Properties of Inverse Opal Photonic Crystals Grown By Atomic Layer Deposition

J.S. King[1], C. W. Neff[1], W. Park[2], D. Morton[3], E. Forsythe[3], S. Blomquist[3], and C. J. Summers[1]

(1) School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA

(2) Department of Electrical and Computer Engineering, University of Colorado, Boulder, CO

(3) U.S. Army Research Laboratory, Adelphi, MD

Outline

I. Rationale

II. Introduction to Photonic Crystals and Atomic Layer Deposition

III. Fabrication Methodology

IV. Characterization

V. Results

VI. Conclusion

VII. Future Work

VIII. Acknowledgements

I. Rationale

Immediate Goal

- Investigate Atomic Layer Deposition (ALD) as an effective infiltration route for fabricating inverse opals for use in the visible

Why?

- Good results with Chemical Bath Deposition, MOCVD (Blanco, Norris, Romanov, etc.): porosity or incomplete filling is often observed.
- We propose ALD as an effective alternate method.
- Flexible deposition technique for oxides, semiconductors and metals
- Easily scalable to mass production (already used in IC fab)

Ultimate Goal

- High dielectric material based luminescent inverse opals with microcavity defects

II. Introduction: Photonic Crystals and Inverted Opals

- PCs offer unprecedented control of light as is well known from the work of Yablonovitch, John, and many others.
  - Highly efficient optic and electro-optic devices; i.e. LEDs, Lasers, Waveguides, luminescent materials
  - Most work has been on 2D structures.
  - 3D luminescent PC's, including microcavity-based structures offer potential for wavelength control and low threshold emission

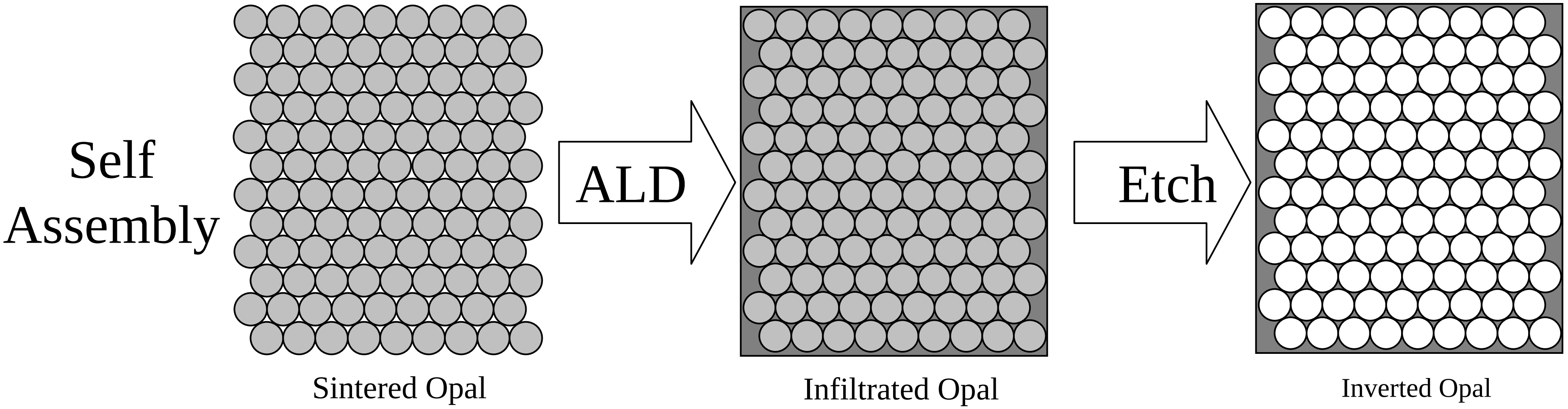
- Inverted Opal Structure (FCC)
  - Predicted by Busch and John
  - As demonstrated in silicon for the IR regime by Blanco, et.al., one of few known 3D structures that should exhibit a full PBG *in the visible*
  - Only structure *currently experimentally practical*

II. Introduction: Photonic Crystals and Inverted Opals

- Requirements
  - 3D periodic structure w/ high refractive index contrast (> 2.8) n>3.5 for 10% PBG
    - GaP, TiO_2, SnS_2, Fe_2O_3, all can be grown using ALD
  - Low optical absorption
  - Lattice constant ~ 140-350 nm
  - **High crystalline quality, conformal coatings**
  - **High filling fractions-** Typical filling fractions ~ 10 – 50 % of available pore volume reported for infiltration schemes

