Luminescent and Tunable 3D Photonic Crystal Structures

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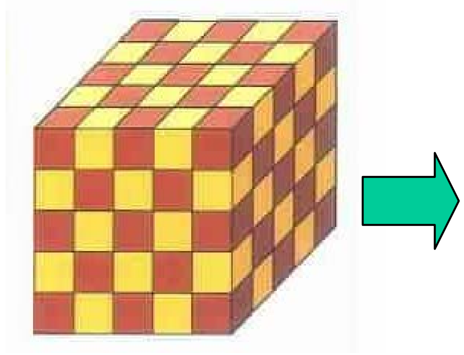
7th Mediterranean Workshop and Topical Meeting
“Novel Optical Materials and Applications”
Cetraro, Italy
May 30th - June 3rd , 2005

Outline

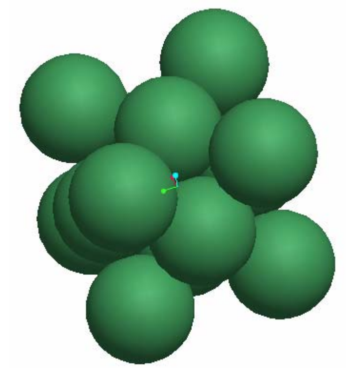
- **Introduction: Photonic Crystals**
  - **- Requirements for highly luminescent materials, PCP**
- **Review of Progress made to get PCP**
  - **Luminescent materials, ZnS:Mn**
  - **Higher Index materials, TiO_2**
  - **Multilayer Combined Infiltrations: ZnS:Mn + TiO_2**
- **Limitations of these structures:**
  - **No Full PBG, Limitations of Geometry**
- **Non-Close Packed Opal Structures**
  - **Theoretical predictions**
  - **Experimental realization**
- **Summary**

Photonic Crystals

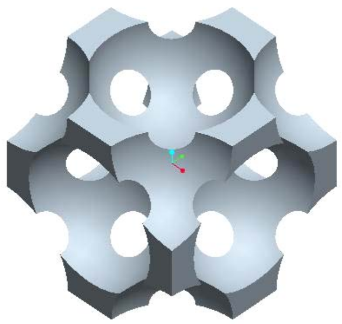
3-D



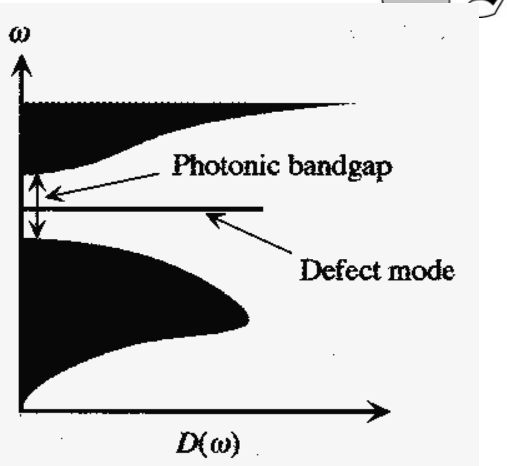
Periodic in three directions



Opal



Inverse Opal



(b) Photonic Crystal

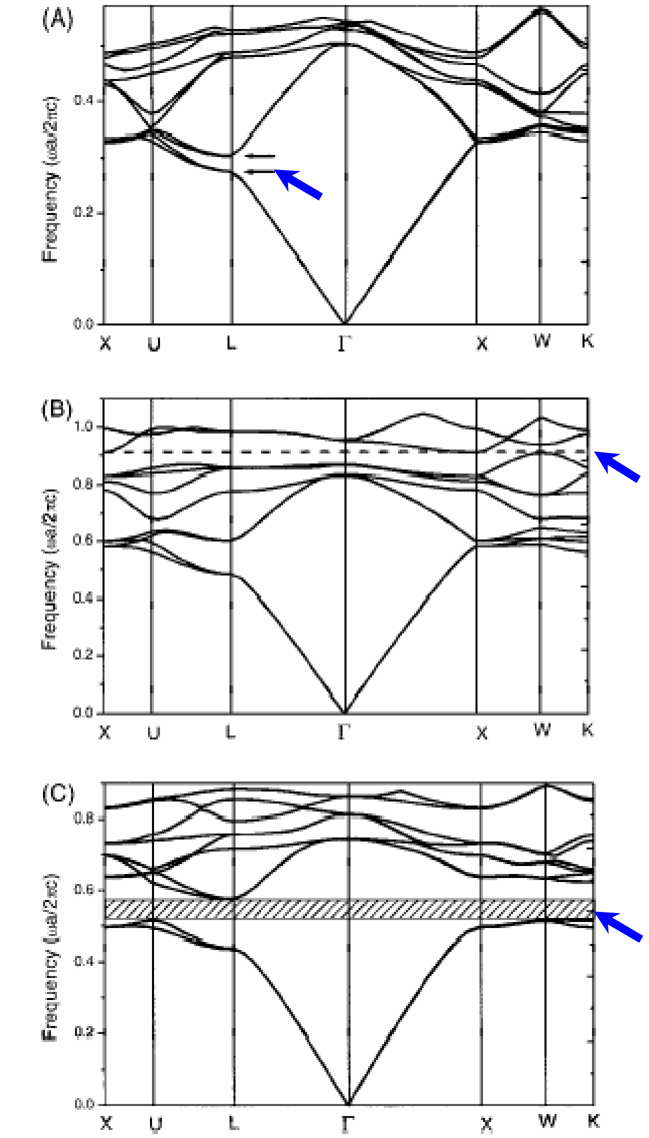
(Sakoda)

- **Photonic Crystal – Periodic modulation of dielectric constant**
- **Formation of Photonic Band Structure and "Photonic Band Gaps" (PBGs)**
- **Properties depend on ω, a, the ratio of dielectric constants and structure**
- **Changing dielectric constant of single "unit" → Dielectric doping (defect mode)**
- **Luminescent 3D PC microcavity structures offer potential for controlling:**

emission wavelength	**efficiency**
time response	**threshold properties**

- **LEDs, Lasers, PC- Phosphors (PCP)**

Band Diagrams: FCC, Inverse FCC, & Diamond-Analog Peanut Structures



- Opal (FCC); Pseudogap between 2nd & 3rd bands
    - High symmetry spherical building block
    - Large filling fraction of high-n material
- Inverse Opal
  - 2.5% band gap between bands 8 & 9
    - High symmetry spherical building block
    - Low filling fraction of high-n material
    - Minimum $n_c = 2.8$
    - Higher PBG if conformal coatings
- Diamond-Analog Peanut
  - >11.2% band gap between 2nd & 3rd bands
    - Minimum $n_c = 2.4$
    - No simple fabrication method
- Chiral and other structures
    - 25% band gap
    - Complex fabrication methods

Challenges for 3D PCPs
(Visible Regime)

Lattice Constant

- Three-dimensional periodic structures difficult to fabricate at the nanometer length scale necessary for operation in visible & near-IR regions

Refractive Index Contrast & Optical Properties

- Few materials with high refractive index, (which leads to PBG effects) and highly transparent and luminescent in the visible region:
  - ZnS n = 2.55 - 2.25
  - TiO_2 n = 3.2 – 2.7, from 400 to 750 nm
  - GaP, SnS_2 and TaN limited coverage in visible

Crystal Structure

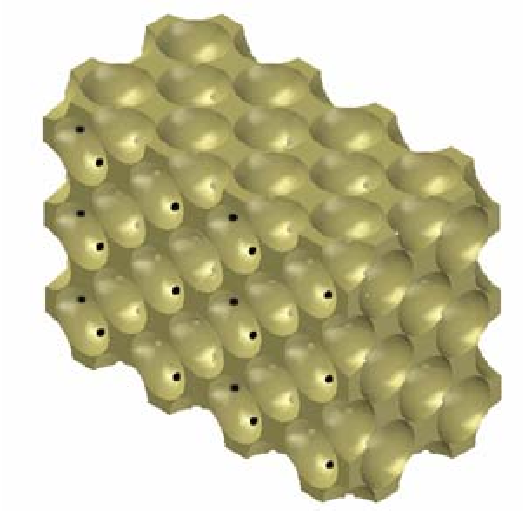
- Diamond structure, calculated to have the widest band gap and best potential for realizing band gap effects, is impossible to form by traditional self-assembly

Filling Fraction of Opals

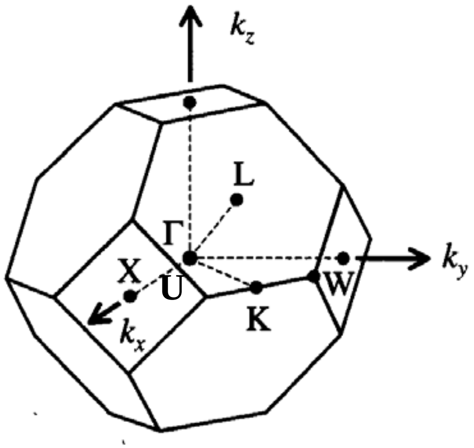
- Optimum structures have low filling fraction of high index material
- Traditional self-assembly of spheres leads to structures with maximum 26% air
- Inverse opals have high index contrast and low filling fractions ~ 74% air

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 (for visible wavelengths)**
- **High filling fractions & crystalline quality, conformal coatings required**

