ATOMIC LAYER DEPOSITION FOR PRECISE, LARGE-SCALE NANOSTRUCTURE FABRICATION

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The Fifth Georgia Tech Conference on Nanoscience and Nanotechnology

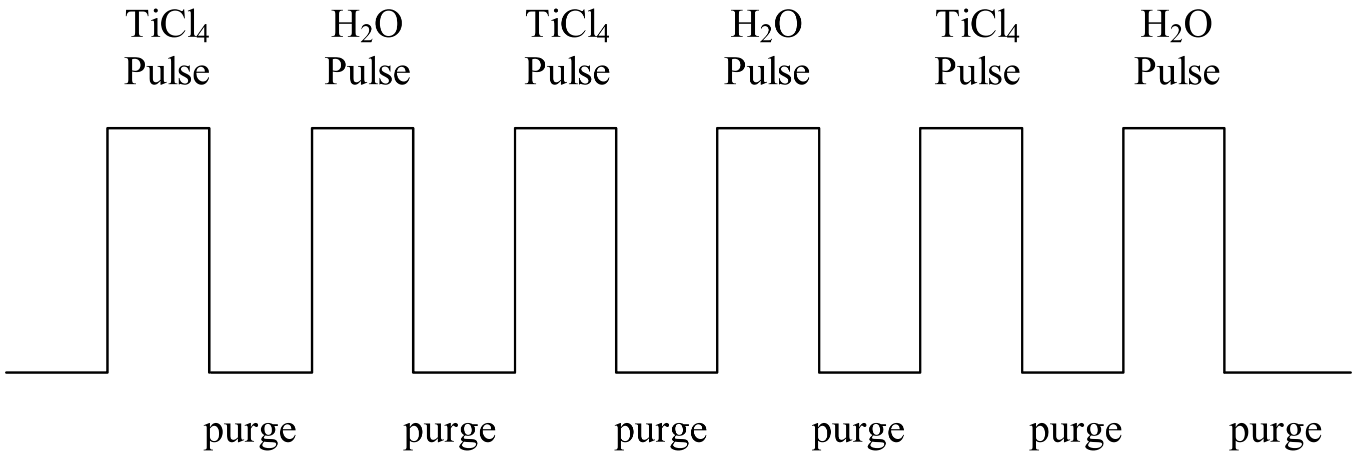
*November 10-11, 2004
Atlanta, Georgia U.S.A.*

Outline

- Introduction to Atomic Layer Deposition
- Introduction to Photonic Crystals
  - Opals
  - Inverse Opal
  - Requirements for Photonic Band Gaps: high filling fraction, smooth, conformal, high refractive index
- Infiltration using ALD
  - Meets above requirements
  - TiO_2 infiltration
  - Novel Structures Fabricated with ALD Template Infiltration
- Summary

Atomic Layer Deposition (ALD)

- Surface limited growth by a modified CVD process.
- Proceeds through cyclic saturative surface reactions and chemical purges resulting in constant thickness increase per cycle.
- Results in conformal growth with digital thickness control.

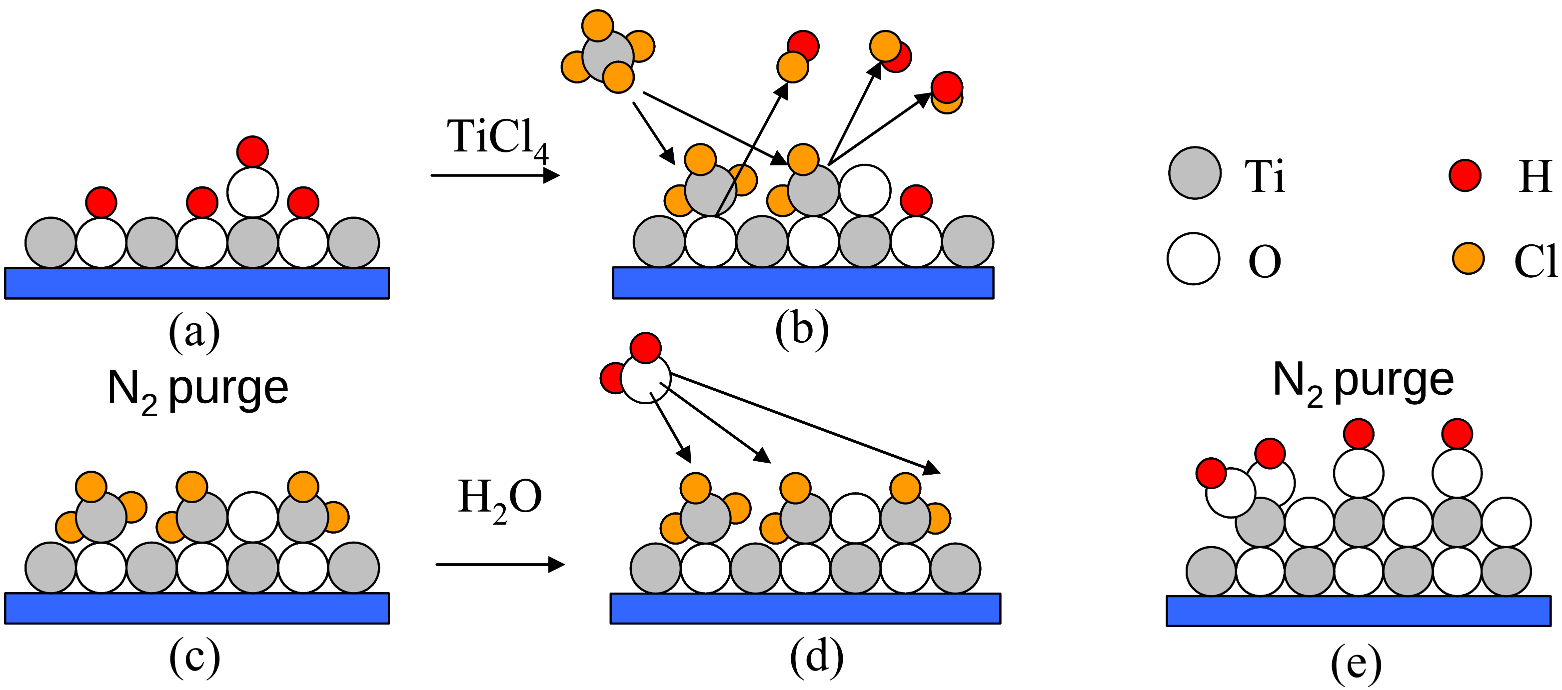


Pulse/Purge Sequence for ALD of TiO_2

Atomic Layer Deposition of TiO_2

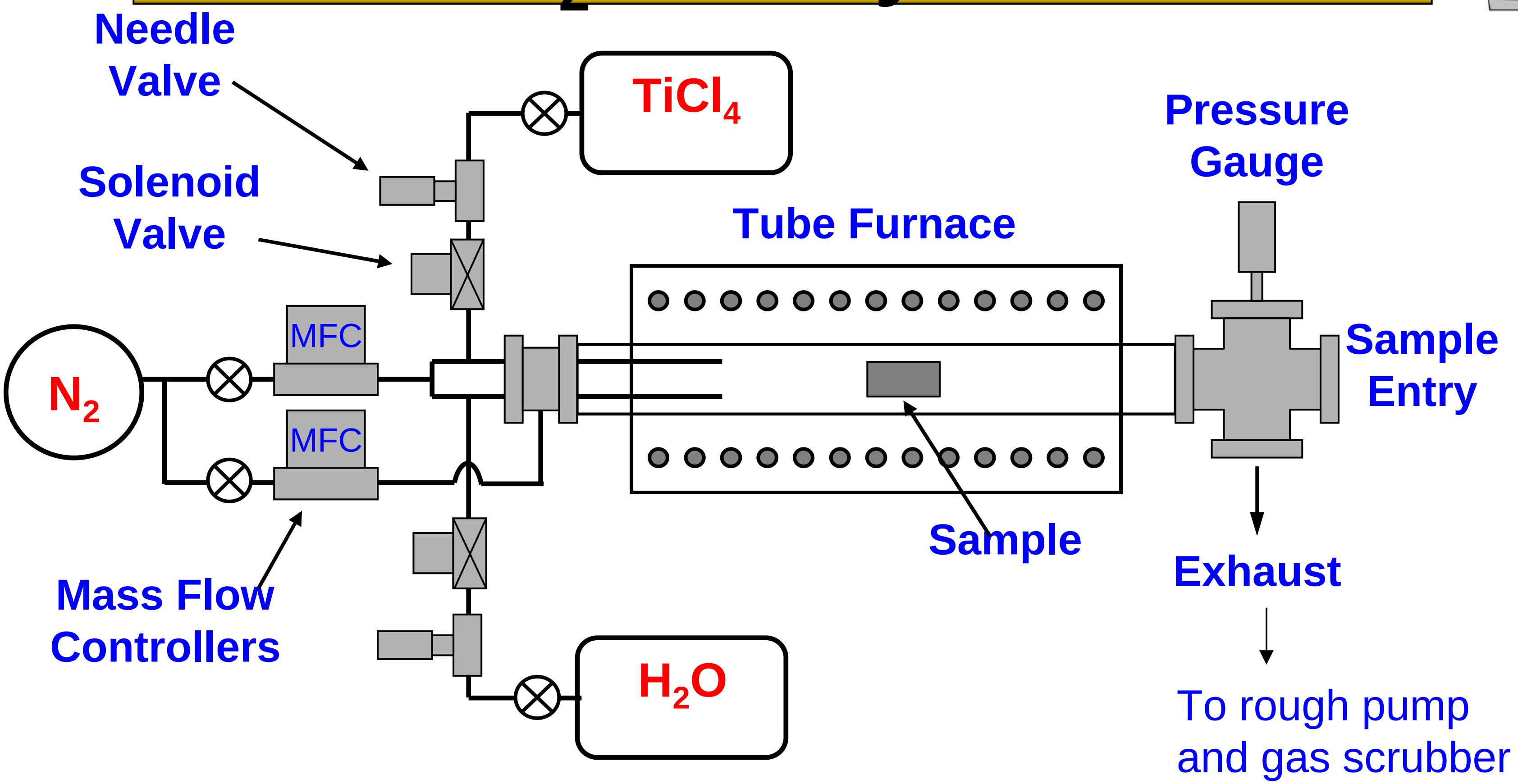
$$n(-OH)(s) + TiCl_4(g) \rightarrow (-O-)_n TiCl_{4-n}(s) + nHCl(g)$$

$$(-O-)_n TiCl_{4-n}(s) + (4-n)H_2O(g) \rightarrow (-O-)_n Ti(OH)_{4-n}(s) + (4-n)HCl(g)$$



- Liquid precursors: high vapor pressure at low T.
- $TiCl_4$ is highly reactive with the oxide film.
- Result: Wide deposition temperature window: RT to 600° C

