Part II. Functional Polymers for Semiconductor Applications

Outline of Part

Polymeric Insulator for Semiconductor Applications

- Introduction of Silicone Chemistry
- Theory of Sol-Gel Chemistry
- Organic-Inorganic Hybrid Polymer
- Semiconductor Insulating Materials
- Nanoporous Polysiloxane Materials
- Summary of Future Trends

Semiconductor Insulating Materials

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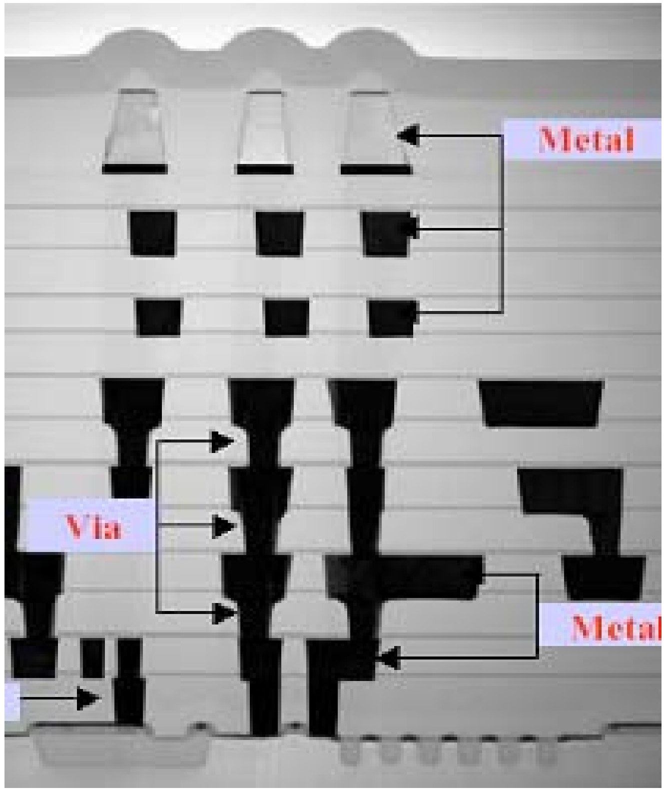
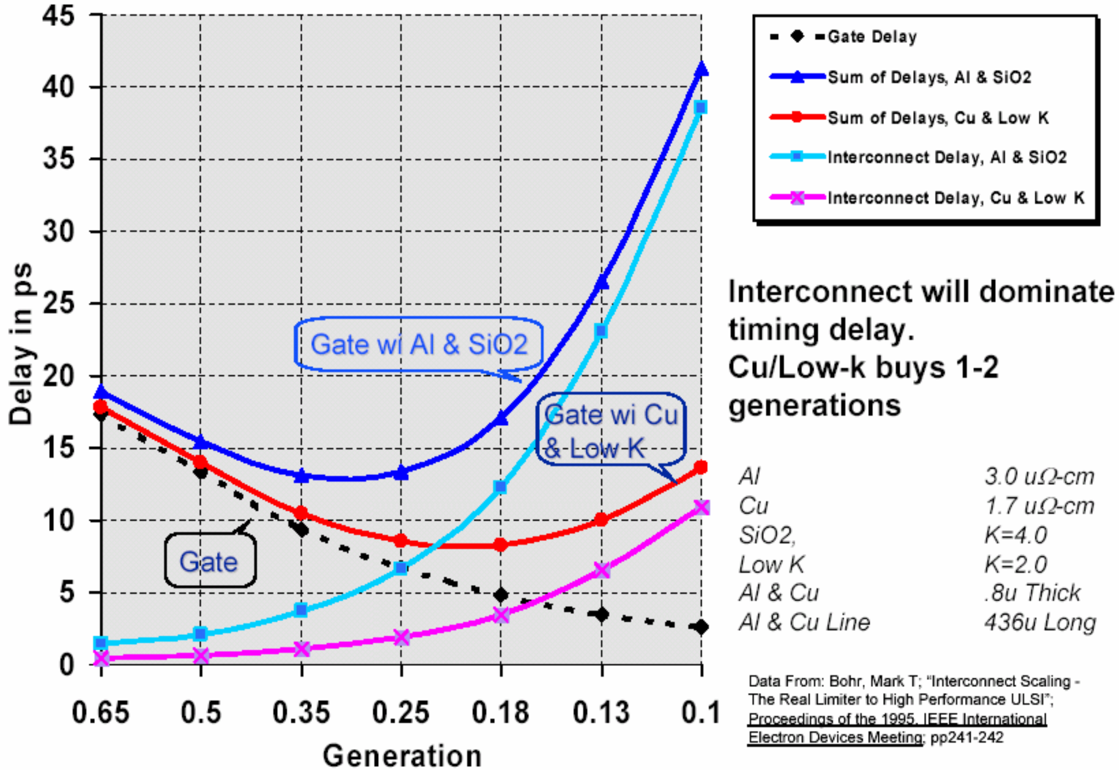
Semiconductor Insulating Materials

Device performance is parasitized by RC delay
in the case of deep sub-micron devices





Why Low-k ?

Materials for the Chip BEOL:
Copper interconnects & low-k dielectrics

$$RC_{delay} = 2\rho\varepsilon\,(4L^2/P^2 + L^2/T^2)$$

R = Line resistance
C = Line capacitance
L = Line length
P = Metal pitch
T = Metal thickness
ρ = Resistivity
ε = Dielectric constant

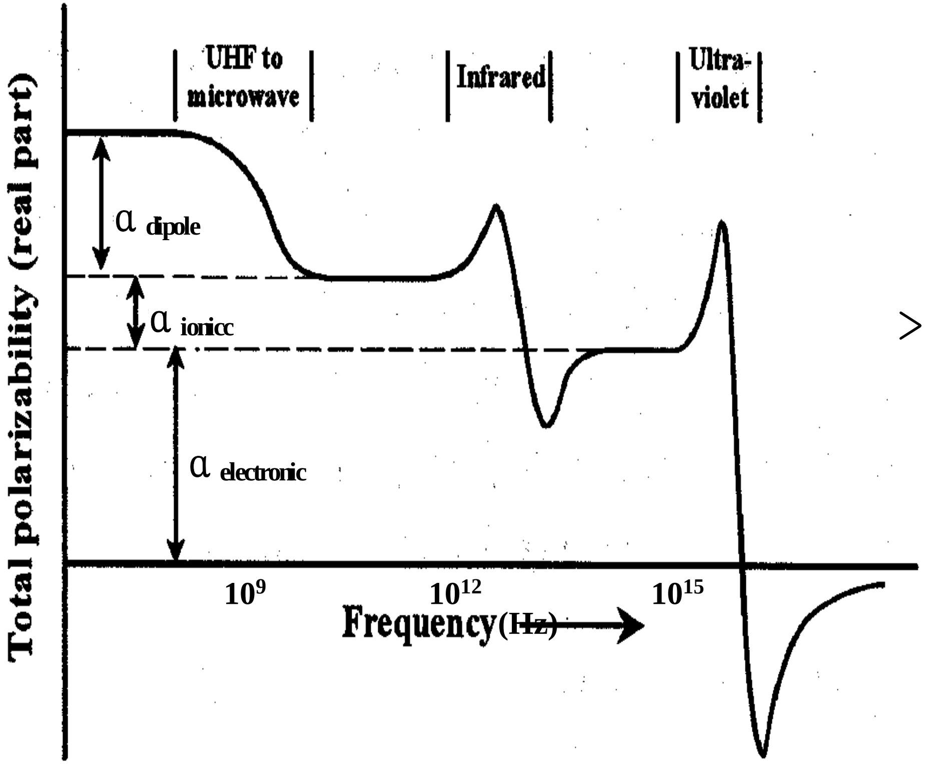
$$Power = CV^2 f$$

f = Frequency
V = Applied Voltage
C = Capacitance

FASTER CHIPS AT LOWER POWER

Dielectric Constant

유전율(ε) vs. polarizability(α)



$$\Delta\varepsilon = \Delta\varepsilon_e + \Delta\varepsilon_i + \Delta\varepsilon_d$$

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\sum N_j \alpha_j$$

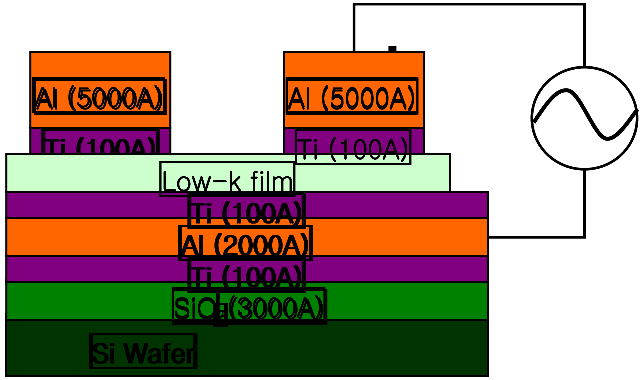
> 유전율 계산

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$

C : capacitance (@100kH

ε : 유전율

> MIM 측정 구조



ITRS Roadmap

Table 6. Changes in ITRS dielectric constant targets

Year	2003	2004	2005	2006	2007	2008	2009
Technology node							
DRAM 1/2 pitch (nm)	100	90	80	70	65	57	50
MPU/ASIC 1/2 pitch (nm)							
Was	107	90	80	70	65	57	50
Is	120	107	95	85	76	67	60
Number of metal levels							
Is	9	10	11	11	11	12	12
Metal 1 wiring pitch (nm)							
Is	240	214	190	170	152	134	120
Interlevel metal insulator (min. expected): effective dielectric constant (*k*)							
Was	3.0–3.6	2.6–3.1	2.6–3.1	2.6–3.1	2.3–2.7		
Is	3.3–3.6	3.1–3.6	3.1–3.6	3.1–3.6	2.7–3.0	2.7–3.0	2.7–3.0
Interlevel metal insulator (min. expected): bulk dielectric constant (*k*)							
Was	<2.7	<2.4	<2.4	<2.4	<2.1		
Is	<3.0	<2.7	<2.7	<2.7	<2.4	<2.4	<2.4

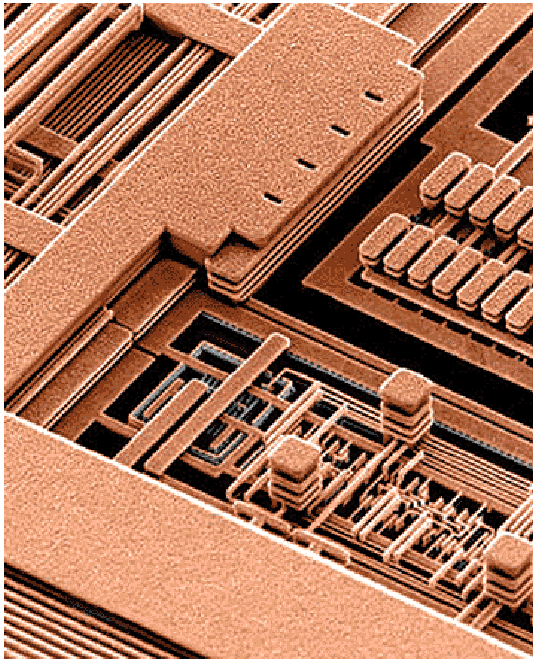
Insulating Materials

- **CVD**
  - **Organic**
    - Parylene (2.5)
    - Polynaphthalene (2.4)
  - **Organo silicate**
    - SiO_2 (4.0)
    - SiOF (3.5)
    - SiOC(2.7)
- **Spin-on**
  - **Organic**
    - BCB (2.7)
    - FLARE (2.8)
    - Polyimide (2.7)
    - Polyphenylene (2.65)
    - Teflon (2.3)
  - **Organo silicate**
    - HSQ (3.1)
    - MSQ (2.7)
    - Xerogel (~2.0)
    - Aerogel (~2.0)

Requirement

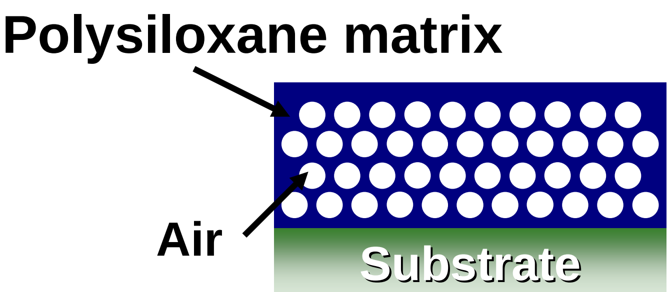
- Good Gap-fill (for Al interconnection)
- Good Thermal Stability (> 500°C)
- Good Adhesion
- No Crack (Mechanical Strength)
- Metal Corrosion Resistance
- Water Resistance
- No issue for integration

Nanoporous Film is Needed!



