ATOMIC LAYER DEPOSITION FOR PHOTONIC CRYSTAL DEVICES

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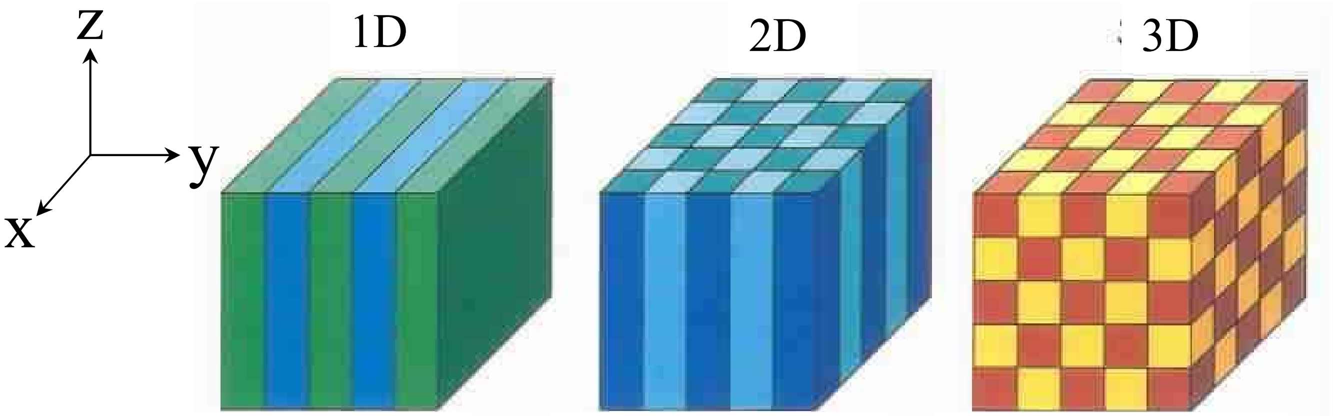
Outline

- Introduction to Photonic Crystals
- Opals
- Inverse Opal
  - Requirements for Photonic Band Gaps: high filling fraction, smooth, conformal, high refractive index
- Infiltration using ALD
  - Meets above requirements
- Results: ZnS:Mn, TiO_2, Multi-layers
- Summary

Photonic Crystals

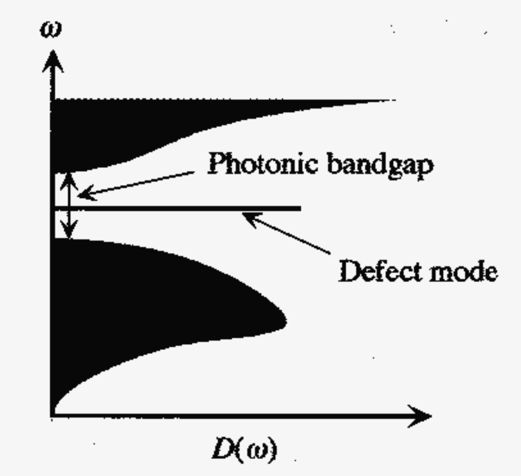


Periodic in one direction

Periodic in two directions

Periodic in three directions

(Joannopoulos)



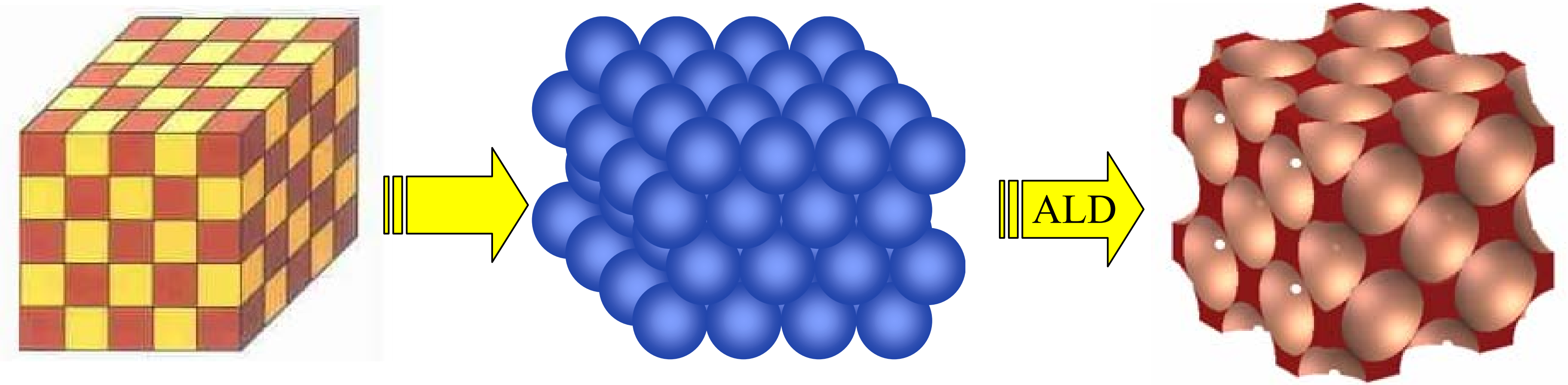
(b) Photonic Crystal

- Photonic Crystal – periodic modulation of dielectric constant
- Exhibits a "Photonic Band Gap" (PBG) where propagation of a range of photon energies is forbidden.
- For visible wavelengths, periodicity on order of 150 – 500 nm.
- Introduction of "dielectric defects" yield modes within the PBG.
- Luminescent 2D & 3D PC structures offer the potential for controlling wavelength, efficiency, time response and threshold properties (phosphors, displays, solid state lighting, etc.).

Real Photonic Crystals:

Opals & Inverse Opals

- For 3D PC's: "top-down" approaches are difficult.
  - "Bottom-up" approach: self-assembly
- Most common 3D photonic crystal is the opal.
  - Close-packed silica spheres in air
- Opal is used as a template to create an inverse opal.
  - Close-packed air spheres in a dielectric material