Schematic of Georgia Tech TiO_2 ALD System

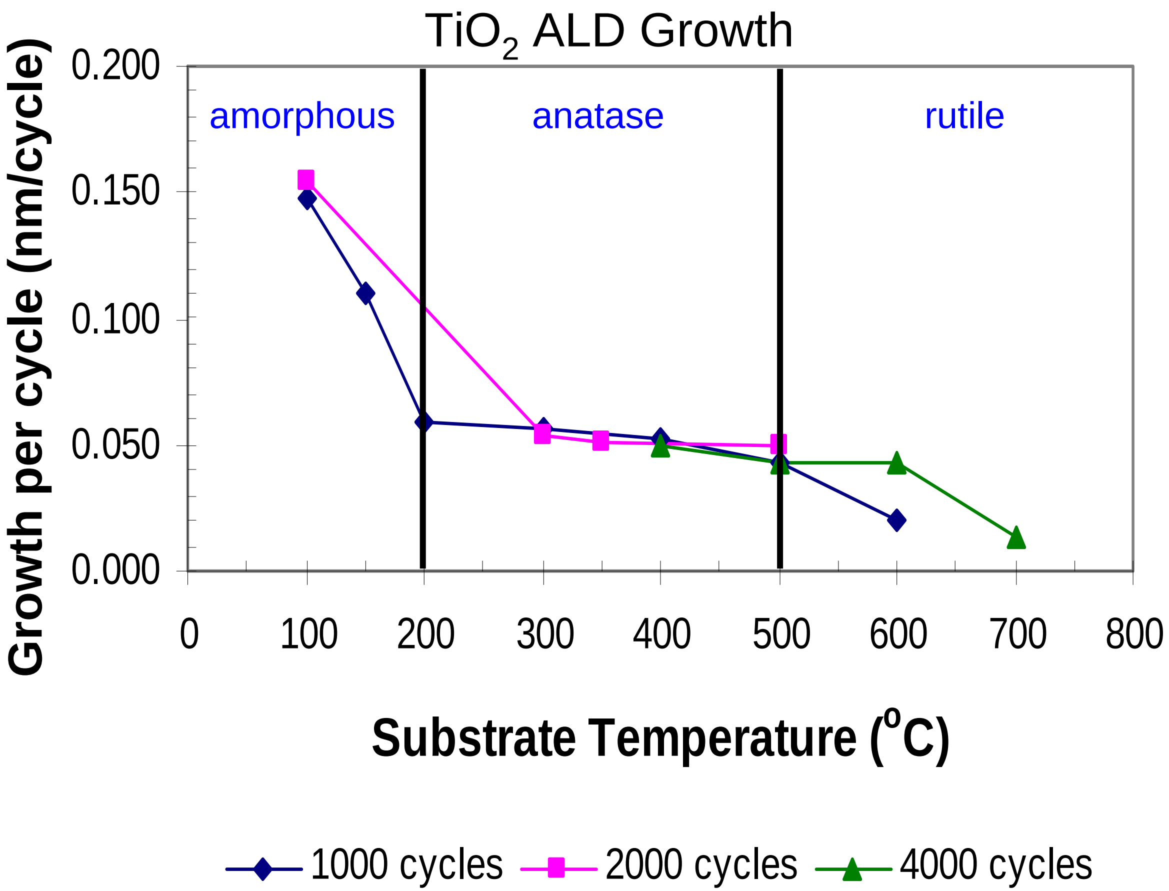


- Pulse lengths and cycles computer controlled
- Deposition temperatures from 75 – 650°C.

Georgia Tech
TiO_2 ALD System

- TiO_2 infiltrations are performed at Georgia Tech using a custom built hot-wall, flow-style reactor.
  - Planar conditions:
    - $TiCl_4/H_2O$ - 1s/1s
    - N_2 purge - 2s
  - **Opal conditions:**
    - **$TiCl_4/H_2O$ - 4s/4s**
    - **N_2 purge - 10s**

Planar Thin Film Growth:
Growth Rate vs. Substrate Temperature



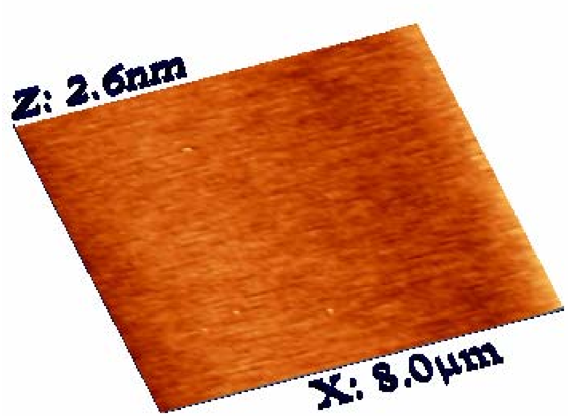
- 3 distinct regions of growth that correspond with development of crystal structure
  - 100 - 200°C amorphous
    - Higher growth rate
  - 200 - 500°C anatase
  - 500 - 700°C rutile
- Decreased density of reactive surface species (-OH groups) at higher temperatures

0.5s H_2O pulse, 1s $TiCl_4$ pulse, 4s purge, 1000 cycles

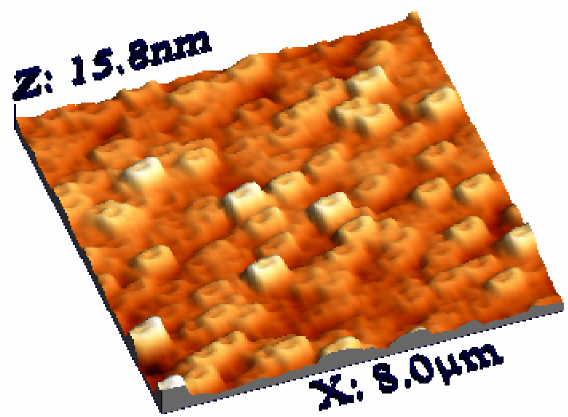
ALD of TiO_2

Surface Roughness: AFM Images

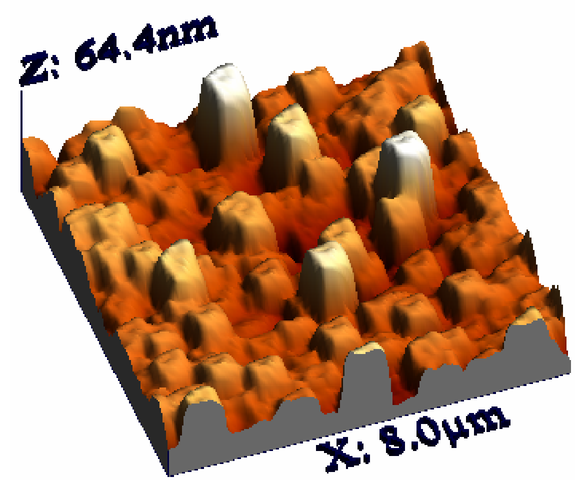
- Formation of polycrystalline structure results in surface roughening of the film, which increases with increased deposition temperature.
- Surface roughness prevents direct high temperature ALD in opals



100ºC
2 Å RMS roughness



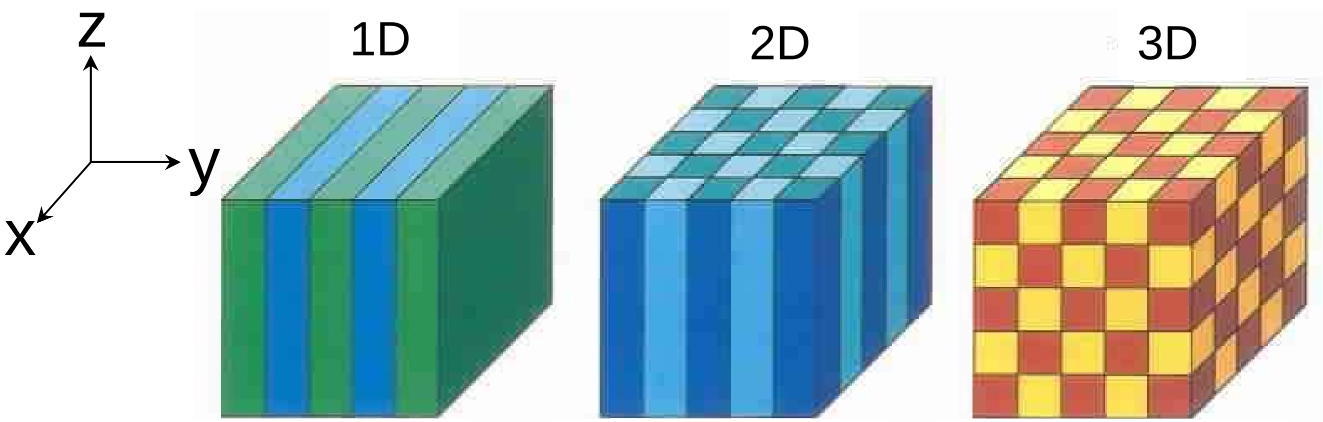
300ºC
21 Å RMS roughness



600ºC
96 Å RMS roughness

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

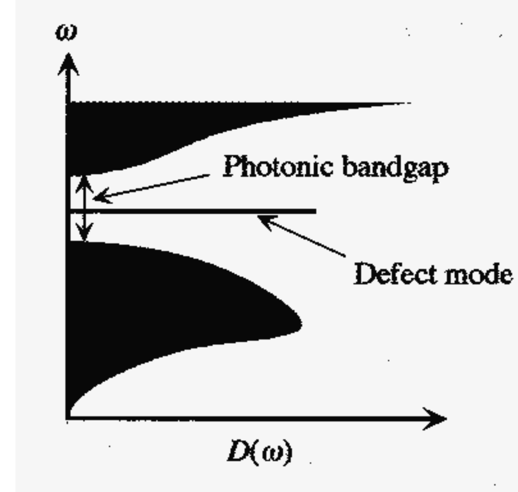
Photonic Crystals



Periodic in one direction

Periodic in two directions (Joannopoulos)