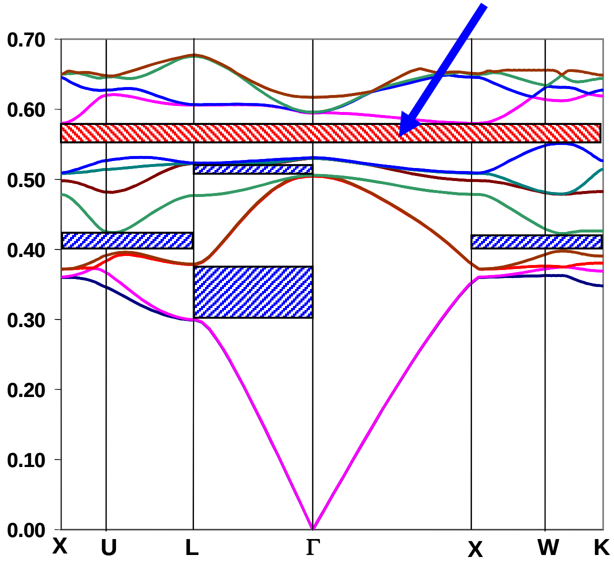


Inverse Opal



FCC Brillouin Zone
Optically: probe Γ-L direction

Full Photonic Band Gap



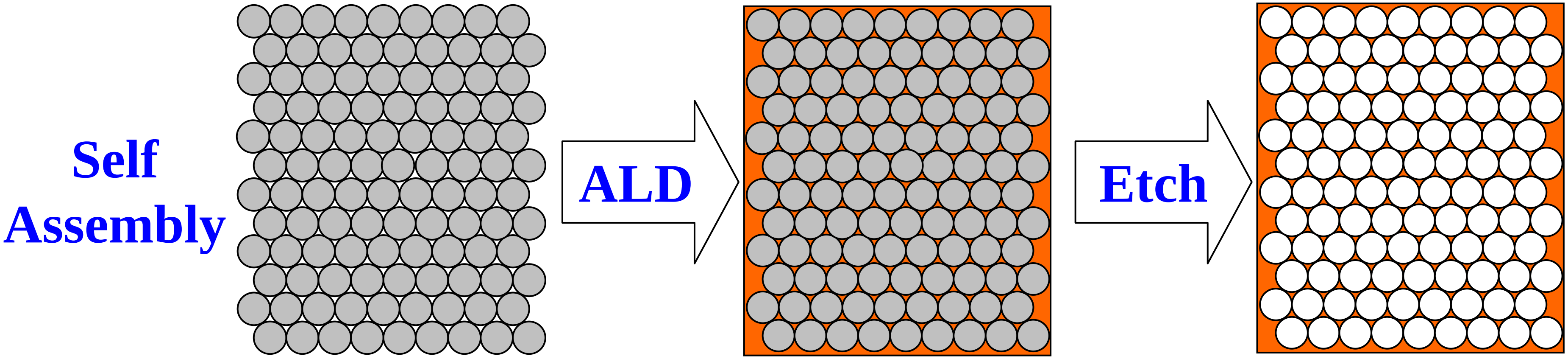
Silicon Inverse Opal
$n_c = 3.46$

Fabrication Objectives

- **Use ALD to form infiltrated & inverse opal photonic crystal phosphors.**
  - Demonstrate PBG and its effects on emission properties.
- **ALD advantages: monolayer control, conformal, flexible**
- **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
- **Investigate TiO_2 to form PBG, transparent, $n > 3.0$ for $\lambda < 450$ nm**
- **Combine ZnS:Mn & TiO_2 into multi-layer films, luminescence & PBG**
- **Characterization: SEM, specular reflectance, PL**
  - Study impact of band structure on reflectance and PL
- **Investigate modifications to Inverse Opals to enhance performance**
  - Photonic band width, tuning, etc

Inverse Opal Fabrication: Infiltration with ALD

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



Self Assembly

ALD

Etch

Sintered Opal

Infiltrated Opal

Inverse Opal

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

Atomic Layer Deposition

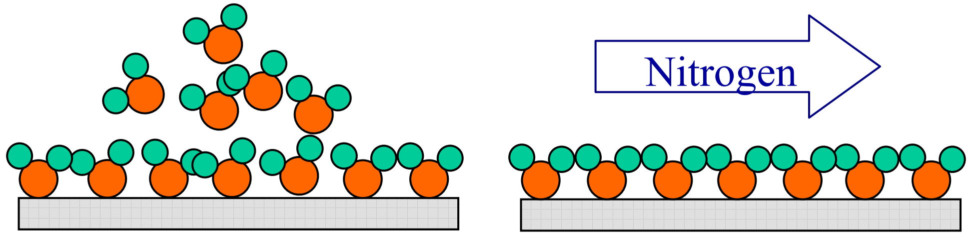
- Thin film surface-controlled growth technique that uses sequential application of reactants to promote monolayer-by-monolayer growth – very conformal coverage

ALD Growth of ZnS:Mn

● Zn^{2+} ● S^{2-} ● H^{+} ● Cl^{-}

(a) $ZnCl_2$ ($MnCl_2$) pulse: several monolayers adsorb on substrate

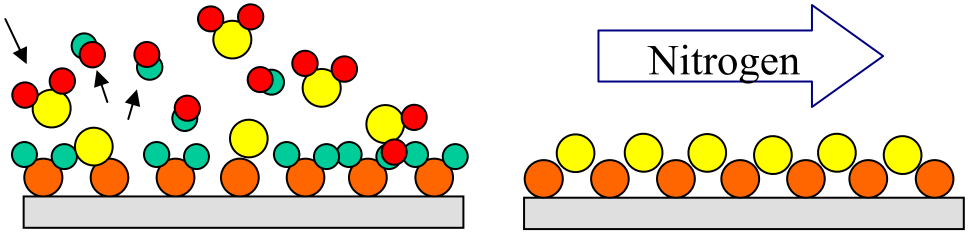
(b) N_2 purge: excess reactant desorbs, monolayer remains



(a) $ZnCl_2$ Pulse (b) N_2 Purge

(c) H_2S pulse: reacts w/ $ZnCl_2$ forming ZnS

(d) N_2 purge: removes excess H_2S, and HCl



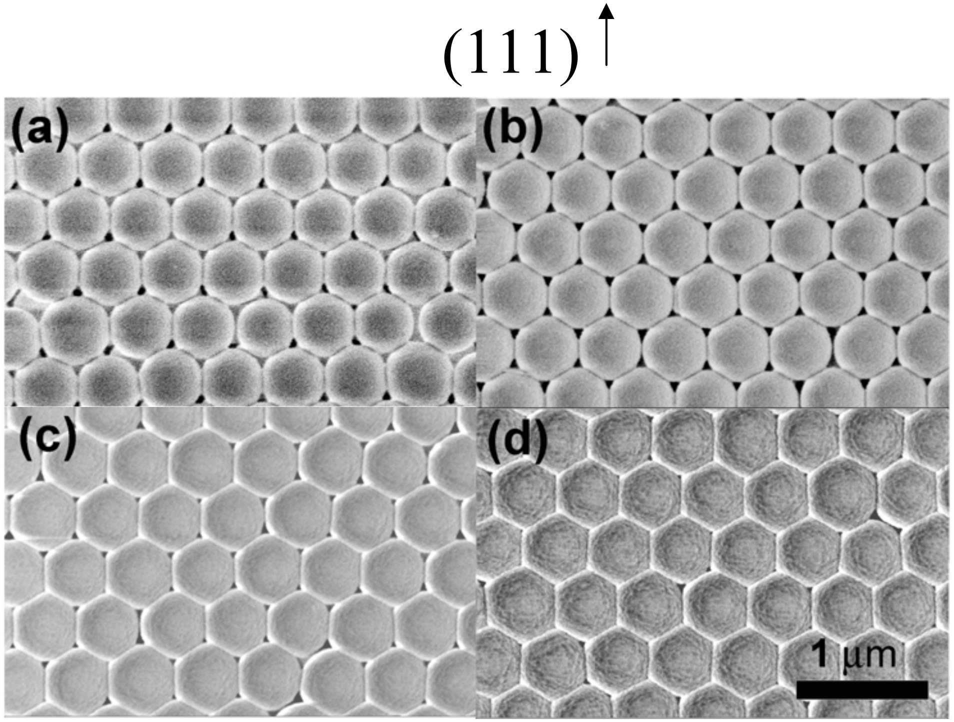
(c) H_2S Pulse (d) N_2 Purge

- Similar Process for TiO_2: using $TiCl_4$ and H_2O, Applicable to semiconductors, oxides & metals

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

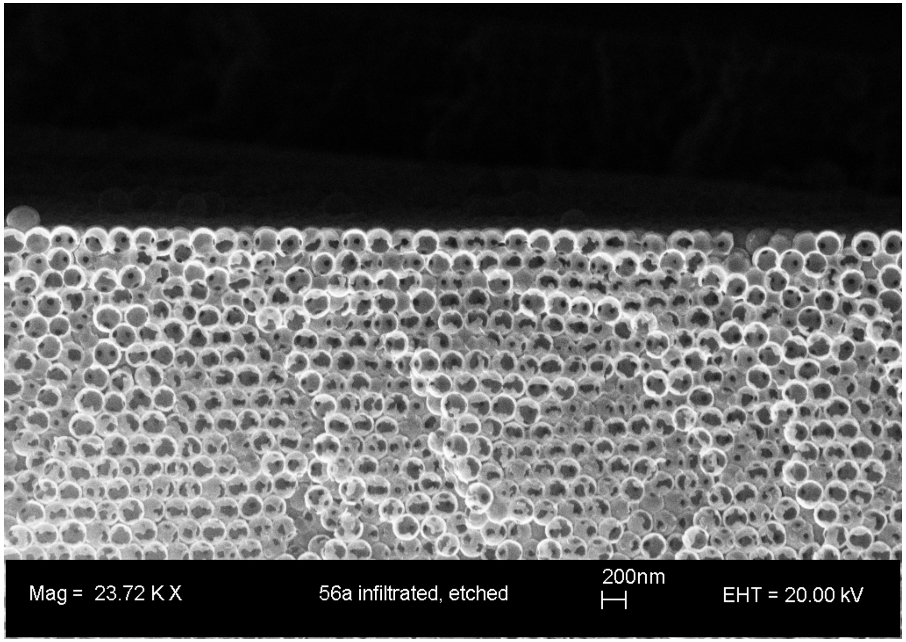
Scanning Electron Microscopy:

ALD of ZnS:Mn



446 nm opal infiltrated with ZnS:Mn at 500°C.