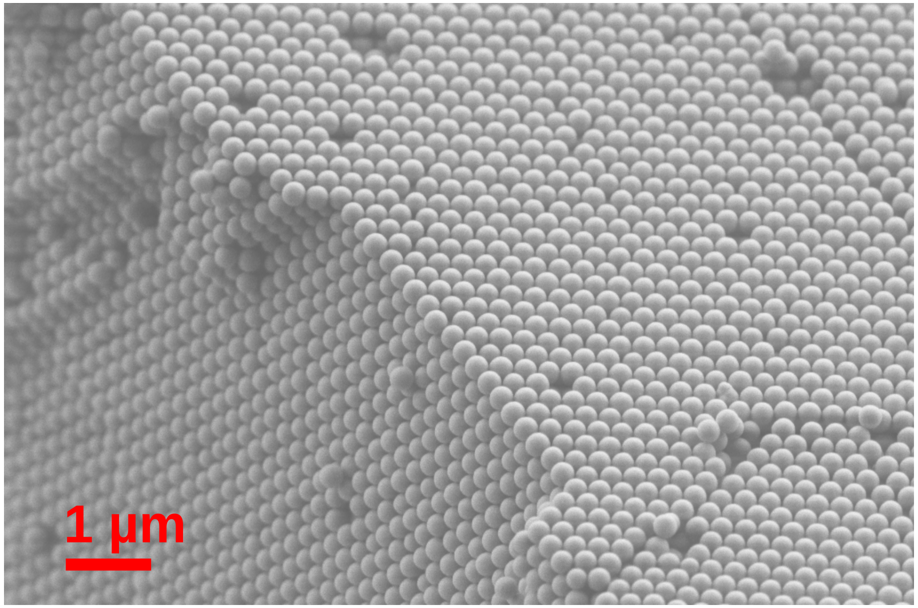
3D-PC

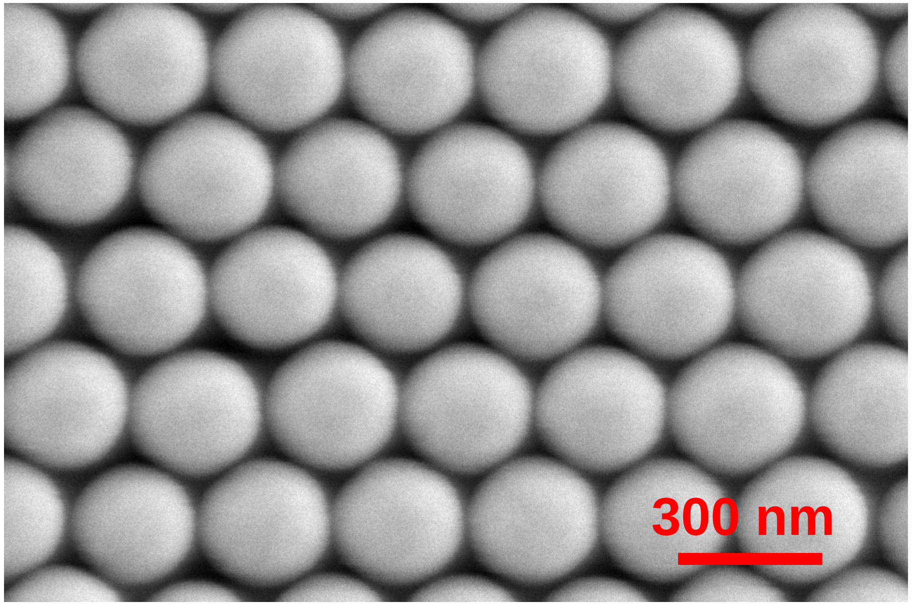
Opal
26% air

Inverse Opal
74% air for high dielectric contrast

SiO_2 Opal Films

- Opal films are polycrystalline, 10 μm thick, FCC films with the (111) planes oriented parallel to the surface.
- For visible spectrum, lattice constant ~ 140 – 500 nm.



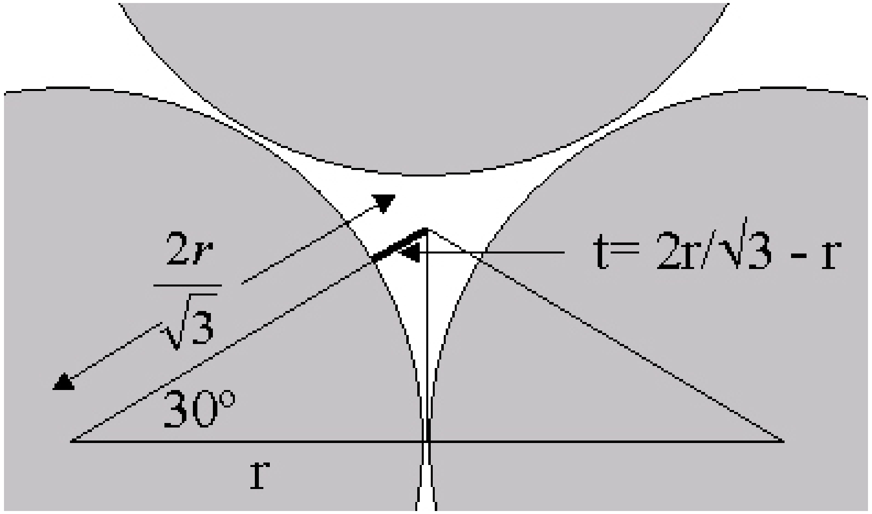


Challenge: growth of uniform films within a dense, highly porous, high surface-area, FCC matrix

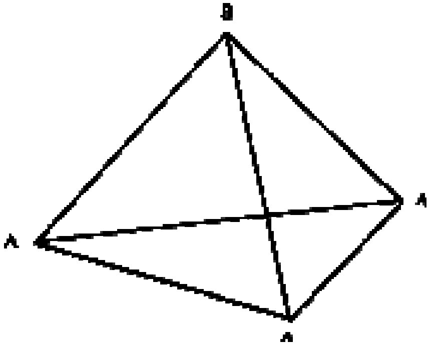
Opal Infiltration: Growth Issues

Geometrical Constraints

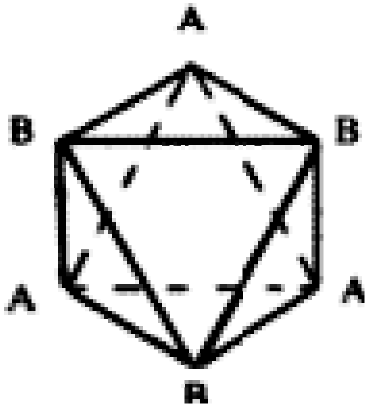
- Narrowest pathway (bottleneck) into opal is through (111) planes.
- Consideration of geometry predicts pore closure at 7.75% of sphere diameter.
- Monte Carlo simulations show this is ~ 86% infiltration of voids.



- Tetrahedral void size is $0.46\times r_{sphere}$ ~ 32–115 nm.



- Octahedral void size is $0.82\times r_{sphere}$ ~ 57–205 nm.



Opal Films: Growth Issues

Increased Surface Area

- Surface area of opal film is much larger than an equivalent planar area:

$$\frac{\mathrm{A}_{\mathrm{opal}}}{\mathrm{A}_{\mathrm{film}}}=\frac{0.74\times l\times \mathrm{w}\times \mathrm{t}}{4/3\pi r^{3}}\times\frac{4\pi r^{2}}{l\times \mathrm{w}}=\frac{2.22\mathrm{t}}{\mathrm{r}}$$

- For a 10 μm thick opal film with 200 nm diameter spheres:

$\mathrm{A}_{\mathrm{opal}}/\mathrm{A}_{\mathrm{film}} = 222$

Opal Infiltration:

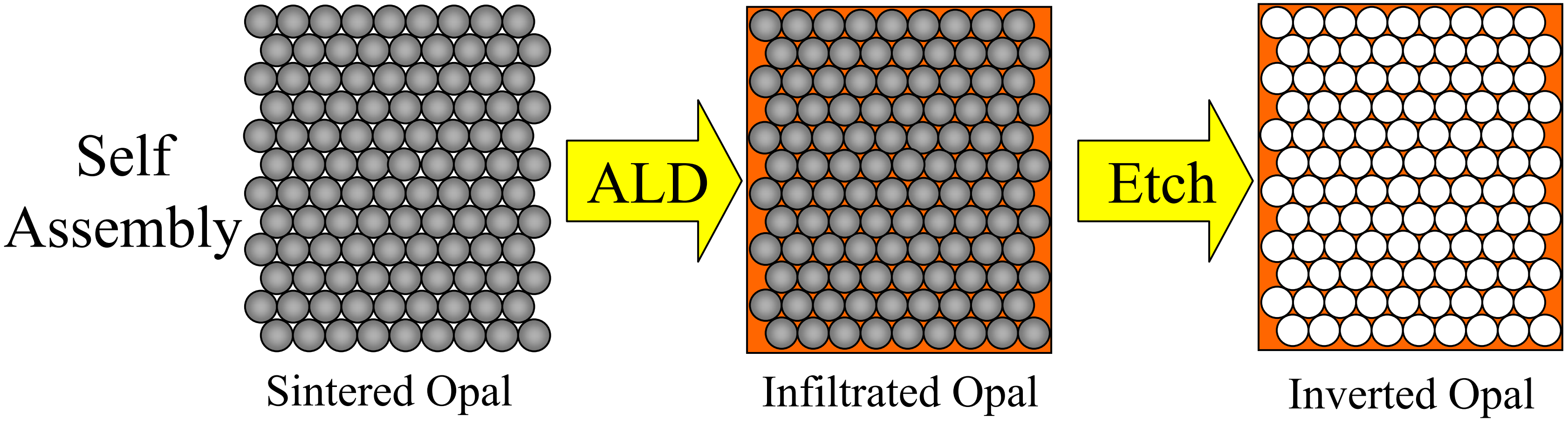
Requirements

- Uniform Infiltration
  - Material must be distributed uniformly throughout the opal
- Controlled Filling Fraction
  - Must be able to precisely control the void space filling
- Conformal and Smooth Surfaces
  - Creates lower porosity infiltrations
  - Creates air pockets at the center of the opal voids, enhancing the PBG
- High Refractive Index, Transparent, & Luminescent Materials
  - For a full PBG, the refractive index contrast (with air) must be > 2.8
- **ALD is the only technique to meet all of these requirements**

Inverse Opal:

Fabrication

- Self-assembled silica opal template
  - – 10 μm thick FCC polycrystalline film, (111) oriented.
- Infiltration of opal with high index materials
  - – ZnS:Mn n~2.5 @ 425 nm (directional PBG)
  - – TiO_2 (rutile) n_{avg}~ 3.08 @ 425 nm (omni-directional PBG)



Opal Infiltration:

Atomic Layer Deposition

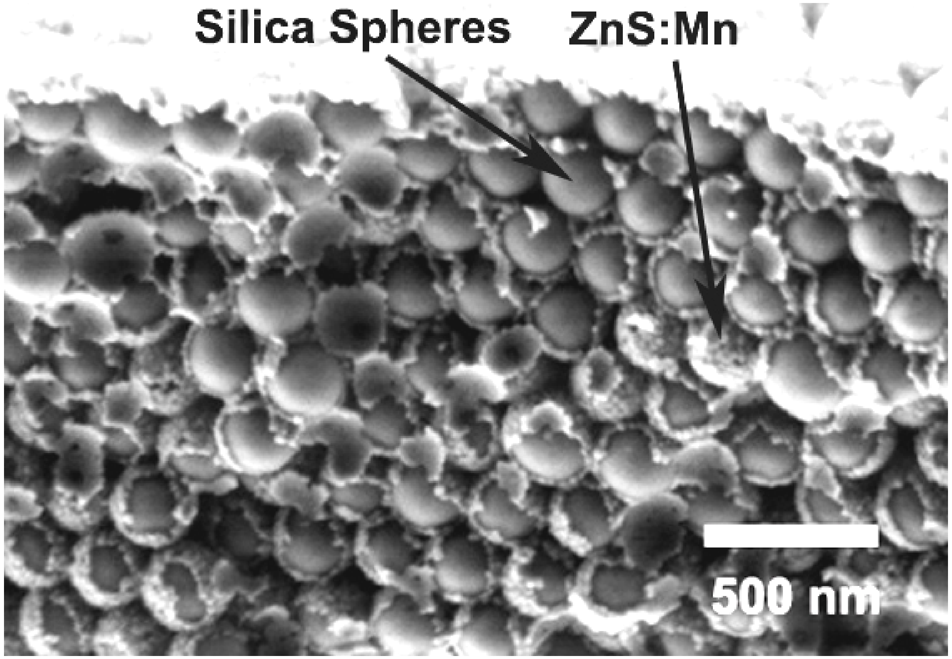
- ZnS:Mn Infiltrations
  - Initial conditions: $ZnCl_2/H_2S$ - 660ms/660ms, N_2 purge - 550ms
  - **Optimum conditions: $ZnCl_2/H_2S$ – 2s/2s, N_2 purge - 2s**
  - 10s $MnCl_2$ pulse every 100th cycle
  - Performed at US Army Research Laboratory (ARL) using a Microchemistry F-120

- TiO_2 Infiltrations
  - Initial conditions: $TiCl_4/H_2O$ - 1s/1s, N_2 purge - 1s
  - **Optimum conditions: $TiCl_4/H_2O$ - 4s/4s, N_2 purge - 10s**
  - Performed at Georgia Tech using a custom built hot-wall, flow-style reactor

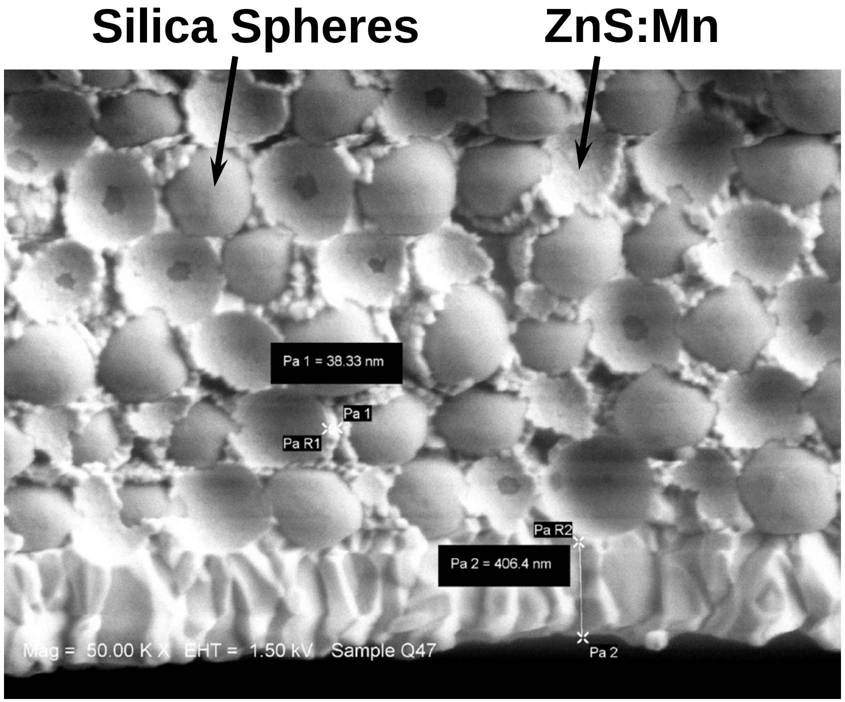
ALD of ZnS:Mn:

Scanning Electron Microscopy

(111)



