Optical and Crystallographic Properties of Inverse Opal Photonic Crystals Grown by Atomic Layer Deposition

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Research Team

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Outline

• Introduction: Photonic Crystals
• Fabrication of Luminescent Inverse Opals
• Atomic Layer Deposition
• Results
  • ZnS:Mn controlled infiltration
  • TiO$_2$ infiltration and heat treatment
  • ZnS/TiO$_2$ multi-layered structure
• Summary
Photonic Crystals

- Photonic Crystal – Periodic modulation of dielectric constant
- Exhibit photonic band gap (PBG).
- Photonic band gap materials can be used to create waveguides, resonators, couplers, filters, etc.

- Luminescent 2D & 3D PC structures offer the potential for controlling wavelength, efficiency, time response and threshold properties (Plasma phosphors, solid state lighting, etc.).
Reflectance measurements probe photonic band structure: PBG, P-PBG
Fabrication: Inverse Opal PC

- Provide template using self-assembled silica opal.
  - 10 µm thick FCC polycrystalline film, (111) oriented.
- Infiltrate interstitial space with high n material.
  - ZnS:Mn $n \approx 2.5$ @ 425 nm (pseudo photonic band gaps)
  - TiO$_2$ (rutile) $n_{avg} \approx 3.08$ @ 425 nm (full photonic band gap possible)
- Etch SiO$_2$ spheres, forming inverse opal.

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Self Assembly

Sintered Opal

ALD

Infiltrated Opal

Etch

Inverted Opal
Luminescent Photonic Crystals

• Inverse opal - Full PBG if $n > 2.8$

• Most luminescent materials do not offer sufficient index.

• High index, luminescent materials required for PCP
  – Combination of two materials offers practical route.
  – ZnS:Mn (luminescent) + TiO$_2$ (high $n$) multi-layer.

• Requires controlled thickness; dense, conformal films.
  – 24.5 % vol. fraction doubles PBG (John & Busch)
  – Atomic Layer Deposition (ALD) fulfills requirements.
Atomic Layer Deposition

ALD is a CVD growth technique utilizing sequential reactant pulses.

**ALD Growth of ZnS**

(a) Chemi + physisorption

(b) Physisorbed layer removal

(c) Formation of ZnS

(d) Removal of H$_2$S and HCl

Surface limited growth: conformal films + monolayer control
ZnS:Mn Stepwise Infiltration

- Previously demonstrated ZnS:Mn full infiltration (MRS 2002, APL 83).
- However, multi-layered opals require infiltration finesse.
- 330 and 460 nm opals were filled with increasing % of ZnS:Mn.
- Deposition @ 500º C with a MnCl$_2$ doping pulse every 32 cycles.
- Shift of P-PBG to longer wavelengths shown in specular reflectance after infiltrations.
ZnS:Mn Stepwise Infiltration

Specular reflectance

Γ-L gap positions

Deviation from theory:
• Coating thickness based on planar growth, not curved surface.
• Reflectivity measured @ 15° from normal.
TiO$_2$ Infiltration

- Need to demonstrate ability to grow high index component by ALD.
- Aarik, et.al. have shown in planar ALD TiO$_2$ growth studies:
  \[<165^\circ\ C = \text{amorphous, } 165^\circ - 350^\circ\ C = \text{anatase, } >350^\circ\ C = \text{rutile}\]
- TiO$_2$ was infiltrated using TiCl$_4$ and H$_2$O pulses.
- Amorphous film growth has advantages over crystalline:
  - **Amorphous films exhibit very smooth surfaces.**
  - Better suited for the conformal infiltration of opals
- Infiltrate at low T, then heat treat to obtain rutile (high index).
- Infiltrations were performed at both 100$^\circ$ C and 500$^\circ$ C.
- Inverse opal formation
  - For amorphous film, ion mill to expose silica (very conformal).
TiO$_2$ Infiltration

Si058 (200 nm Opal)

![Graph showing reflectivity vs wavelength for different infiltration cycles. The graph includes lines labeled 143 cycles, 200 cycles, 250 cycles, and 300 cycles, each indicating different infiltration percentages: 56%, 80%, 86%, and 94%. The x-axis represents wavelength in nm, ranging from 200 to 800.]
Si090A (430 nm)  Si091D (330 nm)
Si083 (273 nm)
**TiO₂ Rutile Conversion - XRD**

Deposited at 500° C  
(initially anatase).  
~50% rutile after HT

Deposited at 100° C  
(initially amorphous).  
~65% rutile after HT
ZnS/TiO$_2$ Inverse Opal

- TiO$_2$ at deposited at 100° C, ZnS:Mn at 500° C.
- Amorphous TiO$_2$ converts to anatase during ZnS:Mn growth.

XRD

Specular Reflectance
ZnS/TiO₂ Infiltrated Opal

ZnS: Mn/TiO₂ multi-layered 330 nm infiltrated opal
ZnS/TiO$_2$ Inverse Opal

ZnS:Mn/TiO$_2$ multi-layered 330 nm inverse opal.
Summary

- Successful formation of ZnS:Mn and TiO$_2$ inverse opals.
- **Precise control of ALD infiltration demonstrated.**
- As-deposited TiO$_2$ can be converted to rutile phase.
- Clearly demonstrated **ability to grow complex luminescent PC structures** at the nanoscale using ALD.
- Future: PL measurements, RTA, more complex structures.
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