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Promising Directions for Developing Nano-structured Photocathodes

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1st Workshop on Photo-cathodes: 300nm-500nm
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U.S. Department of Energy

THE UNIVERSITY OF CHICAGO

Office of Science
U.S. DEPARTMENT OF ENERGY

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Outline

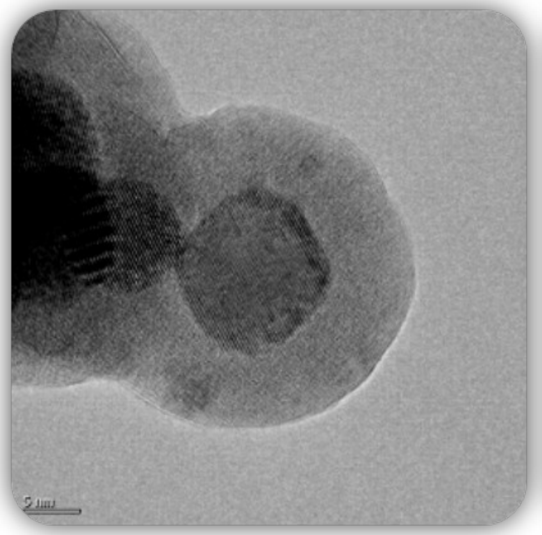
- Issues Arising
- Atomic Layer Deposition (Synthesis)
- Barrier Layers
- Layered Thin Films
- Plasmon Enhanced Absorption

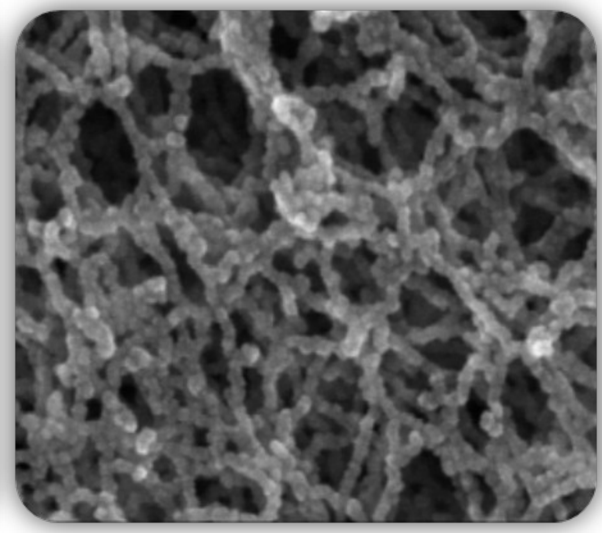
Photocathode Issues

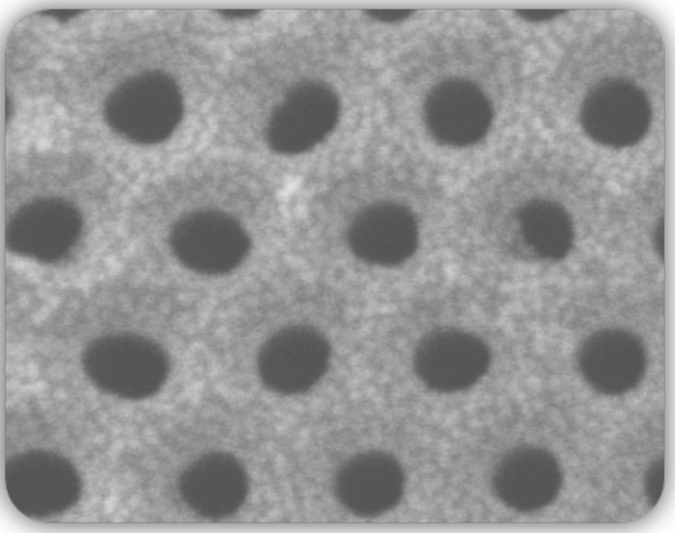
- Conductivity
- Balancing Absorption and Electron Collection
  - Photon Absorption Lengths are long
    - *Nanostructuring*
    - *Plasmonics*
  - Electron Diffusion Lengths are short

Atomic Layer Deposition (ALD)

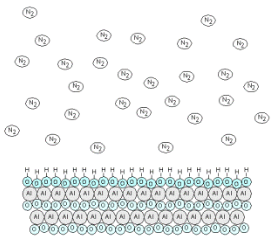
- Layer-by-layer thin film synthesis method
- Atomic level control over thickness and composition (even on very large areas)
- Precise coatings on 3-D objects
- Some unique possibilities for morphology control

