

# Sculptured Thin Films: Nanoengineered Metamaterials

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By

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# Sculptured Thin Films: Nanoengineered Metamaterials

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**Department of Engineering Science and Mechanics**  
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- 
- Nanotechnology
  - Metamaterials
  - Sculptured Thin Films



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# Nanotechnology





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# Nanotechnology

promises to be

- pervasive
- ubiquitous



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# Nanotechnology: Many Initiators

|       |                                 |
|-------|---------------------------------|
| 1850s | Colored glasses (nanoparticles) |
| 1880s | Thin films                      |
| 1910s | Colloidal chemistry             |
| 1960s | Integrated circuits             |
| 1970s | Supramolecular chemistry        |
| 1981  | Scanning tunneling microscopy   |



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# Significant Attributes

- Large surface area per unit volume
- Quantum effects



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# Dimensionality

- 1 D

- Ultrathin coatings

- 2 D

- Nanowires and nanotubes

- 3 D

- Nanoparticles



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# Nanomaterials

- *Lots of potential applications*

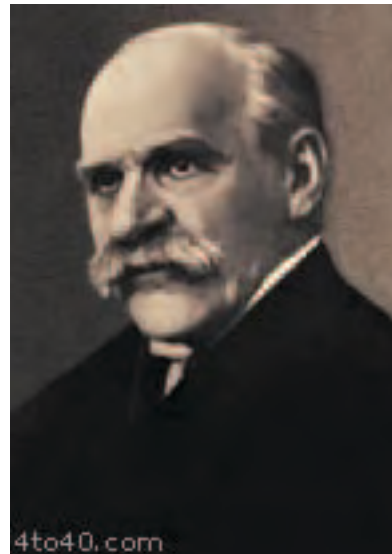


# Metamaterials



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# J.B.S. Haldane



The Creator, if he exists, has ...



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... an inordinate fondness for beetles.





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# Engineers

have had an inordinate fondness

for

composite materials

all through the ages



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# Evolution of *Materials Research*

- Material Properties (< ca.1970)



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# Evolution of *Materials Research*

- Material Properties (< ca.1970)
- Design for Functionality (ca. 1980)



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# Evolution of *Materials Research*

- Material Properties (< ca.1970)
- Design for Functionality (ca. 1980)
- Design for System Performance (ca. 2000)



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# Multifunctionality



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# Multifunctionality





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# Multifunctionality

## Performance Requirements on the Fuselage



1. Light weight (for fuel efficiency)
2. High stiffness (resistance to deformation)
3. High strength (resistance to rupture)



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# Multifunctionality

## Performance Requirements on the Fuselage



1. Light weight (for fuel efficiency)
2. High stiffness (resistance to deformation)
3. High strength (resistance to rupture)
4. High acoustic damping (quieter cabin)



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# Multifunctionality

## Performance Requirements on the Fuselage



1. Light weight (for fuel efficiency)
2. High stiffness (resistance to deformation)
3. High strength (resistance to rupture)
4. High acoustic damping (quieter cabin)
5. Low thermal conductivity (less condensation; more humid cabin)

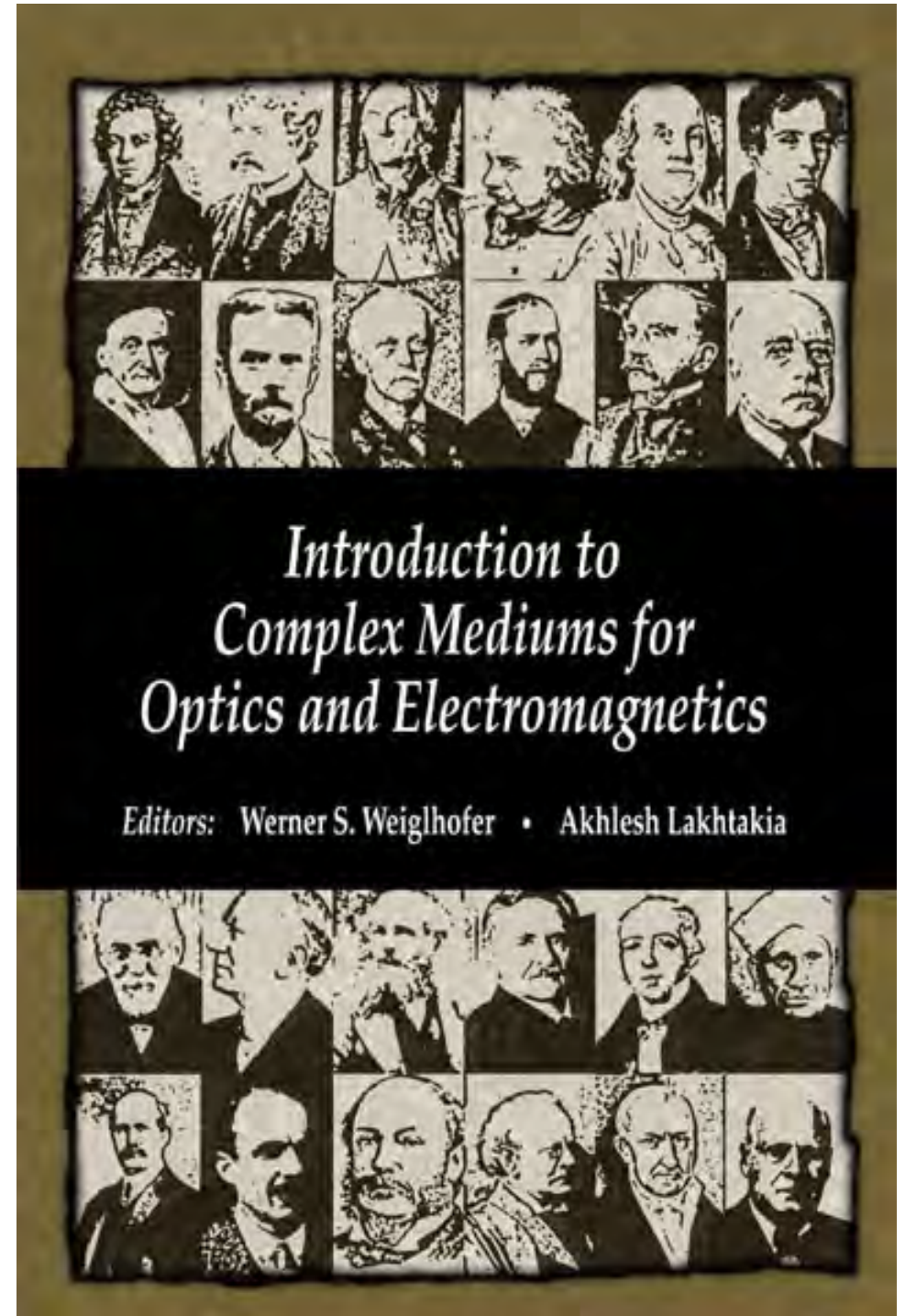


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# Metamaterials

Rodger Walser

*SPIE Press (2003)*





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# “Updated” Definition

**composites** designed to produce an optimized combination of two or more responses to specific excitation



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# Cellularity

# Nanoengineered Metamaterials

**Cellularity**

**Multifunctionality**



**Morphology**

**Performance**

# Nanoengineered Metamaterials

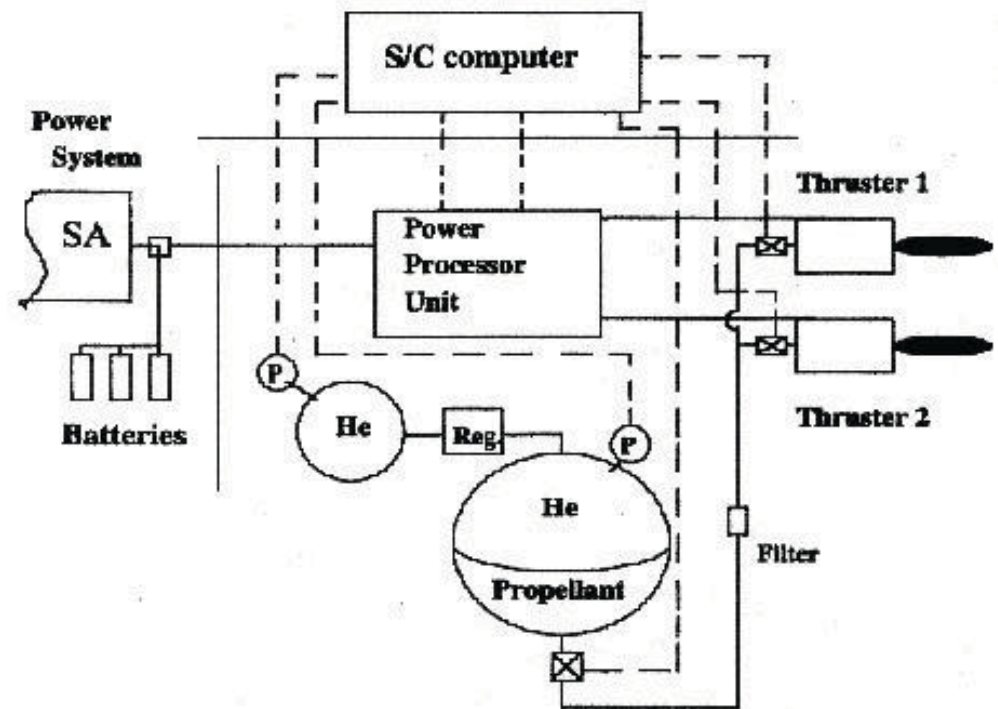
**Multi-component system = Assembly of different components**

Component:

Simple action

Assembly of components:

Complex action



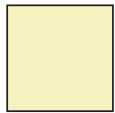


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# Nanoengineered Metamaterials



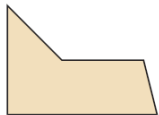
Energy harvesting cell



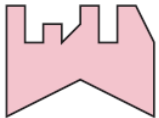
Energy storage cell



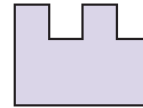
Energy distributor cell



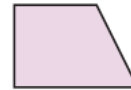
RFcomm cell



IRcomm cell



Chemisensor cell



Force-sensor cell



Shape-changer cell



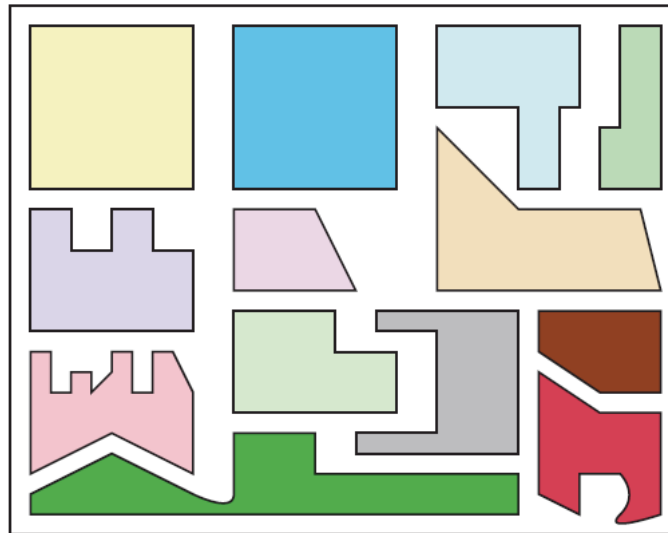
Light-source cell



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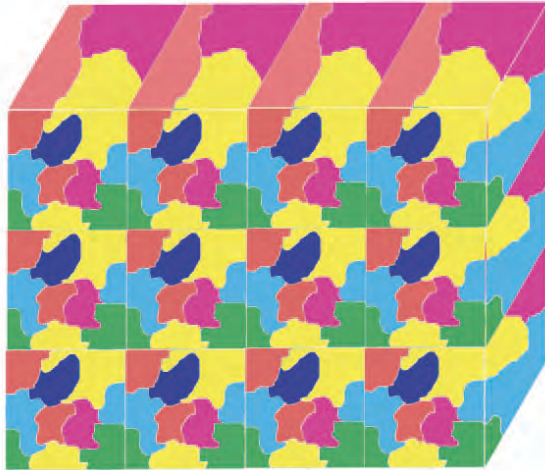
# Nanoengineered Metamaterials

## Supercell

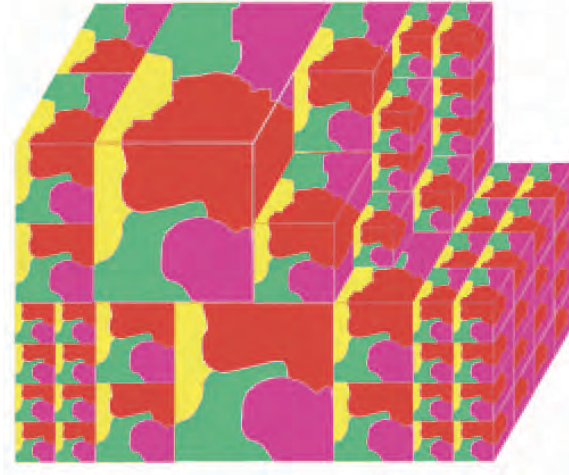


# Nanoengineered Metamaterials

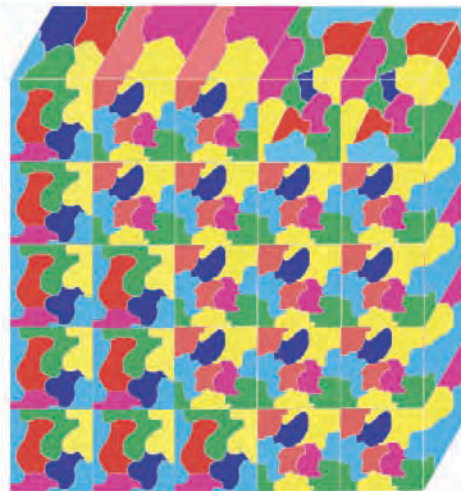
Periodic Arrangement of Supercells



Fractal Arrangement of Supercells

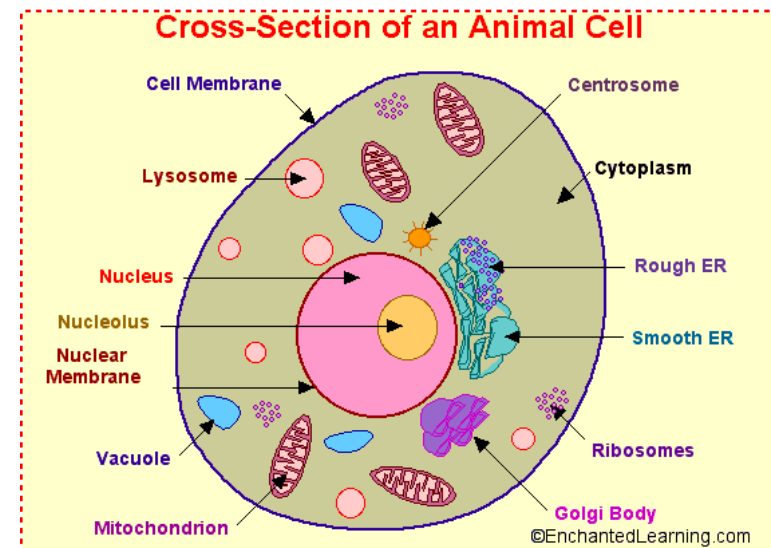
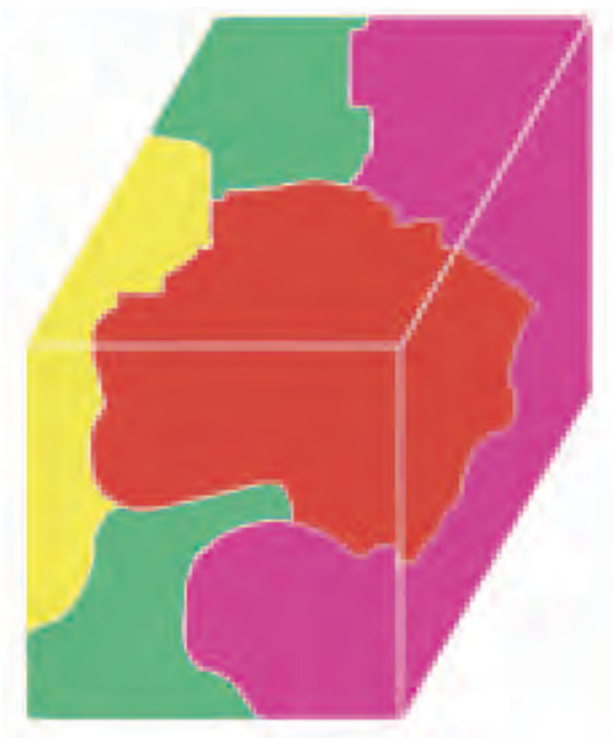