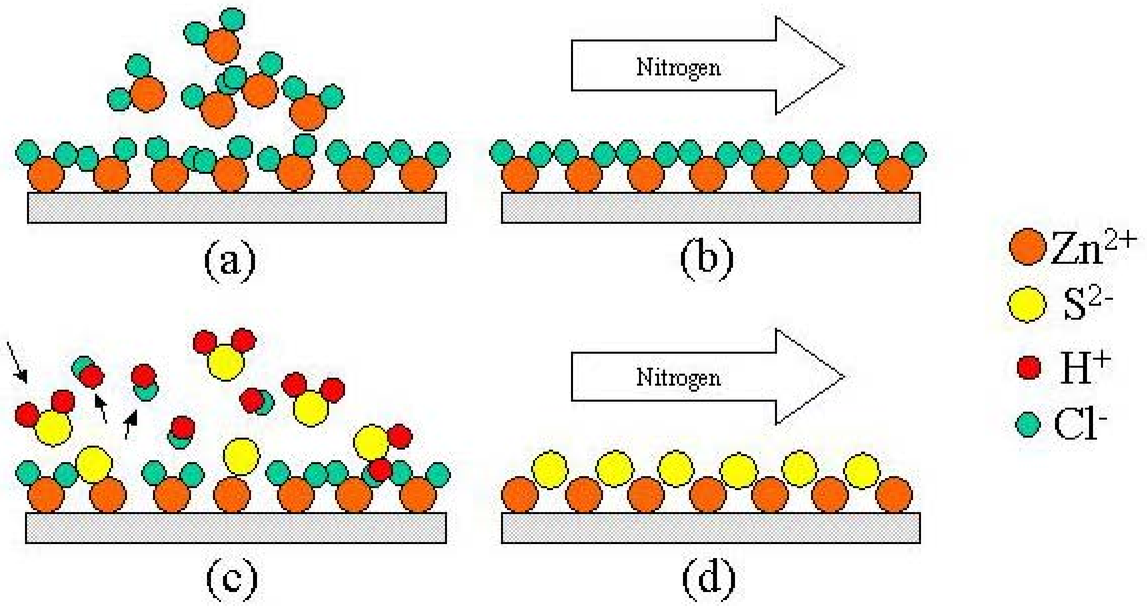
III. Fabrication Methodology

- Self-assembled thin film provides periodicity
  - Sedimentation of monodisperse colloidal silica in a confinement cell followed by sintering to form synthetic opal (modification of method of Gates and Xia)
- After sintering, the opal is then infiltrated with high index material (ALD)
- 2% HF etch used to remove silica spheres, leaving air holes
- Infiltrated material must be compatible with etching scheme



Atomic Layer Deposition

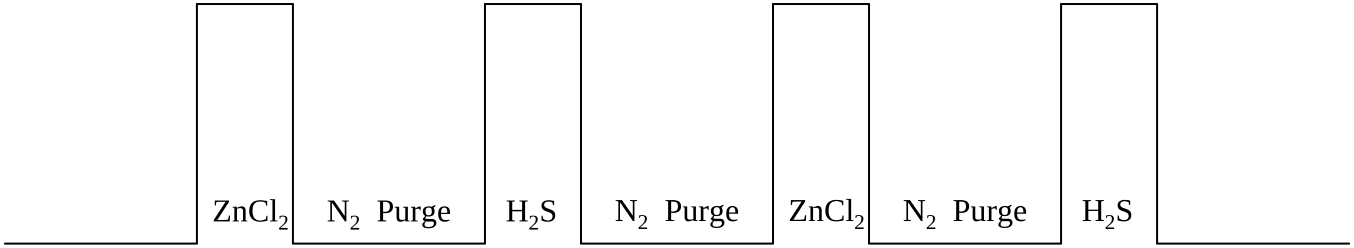
Thin film grown by sequential deposition of reactants results in monolayer-by-monolayer growth



Advantage: surface-controlled growth instead of source-controlled

Atomic Layer Deposition

- Available Materials: ZnS, SiO_2, TiO_2, ZnSe, Fe_2O_3, SnS_2, GaP, W, Ta, . . .
- Multi-layered materials possible, allowing tailoring of refractive index and luminescent behavior
- ZnS:Mn used for initial demonstration: well studied ALD material, but insufficient index (n~2.5) for full PBG: Pseudo-gap behavior
- Luminescent Center: Mn^{2+} doping using $MnCl_2$ every 100th pulse

