Optical and Crystallographic Properties of Inverse Opal Photonic Crystals Grown by Atomic Layer Deposition

J. S. King, C. W. Neff, D. L. Heineman, E. D. Graugnard and C. J. Summers
School of Materials Science and Engineering
Georgia Institute of Technology, Atlanta, GA

MRS Fall Meeting
December 1 - 5, 2003
Boston, Massachusetts

Research Team

Georgia Tech MSE Research Group

Graduate Students

- Davy Gaillot
- Xudong Wang
- Tsuyoshi Yamashita

Army Research Lab

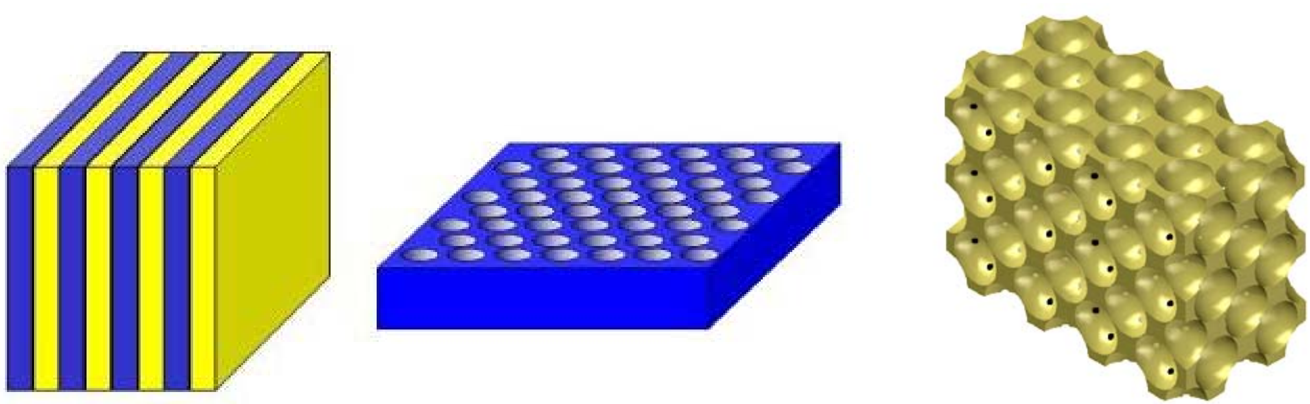
- Steve Blomquist
- Eric Forsythe
- Dave Morton

Outline

- Introduction: Photonic Crystals
- Fabrication of Luminescent Inverse Opals
- Atomic Layer Deposition
- Results
  - ZnS:Mn controlled infiltration
  - TiO_2 infiltration and heat treatment
  - ZnS/TiO_2 multi-layered structure
- Summary

Photonic Crystals

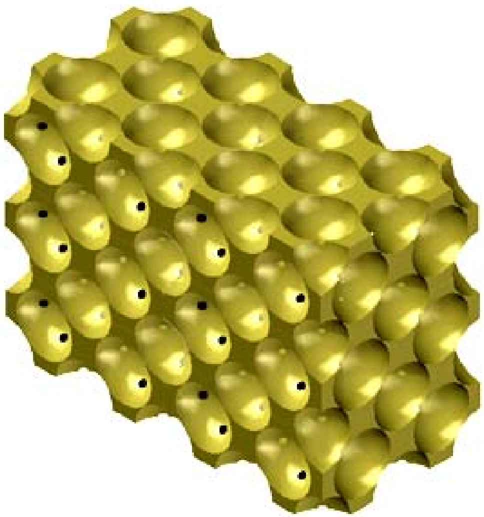
- Photonic Crystal – Periodic modulation of dielectric constant
- Exhibit photonic band gap (PBG).
- Photonic band gap materials can be used to create waveguides, resonators, couplers, filters, etc.
- Luminescent 2D & 3D PC structures offer the potential for controlling wavelength, efficiency, time response and threshold properties (Plasma phosphors, solid state lighting, etc.).

