ZnS-based Photonic Crystal Phosphors Fabricated Using Atomic Layer Deposition

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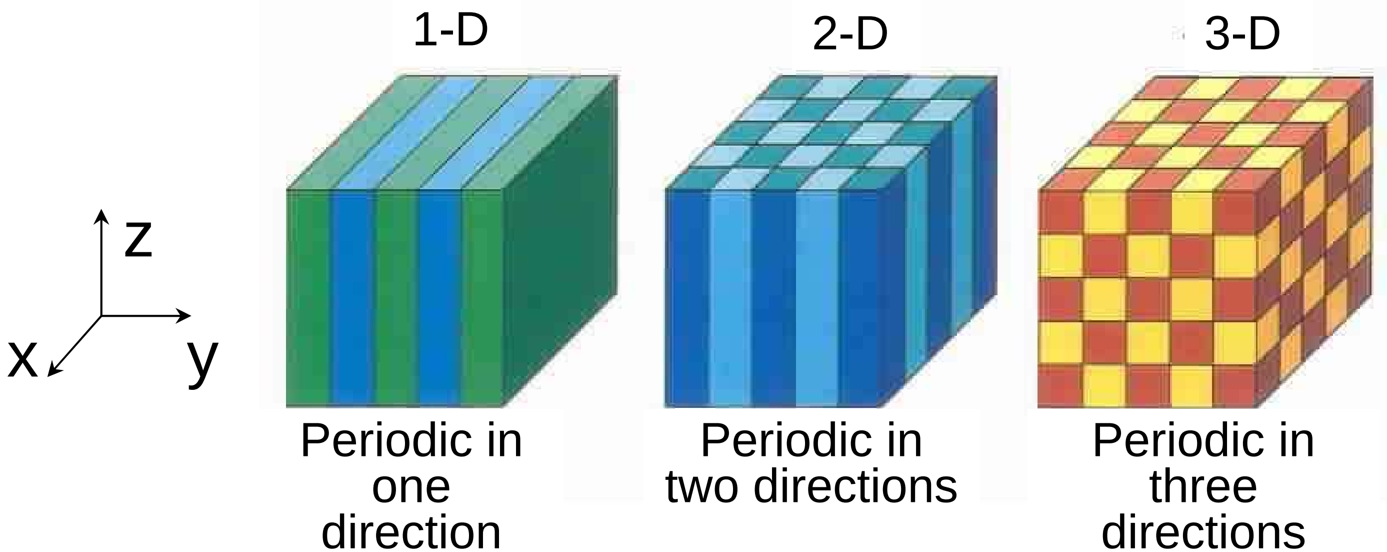
Photonic Crystals



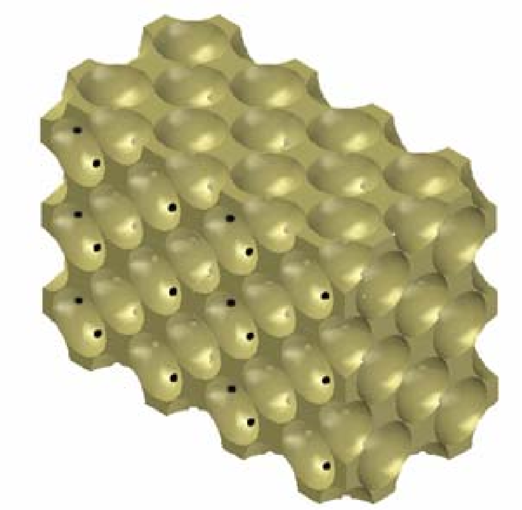
(Joannopoulos)

- Photonic Crystal – Periodic modulation of dielectric constant
- Formation of "Photonic Band Gaps" (PBGs)
- Introduction of "dielectric defects" yield mode within PBG.
- Photonic band gap and associated defect mode are used to create waveguides, resonators, couplers, and filters.
- Luminescent 2D & 3D PC microcavity structures offer the potential for controlling the emission wavelength, efficiency, time response and threshold properties by embedding a defect in a PC structure.(LEDs, Lasers, PC- Phosphors)

