ZnS-based Photonic Crystal Phosphors Fabricated Using Atomic Layer Deposition

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Outline

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• Research Direction
• Inverse Opal Fabrication Methodology
• Atomic Layer Deposition Growth Conditions
• Results
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  • Specular Reflectance
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• Summary
Photonic Crystals

• 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
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.

Atomic Layer Deposition
Materials and Growth Conditions

- ZnS:Mn was infiltrated* using alternating pulses of ZnCl₂ and H₂S, with a MnCl₂ pulse applied every hundredth cycle to dope the film with Mn²⁺ 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

460 nm infiltrated opal

220 nm inverse opal

(111)
Specular Reflectance
Band Diagram

ZnS/SiO$_2$ Infiltrated Opal, $n_{\text{contrast}} = 2.5/1.5$
Specular Reflectance
Comparison with Theory

- 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/SiO₂ Opal
Index contrast 2.5/1.5

- Polycrystalline films: multiple directions probed.
- Both infiltrated and inverse opals exhibit (111) reflectivity peaks
  – shift to lower $\lambda$ as measurement angle increases.
- Confirms existence of PPBGs.
- PPBGs will affect photoluminescence of PCPs.
Photoluminescence
220 nm ALD ZnS:Mn/SiO$_2$ Opal

Detection Angle, $\theta$
(111)

330 nm ZnS band edge excitation
(Xenon Lamp)
Photoluminescence

220 nm ZnS:Mn/SiO₂ Opal

330 nm Excitation

![Graph showing photoluminescence spectra with peaks at various wavelengths. The x-axis represents wavelength in nm, and the y-axis represents intensity in arbitrary units.]
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.