Functionally Graded Arrangement of Supercells



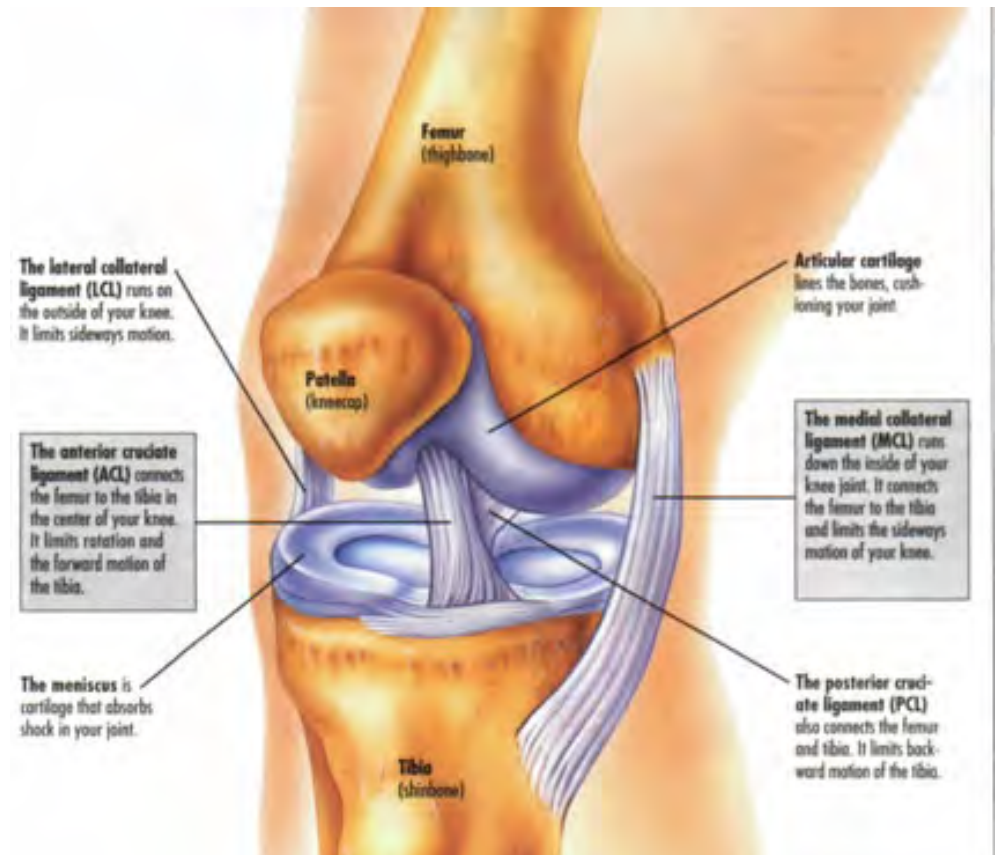
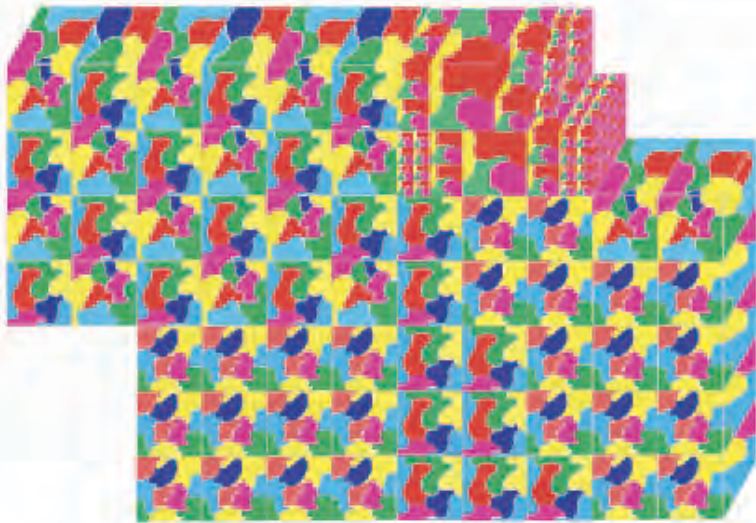
# Nanoengineered Metamaterials

## Biomimesis



# Nanoengineered Metamaterials

## Biomimesis





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# Nanoengineered Metamaterials

## Fabrication

1. Self-assembly
2. Positional assembly
3. Lithography
4. Etching
5. Ink-jet printing
6. ....
7. ....
8. Hybrid techniques

# Sculptured Thin Films



Sculptured Thin Films



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# Sculptured Thin Films

Assemblies of Parallel Curved Nanowires/Submicronwires

Controllable Nanowire Shape

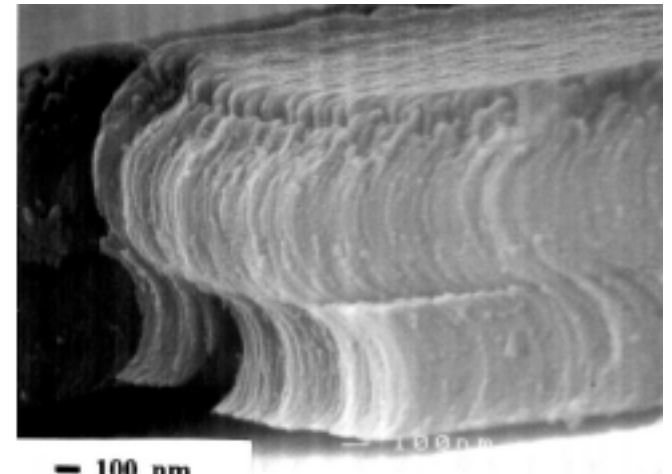
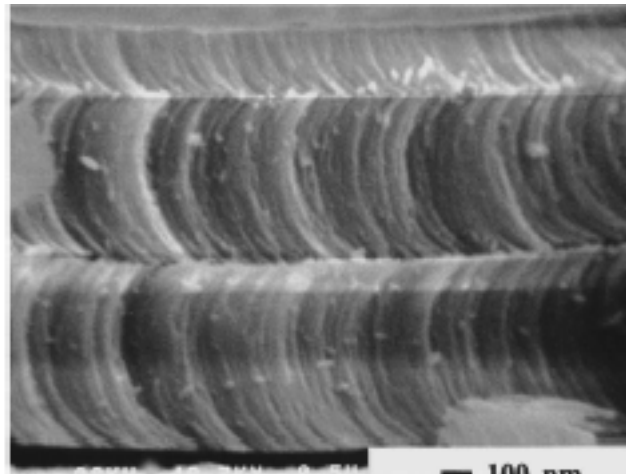
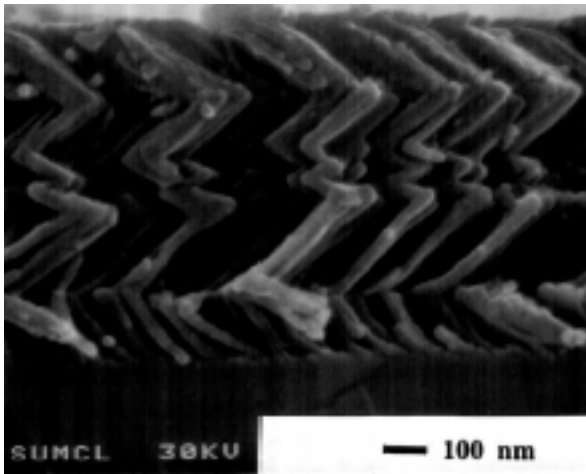


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# Sculptured Thin Films

Assemblies of Parallel Curved Nanowires/Submicronwires

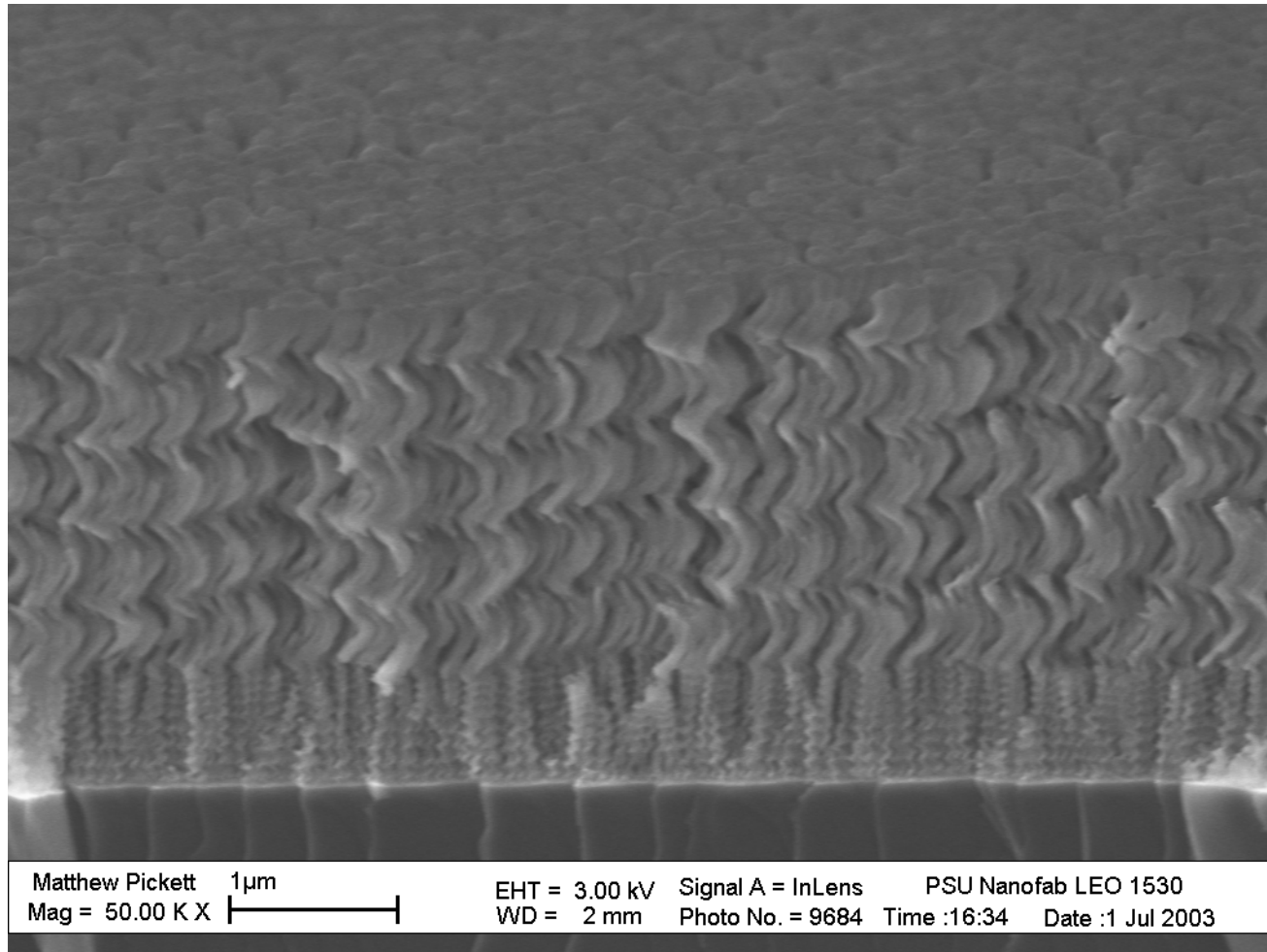
Controllable Nanowire Shape





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# Sculptured Thin Films



Morphological  
Change



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# Sculptured Thin Films

Assemblies of Parallel Curved Nanowires/Submicronwires

Controllable Nanowire Shape

*2-D morphologies*

*3-D morphologies*

vertical sectioning

Nanoengineered Materials (1-3 nm clusters)

*Controllable Porosity (10-90 %)*



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# Sculptured Thin Films

*Antecedents:*

*(i) Young and Kowal - 1959*

*(ii) Niuewenhuizen & Haanstra - 1966*

*(iii) Motohiro & Taga - 1989*

*Conceptualized by Lakhtakia & Messier (1992-1995)*



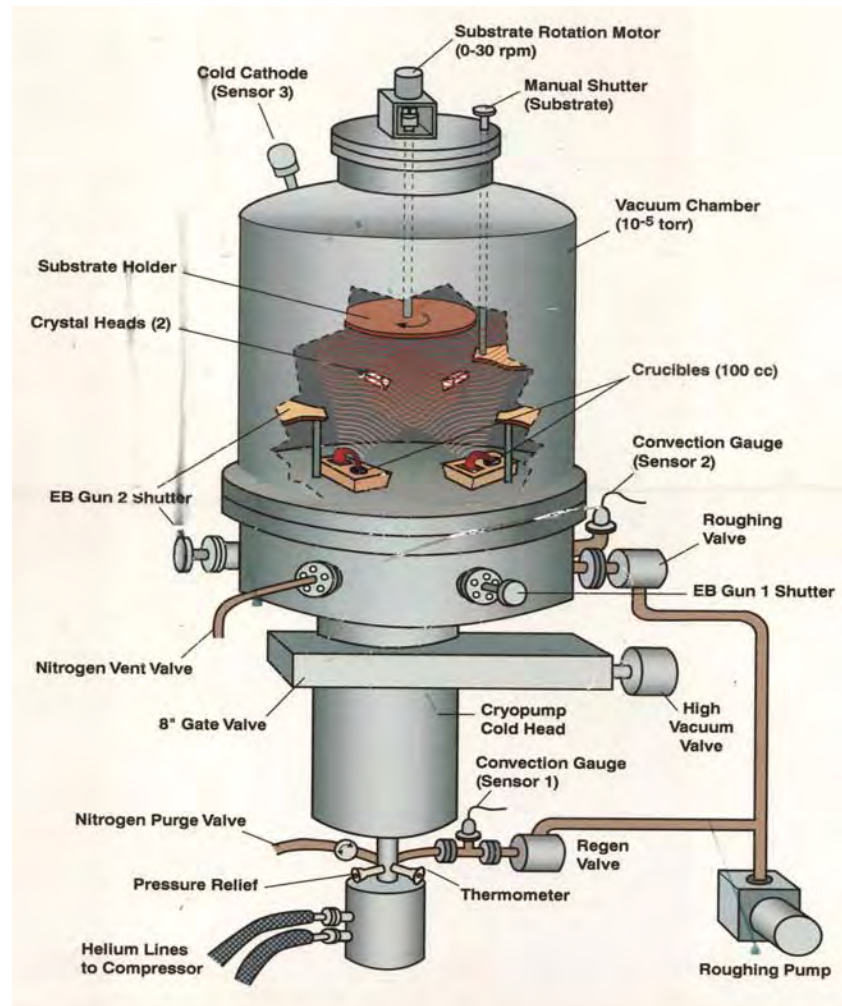
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# Sculptured Thin Films

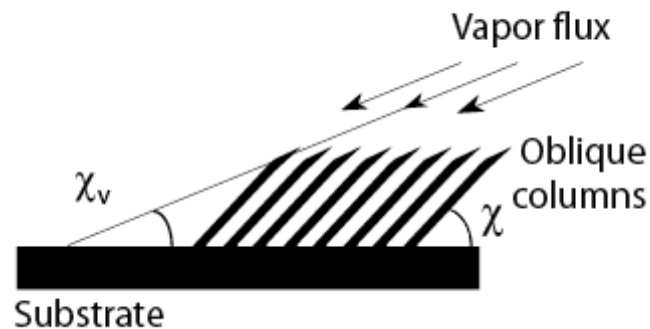
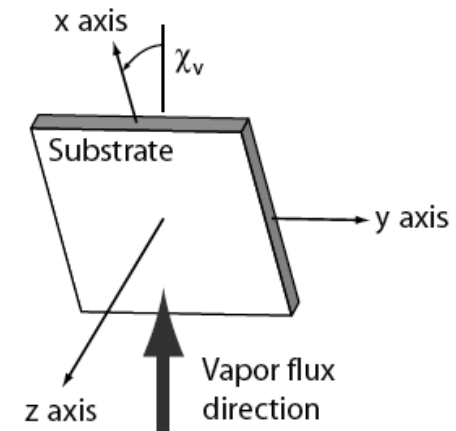
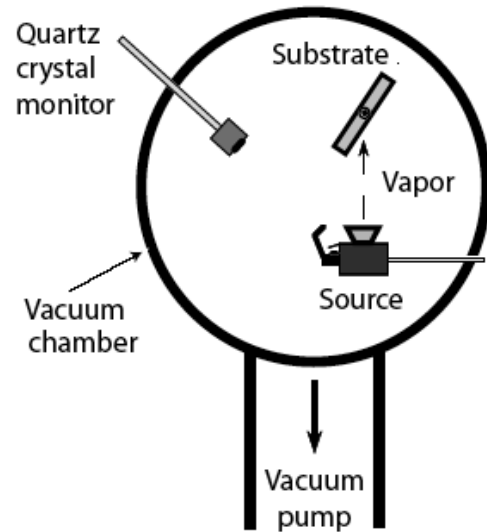
## Research Groups

- (i) *Penn State*
- (ii) *Edinboro University of Pennsylvania*
- (iii) *Lock Haven University of Pennsylvania*
- (iv) *Millersville University*
- (v) *Rensselaer Polytechnic University*
- (vi) *University of Arkansas, Little Rock*
- (vii) *University of Toledo*
- (viii) *University of Georgia*
- (ix) *University of South Carolina*
- (x) *University of Nebraska at Lincoln*
- (xi) *Pacific Northwest National Laboratory*
- (xii) *University of Alberta*
- (xiii) *Queen's University*
- (xiv) *University of Moncton*
- (xv) *National Autonomous University of Mexico*
- (xvi) *Imperial College, London*
- (xvii) *University of Glasgow*
- (xviii) *University of Edinburgh*
- (xix) *University of Leipzig*
- (xx) *ENSMM, Besançon*
- (xxi) *Toyota R&D Labs*
- (xxii) *Kyoto University*
- (xxiii) *Hanyang University*
- (xxiv) *Inha University*
- (xxv) *Dalian University of Technology*
- (xxvi) *National Taipei University of Tech.*
- (xxvii) *Indian Institute of Tech., Kanpur*
- (xxviii) *University of Otago*
- (xxix) *University of Canterbury*
- (xxx) *Ben Gurion Univ. of the Negev*
- (xxxi) *University of Campinas*

