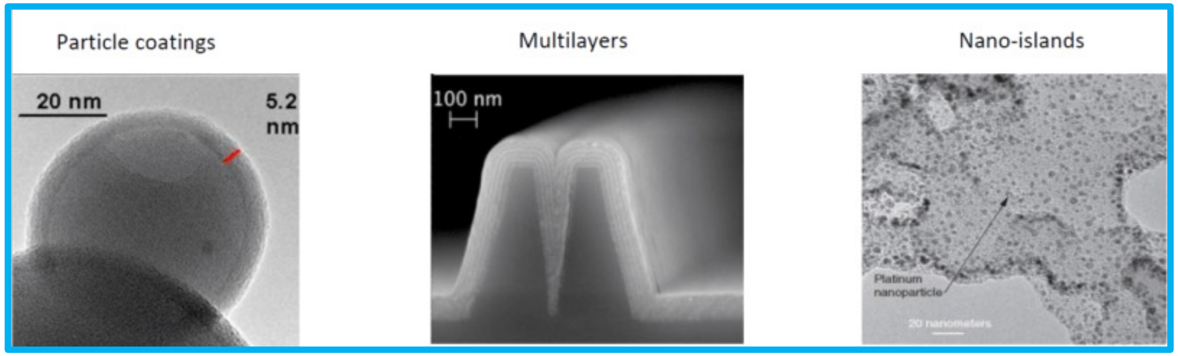
- Scale thickness range for ALD, in comparison to biological components

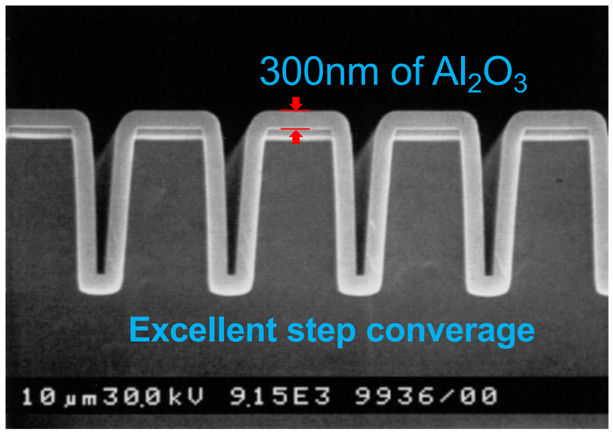
ALD ***vs.*** other coating methods

- ***Comparison of characteristcs: thin film coating methods***



- ***Conformality: ALD´s core benefit***
- ***Examples:*** Si with trench structures (3D substrates); particles; Si with trench structures with multilayers; nano-islands (Pt)





M. Ritala et al., Chem. Vap. Dep., 1999, 5, 7.

- ***Surface controlled processes afford a coverage with constant thickness throughout the structure***

ALD materials application range

- ***The most common ALD materials are metal oxides and metal nitrides***

High-k dielectrics (***Al_2O_3, HfO_2***, ZrO_2, Ta_2O_5, La_2O_3,)
For transistor gates and DRAM capacitors in Si, GaAs, Heterostructures, compound semiconductors
III-V Semiconductor materials, organic transistors, *graphene*, graphite, *nanotubes*, nanowires, molecular electronics

Conductive gate electrodes (Ir, Pt, Ru, TiN)

Metal interconnects and liners (Cu, WN, TaN, WNC, Ru, Ir)
Metallic diffusion barrier layers for copper interconnects and semiconductor vias for transistor gate and memory cell applications, DRAM capacitors, passivation layers

Catalytic materials (Pt, Ir, Co, TiO_2, V_2O_5)
Coatings inside filters, membranes, catalysts (thin economical Pt for automobile catalytic converters), fuel cells ion exchange coatings

Nanostructures (all materials)
Conformal deposition around and inside nanostructures and MEMS (micro-electromechanical-systems)

Biomedical coatings: (TiN, ZrN, CrN, TiAlN, AlTiN)
Biocompatible materials for in-vivo medical devices and instruments

Piezoelectric layers (ZnO, AlN, ZnS)

Transparent Electrical Conductors (ZnO:Al, ITO)

UV blocking layers (ZnO, TiO_2)

OLED passivation (Al_2O_3)

Photonic crystals (ZnO, ZnS:Mn, TiO_2, Ta_2N_5)
Coatings inside porous alumina, inverted opals

Electroluminescent devices (SrS:Cu, ZnS:Mn, ZnS:Tb, SrS:Ce)

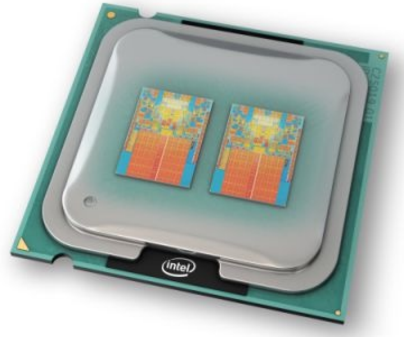
Processing layers (Al_2O_3, ZrO_2)
Etch barriers, ion diffusion barriers, fill layers for magnetic read heads

Optical applications (SnO_2, ZnO)
Photonics, nanophotonics, solar cells, integrated optics, optical coatings

Elemental semiconductors and oxide materials manufactured by ALD increased, mainly driven by ***silicon-based microelectronics***

ALD applications: industrial

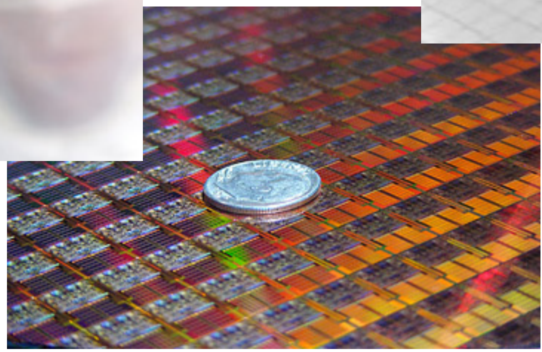
Microelectronics

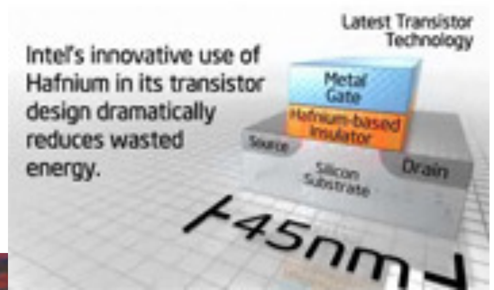


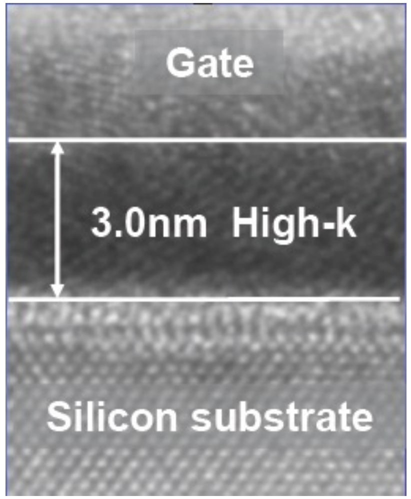
- Intel in 2007 introduced ALD of Hf-based oxide: 45 nm Core processor technology