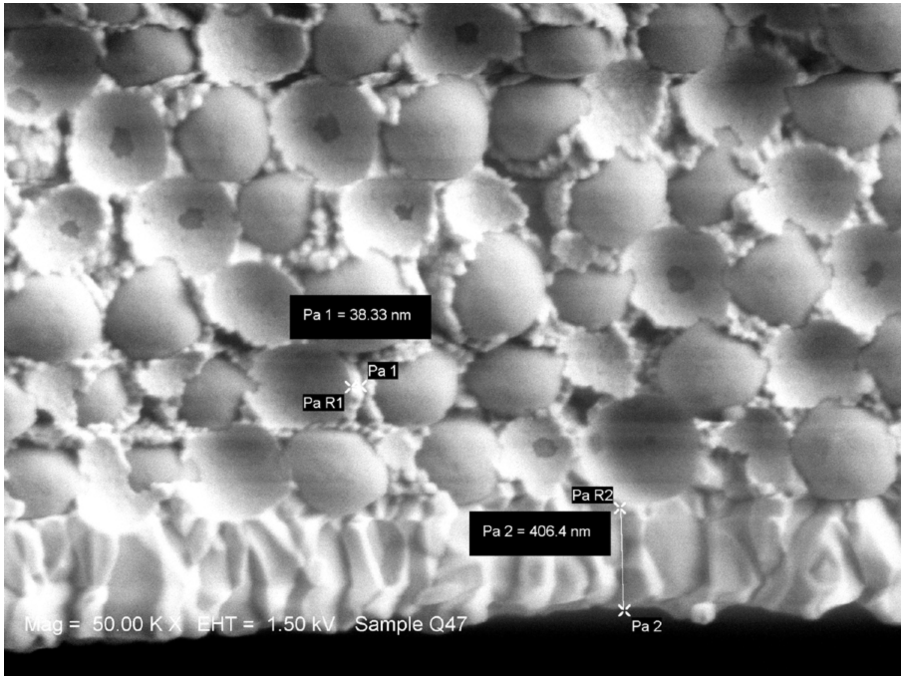


IV. Characterization Methods

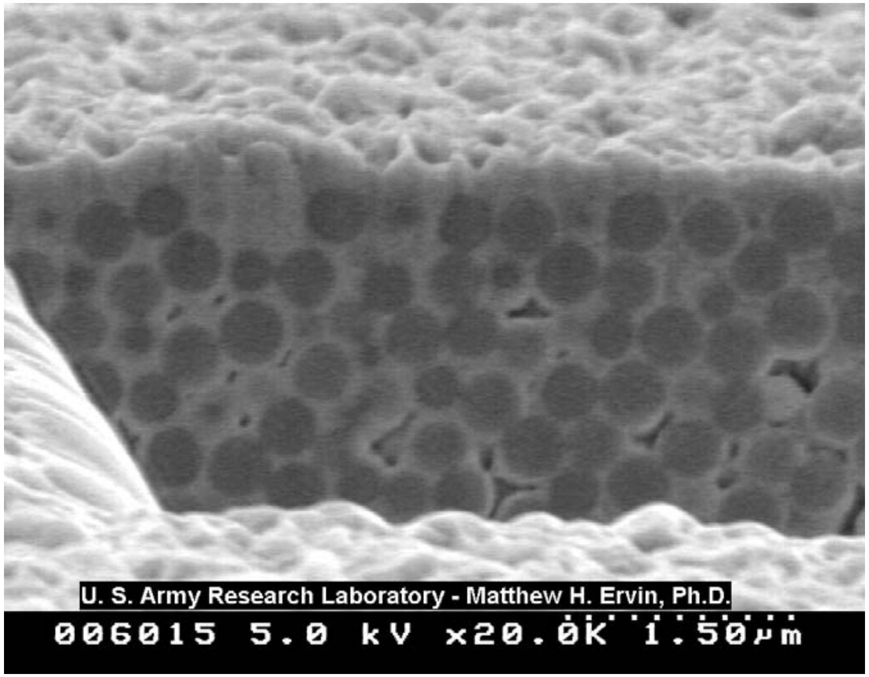
- Scanning Electron Microscopy (SEM)
  - Film quality, conformal nature, sphere sizing
- Optical: Reflectivity (8 degree)
  - lattice constant-sintered opals,
  - filling fraction-infiltrated opals
- Photoluminescence (PL) – Band edge and Mn^{2+} excitation
  - Crystallinity
  - Modulation by photonic crystal
  - Angular dependence