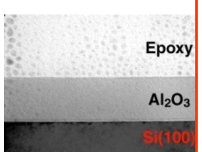




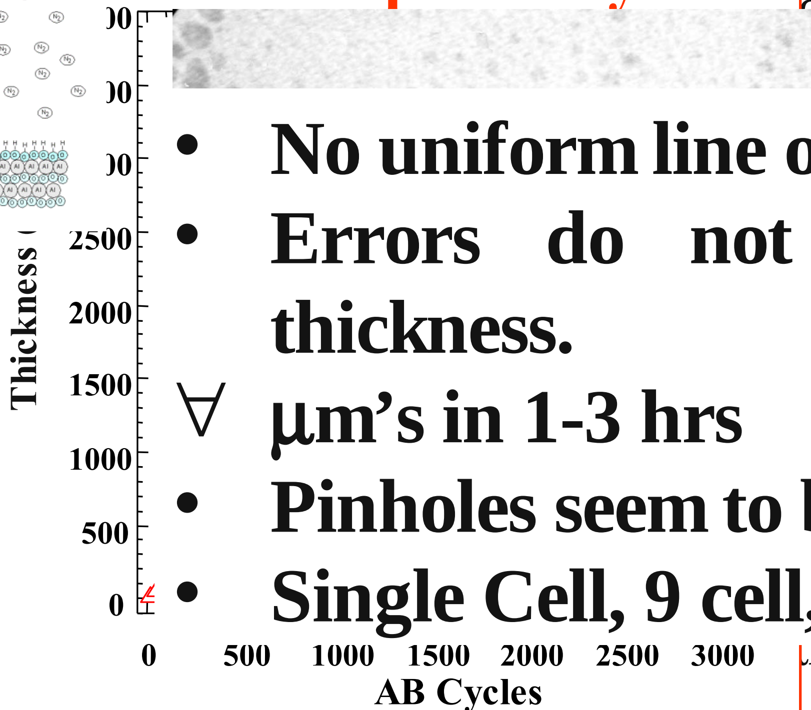


ALD Reaction Scheme





Ellipsometry



Atomic Force Microscopy

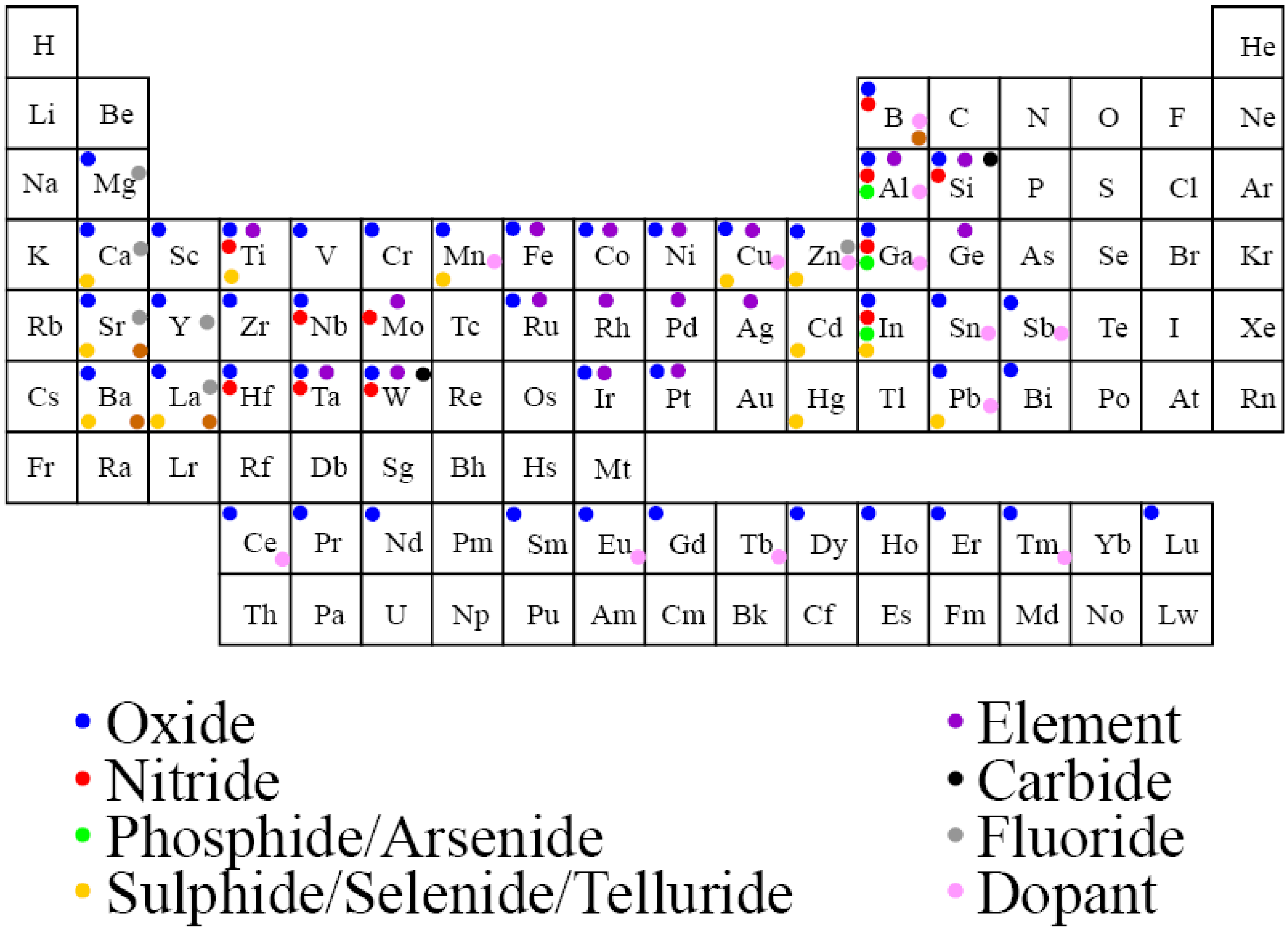
- No uniform line of sight requirement!
- Errors do not accumulate with film thickness.
- ∀ μm's in 1-3 hrs
- Pinholes seem to be removed.
- Single Cell, 9 cell, re-entrant, *in situ*