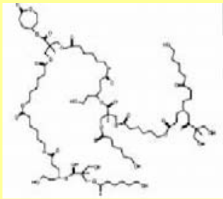
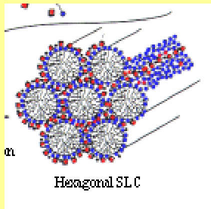
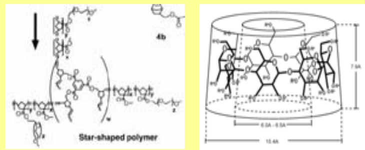
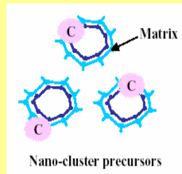
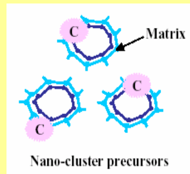
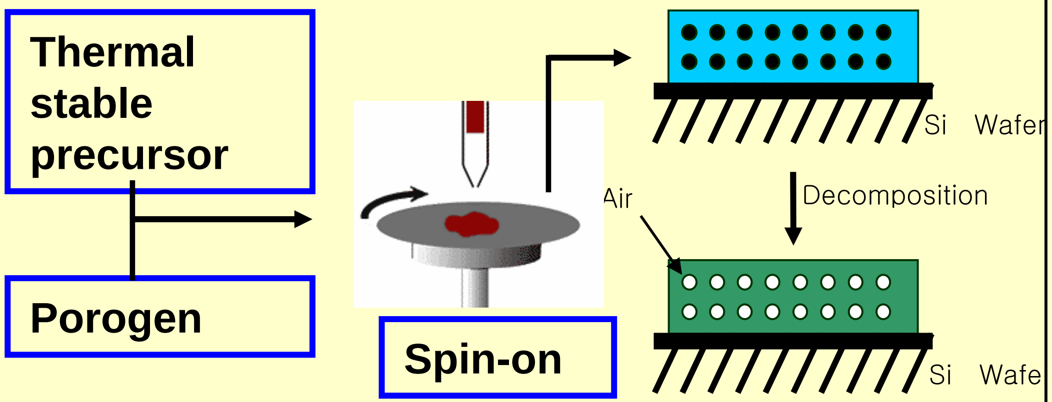
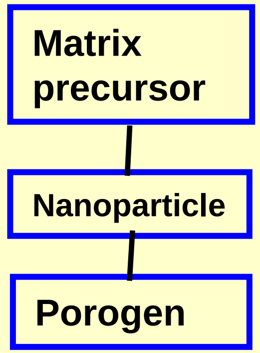
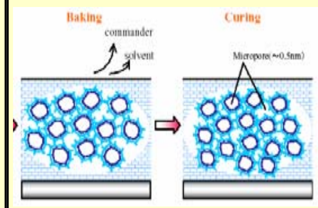
Needs
- ▶ Thermal stability (> 400 ^{o}C)
- ▶ Good mechanical property (>4GPa)
- ▶ Low water uptake
- ▶ Closed cell porosity (< 10 nm)
- ▶ Simplified lithographic processability

Solution
- ▶ High performance siloxane polymer
- ▶ Unique small closed nano pore (<3 nm)
- ▶ Nano pore characterization
- ▶ New pattern process

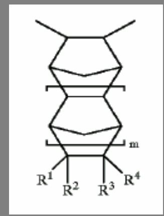


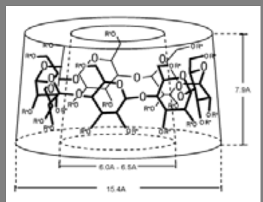
Nanoporous polysiloxane thin film is one of the promising candidates.

How to make porous thin film?

Templating Approach			Hybrid system	Nano Particle
Random PS	Self-assembly	Uni-molecular		
				
				
XLK (Dow Corning) HSG (Hitachi) LKD (JSR)	Lucent Tech. (2002) Philips (2002) JSR (2002)	SAIT (2001) IBM (2003)	SAIT (2003) IBM (2004)	Cal. Univ. (2001) NCS (CCIC)

Various Porogens

2000	2000	2000	2001
 Various polymeric Dendrimer	Decomposable linear Polymer; Polyester, Polystyrene, PMS, Polyacrylate, PMA, Polycarbonate Polyether	 Polynorbone based Polymer	High boiling point organic solvent ex) Tetradecane (b.p~250°C)
IBM	IBM	Georgia Tech	Dow Corning

2001	2002	2002	2002
 Cyclodextrin based derivatives	Polyakylene Oxide Poly(caprolactone) Poly(valeractone) PMMA Mainly PEO/PPO	Ionic Surfactant  C_{16}TMABr Non Ionic surfactant  Cn EOx	Non Ionic surfactant PEO PPO PEO  hydrophilic hydrophilic hydrophobic
SAIT	AlliedSignal Inc.	Lucent Technology	JSR

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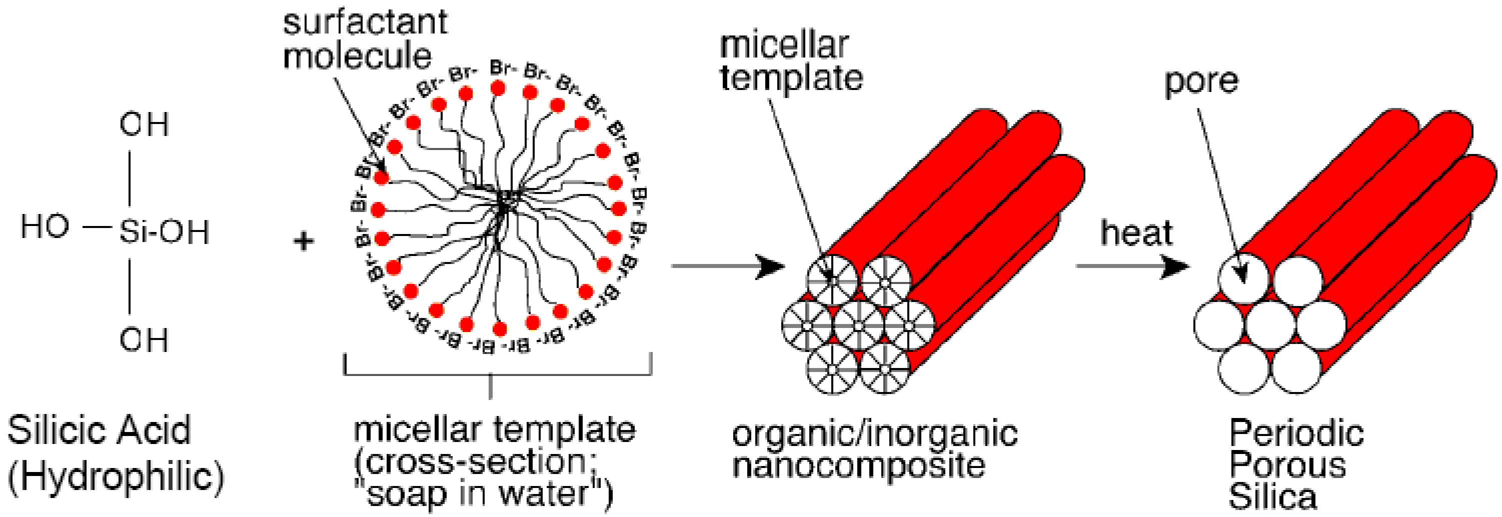
Porous Material via SA

Concept: Sol-Gel Process and Self-Assembly



- Uni-modal pore size distributions
- Controllable pore sizes and pore channel structures (2-10 nm)
- Controllable porosity

Surfactant

Non-ionic Surfactants

(Hydrogen Bonding)

Block Copolymers

$HO-(CH_2CH_2O)_{20}-(CH_2CHO)_{70}-(CH_2CH_2O)_{20}H$, **P123**

CH_3

$HO-(CH_2CH_2O)_{106}-(CH_2CHO)_{70}-(CH_2CH_2O)_{106}H$, **F127**

CH_3

Non-ionic Oligomeric Surfactants

$CH_3(CH_2)_{15}(CH_2CH_2O)_{10}-OH$, B56

Porogen Template Approach

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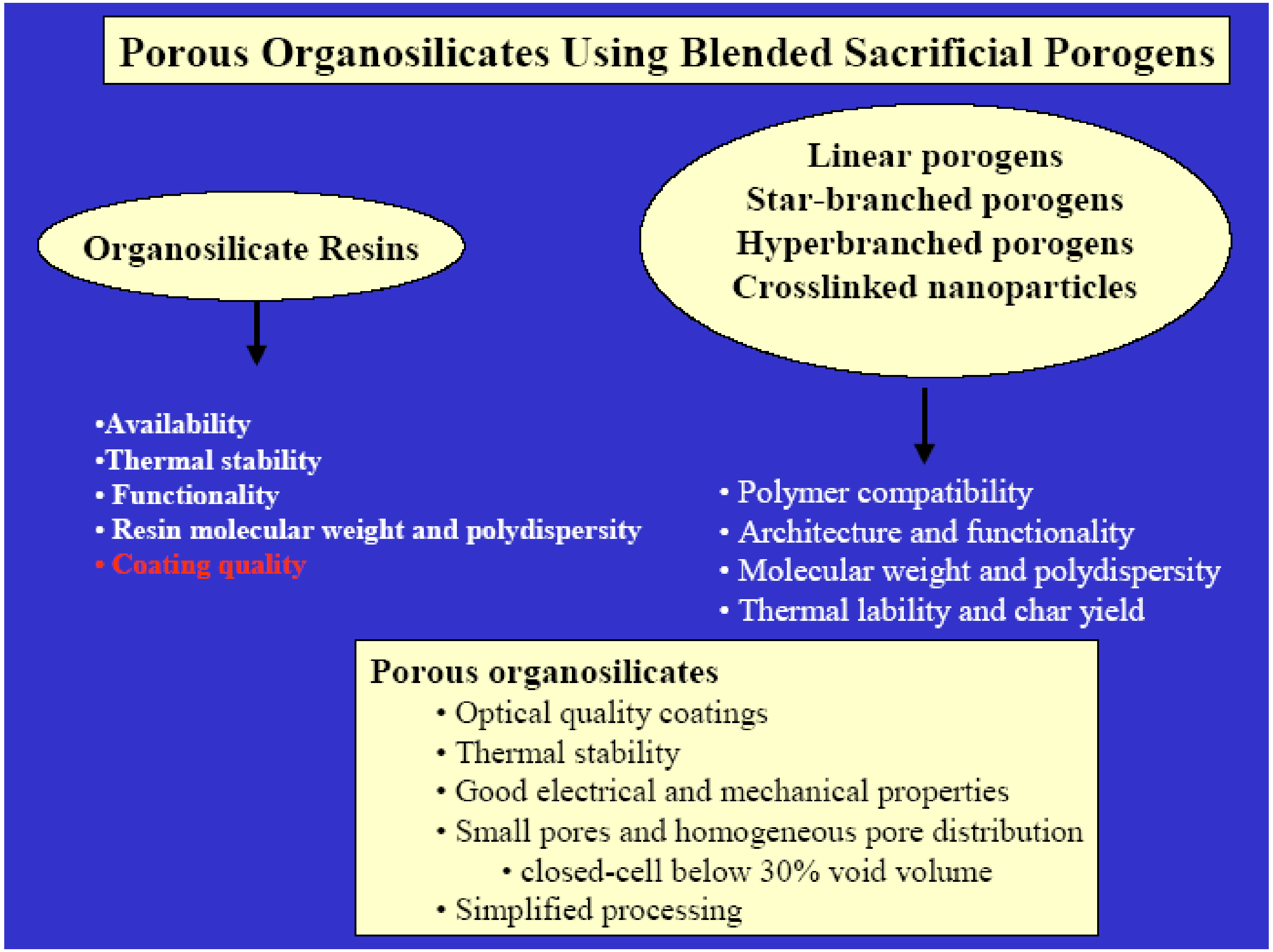
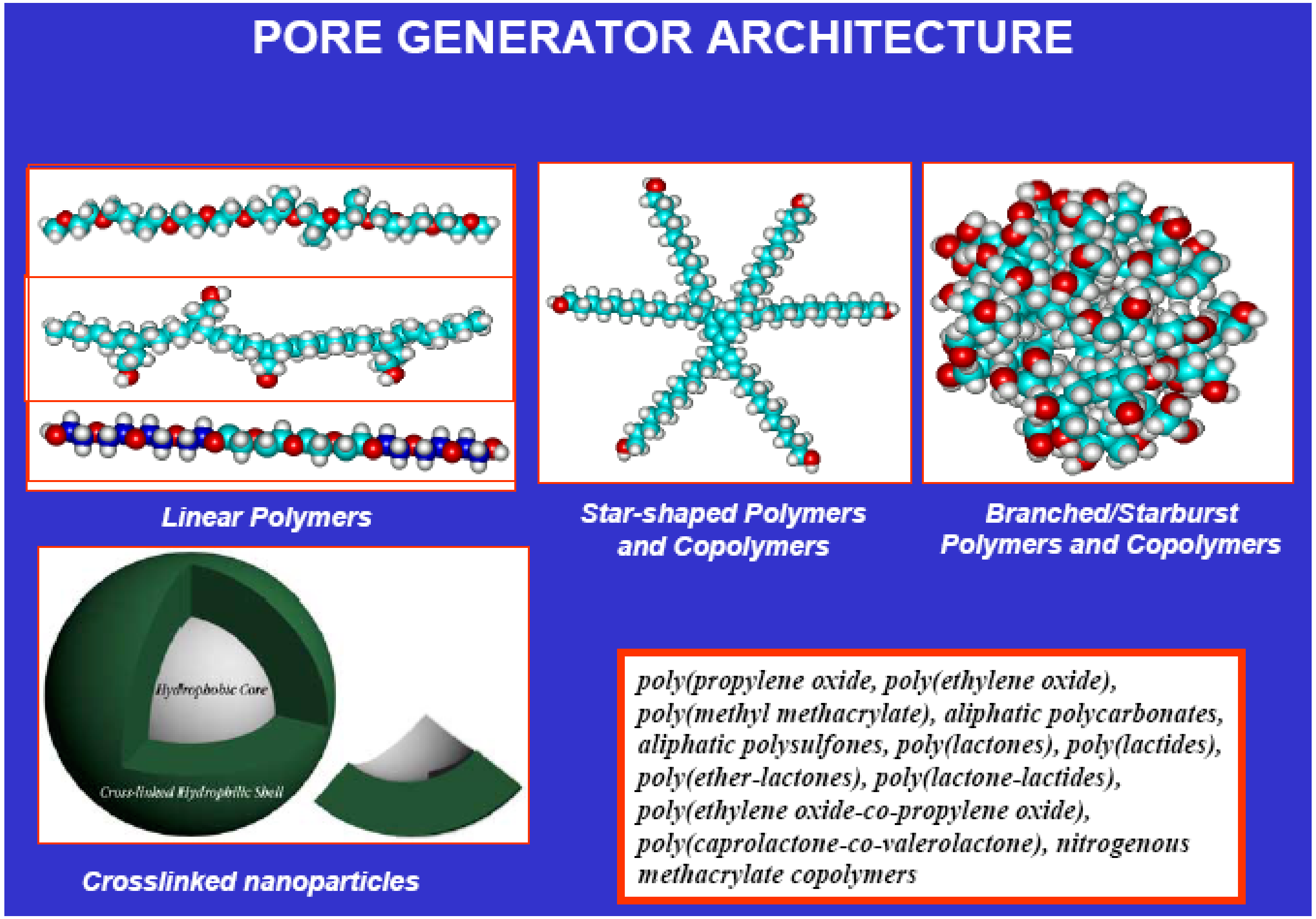
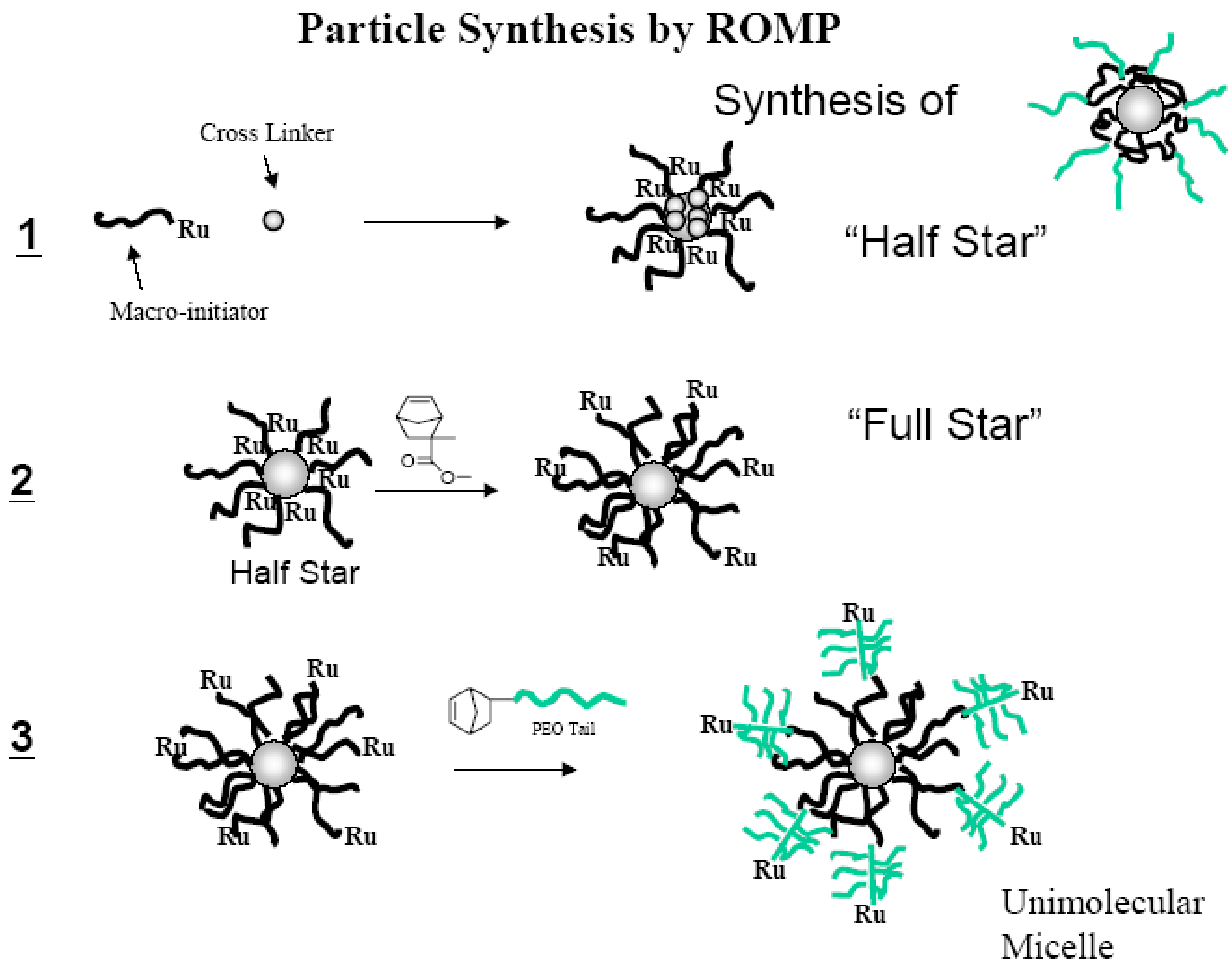
Various Porogens