V. Results SEM – ZnS:Mn Infiltrated Opal

460 nm



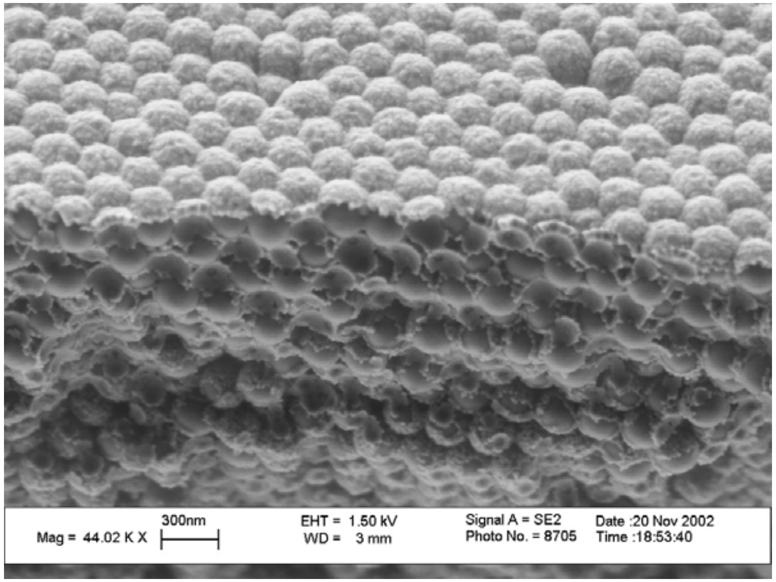
460 nm Sacrificial Sample



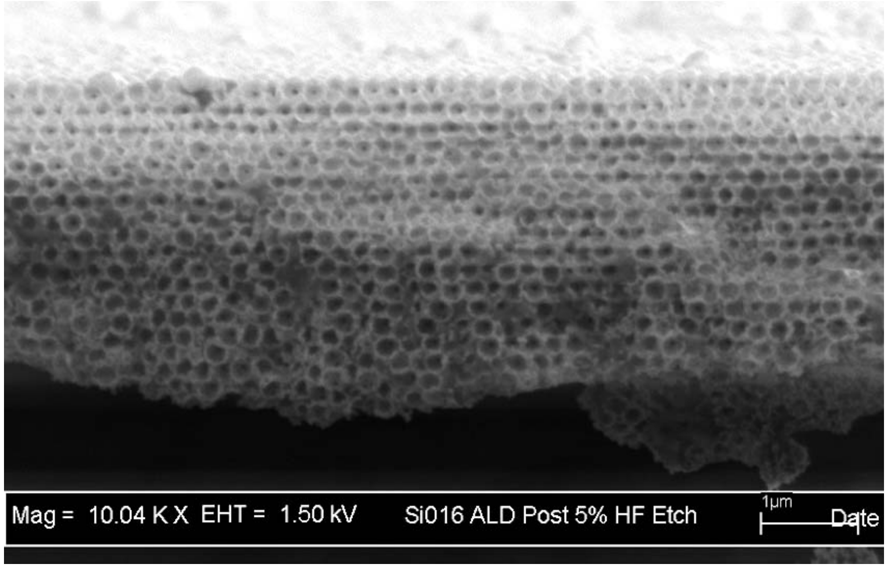
Infiltrated Opal Trench Cut Via FIB

SEM – ZnS:Mn Infiltrated/Inverse Opal

d= 240 nm



d= 220 nm



Calculation of Filling Fraction

–Periodicity yields Bragg diffraction

–Derivative of Bragg law allows calculation of (111) peak position

–Opals grown oriented with (111) planes parallel to substrate

– Resulting peak shift after infiltration allows calculation of filling fraction, *f*

– filling % for ideal FCC = f/0.26 x 100%

$$\lambda = 2d\,0.816\sqrt{\varepsilon_{avg.} - Sin^2\theta}$$

$$\varepsilon_{avg} = \varepsilon_{Silica}0.74 + (0.26 - f)\varepsilon_{air} + f\varepsilon_{ZnS}$$

$$f = \frac{\varepsilon_{avg} - \varepsilon_{silica}\big((0.74)\big) - 0.26}{\varepsilon_{ZnS} - 1}$$

