Complex, 3D Photonic Crystals Fabricated by Atomic Layer Deposition

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MRS Fall Meeting
December 3, 2004
Boston, Massachusetts

Outline

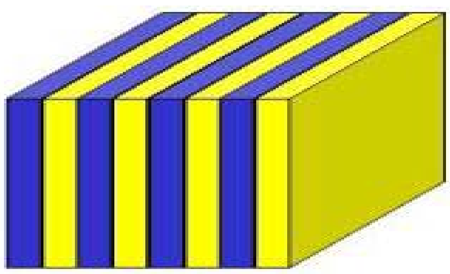
- Research Aims
- Photonic crystals and challenges
- Advanced photonic crystal architectures
- Results
  - ZnS/TiO_2 multi-layered structure
  - Presinter non-close-packed inverse opal
- Summary

Research Aims

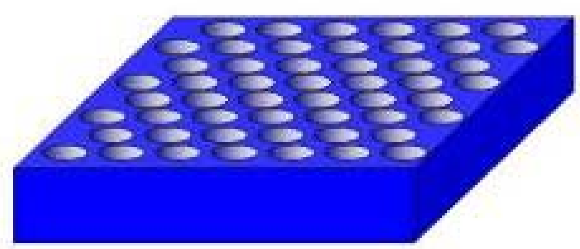
- Development of 3-D photonic crystals through a combination of templating and atomic layer deposition (ALD).
- Advanced architectures:
  - multi-layered inverse opals
  - non-close-packed inverse opals
- Increase functionality: luminescent and high index
- Enhance properties: wider band gaps, decreased minimum refractive index requirements

Photonic Crystals

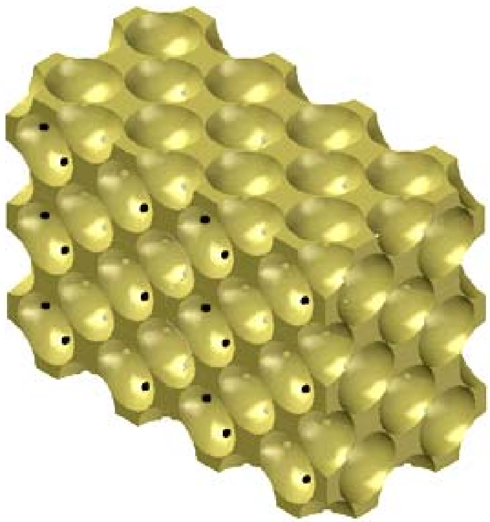
- Photonic Crystal (PC)– Periodic modulation of dielectric constant (refractive index).
- Photonic band gap (PBG) formation
- For visible wavelengths, periodicity on order of 200 – 500 nm.
- Require high contrast in refractive index (n)
- Lattice structure and basis impacts properties.



1D photonic crystal



2D photonic crystal



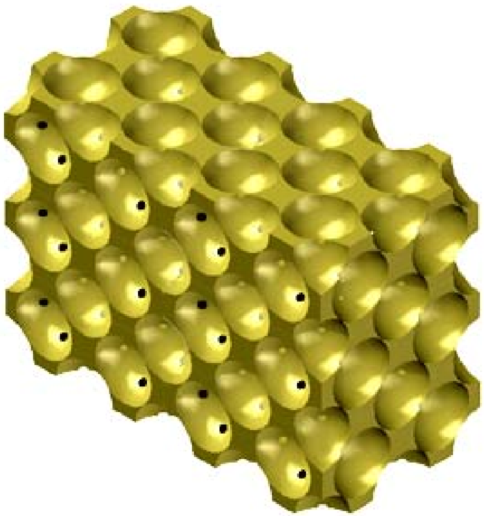
3D photonic crystal

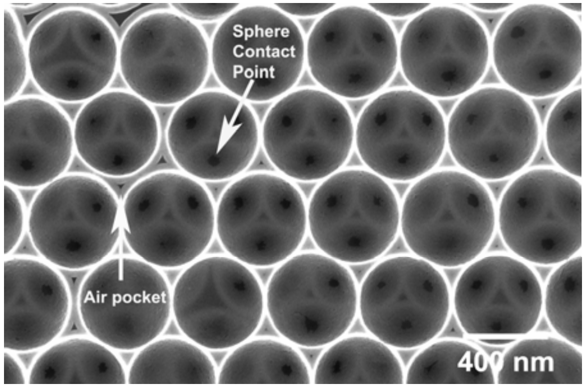
Photonic Crystals: Applications

- **Light guiding**
  - Waveguides, resonators, couplers, filters, self-collimation, giant refraction and superprism effects, slow light applications
- **Light emission control**
  - Microcavities, photonic crystal phosphors and low threshold lasers