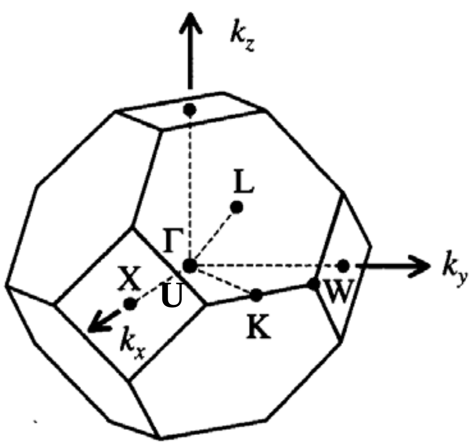
Photonic Crystals

Inverse Opals

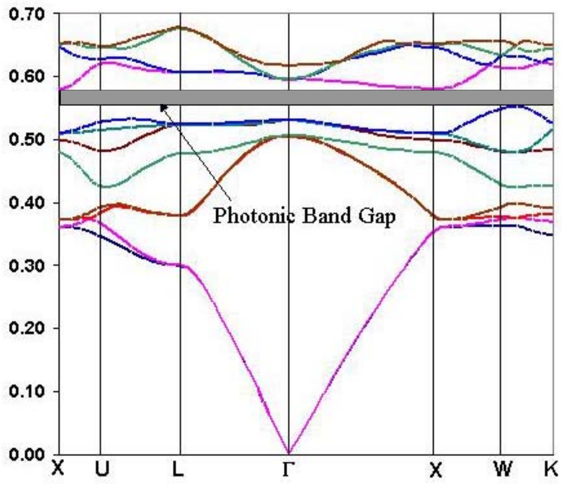
- Inverse Opal- only current experimentally practical 3D structure
- Full PBG requires high refractive index contrast (> 2.8)
- Lattice constant ~ 140-500 nm (visible wavelengths)
- High filling fractions and crystalline quality, conformal coatings
- Dielectric defect = microcavity
- Low optical absorption



Inverse Opal



FCC Brillouin Zone



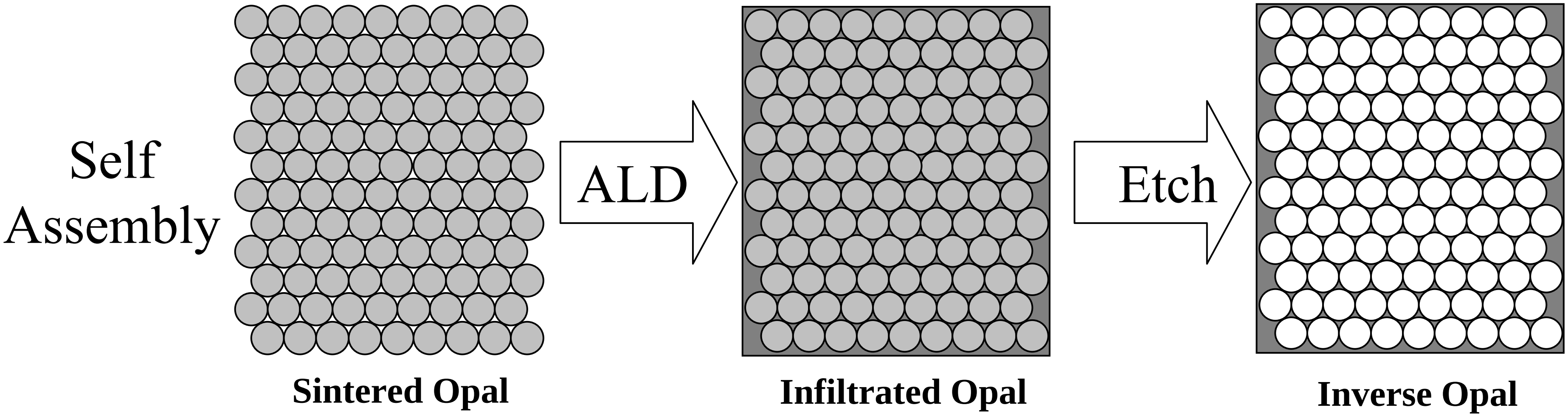
Silicon Inverse Opal

Research Direction

- Use ALD to form infiltrated and inverse opal photonic crystal phosphors.
    - – ALD advantages: monolayer control, conformal, flexible
- Fabricate PC that demonstrates photonic band gap behavior as well as strong photoluminescence.
- Demonstrate PBG effects on emission properties.
- ZnS:Mn used for initial demonstration: well studied ALD material
    - Insufficient index (n~2.5) for full PBG
    - Exhibits pseudo-gap behavior in (111) direction.
- Characterization: SEM, specular reflectance, PL
    - Study impact of band structure on reflectance and PL

Fabrication: Inverse Opal PC

- Provide periodicity using self-assembled film (opal)
  - Sedimentation of monodispersed colloidal SiO_2 in a confinement cell[1] on silicon or quartz substrates, followed by sintering
  - 10 µm thick FCC polycrystalline film, (111) planes parallel to substrate
- Infiltrate interstitial space with high refractive index material (ALD).
- Infiltrate can be a luminescent material to form a PCP.
- Etch SiO_2 spheres, forming inverse opal.