- Flat, Pinhole-Free Film

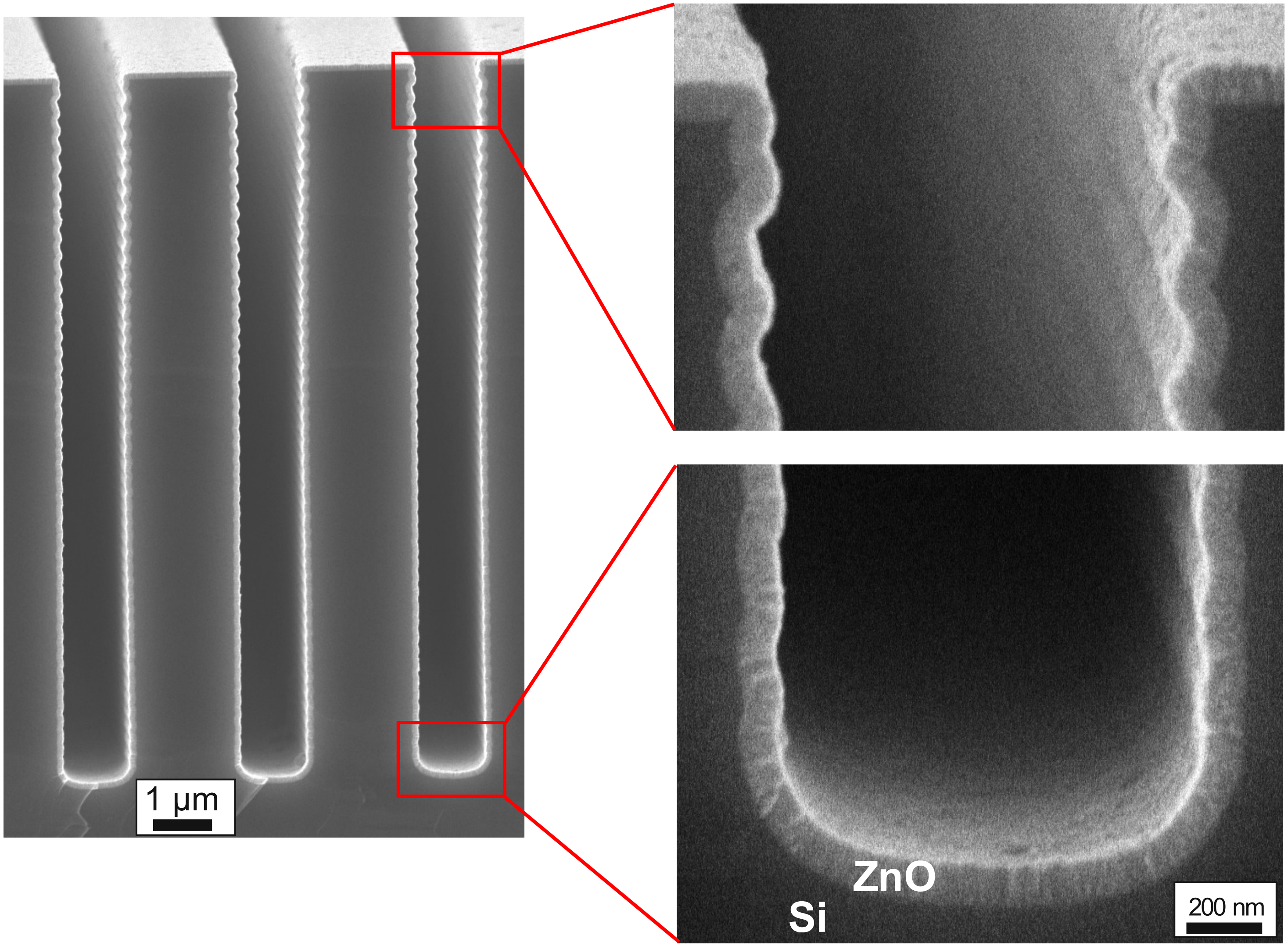
- Film growth is linear with AB Cycles

- RMS Roughness = 4 Å (3000 Cycles)
- ALD Films Flat, Pinhole free

ALD Thin Film Materials



ZnO in Silicon High Aspect Ratio Trench

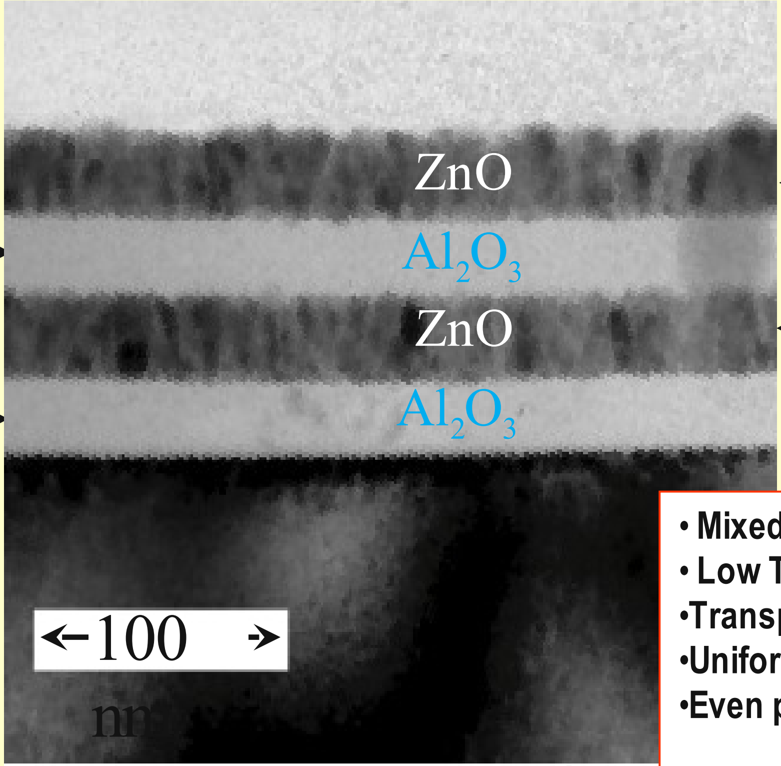


- ALD is *very* good at coating non-planar surfaces

Mixed Oxide Deposition: Layer by Layer

Mass Deposited (ng/cm^2)

[(CH$_3$)$_3$Al // H$_2$O]



[(CH$_3$CH$_2$)$_2$Zn // H$_2$O]

- Mixed Layers w/ atomic precision
- Low Temperature Growth
- Transparent
- Uniform
- Even particles in pores can be coated.

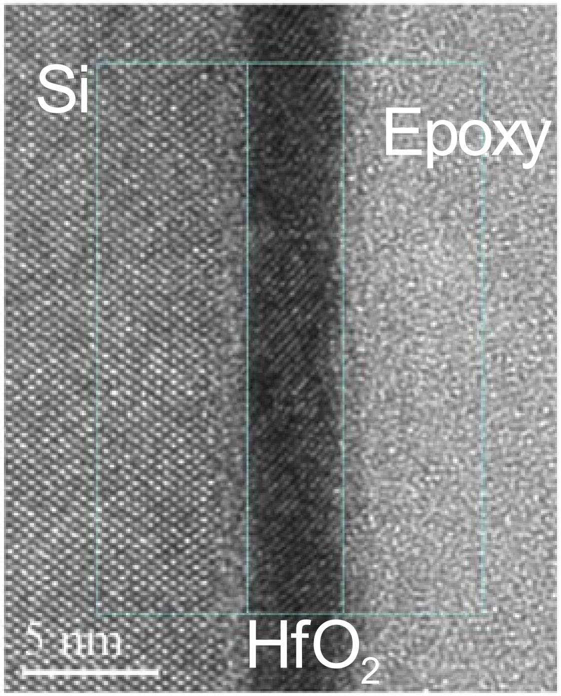
- Films Have Tunable Resistivity, Refractive Index, Surface Roughness, etc.

ALD: Abrupt Semiconductor Dielectric Boundaries

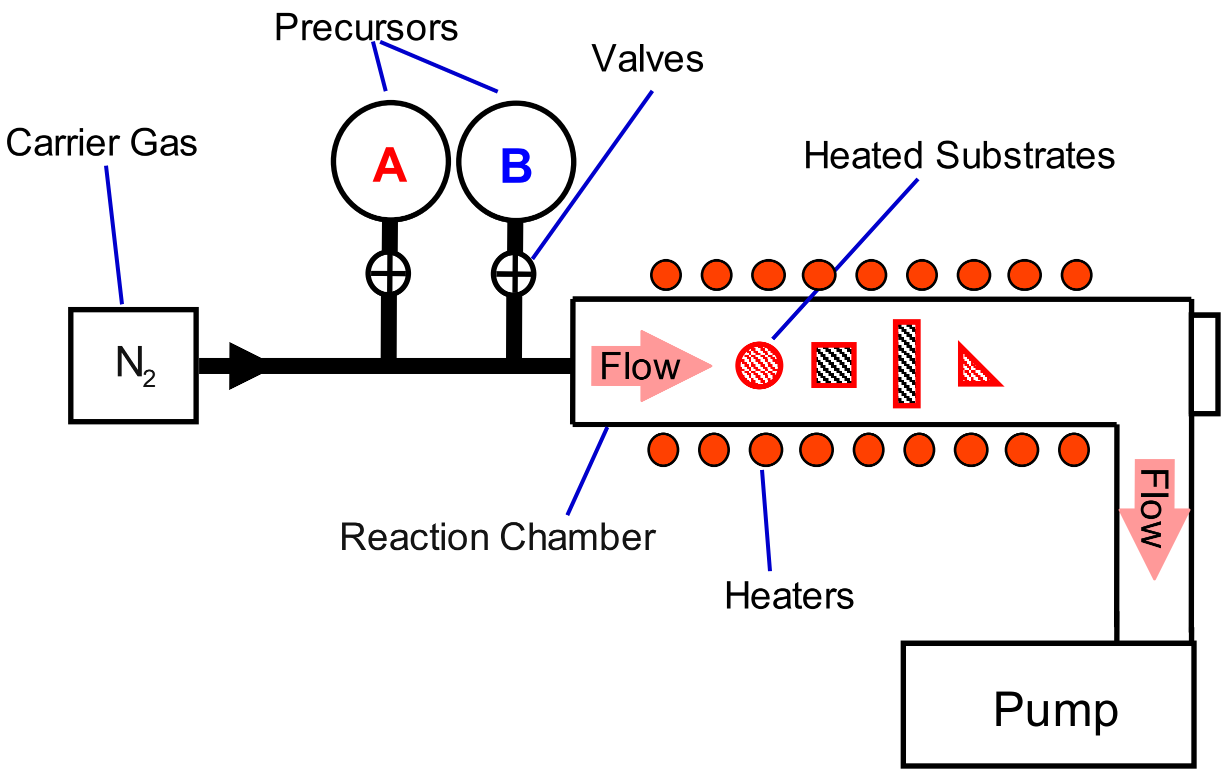
- Semiconductor Industry – a clue
  - Silicon is reactive but oxide is simple and passivates well (but has a low dielectric constant)
  - Gate dielectric oxides are now being used on Si

    metal (and being produced by ALD

    20 m^2 / batch)