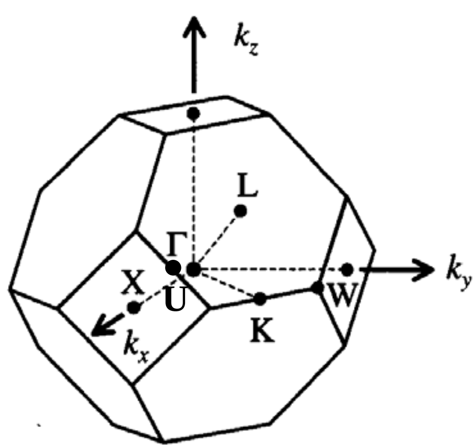


1D 2D 3D

Photonic Crystals

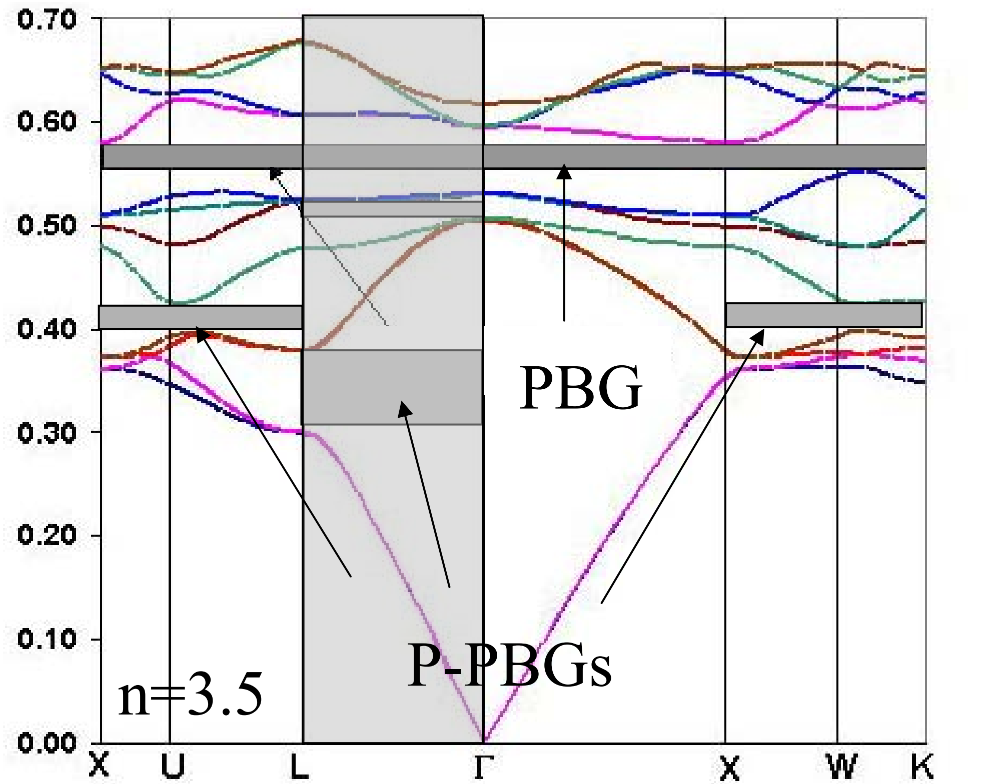
Inverse Opals





FCC Brillouin Zone

Silicon Inverse Opal Photonic Band Diagram



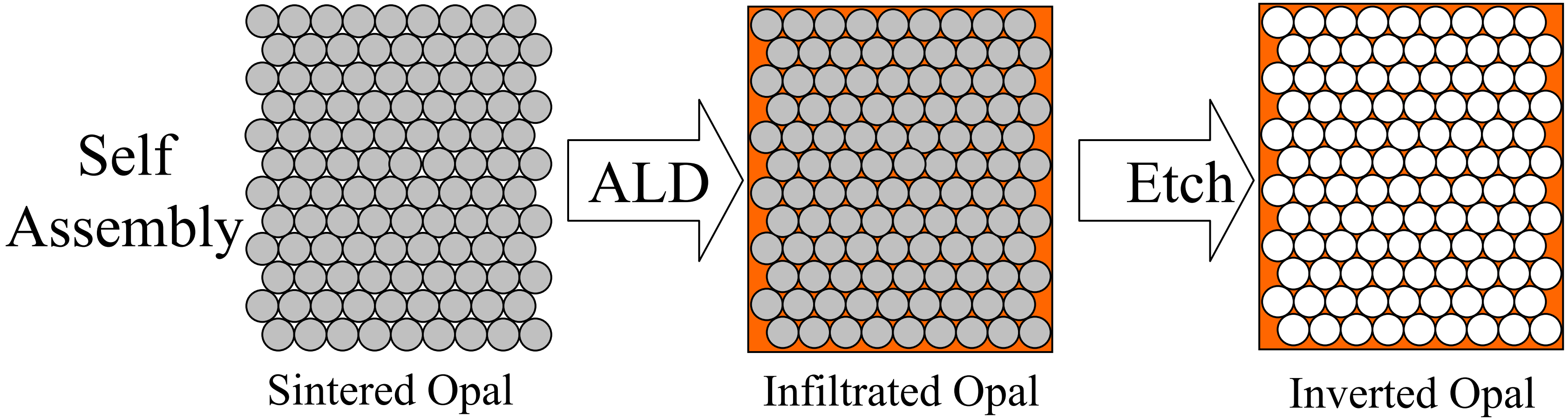
- Reflectance measurements probe photonic band structure: PBG, P-PBG

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.
  – ZnS:Mn n~2.5 @ 425 nm (pseudo photonic band gaps)
  – TiO_2 (rutile) n_{avg}~ 3.08 @ 425 nm (full photonic band gap possible)

- Etch SiO_2 spheres, forming inverse opal.



Luminescent Photonic Crystals

- Inverse opal - Full PBG if $n > 2.8$
- Most luminescent materials do not offer sufficient index.
- High index, luminescent materials required for PCP
  – Combination of two materials offers practical route.
  – ZnS:Mn (luminescent) + TiO_2 (high n) multi-layer.
- Requires controlled thickness; dense, conformal films.
  – 24.5 % vol. fraction doubles PBG (John & Busch)
  – Atomic Layer Deposition (ALD) fulfills requirements.

Atomic Layer Deposition

ALD is a CVD growth technique utilizing sequential reactant pulses.