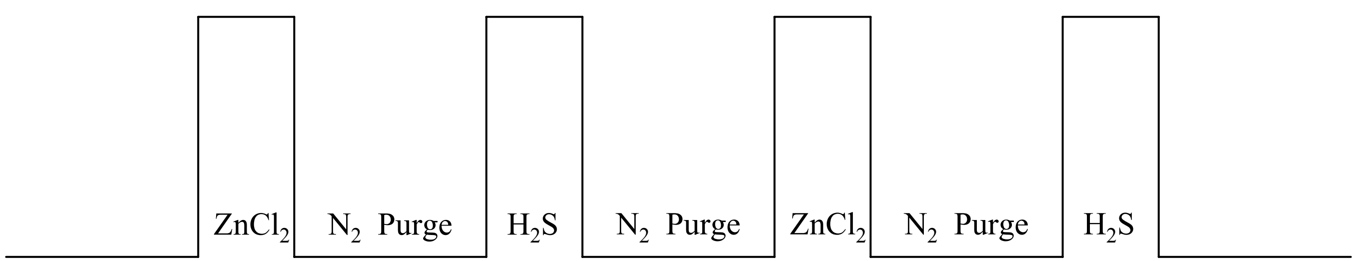


(1) Y. Xia, B. Gates, and S. H. Park, *Journal of Lightwave Technology*, **17** (1999) 1956-1962.

Atomic Layer Deposition

Materials and Growth Conditions

- ZnS:Mn was infiltrated* using alternating pulses of $ZnCl_2$ and H_2S, with a $MnCl_2$ pulse applied every hundredth cycle to dope the film with Mn^{2+} luminescent centers (λ = 585 nm).
- Precursor pulse times, inert gas purge times, and the thickness of the coatings were varied to optimize opal filling.
- 660 ms pulse time, 550 ms purge time, and 500° C substrate temperature were established as optimum conditions.
- Inverse opals were successfully formed by etching with 2% HF.