Periodic in three directions

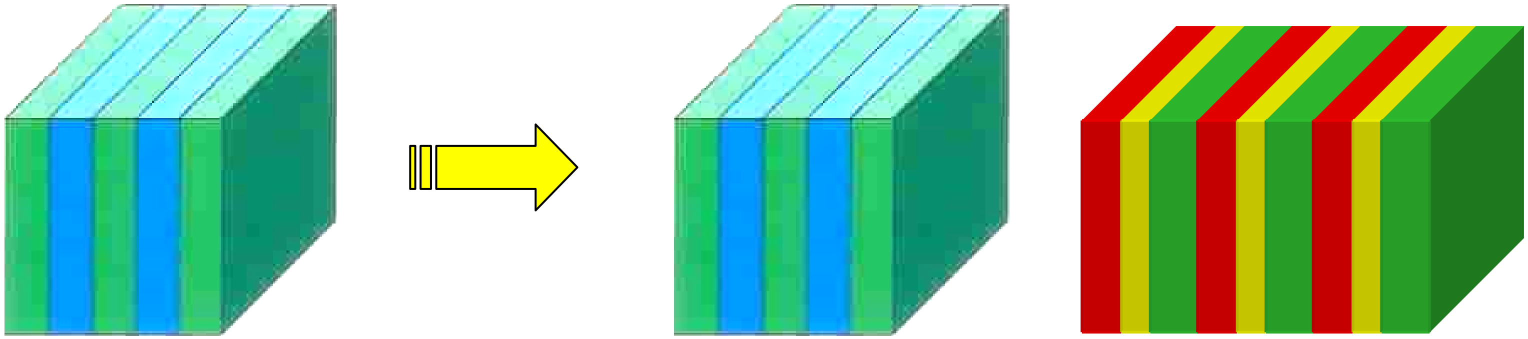


(b) Photonic Crystal

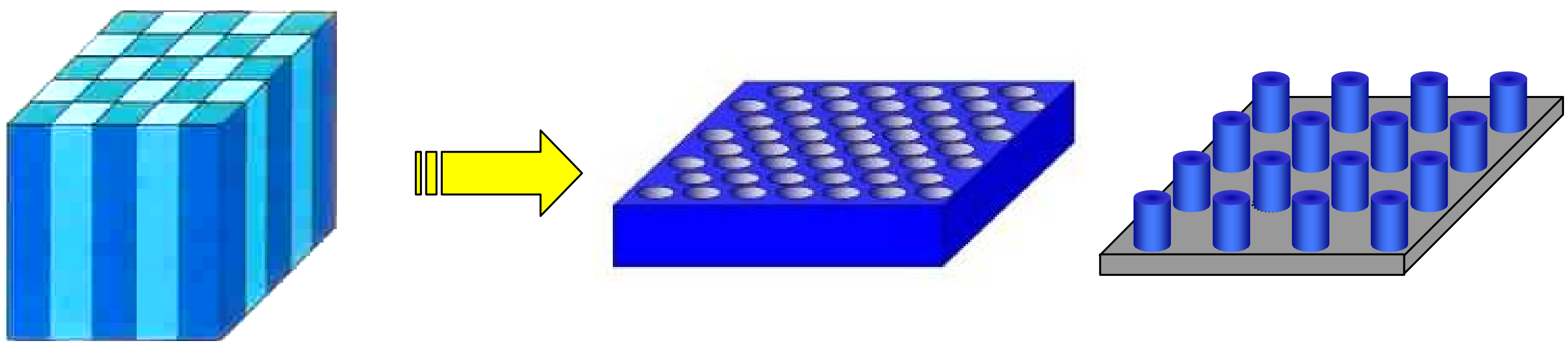
- Photonic Crystal – periodic modulation of dielectric constant
- Exhibits a "Photonic Band Gap" (PBG) where propagation of a range of photon energies is forbidden.
- For visible wavelengths, periodicity on order of 150 – 500 nm.
- Introduction of "dielectric defects" yield modes within the PBG.
- Luminescent 2D & 3D PC structures offer the potential for controlling wavelength, efficiency, time response and threshold properties (phosphors, displays, solid state lighting, etc.).

Real Photonic Crystals:
Applications for thin films

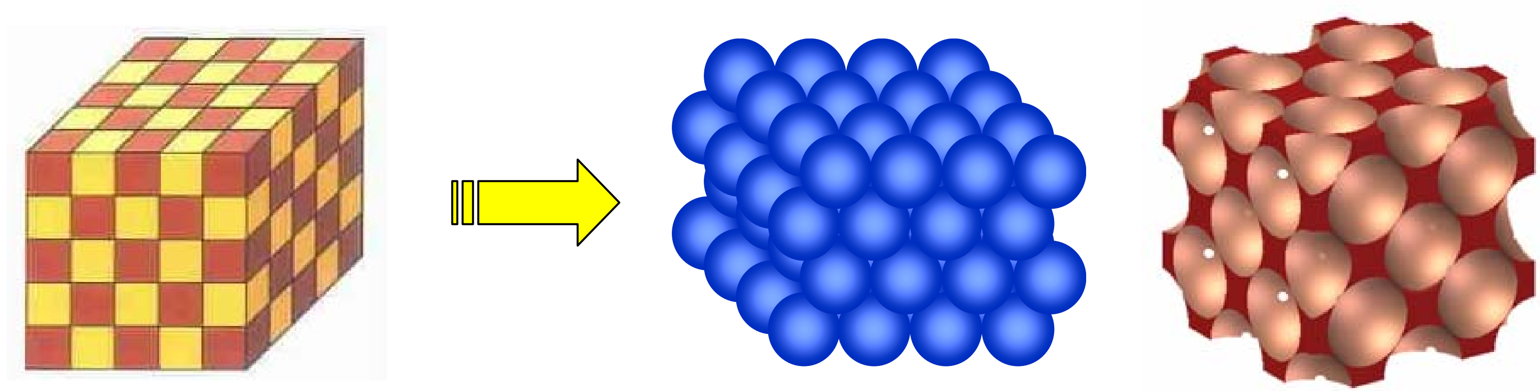
1D



2D



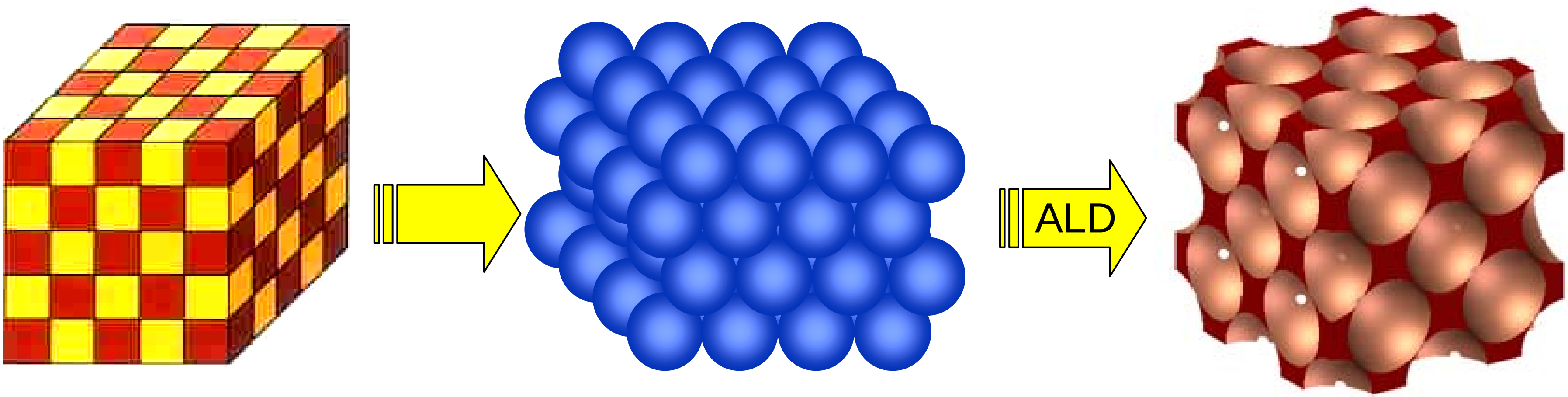
3D



3D Photonic Crystals:

Opals & Inverse Opals

- For 3D PC's: "top-down" approaches are difficult.
  - "Bottom-up" approach: self-assembly
- Most common 3D photonic crystal is the opal.
  - Close-packed silica spheres in air
- Opal is used as a template to create an inverse opal.
  - Close-packed air spheres in a dielectric material



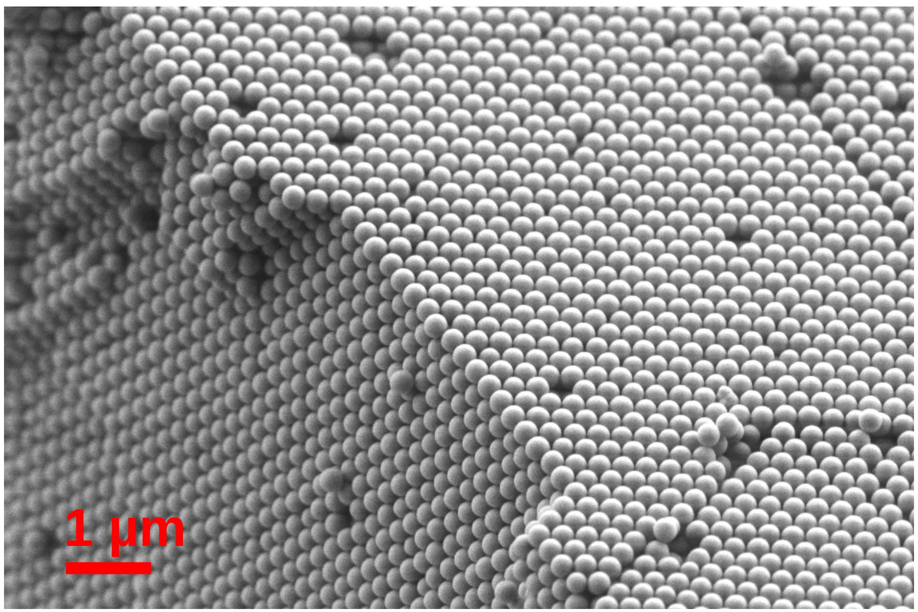
3D-PC

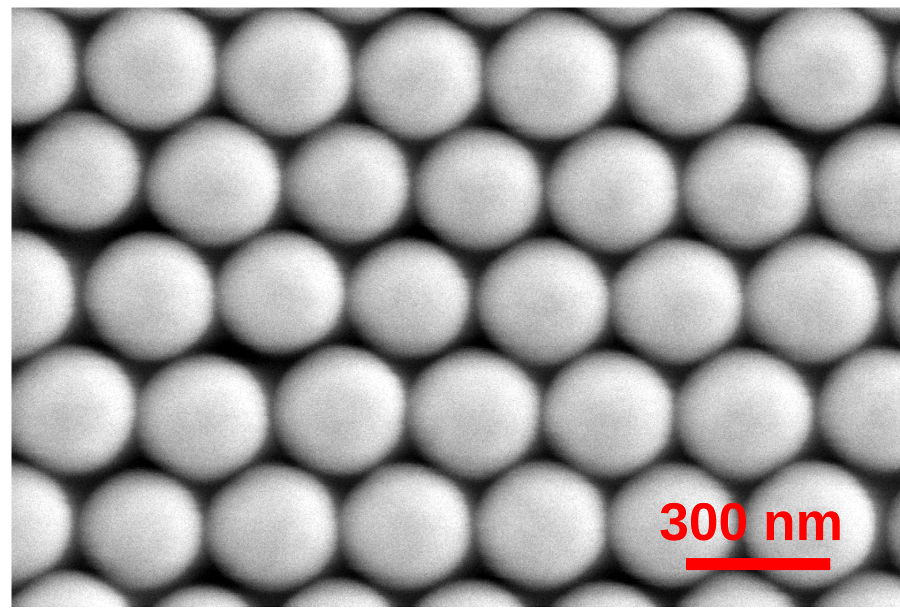
Opal
26% air

Inverse Opal
74% air for high dielectric contrast

SiO_2 Opal Films

- Opal films are polycrystalline, 10 μm thick, FCC films with the (111) planes oriented parallel to the surface.
- For visible spectrum, lattice constant ~ 140 – 500 nm.