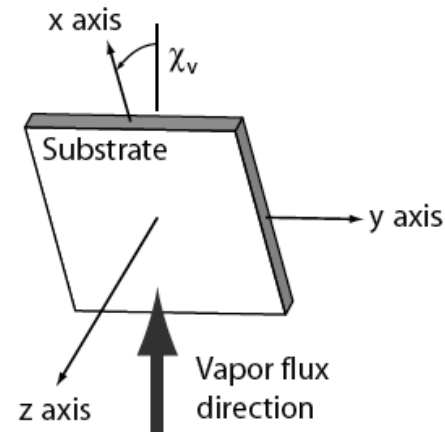
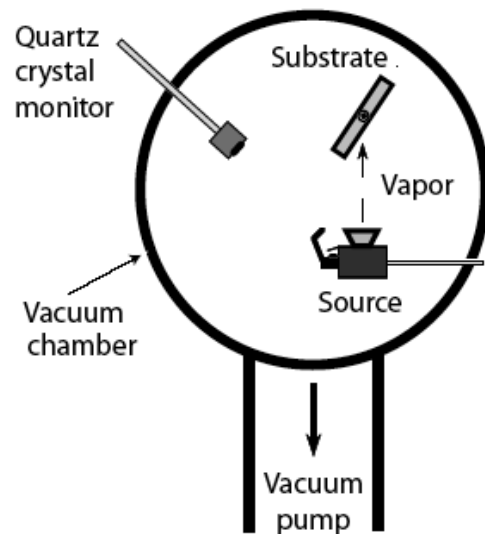
# Physical Vapor Deposition



# Physical Vapor Deposition (Columnar Thin Films)



# Physical Vapor Deposition (Sculptured Thin Films)



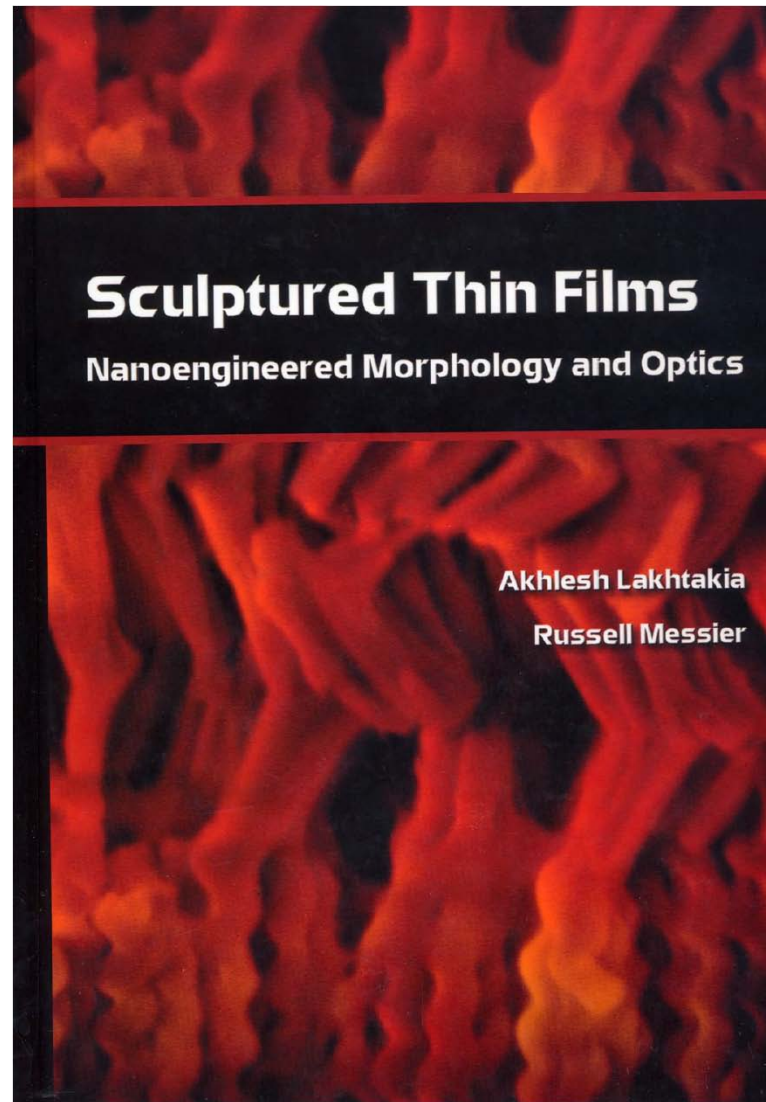
Rotate about  
y axis for  
nematic  
morphology

Rotate about  
z axis for  
helicoidal  
morphology

*Combined  
rotations for  
complex  
morphologies*



# STF Optics



# STF Optics

$$\mathbf{D}(\mathbf{r}, \omega) = \epsilon_0 \underline{\underline{S}}(z) \cdot \left[ \underline{\underline{\epsilon}}_{ref}(\omega) \cdot \underline{\underline{S}}^T(z) \cdot \mathbf{E}(\mathbf{r}, \omega) \right. \\ \left. + \underline{\underline{\alpha}}_{ref}(\omega) \cdot \underline{\underline{S}}^T(z) \cdot \mathbf{H}(\mathbf{r}, \omega) \right],$$

$$\mathbf{B}(\mathbf{r}, \omega) = \mu_0 \underline{\underline{S}}(z) \cdot \left[ \underline{\underline{\beta}}_{ref}(\omega) \cdot \underline{\underline{S}}^T(z) \cdot \mathbf{E}(\mathbf{r}, \omega) \right. \\ \left. + \underline{\underline{\mu}}_{ref}(\omega) \cdot \underline{\underline{S}}^T(z) \cdot \mathbf{H}(\mathbf{r}, \omega) \right],$$

**Dielectric,  
Magnetic, &  
Magnetoelectric  
Properties**

**Substrate  
Motion**

$$\underline{\underline{S}}_x(z) = \mathbf{u}_x \mathbf{u}_x + (\mathbf{u}_y \mathbf{u}_y + \mathbf{u}_z \mathbf{u}_z) \cos \xi(z) \\ + (\mathbf{u}_z \mathbf{u}_y - \mathbf{u}_y \mathbf{u}_z) \sin \xi(z), \\ \underline{\underline{S}}_y(z) = \mathbf{u}_y \mathbf{u}_y + (\mathbf{u}_x \mathbf{u}_x + \mathbf{u}_z \mathbf{u}_z) \cos \tau(z) \\ + (\mathbf{u}_z \mathbf{u}_x - \mathbf{u}_x \mathbf{u}_z) \sin \tau(z), \\ \underline{\underline{S}}_z(z) = \mathbf{u}_z \mathbf{u}_z + (\mathbf{u}_x \mathbf{u}_x + \mathbf{u}_y \mathbf{u}_y) \cos \zeta(z) \\ + (\mathbf{u}_y \mathbf{u}_x - \mathbf{u}_x \mathbf{u}_y) \sin \zeta(z).$$

# STF Optics

## Dielectric Materials

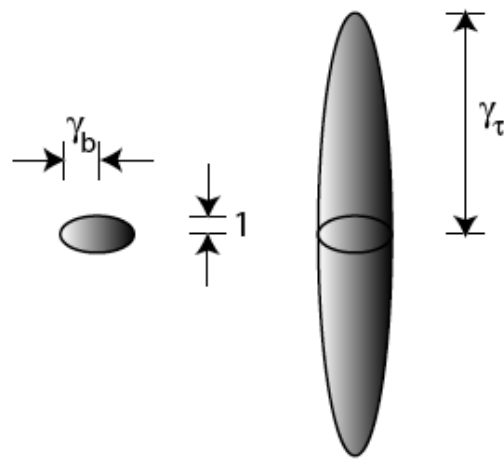
$$\begin{aligned}\mathbf{D}(\mathbf{r}, \omega) &= \epsilon_0 \underline{\underline{\epsilon}}_r(z, \omega) \cdot \mathbf{E}(\mathbf{r}, \omega) \\ &= \epsilon_0 \underline{\underline{S}}(z) \cdot \underline{\underline{\epsilon}}_{ref}(\omega) \cdot \underline{\underline{S}}^T(z) \cdot \mathbf{E}(\mathbf{r}, \omega), \\ \mathbf{B}(\mathbf{r}, \omega) &= \mu_0 \mathbf{H}(\mathbf{r}, \omega).\end{aligned}$$

$$\underline{\underline{\epsilon}}_{ref}(\omega) = \underline{\underline{\hat{S}}}_y(\chi) \cdot \underline{\underline{\epsilon}}_{ref}^o(\omega) \cdot \underline{\underline{\hat{S}}}_y^T(\chi)$$

$$\underline{\underline{\epsilon}}_{ref}^o(\omega) = \underline{\underline{\epsilon}}_{ref}(\omega) \Big|_{\chi=0} = \epsilon_a(\omega) \mathbf{u}_z \mathbf{u}_z + \epsilon_b(\omega) \mathbf{u}_x \mathbf{u}_x + \epsilon_c(\omega) \mathbf{u}_y \mathbf{u}_y$$

$$\underline{\underline{\hat{S}}}_y(\chi) = \mathbf{u}_y \mathbf{u}_y + (\mathbf{u}_x \mathbf{u}_x + \mathbf{u}_z \mathbf{u}_z) \cos \chi + (\mathbf{u}_z \mathbf{u}_x - \mathbf{u}_x \mathbf{u}_z) \sin \chi$$

# STF Optics



**Homogenize a  
collection  
of parallel ellipsoids  
to get  $\epsilon_{ref}^o(\omega)$**

# STF Optics

## Wave Propagation

$$\mathbf{E}(\mathbf{r}, \omega) = \mathbf{e}(z, \kappa, \psi, \omega) \exp [i\kappa(x \cos \psi + y \sin \psi)]$$

$$\mathbf{H}(\mathbf{r}, \omega) = \mathbf{h}(z, \kappa, \psi, \omega) \exp [i\kappa(x \cos \psi + y \sin \psi)]$$

# STF Optics

## Wave Propagation

$$\mathbf{E}(\mathbf{r}, \omega) = \mathbf{e}(z, \kappa, \psi, \omega) \exp [i\kappa(x \cos \psi + y \sin \psi)]$$

$$\mathbf{H}(\mathbf{r}, \omega) = \mathbf{h}(z, \kappa, \psi, \omega) \exp [i\kappa(x \cos \psi + y \sin \psi)]$$

$$\nabla \times \mathbf{E}(\mathbf{r}, \omega) = i\omega \mathbf{B}(\mathbf{r}, \omega),$$

$$\nabla \times \mathbf{H}(\mathbf{r}, \omega) = -i\omega \mathbf{D}(\mathbf{r}, \omega),$$

$$\begin{aligned} \mathbf{D}(\mathbf{r}, \omega) &= \epsilon_0 \underline{\underline{\epsilon}}_r(z, \omega) \cdot \mathbf{E}(\mathbf{r}, \omega) \\ &= \epsilon_0 \underline{\underline{S}}(z) \cdot \underline{\underline{\epsilon}}_{ref}(\omega) \cdot \underline{\underline{S}}^T(z) \cdot \mathbf{E}(\mathbf{r}, \omega), \\ \mathbf{B}(\mathbf{r}, \omega) &= \mu_0 \mathbf{H}(\mathbf{r}, \omega). \end{aligned}$$

# STF Optics

## Wave Propagation

$$\mathbf{E}(\mathbf{r}, \omega) = \mathbf{e}(z, \kappa, \psi, \omega) \exp [i\kappa(x \cos \psi + y \sin \psi)]$$

$$\mathbf{H}(\mathbf{r}, \omega) = \mathbf{h}(z, \kappa, \psi, \omega) \exp [i\kappa(x \cos \psi + y \sin \psi)]$$

$$\nabla \times \mathbf{E}(\mathbf{r}, \omega) = i\omega \mathbf{B}(\mathbf{r}, \omega),$$

$$\nabla \times \mathbf{H}(\mathbf{r}, \omega) = -i\omega \mathbf{D}(\mathbf{r}, \omega),$$

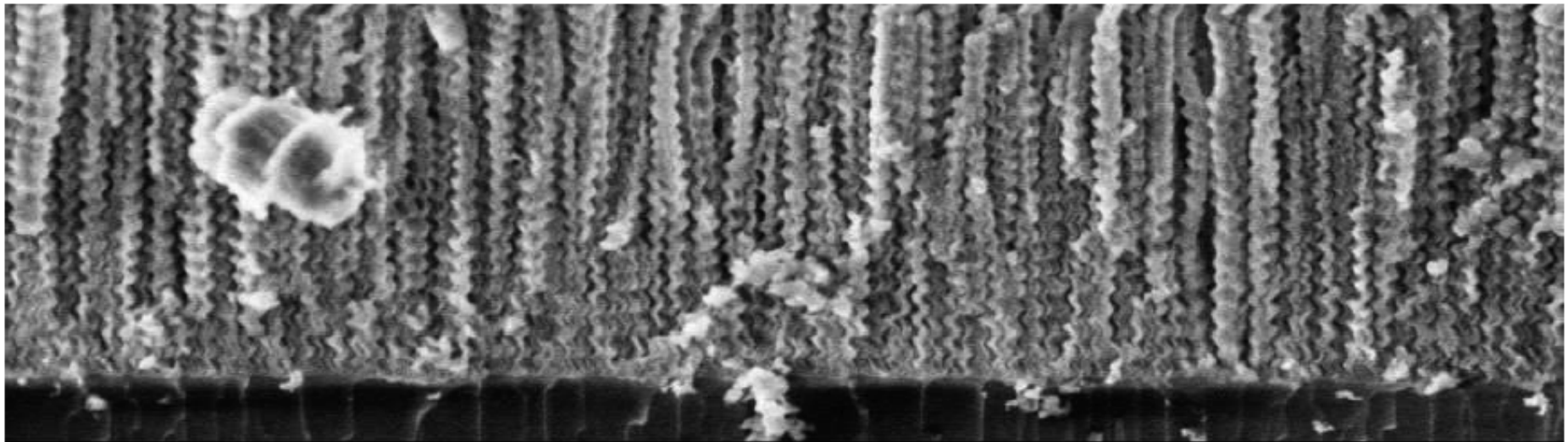
$$\begin{aligned} \mathbf{D}(\mathbf{r}, \omega) &= \epsilon_0 \underline{\underline{\epsilon}}_r(z, \omega) \cdot \mathbf{E}(\mathbf{r}, \omega) \\ &= \epsilon_0 \underline{\underline{S}}(z) \cdot \underline{\underline{\epsilon}}_{ref}(\omega) \cdot \underline{\underline{S}}^T(z) \cdot \mathbf{E}(\mathbf{r}, \omega), \\ \mathbf{B}(\mathbf{r}, \omega) &= \mu_0 \mathbf{H}(\mathbf{r}, \omega). \end{aligned}$$

$$\frac{d}{dz} [\mathbf{f}(z, \kappa, \psi, \omega)] = i[\mathbf{P}(z, \kappa, \psi, \omega)] [\mathbf{f}(z, \kappa, \psi, \omega)].$$

$$[\mathbf{f}(z, \kappa, \psi, \omega)] = \begin{bmatrix} e_x(z, \kappa, \psi, \omega) \\ e_y(z, \kappa, \psi, \omega) \\ h_x(z, \kappa, \psi, \omega) \\ h_y(z, \kappa, \psi, \omega) \end{bmatrix}$$

# Optical Filters

## Chiral STF



Mag = 15.00 K X  
1  $\mu$ m

EHT = 2.00 kV  
WD = 1 mm

Signal A = InLens  
Photo No. = 9780

PSU Nanofab LEO 1530  
Time :14:59 Date :16 Jul 2003

# Optical Filters

## Chiral STF as CP Filter

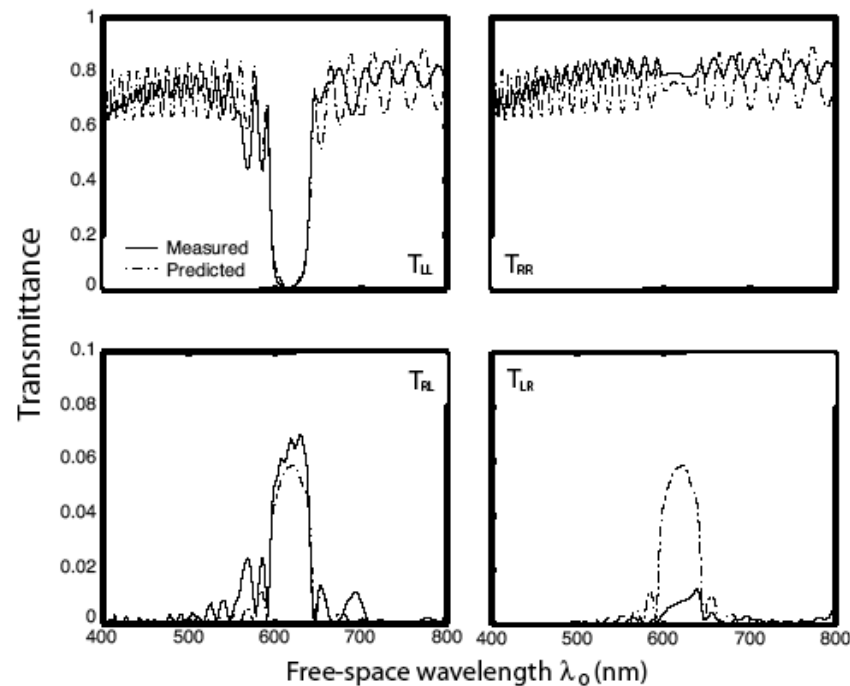


Figure 10.2: Predicted and measured transmittances of a circular polarization filter as functions of the free-space wavelength  $\lambda_0$  for normal incidence. The filter is a chiral STF of patinal titanium oxide. The reference permittivity dyadic was predicted with  $\epsilon_s = 6.3 + i0.012$ ,  $\epsilon_v = 1$ ,  $f_v = 0.421$ ,  $\gamma_\tau^{(s)} = \gamma_\tau^{(v)} = 20$ , and  $\gamma_b^{(s)} = \gamma_b^{(v)} = 1.06$  set in Program 6.1. The other parameters are  $\chi = 47$  deg,  $h = -1$ ,  $\Omega = 173$  nm,  $L = 30$   $\Omega$ , and  $\psi = 0$  deg. (Adapted from Sherwin et al. [109] with permission of Elsevier.)