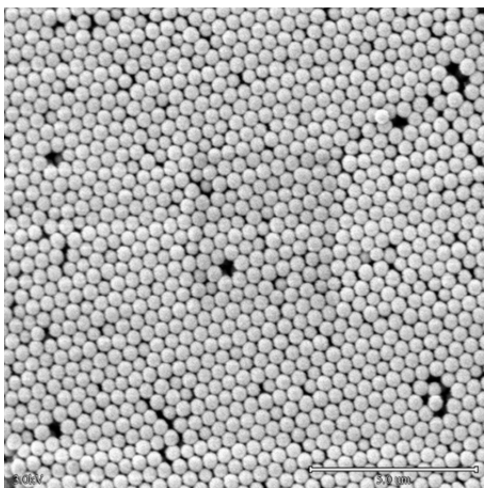


* ZnS depositions performed at US. Army Research Lab, Adelphi, MD

Scanning Electron Microscopy

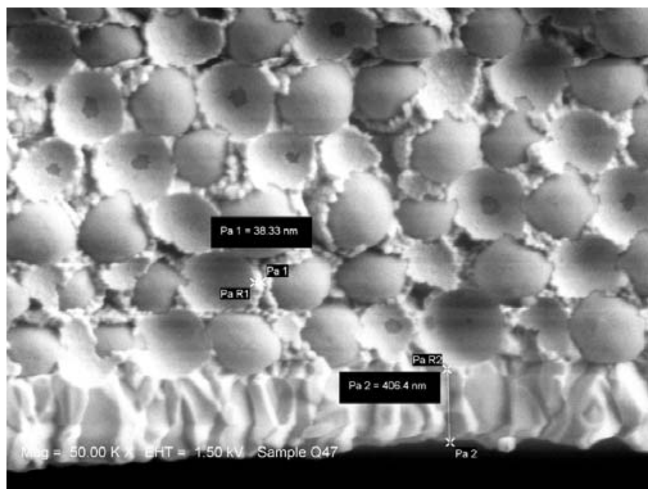
460 nm sintered opal

(111) ⊙



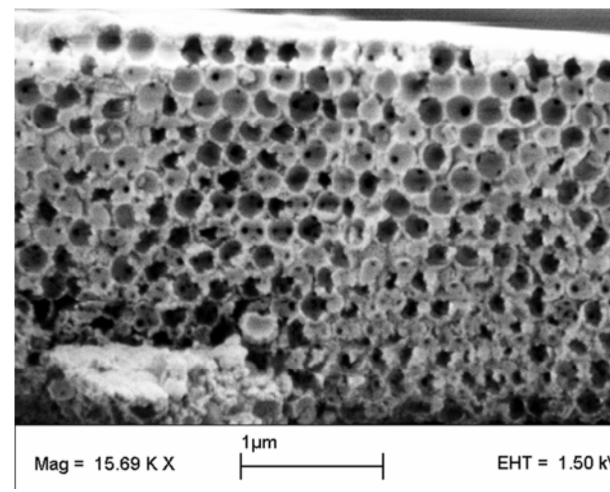
460 nm infiltrated opal

(111) ↑