d= silica sphere diameter

ε_{ZnS} = ZnS bulk dielectric constant

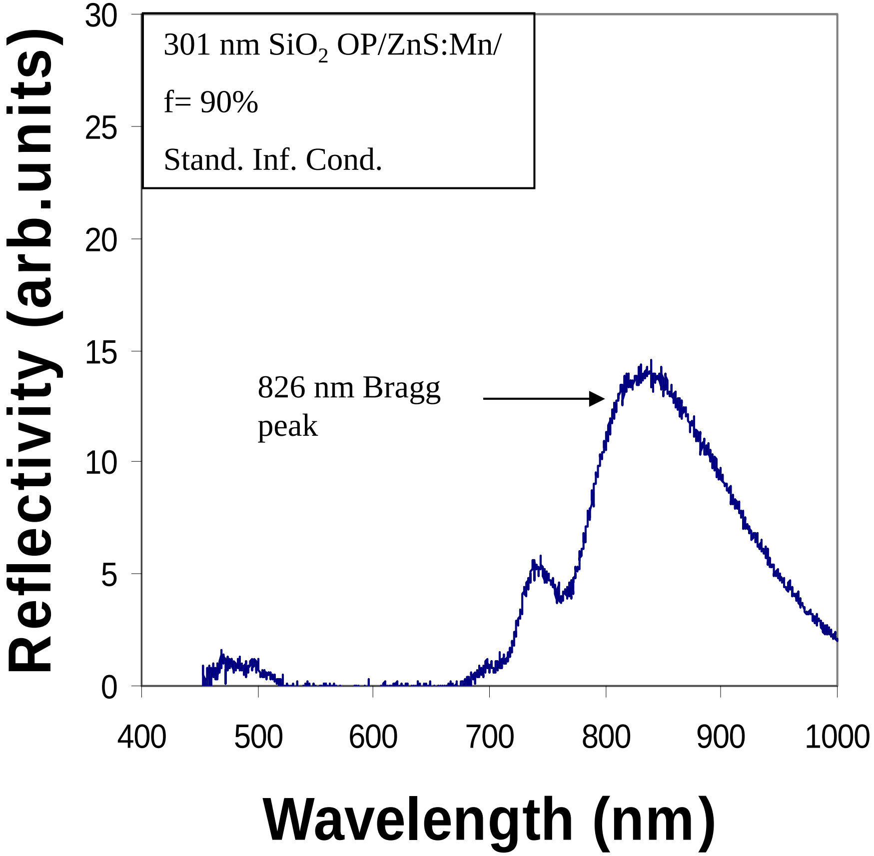
ε_{avg} = effective dielectric constant

θ = angle of incidence

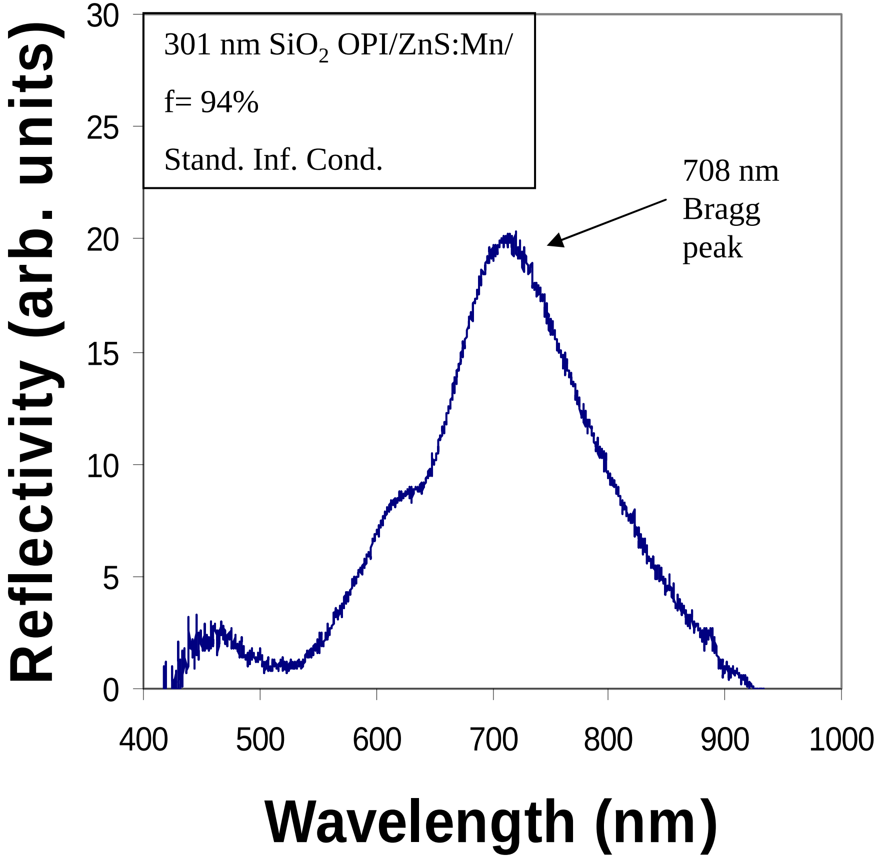
Reflectivity – 300 nm ZnS:Mn Opal