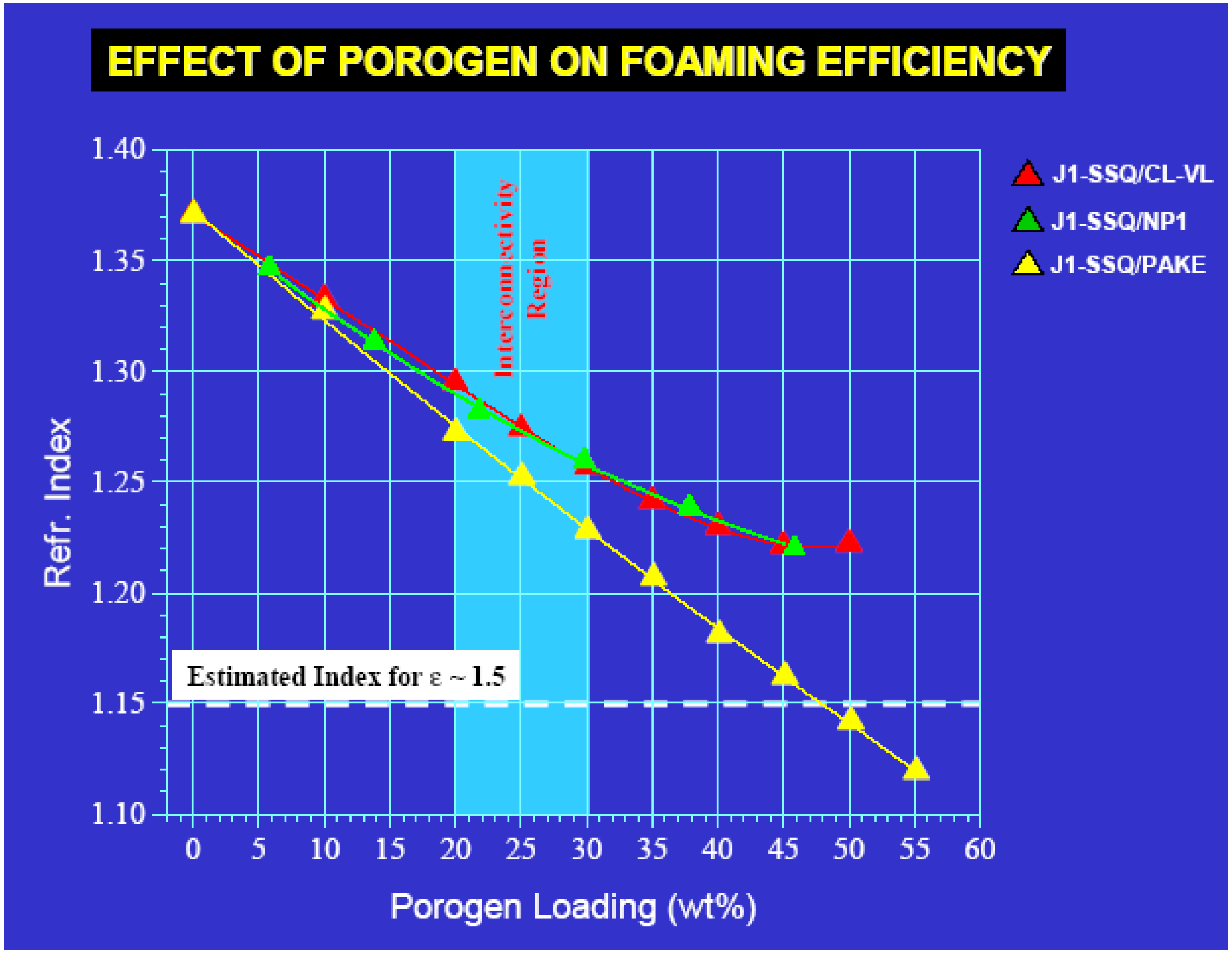
Polymeric Porogens



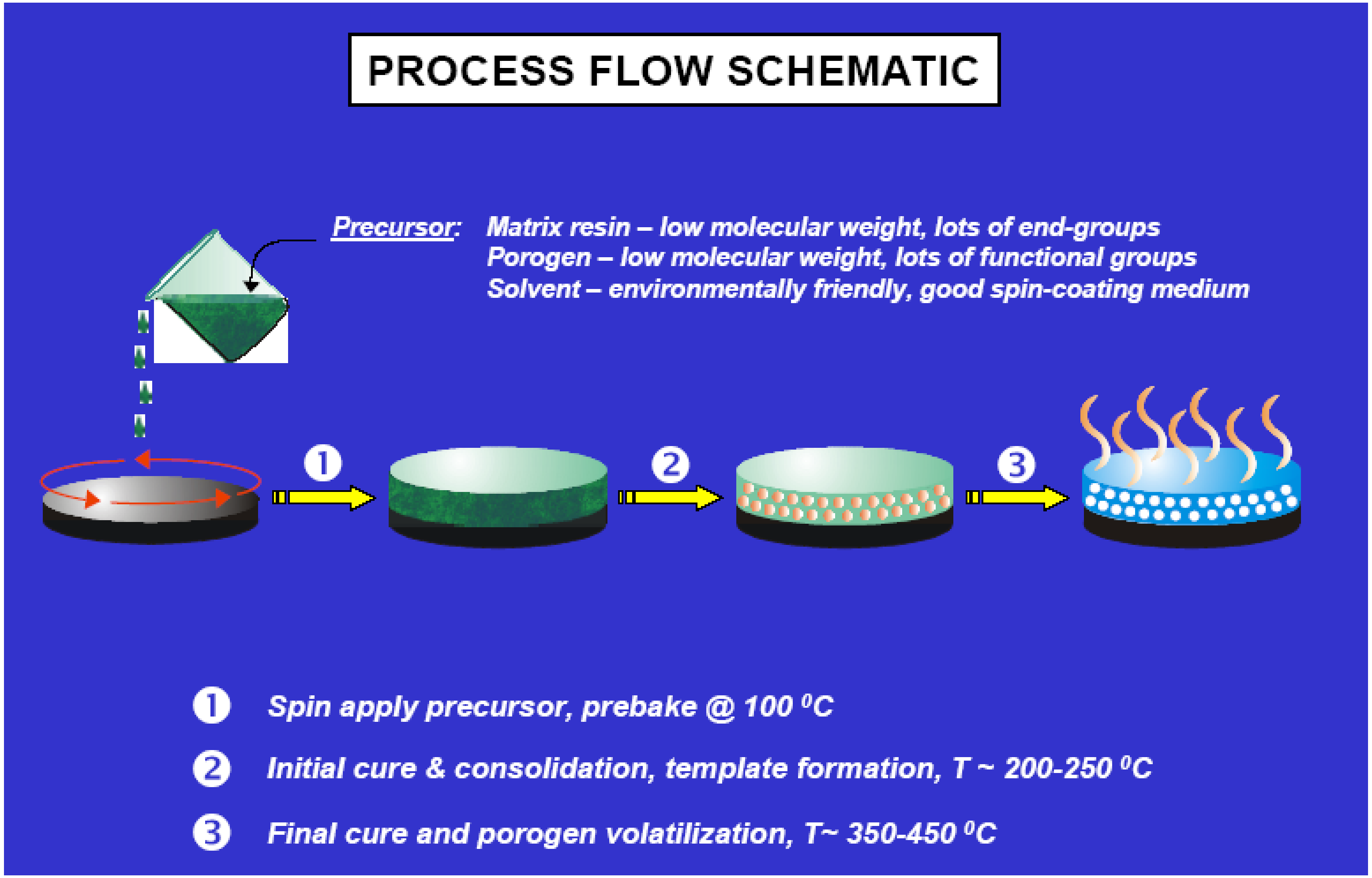
Nanoparticle porogen via ROMP



Forming Efficiency

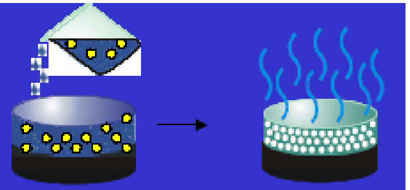


Porogen Template Method

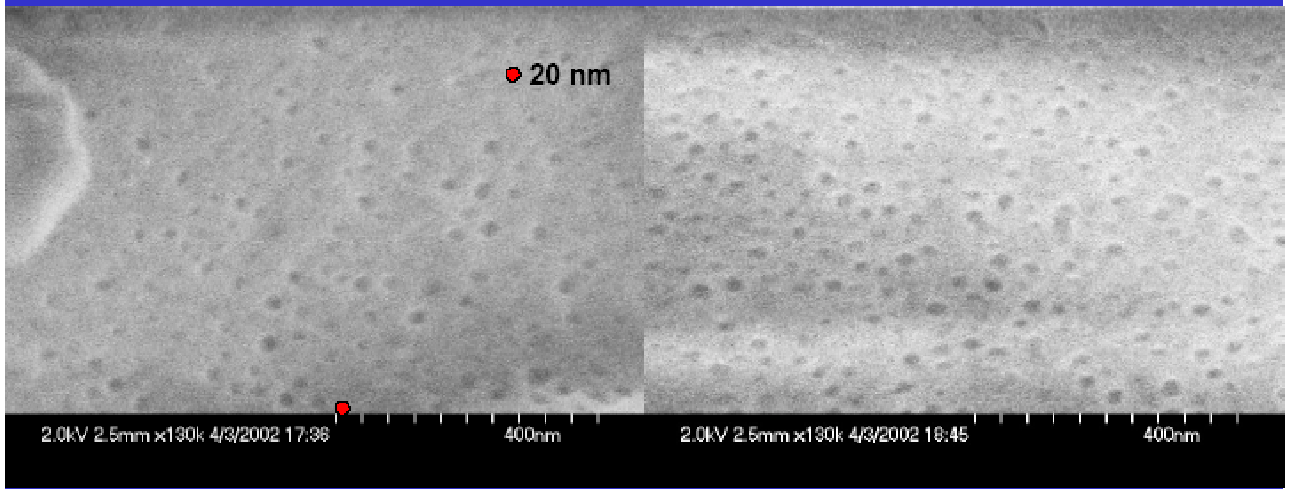


Closed Nanopore

FE-SEM Pictures.
25 nm templates in cured MSSQ resin

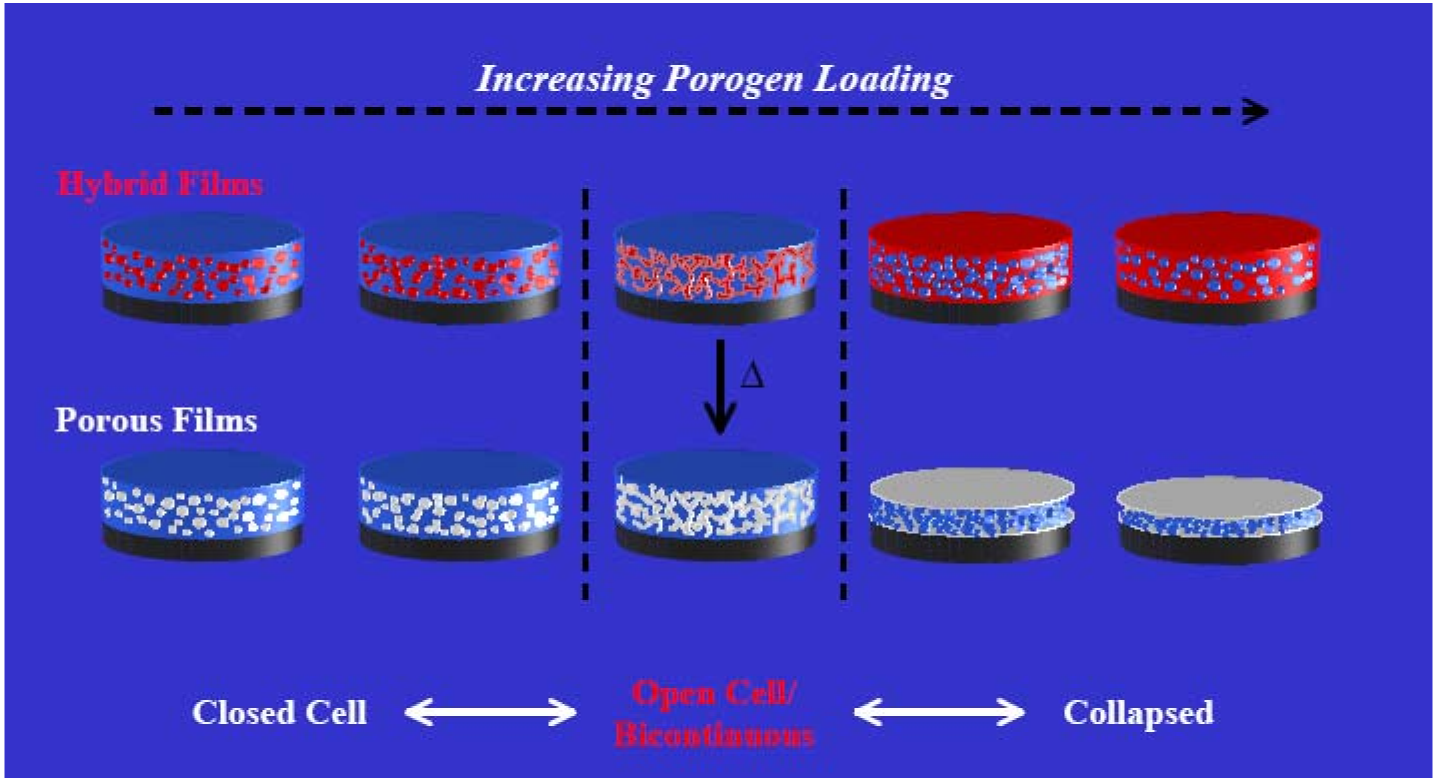