Photonic Crystals

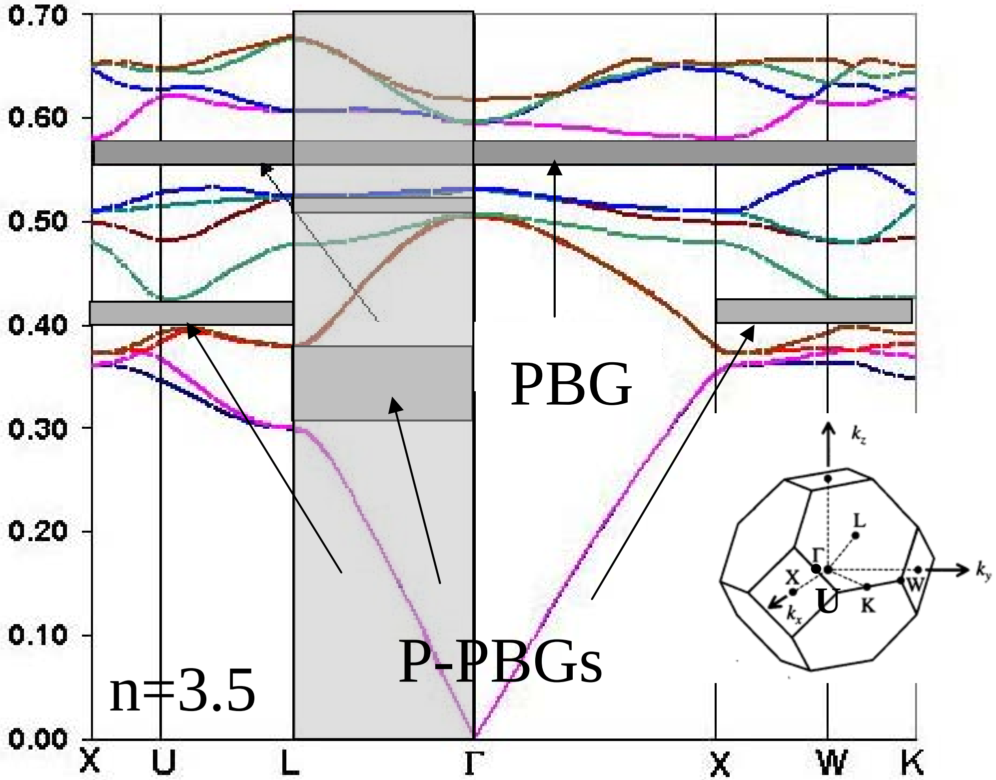
Inverse Opals





(111)

Silicon Inverse Opal Photonic Band Diagram

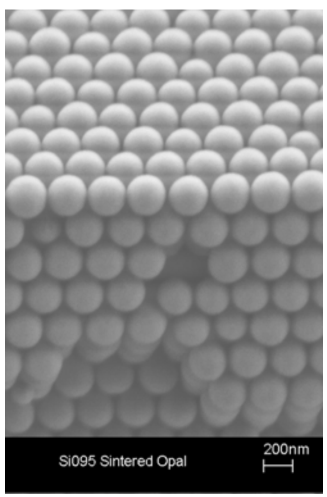


- Reflectance measurements probe photonic band structure: PBG, P-PBG

Fabrication: Inverse Opal PC

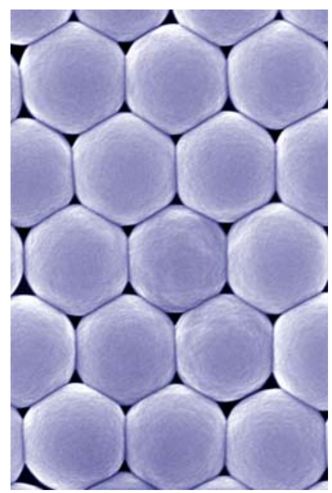
- Provide template using self-assembled silica opal.
  – 10 μm thick FCC polycrystalline film, (111) oriented.
- Infiltrate interstitial space with high n material.
- Etch SiO_2 spheres, forming inverse opal.

Self Assembly



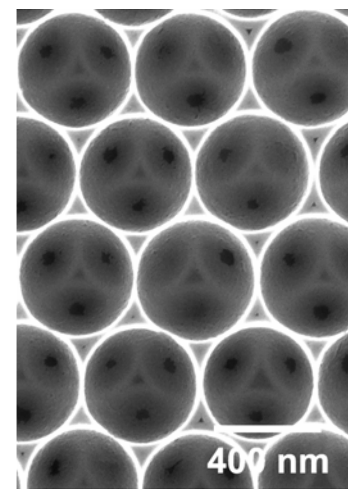
Sintered Opal

Inf.