ZnS Background subtracted

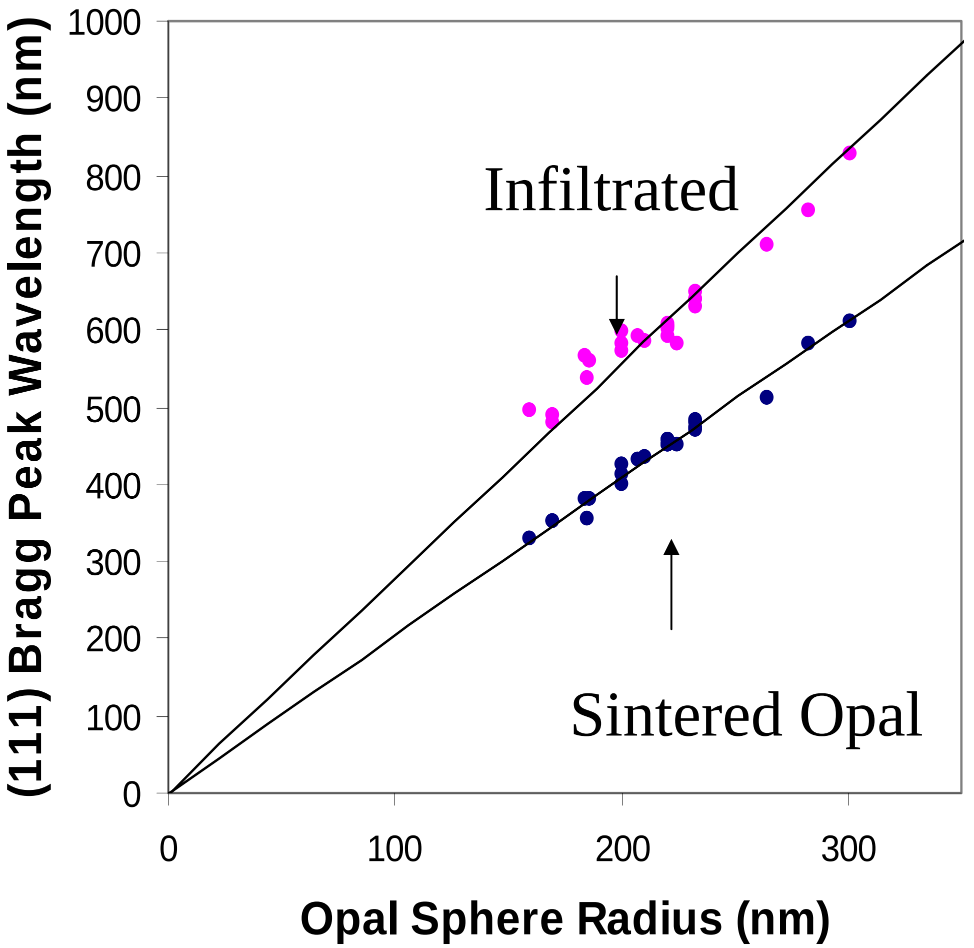
Infiltrated



Etched



Reflectivity - Summary



From the trendline, the average fill fraction is 90%

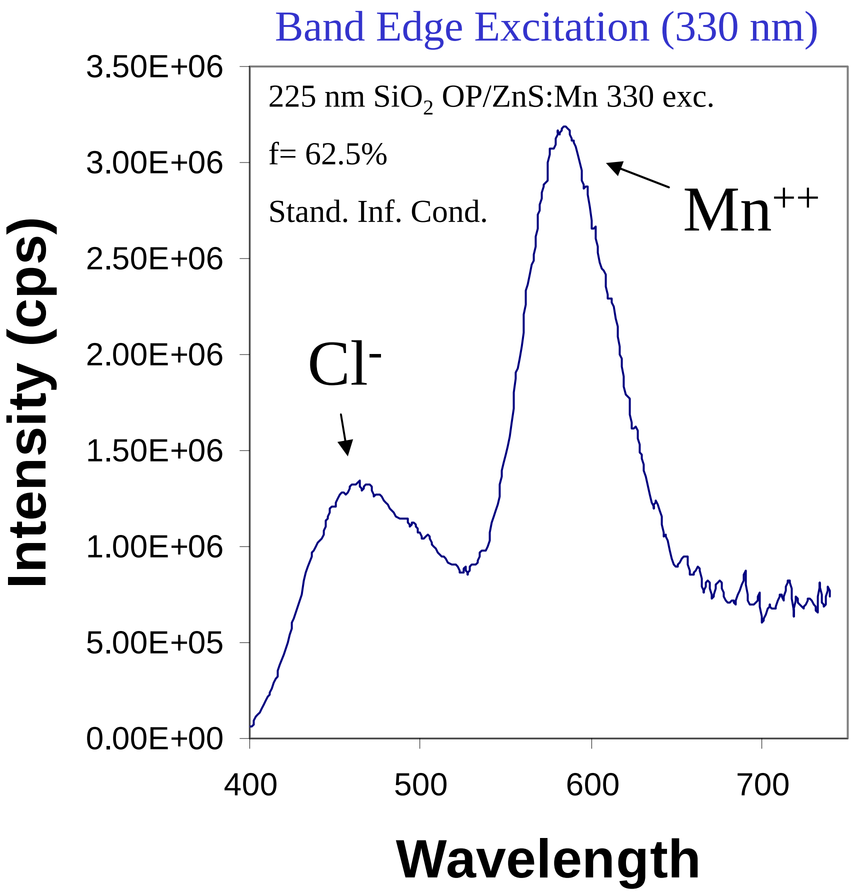
Increased deviation as sphere size decreases