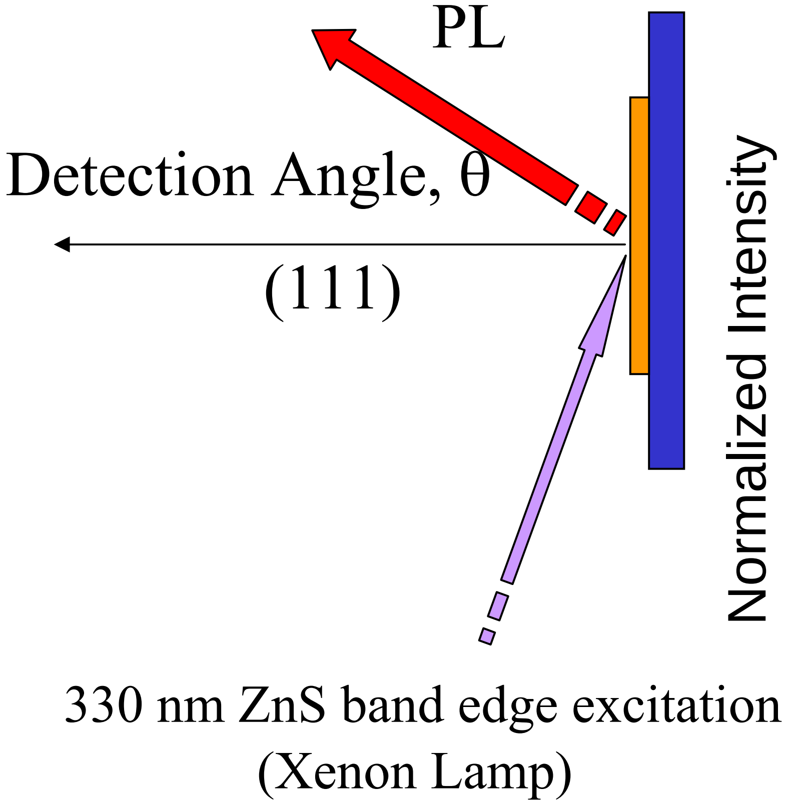
SEM images of (111) surface of SiO2 466 nm opals after infiltration with (a) 2.5, (b) 5, (c) 10, and (d) 20 nm of ZnS:Mn.



220 nm ZnS inverse opal deposited at 500°C

X-ray data confirmed material composition: - grain sizes 2 – 5 nm

Photoluminescence Modification
466 nm ZnS:Mn/SiO$_2$ Opal

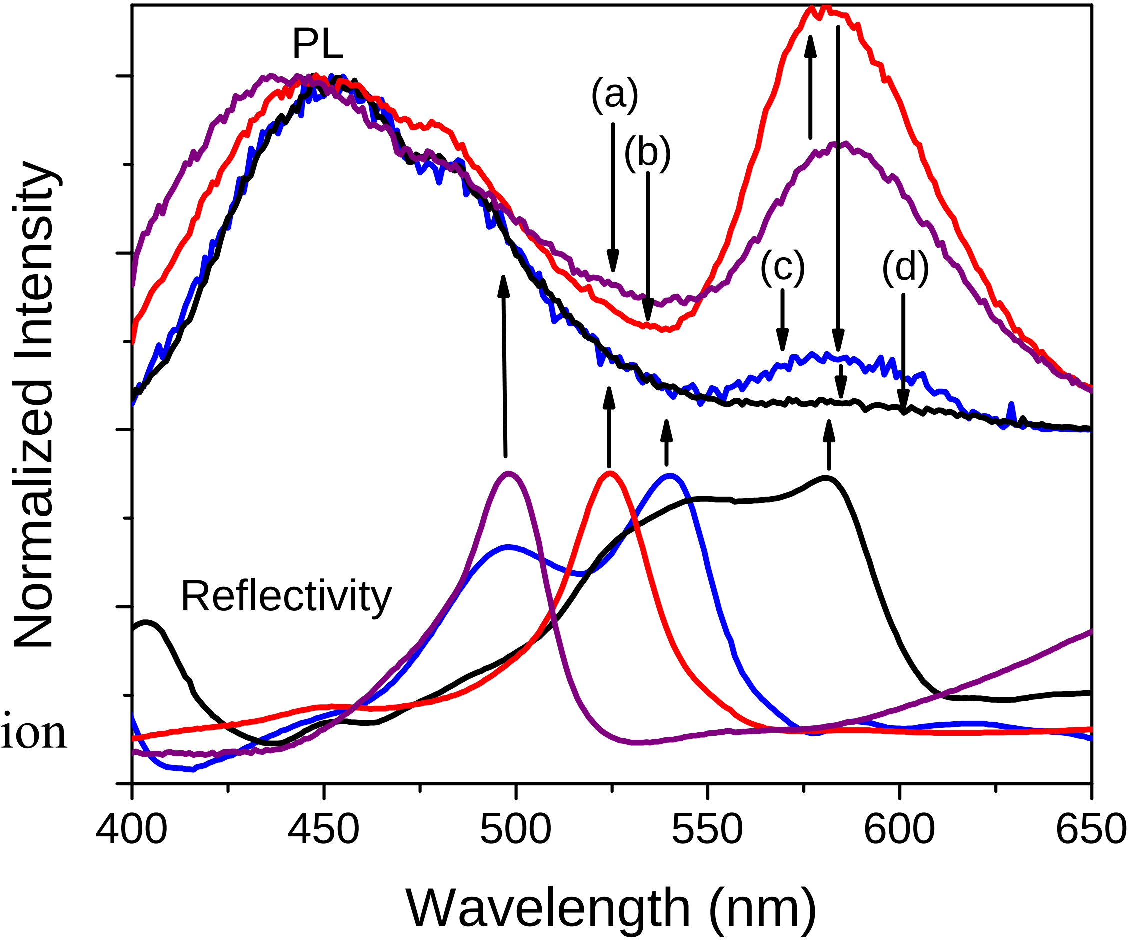


PL

Detection Angle, θ

(111)

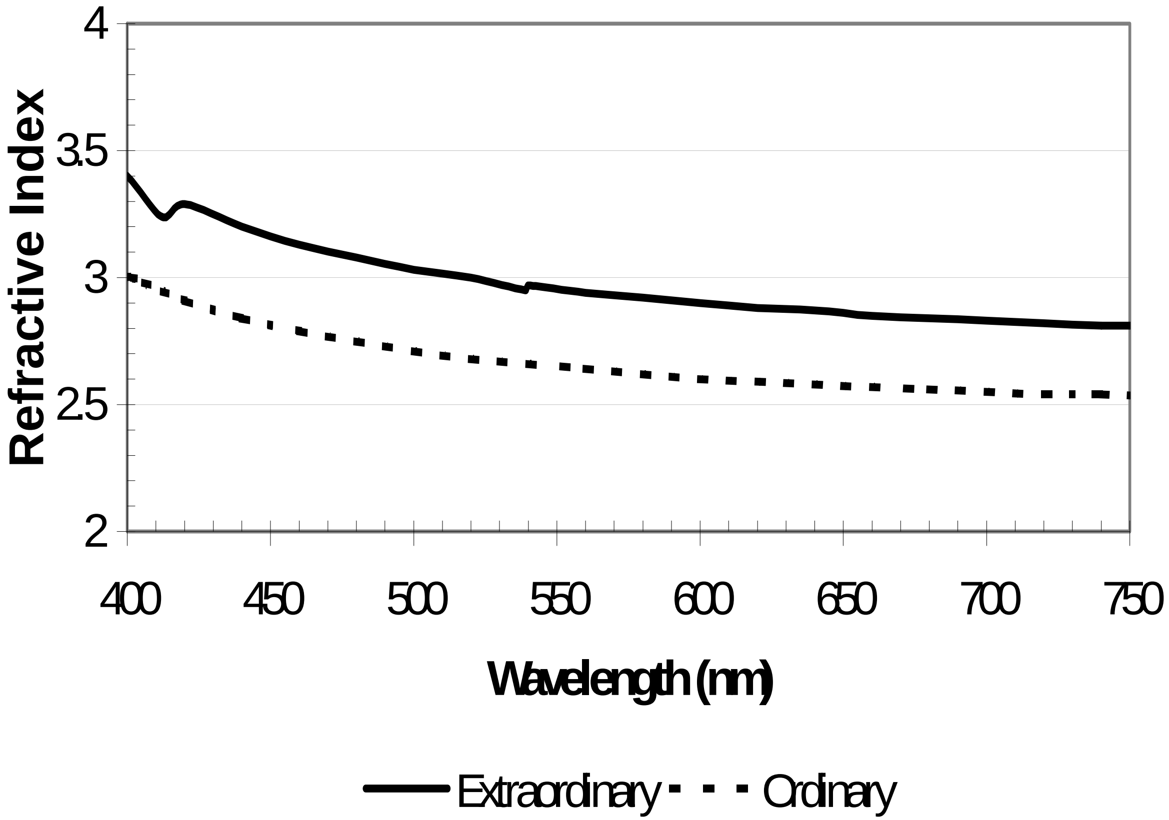
330 nm ZnS band edge excitation
(Xenon Lamp)