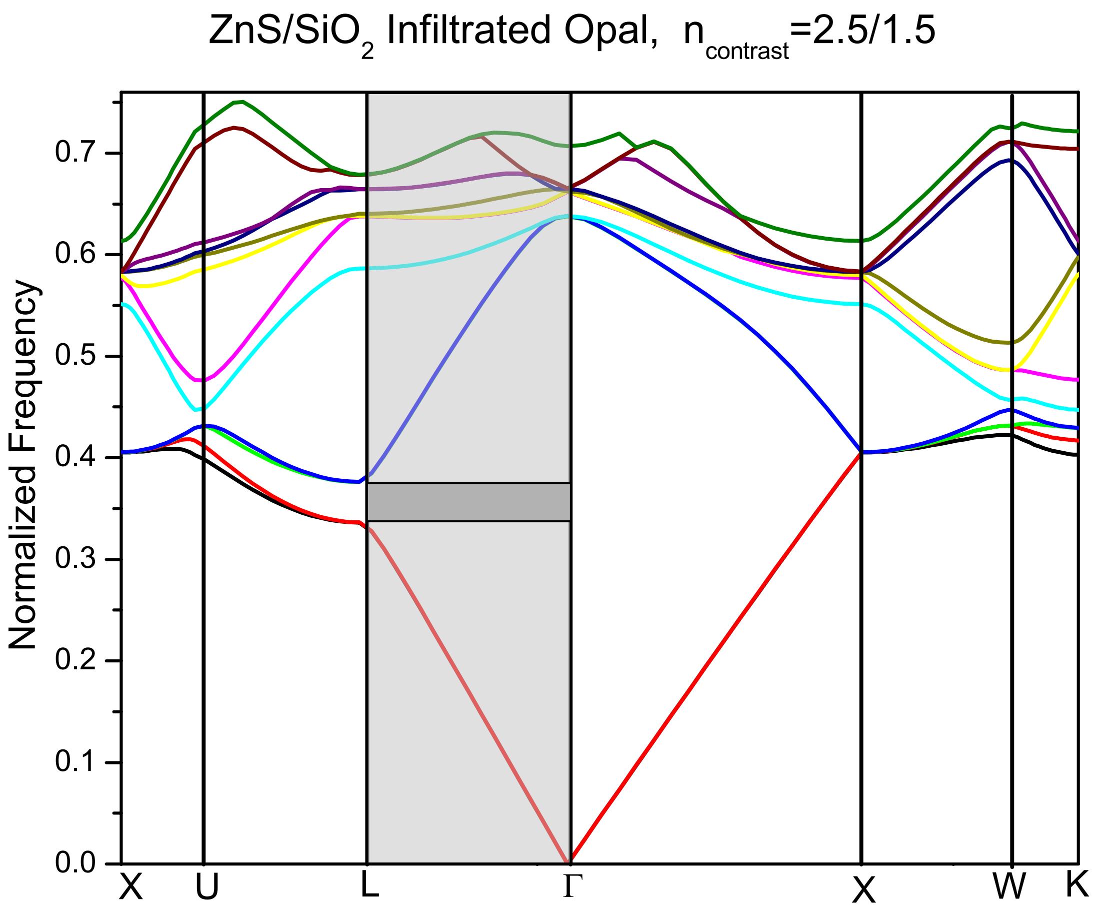
220 nm inverse opal

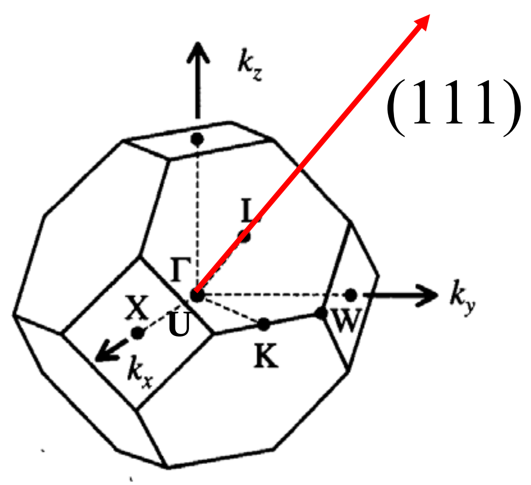
(111) ↑



Specular Reflectance

Band Diagram



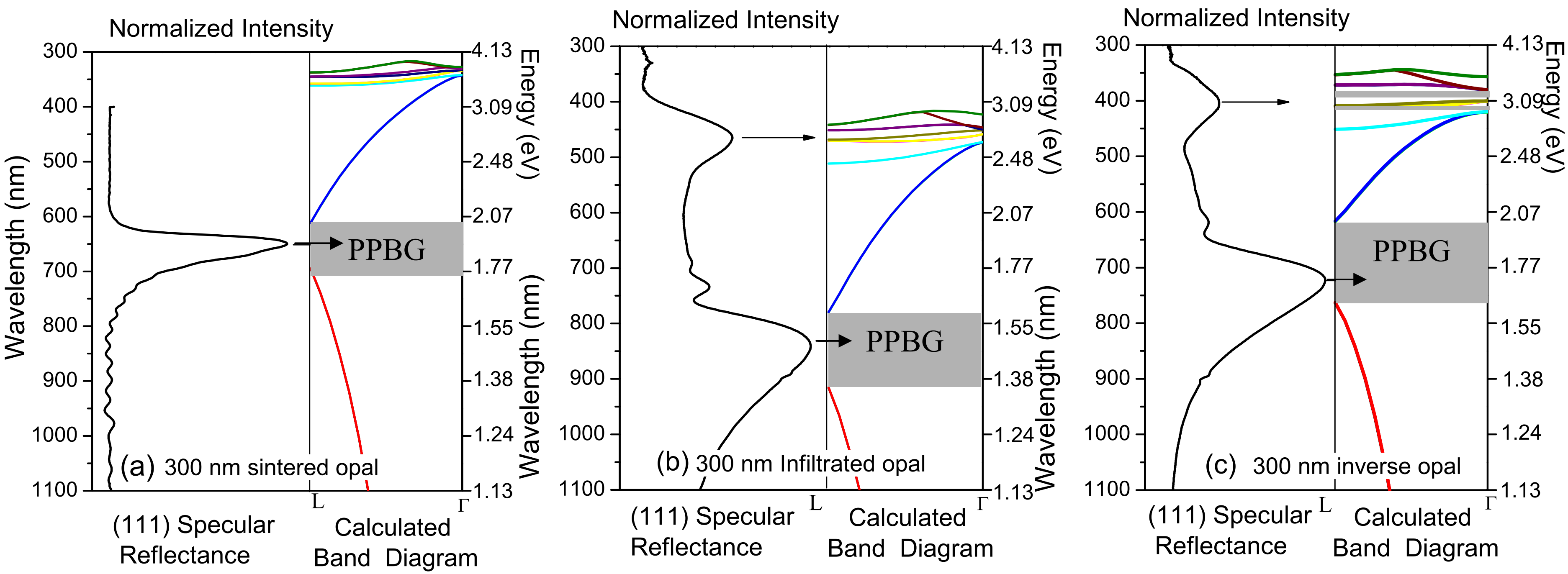


Specular Reflectance
Comparison with Theory

SiO_2 opal $n_{contrast}$= 1.5:1

SiO_2/ZnS:Mn opal $n_{contrast}$=2.5:1.5