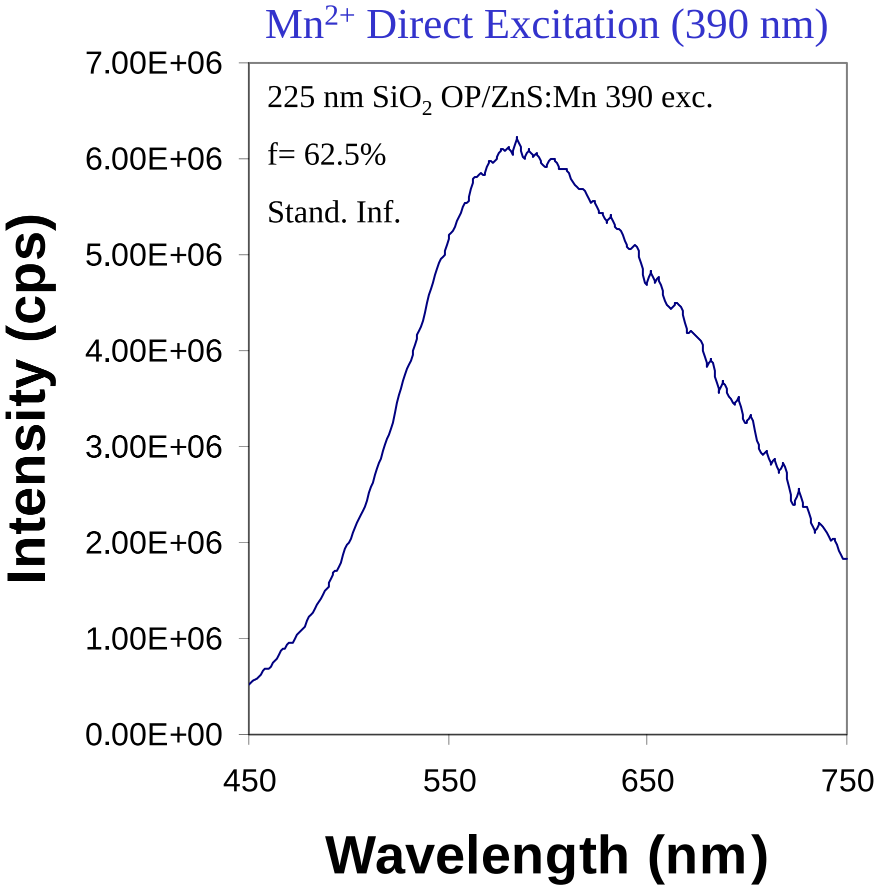
- Uncertainty in measurements of sphere size and wavelength