# Optical Filters

## Chiral STF as CP Filter

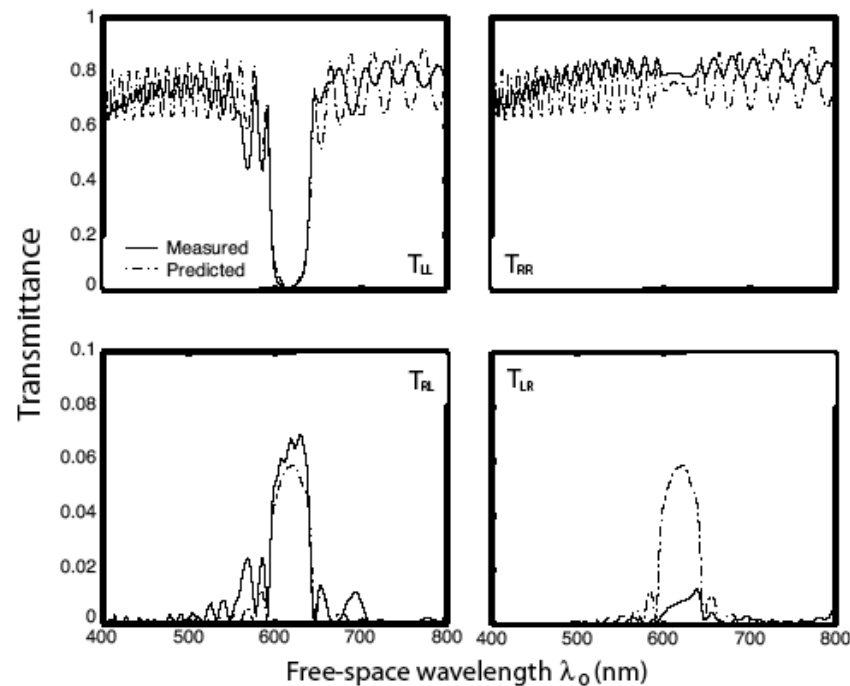


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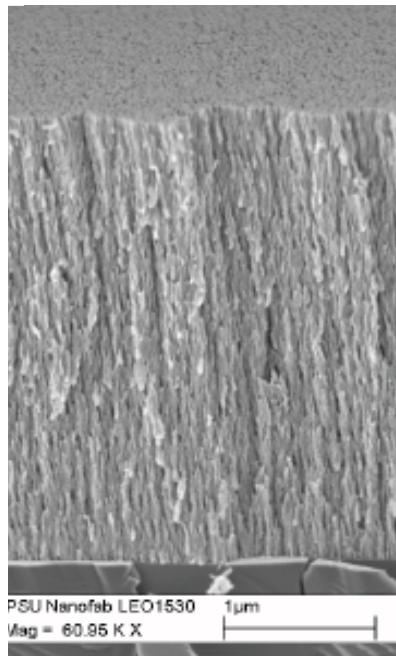
# Optical Filters

## Chiral STF as CP Filter

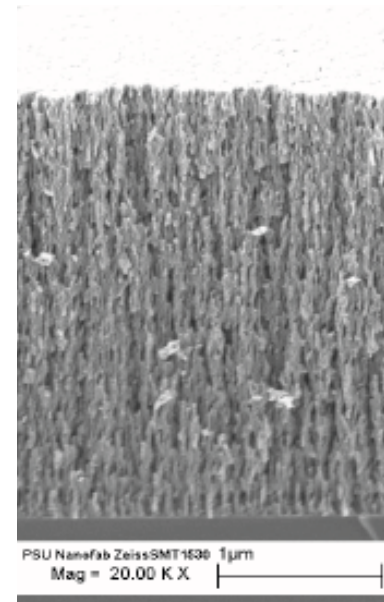
### Post-Deposition Engineering of Bragg Regime

#### Annealing

*before*



*after*



# Optical Filters

## Chiral STF as CP Filter

### Annealing

#### Blue-shift factors:

- (i) Decreases pitch
- (ii) Thins nanowires

#### Red-shift factors:

- (i) Increases permittivity

# Optical Filters

## Chiral STF as CP Filter

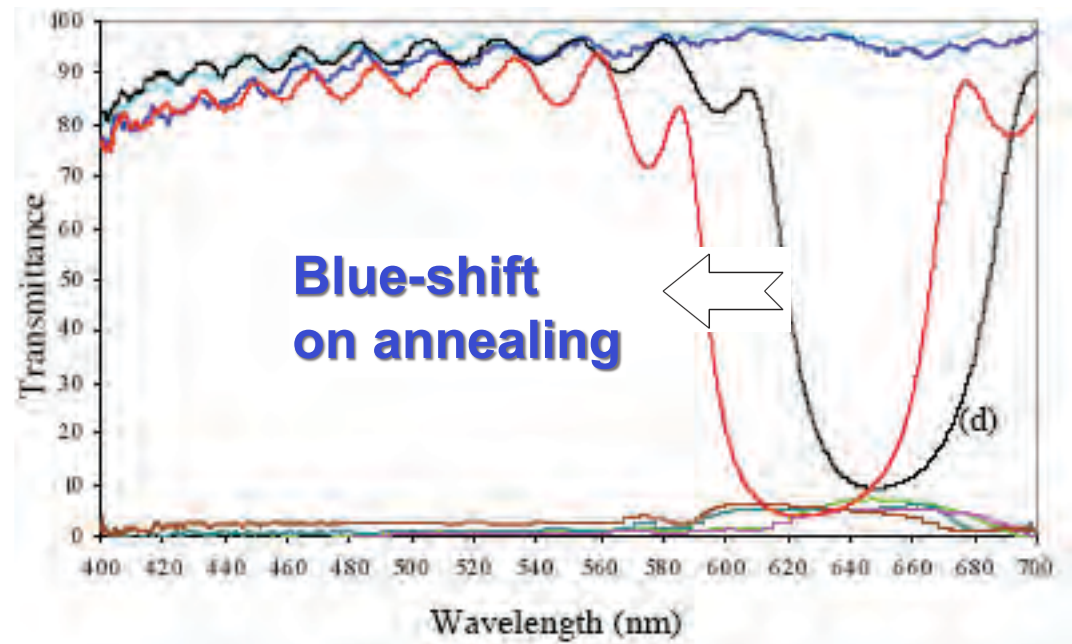
### Annealing

#### Blue-shift factors:

- (i) Decreases pitch
- (ii) Thins nanowires

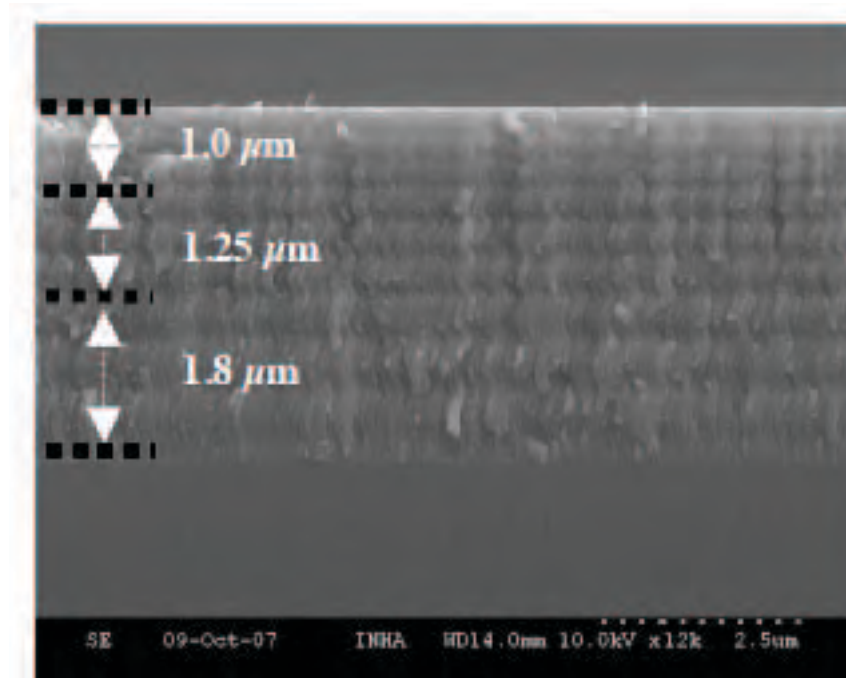
#### Red-shift factors:

- (i) Increases permittivity



# Optical Filters

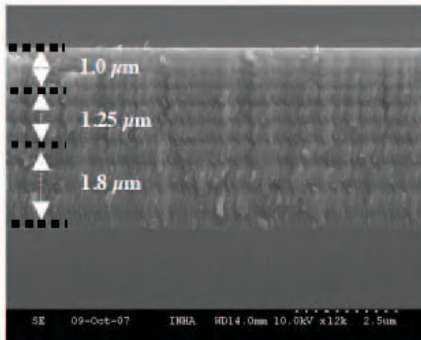
## Multiband CP Filter



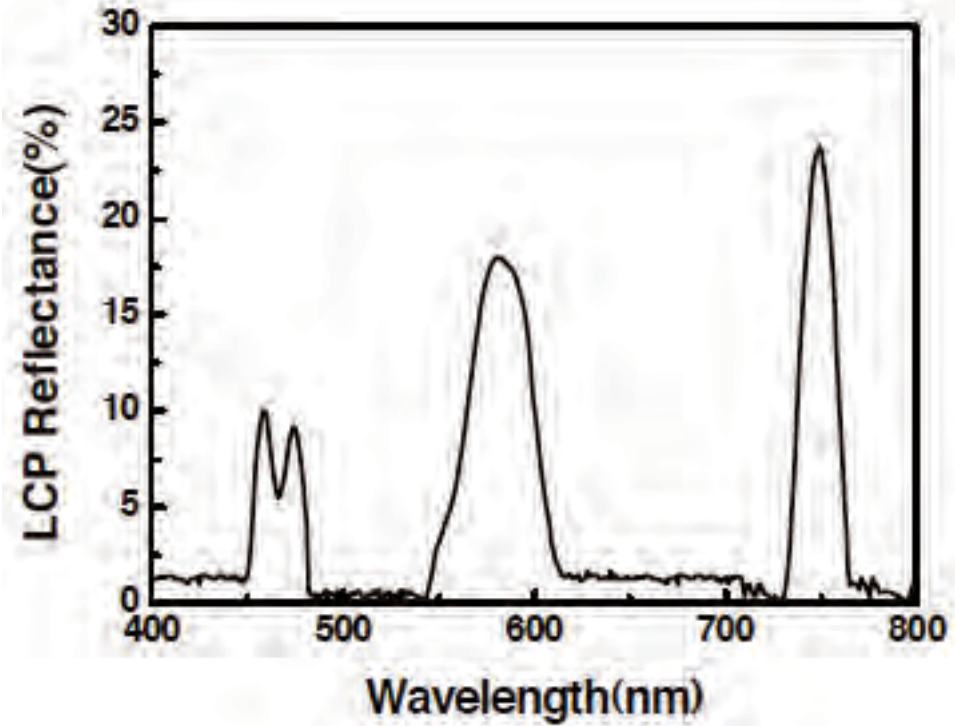
## Stack of 3 chiral STFs

# Optical Filters

## Multiband CP Filter



Stack of 3 chiral STFs



# Optical Filters

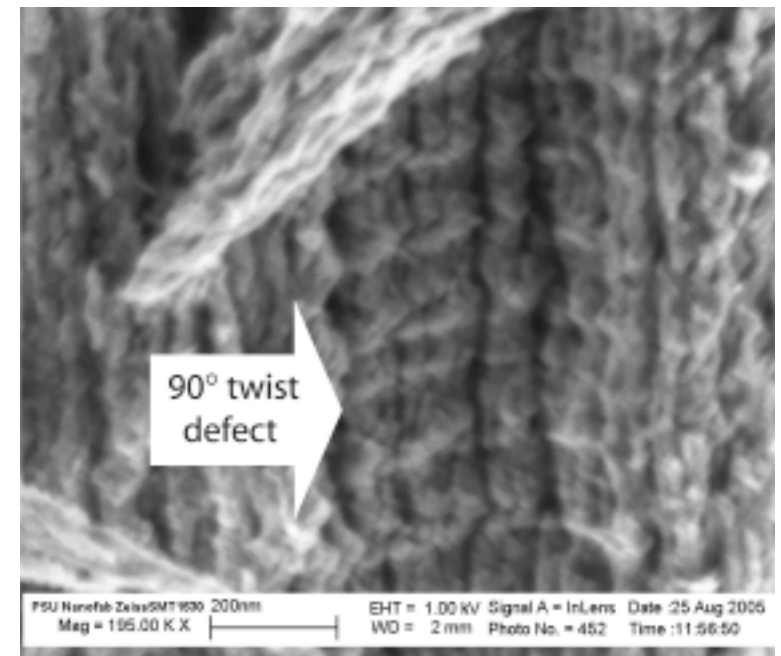
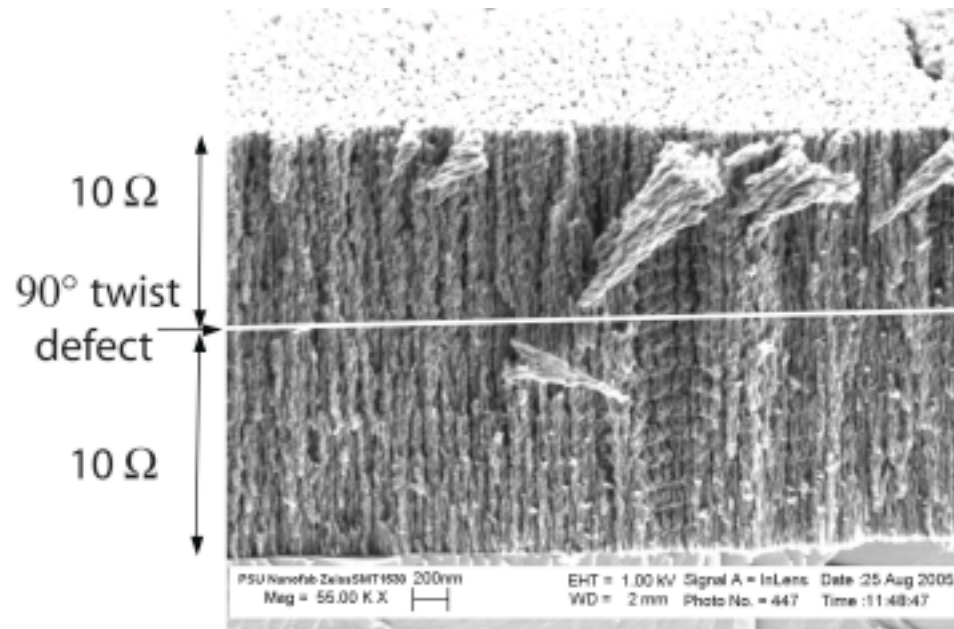
## Spectral Hole Filter

### Central Phase Defect in a Chiral STF

- Homogeneous-layer defect
  - *Isotropic*
  - *Anisotropic*
- Twist defect
- Structurally-chiral-layer defect

# Optical Filters

## Spectral Hole Filter



# Optical Filters

## Spectral Hole Filter

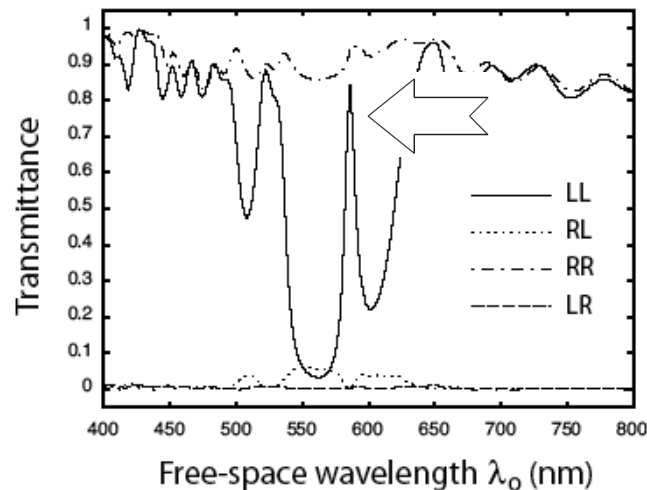
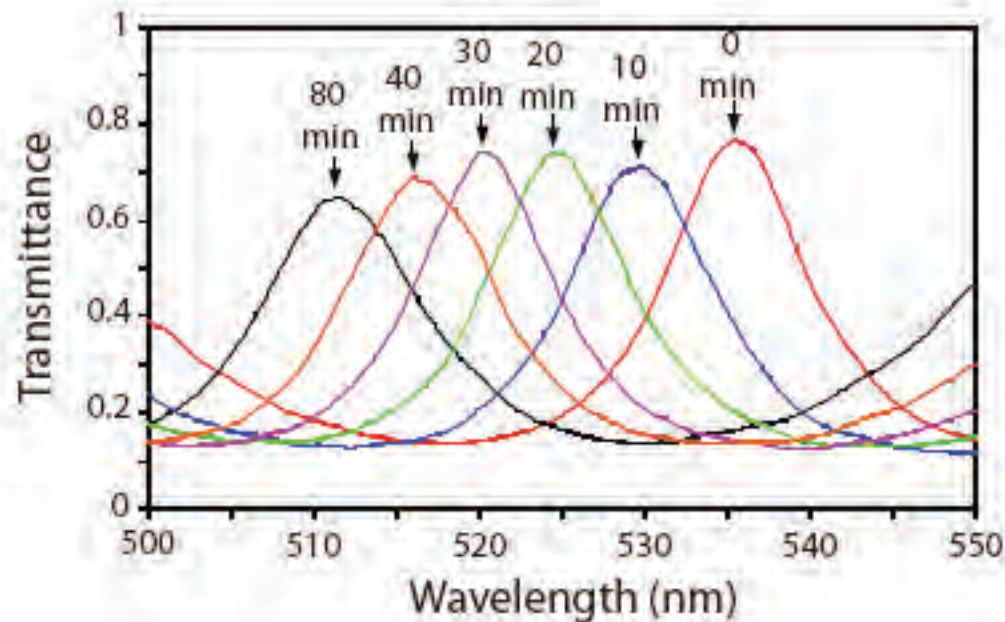


Figure 10.10: Measured transmittances of a narrow bandpass filter comprising an isotropic homogeneous spacer of hafnium oxide interposed between two identical, structurally left-handed, chiral STF sections of titanium oxide. Evidence of a hole in the spectrum of  $R_{LL}$  at 580-nm wavelength is provided by the spectrum of  $T_{LL}$ . (Adapted from Hodgkinson et al. [125] with permission of Elsevier.)