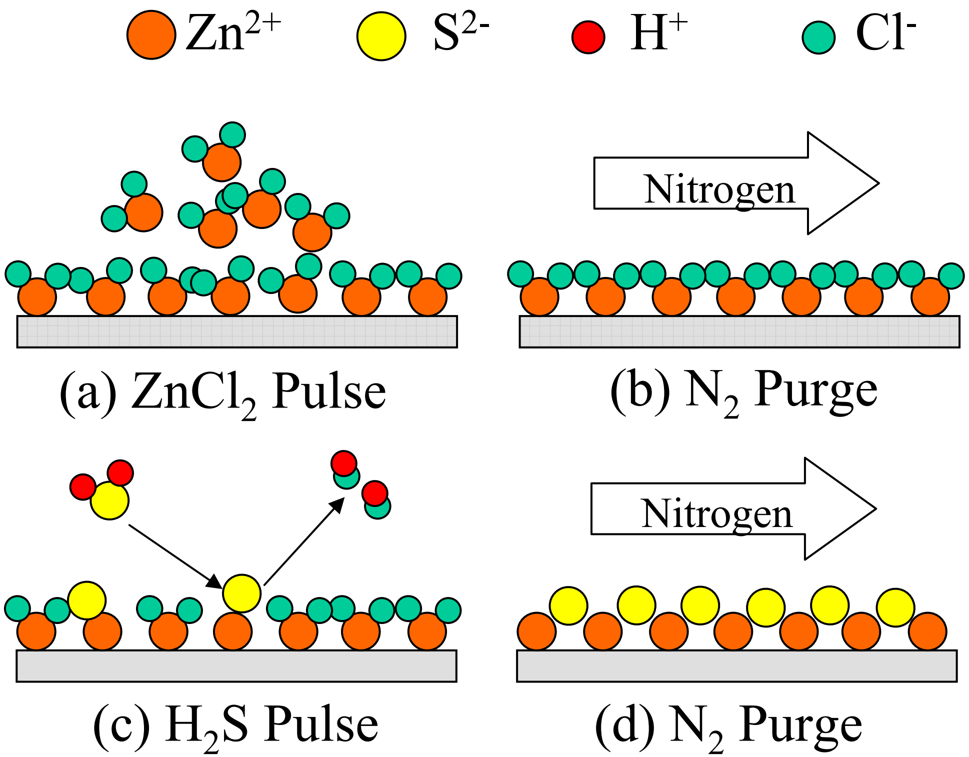
ALD Growth of ZnS

(a) Chemi + physisorption

(b) Physisorbed layer removal

(c) Formation of ZnS

(d) Removal of H_2S and HCl

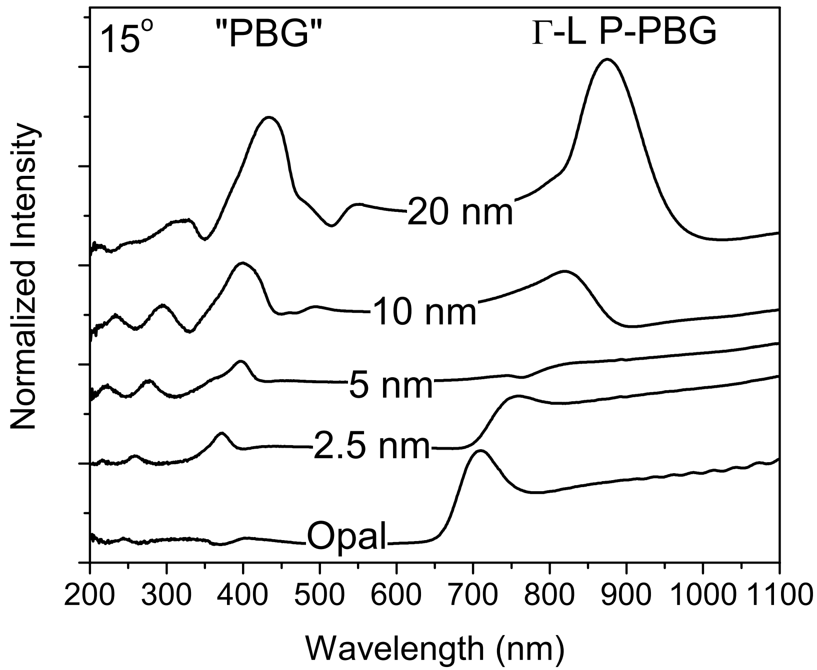


Surface limited growth: conformal films + monolayer control

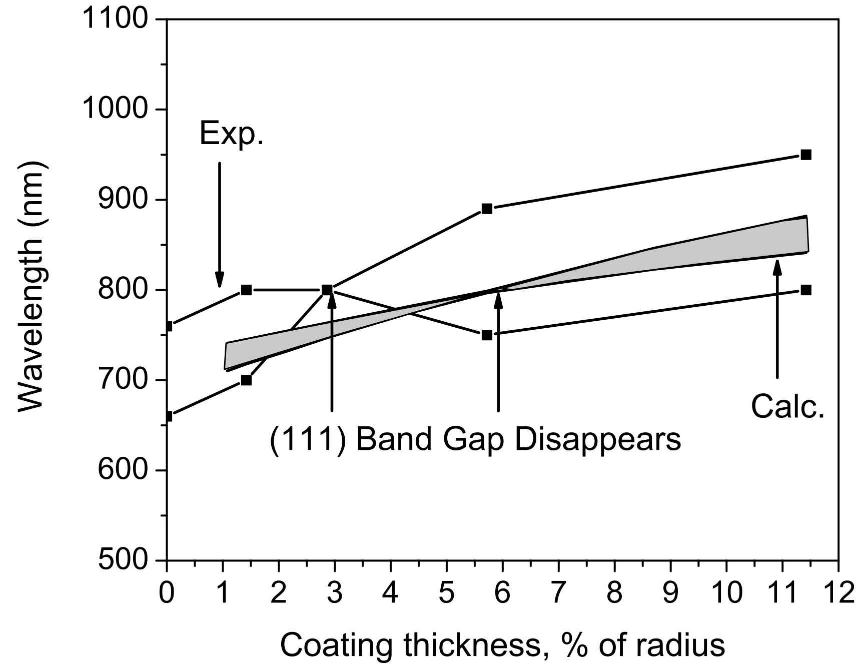
ZnS:Mn Stepwise Infiltration

- Previously demonstrated ZnS:Mn full infiltration (MRS 2002, APL 83).
- However, multi-layered opals require infiltration finesse.
- 330 and 460 nm opals were filled with increasing % of ZnS:Mn.
