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

Hybrid Organic-Inorganic Materials

Traditional composite materials : multiphase material brought about by combining materials that differ in composition or form in order to obtain specific characteristics and properties.

- retain their identities and properties
- act in concert to achieve improved synergistic properties

These traditional composite materials, and in particular materials with I fillers in O matrix, have macroscale domain size of micrometer and even millimeter scale.

HOIM or **nanocomposites** or **molecular composites** : a new class of composite materials with the physical constraint of few nanometers as the maximum size of the I and/or O component.

- I/O interface tends towards infinite.
- original properties, such as optical transparency.

Why HOIM??

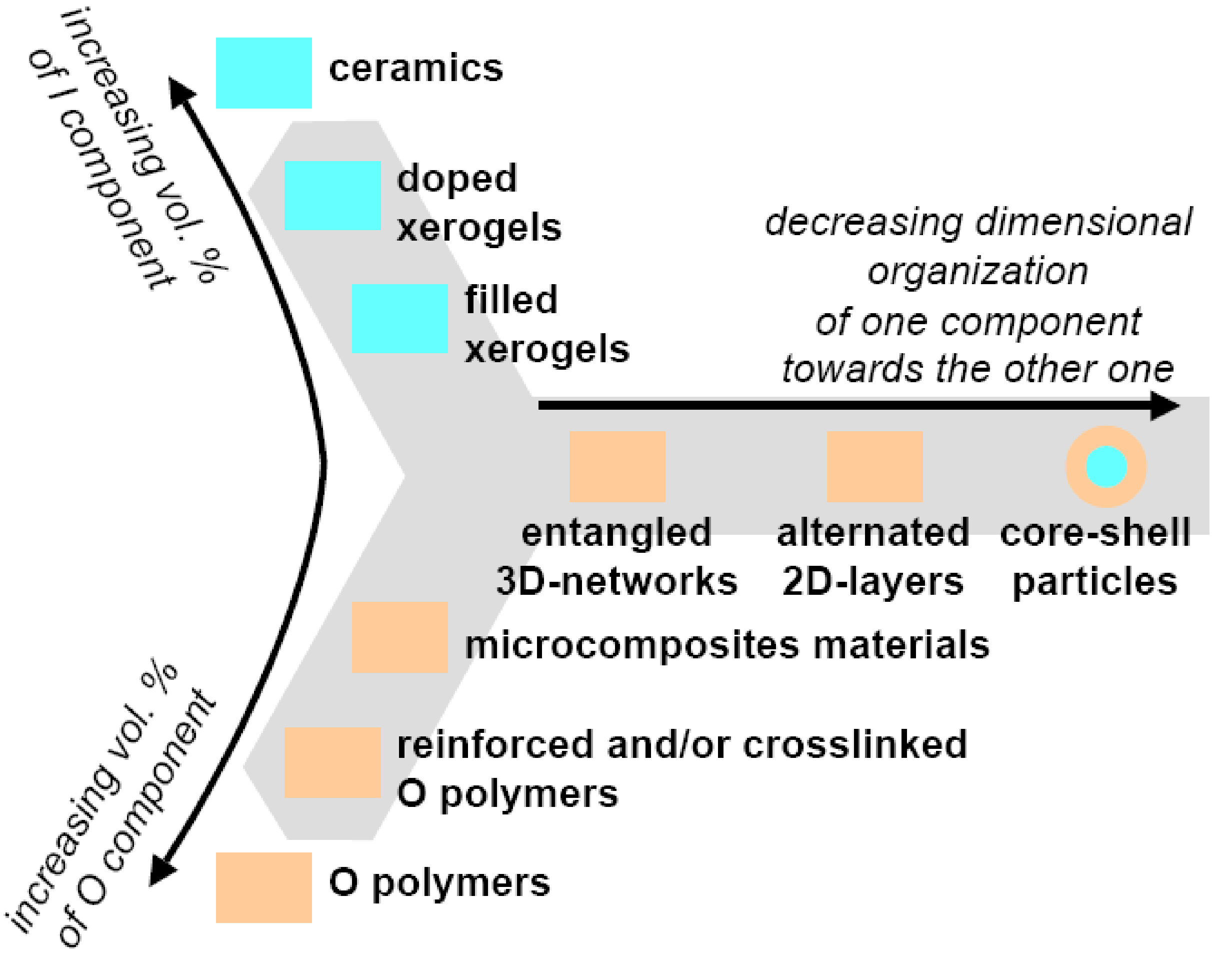
- I component acts as **network former** : chemical resistance, mechanical resistance, optical transparency…
- O component acts as **network former** or **network modifier** : processability, hydrophobic/hydrophilic balance, specific property as NLO response, biological activity…