ZnS:Mn inverse opal $n_{contrast}$=2.5:1



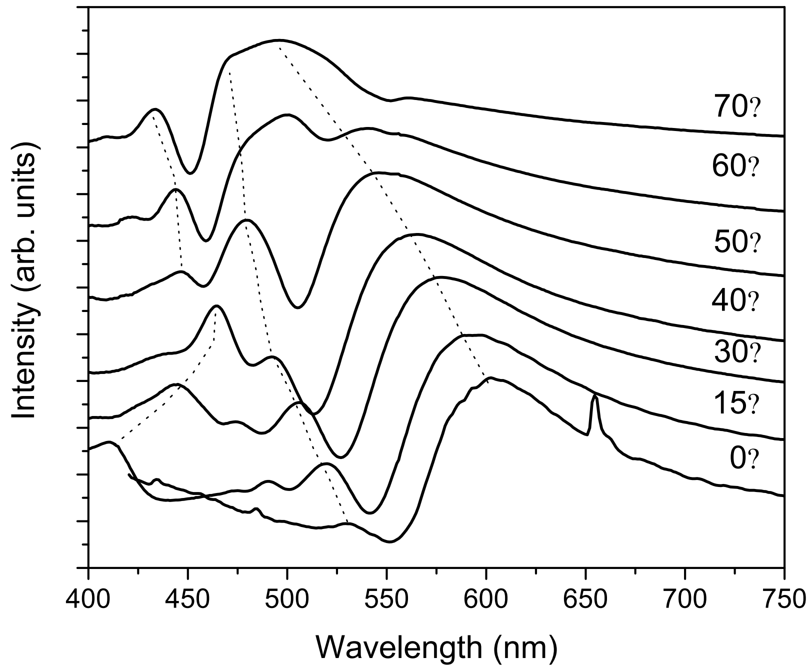
- Reminder: inverse opal full PBG occurs between high energy bands.

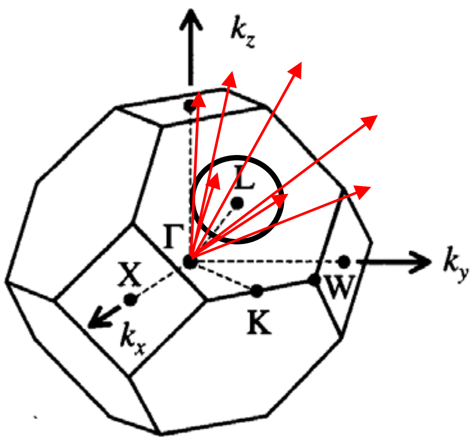
Band diagrams calculated using MIT Photonic Band software package.
(Plane wave expansion method)