- Deposition @ 500º C with a $MnCl_2$ doping pulse every 32 cycles.
- Shift of P-PBG to longer wavelengths shown in specular reflectance after infiltrations.

ZnS:Mn Stepwise Infiltration



Specular reflectance



Γ-L gap positions

Deviation from theory:

- Coating thickness based on planar growth, not curved surface.
- Reflectivity measured @ 15° from normal.

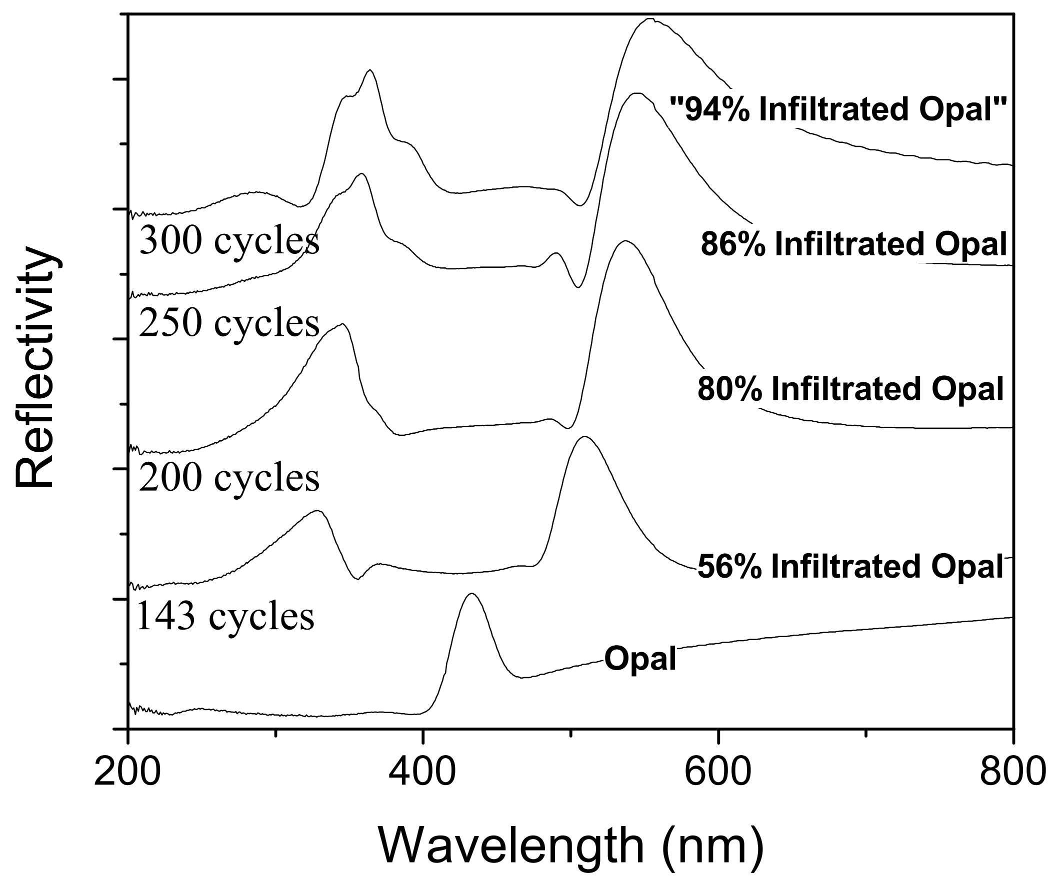
TiO_2 Infiltration

- **Need to demonstrate ability to grow high index component by ALD**.
- Aarik, et.al. have shown in planar ALD TiO_2 growth studies:

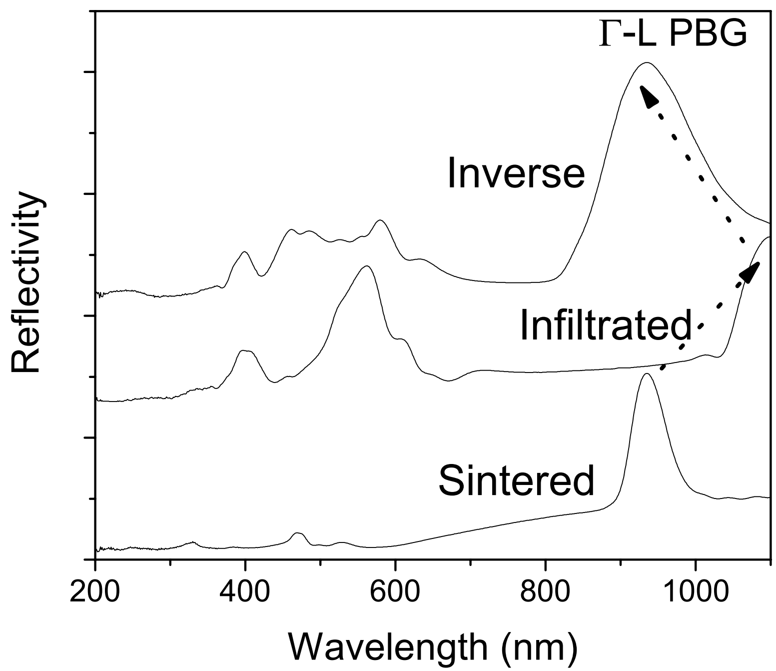
  <165º C = amorphous, 165º - 350º C = anatase, >350º C= rutile
- TiO_2 was infiltrated using $TiCl_4$ and H_2O pulses.
- Amorphous film growth has advantages over crystalline:
  - **Amorphous films exhibit very smooth surfaces.**
  - Better suited for the conformal infiltration of opals
- Infiltrate at low T, then heat treat to obtain rutile (high index).
- Infiltrations were performed at both 100º C and 500º C.
- Inverse opal formation
  - For amorphous film, ion mill to expose silica (very conformal).

TiO_2 Infiltration

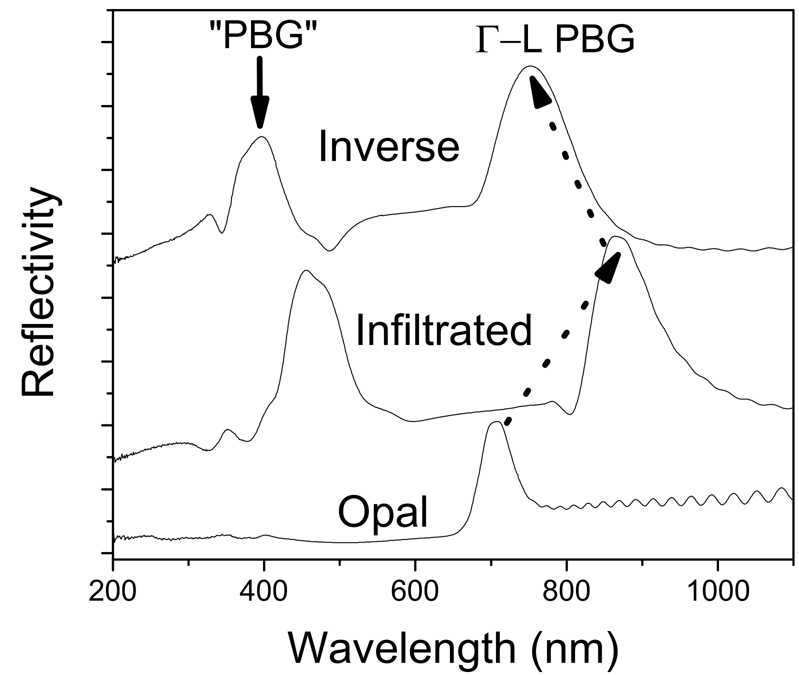
Si058 (200 nm Opal)



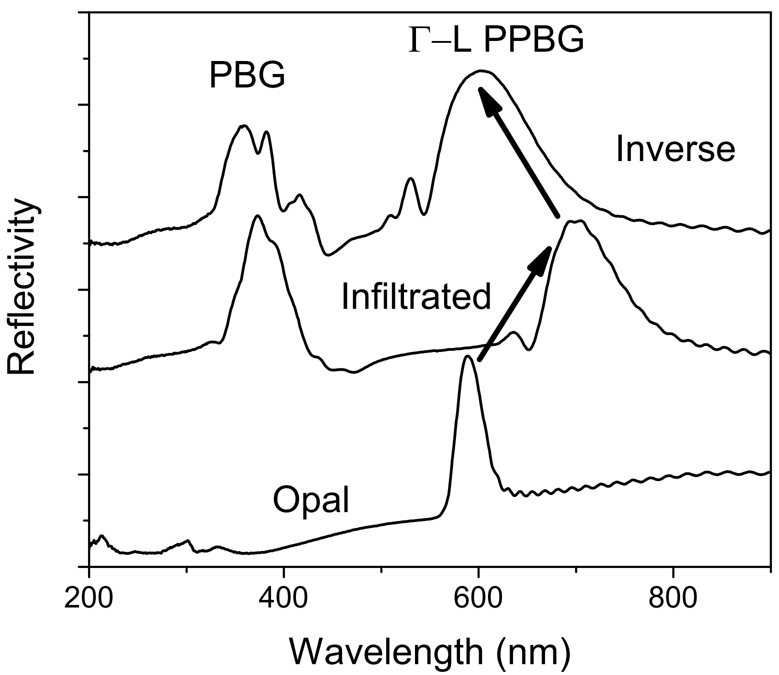
Si090A (430 nm)



Si091D (330 nm)