# Optical Filters

## Spectral Hole Filter

### Chemical Etching Columnar Thinning Blue Shift



# Snapshots

# Snapshots

## 1. Fluid Concentration Sensor

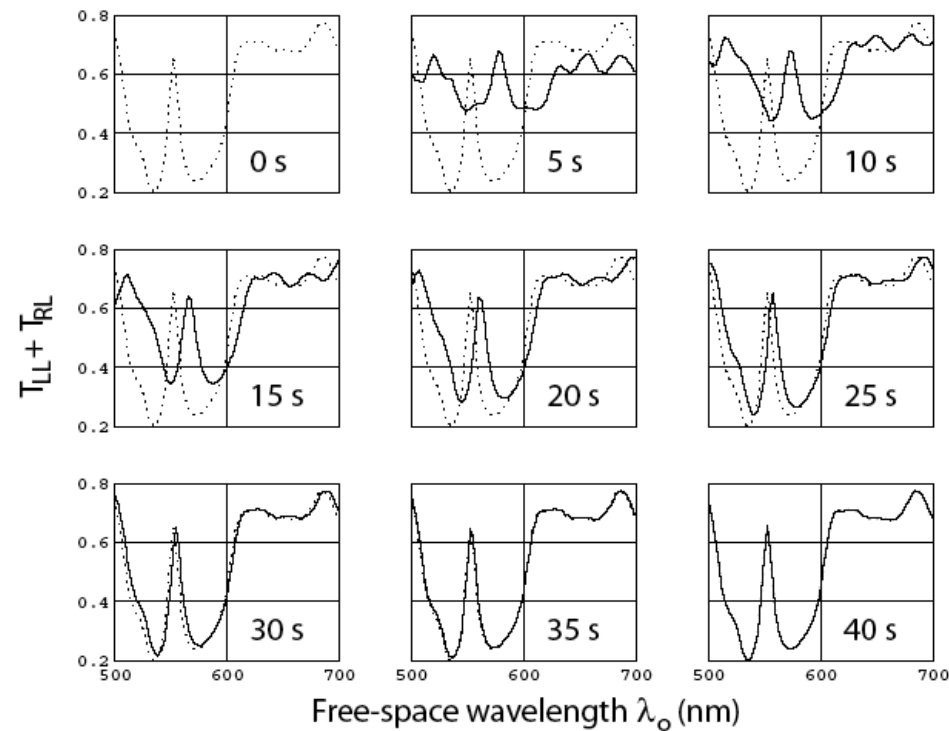
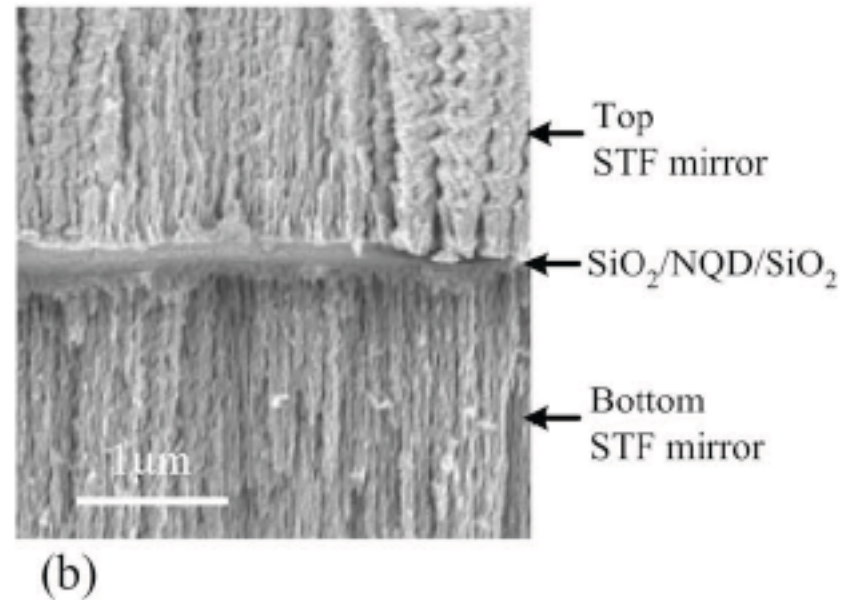
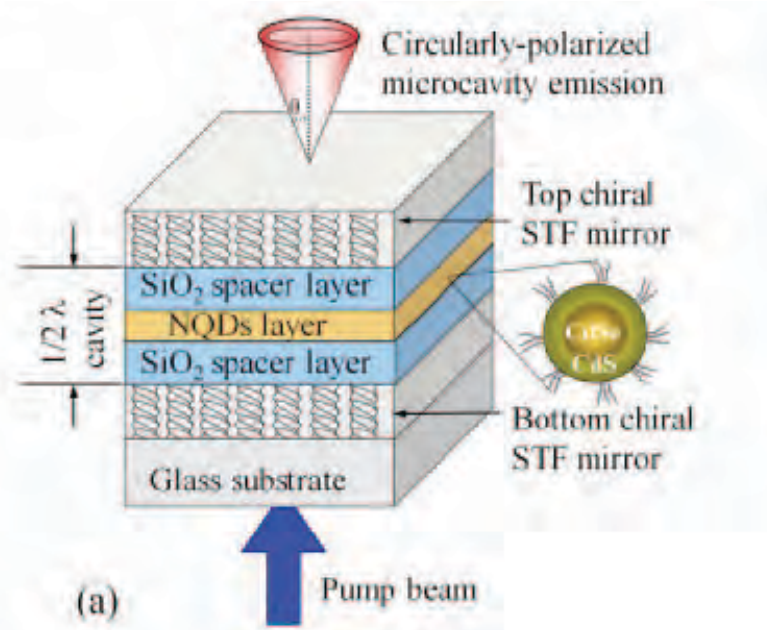


Figure 10.22: Optical response of a narrow bandpass filter, described by Eq. (10.17) and made of two structurally left-handed chiral STF sections, on infiltration by water vapor. The dotted lines indicate the measured transmittance spectrum when the filter was dry. The filter was flooded with water and then allowed to recover by evaporation in air. Transmittance spectra recorded at 5-s intervals after the flooding are shown. (Adapted from Lakhtakia et al. [105] with permission of Elsevier.)

# Snapshots

## 2. CP-Light Emitting Cavity

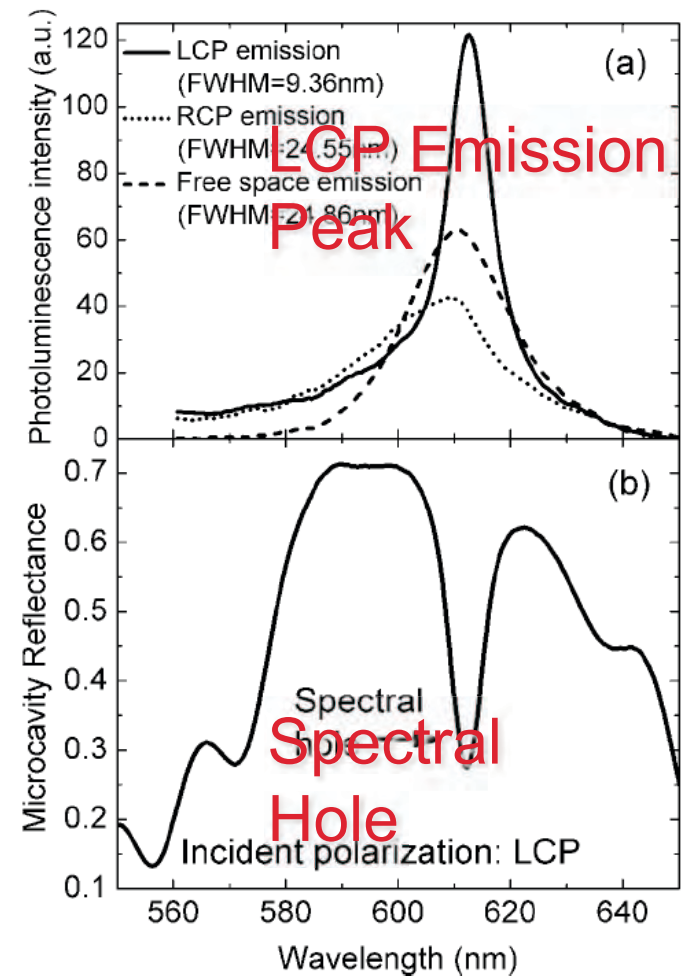
- Quantum dots inserted in a cavity between two left-handed chiral STFs



# Snapshots

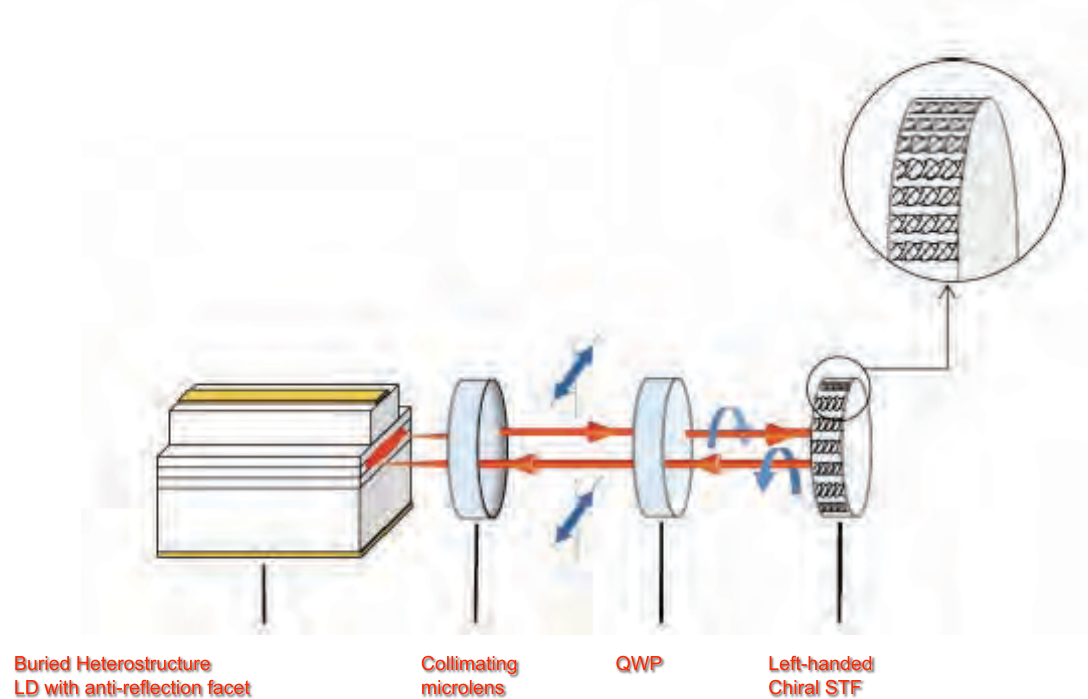
## 2. CP-Light Emitting Cavity

- Quantum dots inserted in a cavity between two left-handed chiral STFs



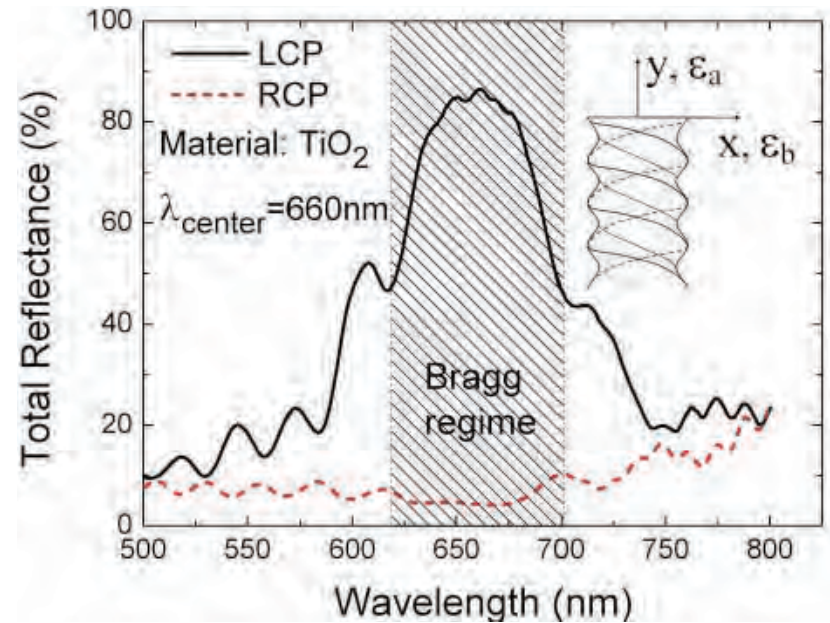
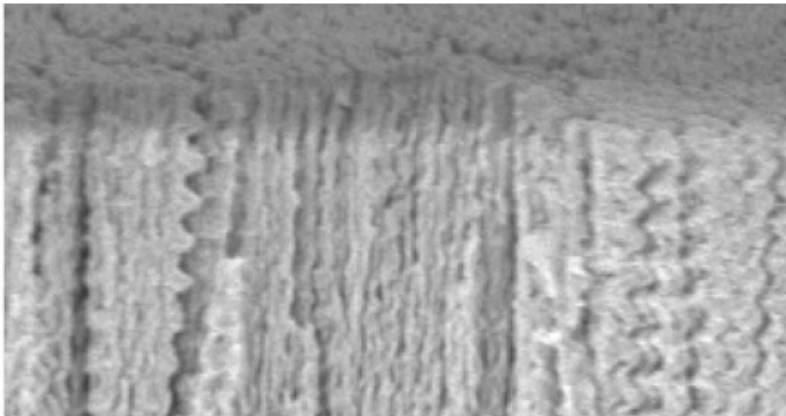
# Snapshots