220 nm infiltrated opal

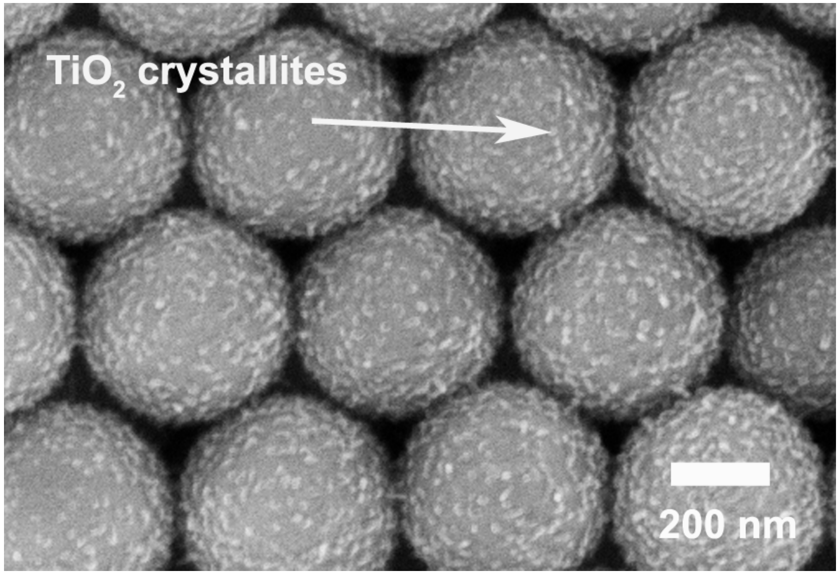


460 nm infiltrated opal

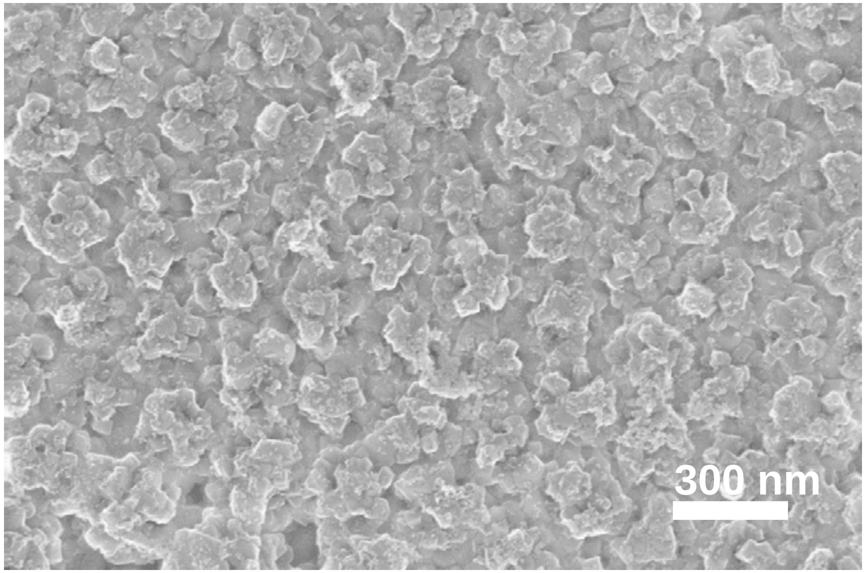
Growth Conditions: 500ºC, $ZnCl_2$ – 660 ms, H_2S – 660 ms

ALD of TiO_2

(111) ⊙



433 nm opal with TiO_2
crystallites deposited at 600ºC.



224 nm opal with TiO_2
deposited at 500ºC.

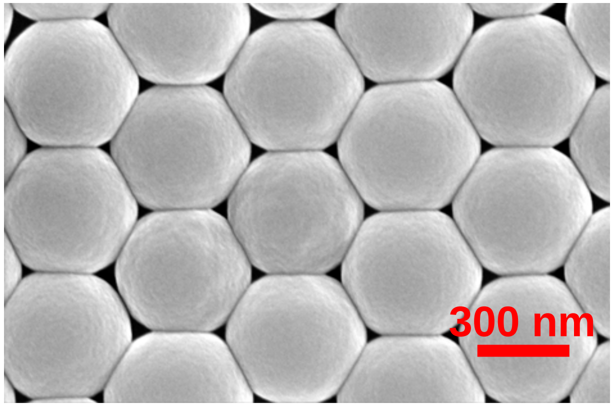
Polycrystalline TiO_2 grown at high temperatures produces very rough surface coatings.

The opal structure is lost at the outer surface for complete TiO_2 infiltrations at high temperatures.