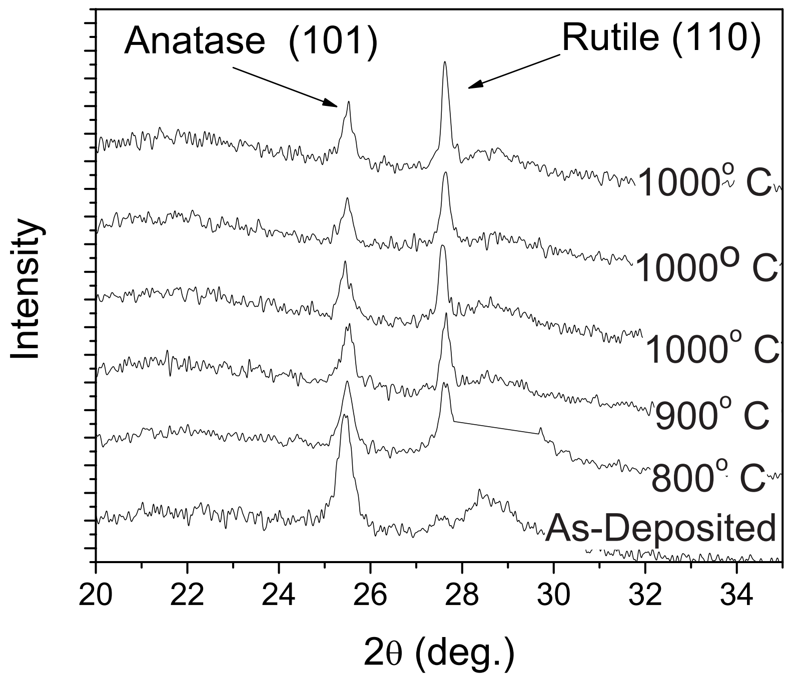


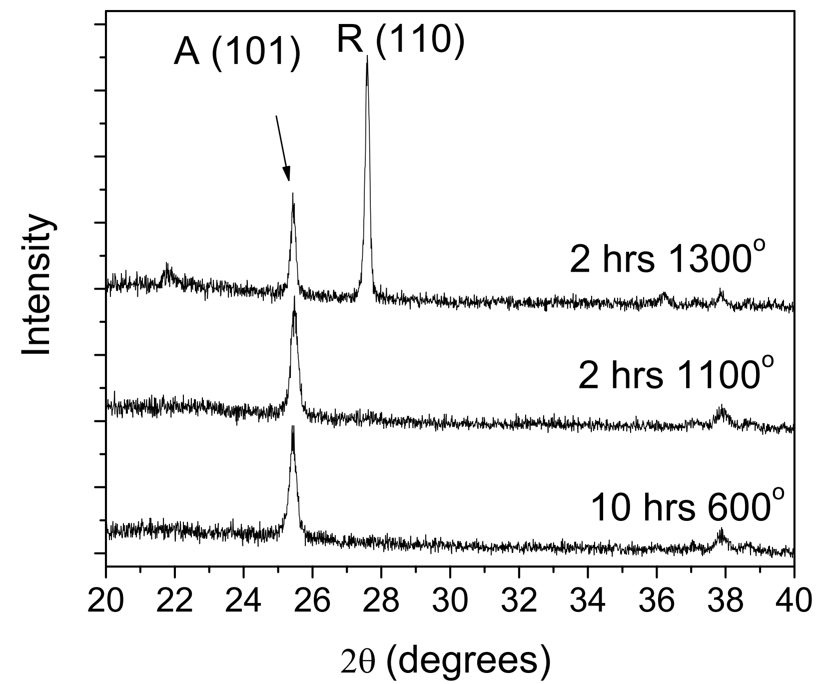
Si083 (273 nm)



Γ–L PPBG
PBG
Inverse
Infiltrated
Opal
Reflectivity
200
400
600
800
Wavelength (nm)