TiO_2 Infiltrated Opal

Etch



TiO_2 Inverse Opal

King, et. al. *Adv. Mat. (in press)*

Inverse Opal Challenges

- High index contrast for complete gap to exist (> 2.8)
- For emissive applications: luminescent materials with low absorption in visible and sufficient index unavailable.
- Two solutions:
  – Multi-layered inverse opals (luminescent + high n)
  – Non-close-packed inverse opals* (widen PBG, decrease index requirements)

* Doosje, et. al. (2000)

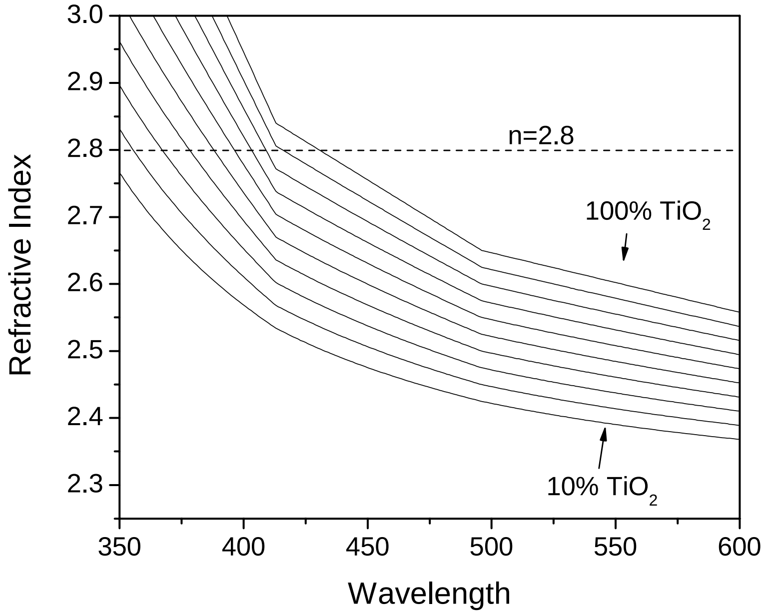
Multilayer: Design Considerations

- Combination of two materials offers practical route
- ZnS:Mn (luminescent) + TiO_2 (high n) "composite" PC.
- At 400 nm, ZnS/anatase TiO_2 PC: full PBG if $X_{ZnS} < 26\%$.

$$n_{avg} = x_1 n_1(\lambda) + x_2 n_2(\lambda)$$

Requires nano-scale control of infiltration amounts; dense, conformal films

ZnS + TiO_2 refractive index



Atomic Layer Deposition

ALD is a CVD growth technique utilizing sequential reactant pulses.