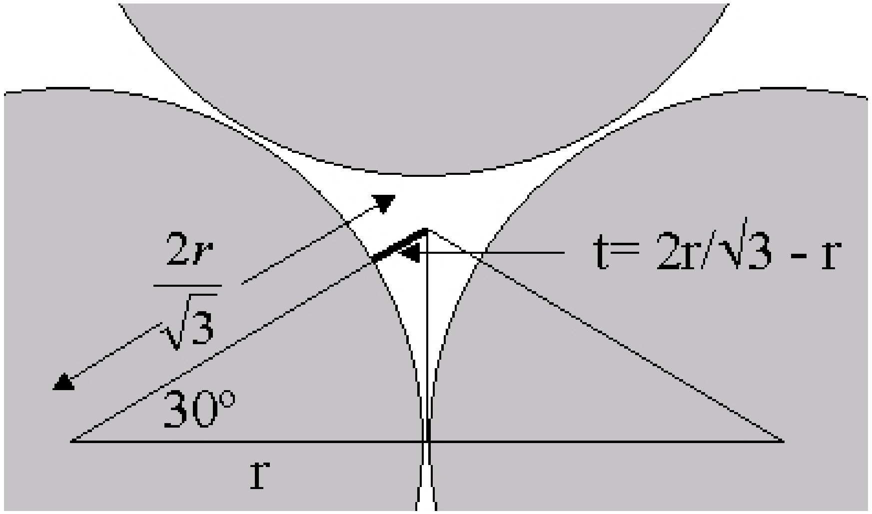


Challenge: growth of uniform films within a dense, highly porous, high surface-area, FCC matrix

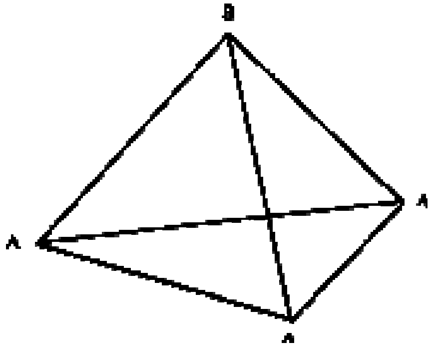
Opal Infiltration: Growth Issues

Geometrical Constraints

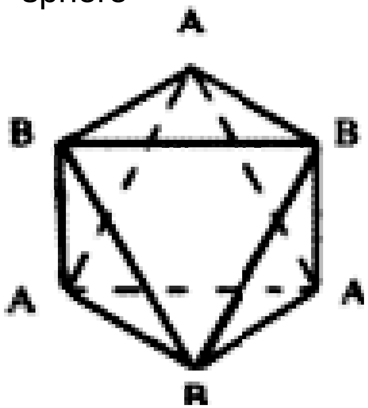
- Narrowest pathway (bottleneck) into opal is through (111) planes.
- Consideration of geometry predicts pore closure at 7.75% of sphere diameter.
- Monte Carlo simulations show this is ~ 86% infiltration of voids.



- Tetrahedral void size is $0.46 \times r_{sphere}$ ~ 32–115 nm.



- Octahedral void size is $0.82 \times r_{sphere}$ ~ 57–205 nm.



Opal Films: Growth Issues

Increased Surface Area

- Surface area of opal film is much larger than an equivalent planar area:

$$\frac{A_{\text{opal}}}{A_{\text{film}}} = \frac{0.74 \times l \times w \times t}{4/3\pi r^3} \times \frac{4\pi r^2}{l \times w} = \frac{2.22t}{r}$$

- For a 10 μm thick opal film with 200 nm diameter spheres:

$A_{opal}/A_{film} = 222$

$A_{opal} = 0.089\ m^2$

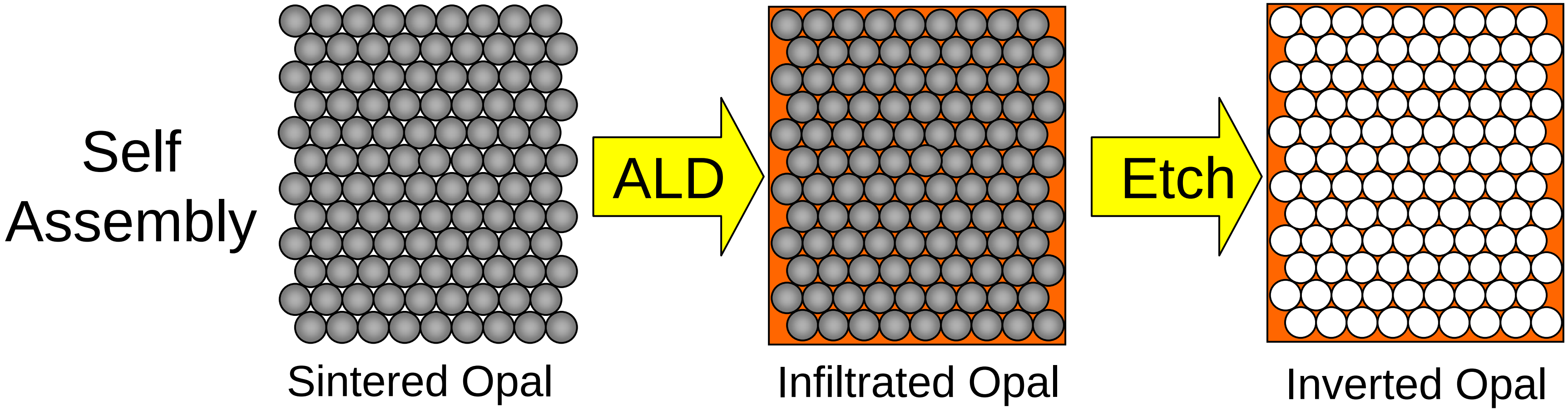
Georgia Institute of Technology

Opal Infiltration:
Requirements

- Uniform Infiltration
  – Material must be distributed uniformly throughout the opal
- Controlled Filling Fraction
  – Must be able to precisely control the void space filling
- Conformal and Smooth Surfaces
  – Creates lower porosity infiltrations
  – Creates air pockets at the center of the opal voids, enhancing the PBG
- High Refractive Index, Transparent, & Luminescent Materials
  – For a full PBG, the refractive index contrast (with air) must be > 2.8
- **ALD is the only technique to meet all of these requirements**

Inverse Opal:
Fabrication

- Self-assembled silica opal template
  - 10 μm thick FCC polycrystalline film, (111) oriented.
- Infiltration of opal with high index materials
  - ZnS:Mn n~2.5 @ 425 nm (directional PBG)
  - TiO_2 (rutile) n_{avg}~ 3.08 @ 425 nm (omni-directional PBG)

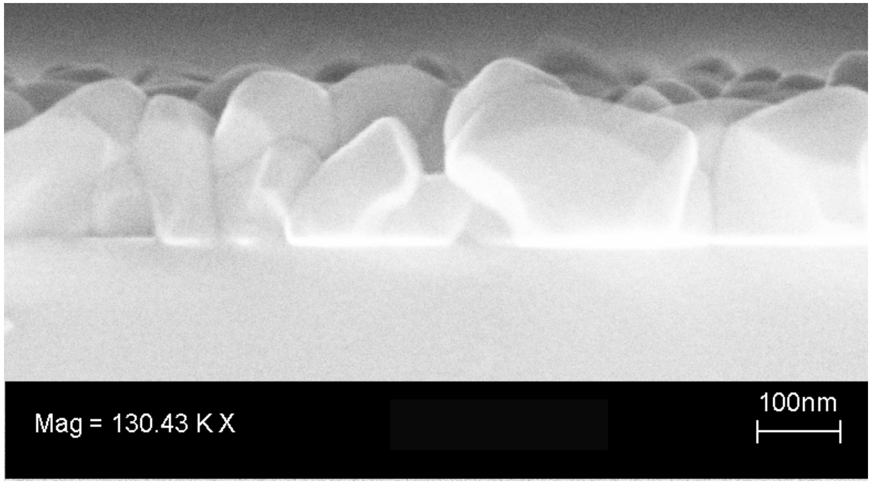


ALD of TiO_2

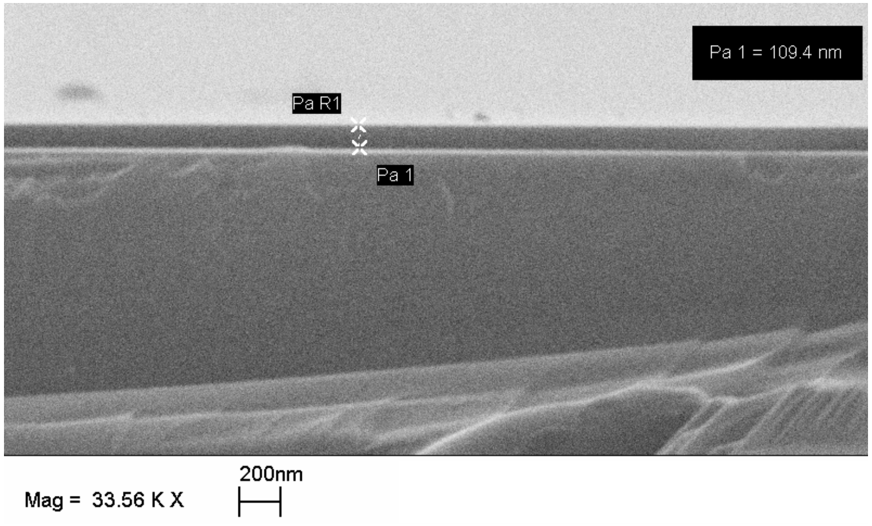
Surface Roughness: planar TiO_2 films

- Large ALD temperature window allows optimization of surface morphology.
- Below 150° C, ultra-smooth amorphous film results (2 Å RMS roughness).
- 400°C, 2 hr. heat treatment forms anatase, Roughness increase of only 2 Å!
  - Refractive index increases from 2.5 to 2.85 (@425 nm).

500° C Deposition



100° C Deposition

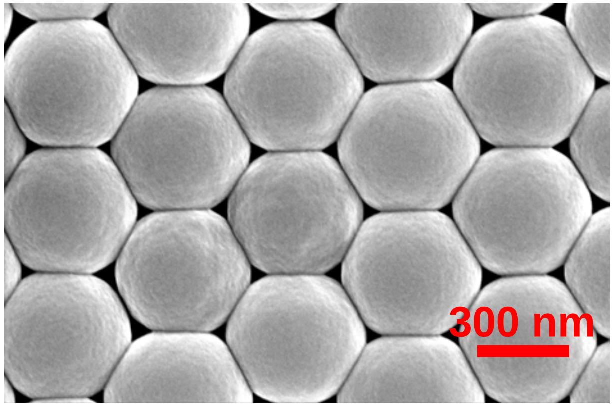


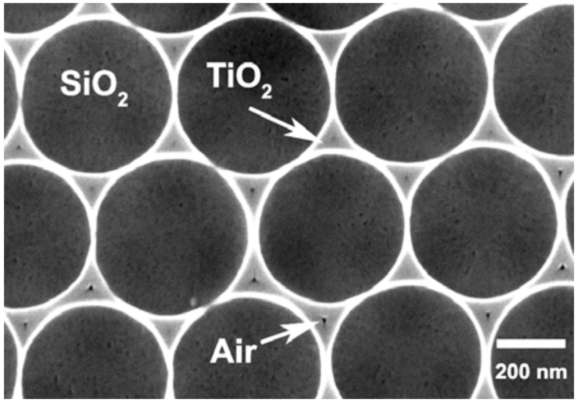
Low T ALD + Heat Treatment = Smooth, conformal, high index!