## 3. CP-Light External Cavity Diode Laser



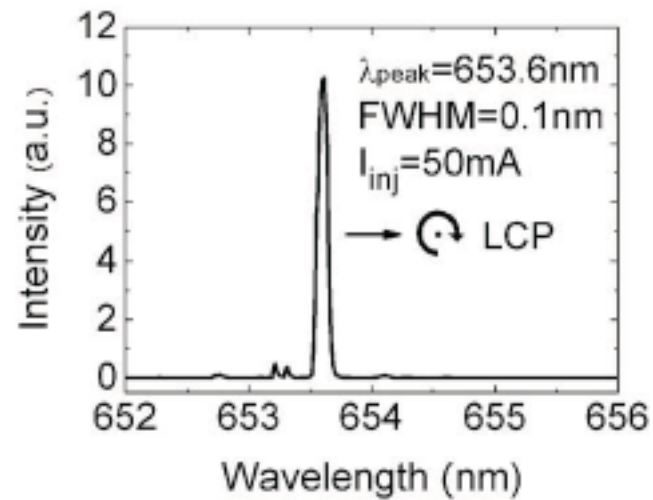
# Snapshots

## 3. CP-Light External Cavity Diode Laser



# Snapshots

## 3. CP-Light External Cavity Diode Laser



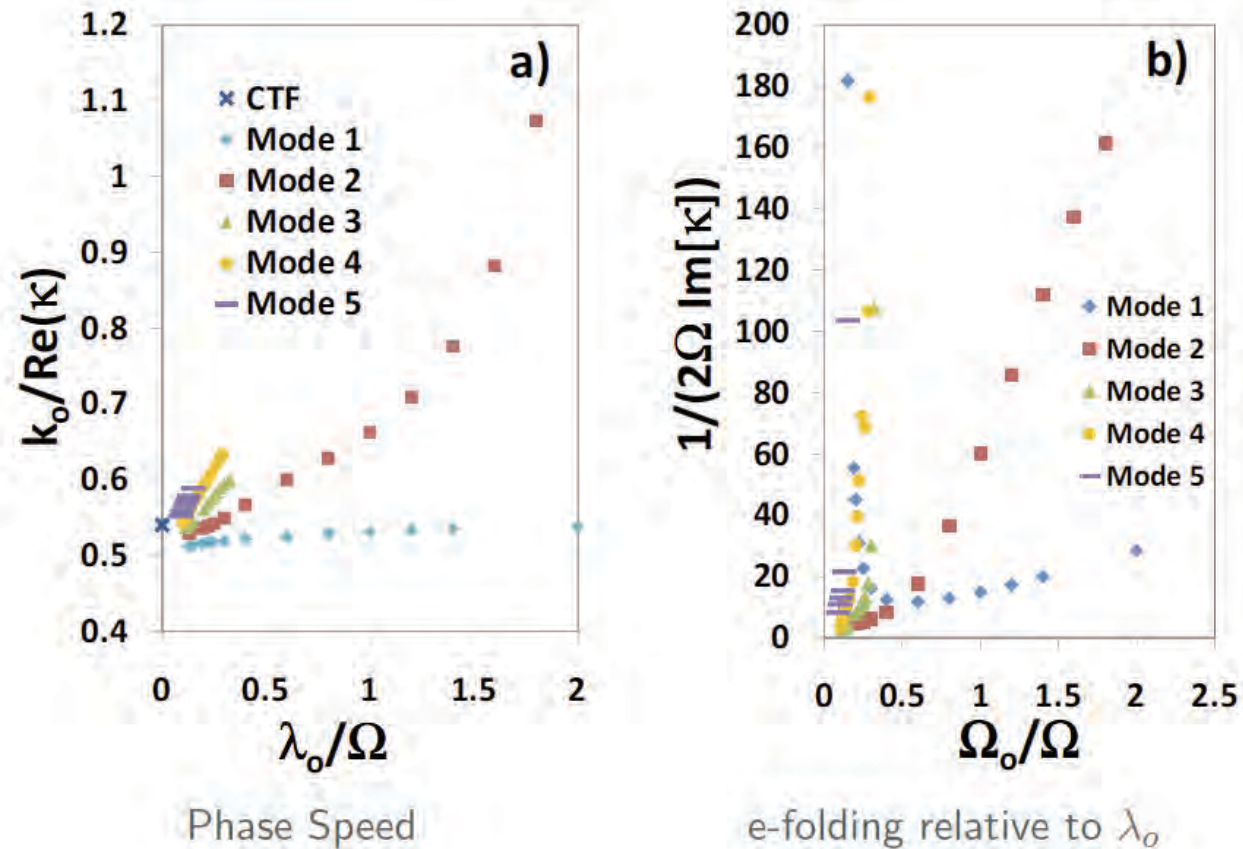
# Snapshots

## 4. Multiple Surface-Plasmon-Polariton Waves



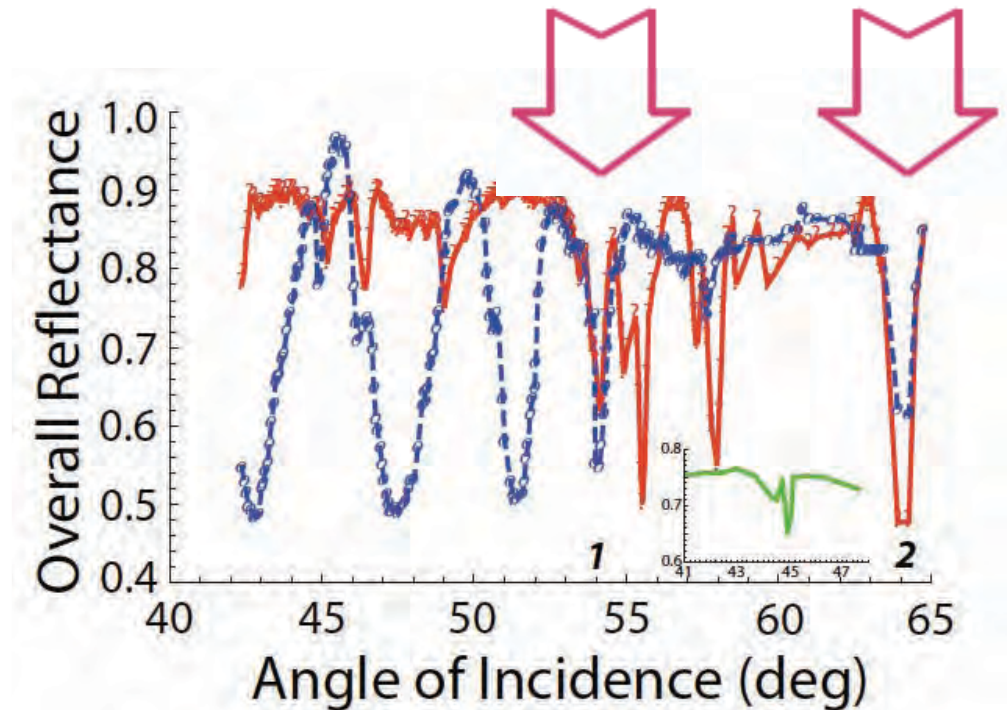
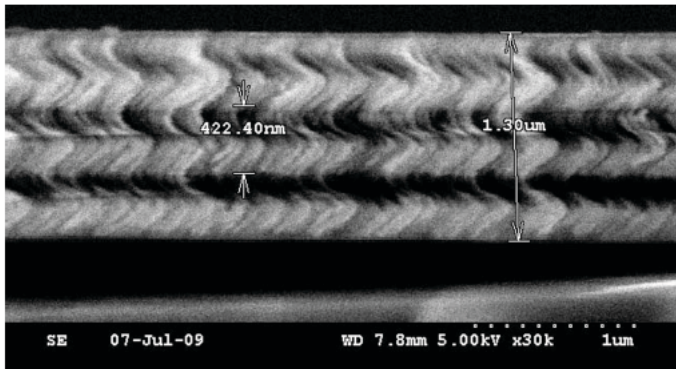
# Snapshots

## 4. Multiple Surface-Plasmon-Polariton Waves



# Snapshots

## 4. Multiple Surface-Plasmon-Polariton Waves



# Snapshots

## 4. Multiple Surface-Plasmon-Polariton Waves

**Multiple trains of same-color  
surface plasmon-polaritons guided by the planar  
interface of a metal and a sculptured nematic thin film**

**Michael A. Motyka<sup>a</sup> and Akhlesh Lakhtakia<sup>b</sup>**

# Snapshots

## 4. Multiple Surface-Plasmon-Polariton Waves

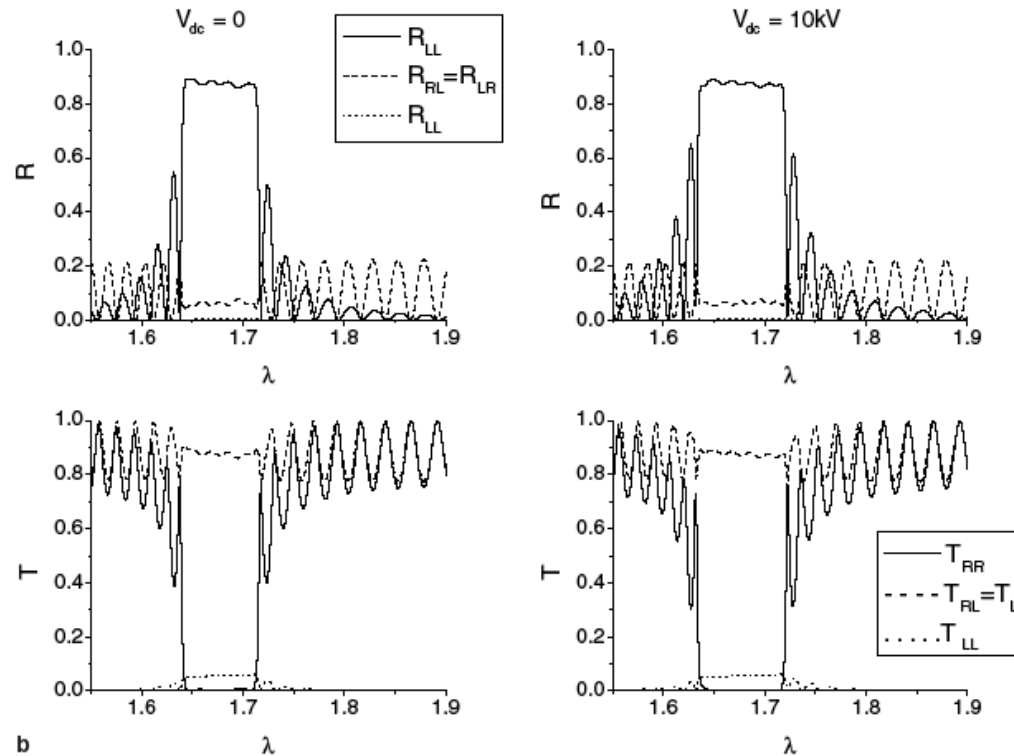
**Multiple trains of same-color surface plasmon-polaritons guided by the planar interface of a metal and a sculptured nematic thin film. Part III: Experimental evidence**

**Akhlesh Lakhtakia,<sup>a</sup> Yi-Jun Jen,<sup>b</sup> and Chia-Feng Lin<sup>c</sup>**

# Snapshots

## 5. Electro-Optic Chiral STFs

$$\epsilon_1^{(0)} = 2.7, \epsilon_3^{(0)} = 3.2, r_{41} = 9 \times 10^{-12} \text{ mV}^{-1}, r_{63} = 3r_{41}, \text{ and } h = 1.$$



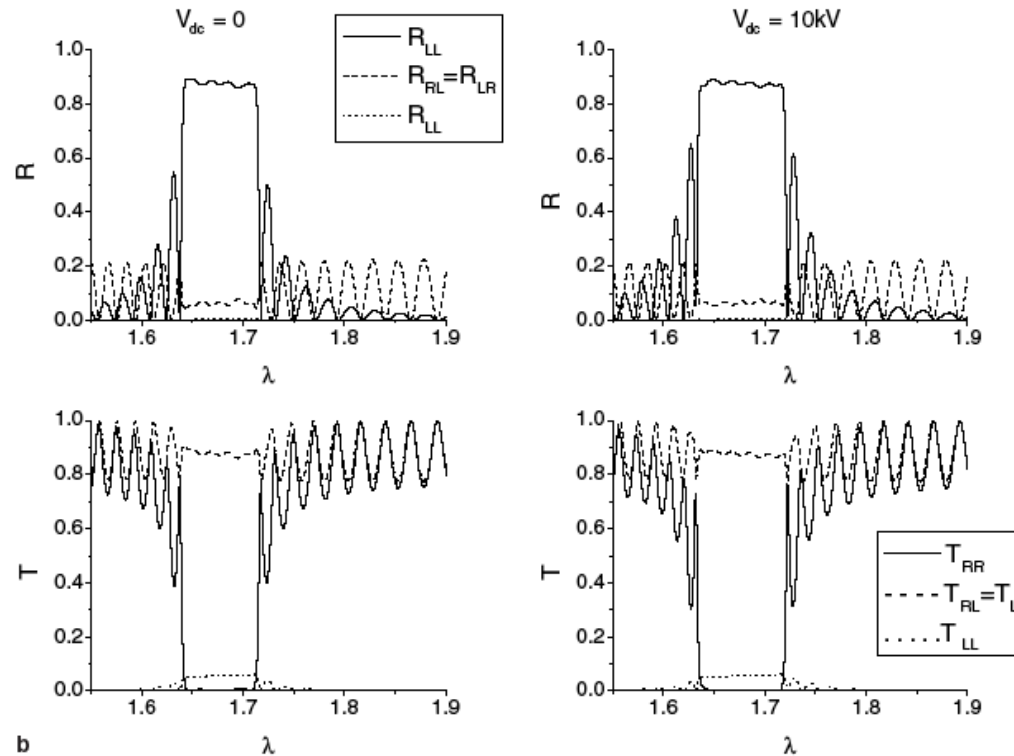
Without dc voltage

With dc voltage

# Snapshots

## 5. Electro-Optic Chiral STFs

$$\epsilon_1^{(0)} = 2.7, \epsilon_3^{(0)} = 3.2, r_{41} = 9 \times 10^{-12} \text{ mV}^{-1}, r_{63} = 3r_{41}, \text{ and } h = 1.$$