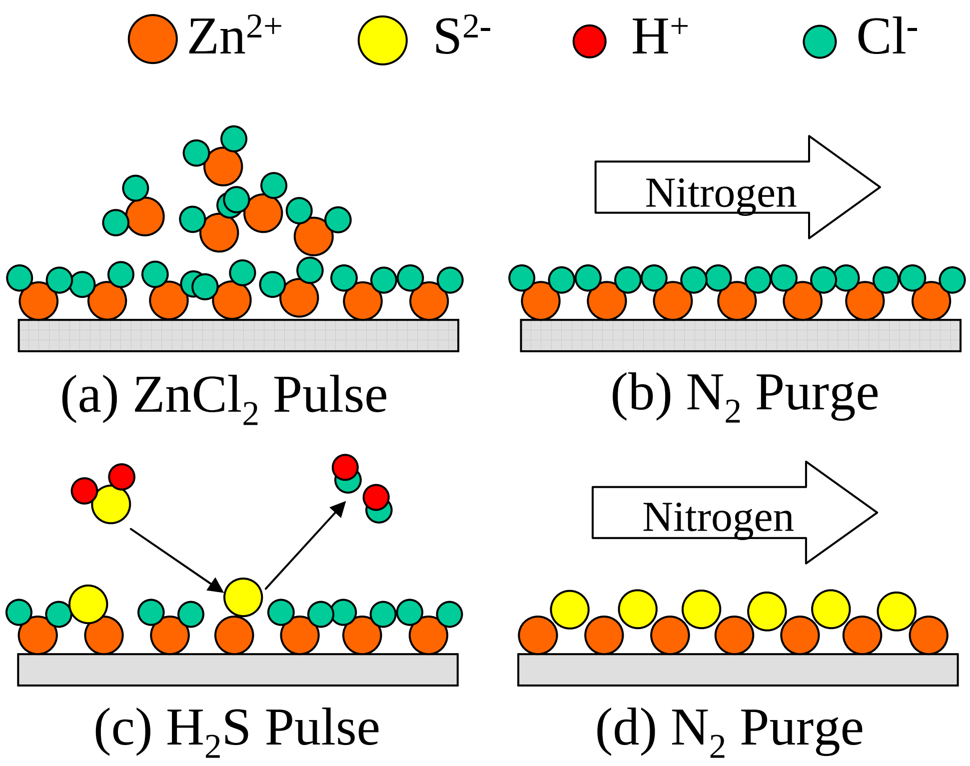
<u>ALD Growth of ZnS</u>

(a) Chemi + physisorption

(b) Physisorbed layer removal

(c) Formation of ZnS

(d) Removal of H_2S and HCl



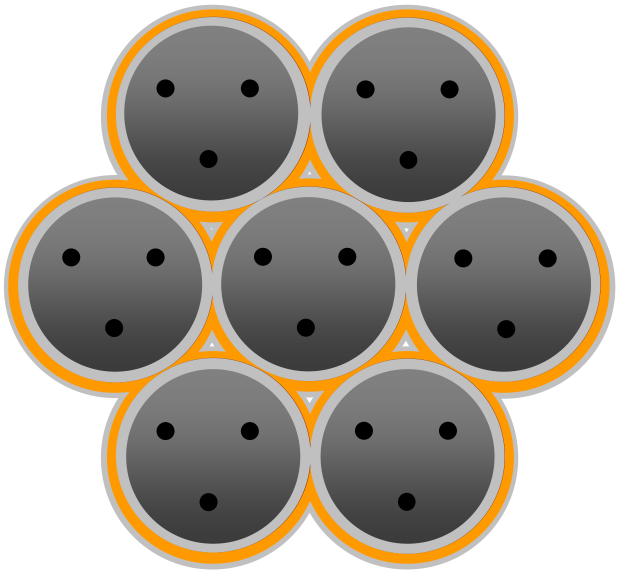
Surface limited growth: conformal films + monolayer control

Fabrication of ML Inverse Opal

- ZnS:Mn first deposited on bare opal.
- TiO_2 layer next deposited in remaining interstitial volume.
- Inverse opal formed by HF etch.
- 3rd step: back-filled inverse opal, yielding 3-layer structure.
  - Enabled by ALD's characteristics: conformal and precise