  - synthesis and application of HOIM have attracted
    - polymer scientists
    - solid state chemists
    - ceramists
    - inorganic chemists
    - organ(ometall)ic chemists

    and

    - physicists
    - biologists

Classification of HOIM



Approach of HOIM

- **Sol-gel-derived hybrid organic-inorganic materials**
  - Incorporation of small organic molecules or organic groups/functions in inorganic networks
  - Sol-gel process in combination with organic polymers and/or free-radical polymerization reactions
  - Incorporation of micrometric size "objects" in inorganic networks

- **Intercalation chemistry background**
  - General considerations
  - The kinetics and mechanism of intercalation
  - Synthetic methods

Organic-Inorganic Hybrid Materials

Figure 1. Hybrid organic–inorganic materials can be readily prepared as monolithic structures as well as thin films, fibers, particles, or powders.

- **Homogeneous System**:

  from monomer or miscible system

- **Heterogeneous System**:

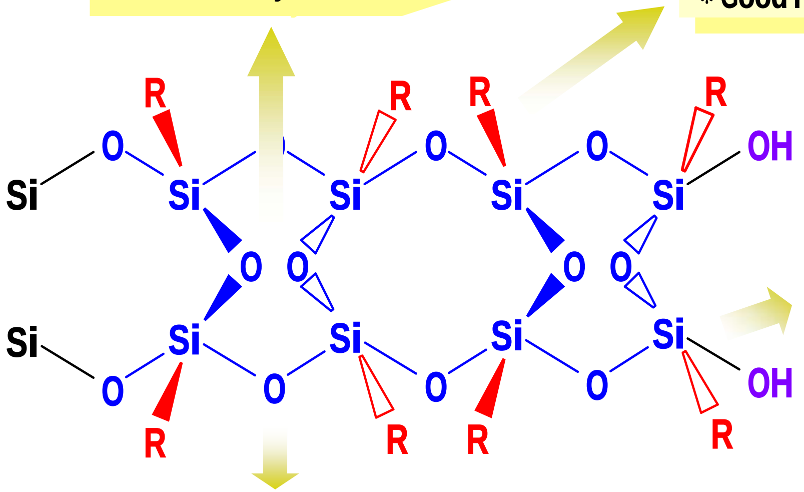
  Phase separated system with domain ~μm

- **Preparation route**

  Solution mixing, Solid state RXN,

  Sol-Gel Process, In-situ polymerization

Organic Inorganic Hybrid System: SSQ



Ladder structure;

- ∗ High thermal stability
- ∗ High Tg.
- ∗ Low viscosity

Pendant group

- ∗ Excellent thermal stability
- ∗ Low moisture absorption
- ∗ Low conductivity/ Low dielectric constant
- ∗ Good hardness

End group(Si-OH);

- ∗ Thermoset (120 – 350°C)
- ∗ Versatility to organic reaction

Si-O-Si bond;

- ∗ Optical transparency
- ∗ Oxygen plasma resistance
- ∗ Compatibility with inorganic material

Nomenclature I

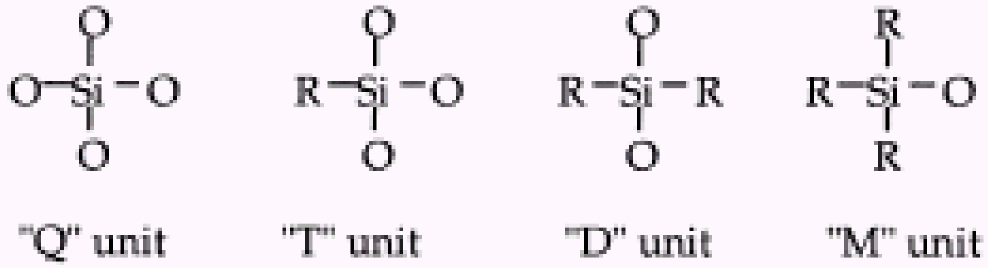


Chart 1.