10% porogen loading **20% porogen loading**

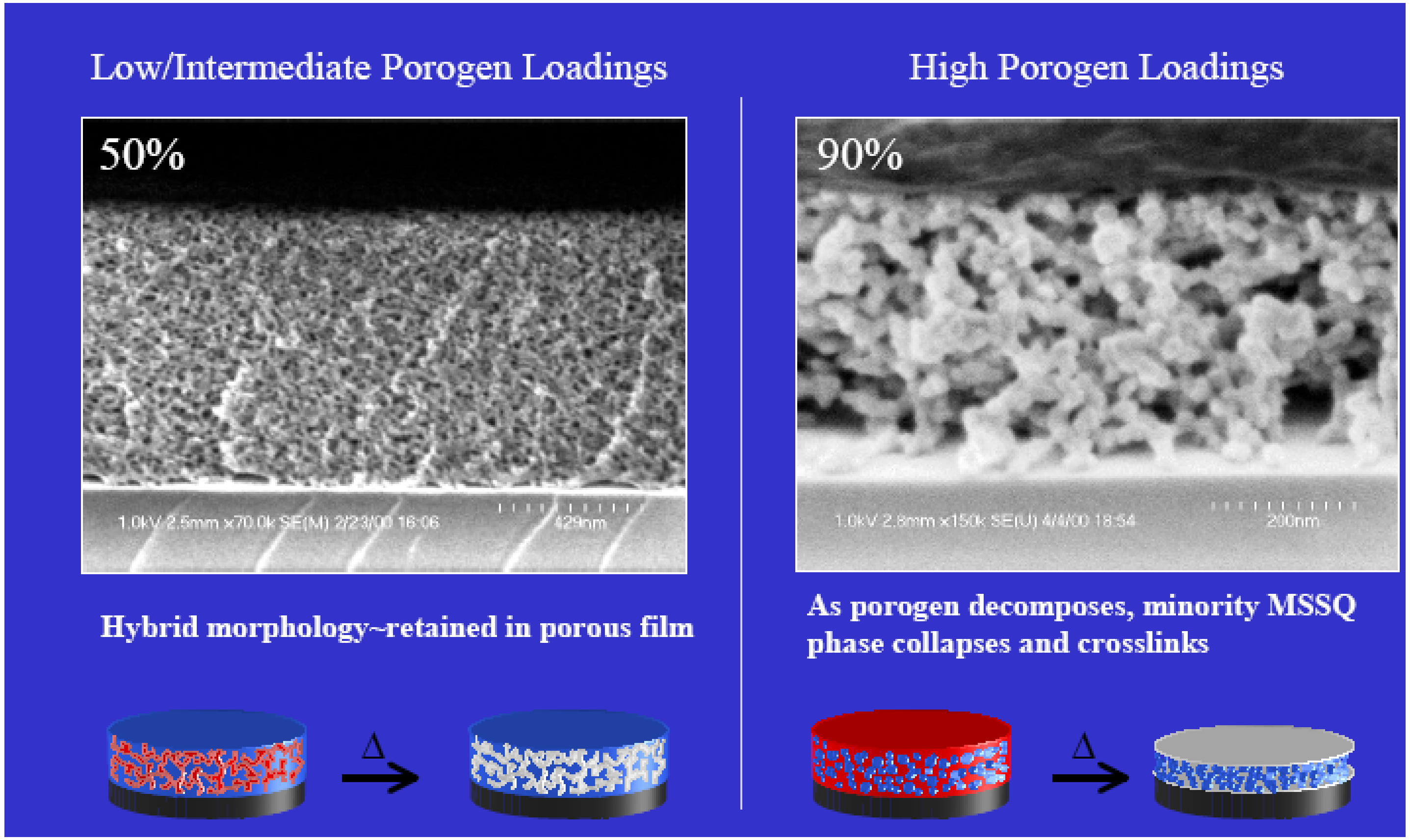


Constant pore size is typical for templating
rather than nucleation and growth

Morphological Transition



Bicontinuous/Collapse Transition



Sol-gel Approach

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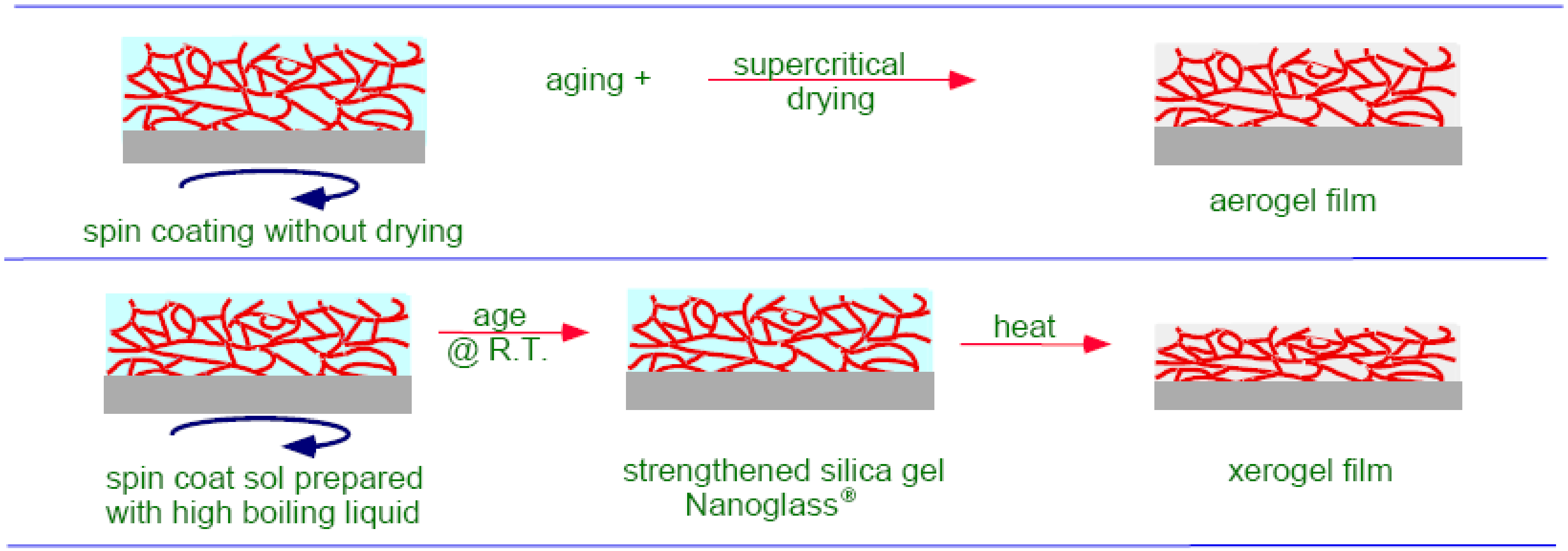
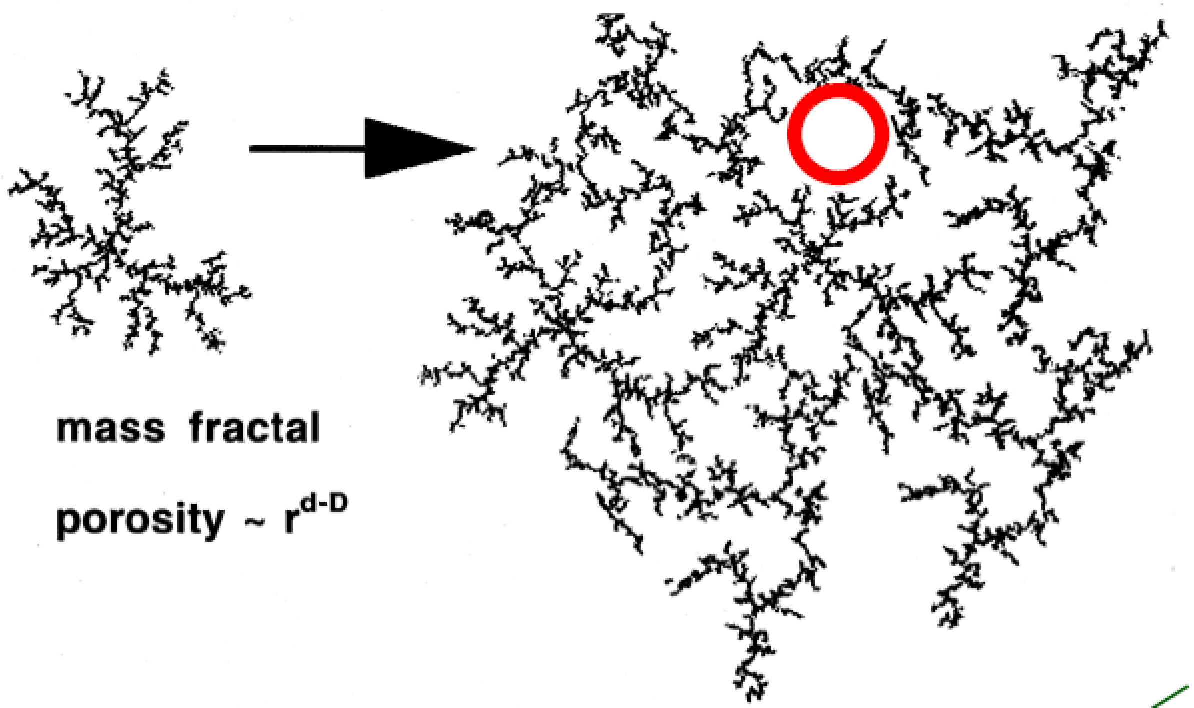
Sol-gel Route to Porous Film