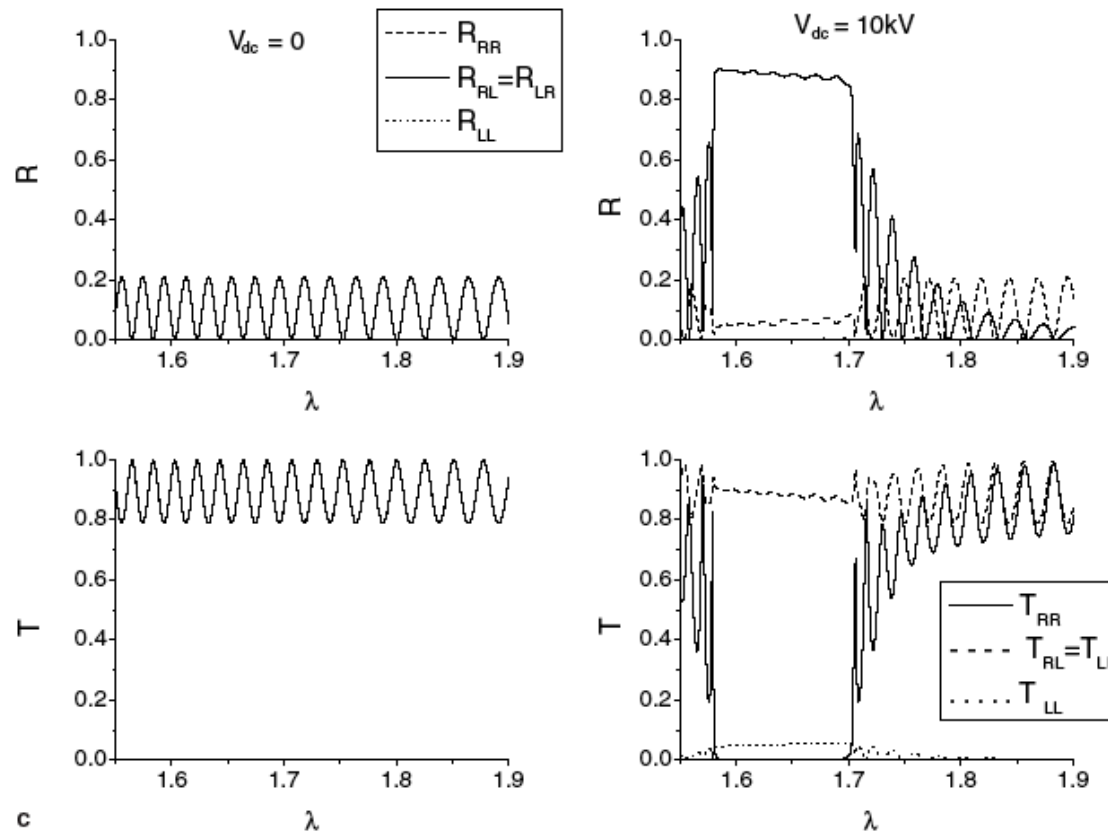
Without dc voltage

With dc voltage

# Snapshots

## 5. Electro-Optic Chiral STFs

Pseudo-  
Isotropic  
Point



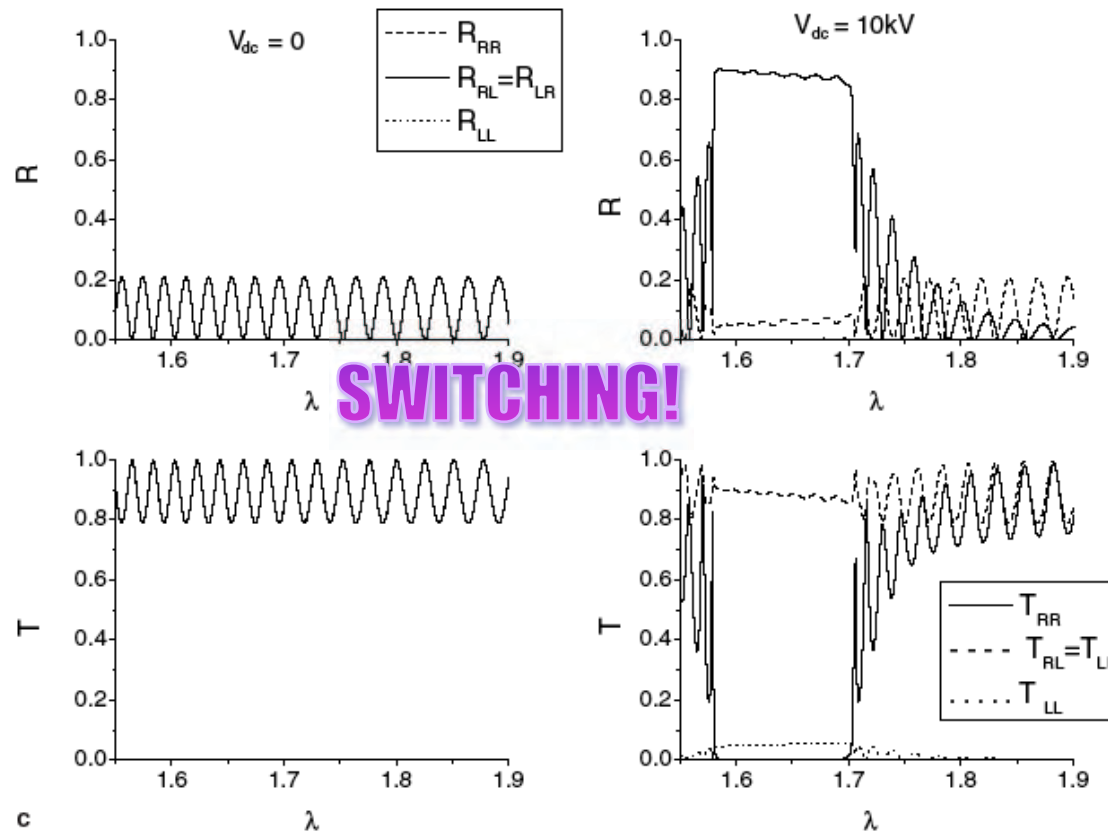
Without dc voltage

With dc voltage

# Snapshots

## 5. Electro-Optic Chiral STFs

Pseudo-  
Isotropic  
Point



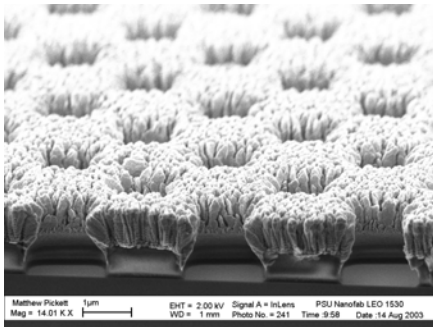
Without dc voltage

With dc voltage

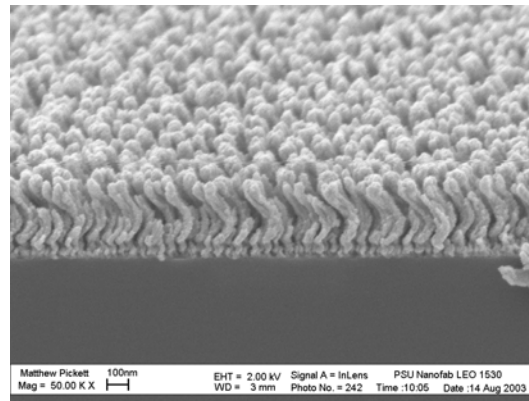
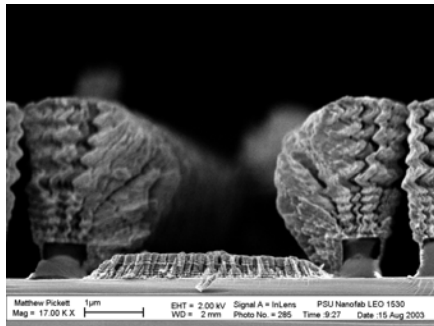
# Snapshots

## 6. 2D and 3D Photonic Crystals

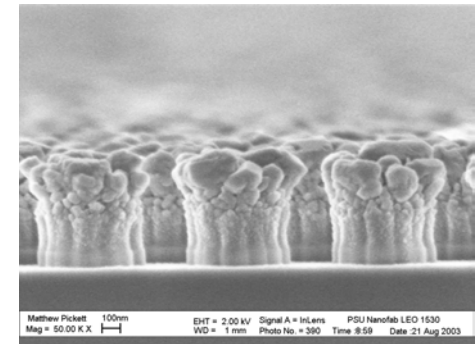
### MetalS TFson Topographic Substrates



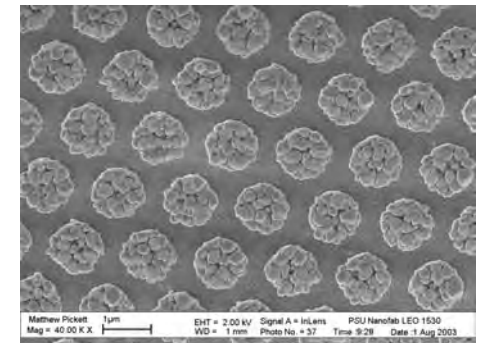
**Chromium**



**Molybdenum**

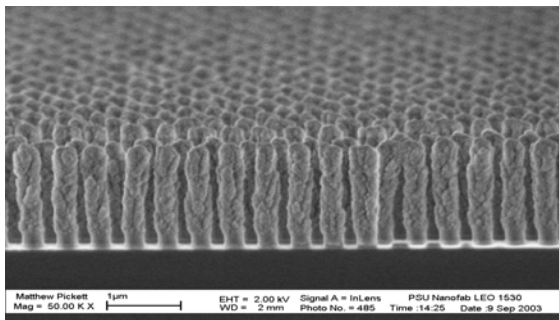


**Aluminum**



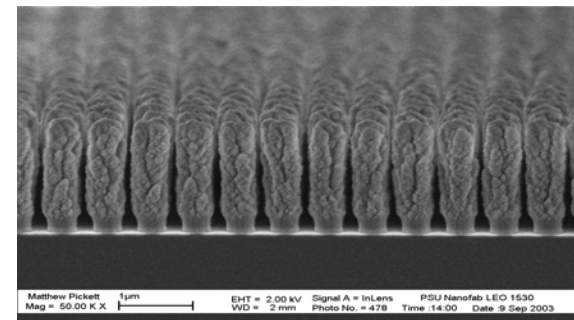
# Snapshots

## 6. 2D and 3D Photonic Crystals

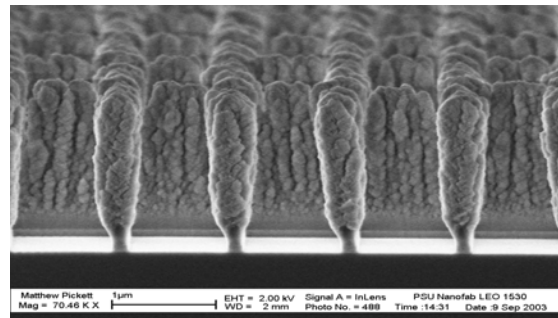


HCP array of SiO<sub>x</sub> nanocolumns

### Dielectric STFs on Topographic Substrates



BCC array of SiO<sub>x</sub> nanocolumns

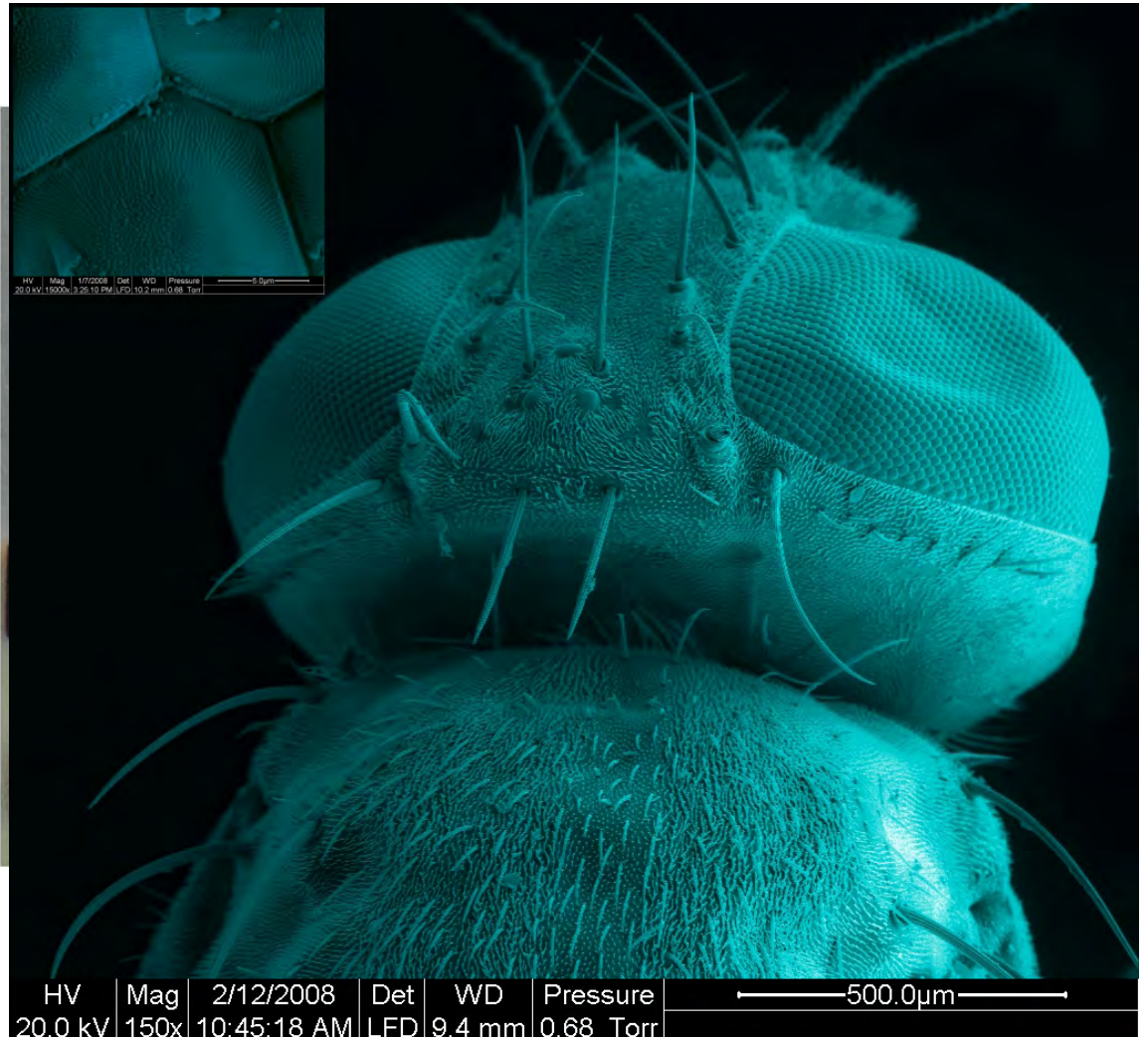


1 μm x 1 μm mesh of SiO<sub>x</sub> nanolines

Horn *et al.*, *Nanotechnology* **15**, 303 (2004).

# Snapshots

## 7. Bioreplication



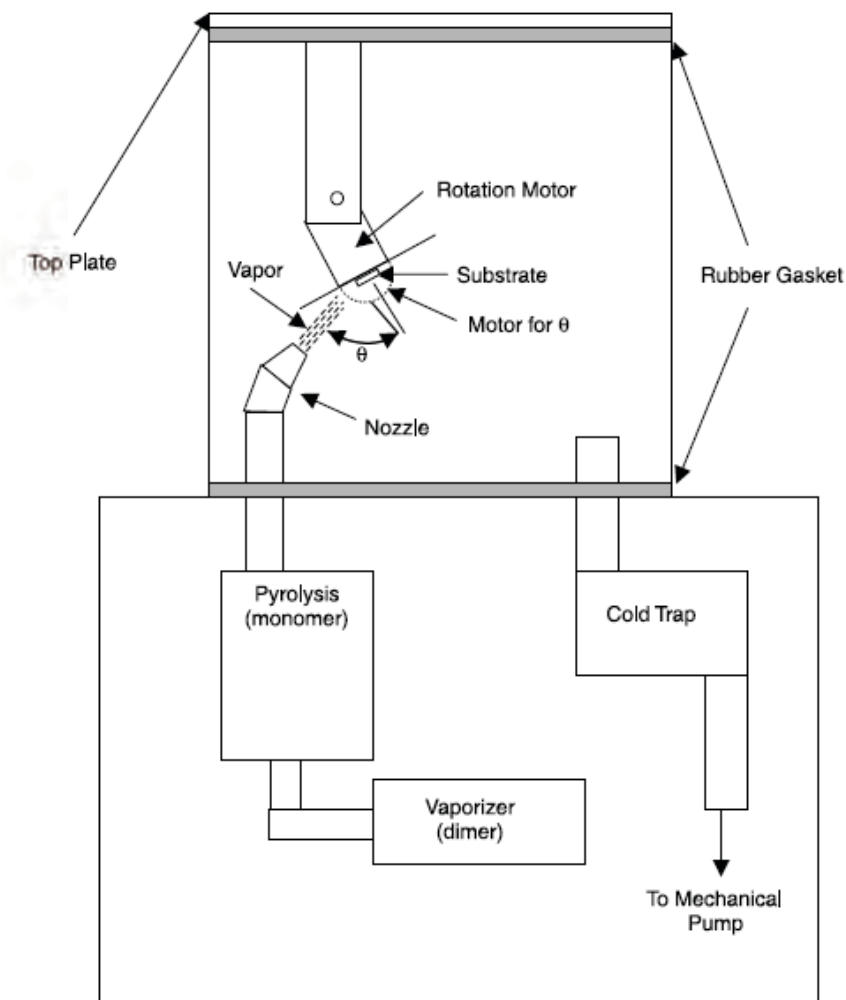
Martín-Palma et al., *Nanotechnology*  
**19**, 355704 (2008)



A. Lakhtakia

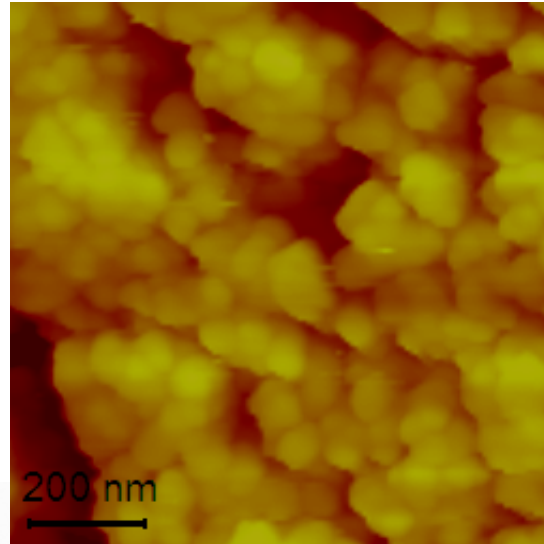
# Polymeric STF's

# PARYLENE-C STFs: COMBINED CVD+PVD TECHNIQUE

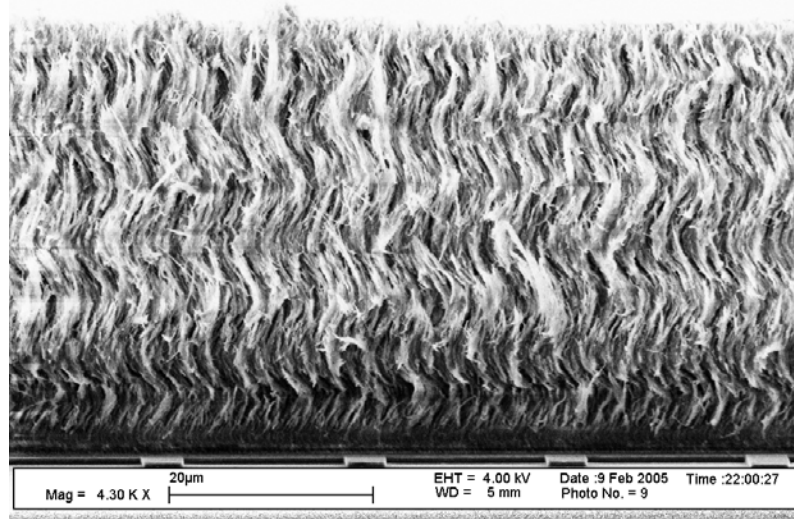


Pursel *et al.*, *Polymer* **46**, 9544 (2005)