Toughness Increase
Polarizability Decrease

Hardness/Modulus Increase

Molecular Structure

“Q” Structure “T” Structure “D” Structure

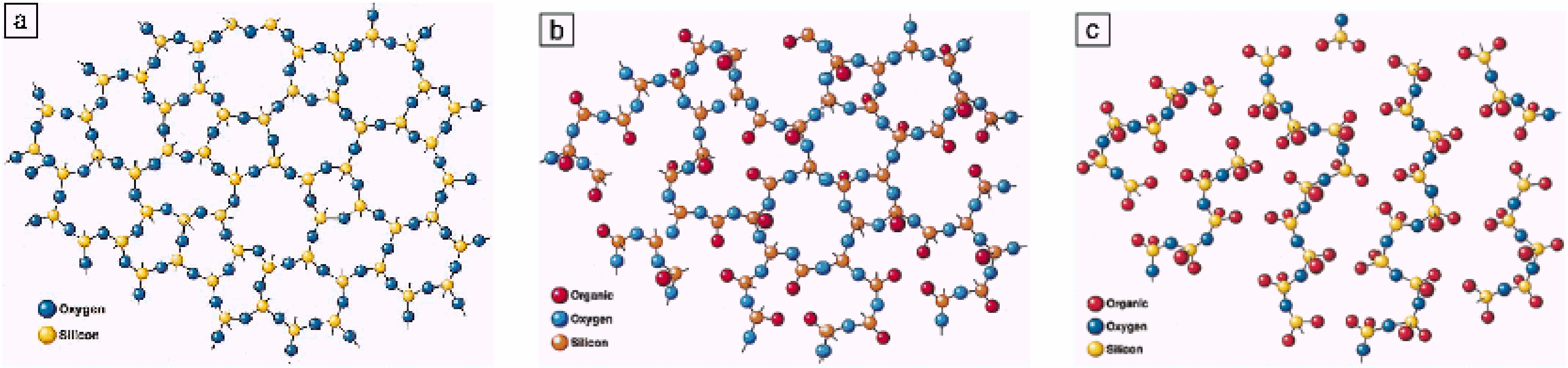
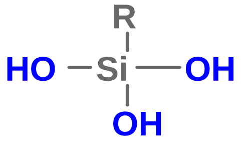
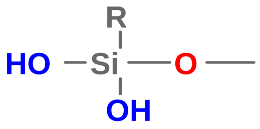
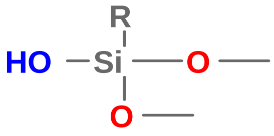
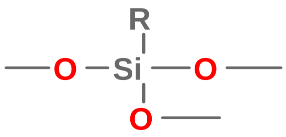


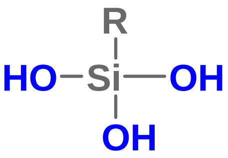
Figure 1. Hybrid organic–inorganic polymers can be visualized as successive organic substitutions of polyoxymetallates. (a) A “Q” structure, where four oxygen atoms are bound to a metal atom (silicon dioxide, or quartz in the example of silicon), gives rise to (b) a less rigid “T” resin when there is one organic substituent on each metal atom, and (c) linear “D” resins when there are two organic substituents on each metal atom (exemplified in the case of silicon by silicone oils).

Nomenclature II

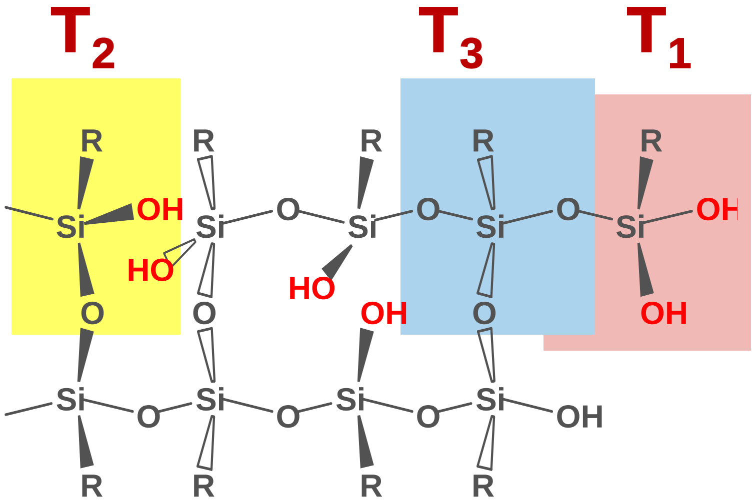
T : Tri-functional group
i : The number of oxygen bridging atoms (0~3)

