Photonic Crystal-Based Optical Devices

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Photonics Today: Interesting, but Exciting?

It's hard to get excited about 2-D.
Current 2-D Optical Network Devices

“Innovate to manipulate photons in a flexible, compact way.”
Lucent's (canceled) WaveStar™ LambdaRouter

2.5 dimensional?

Close-up of single mirror.

Array of microscopic mirrors, each able to tilt in various directions, to steer light.
So, how to get to 3-D?

**Colloidal self-assembly**

Ref: many, many groups!

**Multiphoton polymerization**


**3-D Applications**

- Low-loss waveguides
- Optical cavities
- Zero-threshold microlasers
- Light-emitting diodes
- All-optical transistors
- Improved photoreactors
- Tunable filters

Prof. John Joannopoulos
http://ab-initio.mit.edu/photons/index.html

**Lithography**


**4-beam holography**

Requirements for a Photonic Crystal: 1) Periodicity in the dielectric constant; 2) Domain sizes ~ $\lambda$

Properties of a Photonic Crystal:

- **Bragg Diffraction**
  - $m\lambda = 2d (n_{eff}^2 - \sin^2 \Phi)^{1/2}$

- **Light Modulation**
  - weak
  - $\uparrow$ index contrast
  - strong
  - appropriate geometry

Figures modified from: http://www.elec.gla.ac.uk/groups/opto/photoniccrystal/Welcome.html

J. Joannopoulos et al. *Photonic Crystals*, 1995, p. 82
Example PBG Application: Waveguiding

Current Principle:
Total Internal Reflection

PBG-Based:
Frequency Confinement

Inherent losses typically > ~ 0.2 db / km

Cannot tolerate bend radii < 5 cm

Require periodic amplification of signal

Not suitable for small bend radii

Defects create states in the bandgap

Forbidden frequencies are confined within defects

100% transmission around bend radii ~ λ!

http://ab-initio.mit.edu/photons/index.html
3-D Self-Assembly: Colloidal Crystals (Opals)

- Natural Opals consist of periodically arranged silica spheres in a matrix
- The colors of an opal are due to Bragg diffraction of light by planes of silica spheres
- Synthetic Opals are formed by careful assembly of silica spheres from solution


Reflectance / %

0 20 40 60

Wavelength / nm

400 500 600 700 800 900 1000
Colloidal Crystals – Diffraction Yields Color

White light illumination at varying angles

Effect of particle diameter

Blue: 570 nm diameter colloids
Red: 590 nm diameter colloids

FWHM ~100nm
Peak Reflectance ~70-75%
Defects in Colloidal Crystals?

Image courtesy of Satoshi Takeda, Pierre Wiltzius
A Better Colloidal Crystal – Nanoparticle Mediated Colloidal Epitaxy


Colloidal epitaxy → low defect density & defined orientation with respect to the substrate
Gravity Driven Nanoparticle Mediated Colloidal Epitaxy

Silica ($\phi=1.18\mu m$, 0.5vol%) Zirconia ($\phi\sim3nm$, 0.03vol%)

Phase behavior
microsphere-nanoparticle size ratio 197

Nanoparticle volume fraction ($\phi_{nano}$)

Microsphere volume fraction ($\phi_{micro}$)

Tohver, V. PNAS 2001, 98, 8950
Tohver, V. Langmuir 2001, 17, 8414
Vacancy concentration ~1 per 200 particles

Patterned substrate
- $\phi_{\text{micro}} = 10^{-3}$
- $\phi_{\text{micro}} = 2.5 \times 10^{-3}$

Layer number (#)

Vacancy concentration (#/microsphere)

Langmuir, In press, 2004
But, defined defects in colloidal crystals?