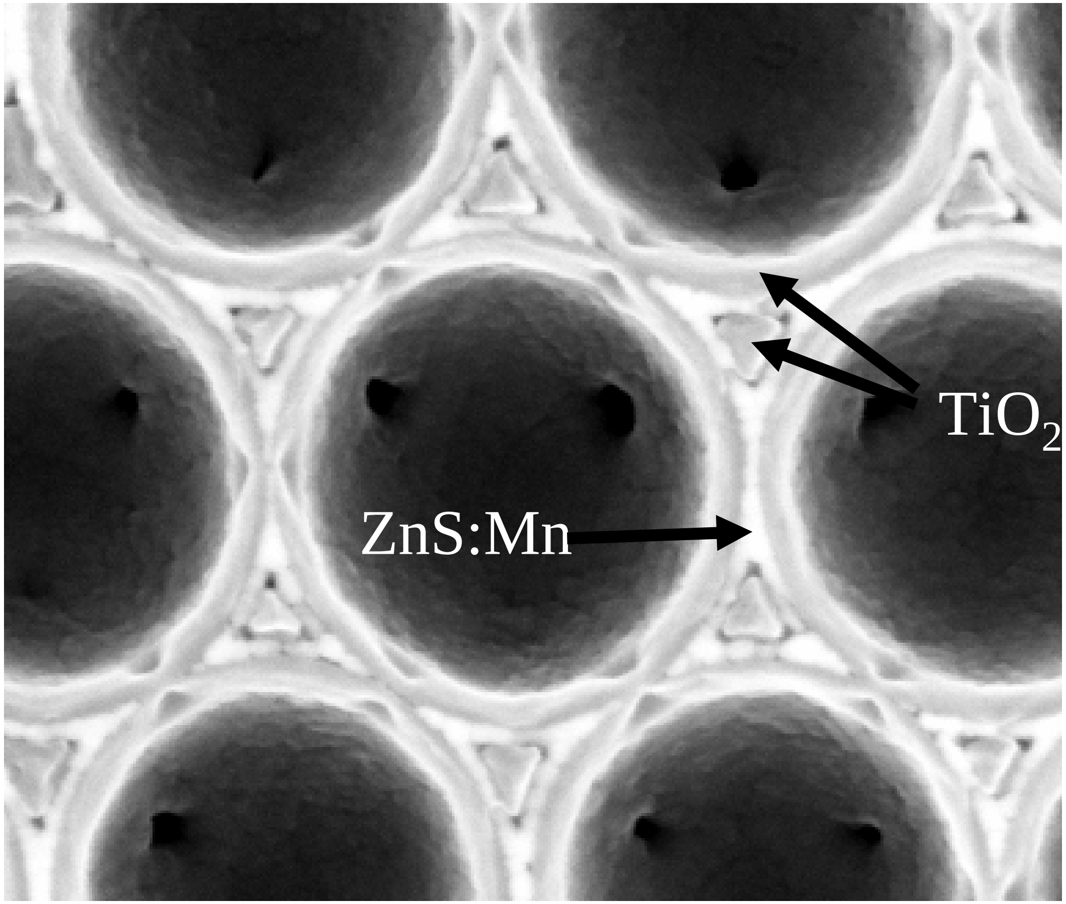
ZnS:Mn layer

TiO_2 layers



TiO_2 ALD: $TiCl_4 + H_2O$

ML Inverse Opal: SEM Images

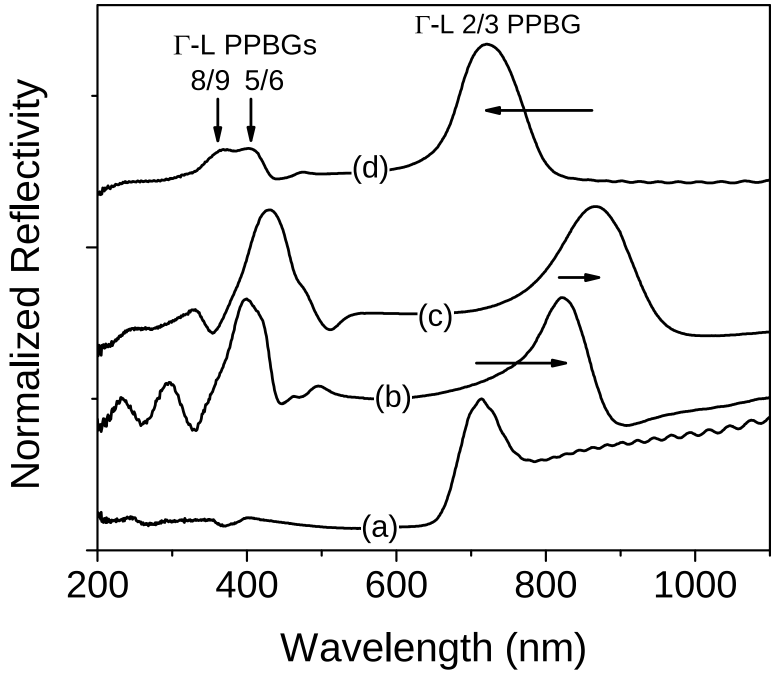


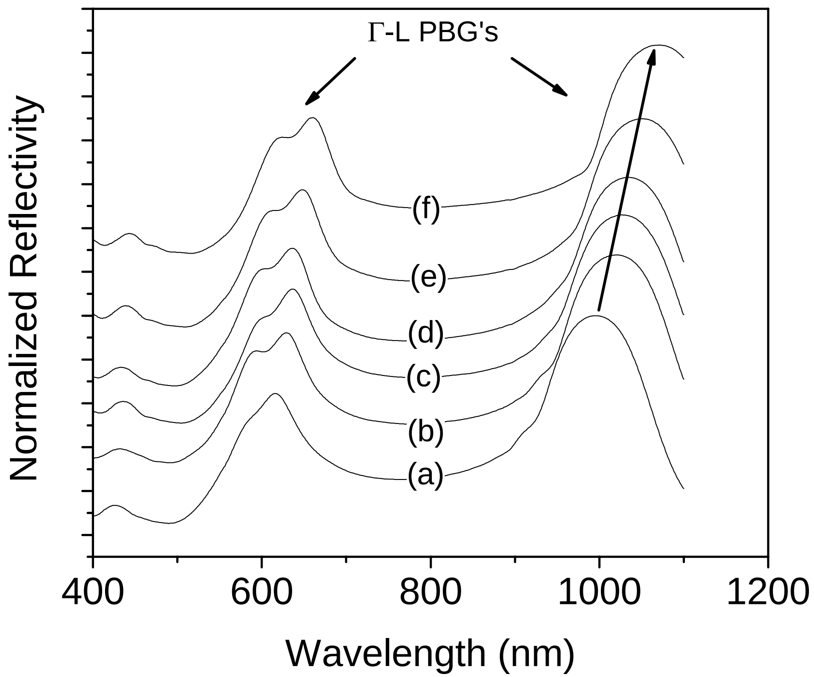
23 nm TiO_2/10 nm ZnS:Mn/20 nm TiO_2 Inverse 433 nm Opal

King, et. al. *Adv. Mat. (submitted)*

ML Inverse Opal: Specular Reflectance

330 nm opal 15° from [111] 433 nm opal





(a) sintered
(b) ZnS:Mn infiltrated
(c) ZnS:Mn/TiO_2 infiltrated, and
(d) ZnS:Mn/TiO_2 inverse opal.