Structure	Formula	Nomen-clature
 $HO-Si(R)(OH)-OH$	$RSi(OH)_3$	T_0
 $HO-Si(R)(OH)-O-$	$RSiO(OH)_2$	T_1
 $HO-Si(R)(O-)-O-$	$RSiO_2OH$	T_2
 $-O-Si(R)(O-)-O-$	$RSiO_{3/2}$	T_3

T_0

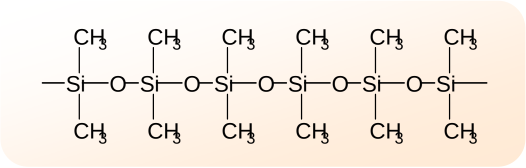


$HO-Si(R)(OH)-OH$

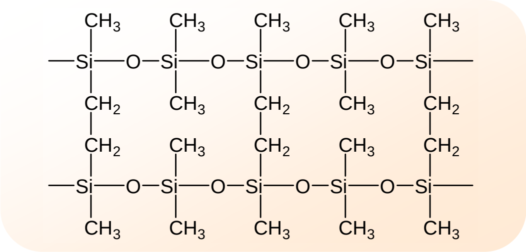


Various Silicone Structure

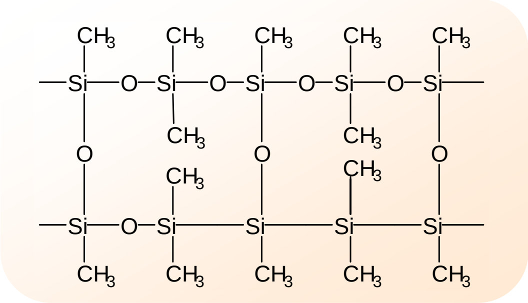
Silicone Oil

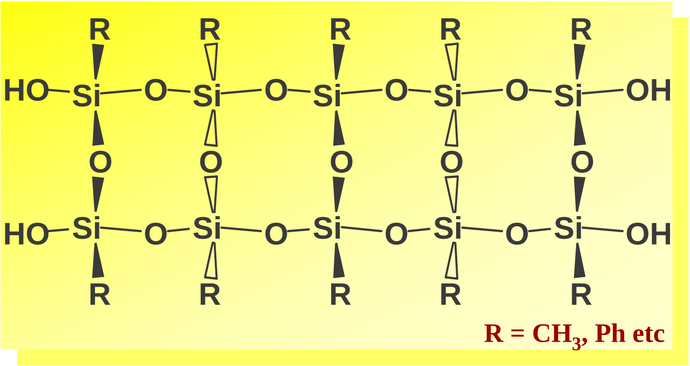


Silicone Rubber



Silicone resin

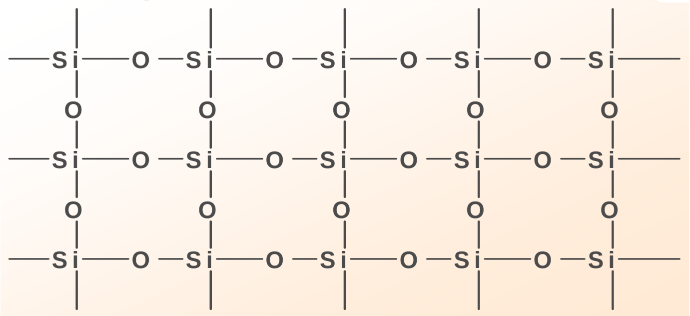




R = CH_3, Ph etc

Silicone Ladder Polymer
Polyorganosilsesquioxane (SSQ)

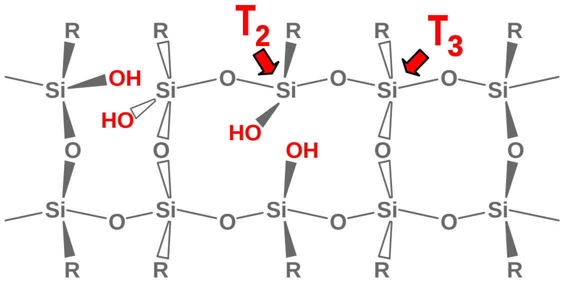
Silica glass



Functionality Control

Structures

- ⁎ Ladder-like Polymer
  or with defects structure
  or with random structure
- ⁎ Branched Ladder Polymer
- ⁎ Cured Ladder Polymer
- ⁎ Perfect Ladder Polymer