ALD in dow-scaling miroelectronics features

- **Hafnium oxide *(HfO_2)*** based high-k gate oxides in CMOS transistors



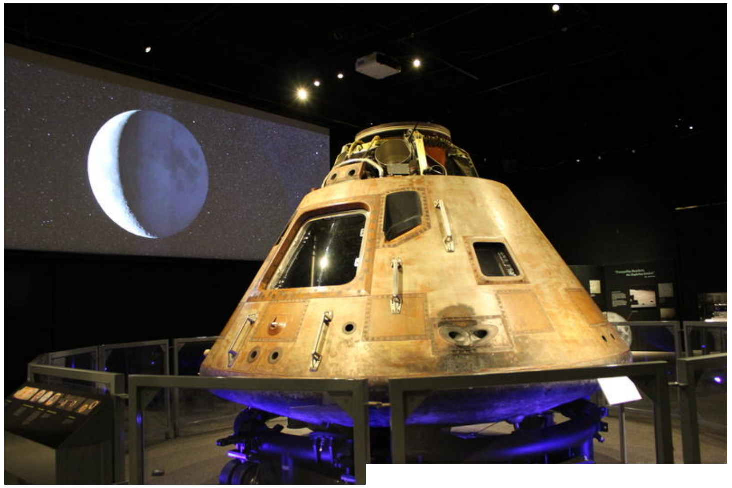




Merits:
Reduces leakage current
Cooler transistors

- **ALD is capable of producing ultra-thin films with exact composition and thickness control at the sub-nanometer level**

FunFact – did you know?



Your smartphone has more computing power than Apollo 11 did during its moon landing

Apollo Guidance Computer (AGC) **vs.** Apple iPhone 5s

Dimensions: 24 x 12.5 x 6.5 inches
Weight: 70 pounds
Processor speed: 1 MHz
Memory: 2,048 words (32,768 bits or roughly 4kB)
Display: Seven-segment numeric
Price: $150,000 (est.)

Dimensions: 4.87 inches x 2.31 inches
Weight: 3.95 ounces
Processor speed: 1.3GHz, dual-core
Memory: 64GB
Display: 4-inch diagonal Multi-Touch display, 1136 x 640 pixel resolution at 326 ppi
Price: $399

Menory type

Core rope menory, wires running through magnets

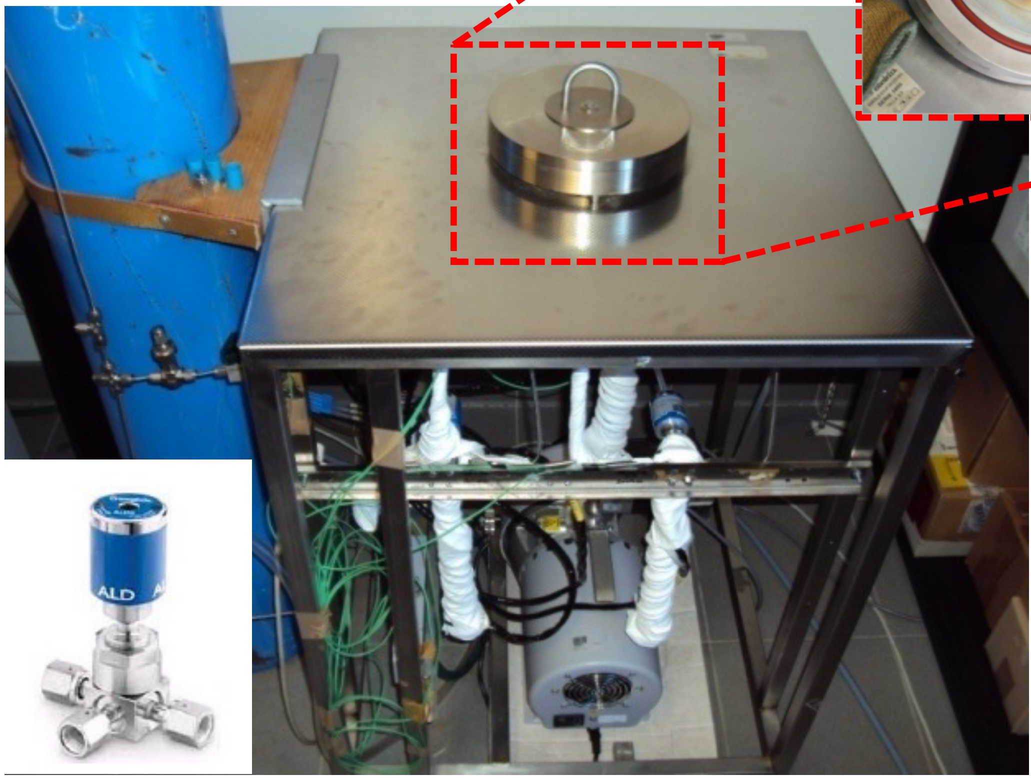
Silicon-based menory chips

ALD tool in UA

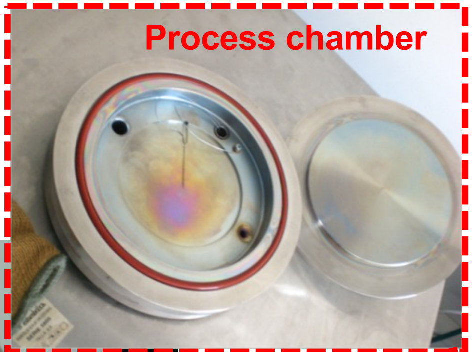
universidade de aveiro ciceco

- Custom-made cross-flow ALD reactor (inorganic materials)

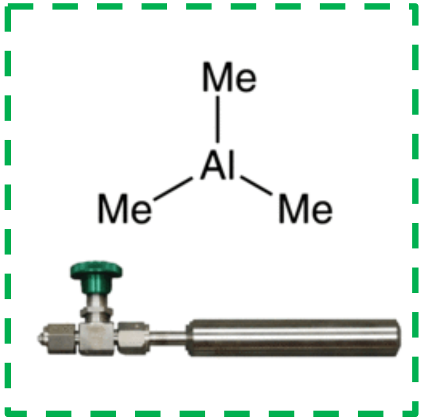
  - ***Thermal ALD***



ALD pneumatic valve – precursor pulse

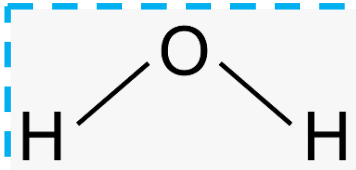


Metal precursor (TMA)



ALD ss-canister for precursor chemicals

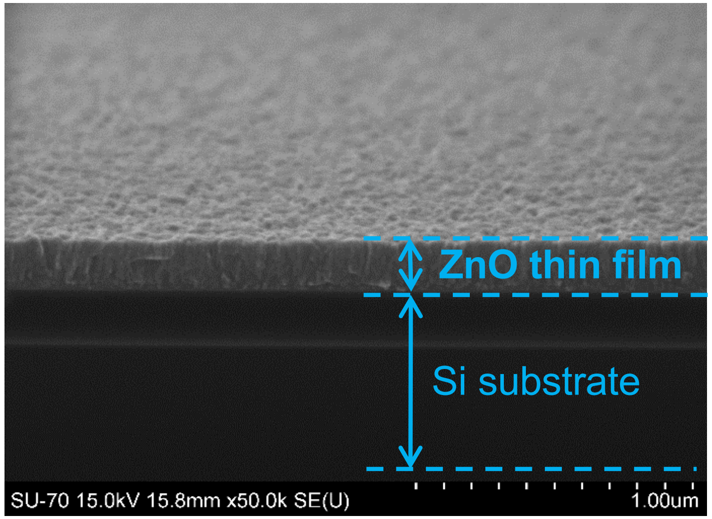
Oxygen source (H_2O)