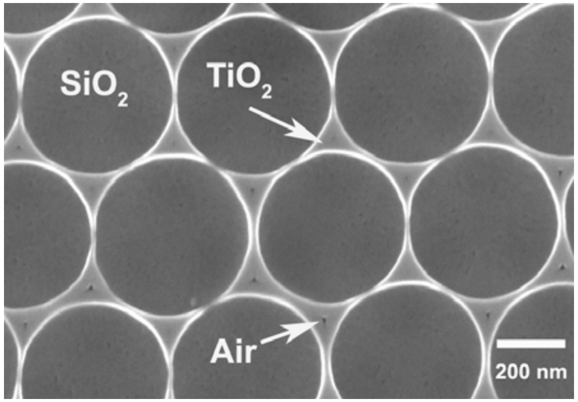
ALD of TiO_2 at 100ºC

(111) ⊙

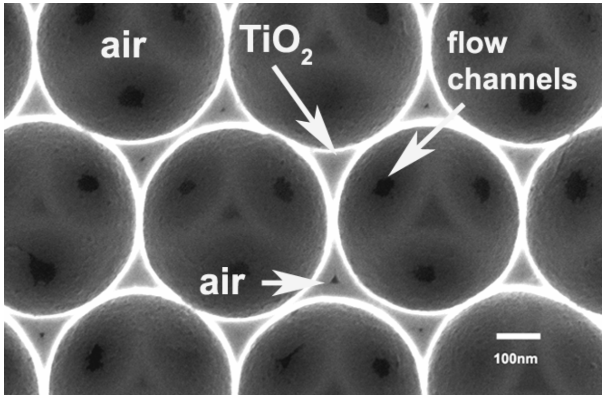
Cross-sections



433 nm opal infiltrated
with 20 nm of TiO_2



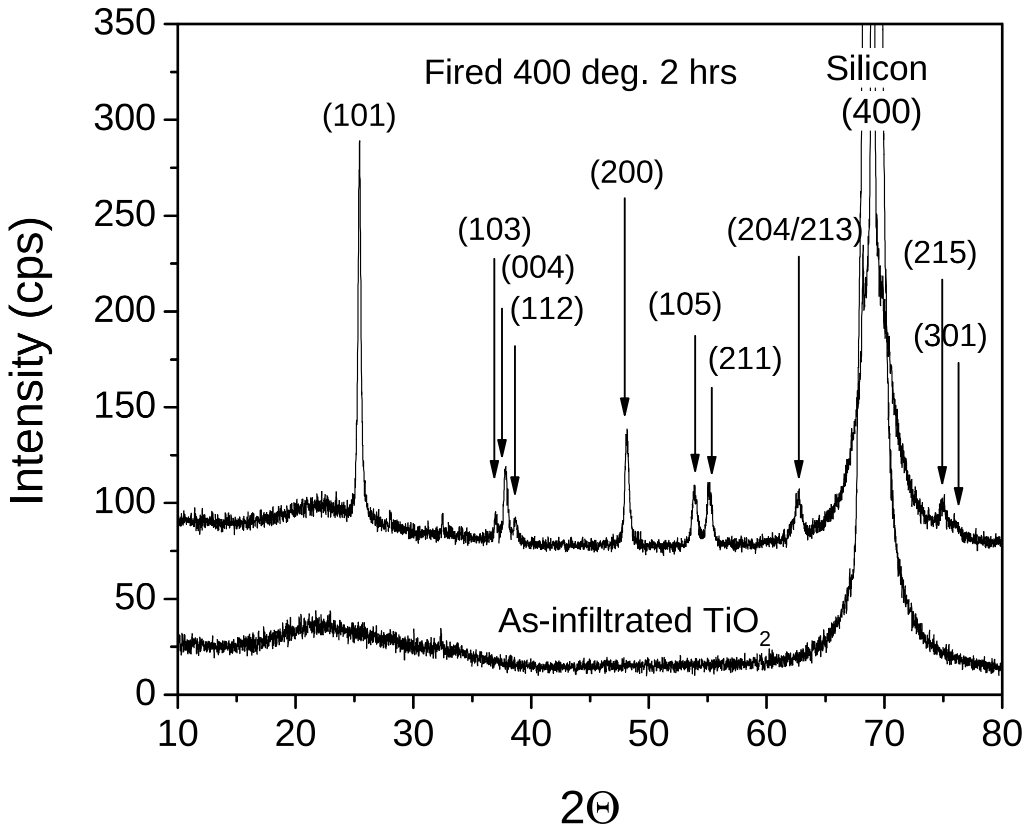
433 nm opal infiltrated
with TiO_2



433 nm TiO_2 inverse opal

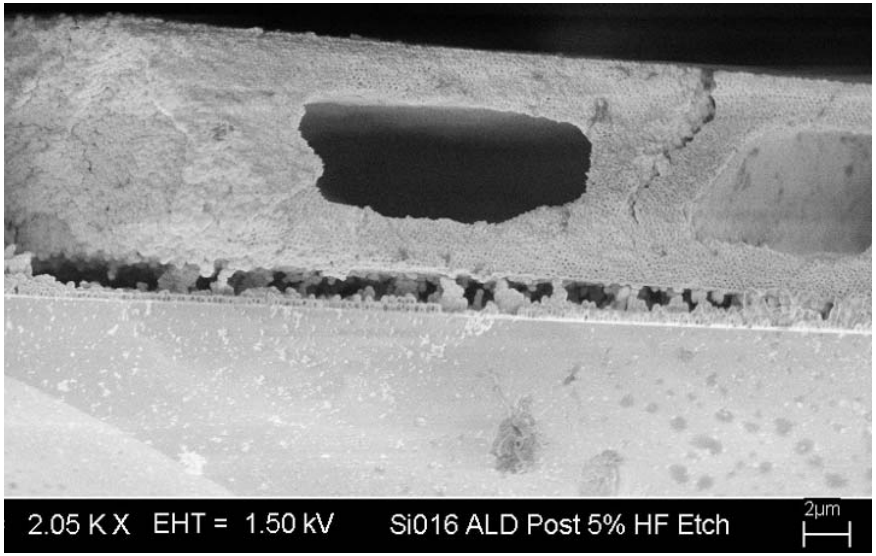
- TiO_2 infiltration at 100ºC produces very smooth and conformal surface coatings with rms roughness ~2Å.
- Heat treatment (400C, 2 hrs.) of infiltrated opal converts it to anatase TiO_2, increasing the refractive index from 2.35 to 2.65, with only a 2Å increase in the rms surface roughness.

XRD of Infiltrated Opals

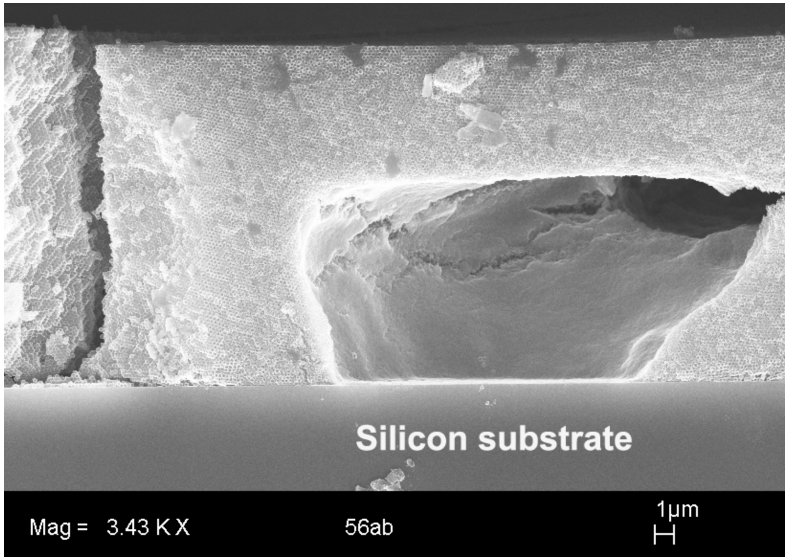


- XRD data for 100°C 433 nm infiltrated TiO_2 opal (lower curve), and same sample after 400°C 2 hour heat treatment (upper curve).