Pendant group

- ⁎ Methyl(Polymethylsilsesquioxane;PMSQ)
- ⁎ Phenyl(Polyphenylsilsesquioxane;PPSQ)
- ⁎ Protone(Polyhydrogensilsesquioxane;PHSQ)

Silicone modified organic polymer

- ⁎ Alkyl
- ⁎ Epoxy
- ⁎ Polyester
- ⁎ Phenol
- ⁎ Acrylic

Proposed applications:
Optics,adhesives,
abrasive resistant coating etc

Recent Publications

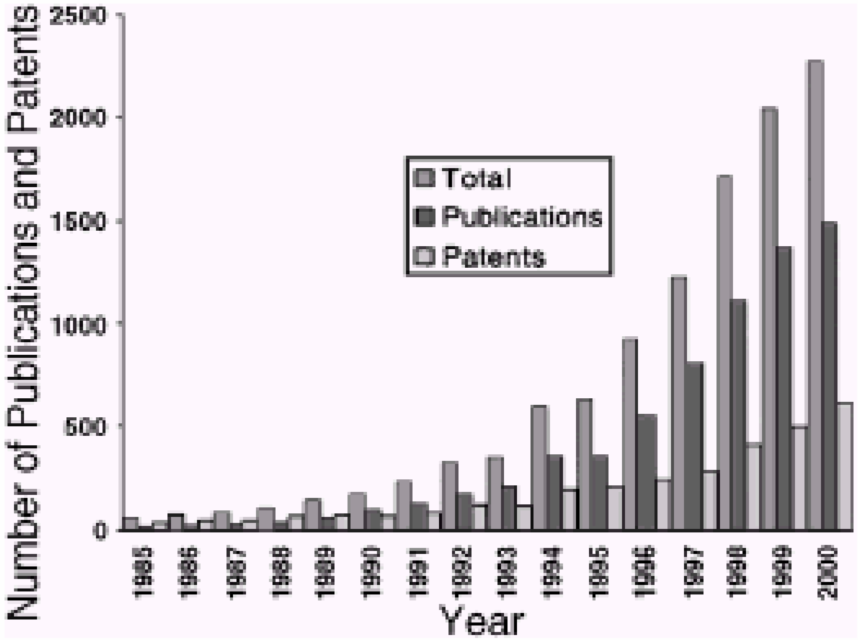
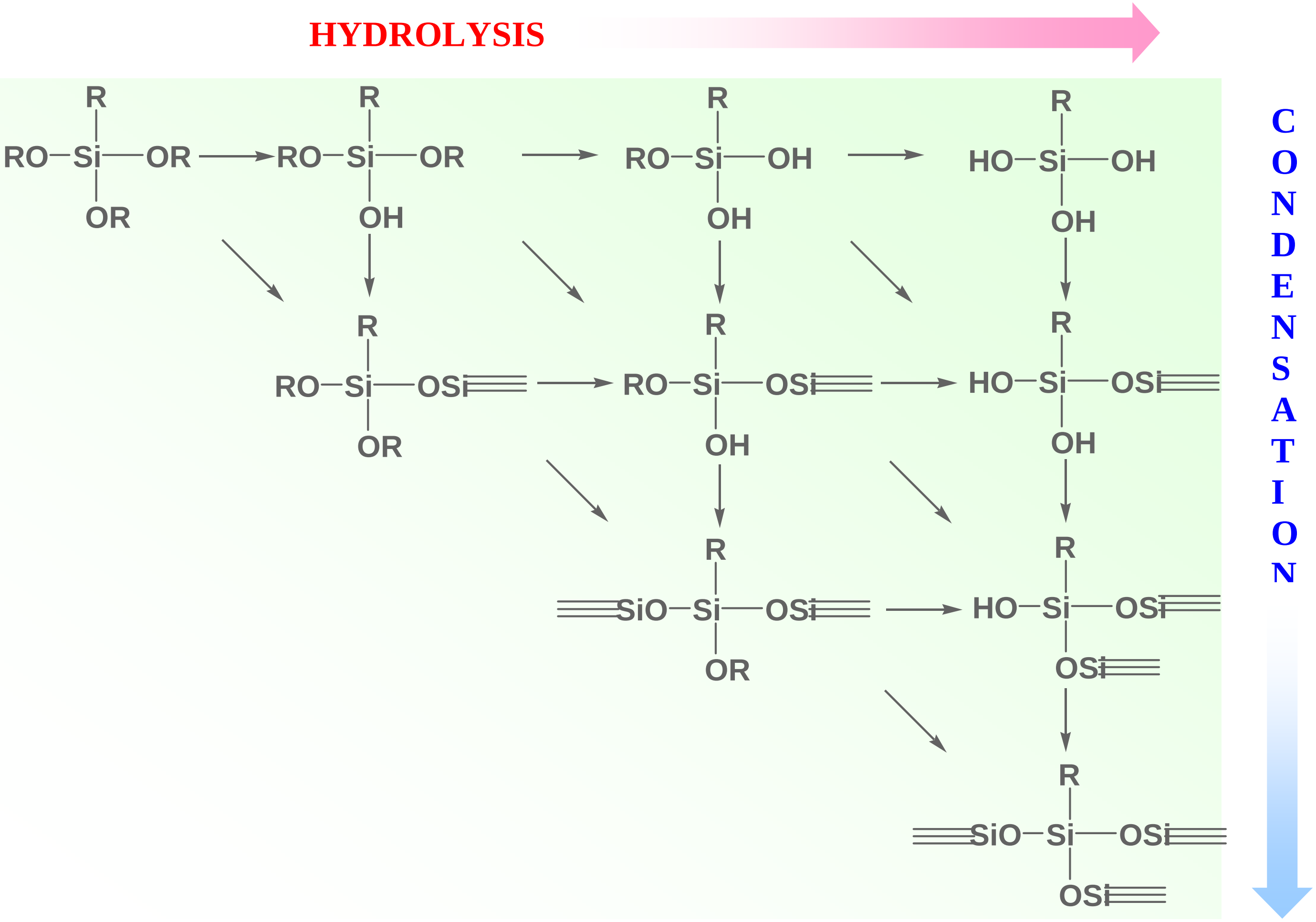
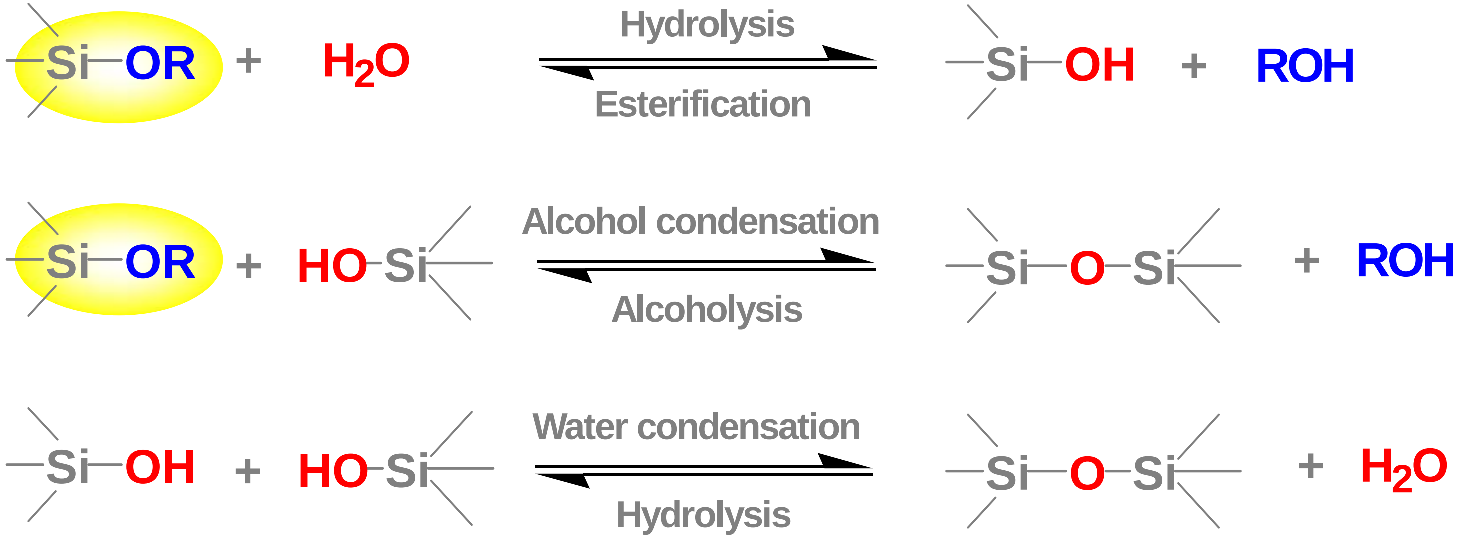


Figure 2. The number of publications and patents each year that include the term "hybrid organic–inorganic" or its synonyms in their abstracts or as key words.