Components of ALD System

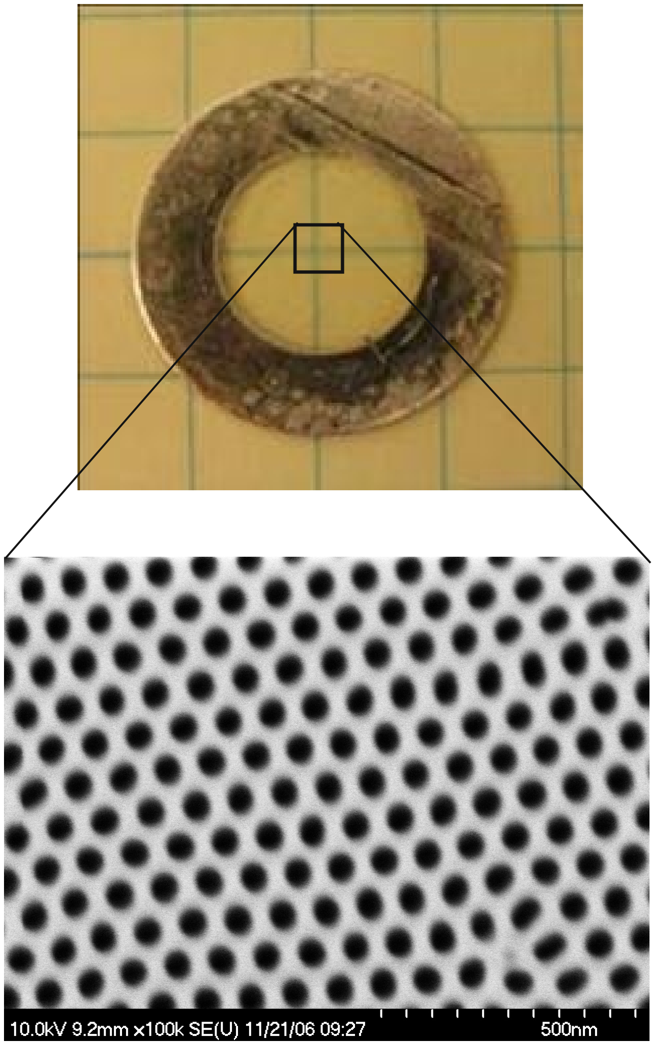


- Equipment is simple
- Scale up is straightforward

ALD Viscous Flow Reactors at ANL

- 10 chemical precursor channels
  - gas, liquid, or solid
  - precursor temperature to 300°C
  - ozone generator
- Reaction temperature to 500°C (1000°C)
- In-situ measurements
  - thickness (quartz microbalance)
  - gas analysis (mass spectrometer)
- Coat flat substrates (Si), porous membranes, powders, etc.

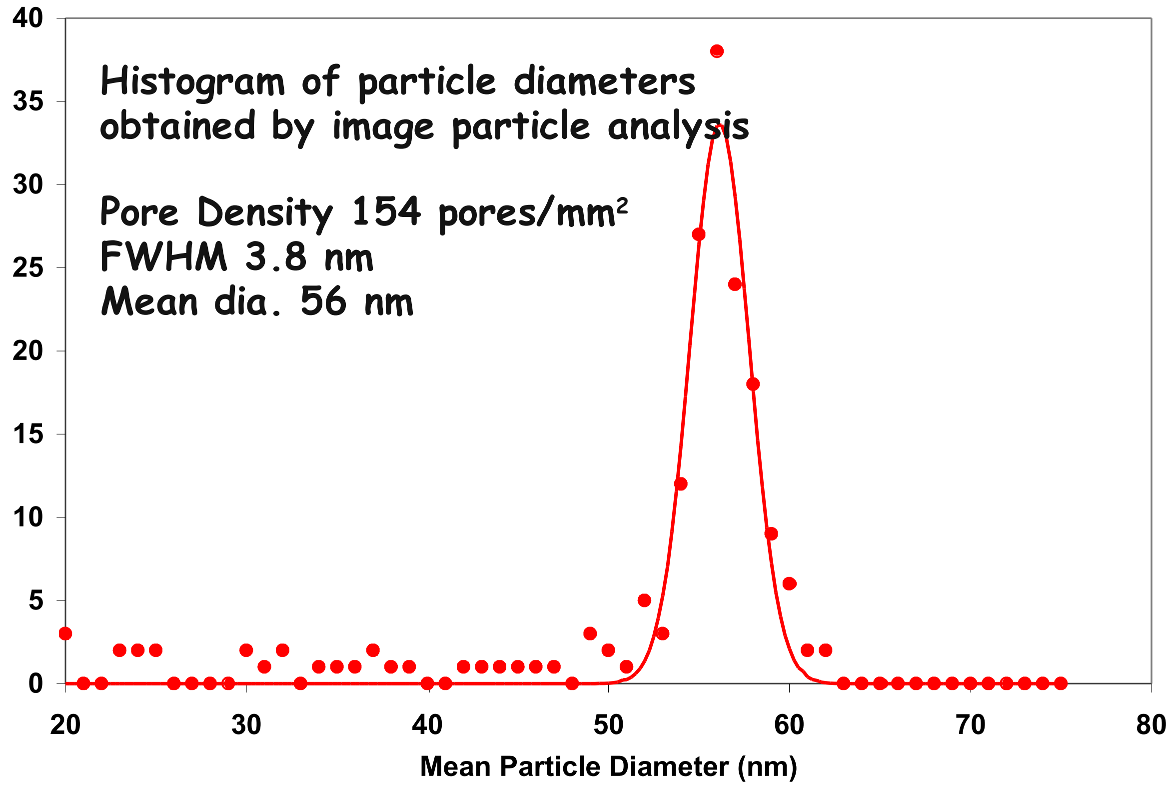
Anodic Aluminum Oxide Membrane Properties