Incomplete Opal Penetration



220 nm ZnS:Mn inverse opal

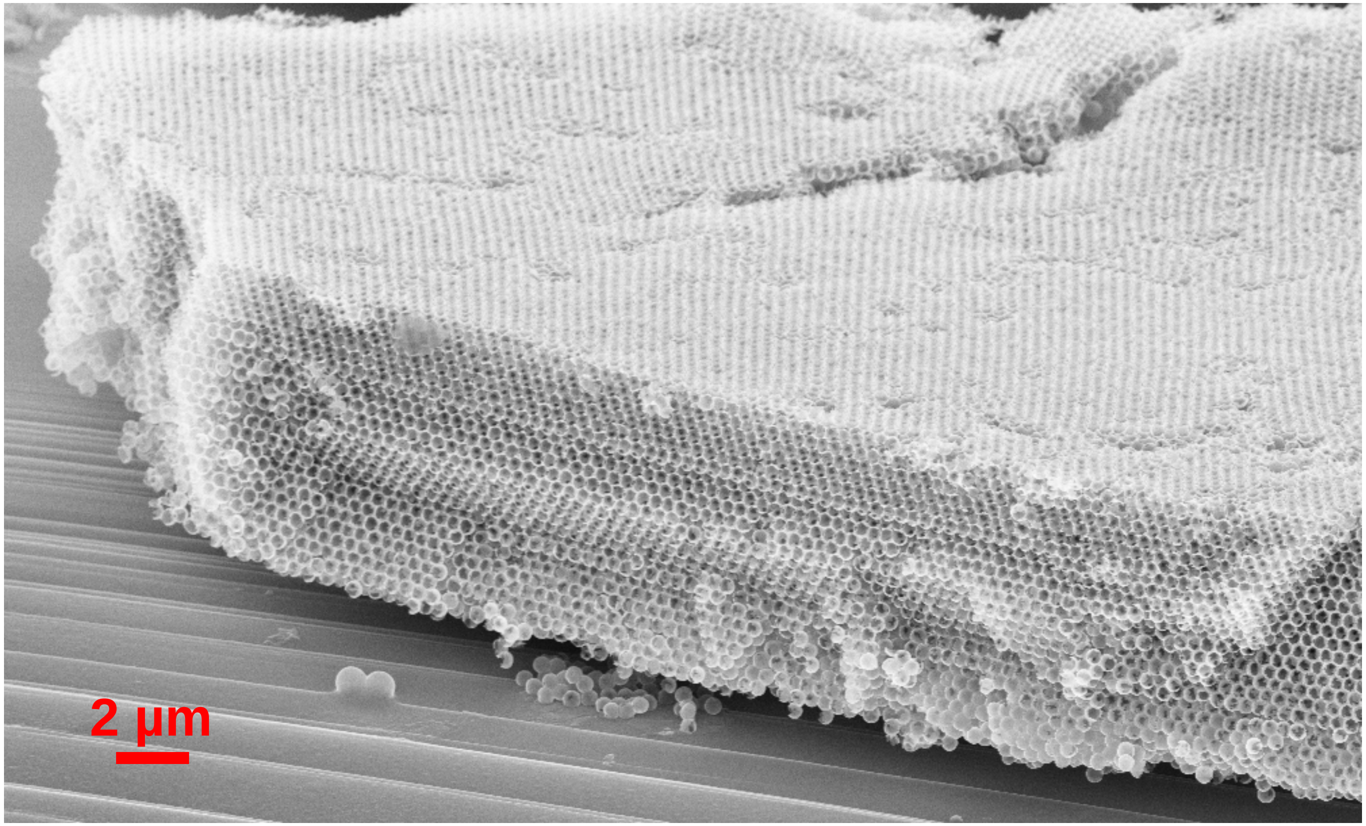


200 nm TiO_2 inverse opal

- For small opal sphere sizes, uniform infiltration becomes difficult creating air cavities when the opal is inverted.

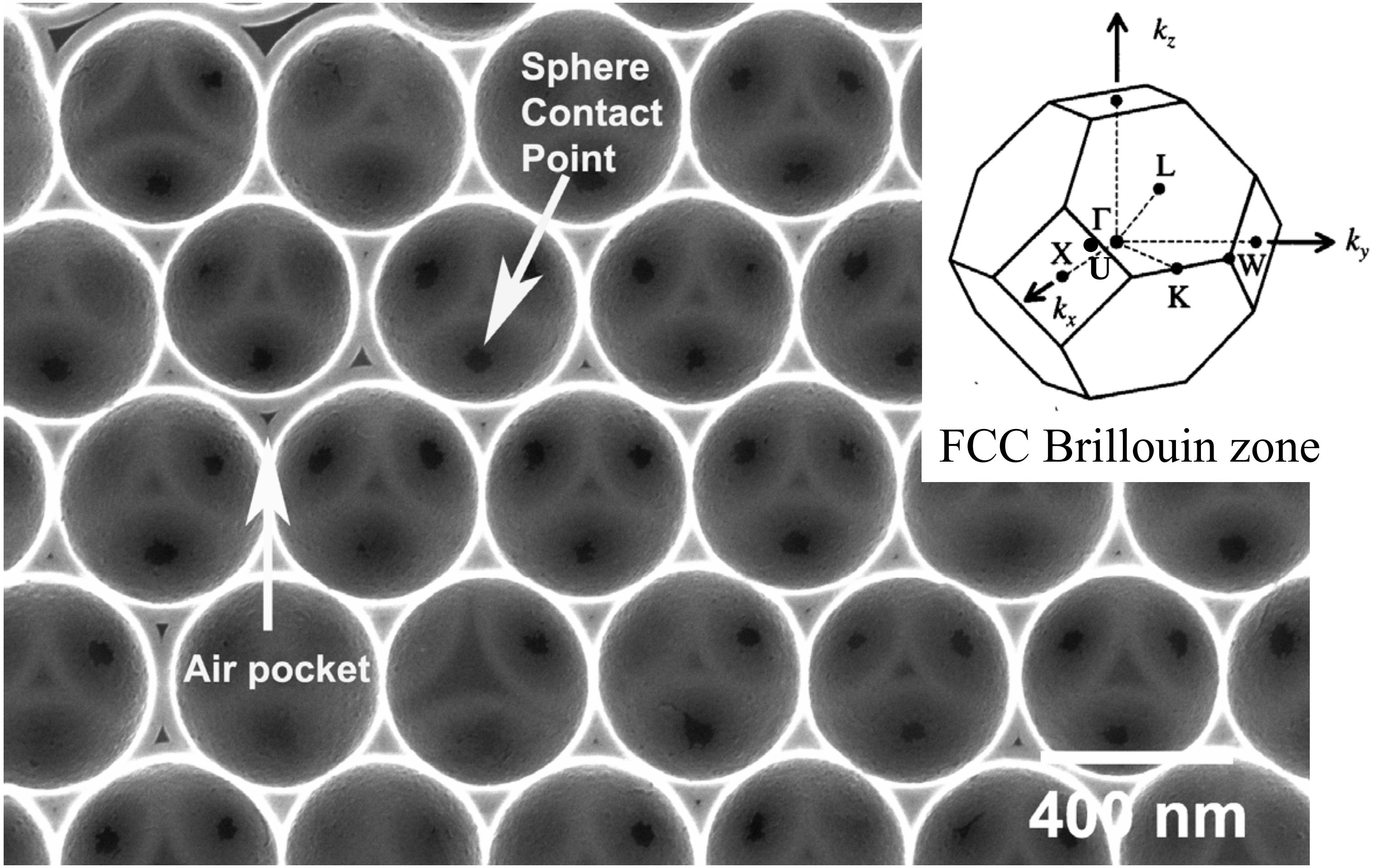
Optimized TiO_2 Infiltration

- Pulse and purge times were increased to optimize infiltration in opals with small sphere sizes.