- 466 nm ZnS opal infiltrated with 2.5, 5.0, 10.0 and 20.0 nm of ZnS

Properties of TiO_2

- Titania: one of few materials that meets both refractive index and transparency requirements for the existence of a full-PBG in the inverse FCC structure



Polymorphs of titania

Brookite – index 2.3

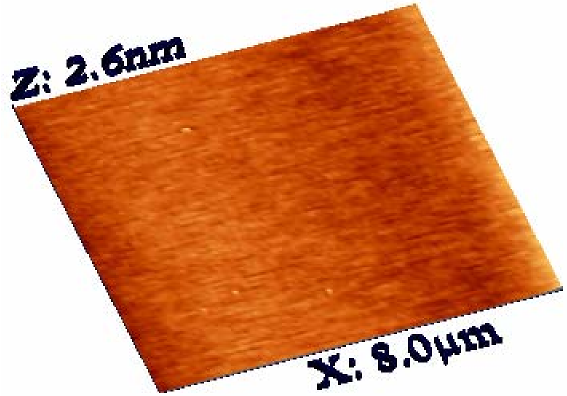
Anatase – index 2.65

Rutile → high temp, high index polymorph >2.9 for wavelengths shorter than 450 nm

Refractive Index versus Wavelength for Rutile Structure

Thin Film Growth: Film Morphology – AFM

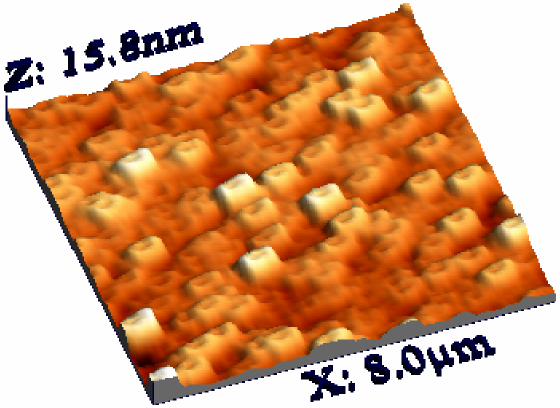
- Growth of polycrystalline films result in surface roughening, which increases with increased deposition temperature.
- Surface roughness prevents direct high temperature ALD in opals.



100ºC

$r_{RMS} = 0.2$ nm

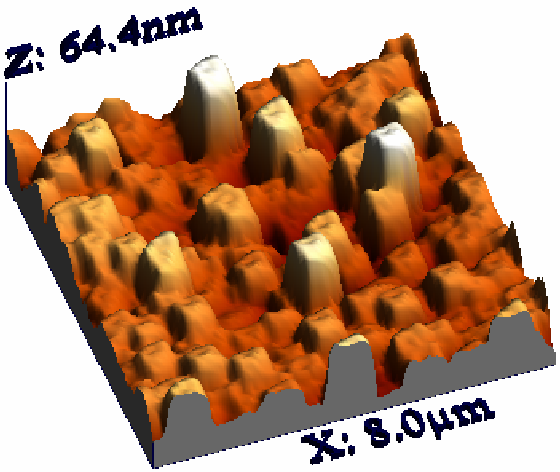
Amorphous



300ºC

$r_{RMS} = 2.1$ nm

Anatase



600ºC

$r_{RMS} = 9.6$ nm

Anatase/Rutile

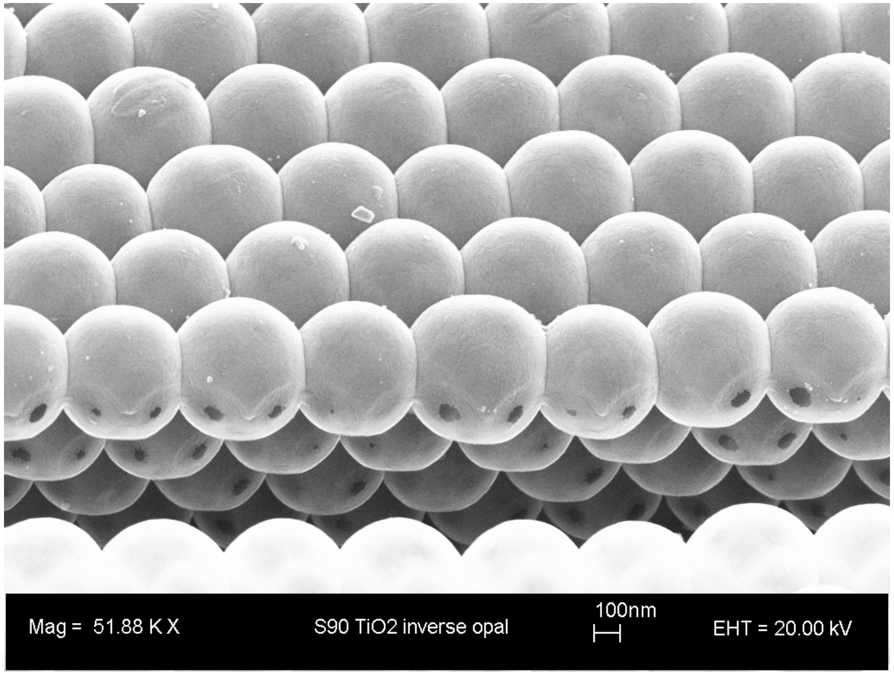
AFM images acquired with a Park Instruments Inc. CP Autoprobe and processed with WSxM 3.0 from Nanotec Electronica S.L.

TiO$_2$ Thin Film Growth: Summary

- Growth at 100ºC
  - Amorphous film
  - Lowest surface roughness: ~0.2nm
  - ***Produces the most conformal films***
- Growth at 300ºC
  - Anatase crystal structure
  - Growth rate reaches saturation at pulse lengths <150ms
- Growth at 600ºC
  - Inconsistent film quality despite uniform growth rate
  - Anatase/Rutile Mixed Phase --- from 29 to 78%
- ***Low temp ALD deposition followed by 400-500 C/2 hr anneal***
  - ***Smooth films with higher index -- mixed Anatase/Rutile phases***

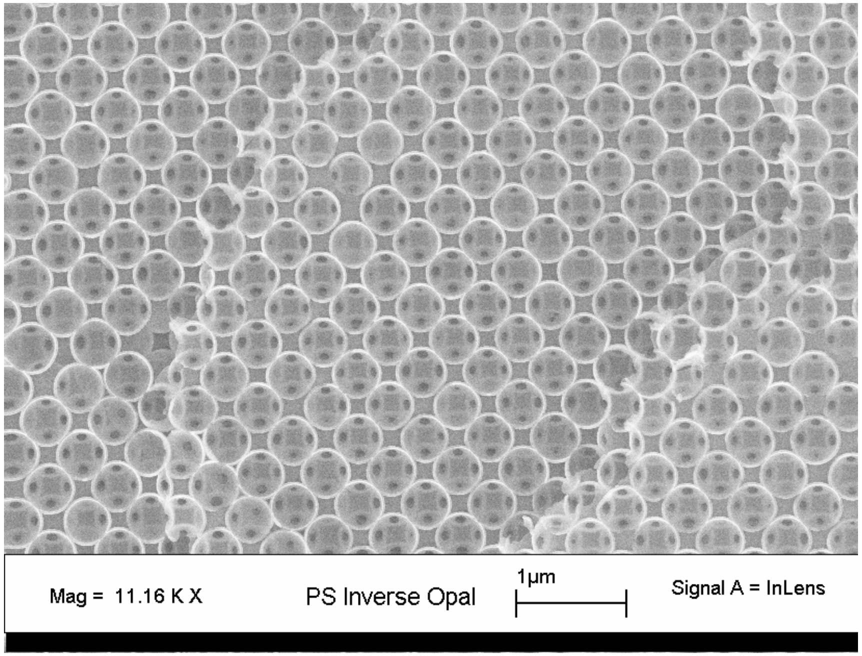
Scanning Electron Microscopy: Low Temperature ALD of TiO_2

(111) Angled plane



466 nm opal fully infiltrated with TiO_2 grown at 100 C

(100) plane

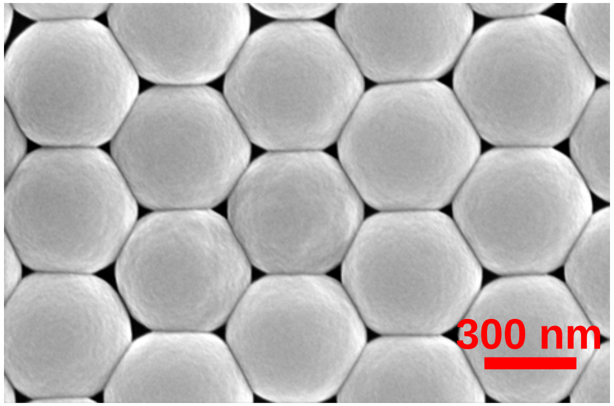


470 nm TiO_2 inverse opal formed on PS at 80 C

TiO_2 infiltration at <100ºC + anneal, produces very smooth conformal surface coatings

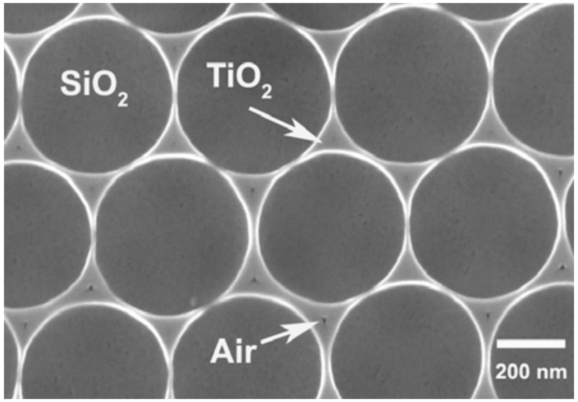
Scanning Electron Microscopy: Low Temperature ALD of TiO_2