Optical cavities & Waveguides?
Two-Photon Polymerization (TPP)

**Motivation:** Need method for generation of embedded 3D defect features in self-assembled photonic crystals

Absorption Probability \( \alpha P^n \)

\( P = \) Laser intensity
\( n = \) Number of photons involved in the excitation process

Multi-Photon Excitation Volume \( \alpha \lambda^3 \)

Photopolymerization of high-resolution three-dimensional free-form structures

**System Characteristics**

**Beam:**
- Ti:Sapphire
- Pulsed, mode-locked
- \( \lambda = 780 \text{ nm} \)
- \( \tau \sim 100 \text{ fs} \)
- \( F = 82 \text{ MHz} \)
- \( P \sim 20-200 \text{ mW} \)
- N.A. \( \sim 1.32 \)

**Initiator:**
- \( \sigma \sim 9 \times 10^{-47} \text{ cm}^4 \text{ s} / \text{ photon molecule} \)
- \( \lambda_{\text{max}} \sim 780 \text{ nm for two photon excitation} \)

**Monomer:**
- Trimethylolpropane triacrylate (TMPTA)

*Courtesy of Air Force Research Laboratory (e.g. R. Kannan et al. Chem. Mater. **2001**, 13, 1896-1904)*
Optics for Multiphoton Polymerization

- Nd:YAG
- Ti:Sapphire
- Beam Expander
- Spectrum Analyzer
- Shutter
- EOM
- Galvometer Stage
- Objective
- Scanning Mirrors
- Region of Interest (defined in software)
- Pulse Amplifier
- Pulse Compression Sequence
- Objective
- High/Low
- Objective
- Objective
- Region of Interest
- Region of Interest
- Region of Interest
3-D Pattern Formation in Colloidal Crystals – Procedure

1. Settling of colloids onto template
   - Formation of colloidal crystal
   - Image using confocal
   - Drying and stabilization of colloidal crystal
   - Addition of monomer and photoinitiator

2. Rinse away unpolymerized material
   - Fill with dye for imaging
   - Invert and photopolymerize
   - Objective
Sedimentation of colloidal crystal

Multi-photon polymerization

Remove unpolymerized materials

LSCM, top view

LSCM, side view

SEM

Edge resolution ≤ 100nm

W. Lee, S. A. Pruzinsky, P. V. Braun,
2-photon Polymerization in and out of Colloidal Crystals

**xy slice**

**xz slice**

Colloidal Crystal

polymer

150 nm
Successful fabrication of embedded waveguide structures in self-assembled photonic crystals!

**Press Reports:**
Selenium – a High Refractive Index Filler

1.6 μm silica colloid settled on a 1.66 μm template. Index matched with DMF (n ~ 1.43). White light illumination

Results in high refractive index contrast, highly oriented photonic band gap materials

True fcc colloidal crystal created by settling on a patterned substrate. The colloidal crystal nucleates and grows perpendicular to the 001 face, therefore no stacking faults form.

Selenium – a High Refractive Index Filler

Dielectric contrast enhancement: Melt Imbibing of Selenium

LSCM image of polymer feature

Melt selenium (~250 C)

Pressurize

Etch silica (HF)
Next Step

Characterization of transmission through embedded waveguides
Inserted Planar Defects in Colloidal Crystals

Defect thickness
130 nm
230 nm
280 nm


Integrated Photonics?


FWHM = 1 nm (0.25 nm possible)

48-channel echelle grating demultiplexer chip.
Metallic Photonic Crystals

Enhance blackbody emission?

S. Y. Lin, Nature 2002

Electrodeposited Ni inverse Opal
Templated by 466 nm PS spheres
Yun-Ju Lee, P. V. Braun unpublished
After semiconductor electrodeposition, the colloidal particles are removed via solvent.
Possible Stimulus
pH
Ionic strength
Solvent
Binding

Because \( \Delta \lambda \sim \Delta d \), swelling enables sensing

\[
\lambda = 2dn_{eff} \approx 2d \left( \sum_i n_i^2 V_i - \sin^2 \phi \right)^{1/2}
\]

- \( d \) = interlayer distance
- \( n_i \) = refractive index of component \( i \)
- \( V_i \) = volume fraction of component \( i \)
- \( \phi \) = angle between incident beam and sample normal