433 nm TiO_2 inverse opal

Anatase TiO_2 Inverse Opal

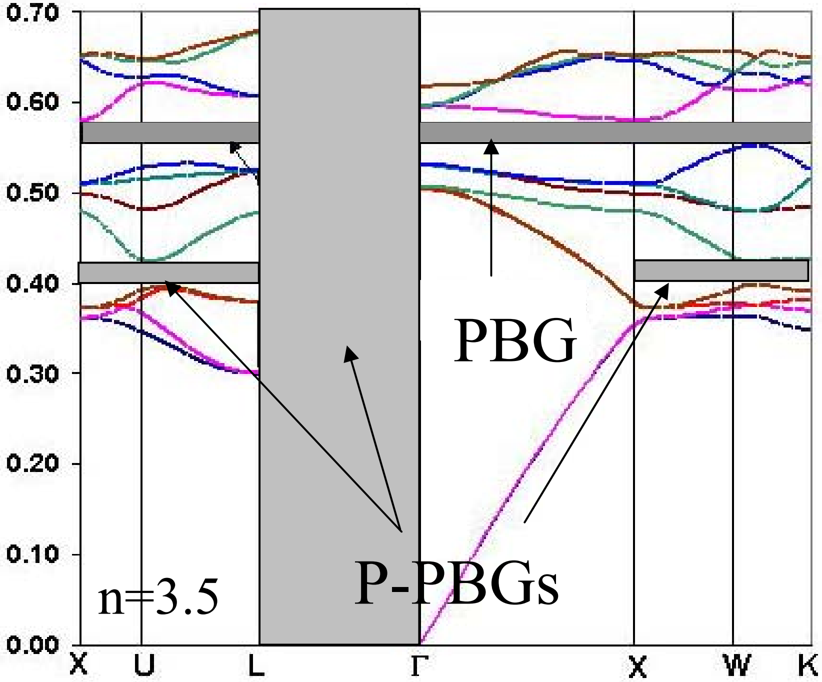


FCC Brillouin zone

433 nm inverse opal, ion milled (111) surface

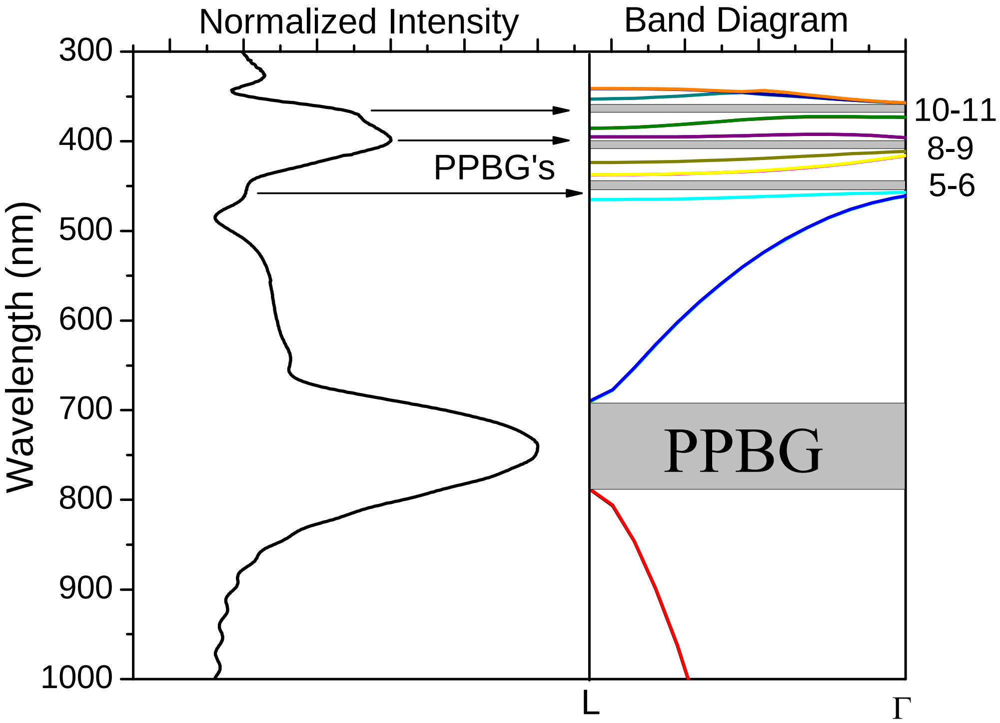
Inverse Opal Reflectivity:
Theoretical Comparison

Silicon Inverse Opal Photonic Band Diagram



- Full PBG between bands 8 & 9
- PPBGs between other bands

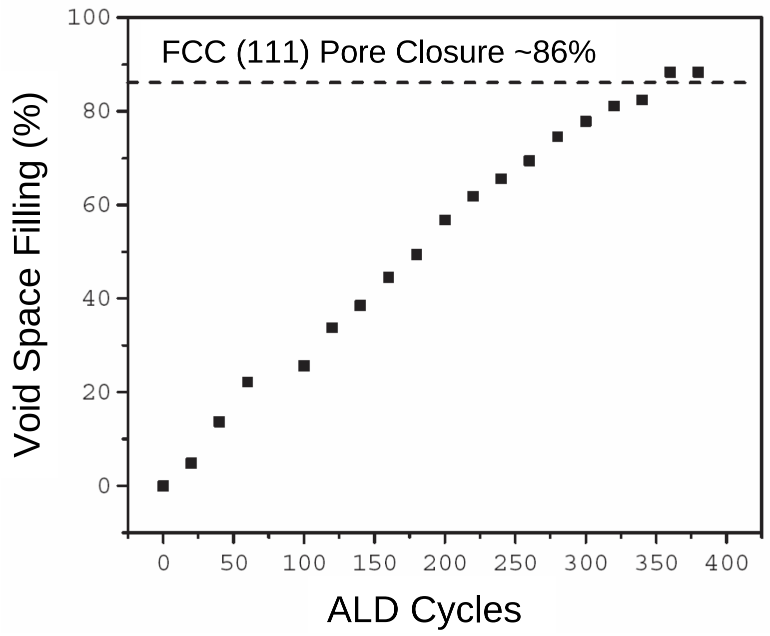
TiO_2 Inverse Opal Reflectivity and Photonic Band Diagram



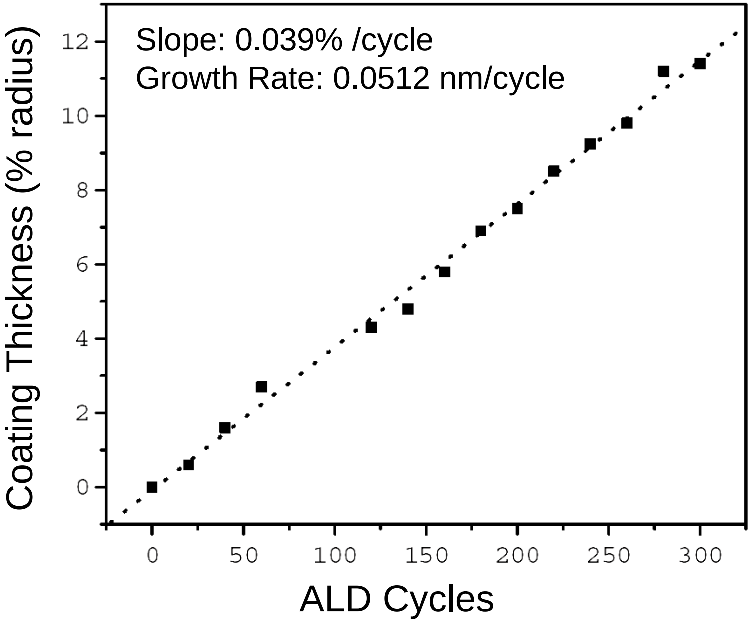
- 330 nm opal
- ~88% filling fraction
- 2.65 Refractive Index

Precise Digital Opal Infiltration

Void filling fraction of opal as function of ALD Cycles calculated from reflectivity