Specular Reflectance

Angular Dependence

220 nm $ZnS:Mn/SiO_2$ Opal
Index contrast 2.5/1.5

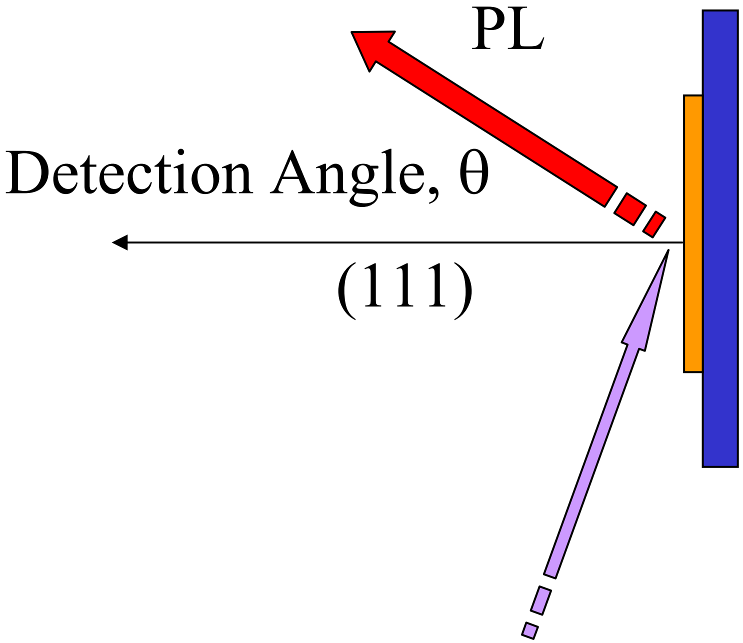




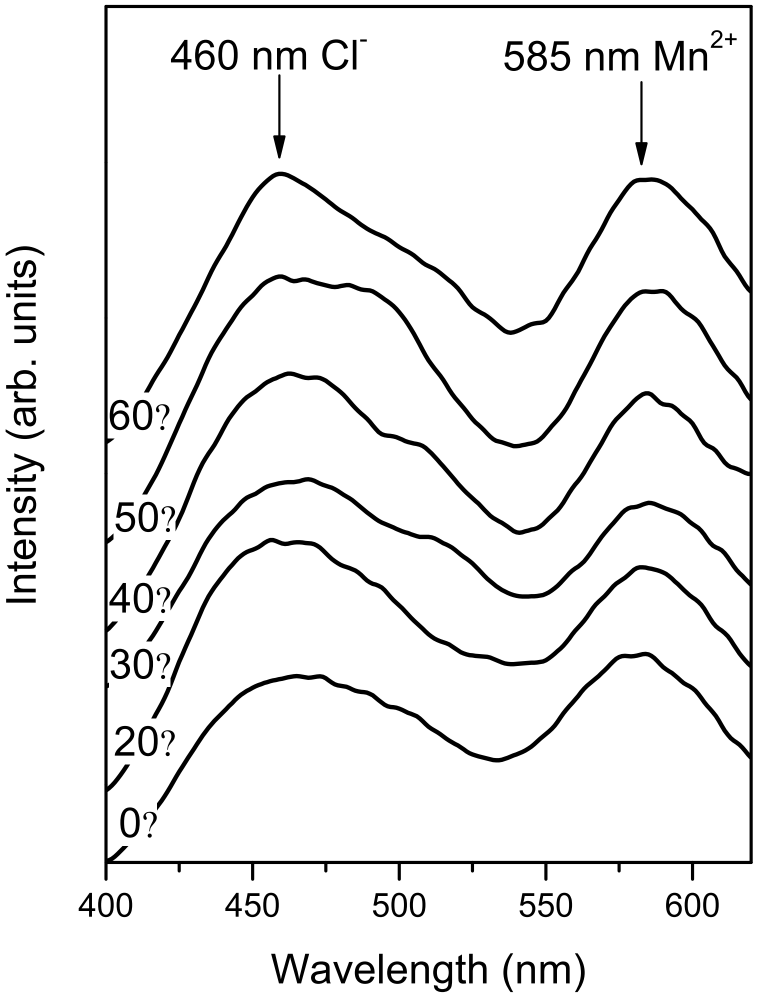
- Polycrystalline films: multiple directions probed.
- Both infiltrated and inverse opals exhibit (111) reflectivity peaks
  - – shift to lower λ as measurement angle increases.
- Confirms existence of PPBGs.
- PPBGs will affect photoluminescence of PCPs.

Photoluminescence

220 nm ALD ZnS:Mn/SiO_2 Opal



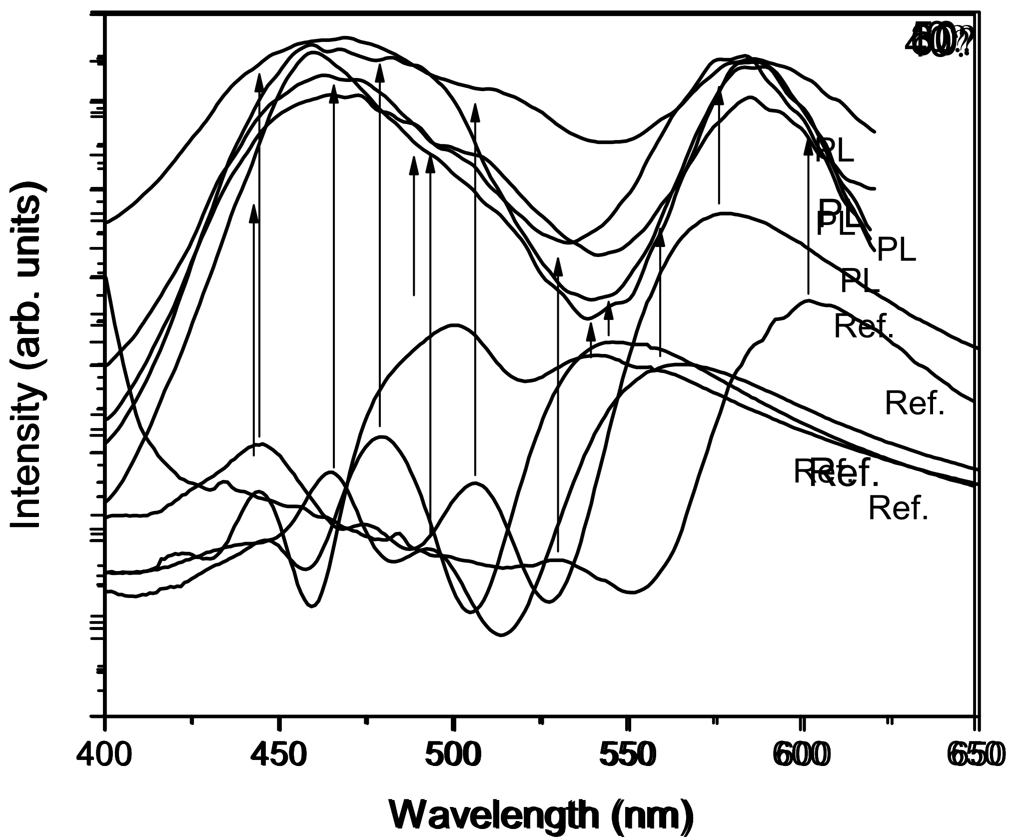
330 nm ZnS band edge excitation
(Xenon Lamp)