High Surface area substrates for increased absorption

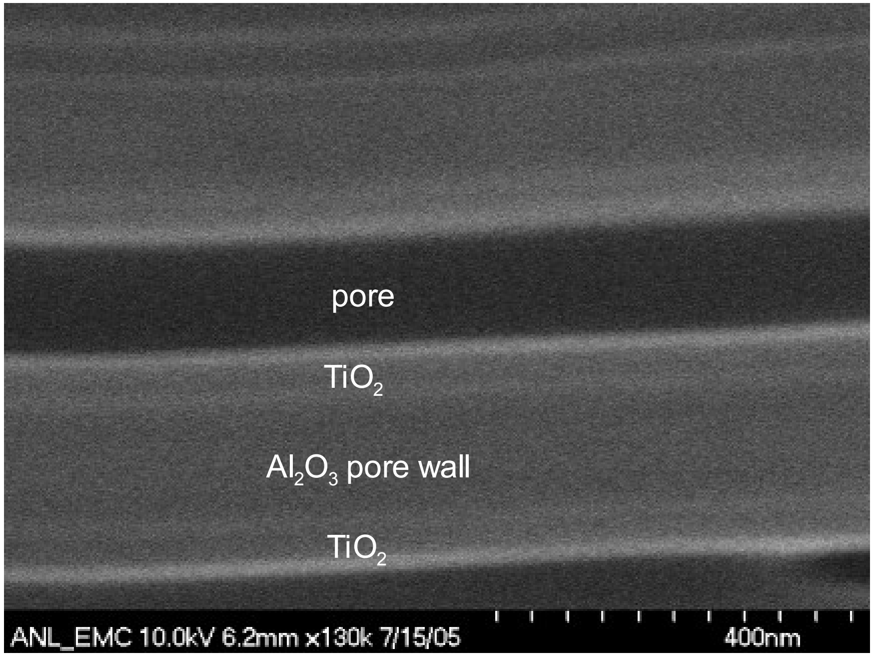
<u>Typical membrane properties</u>

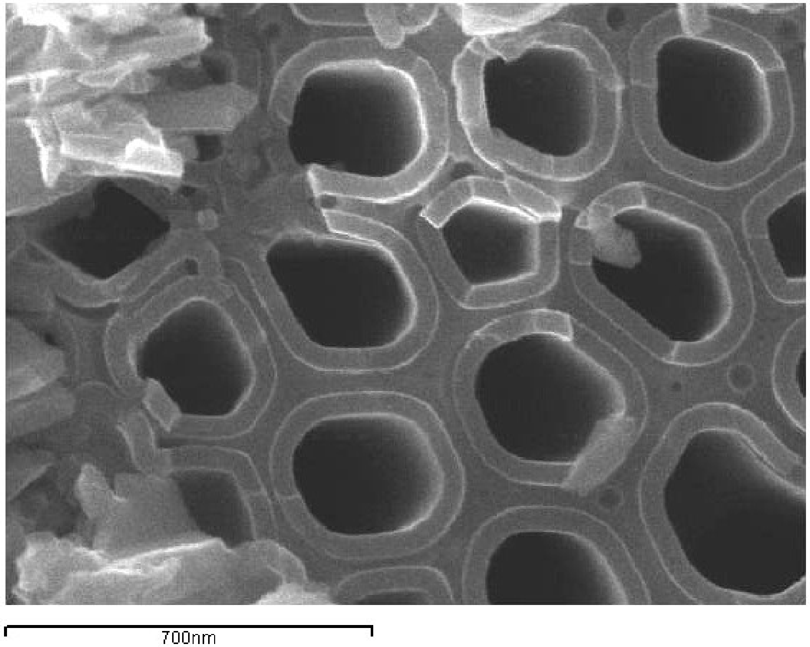
- Membrane thickness = 75 μm
- Conductance ~ 0.2 sccm/torr (N_2 @ 1 atm)



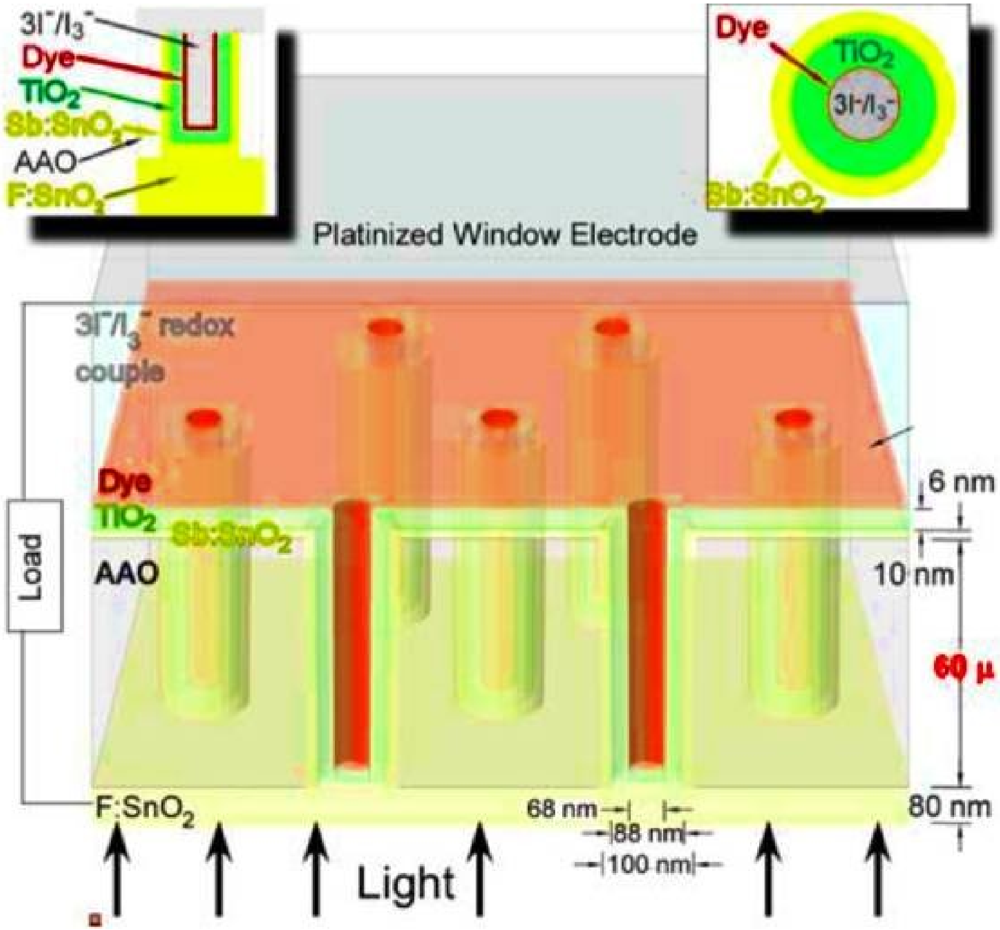
Combining AAO and ALD

- Conformal deposition of a wide variety of metals and metal oxides
- Extraordinary control over layer thickness





AAO/ALD Electrode Design Incorporating Transparent Conducting Oxide (TCO)