(111) ⊙

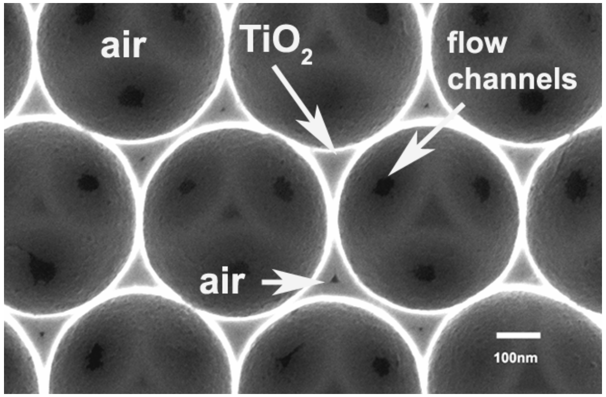


433 nm opal infiltrated with 20 nm of TiO_2

Cross-sections



433 nm opal infiltrated with TiO_2



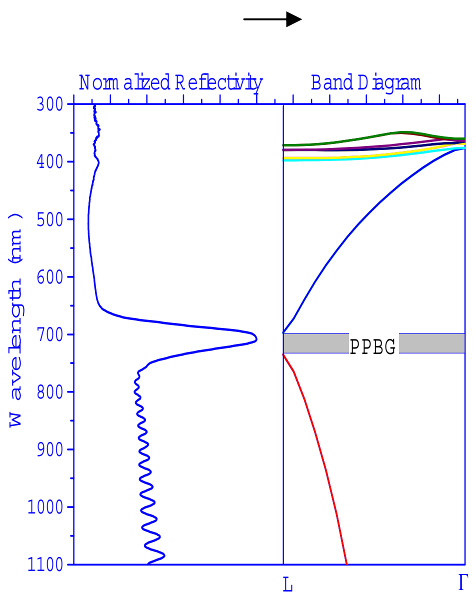
433 nm TiO_2 inverse opal

TiO_2 infiltration at 100ºC produces very smooth and conformal surface coatings.

Specular Reflectance: Agreement with Theory

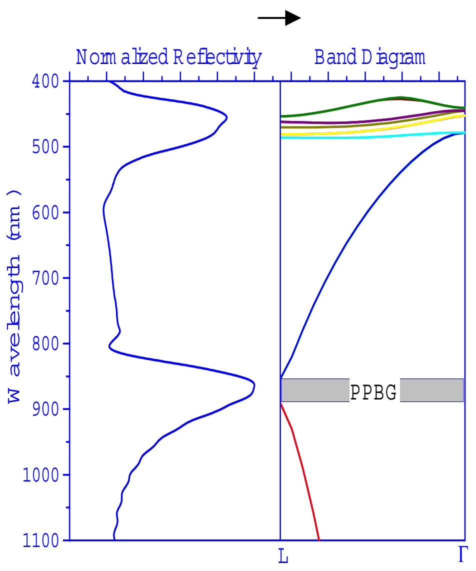
SiO_2 opal

$n_{contrast}$= 1.46:1



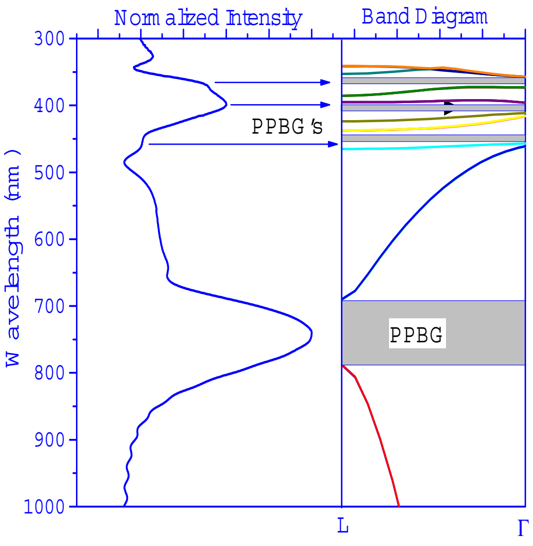
SiO_2/TiO_2 opal

$n_{contrast}$=2.5:1.46



TiO_2 inverse opal

$n_{contrast}$=2.6:1

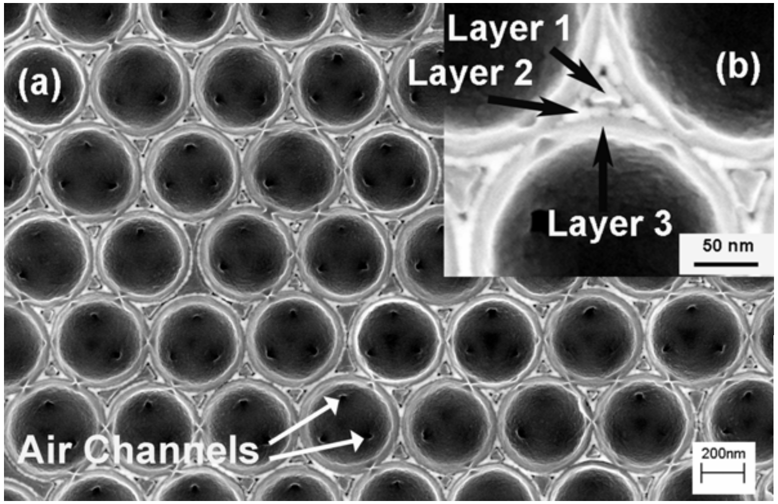


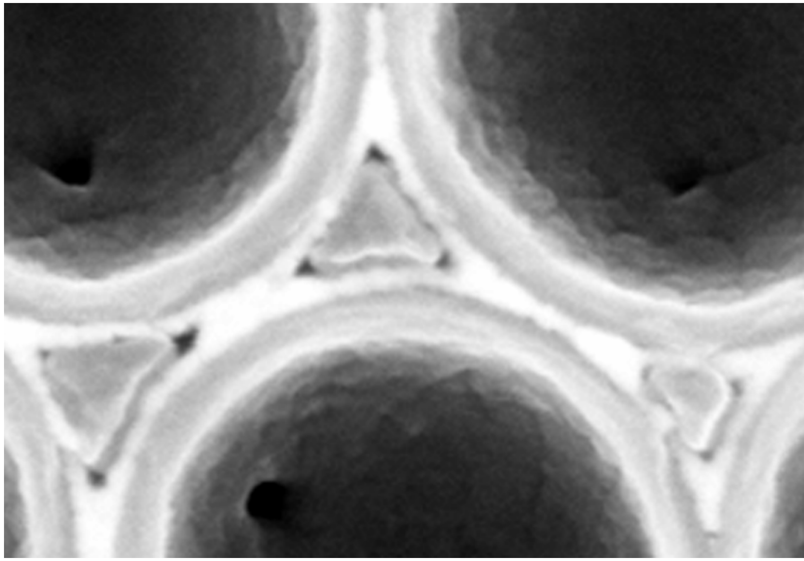
- Inverse opal full PBG occurs between high energy bands.
- Shift of PPBG indicates ~95% infiltration.

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

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

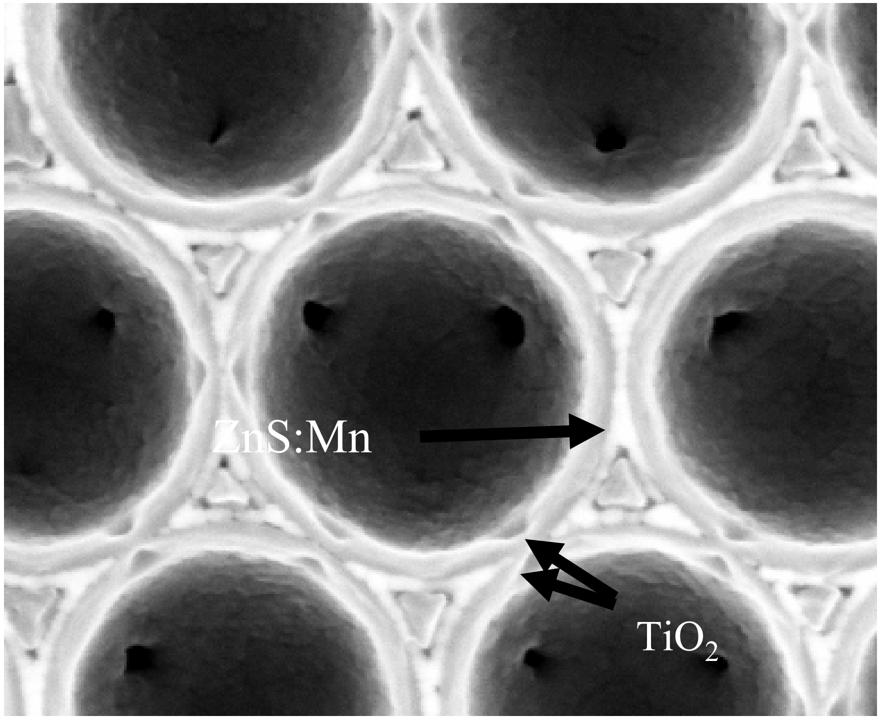
- SEM of $TiO_2/ZnS:Mn/TiO_2$ inverse opal, and (b) high magnification of layered region