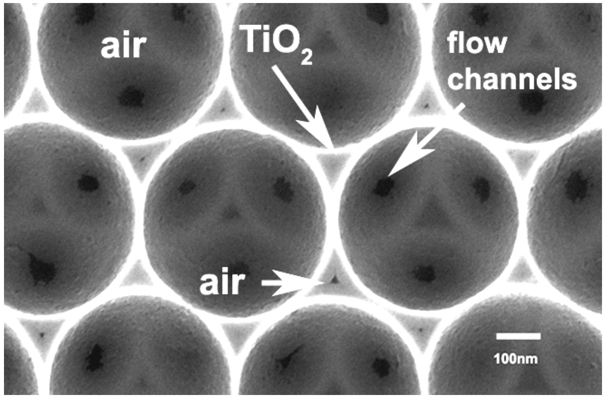
ALD of TiO_2 at 100ºC

(111)⊙

Cross-sections







433 nm opal infiltrated with 20 nm of TiO_2

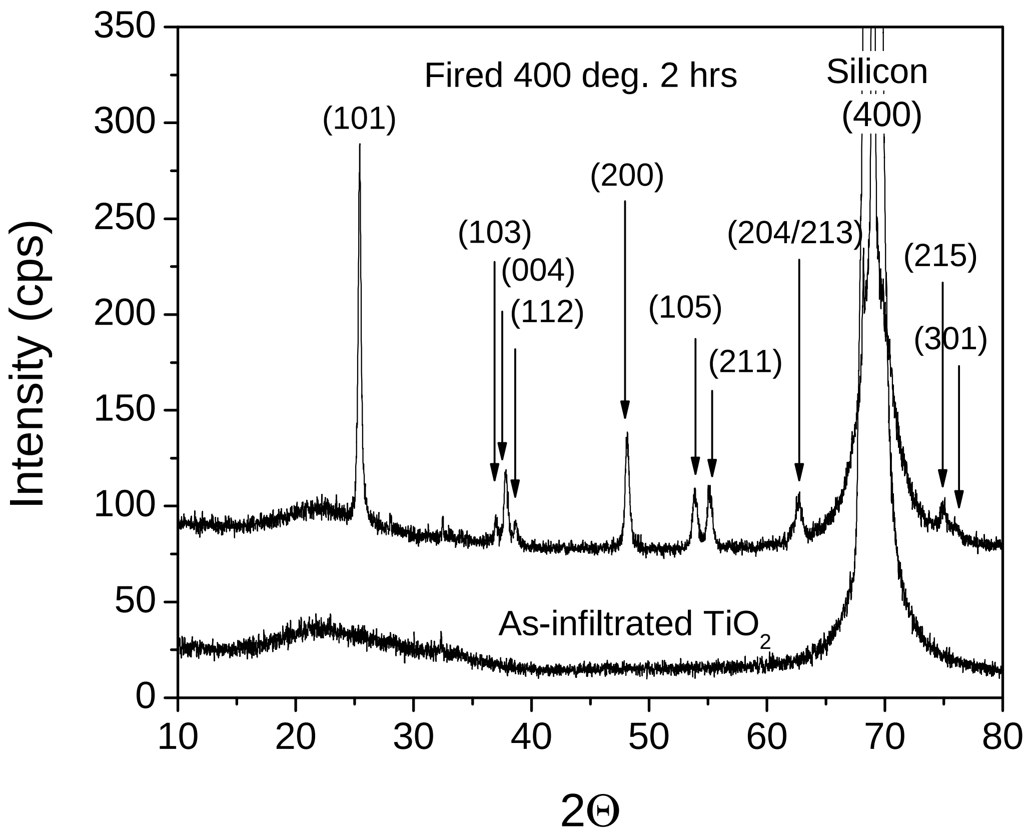
433 nm opal infiltrated with TiO_2

433 nm TiO_2 inverse opal

- TiO_2 infiltration at 100ºC produces very smooth and conformal surface coatings with rms roughness ~2Å.
- Heat treatment (400C, 2 hrs.) of infiltrated opal converts it to anatase TiO_2, increasing the refractive index from 2.35 to 2.65, with only a 2Å increase in the rms surface roughness.

J.S. King, *et al*., *Adv. Mater.* (in press).

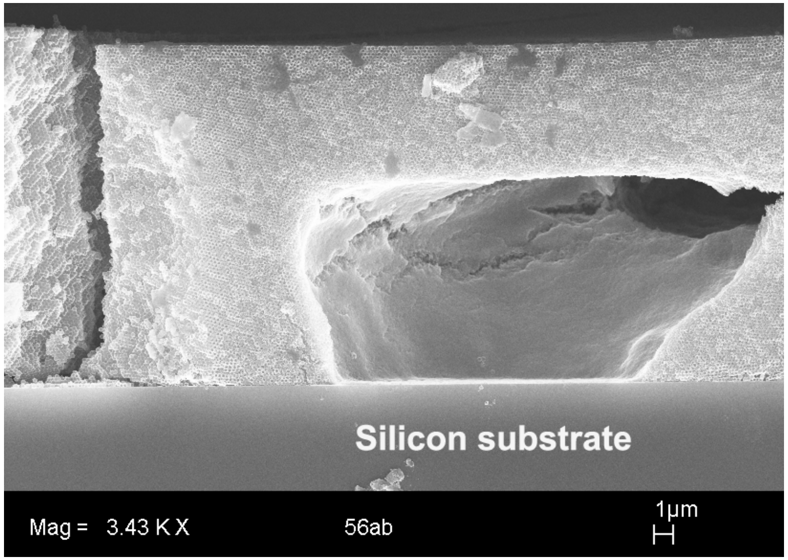
XRD of Infiltrated Opals



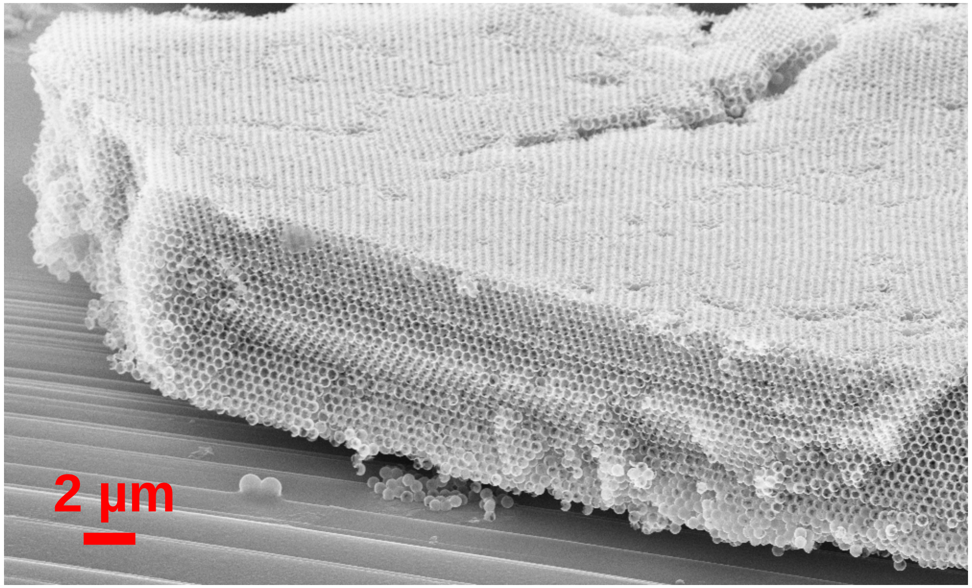
- XRD data for 100°C 433 nm infiltrated TiO_2 opal (lower curve), and same sample after 400°C 2 hour heat treatment (upper curve).

Optimized TiO_2 Infiltration

- For small opal sphere sizes, uniform infiltration becomes difficult creating air cavities when the opal is inverted.
- Pulse and purge times were increased to optimize infiltration in opals with small sphere sizes.