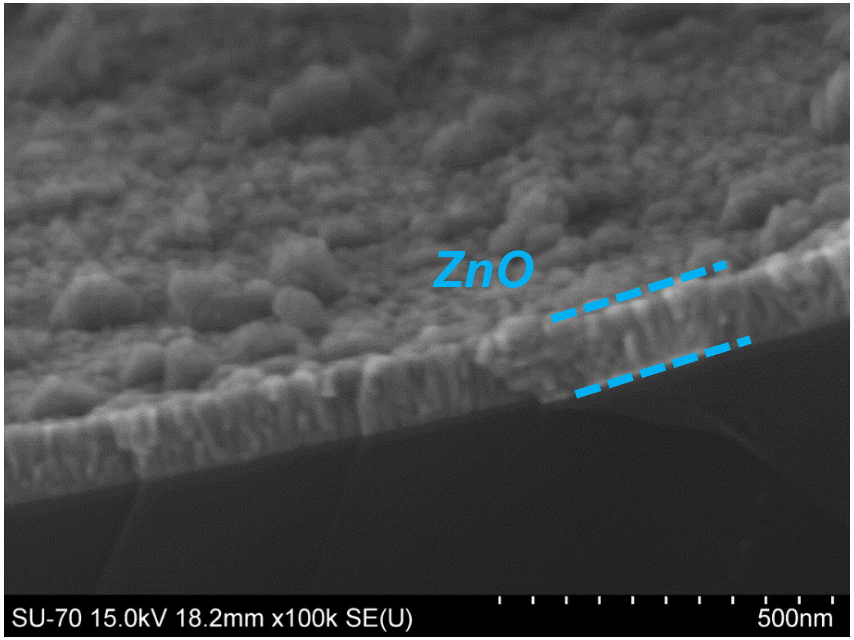


- *ALD – Tool for nanostructured materials*
  - Selected examples *("made in UA")*
  - *From planar substrates to 3D substrates*

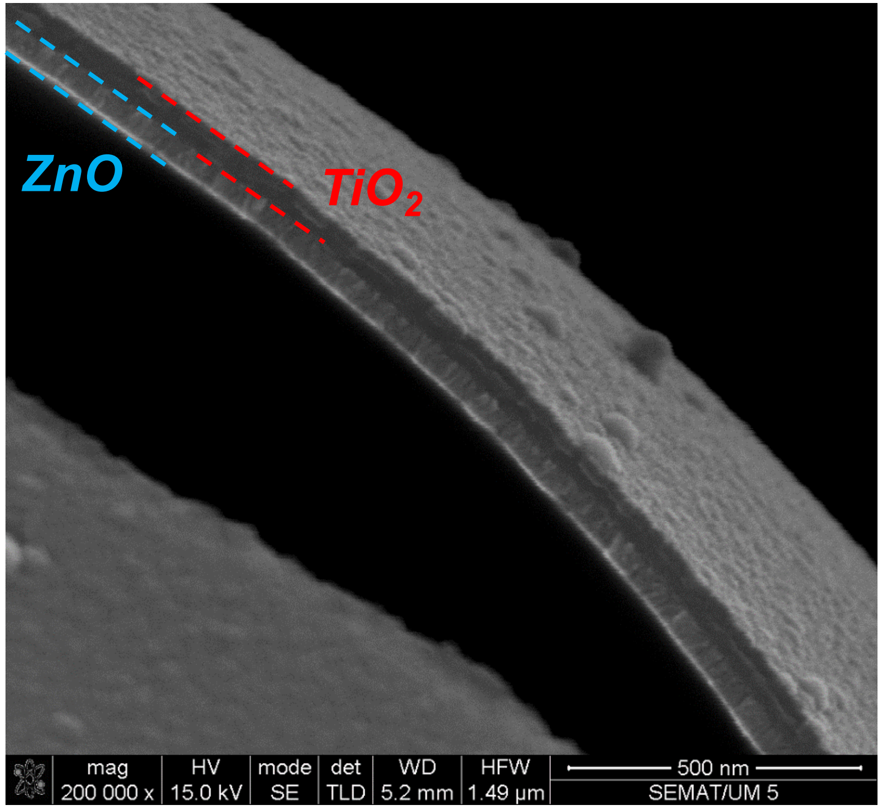
ALD of nanostructured materials:

- ***Si/SiO$_2$ coated with ZnO***



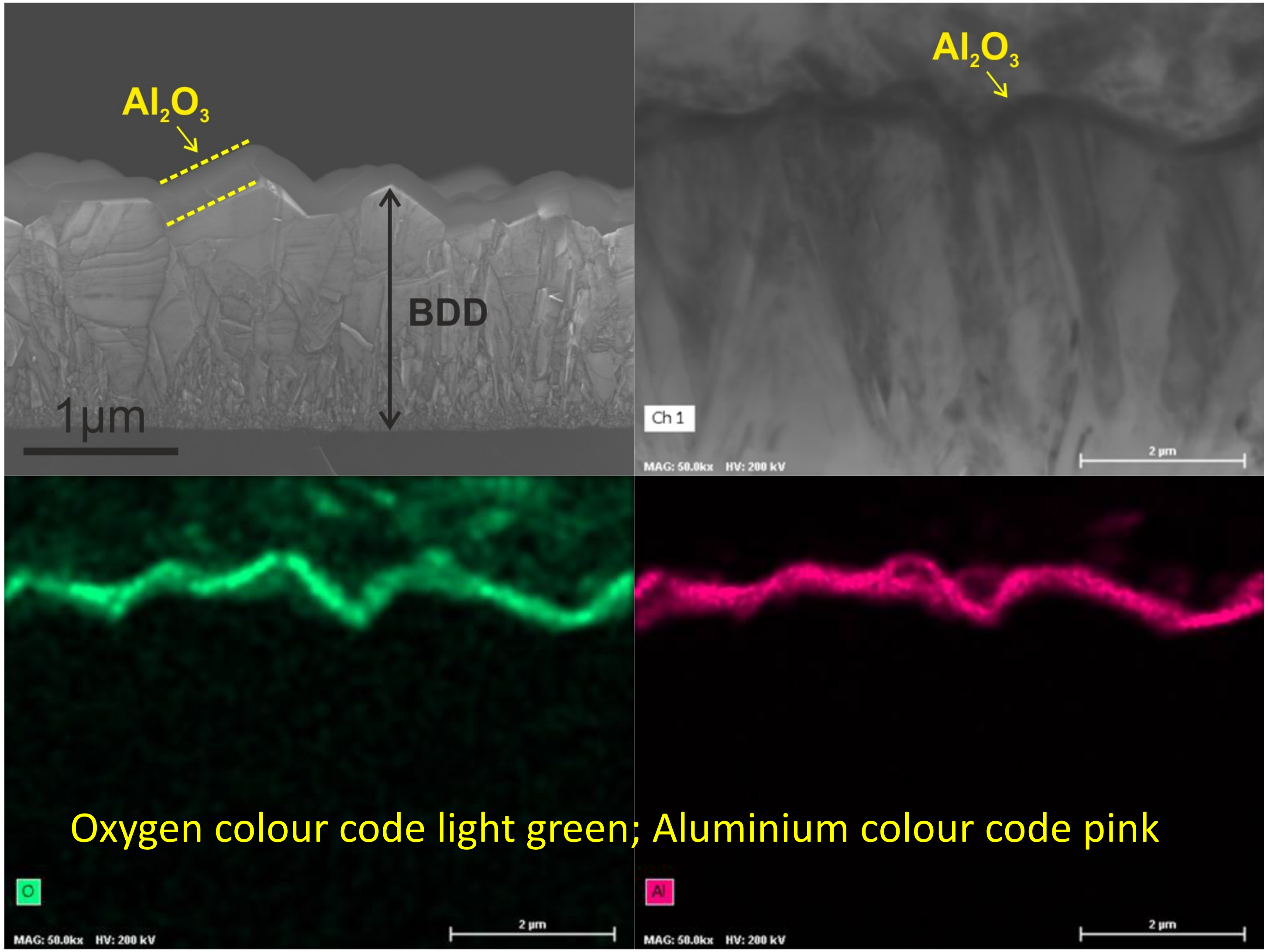


- ***Multilayer: ZnO/TiO$_2$***

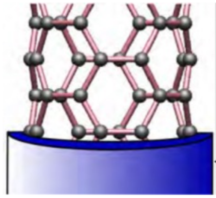


ALD of nanostructured materials:

- ***HFCVD - BDD coated with Al_2O_3 ($T_{deposition}$= 200ºC)***

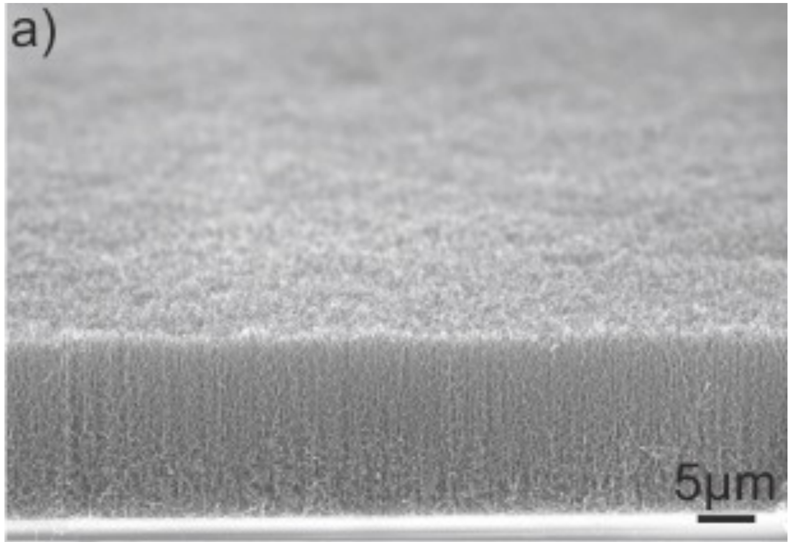


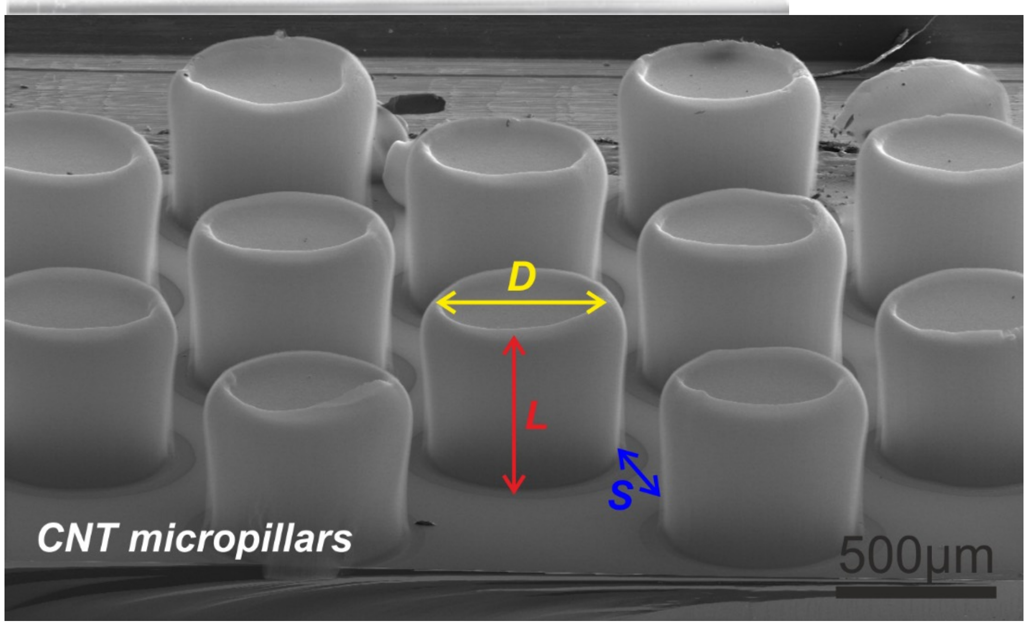
ALD of nanostructured materials:



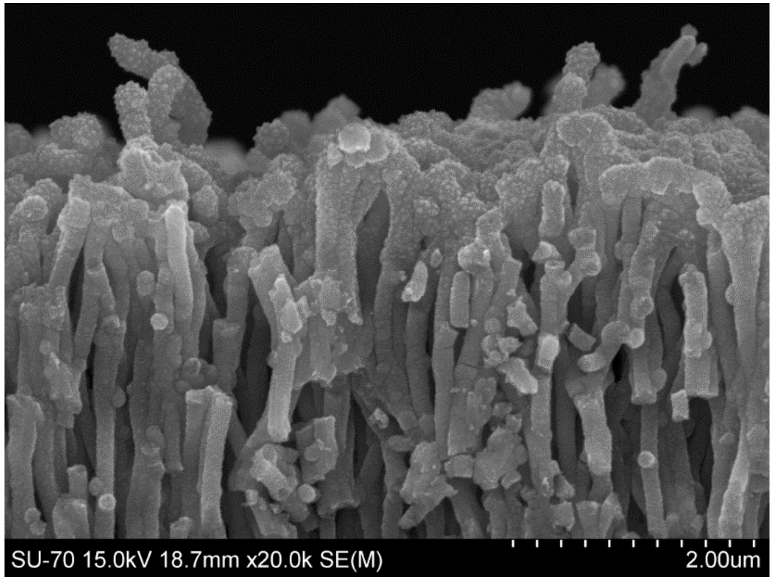
- ***VACNTs coated with ZnO***

Uncoated VACNTs forest grown by TCVD from Fe catalyst

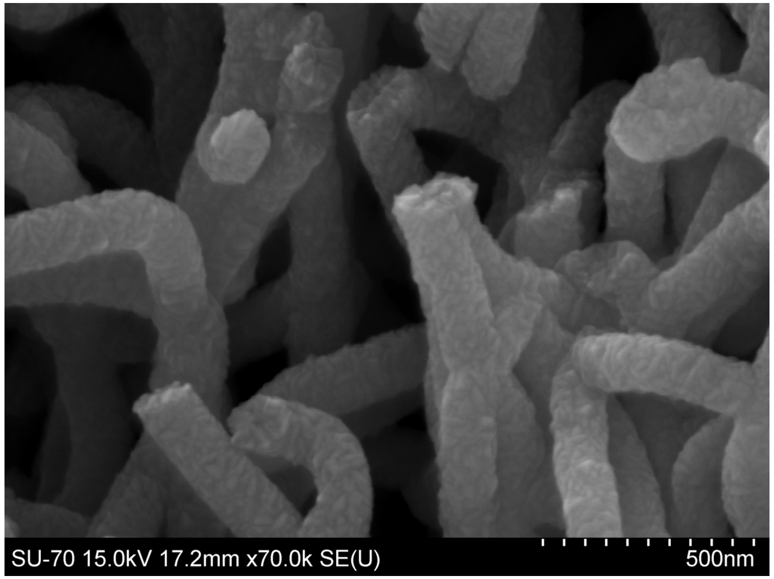




Coated VACNTs forest with ZnO

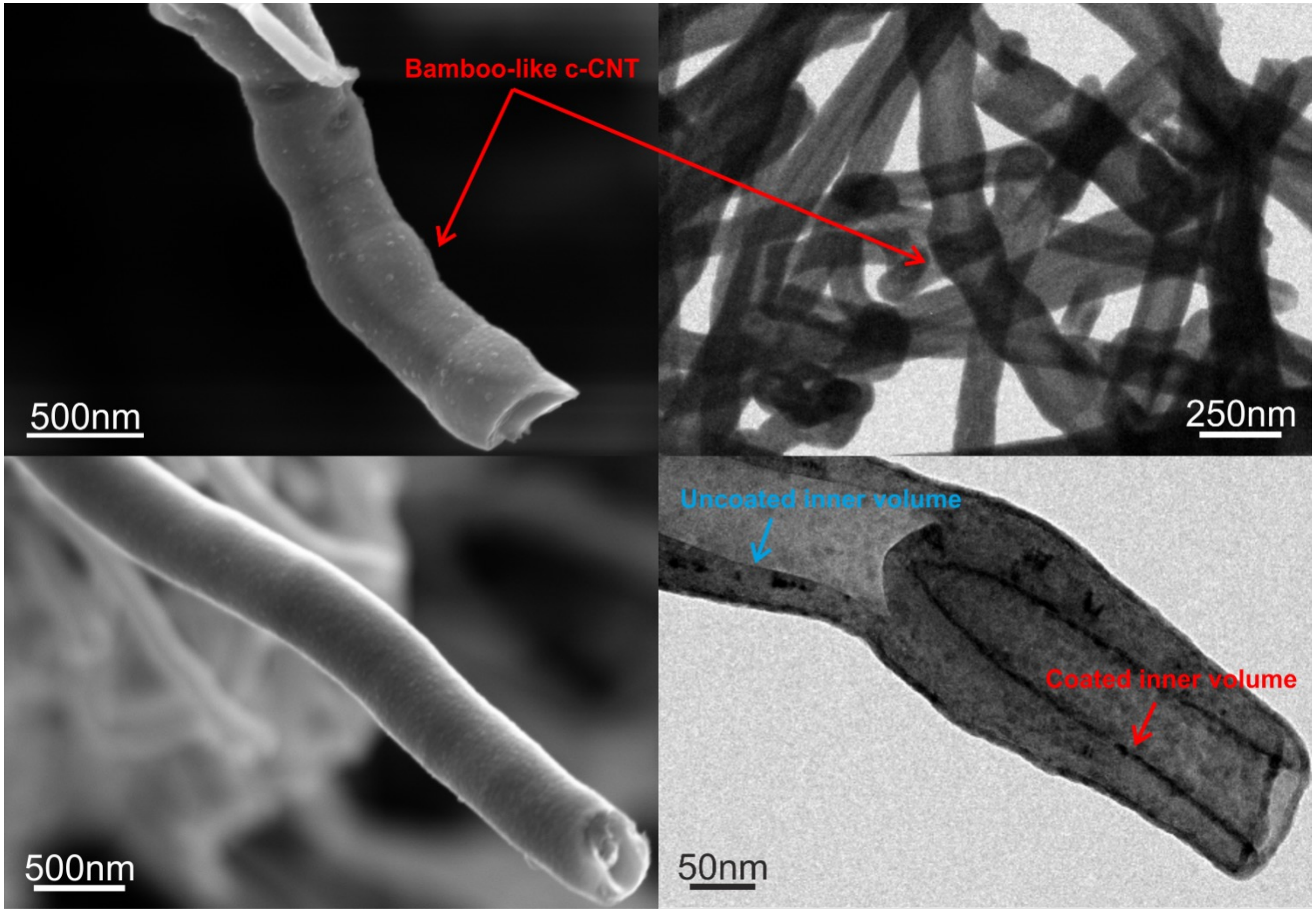


Top-CNTs forest/ZnO particule-like morphology



ALD of nanostructured materials:

• ***Commercial-CNTs (bamboo-like structure) coated with Mn_3O_4***

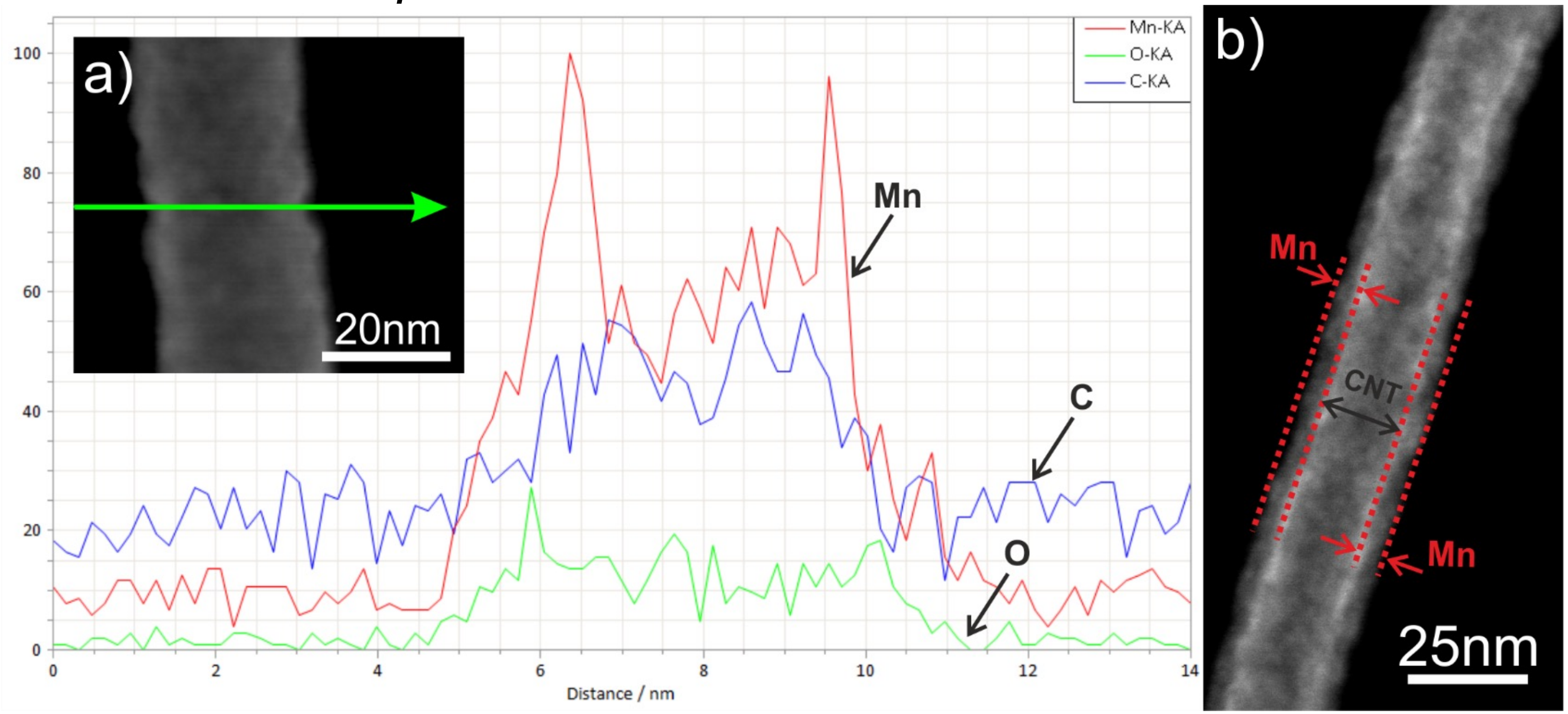


• *The dark contrast in BF-TEM images indicates a uniform and conformal coating of Mn_3O_4*
• *It can be seen that the original shape preserved*