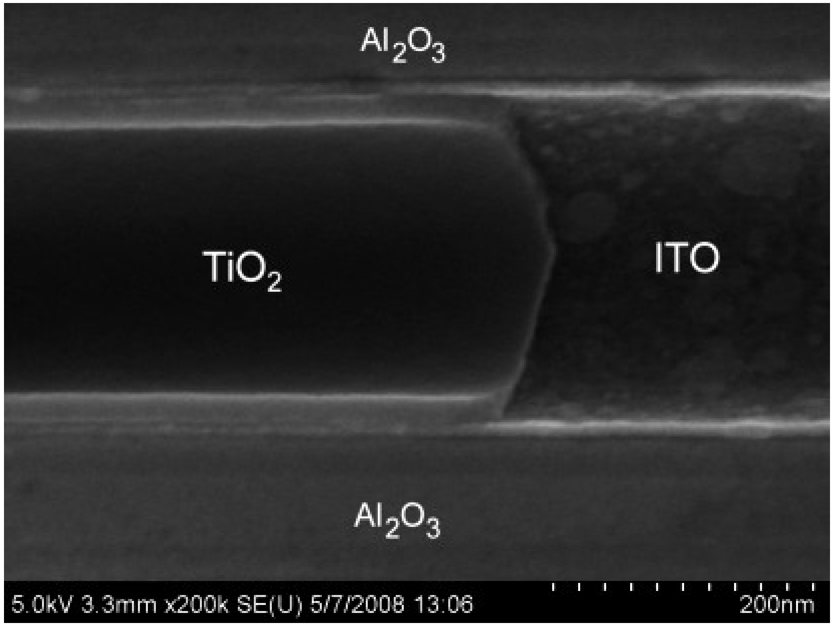


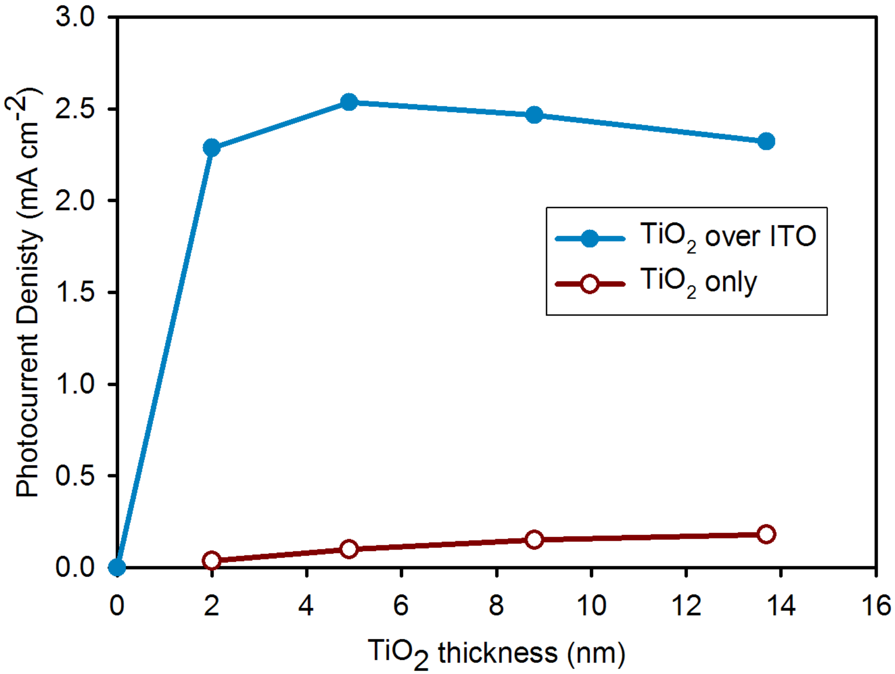
Key feature:

w/o TCO ➡60 µm e⁻ path thru semi-conductor: ***longitudinal*** *transport*

with TCO ➡6 nm e⁻ path thru semi-conductor: ***radial*** *transport*

Enhanced Performance From Radial Charge Collection





- Higher photocurrents (x20) with interdigitated TCO
- Radial charge collection:
  - Accelerates electron transport
  - Reduces electron-hole recombination

Plasmonic Photocathode Demonstration

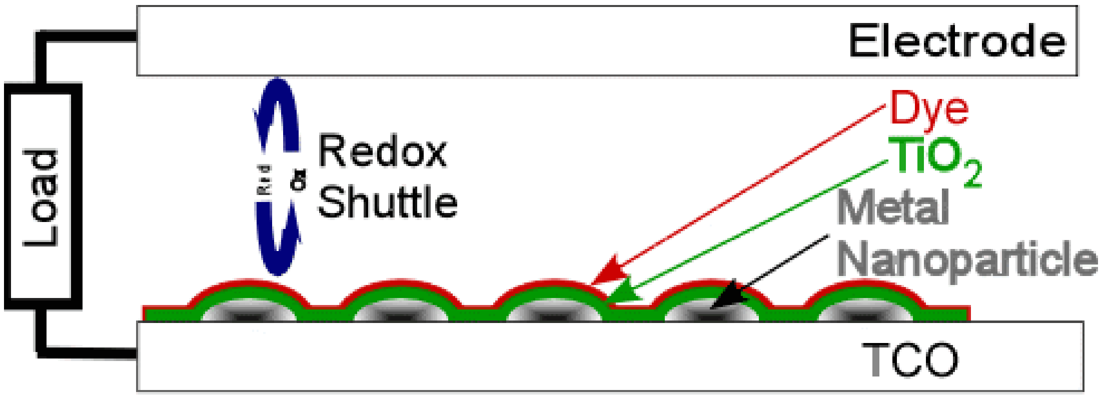


Fig. 18. A schematic representation of field enhanced metal nanoparticle solar cell geometry is shown. In this design, serve only as plasmonic amplifiers. In future designs, interconnected particle arrays will also serve as current collectors, enabling the TCO to be omitted.

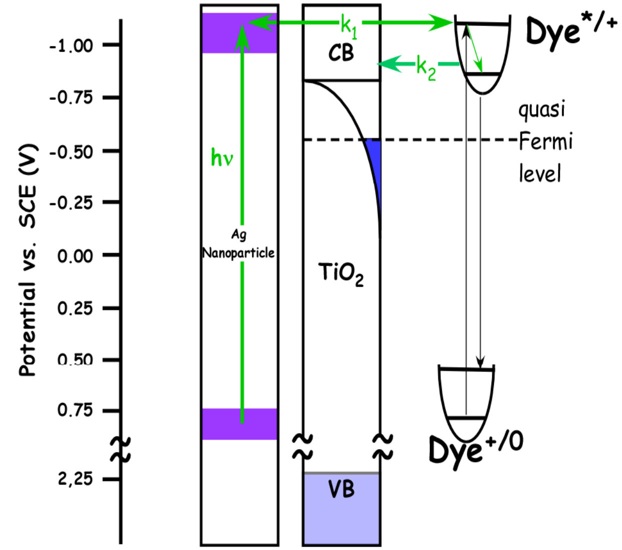


Figure 1. Plasmonic energy transfer scheme. Ag plasmonic absorbers are excited by the absorption of a photon. Excitation is short lived in a plasmon normally with internal conversion losing the excitation to heat in a few 10's of fs.** In a solar cell, a second route to de-excitation of the plasmon is energy transfer to a nearby dye (k_1). Rapidly this excitation results in electron transfer to the wide band gap semiconductor, k_2, (~ 3 fs)* or intersystem crossing to a triplet dye state and then e transfer.