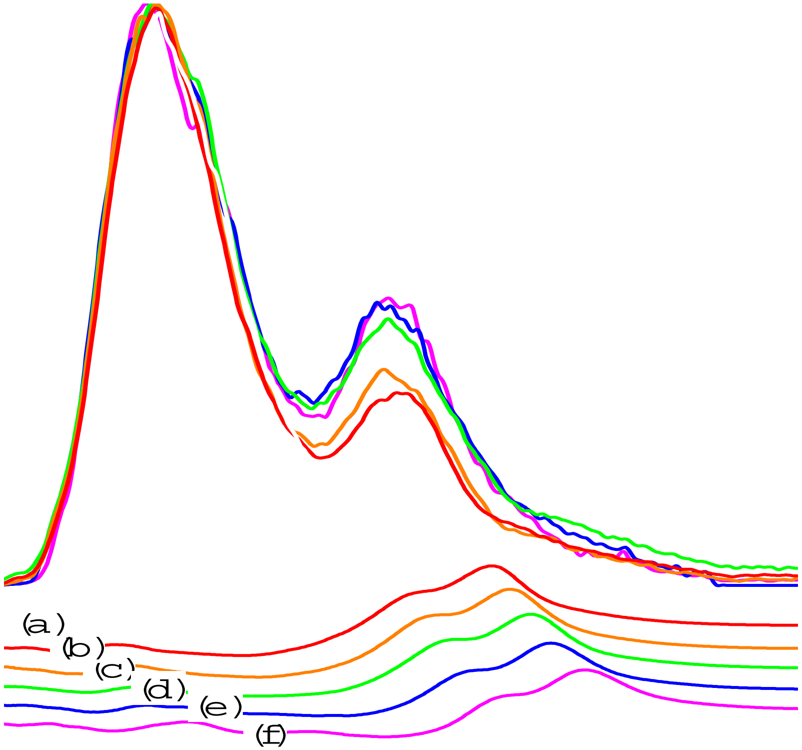




- 330 nm sphere size

Luminescent & Tunable Multi-Layered Photonic Crystals





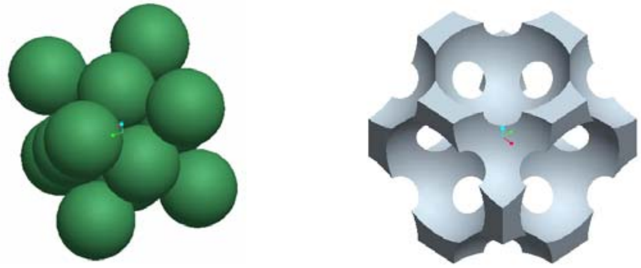
- Change in PL spectrum as “Back-fill” with additional layers of TiO_2
    - Thicknesses of ~ 1, 2, 3, 4 and 5 nm
- ***Photoluminescence intensity increases by 108%***

Photonic Crystal Phosphors: Summary

- Achieved fabrication objectives:
  - Luminescent ZnS:Mn inverse opals fabricated by ALD
    - *Photonic Crystal Phosphor!*
  - High index ultra-smooth TiO_2 inverse opals fabricated by ALD
  - Multi-layer inverse opals fabricated by combining ALD of ZnS:Mn and TiO_2
  - *Independent control of refractive index and luminescence*
  - Modification of luminescence with high-order photonic bands
  - Controlled ALD allowed 108% tuning of luminescence intensity from a multi-layer PCP
- Still small to no full photonic band gap
- Limited volume available for infiltration
- *Need new structures & geometries for improved & tunable devices!*

New Structures:
Non-Close Packed Inverse Opals

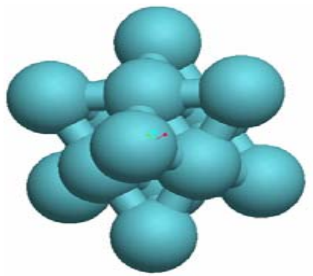
Close-packed structures



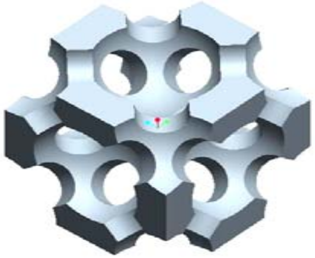
Non-close-packed structures

(Busch & John, PRB (1998)

Doosje et al., J. Opt. Soc. Am. B, V17,(2000))



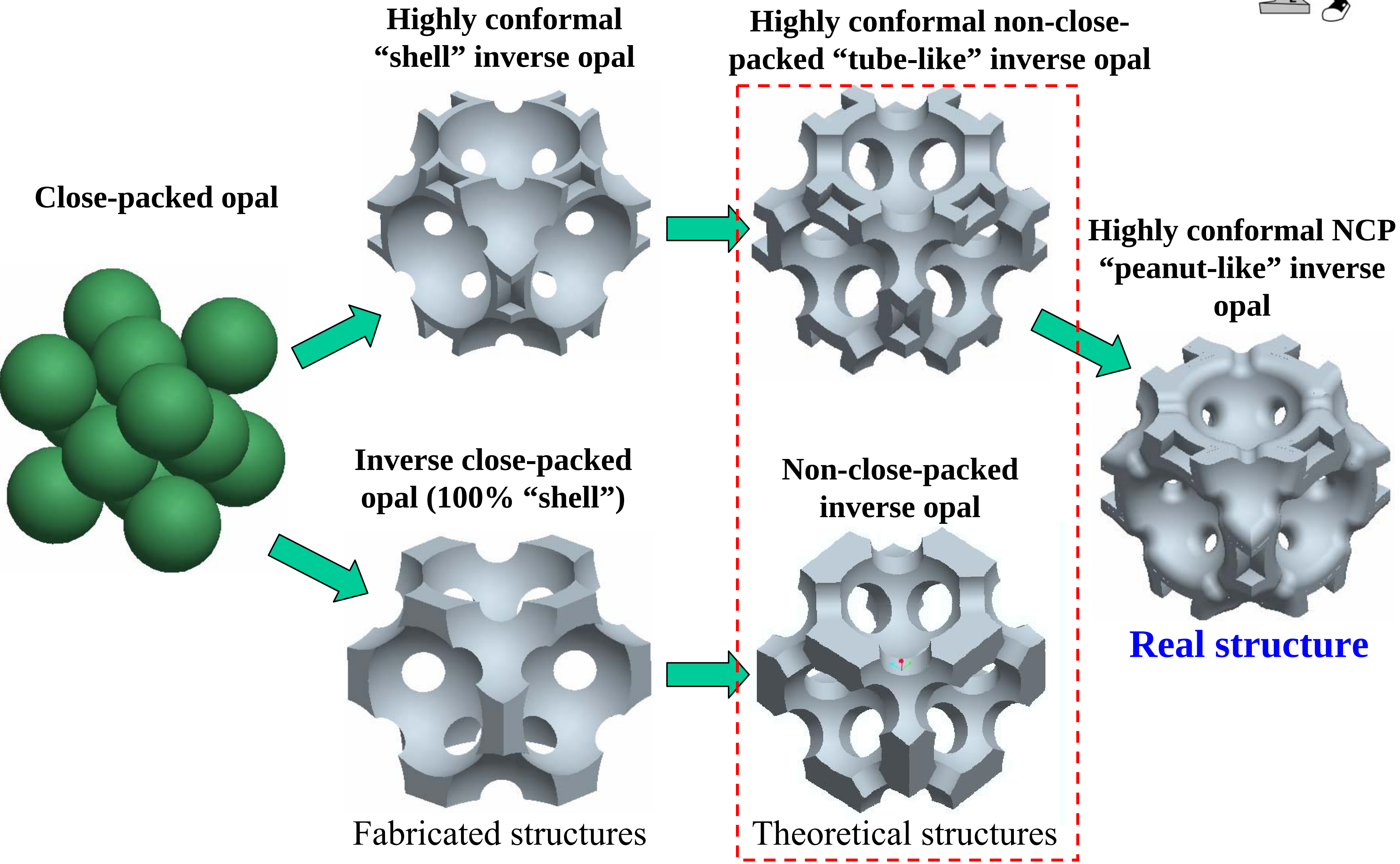
Air network in an
inverse NCP opal



Dielectric network in
an inverse NCP opal

- **NCP:** 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.**
  - Increase in PBG with Rc
  - Reduced refractive index requirement to form PBG

3D Opal-Based NPCs



Close-packed opal

Highly conformal "shell" inverse opal

Inverse close-packed opal (100% "shell")

Highly conformal non-close-packed "tube-like" inverse opal

Non-close-packed inverse opal

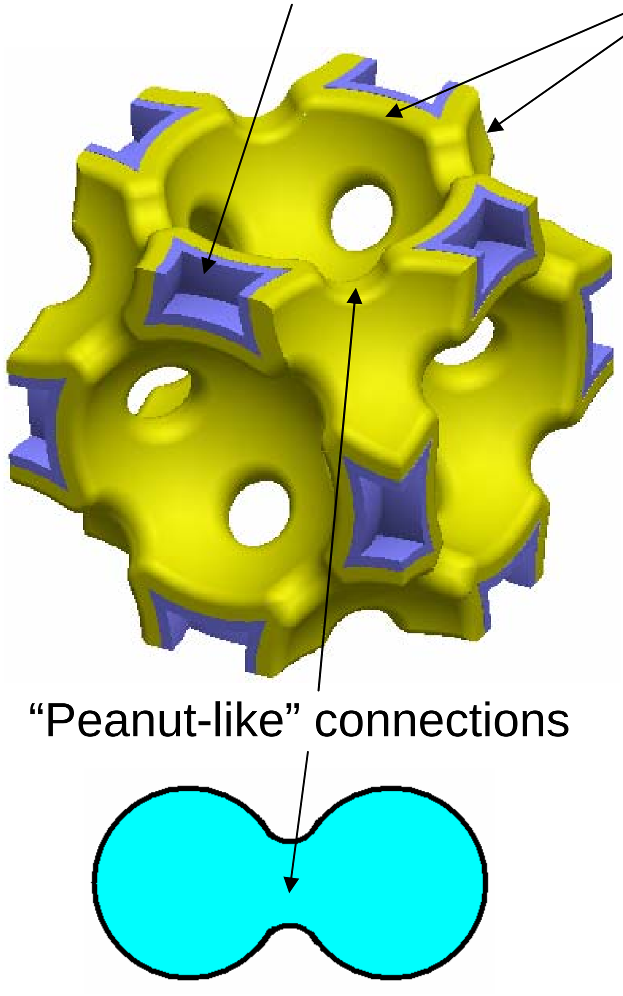
Highly conformal NCP "peanut-like" inverse opal