ALD of nanostructured materials:

- ***VA-CNTs coated with Mn_3O_4***

STEM/EDS line scan profile

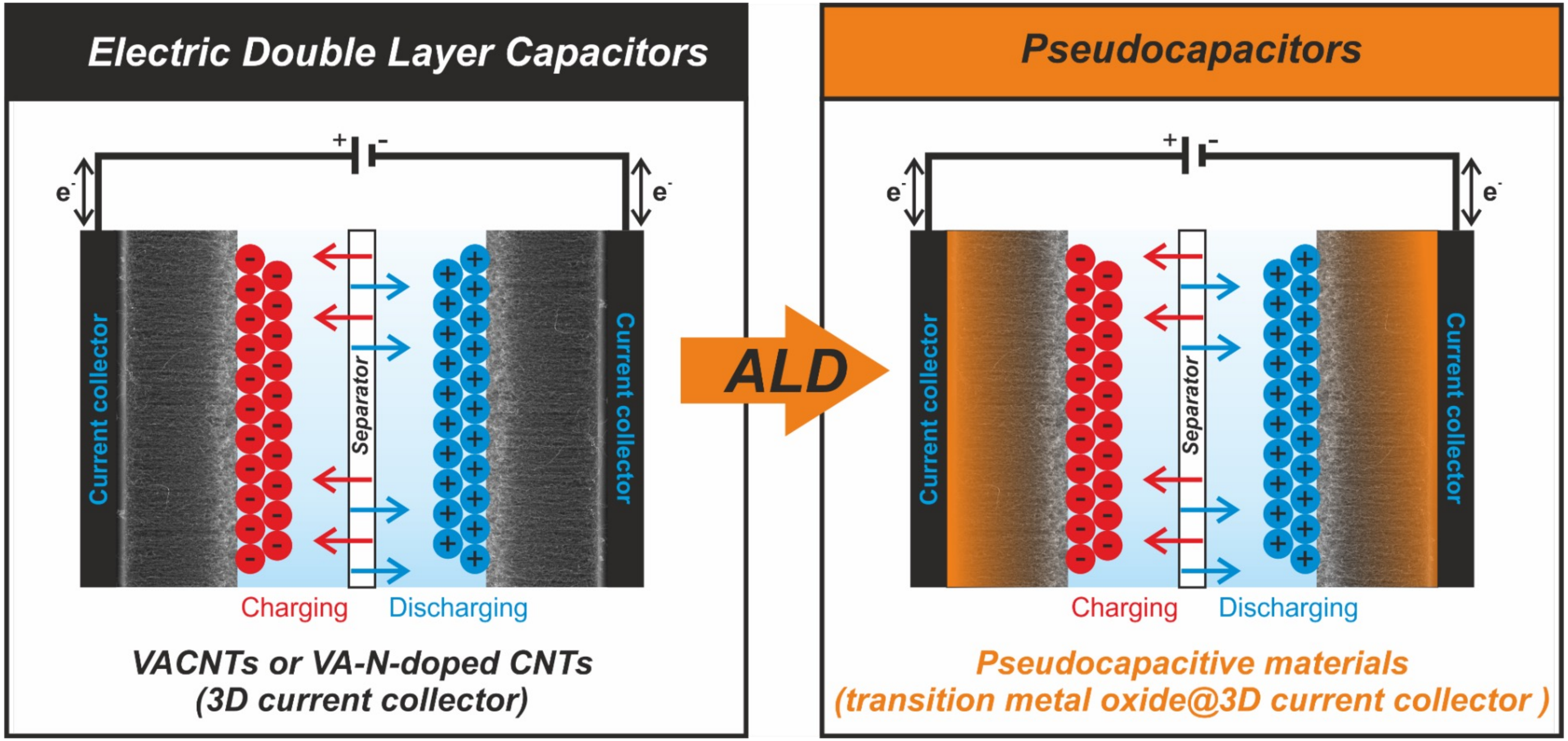


- ***Core-shell configuration: CNT/Mn_3O_4***
- ***Practical Application?***

ALD of nanostructured materials:

- ***VACNTs coated with Mn_3O_4 – Practical Application***

- ***Supercapacitor – A Class of Energy Storage Devices – Electrodes***

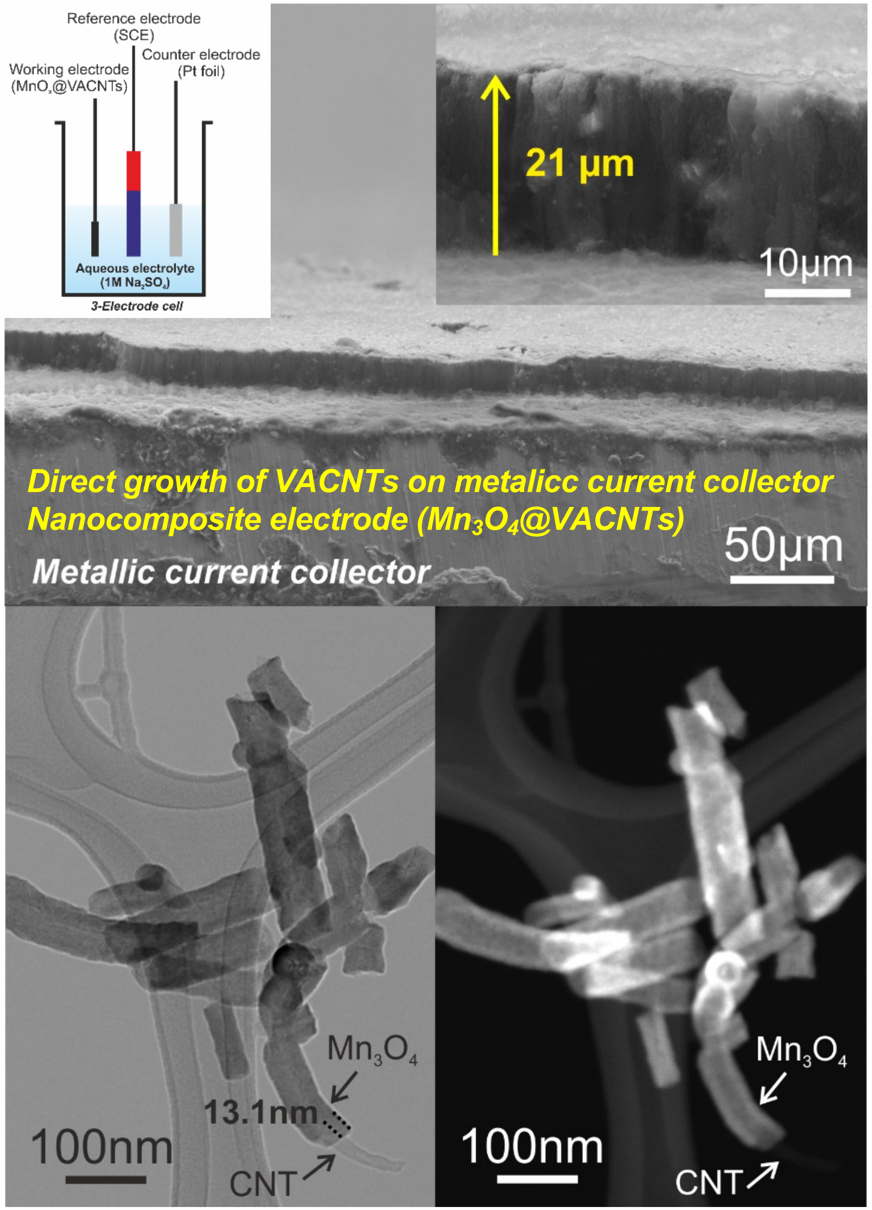


- Supercapacitor consists of two electrodes immersed in a electrolyte solution, with a voltage potential across the current collectors and a dielectric separator between the two electrodes