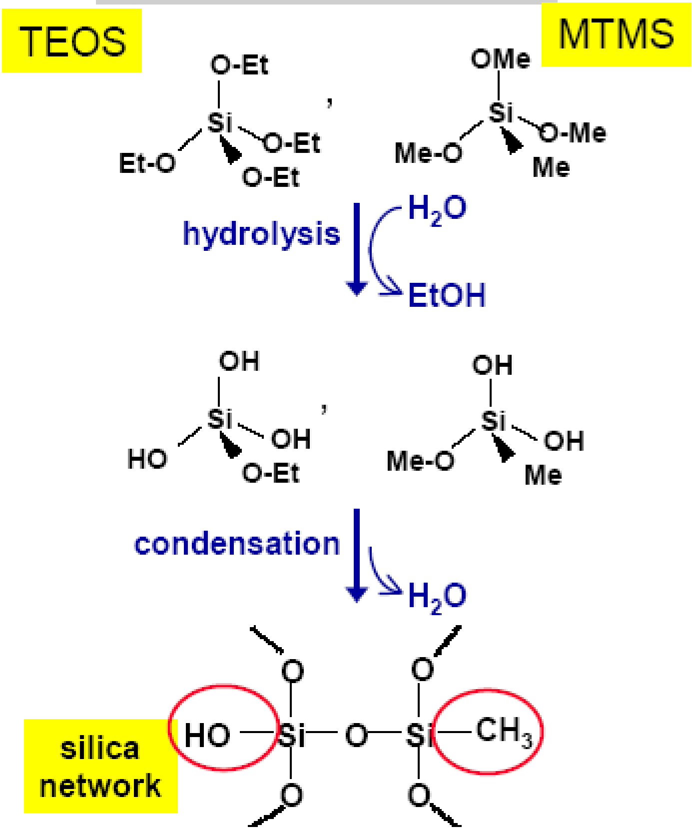
Aerogel: Disordered Fractal Network



- Weakly mechanically connected → low modulus, low thermal cond.
- Modulus scales as 3rd or 4th power of density

Self Assembly

basic sol-gel reactions

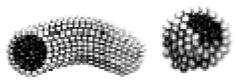


surfactant-templating

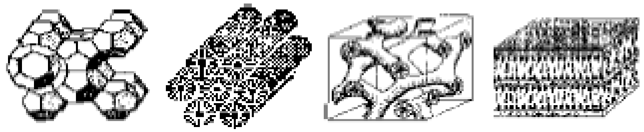
Surfactant

• cationic (CTAB) or non-ionic (Brij 76, F127)

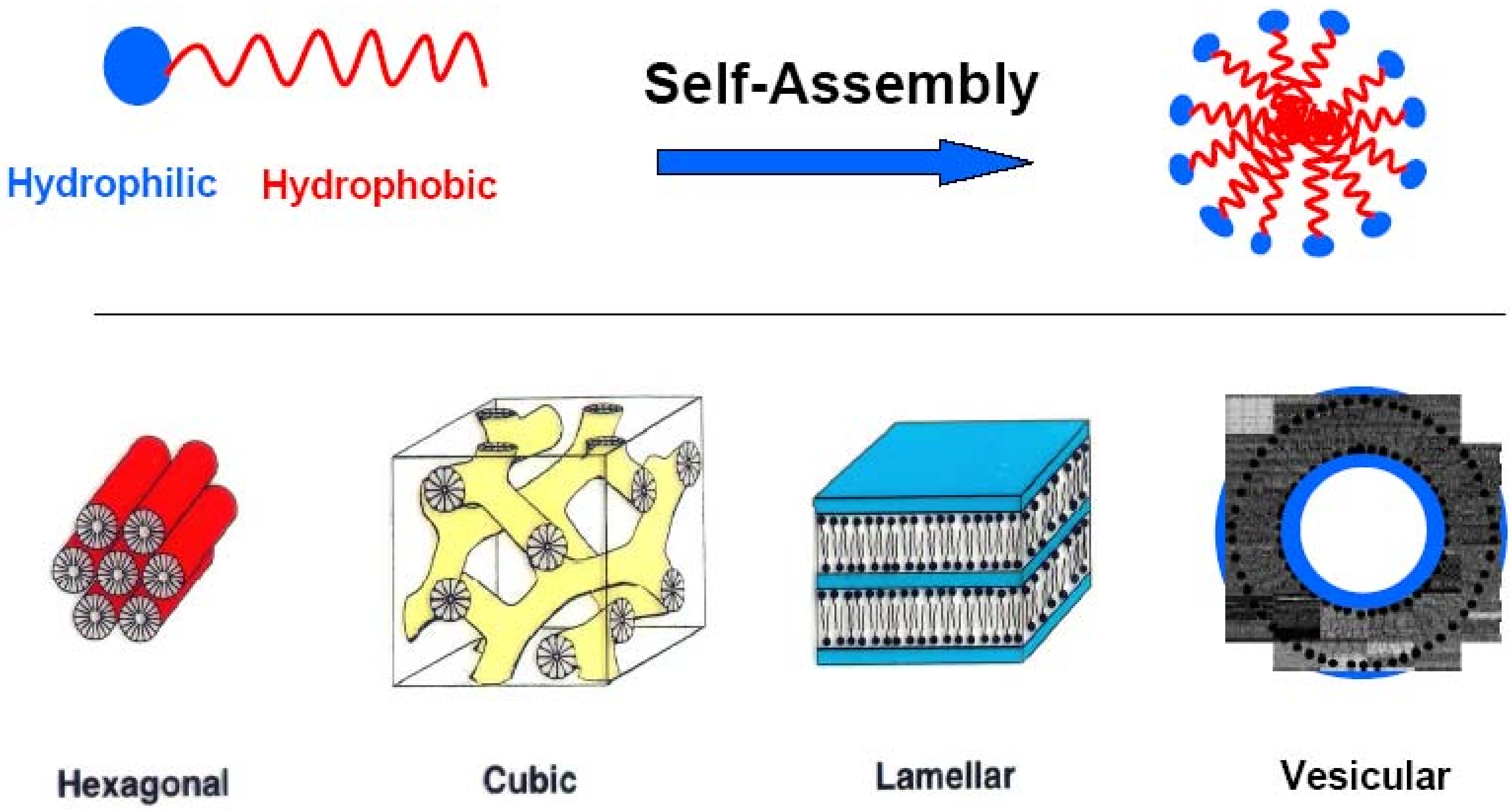
micelles



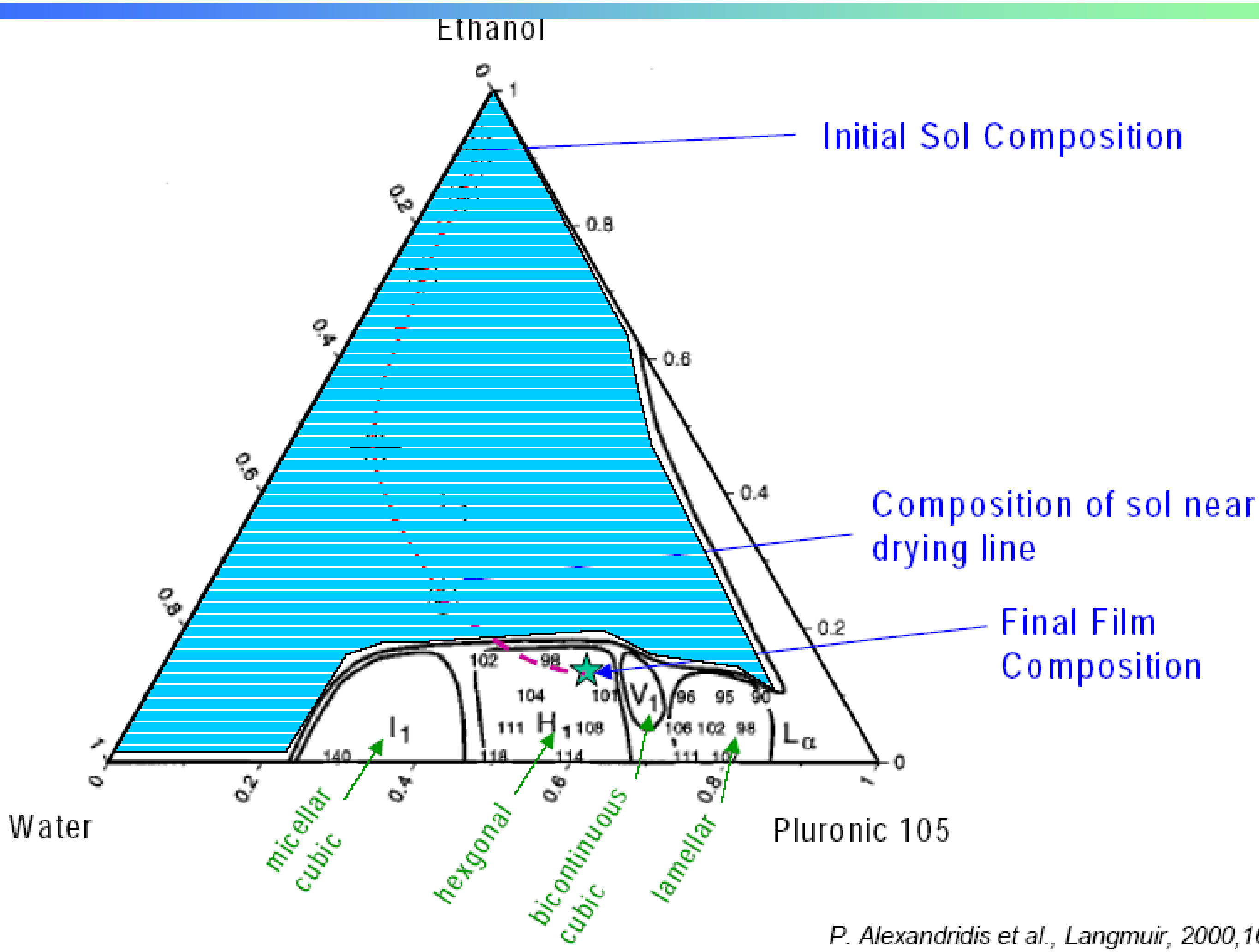
ordered mesophase



Pore Structure

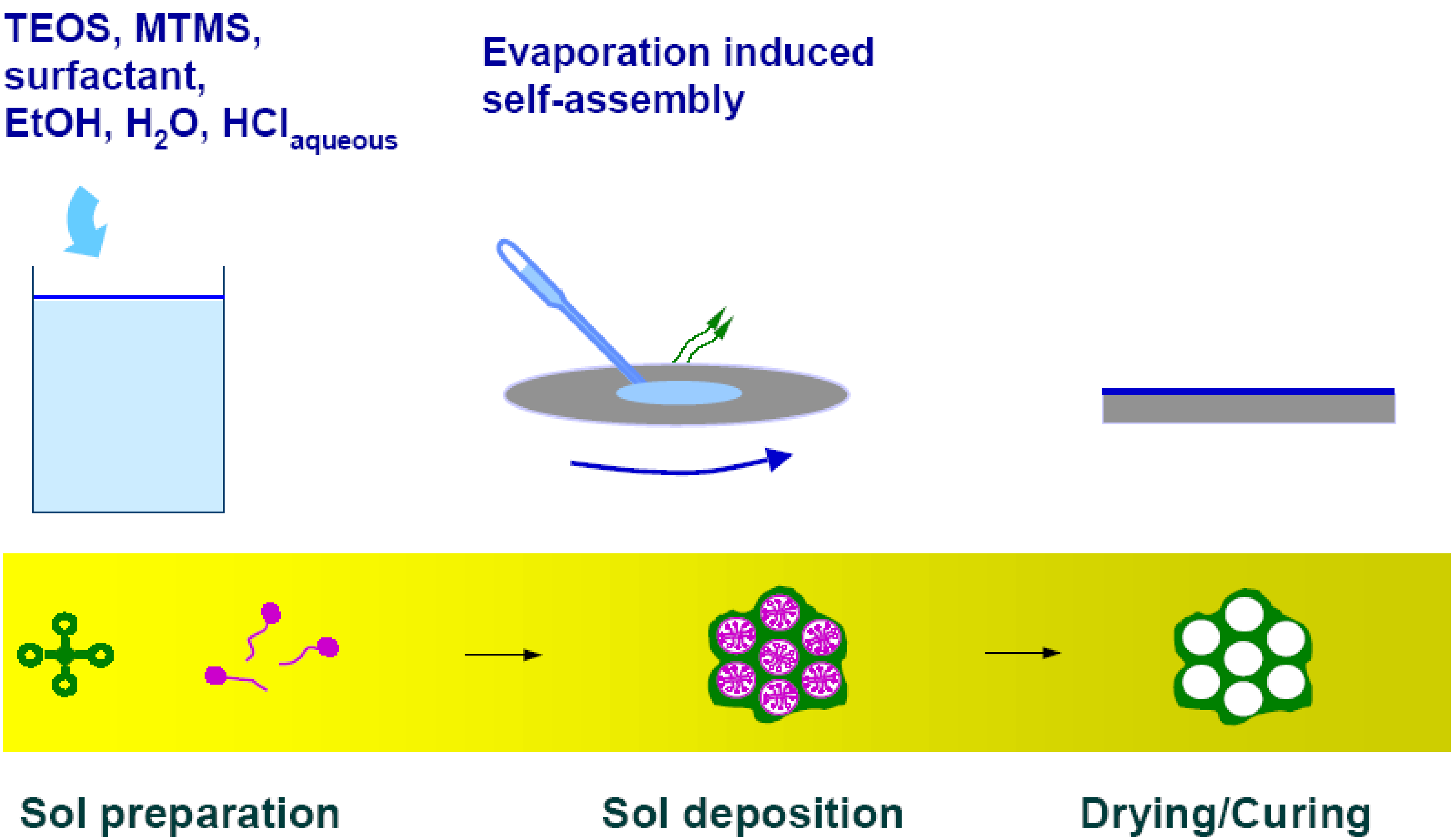


Evaporation Induced Self Assembly (EISA)