Real structure

Fabricated structures

Theoretical structures

Highly Conformal Non-Close-Packed "Peanut-Like" Inverse Opal



Initial Inverse Backbone

Backfilled Layer

"Peanut-like" connections

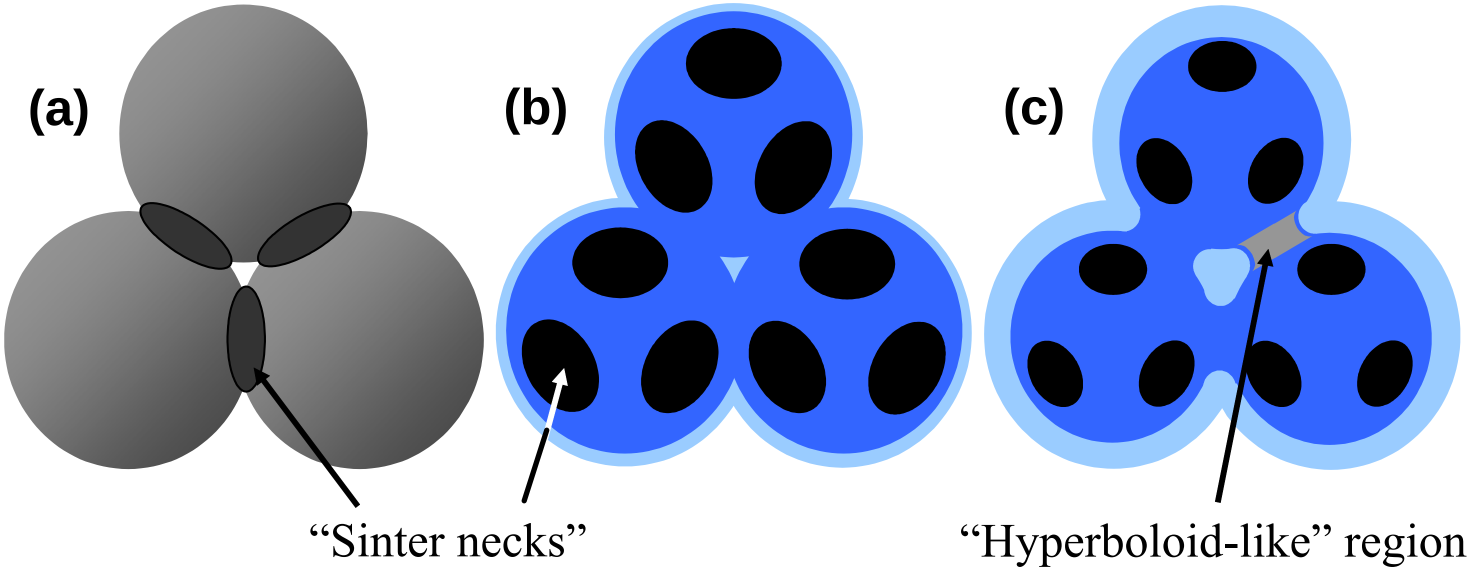
- Combination of heavy sintering and conformal infiltration after removal of template allows higher geometry and PBG tunability.
- Desired geometries can be achieved by a heavy sintering treatment yielding a high degree of control over dielectric/air backbone.
- Backfilling infiltration yields "peanut-like" connections not "tube-like" connections due to conformal deposition.
- Computations predict gap widths as high as 7.5% for Si
- Refractive index contrast requirement of n~2.7 for PBG

Fabrication possible !!!!

NCP: Sintered Fabrication Route

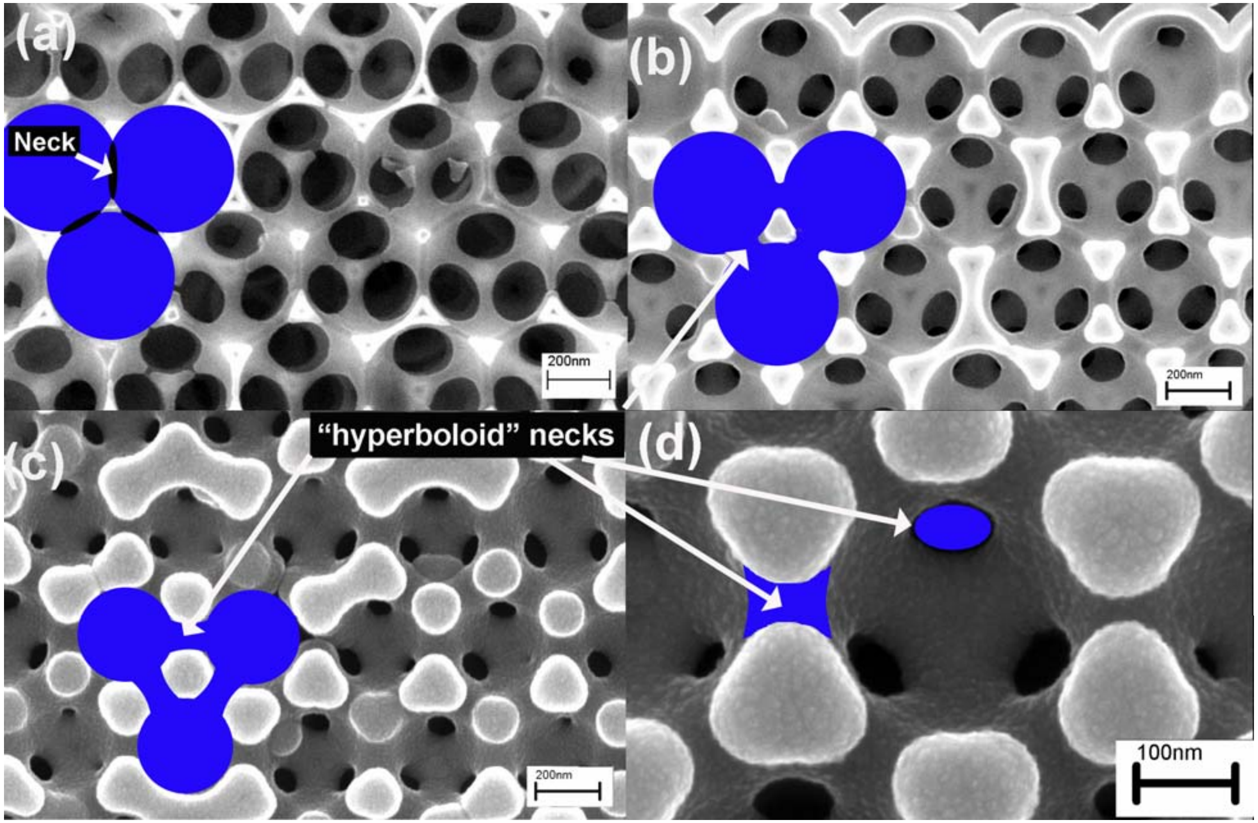
Presintering (PSNCP)

- Sinter opal prior to infiltration
  - Increases diameter of necks between spheres
  - After infiltration, connectivity pores are larger.
- Infiltrate with TiO_2
- Etch SiO_2 with HF to form inverse NCP opal
- Back-fill with TiO_2, thus creating air cylinders

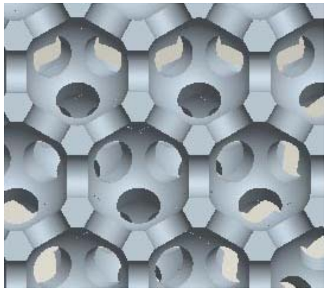


(a) heavily sintered opal template (b) resulting inverse opal and (c) non-close-packed inverse opal after ALD backfilling.