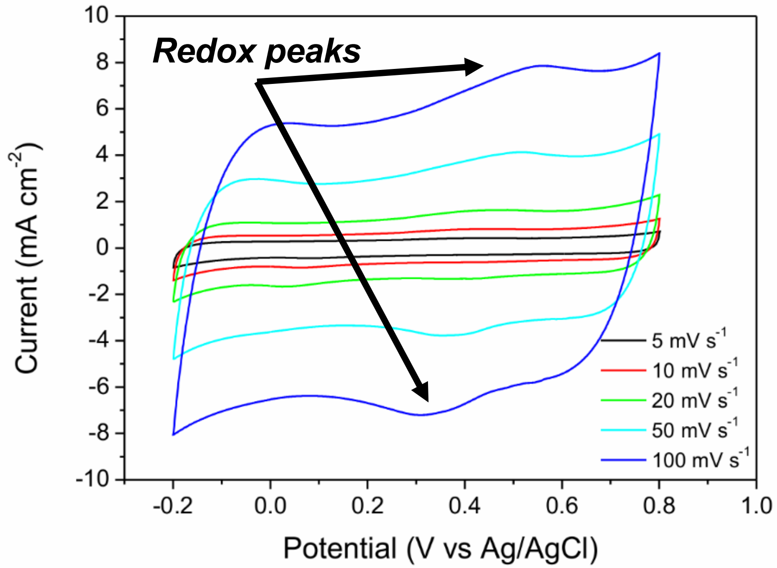
ALD of nanostructured materials:

Micro-scale energy systems
Area-limited configurations

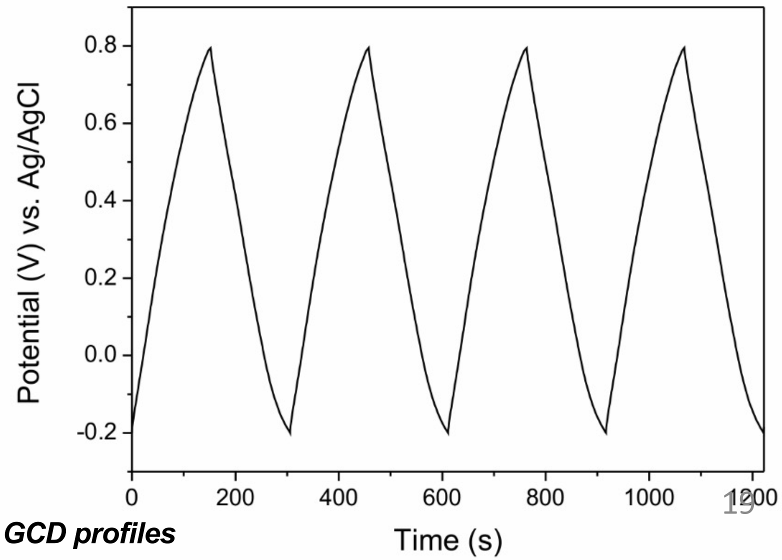
- ***Supercapacitor - Electrode - Microstructure***



C_{sp} is proporcional to the area under the CV curves



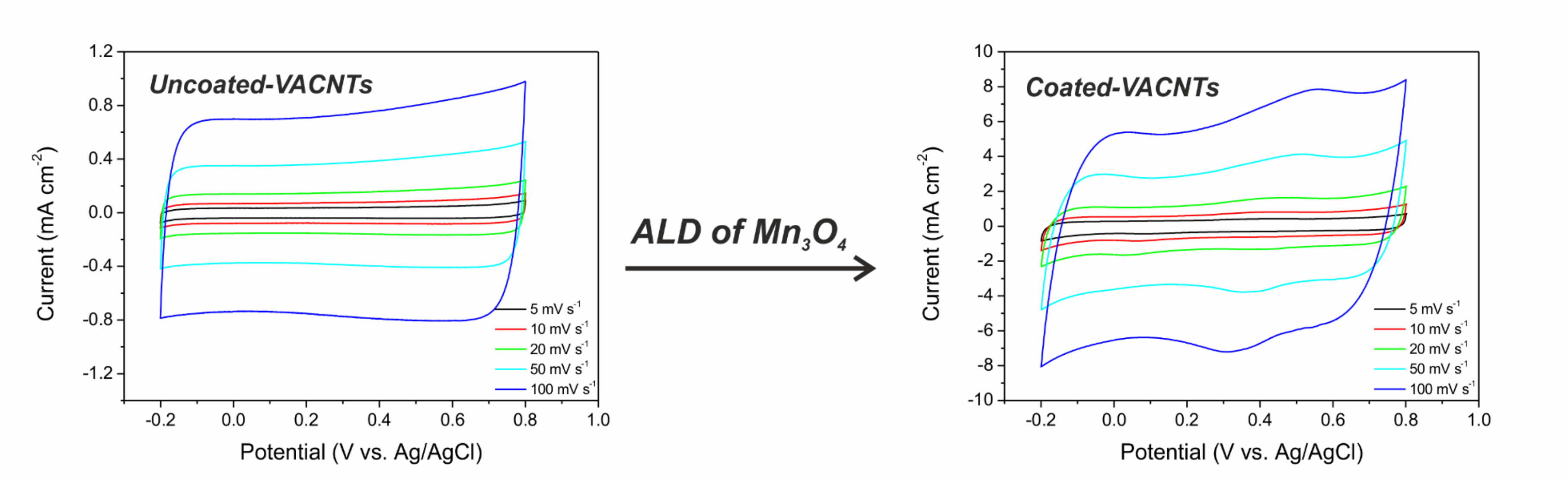
Good capacitance retention upon cycling (long term use)



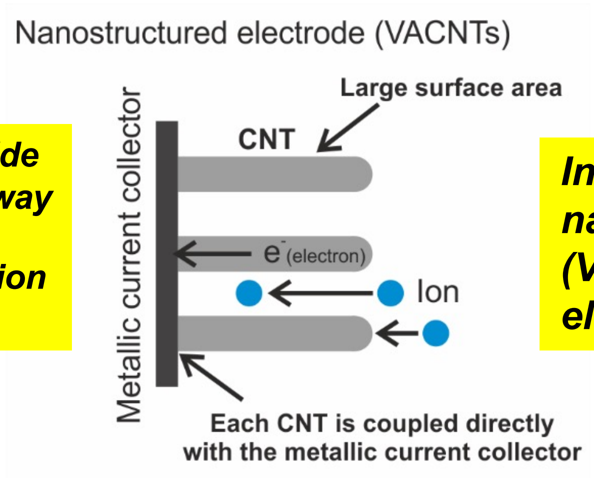
Linear GCD profiles

ALD of nanostructured materials:

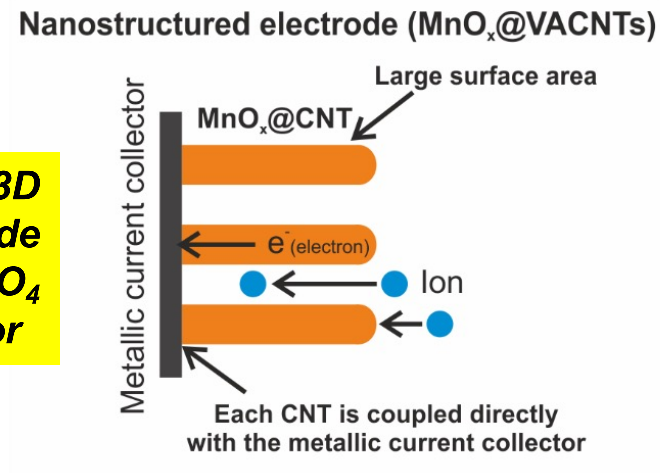
- ***Supercapacitor - Electrode - Performance***



VACNTs provide direct 1D pathway for electron transport and ion diffusion

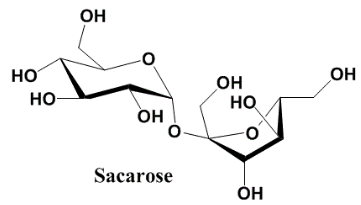


Influence of the 3D nanostructured electrode (VACNTs) on the Mn_3O_4 electrochemical behavior

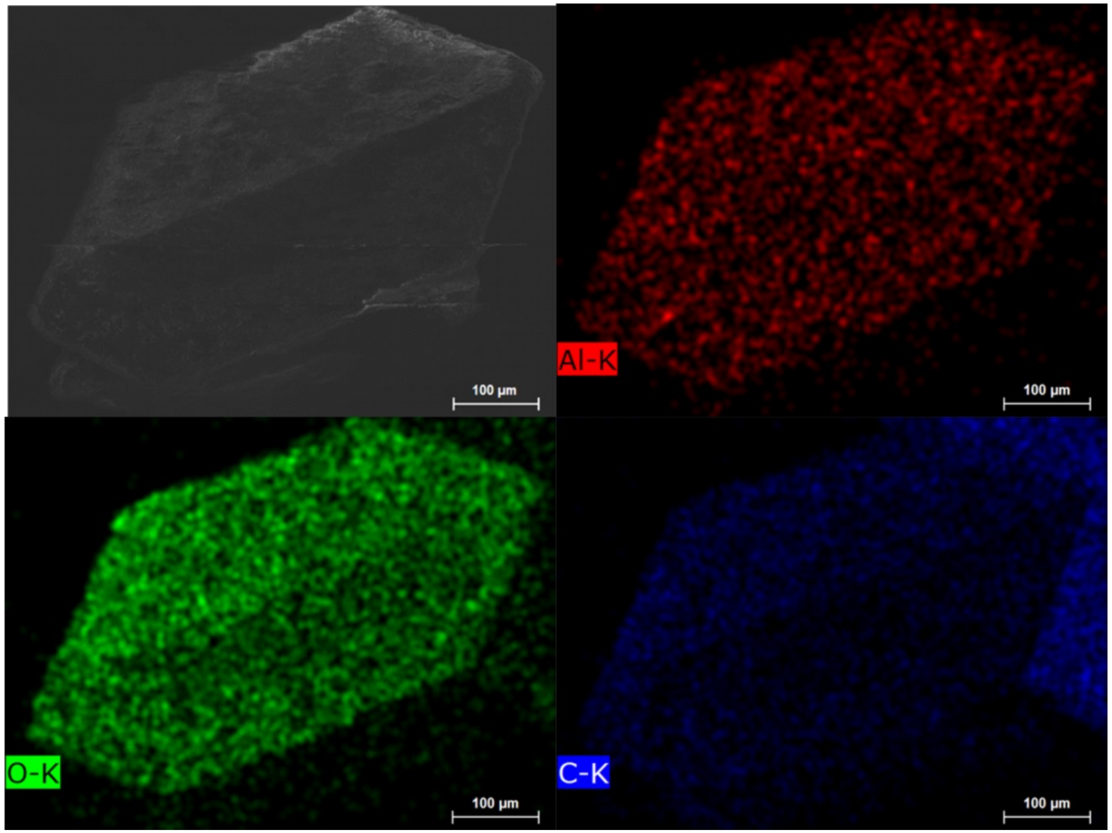


- ***Binder-free electrodes for supercapacitors; taking advantage of both materials***

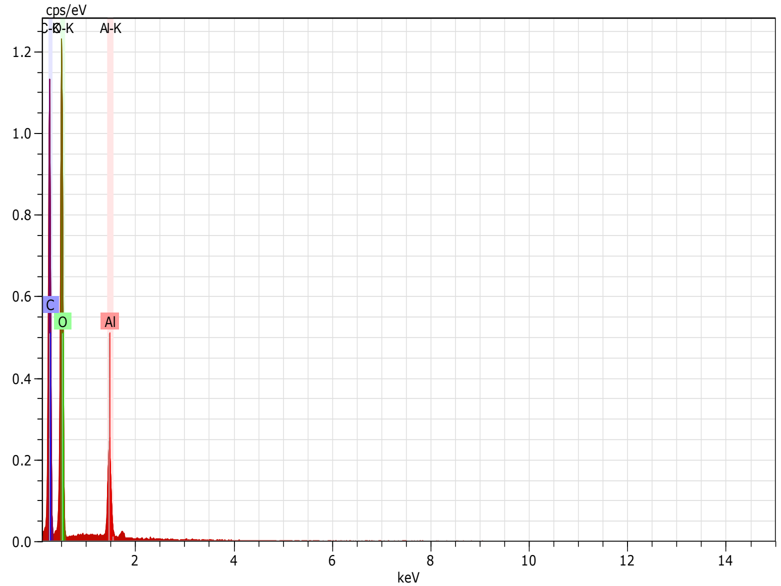
ALD of nanostructured materials:



- ***Sugar grain coated with ALD of Al_2O_3***

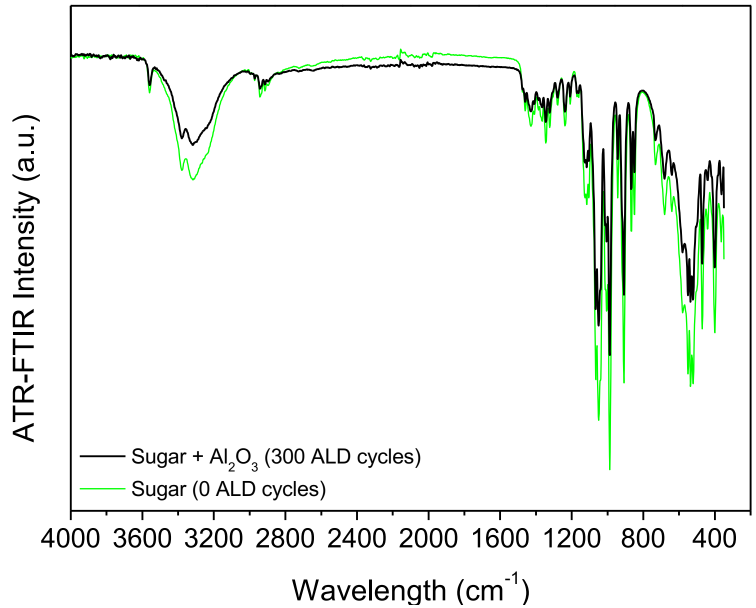


EDS – elemental composition



It can be seen that the original shape preserved

- <u>Heat-sensitive materials: polymers</u>



Final remarks

- ALD is a thin film technology for:

  - Surface modification *(active film or interfacial layer)*

  - Fabrication of complex nanostructured materials

  - Development of nanostructured materials for different applications fields

  - ***Conformality is, in fact, the ALD´s core benefit***

- ***Limitations:***

  Expensive equipment

  Low effective deposition rate

Thank you for your attention!