# PARYLENE-C STFs: COMBINED CVD+PVD TECHNIQUE

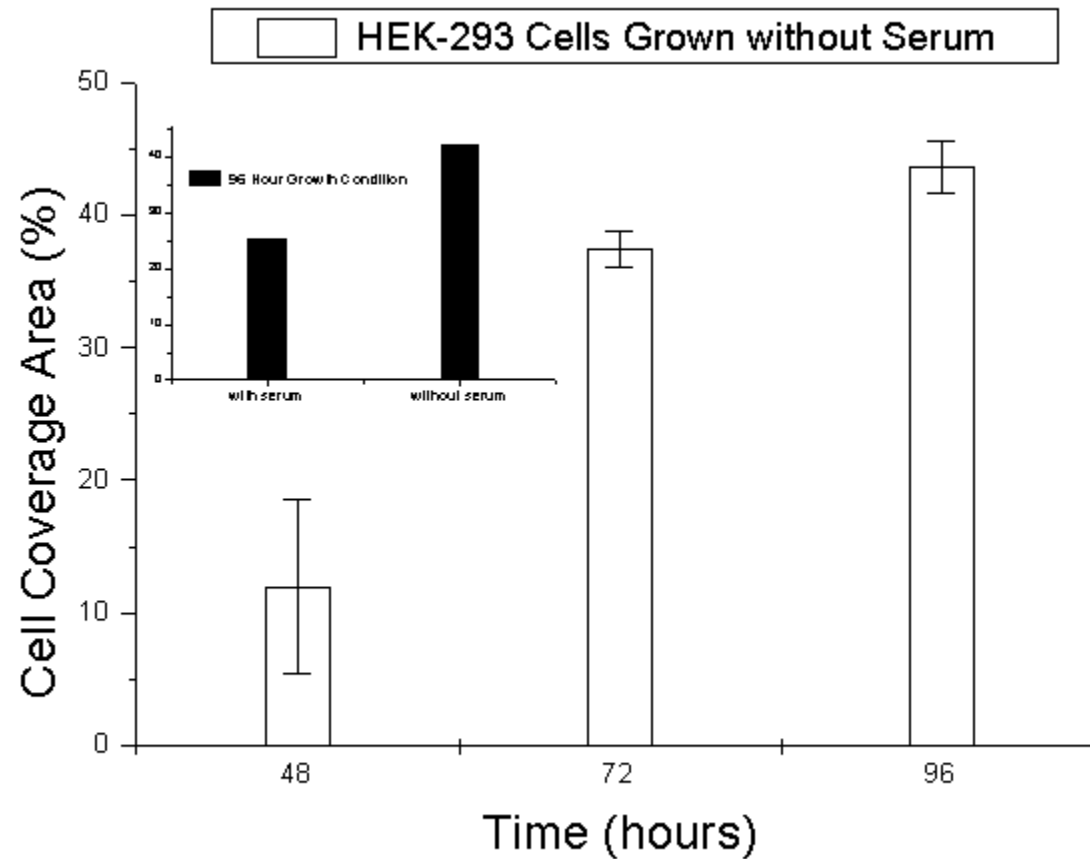


**Nanoscale  
Morphology**

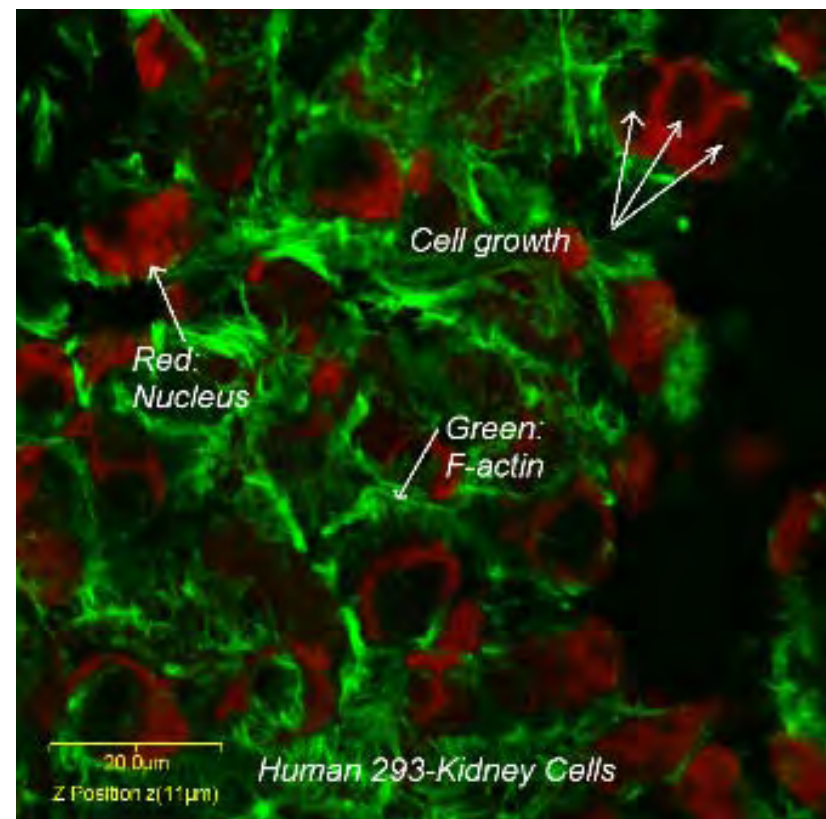
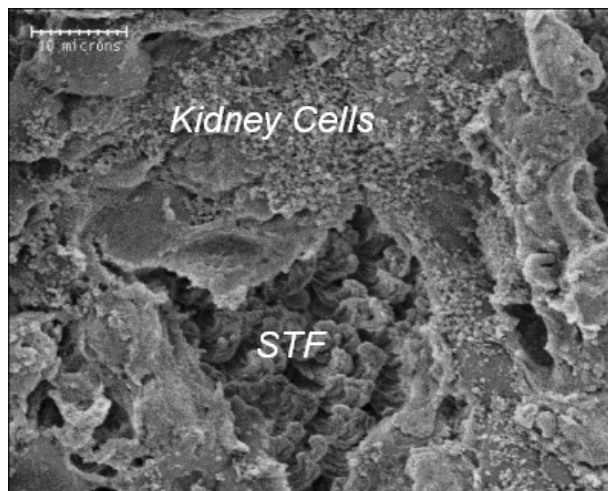


**Ciliary Structure**

# BIOSCAFFOLDS



# BIOSCAFFOLDS





A. Lakhtakia

# Applications of Parylene STFs

- Cell-culture substrates
- Coatings for prostheses (e.g. stents)
- Coatings for surgical equipment (e.g., catheters)
- Biosensors
- Tissue engineering for controlled drug release

*Volumetric functionalization*

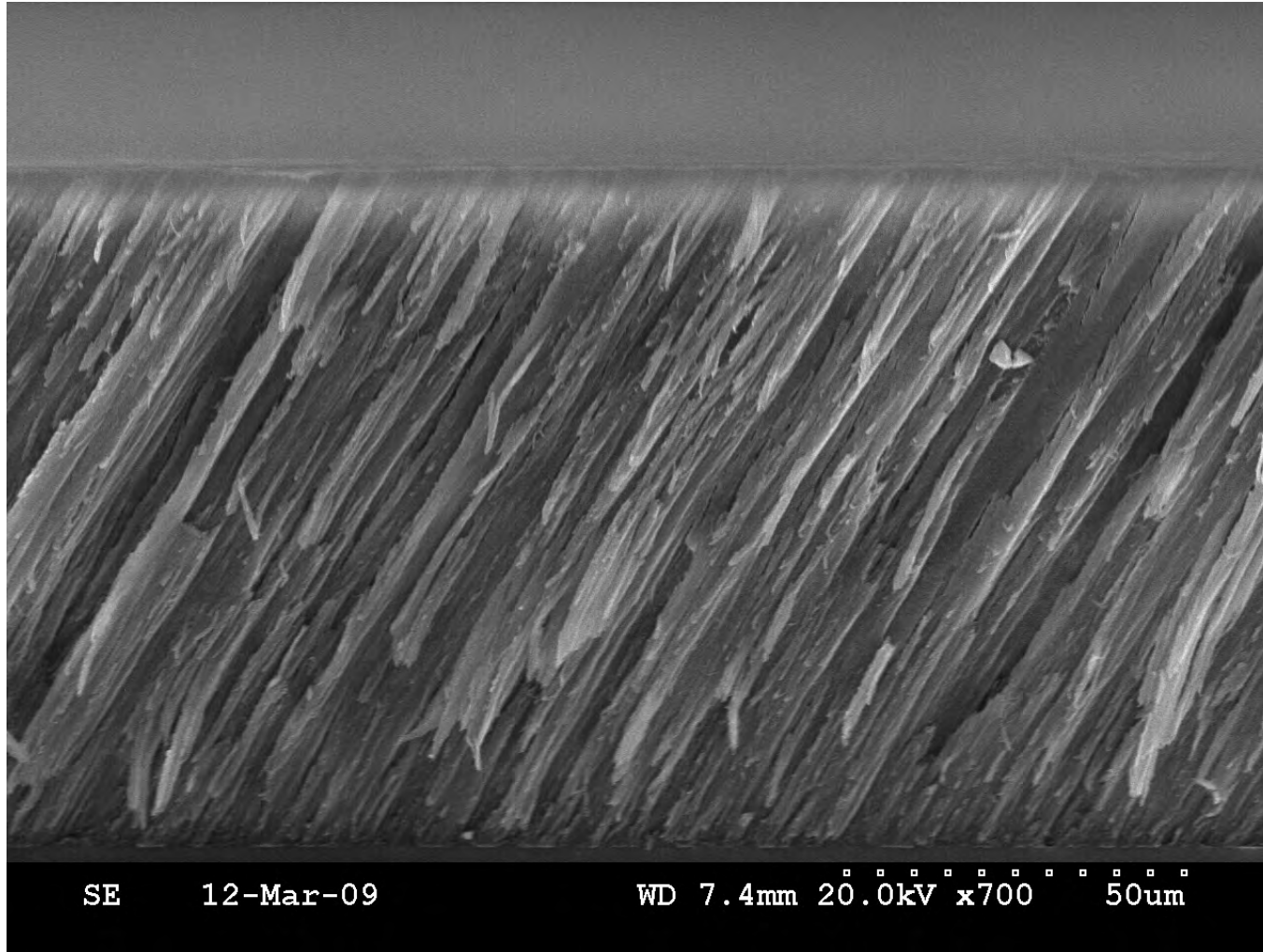
*IR monitoring*



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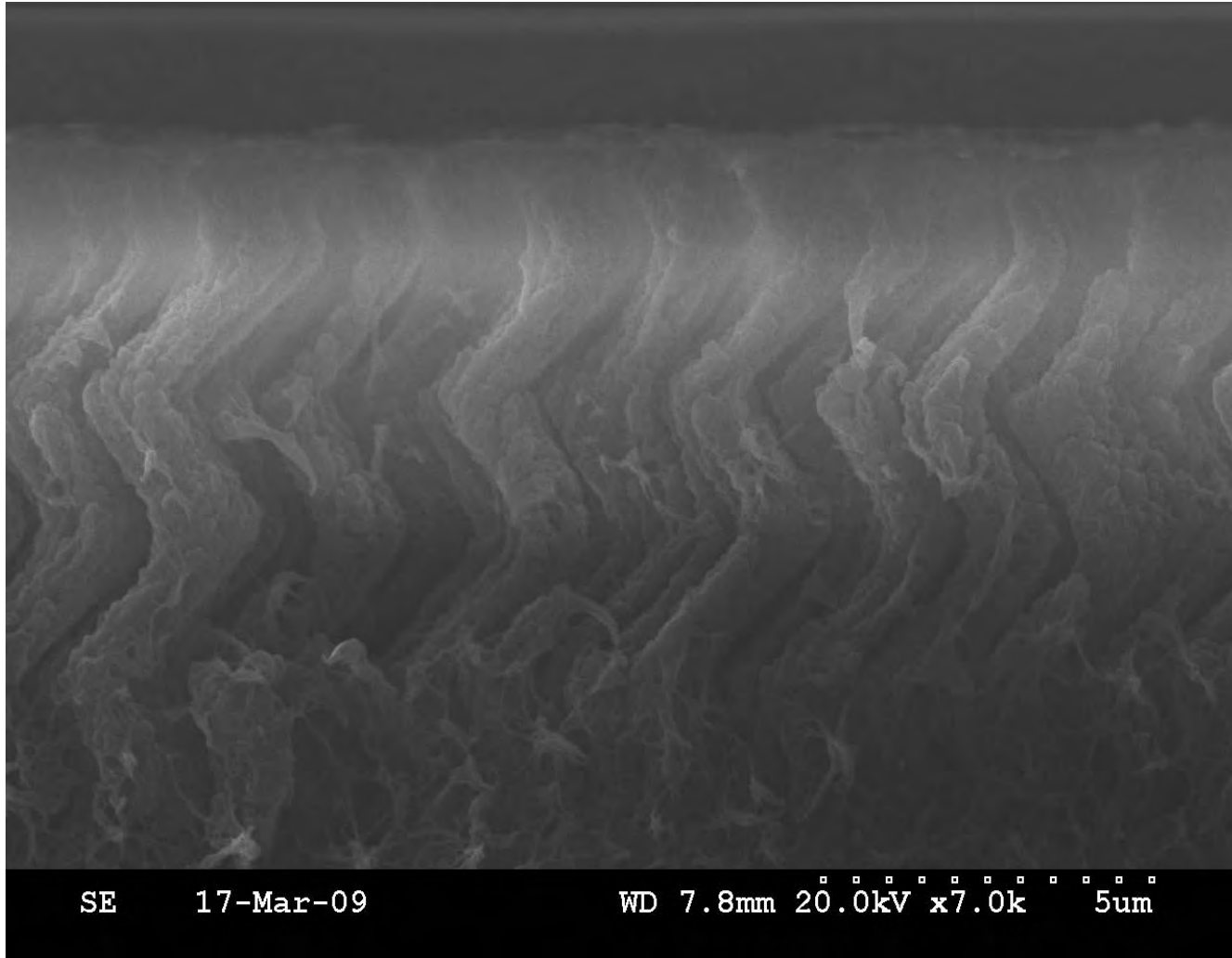
# STFs for Ultrasonics

## STFs for Ultrasonics



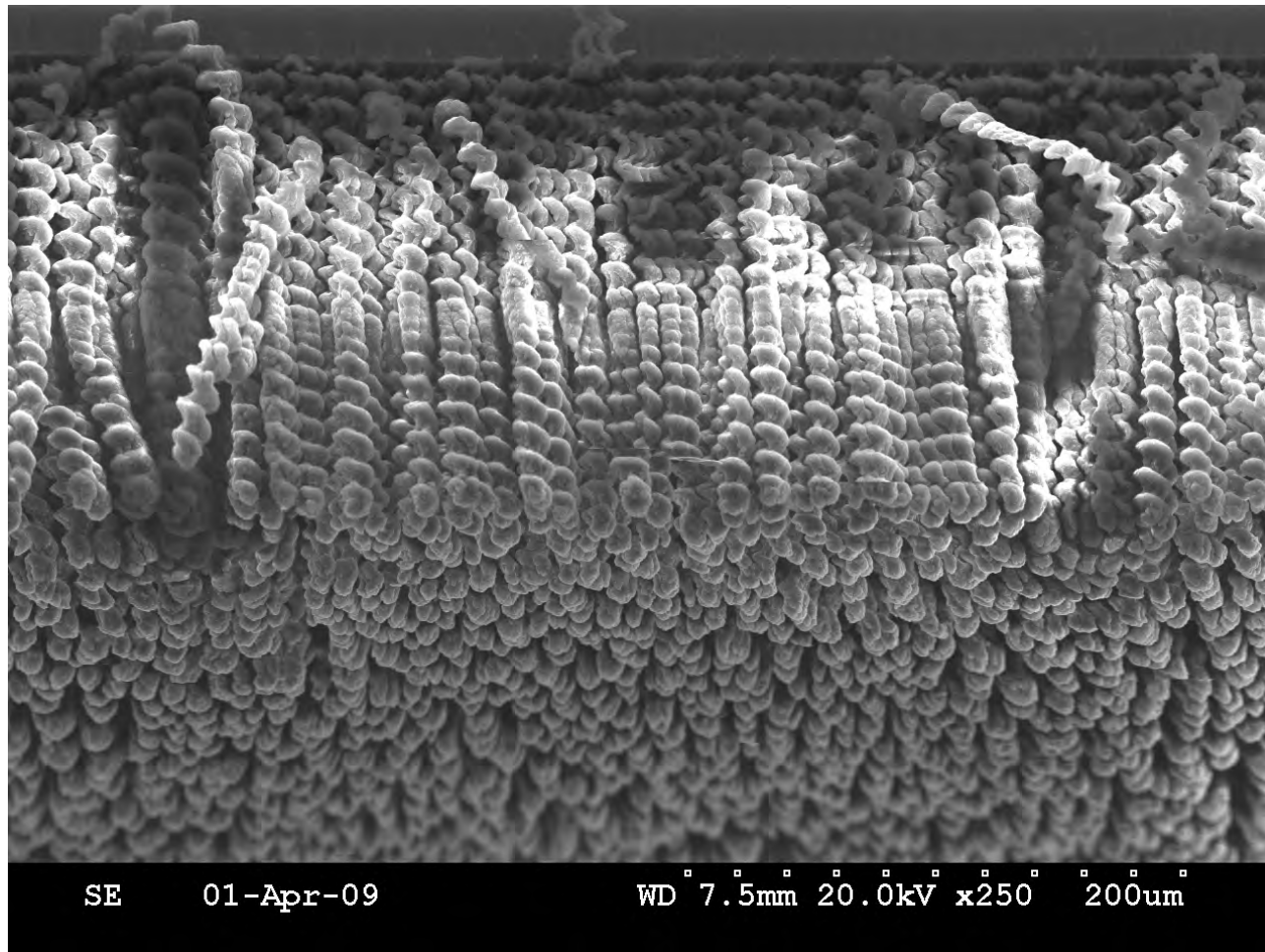
**80-micron thick parylene CTF**

## STFs for Ultrasonics



**15-micron thick parylene chevronic STF**

## STFs for Ultrasonics



**200-micron thick parylene chiral STF**



A. Lakhtakia





A. Lakhtakia