Note: See lectures by Prof. Sandy Asher
Pioneered the field
1. Assemble colloidal crystal in flow cell
2. Infiltrate with monomer mixture
3. UV irradiate (356 nm, 50 min)
4. CHCl₃ etch (24 hours)
5. Solvent exchange
6. Structural and optical characterization

Polymerization of Templated Hydrogels

Glucose Sensing with Mesoscale Photonic Crystals

Can also do pH sensing (Adv. Mater. 2003)

PBA (phenylboronic acid)

Glucose-PBA complex

[Glucose]

0 mM $\rightarrow$ 100 mM

![Reflection vs Wavelength](image)

Inflow from syringe pump

Outflow

Flow cell

Hydrogel

SEM of templated hydrogel

Y.-J. Lee et al. *Langmuir*, 2004
Kinetics of Glucose Sensing

Increasing [Glu] Diffraction Shift Kinetics

- $10 \rightarrow 100$ mM, $t_{eq} \approx 250$ s
- $1 \rightarrow 10$ mM, $t_{eq} \approx 1100$ s
- $0.1 \rightarrow 1$ mM, $t_{eq} > 1500$ s

Normalized diffraction shift vs. elapsed time (s)

Inset: Diffraction wavelength (nm) vs. elapsed time (s)
Reflection Spectra of 6.25% APBA Hydrogel

Dramatic Decrease in Diffraction Efficiency with Swelling

WHY?

Reflection Spectra of 5mol% AA Hydrogel

[Glucose] (in buffer)
0 mM → 100 mM

Dramatic Decrease in Diffraction Efficiency with Swelling

WHY?

Reflection Spectra of 6.25% APBA Hydrogel

[Glucose] (in buffer)
0 mM → 100 mM

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Dramatic Decrease in Diffraction Efficiency with Swelling

WHY?
Simple Models for Hydrogel Swelling → Diffraction Response

Reflectance (%) vs. \( \lambda / \lambda_0 \)

- **Initial State**
- **Constant Volume**
- **Pore Swelling**
- **Pore Shrinkage**

The graph shows the reflectance (%) as a function of the ratio \( \lambda / \lambda_0 \) for different states of the hydrogel:

- **Initial State**
- **Constant Volume**
- **Pore Swelling**
- **Pore Shrinkage**
1. Synthesize Acrylated Rhodamine B
   Rhodamine B-ITC + 2-Aminoethylmethacrylate·HCl

2. Polymerize hydrogel in colloidal crystal (PS, d = 3 μm, t = 25 μm) HEMA + 5% AA + 0.66% EDGM + ~10 μM acrylated Rhodamine B

3. Etch colloids

4. Image with 2-photon confocal microscopy
Two-photon Imaging – Bottom Layer

fcc (111), bottom layer

Pore deformation at pH >= 4.5
Partial pore closure at high pH
- Substrate pinning
Two-photon Imaging Results – Layer 2

fcc (111), 2nd layer

pH 3.4

pH 4.5 (~ pK_a)

pH 5.0

pH 5.7

pH 6.6

Pore deformation below pH 4.5
Nearly complete collapse at pH 6.6
Finite Element Analysis

Parameters
- ¼ of an inverse fcc unit cell modeled
- Periodic boundary conditions
- Bottom surface does not move vertically
- Thermal strain applied → 59% volume change
- $E = 10^6$ N/m$^2$, $\nu = 0.499$

So, how will this impact the optical response?
Conclusions and Acknowledgements

Colloidal Epitaxy
Binary nanoparticle-colloid suspensions enable the formation of crack-free, low defect density dry colloidal crystals
Dr. Wonmok Lee, Dr. Michael Bevan, Prof. Jennifer Lewis

Waveguides
Direct writing of 3-D structures in colloidal crystals through multiphoton polymerization
Stephanie Pruzinsky, Dr. Wonmok Lee

Chemical Sensors
Optically active structures formed from chemically responsive inverse opal hydrogels
Yun-Ju (Alex) Lee, Stephanie Pruzinsky, Carla Heitzman, Walter Frey, Prof. Harley Johnson

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