Δd ~ 5-10 nm Δλ ~ 5 nm

PL Results – ZnS:Mn Infiltrated Opal

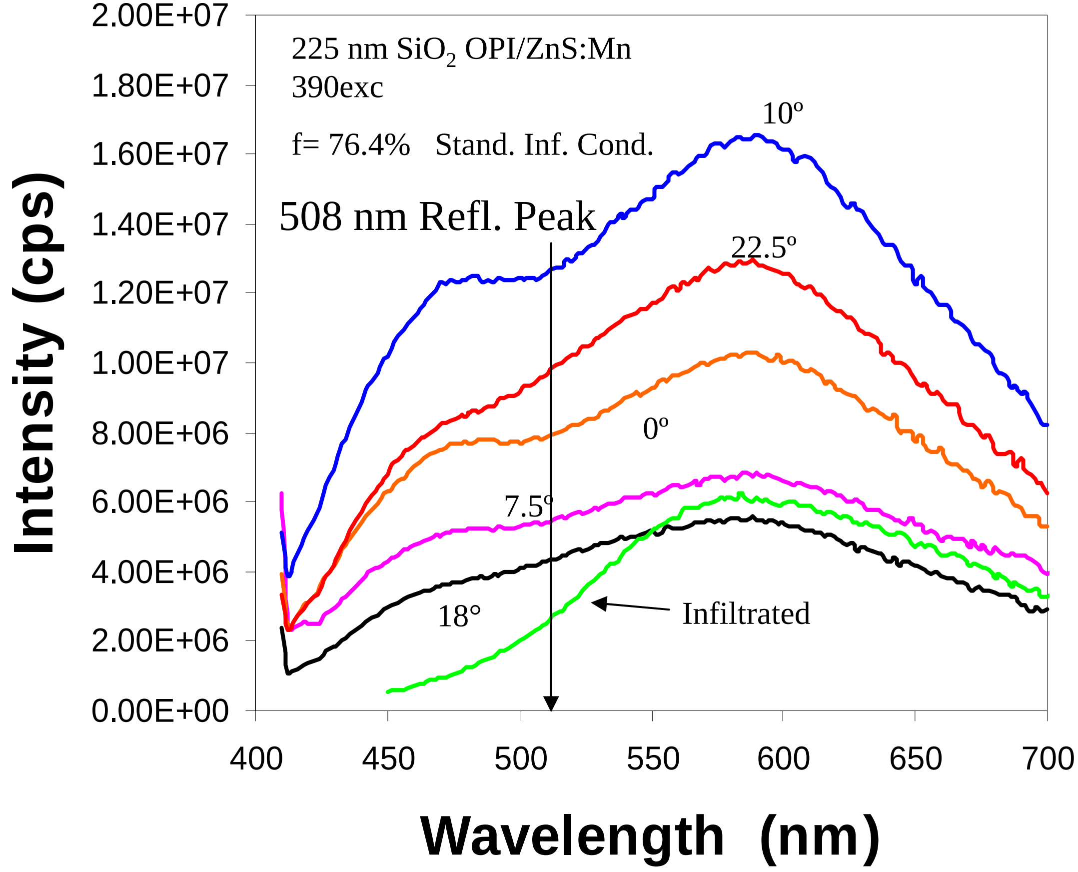
PL standard collection angle = 22.5°

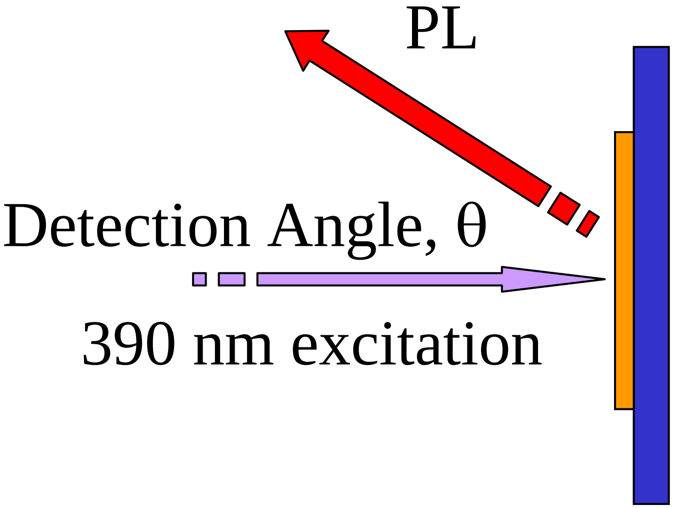

Band Edge Excitation (330 nm)


Mn^{2+} Direct Excitation (390 nm)

Angle Dependent PL Results – ZnS:Mn Inverse Opal

d=225 nm





VI. Conclusions

I. Successful ALD ZnS:Mn infiltration of opals

- Filling fractions close to 100% achieved, calculated using Reflectance
- SEM confirms high quality, conformal coatings

II. Etched silica spheres to form inverted opal

- Resulting inverted opal ~ 3 – 5 microns thick, robust

III. Luminescent Properties

- PL confirms high crystalline quality
- PL shows interesting changes, angle dependence

VII. Future Work

I. Further optimization of ALD process for smaller opals to maximize depth of penetration of high index material

II. Thorough investigation of angular dependence of reflectivity and PL

III. Use ALD to fabricate inverted opals in high-n materials systems, i.e. TiO_2, Fe_2O_3, SnS_2 GaP, etc.

IV. Work on incorporation of “dopant” spheres in opal for microcavity fabrication

VIII. Acknowledgements

Work supported by:

U.S. Army Research Office

- MURI Contract# DAAA19-01-1-0603

Sandia National Laboratories

- Contract # 18499