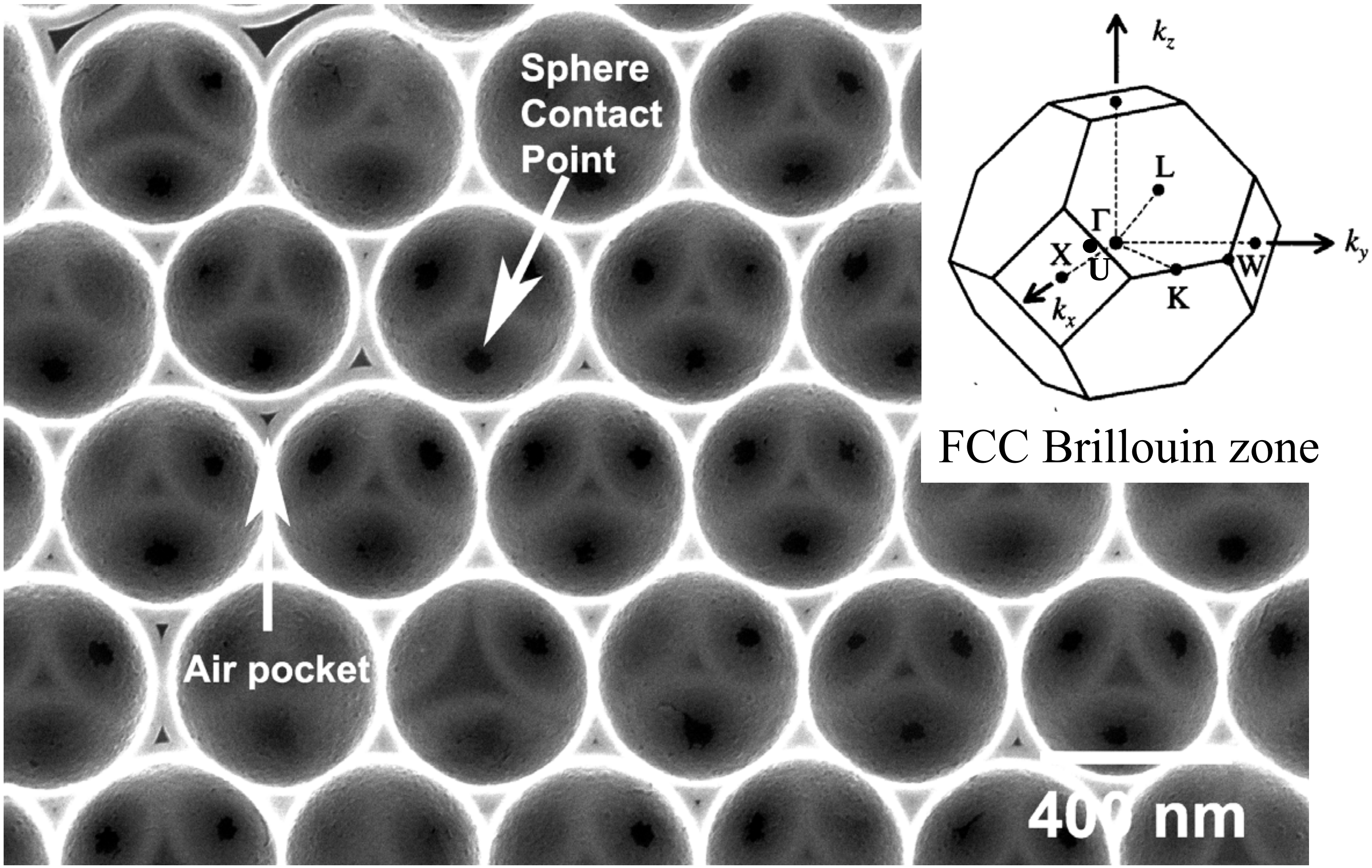


200 nm TiO_2 inverse opal



433 nm TiO_2 inverse opal

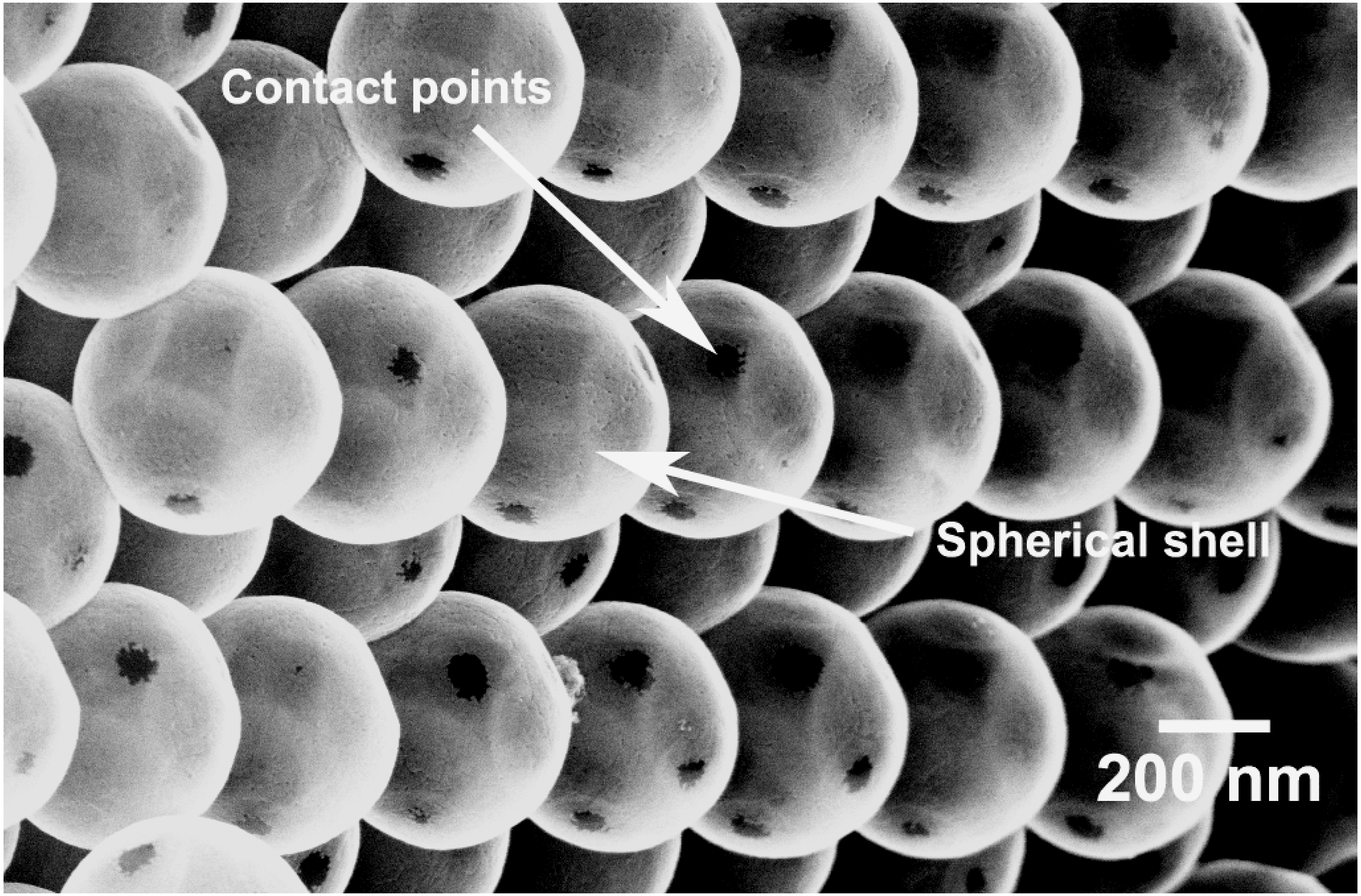
Anatase TiO_2 Inverse Opal



FCC Brillouin zone

433 nm inverse opal, ion milled (111) surface

Anatase TiO_2 Inverse Opal

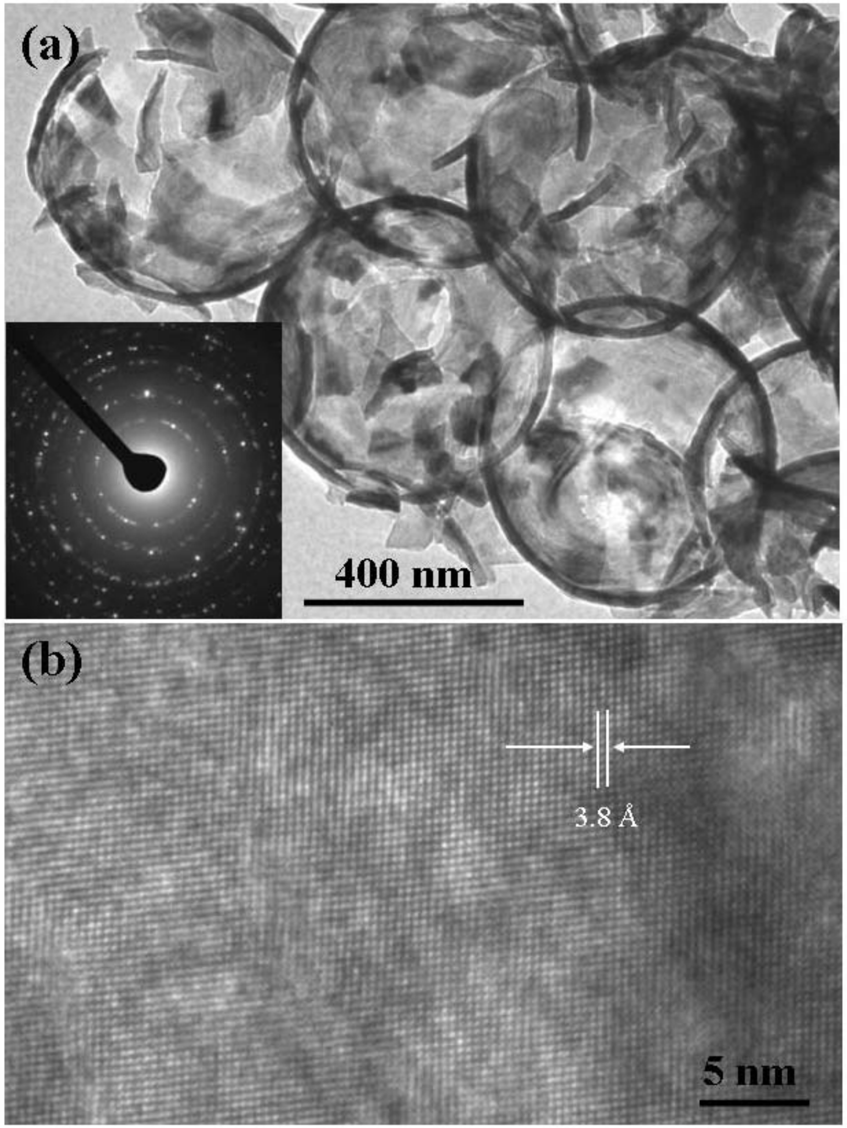


433 nm inverse opal fracture surface

TEM of TiO_2 Shells

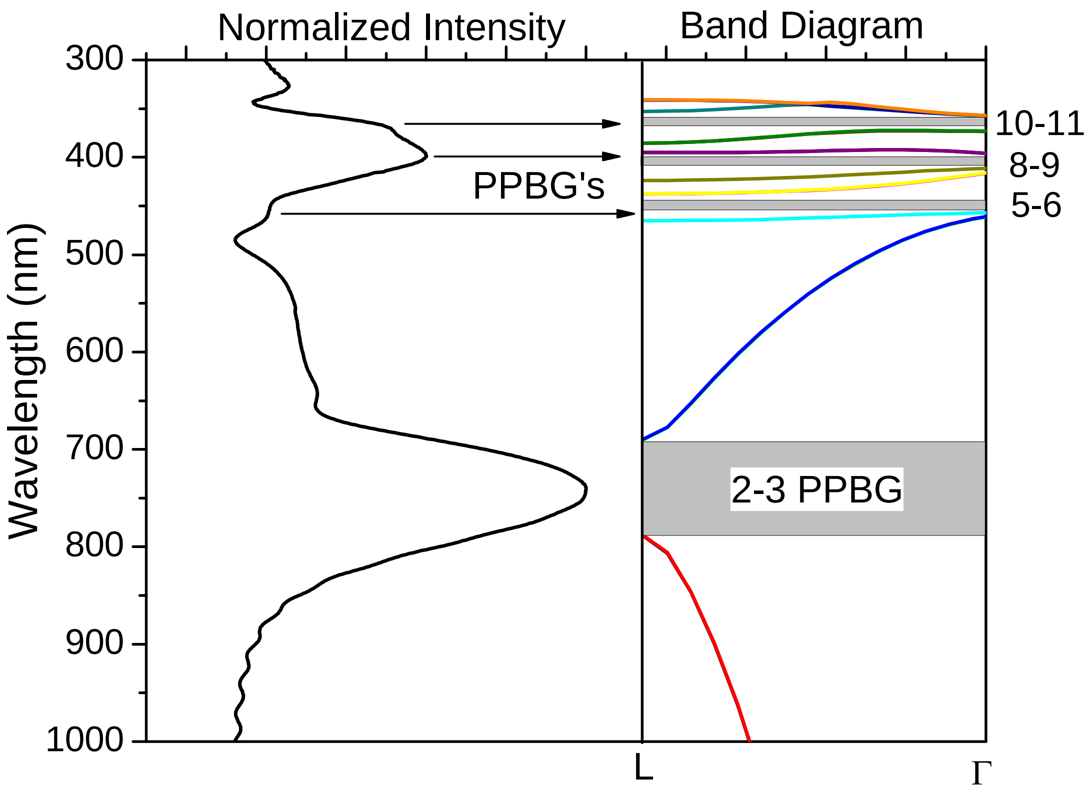
- (a) TEM image of TiO_2 shell structures after annealing. The inset shows an electron diffraction pattern confirming the polycrystalline structure.

- (b) HR-TEM image showing lattice fringes that match the (101) planes of anatase TiO_2.