Plasmonic Absorption Enhancement

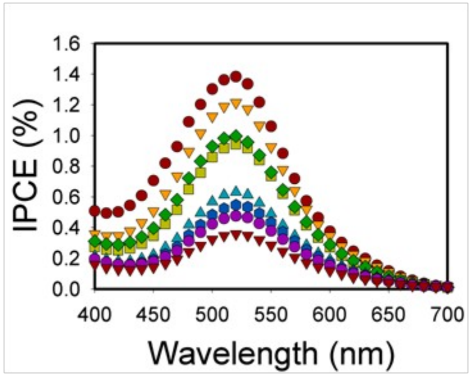


Fig.17. Plasmonic enhancement of photocurrent generation for a nominally flat photoelectrode featuring ALD coated (TiO_2) silver nanoparticles as amplifiers. Currents are lowest with thick ALD coatings (little plasmon amplification) and highest with thin ALD coatings (substantial plasmon amplification).

Fig. 16. a) N719 dye on low-area (flat) TiO_2 electrode, b) silver nanoparticle-coated, low-area (flat) TiO_2 electrode, c) N719 dye on TiO_2 (ALD)-coated silver nanoparticle layer on electrode. Quantitative measurements indicated ca. 5 to 7 fold enhancement in dye absorption in the presence of silver particles.

Combination Contact and Enahncer

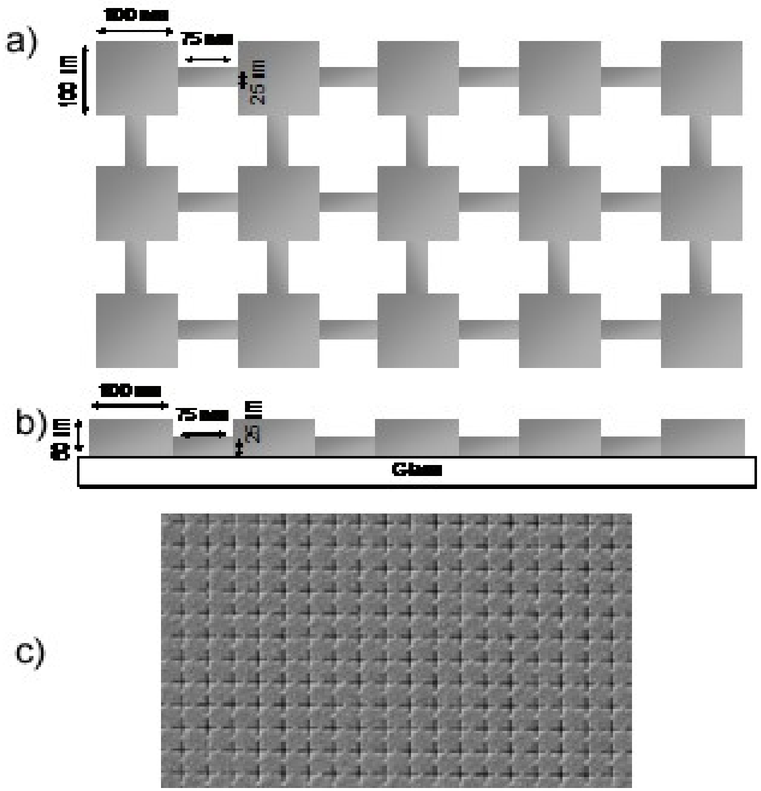
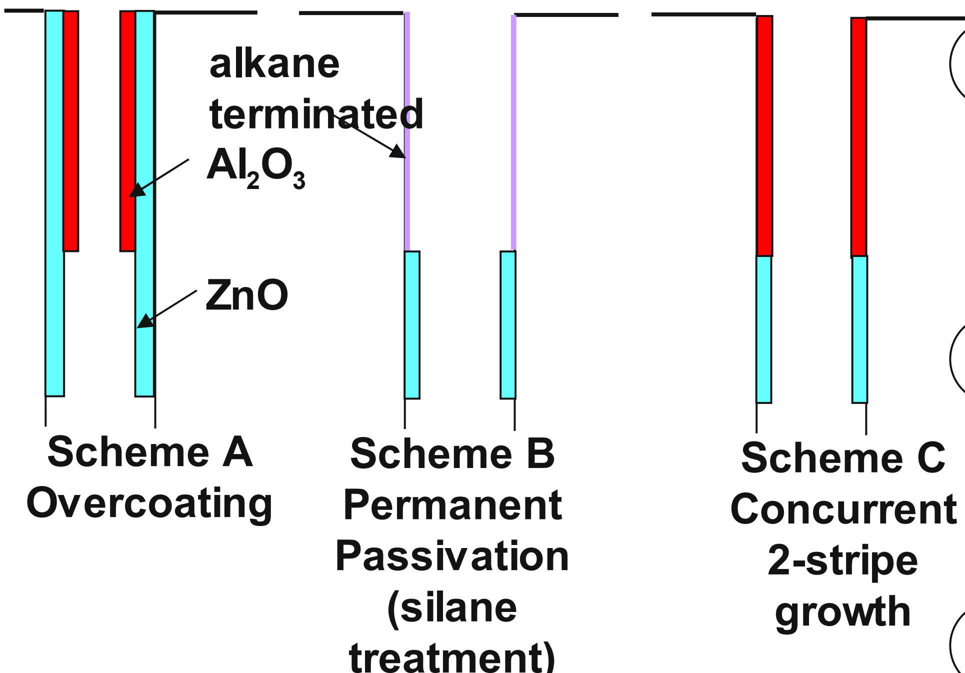


Fig. 20. Interconnected metal particle arrays for combined light enhancement and electron collection. Schematic A) top view; b) side view, c) SEM image of a test Ag structure.

Internal Stripes

Internal Stripe Deposition Concept

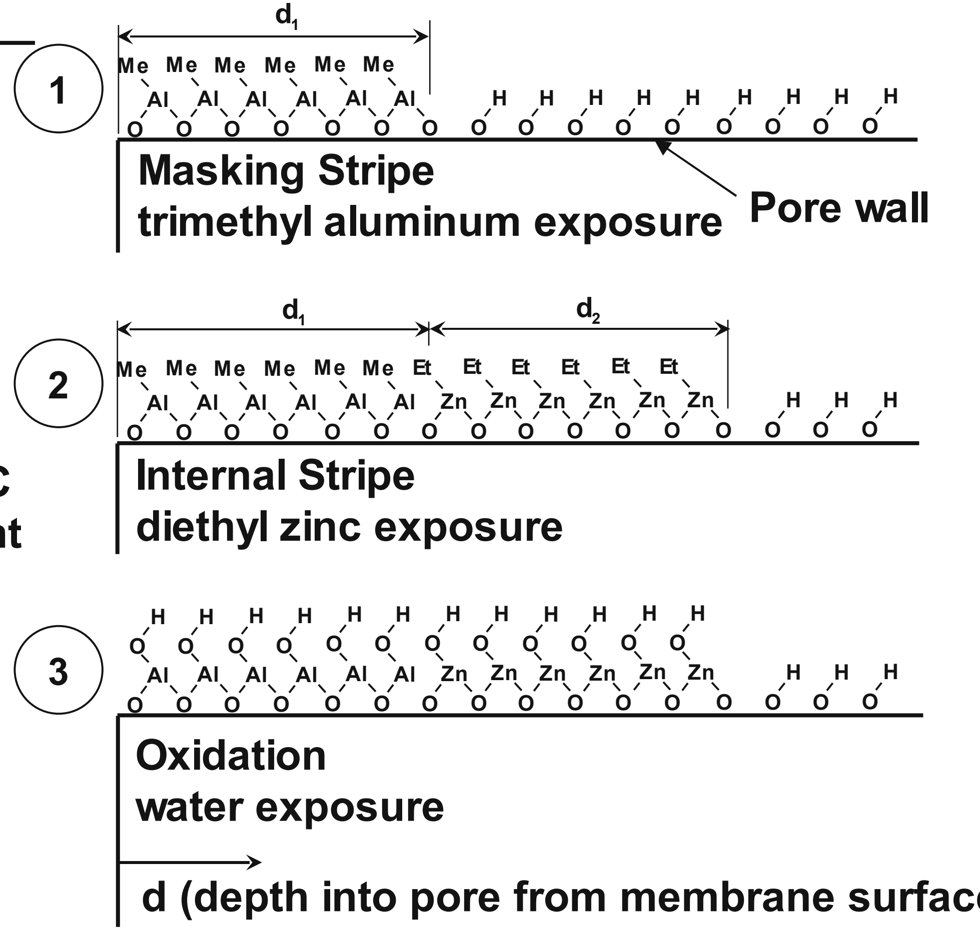
- **Objective : deposit specified surface species at arbitrary depths in the membrane. Several schemes are possible to achieve this:**