(a) ZnS:Mn/TiO_2 inverse opal and after backfilling with (b) 20 (c) 40 (d) 60 (e) 80 (f) 100 total ALD cycles. (1-5 nm)

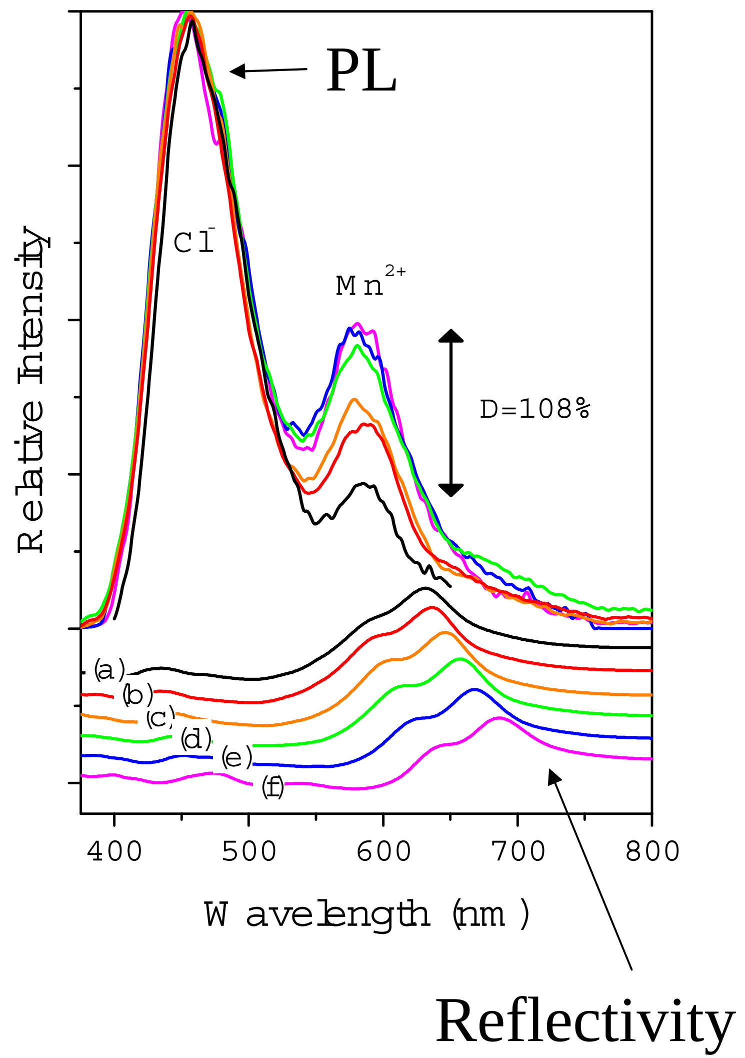
PL: ML Inverse Opal

3-layer $ZnS:Mn/TiO_2$ inverse opal (433 nm)

(a) TiO_2 (14 nm)/ ZnS:Mn (20 nm)/air inverse opal
after backfilling with TiO_2 layers of
(b) 1 nm
(c) 2 nm
(d) 3 nm
(e) 4 nm
(f) 5 nm, thickness

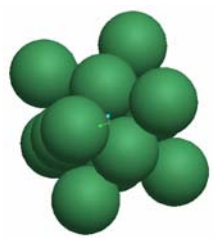
- **High-order photonic band PL modulation**
- 108% increase in relative intensity

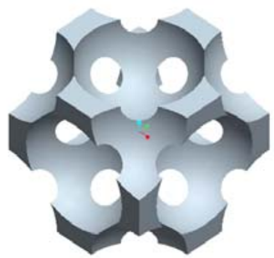
433 nm opal, 337 nm N_2 laser excitation



Non-Close Packed Inverse Opals

- Increases PBG gap width (up to 100%)*
- Reduces minimum index requirements





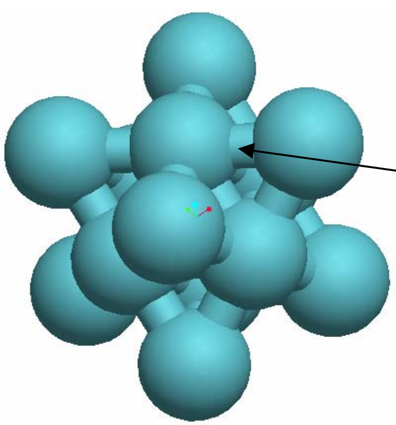
← Close-packed Structures

2 parameters define the geometry of the structure instead of one.