SEM of (111) Plane of Ti$_2$O NCP Opal

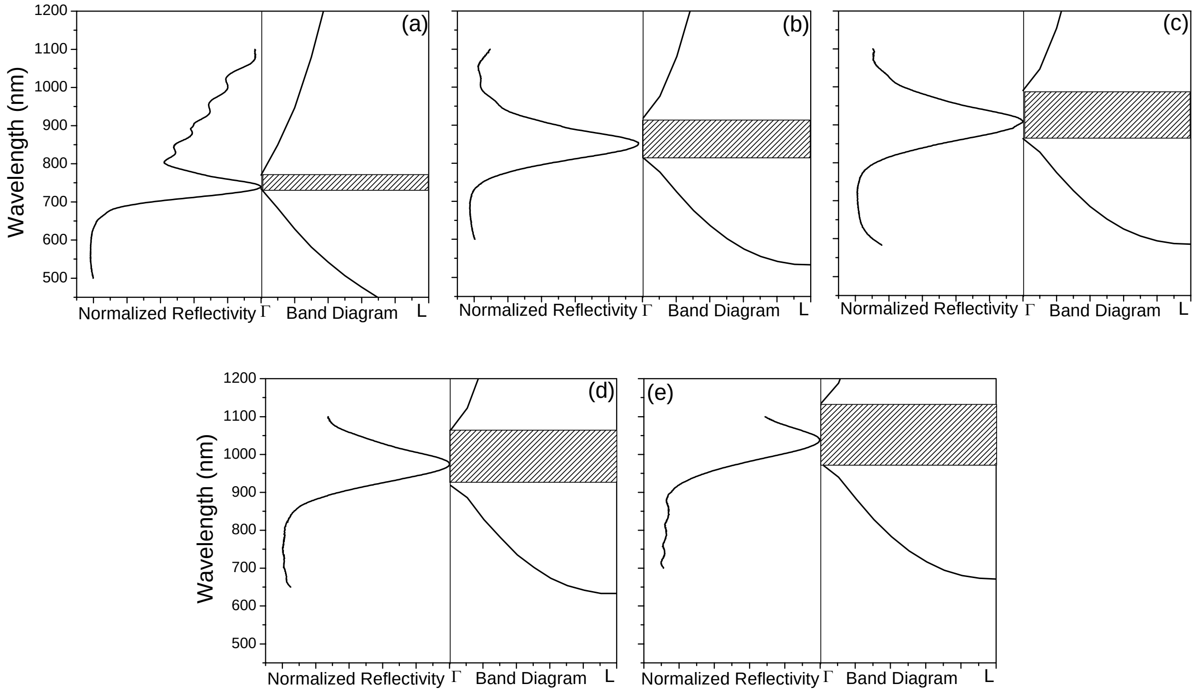


Optimized Theoretical NCP Structure



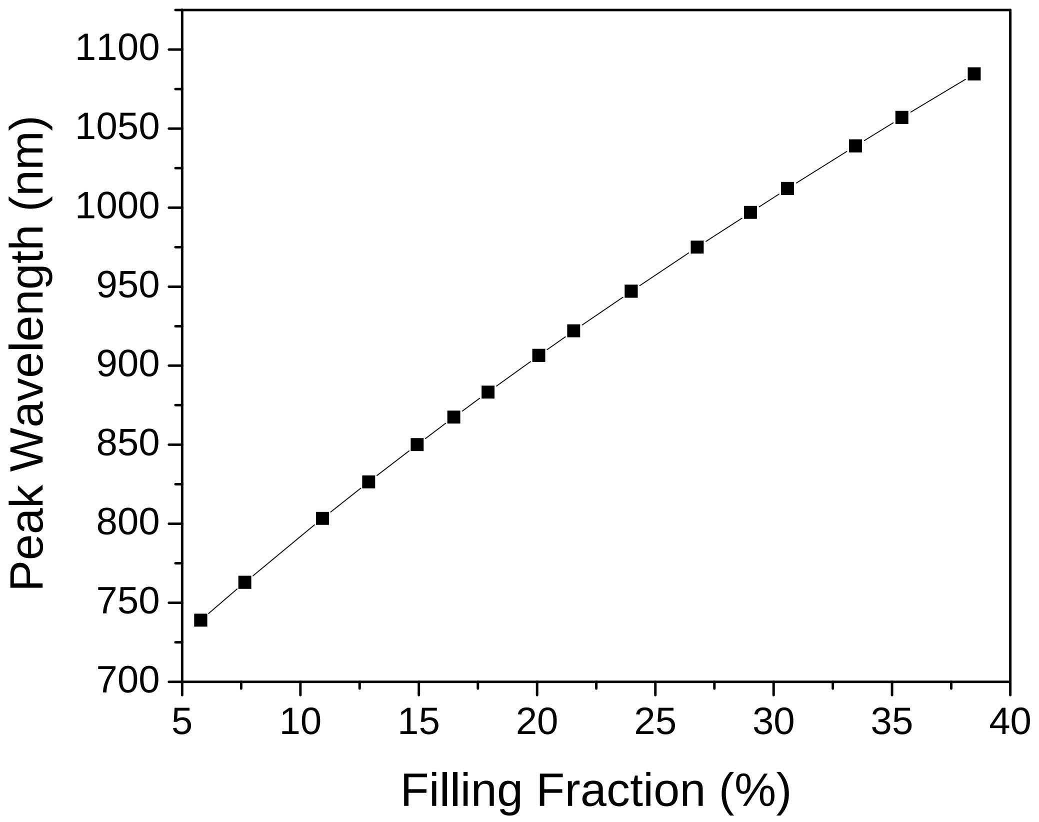
(a) TiO$_2$ inverse opal, formed from a heavily sintered 460 nm SiO$_2$ opal,
(b) Non-close-packed inverse opal formed after 240 TiO$_2$ ALD backfilling cycles
(c) Non-close-packed inverse opal formed after 560 TiO$_2$ ALD backfilling cycles
(d) Higher magnification of structure

Reflectivity and PBG Calculations



- Comparison of reflectivity spectra with calculated positions of 2nd & 3rd photonic bands of:
  - (a) the 5.9% filling fraction TiO_2 NCP inverse opal and after backfilling with
  - (b) 160 (c) 280 , (d) 400, and (e) 520 ALD cycles, respectively.
- For all calculations $n_{an} = 2.65$, $n_{am} = 2.45$. (15°). Longer sintering time yields larger interconnecting pore diameter

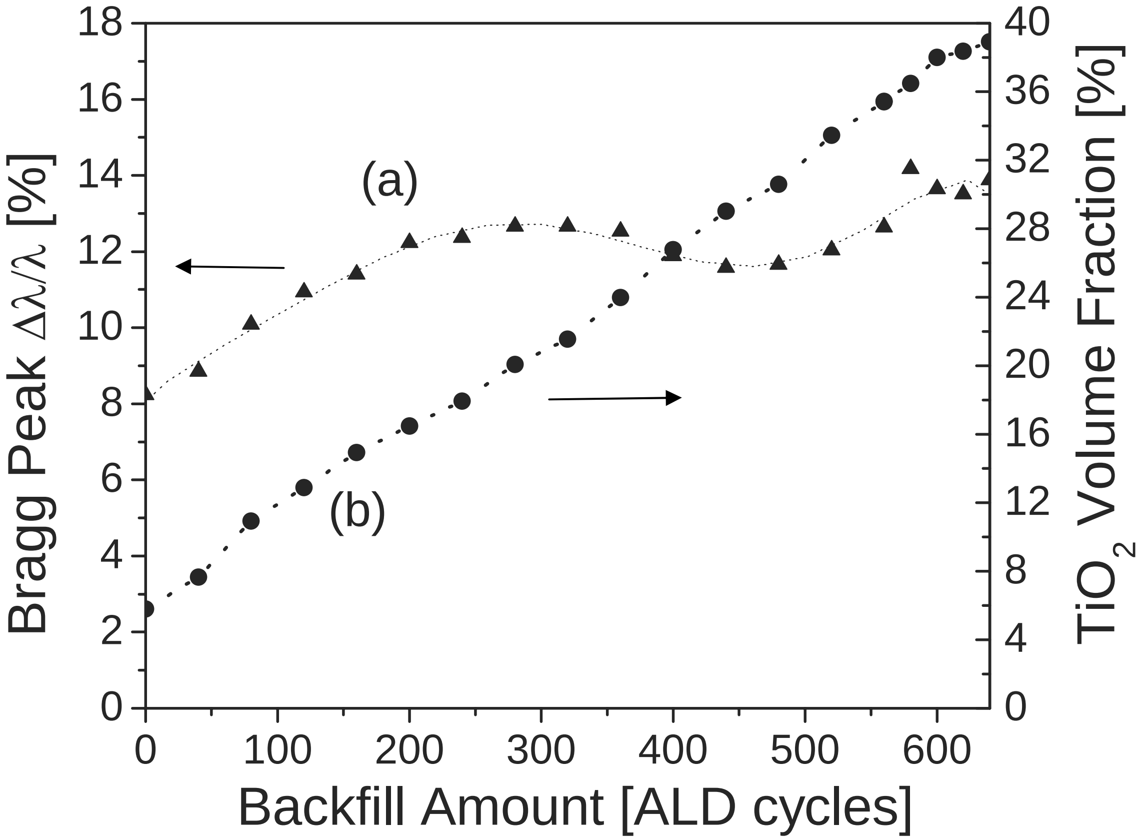
Bragg Peak Position as a Function of TiO_2 Filling Fraction



Tuning from:
730 nm to 1080nm
~ 350 nm

- Bragg peak (Γ-L PPBG) as a function of the TiO_2 backfilling fraction (New Technique gives further ~2X)

Bragg Peak Relative Width & TiO_2 Filling Fraction vs. ALD cycles



Increase in PPBG: Bragg Peak Width from 8 to 13.5%

- Bragg peak (Γ-L PPBG) relative width (Δλ/λ) (left axis) and the corresponding TiO_2 filling fractions (right axis) as a function of number of ALD cycles
- Backfilling is ~ 40% of available volume

Summary

- **ALD - effective infiltration method for fabricating inverse opal PCs.**
  - >95% infiltration of pore volume achieved for ZnS and TiO_2
  - PPBGs demonstrated in inverse ZnS, TiO_2 & multilayered PCs luminescent & high index materials
  - Reflectance agrees well with theory.
- **Strong PL modulation demonstrated in ZnS:Mn**
  - Well correlated with reflectance/PPBGs
- **Practical pathway to grow complex *luminescent* photonic crystal structures and optical microcavities.**
- **Developed Non-Close Packed multi-layered PCs**
  - Highly Tunable Reflectance – over twice initial wavelength
  - Enhanced bandwidth – by approximately 50%
- **Future Work - Extension to:**
  - Luminescent & dynamically tunable devices: 3D photolithographic derived structures: Defect Microcavities Modes: 2D PCs

Acknowledgements

Research Group

Graduate Students

- Curtis Neff
- Tsuyoshi Yamashita
- Davy Gaillot
- Xudong Wang
- Swati Jain

Postdoctoral Researchers

- Elton Graugnard, Jeff King

Collaborations

- Drs. D. Morton, E. Forsythe, S. Blomquist, W. Park and I. C. Khoo
- U.S. Army Research Office - MURI Contract# DAAA19-01-1-0603

Thank You!