- **In A, additional pore narrowing must be tolerated which is undesirable because the diffusion depth is a strong function of pore diameter.**
- **Scheme B not effective for many subsequent ALD cycles; difficult to achieve complete passivation and inertness to oxidizer.**

Scheme C:

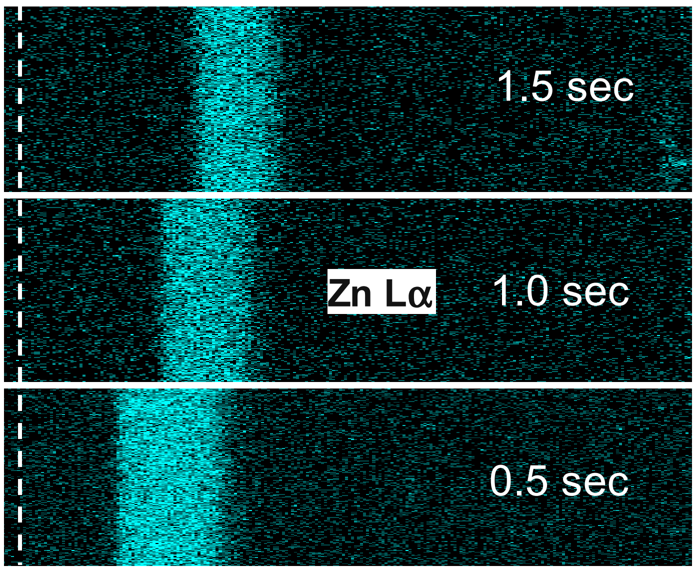
- This scheme is implemented in three steps:

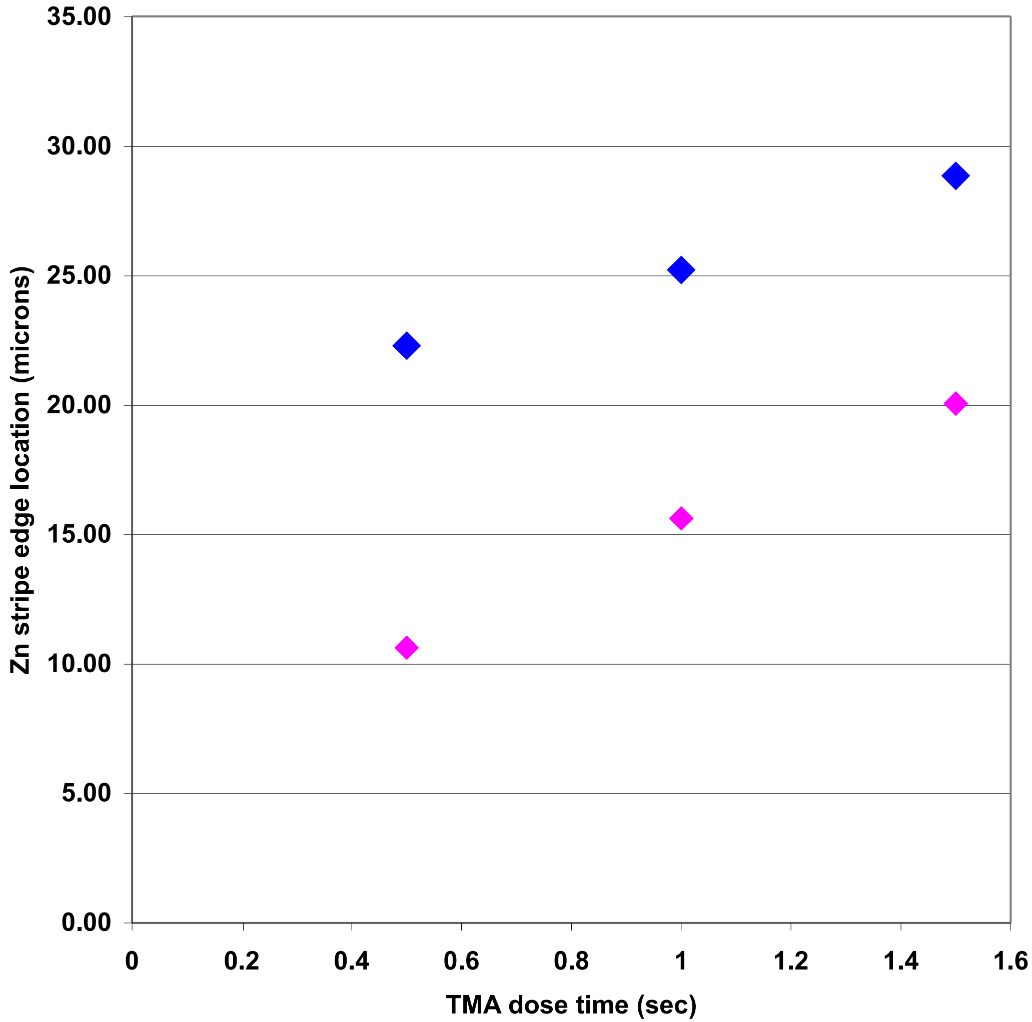


Internal ZnO Stripes Positioning

Depth Positioning

- **The TMA mask stripe depth was varied keeping all other growth parameters constant**
- **Timing: 20c(x-5-4-10-5-15) (TMA-purge-DEZ-purge-H_2O-purge)**
- **The delay caused by the increasing depth of the passivating stripe causes a narrowing of the Zn stripe width.**





Benefits of Argonne Nanostructured PV Technology

- Lower manufacturing cost than other PV technologies
- Non-vacuum, low temperature fabrication
- Very tolerant to impurities (no clean room necessary) – light absorption and charge separation occur close to interface
- Inexpensive, abundant, benign materials (e.g. TiO_2, ZnO)
- Robust nanoscale process