TiO_2 Rutile Conversion - XRD



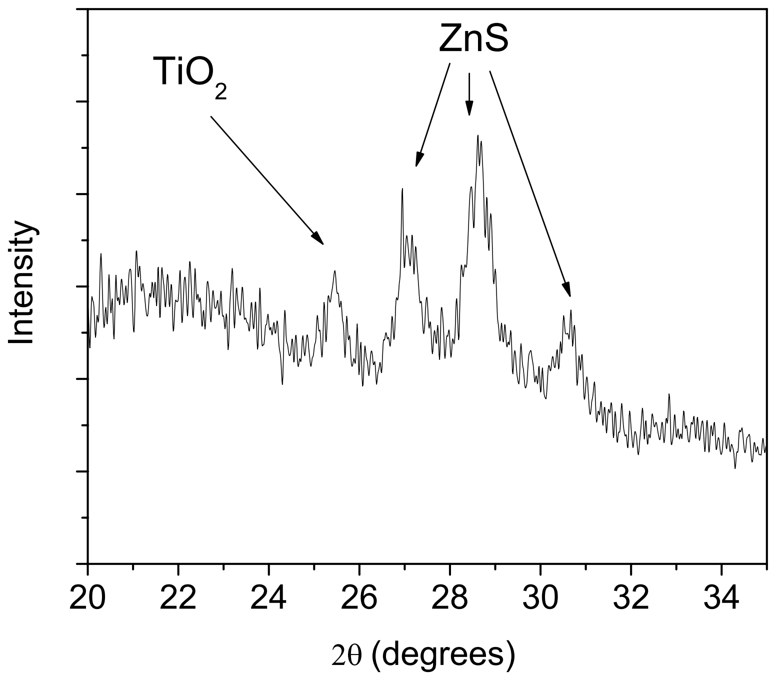


Deposited at 500º C (initially anatase). ~50% rutile after HT

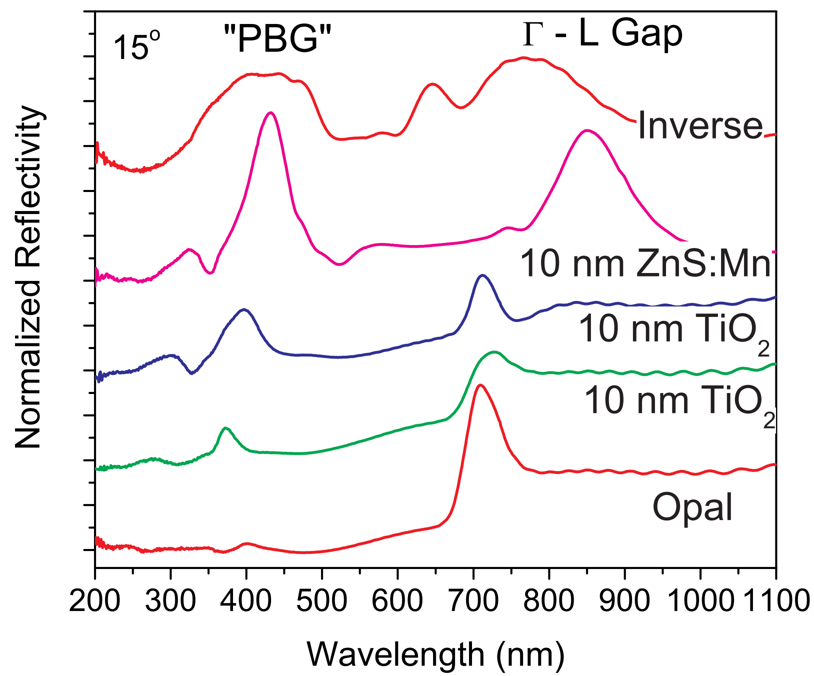
Deposited at 100º C (initially amorphous). ~65% rutile after HT

ZnS/TiO_2 Inverse Opal

- TiO_2 at deposited at 100º C, ZnS:Mn at 500º C.
- Amorphous TiO_2 converts to anatase during ZnS:Mn growth.