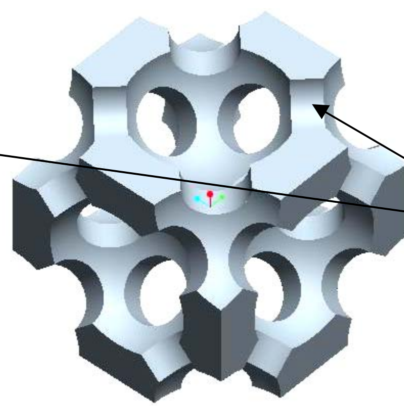
- Radius of sphere: R/a
- Radius of connecting cylinder: Rc/a

(a is the cubic lattice constant)

Rc was proven to greatly affect gap size compared to R.



Air network in an inverse NCP opal



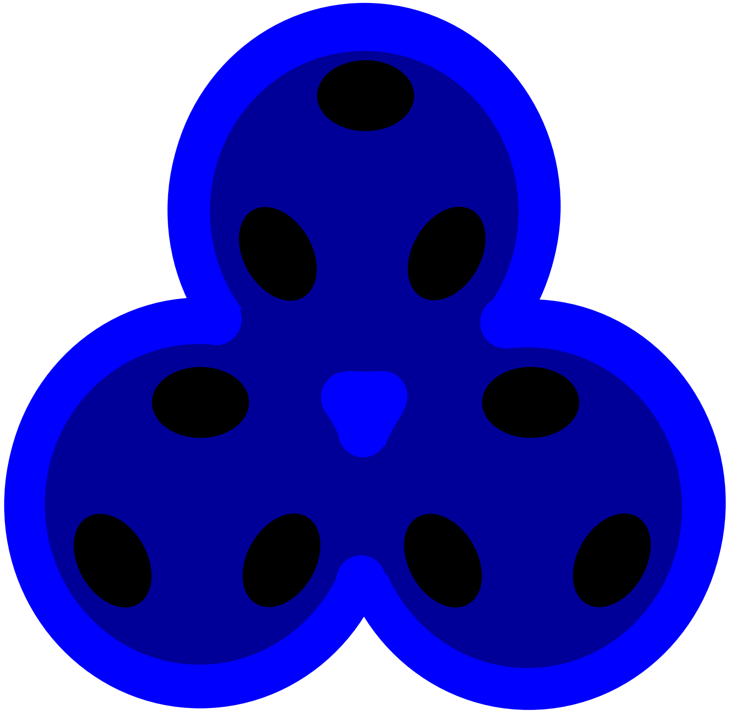
Dielectric network in an inverse NCP opal

* *Doosje et al.*

Non-Close Packed Inverse Opals

Fabrication Scheme:

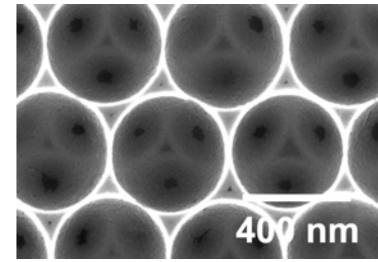
- Sinter opal prior to infiltration
- After etching, sphere connectivity is large
- Back-fill inverse opal to create cylinder-like connectivity