P. Alexandridis et al., Langmuir, 2000,16, 3676-89

Typical Process

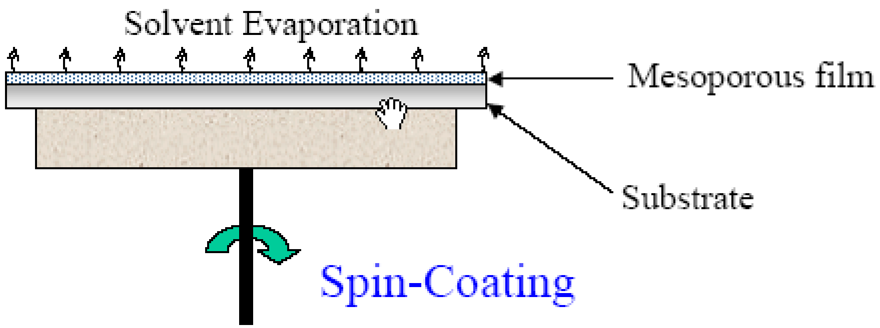


Characteristics of EISA

Self-assembly through surfactant enrichment by solvent evaporation during spin-coating process

Sols containing:

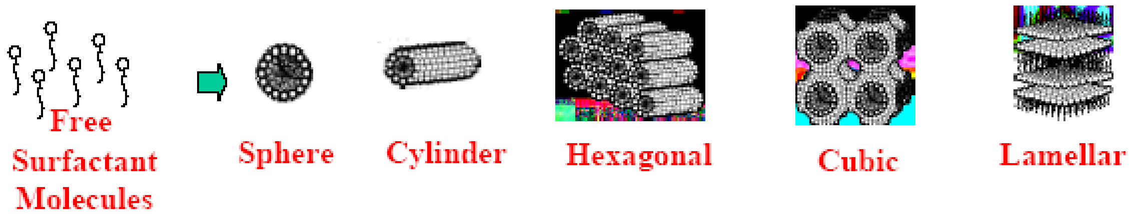
- Ethanol/Water
- Polymeric silica source*
- Surfactant (<< *CMC*)



Features

- Fast (few seconds)
- Controlled Structure (Depends on initial surfactant concentration)

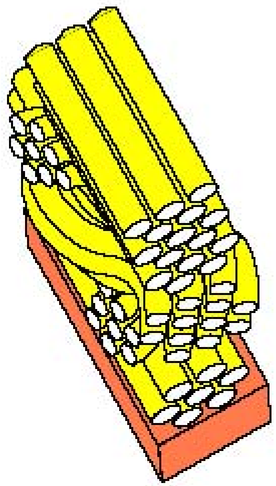
→ Evaporation induced mesostructure development during spin coating



*Designed to minimize siloxane condensation

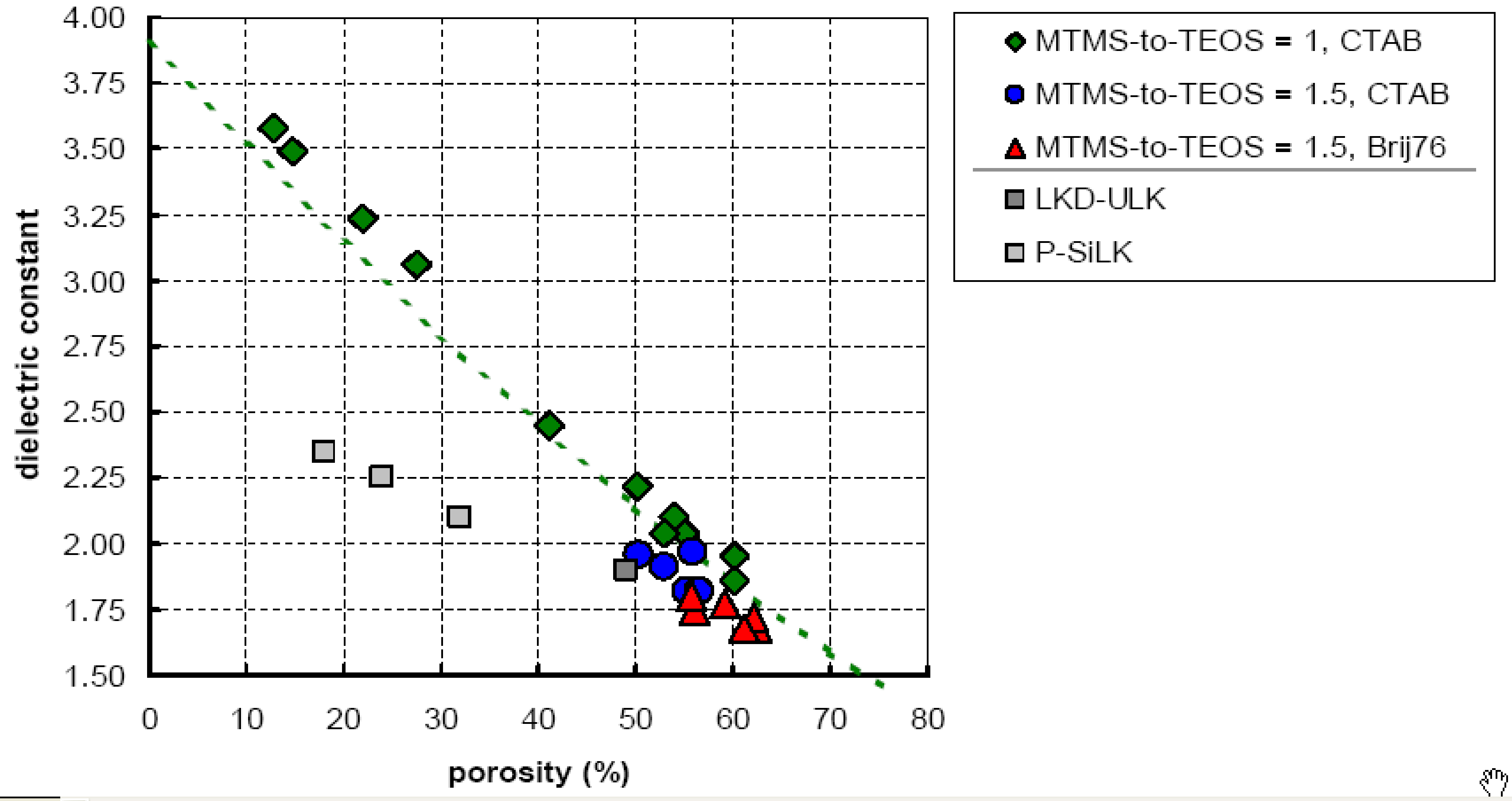
US Patent Issued Jan. 99
Lu et al., Nature, Sept. 97

Material Structure-Property Relationships

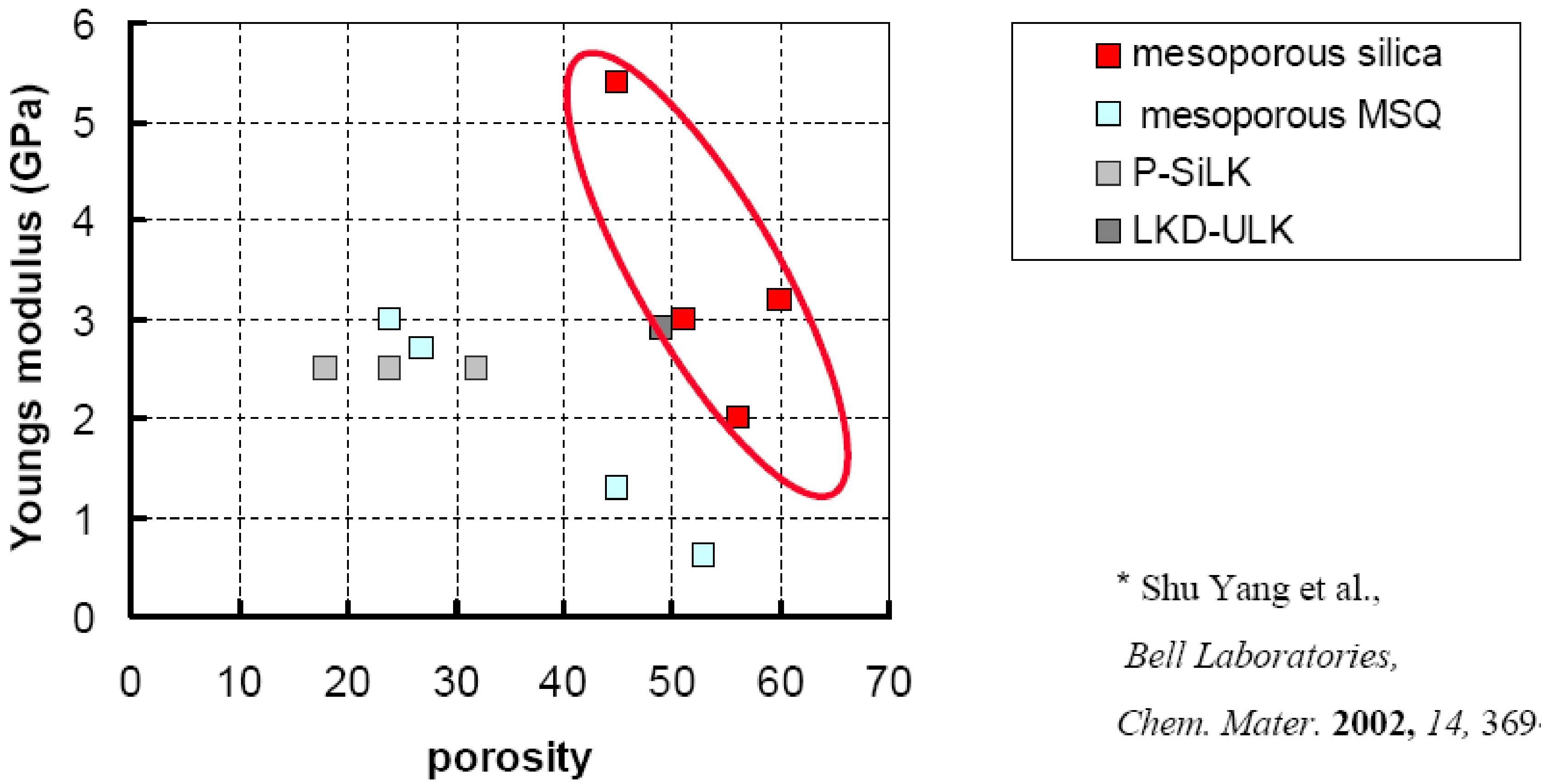


TEM cross-section through 500 nm mesoporous silica (surfactant: F127)