Inverse Opal Reflectivity:
Theoretical Comparison

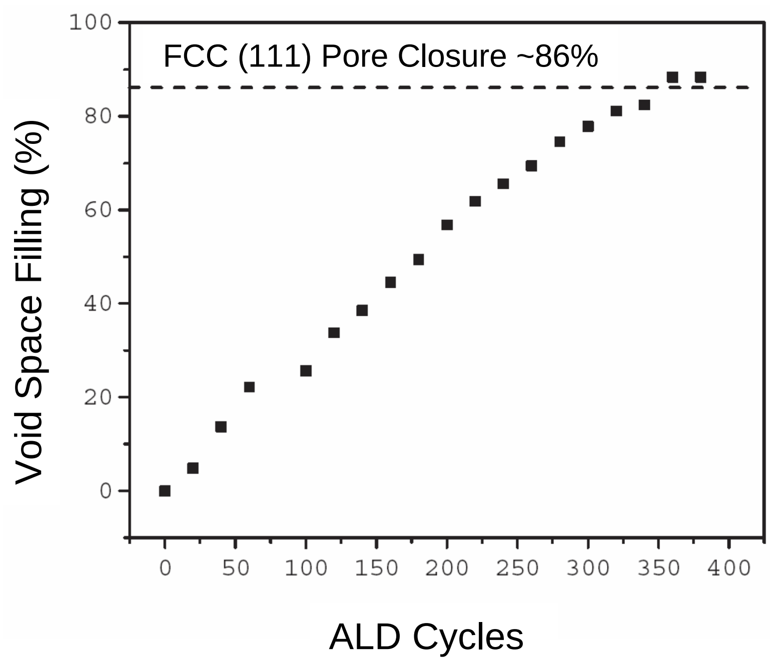
TiO_2 Inverse Opal Reflectivity and Photonic Band Diagram



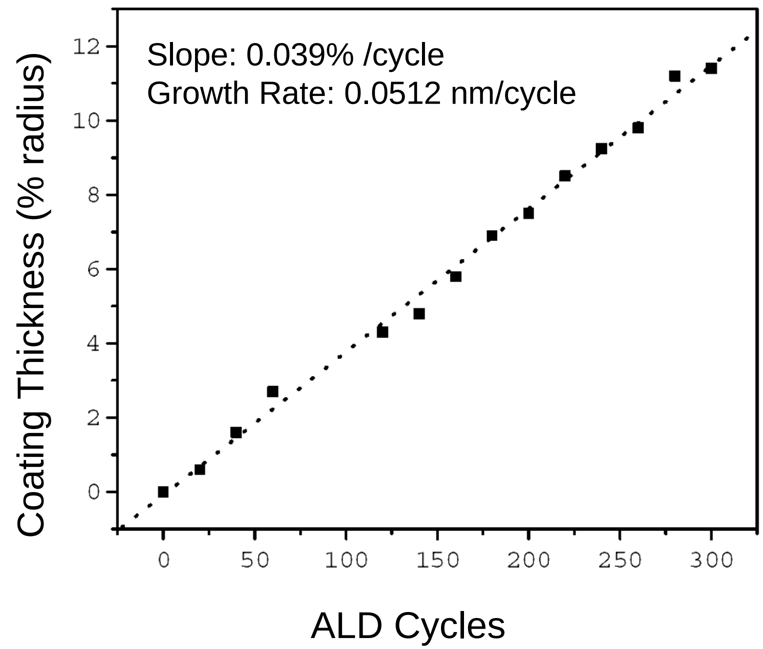
- TiO_2 infiltration of 330 nm opal with ~88% filling fraction
- 2.65 Refractive Index
- Agreement: full index attained!

Precise Digital Opal Infiltration

Void filling fraction of opal as function of ALD Cycles calculated from reflectivity



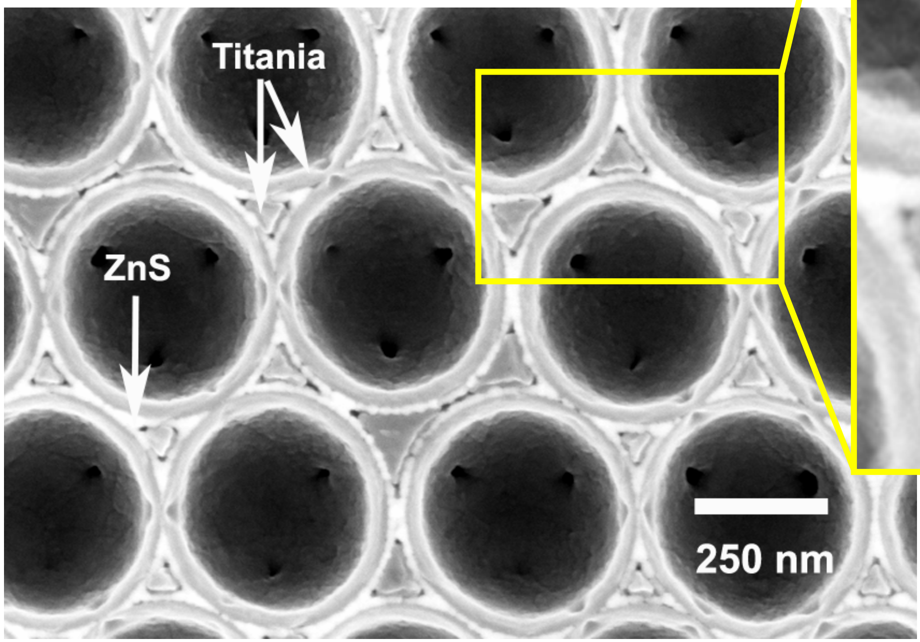
TiO_2 Coating Thickness as function of ALD cycles

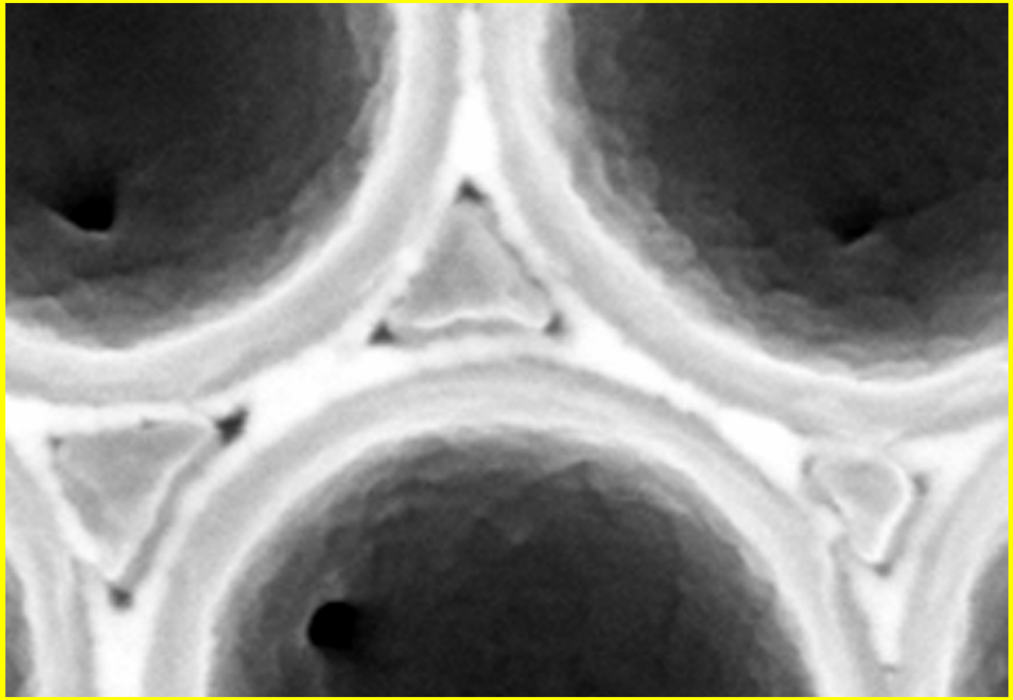


- **Optical verification of maximum filling fraction.**
- **ALD allows for ultra-fine control of opal infiltration.**

Multi-Layer Inverse Opals

- SEM of TiO_2/ZnS:Mn/TiO_2 inverse opal





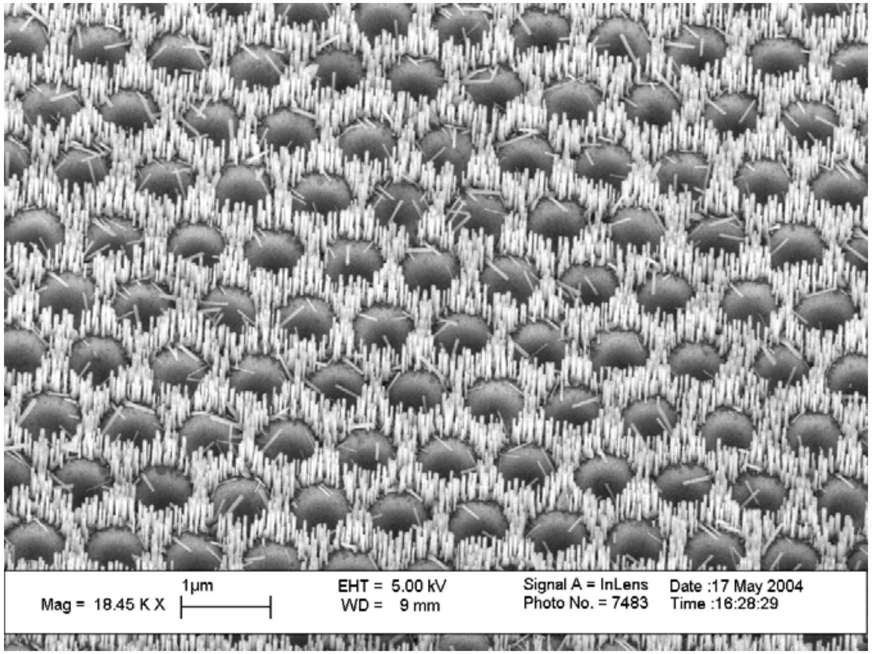
330 nm sphere diameter

Luminescent, high index multi-layered inverse opals fabricated using ALD

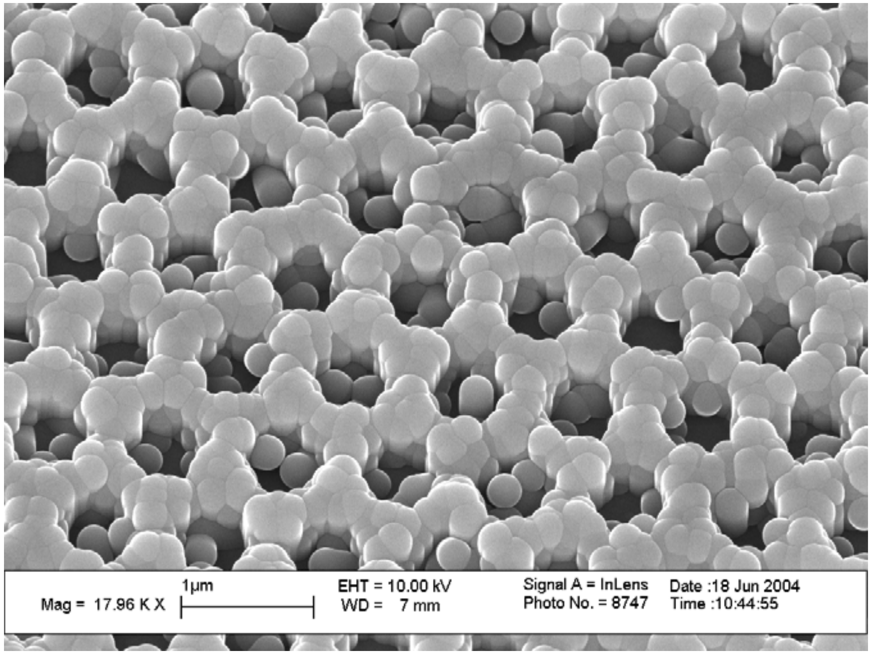
J.S. King, *et al*., submitted to *Adv. Mater.*