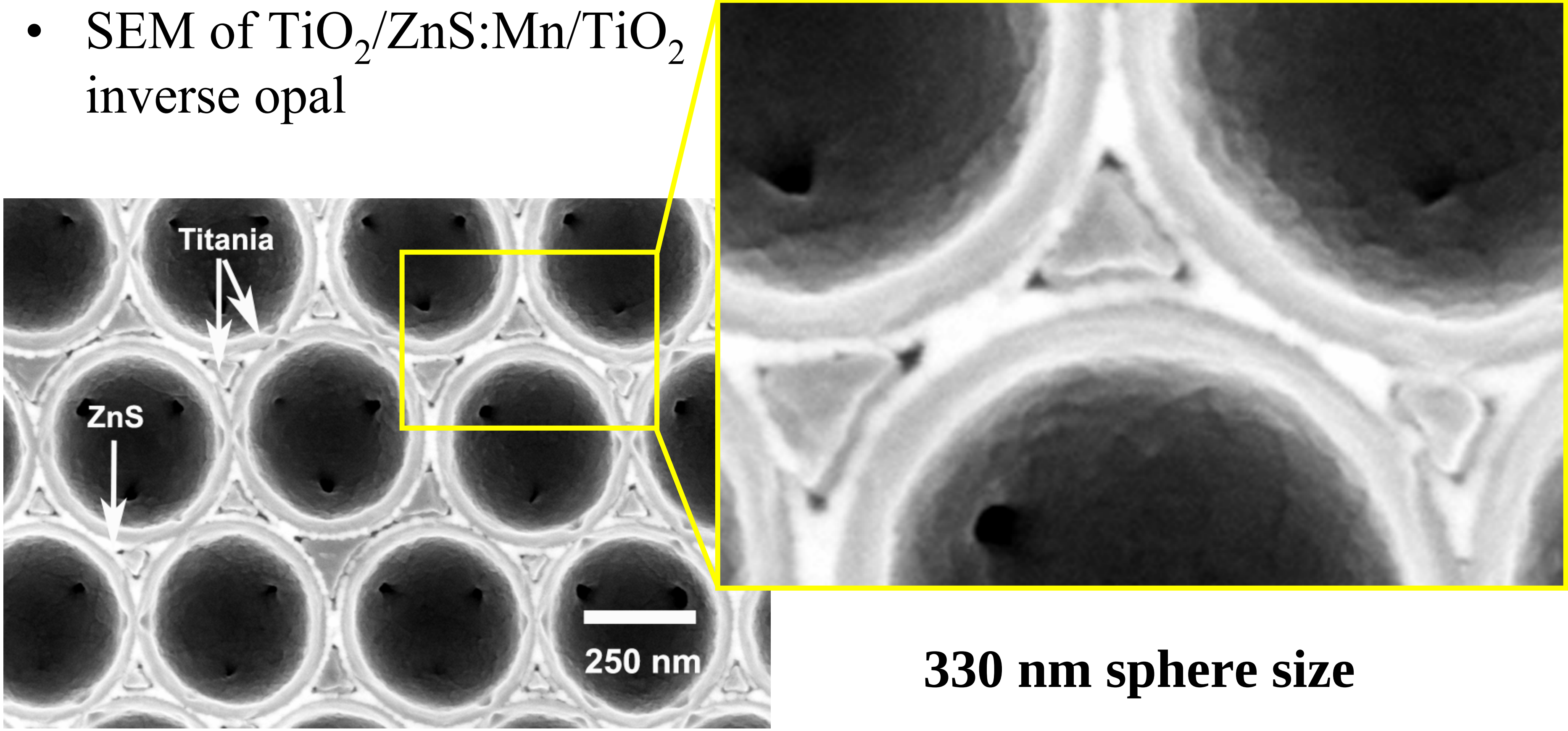
TiO_2 Coating Thickness as function of ALD cycles



- **Optical verification of maximum filling fraction.**
- **ALD allows for ultra-fine control of opal infiltration.**

Multi-Layered Inverse Opal: $TiO_2/ZnS:Mn/TiO_2$

- SEM of $TiO_2/ZnS:Mn/TiO_2$ inverse opal



330 nm sphere size

Luminescent multi-layered inverse opals fabricated using ALD

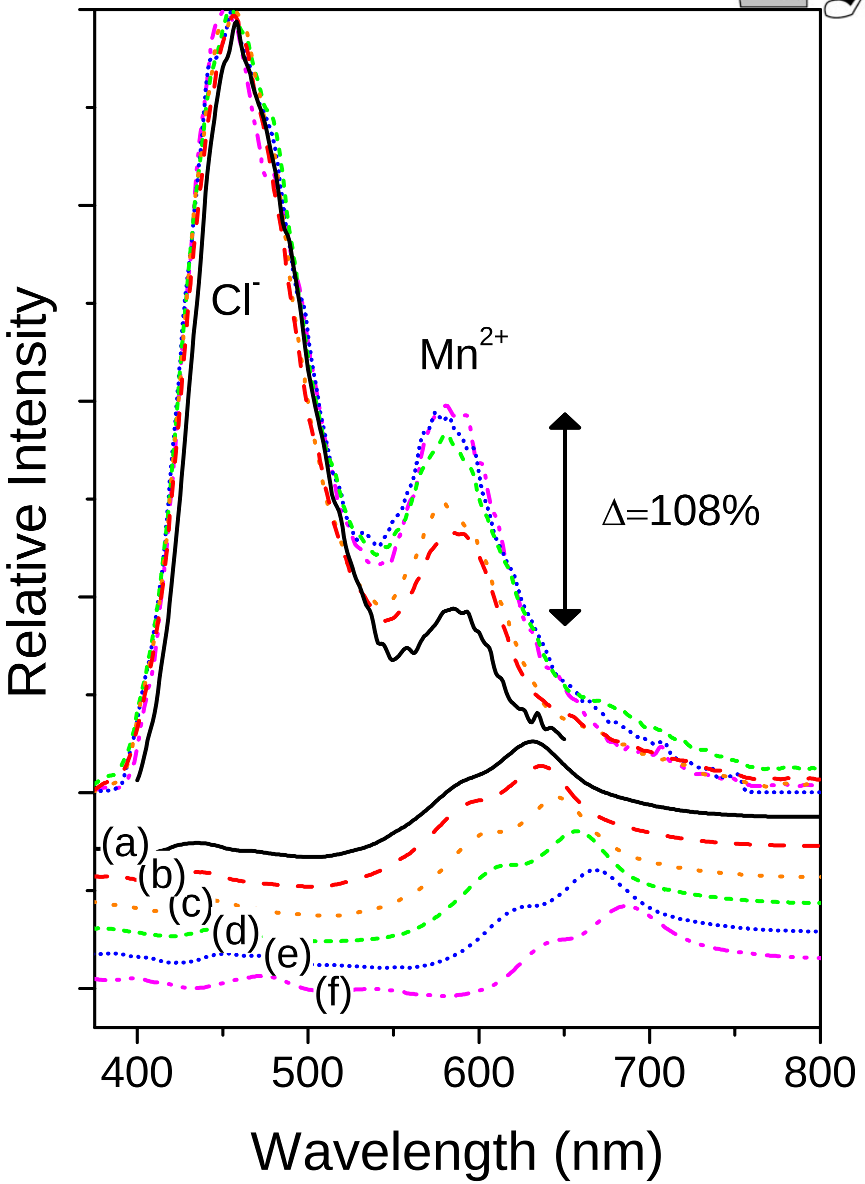
Photoluminescence:
ZnS:Mn/TiO_2 Composite

- 433 nm opal
- 337 nm N_2 laser excitation
- Detection normal to surface

(a) 2-layer TiO_2/ZnS:Mn/air (14 nm/20 nm) inverse opal

(b-f) 3-layer TiO_2/ZnS:Mn/TiO_2 inverse opal after backfilling with TiO_2 by

- (b) 1 nm
- (c) 2 nm
- (d) 3 nm
- (e) 4 nm
- (f) 5 nm



Summary

- Fabricated high quality inverse opal photonic crystals in the visible spectrum using ALD.
- TiO_2 ALD conditions optimized for complete, uniform infiltrations with smooth and conformal coatings.
  - Growth/Anneal protocol developed to form anatase inverse opals
- Precise control enables novel photonic crystal structures:
  - Inverse opals with void space air pockets (enhanced PBG)
  - Achieved maximum infiltration of 86%
  - Perfect match between reflectivity and calculated band structure
  - Multi-layered luminescent inverse opals
- Modification of photoluminescence by precise infiltration
  - Increased Mn^{2+} peak intensity by 108%
- **Pathway for photonic crystal band gap engineering.**

Acknowledgments

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