Dielectric constant vs Porosity



Mechanical Property



* Shu Yang et al.,

Bell Laboratories,

Chem. Mater. **2002,** *14,* 369-374

Nanoparticle Approach

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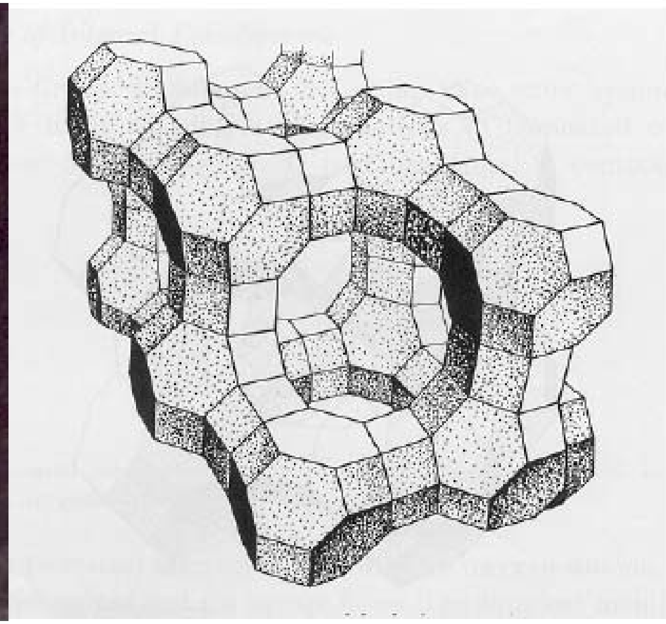
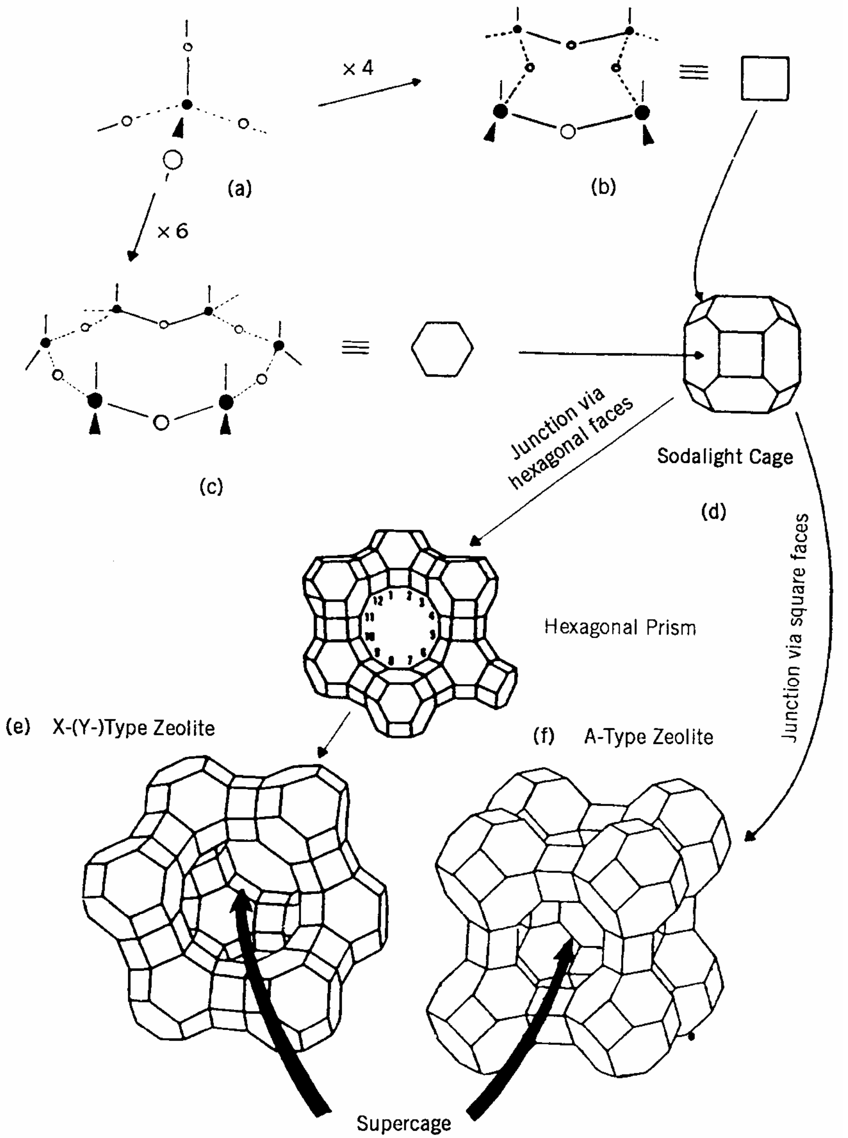
Zeolite ?



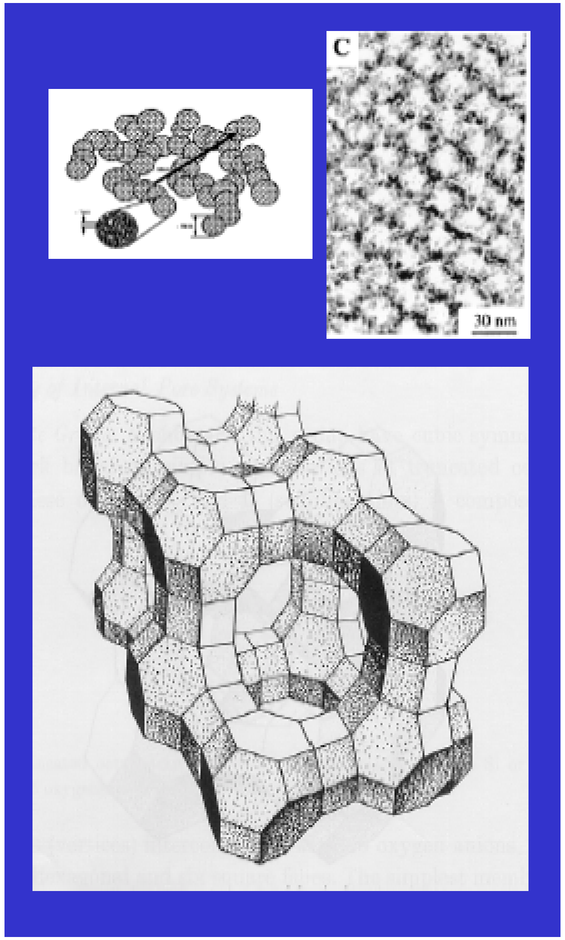
- Inorganic
- Crystalline

- Uniform, molecular-sized pores
- Various pore size and porosity
- Current use
  - Catalysis and separation
  - pellets and granules


× 4
(a)
(b)
× 6
(c)
Junction via hexagonal faces
Sodalight Cage
(d)
Hexagonal Prism
Junction via square faces
(e) X-(Y-)Type Zeolite
(f) A-Type Zeolite
Supercage

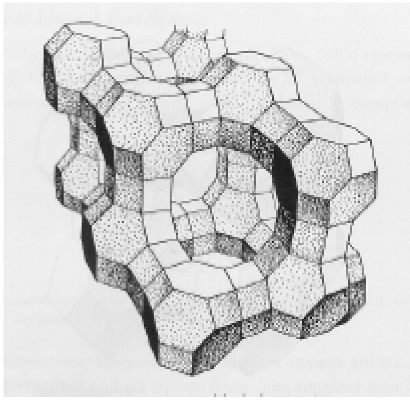
Various Porous Film

- Sol-gel silica
  - Very low k
  - Low mechanical strength
  - Low heat conductivity
  - Electrical breakdown
  - Hydrophilic
- Mesoporous silica
- Zeolites

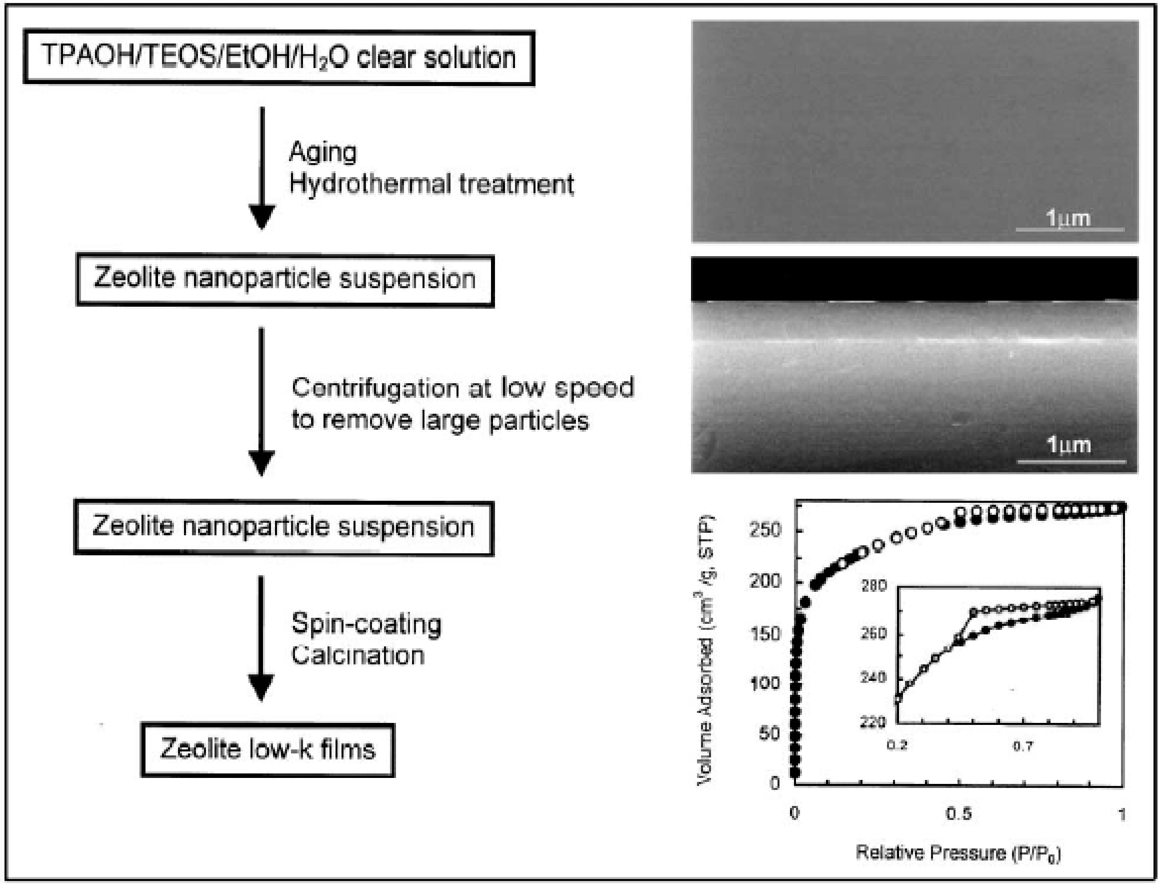


Characteristics

- Microporous *crystalline* silica
  - High thermal stability
  - High heat conductivity
  - High mechanical strength
  - Could be hydrophobic
  - Uniform molecular-sized pores

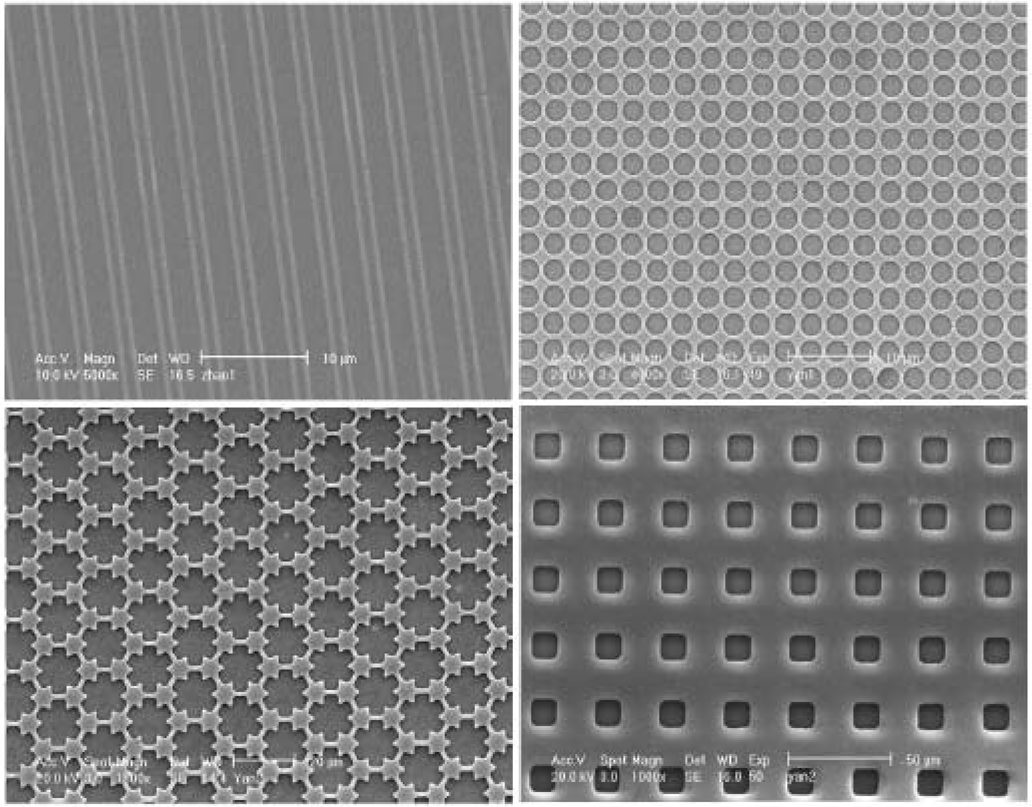


Typical Process



- k=2.0 – 2.2
- Elastic modulus = 16-18 GPa
- Total spin-on process
- Film thickness = 0.45 μm

Patterned Structure



Huang L. et al. *J. Am. Chem. Soc.* 2000. 122:3530-3531

Summary of Zeolite low-k

- Lowest k=2.0 – 2.1
- Mechanically strong (modulus = 16-18 GPa)
- Commercially feasible spin-on process
- Extendable to lower k value

Nanopore Analysis

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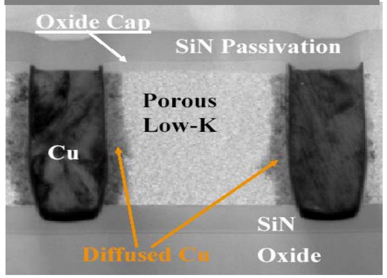
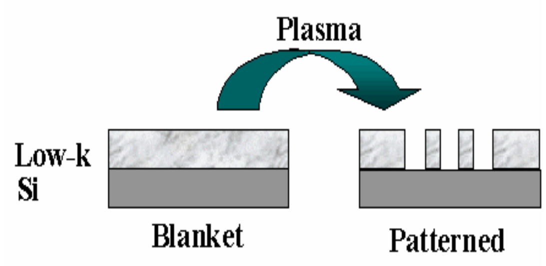
Nanopore Engineering

Barrier Metal Issue

Cu Diffusion Issue



Ashing Damage Issue

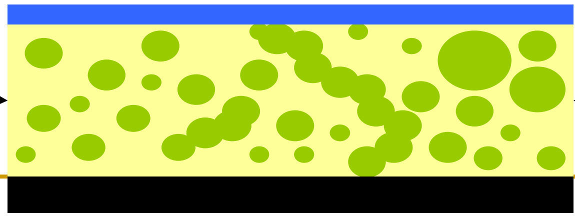


Blanket Film

- Electrical Properties; k, Leakage current, Breakdown voltage
- Young's Modulus; Modulus, Hardness, Toughness

Overall Properties

- Film thickness
- Refractive index
- Film density & Porosity
- Surface Area
- Young's Modulus



Pore Structure

- Open & closed pore size
- Pore size distribution
- Interconnectivity
- Open & closed pore volume