Photoluminescence

220 nm ZnS:Mn/SiO_2 Opal

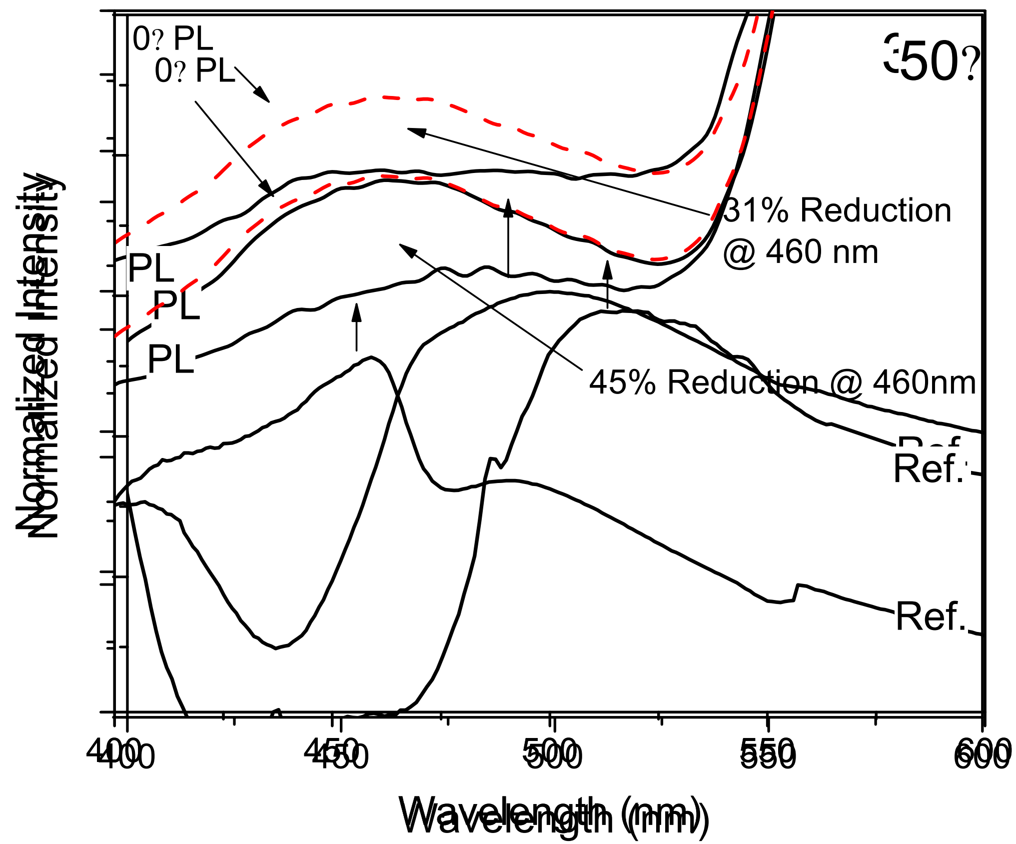
330 nm Excitation



Photoluminescence

220 nm ZnS:Mn Inverse Opal

330 nm Excitation



Summary

- Luminescent PC structures (including microcavity structure) offer potential for control of emission wavelength, efficiency, time response and threshold properties.
- ALD is an effective infiltration method for fabricating inverse opal PCs.
- Pseudo band gap effects have been demonstrated in infiltrated and inverse ZnS-based opal PCPs.
- As a consequence, anisotropic PL has been demonstrated.