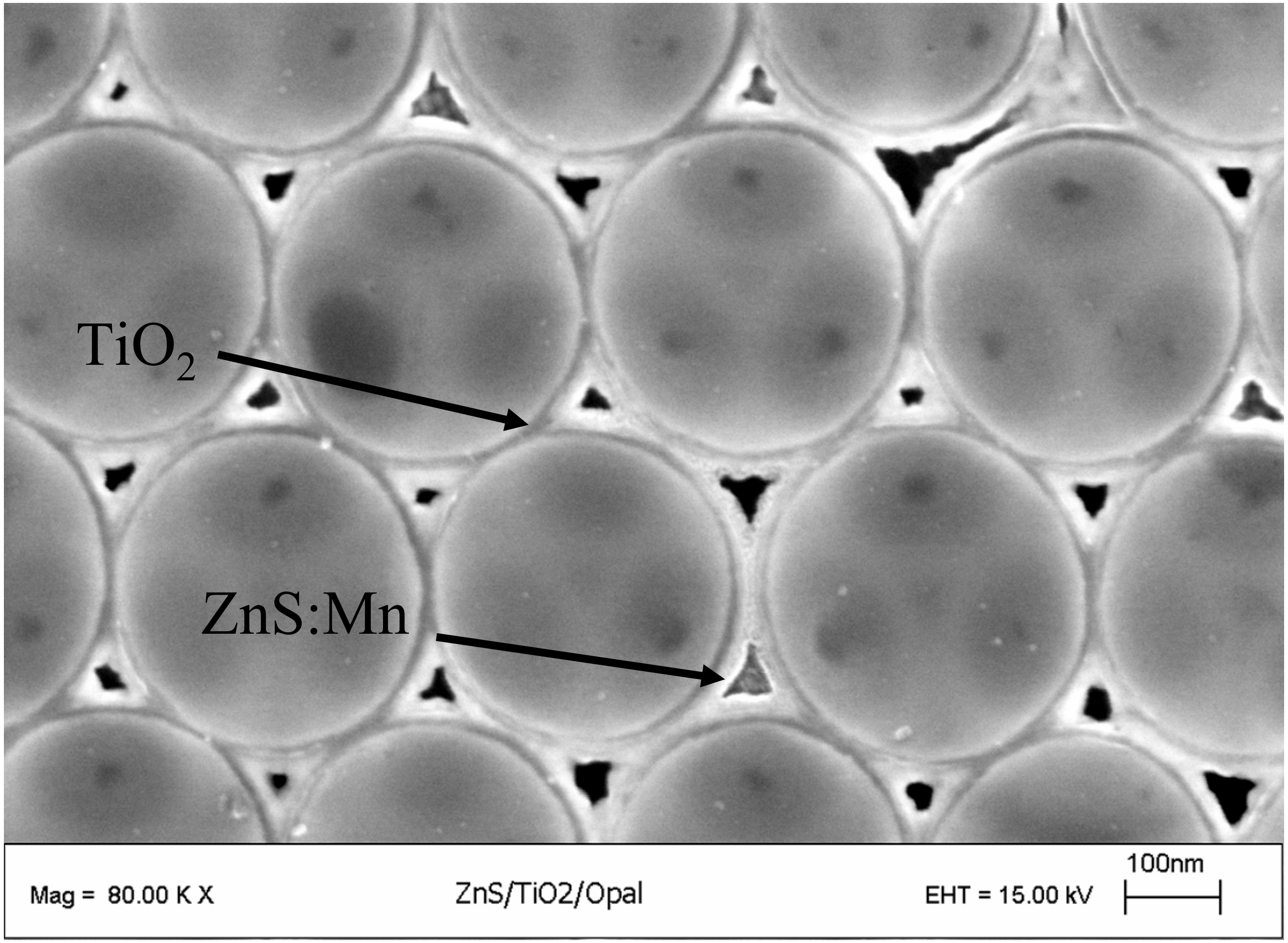


XRD



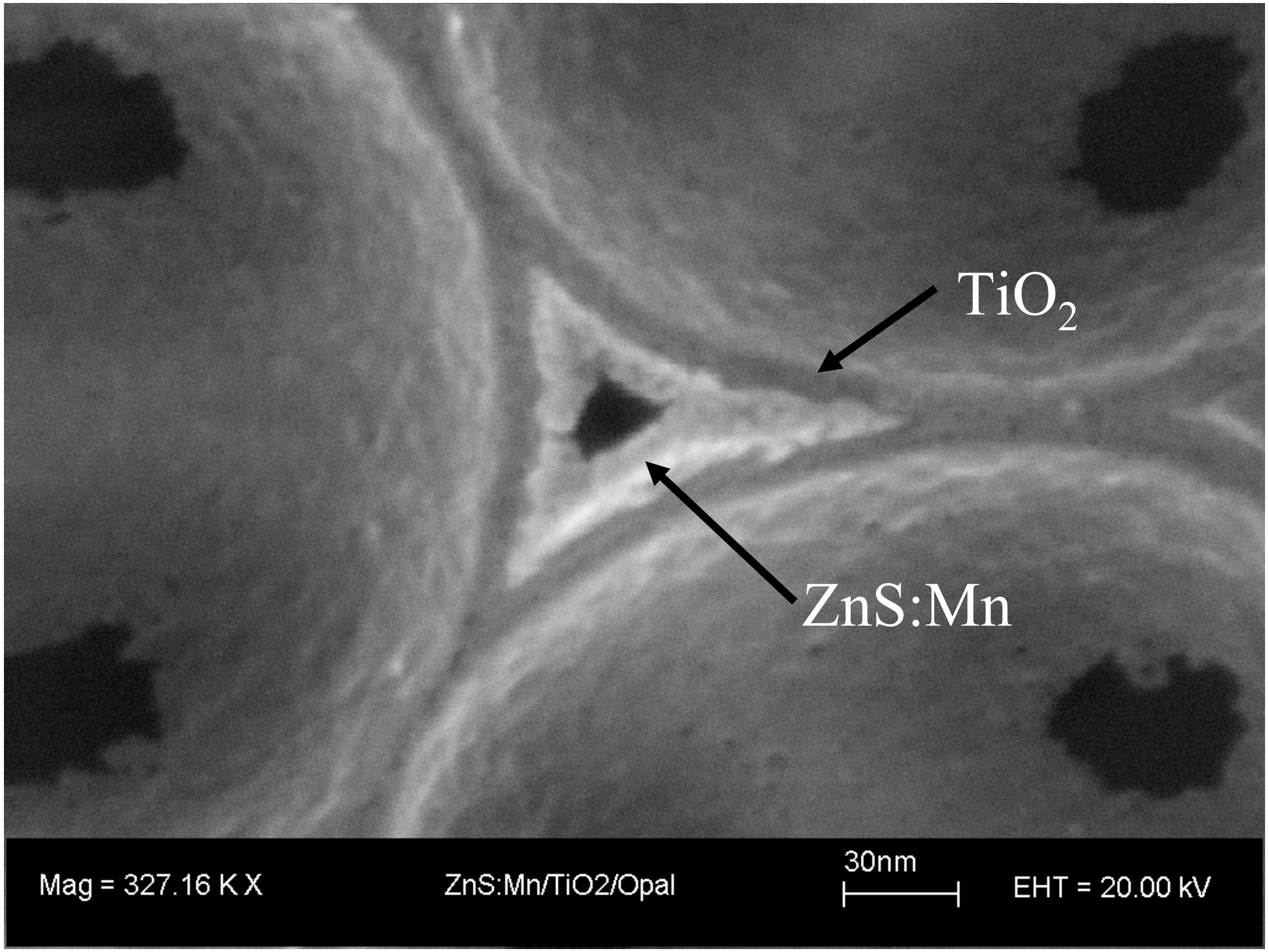
Specular Reflectance

ZnS/TiO_2 Infiltrated Opal



$ZnS{:}Mn/TiO_2$ multi-layered 330 nm infiltrated opal

ZnS/TiO_2 Inverse Opal



$ZnS:Mn/TiO_2$ multi-layered 330 nm inverse opal.

Summary

- Successful formation of ZnS:Mn and TiO_2 inverse opals.
- **Precise control of ALD infiltration demonstrated.**
- As-deposited TiO_2 **can be converted to rutile phase**.
- Clearly demonstrated **ability to grow complex *luminescent* PC structures** at the nanoscale using ALD.
- Future: PL measurements, RTA, more complex structures.

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