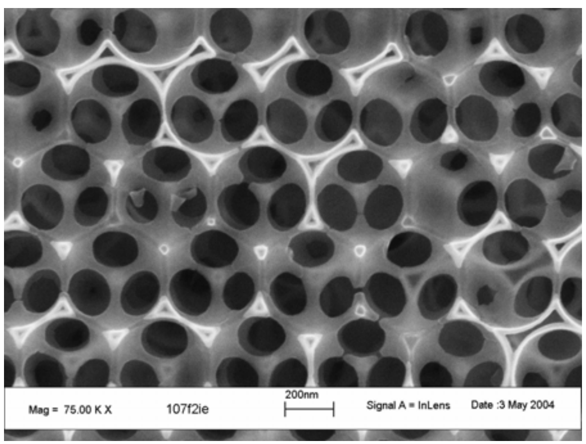
NCP Inverse Opals: SEM Results

1050º C 3 hour pre-infiltration heat treatment

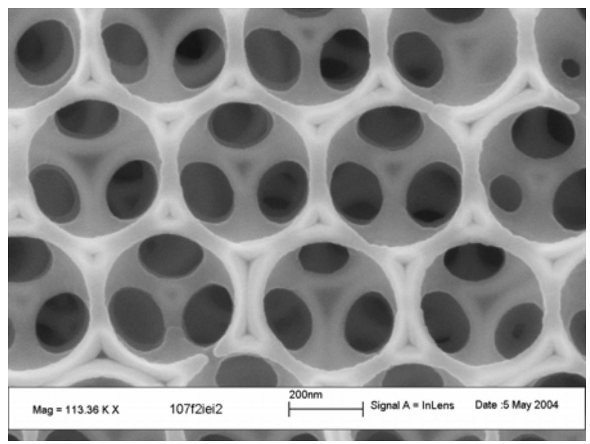
TiO_2 NCP inverse opal formation



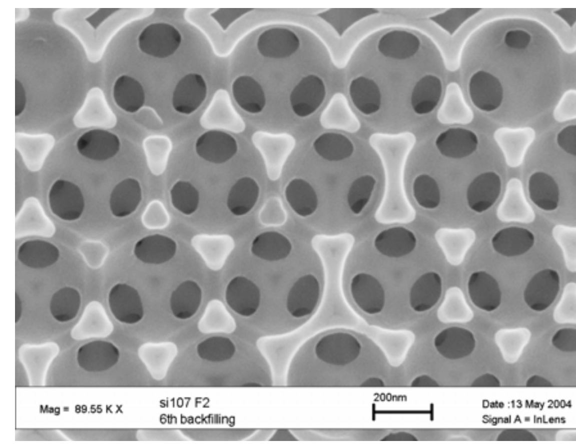
Close-packed inverse Opal



PrS inverse opal



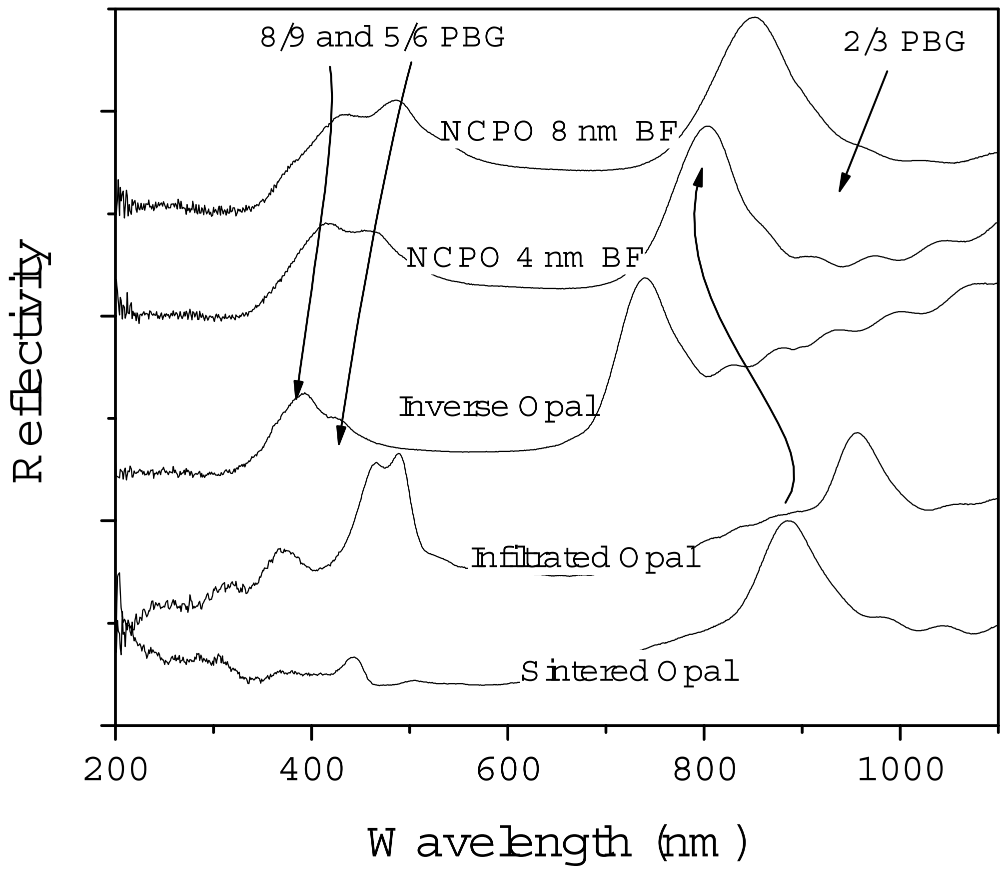
PrS inverse opal, backfilled 80 ALD cycles



PrS inverse opal, backfilled 160 ALD cycles

NCP Inverse Opal: Reflectivity

433 nm opal 15° from [111]



Summary

- Increased PC functionality by formation of
  - ZnS:Mn/TiO_2 multi-layered inverse opals
- Improved photonic band properties by formation of
  - Non-close-packed TiO_2 inverse opals
- Demonstrated tuning of luminescent and photonic band properties.
- Established **ability to grow complex *luminescent* PC structures** at the nanoscale using ALD.
- Future: Non-close-packed multi-layer PCs.

Acknowledgements

U.S. Army Research Office

- MURI Contract DAAA19-01-1-0603

Georgia Institute of Technology Molecular Design Institute

- Office of Naval Research Contract N00014-95-1-1116