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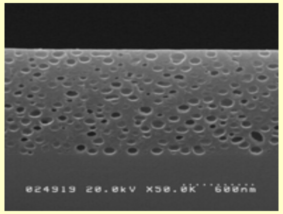
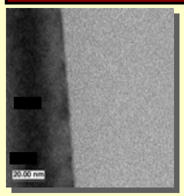
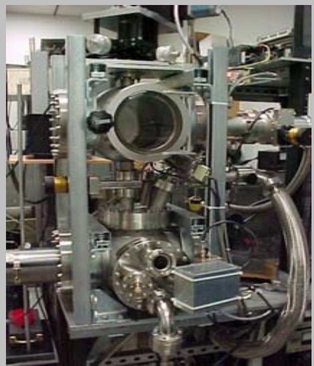
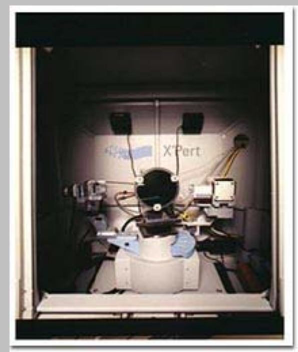
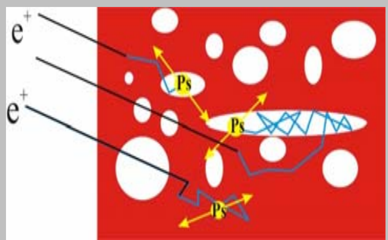
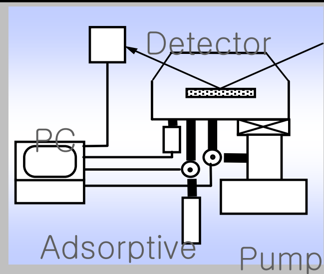
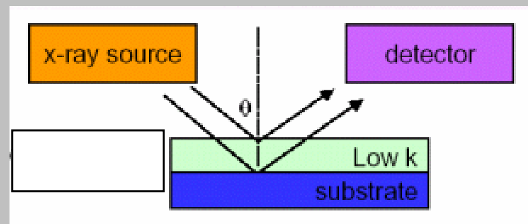
Nanopore Analysis

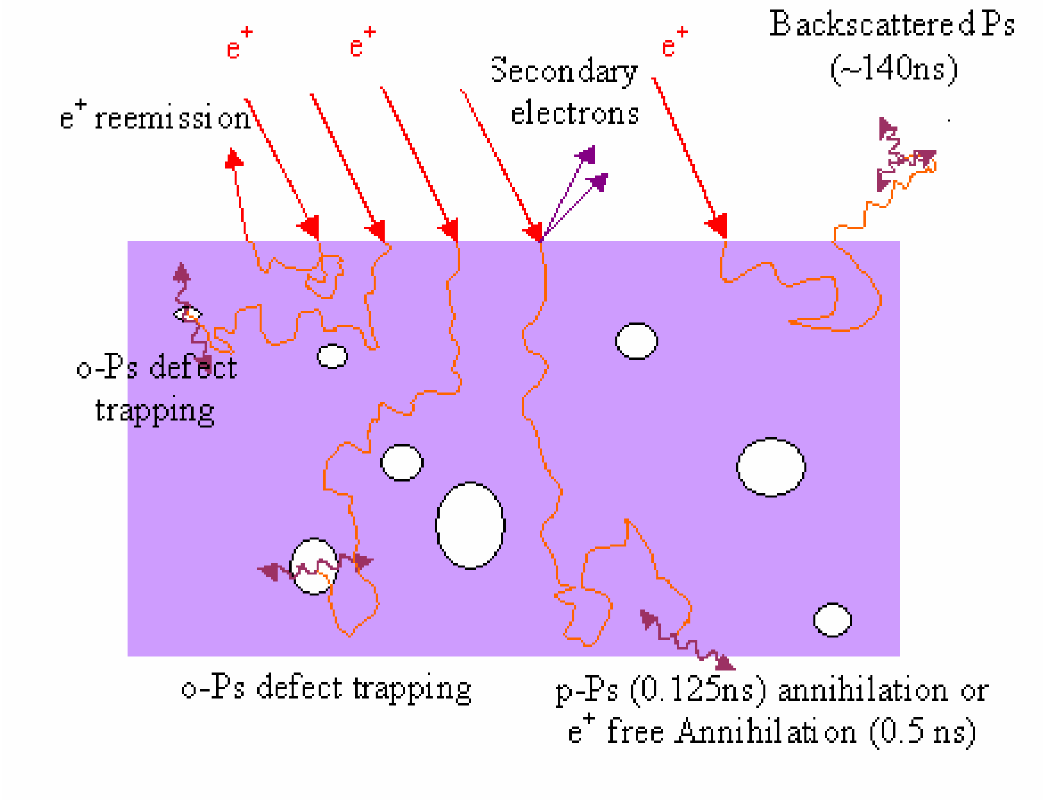
Stereological Analysis	Intrusive Method	Non-intrusive Method
SEM, FE-SEM   **TEM, HR-TEM**  	**Gas Adsorption** **Mercury Porosimetry** **Calorimetric Method** **J. Rouquerol et al., *Pure Appl. Chem.*, 66, 1739 (1994)** **Ellipsometric Porosimetry** **M.R. Baklanov et al., J. Vac. Sci. *Tecnol.*, 18, 1385 (2000)**	**PALS, PAS** **D. W. Gidley et al., *Appl. Phys. Lett.*, 76, 1282 (2000)** **XRR/SANS** **W. Wu et al., *Appl. Phys. Lett.*, 87, 1193 (2000)** **XRR/SAXS** **T.P. Russel., *MRS Bull.*, Jan. 49 (1996)**
– Qualitative analysis – Low contrast in amorphous materials (Low sensitivity) – Pore structure changing in the sample preparation	– Limitation of closed pore system – Swelling issue of polymer film – Destructive method	– Need of radiation beam generator (Big facility) – PALS; Materials dependency (No generation and diffusion of Ps)

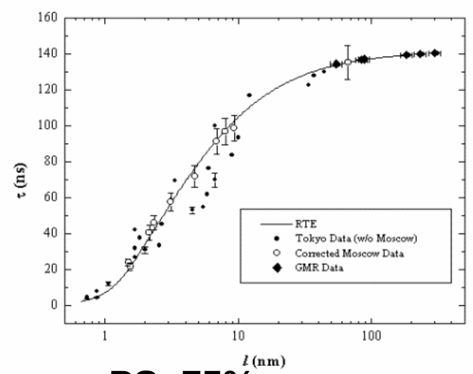
Nanopore Analysis

PALS (Michigan Univ.)	EP (IMEC)	XRR/SANS (NIST)
		
		
- Pore Size, PSD - Closed/Open Pore Shape - Interconnection Length	- Porosity - Pore Size, PSD - Open/Closed Pore Volume - Young's Modulus	- Porosity - Pore Size, PSD

PALS

PALS technique provide: average pore size, PSD, pore shape (interconnectivity)





<u>o-PS: 75%</u>

(1) Micro pore Traped
τ = 1-10 ns

(2) Meso pore Traped
τ = 10-140 ns

(3) Escape to Vacuum
τ = ~140 ns

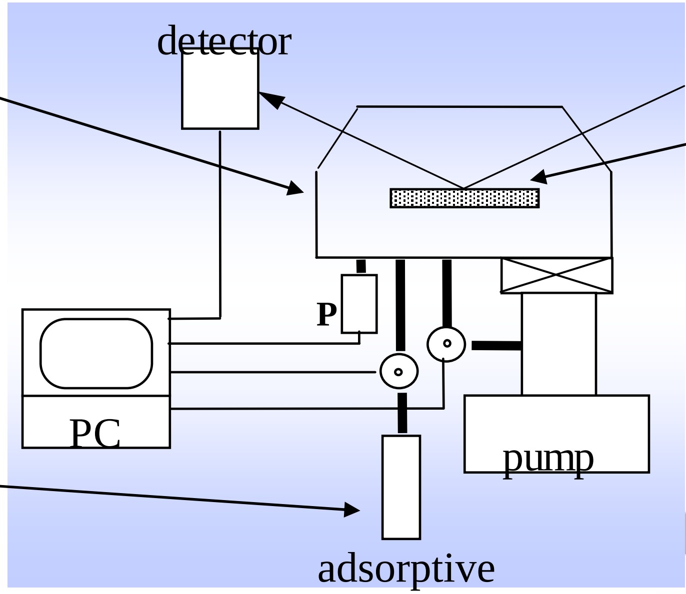
(4) Backscattered o-Ps
τ = 142 ns

<u>p-Ps: 25%</u>
τ = 0.125ns

EP

EP technique provide: average pore size, PSD, porosity, shape info., modulus

Simple vacuum equipment fits in-line process diagnosis

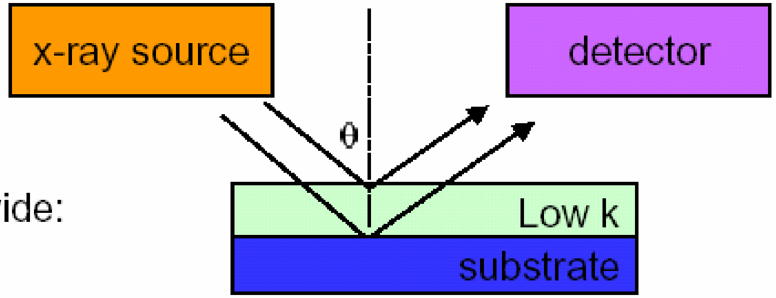


No need for film scratch

Non-hazardous adsorptive

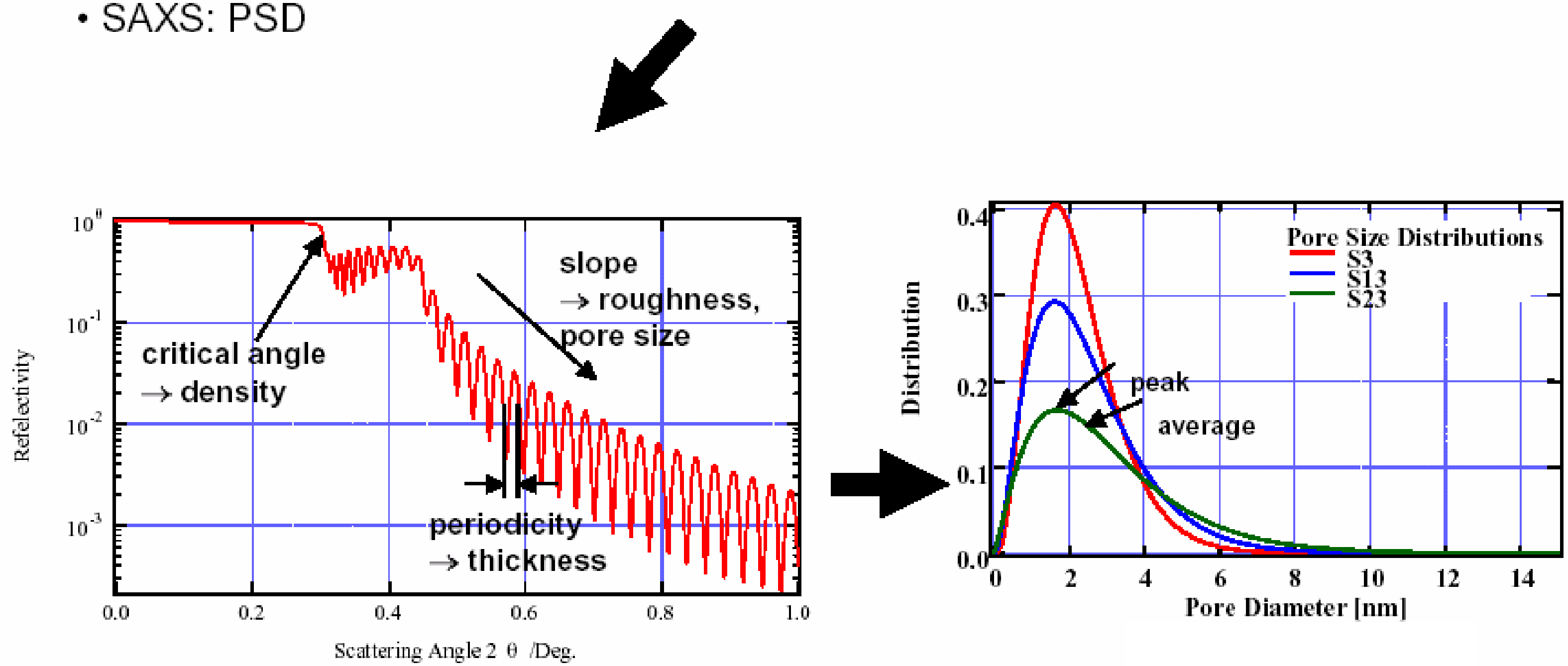
Laser probe **determines the adsorbate amount.**
No need **in large surface area**

XRR/SANS



X-ray techniques provide:

- XRR: density and thickness
- SAXS: PSD



Summary

- A variety of sacrificial porogen classes are compatible with low Mw SSQ derivatives
- Thermal processing and pore generation is exceptionally simple
- Thermal and morphological stability is excellent (> 450 C)
- Measured thermal conductivities of porous organosilicates is comparable to porous silica in the same dielectric range
- Porous organosilicates have acceptable electrical properties
    - (leakage and breakdown) for dielectric applications
- Dielectric constants < 1.5 have been demonstrated for porosities <60%
- Dielectric targets of 2.0-2.2 can be reached with closed -cell porosity
- Percolation thresholds range from 20-30% porosity and depend on resin structure
- Pore sizes can be varied over a large range on a nanoscopic scale
- Porous organosilicates are intrinsically hydrophobic without chemical treatment.
- Resin mechanical properties vary strongly with structure