TiO_2 Coated ZnO Arrays

Template patterned growth, followed by ALD of TiO_2 was used to create novel 2D structures

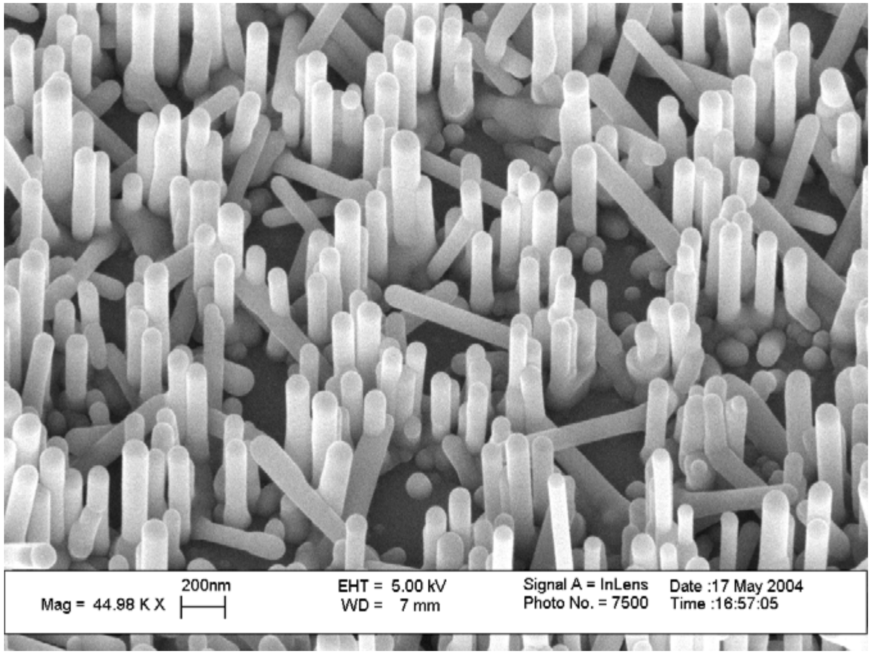


Aligned ZnO nano-rods in a hexagonal matrix on a sapphire substrate.

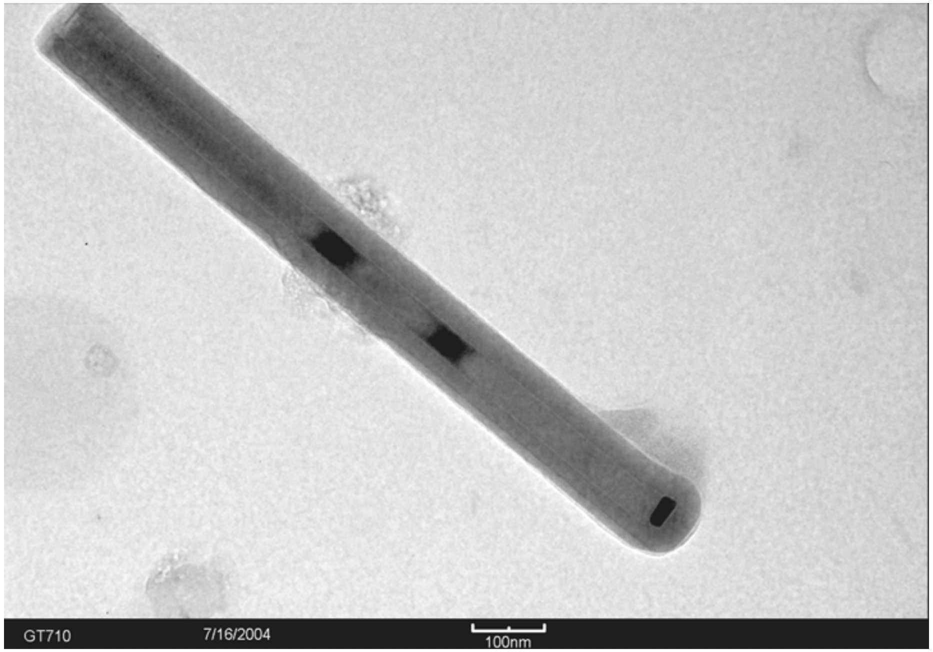


Aligned ZnO nano-rods coated with 100 nm of TiO_2 at 100°C.

TiO_2 Coated ZnO Arrays



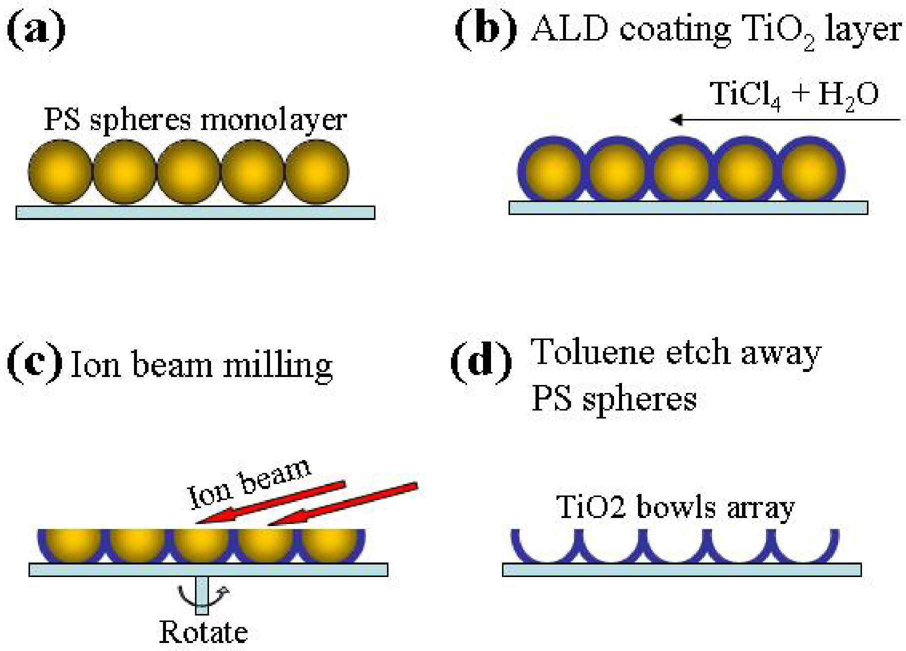
Aligned ZnO nano-rods coated with 50 nm of TiO_2 at 100°C.

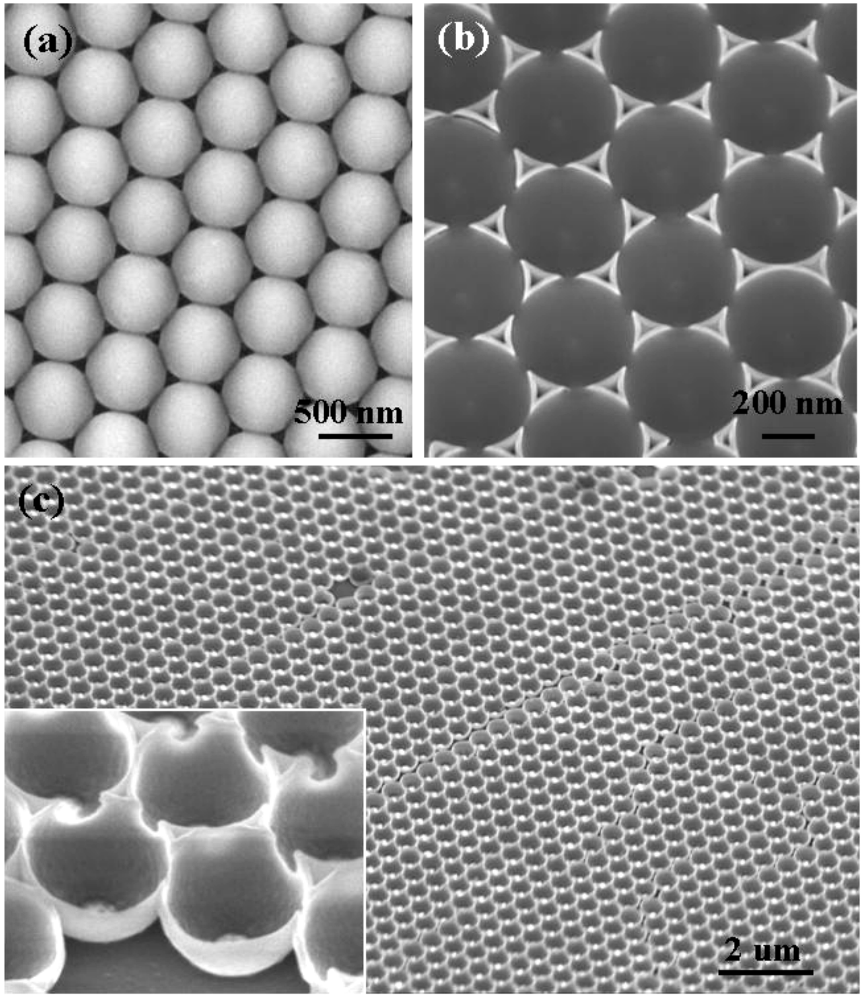


TEM image of a TiO_2 coated ZnO nano-rod.

TiO_2 Bowl Arrays

- Self-assembly for template patterning.





X.D. Wang, *et al*., 1:30 pm Today

X.D. Wang, *et al*., *Nano Letters* (2004).

Summary

- ALD is an ideal deposition method for PC fabrication.
- Fabricated high quality inverse opal photonic crystals in the visible spectrum using ALD.
- TiO_2 ALD conditions optimized for complete, uniform infiltrations with smooth and conformal coatings.
  – Growth/Anneal protocol developed to form anatase inverse opals
- Precise control enables novel photonic crystal structures:
  – Inverse opals with void space air pockets (enhanced PBG)
  – Achieved maximum infiltration of 86%
  – Perfect match between reflectivity and calculated band structure
  – Multi-layered, luminescent, high index inverse opals
- Novel structures created with ALD
  – TiO_2/ZnO aligned nano-rod arrays
  – TiO_2 nano-bowl arrays
- **ALD template infiltration is a pathway for photonic crystal band gap engineering.**

Acknowledgments

- Curtis Neff
- Davy Gaillot
- Tsuyoshi Yamashita
- US Army Research Lab: S. Blomquist, E. Forsythe, D. Morton
- Dr. Won Park, U. Colorado

- Dr. Mike Ciftan, US Army Research Office: MURI “Intelligent Luminescence for Communication, Display and Identification”