Sol-Gel process



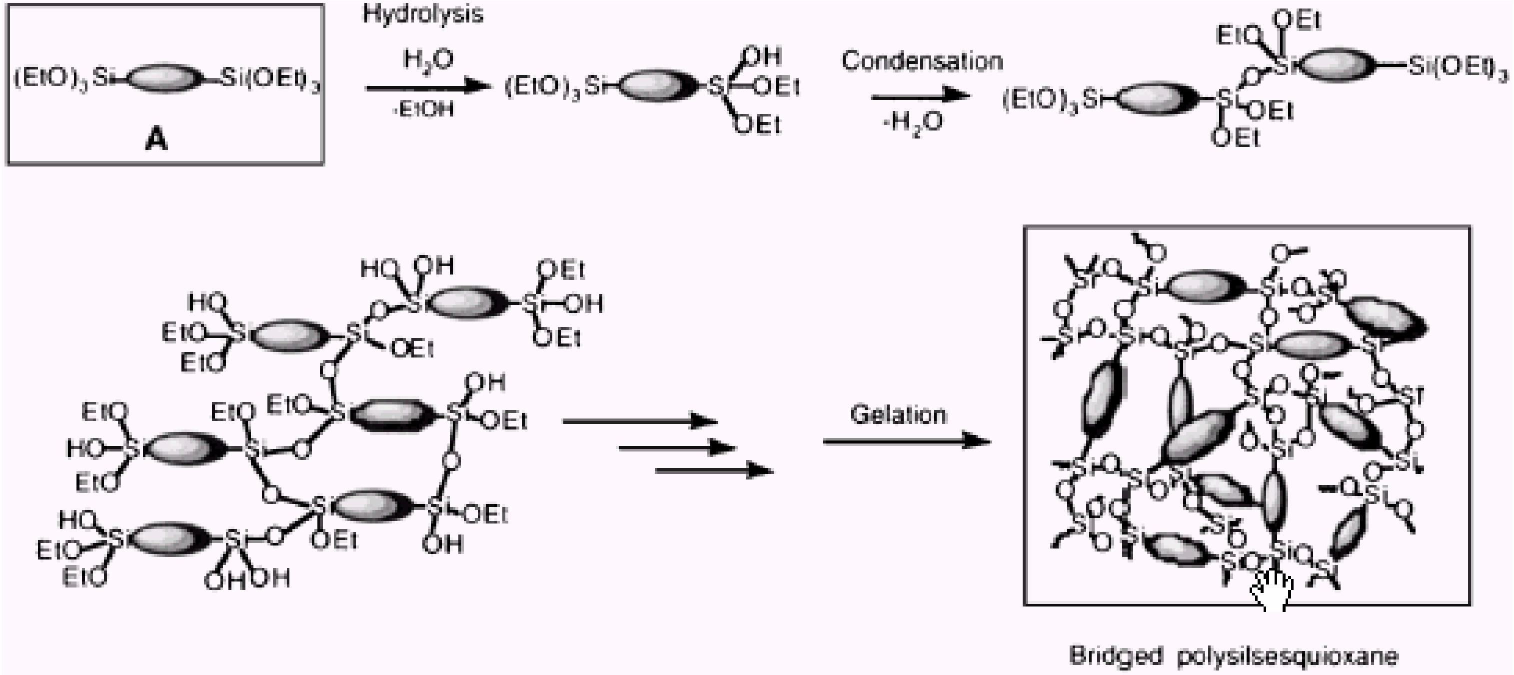
Sol-Gel process



- **Again condensation table place before the completion of hydrolysis**

Brinker and Scherer, “Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing”, Academic Press, San Diego (1990).

Homogeneous System



Scheme I. Formation of bridged polysilsesquioxanes by the hydrolysis and condensation of monomers with two or more trihalosilyl (not shown) or trialkoxysilyl groups attached to organic bridging groups.

Organic Functional Groups

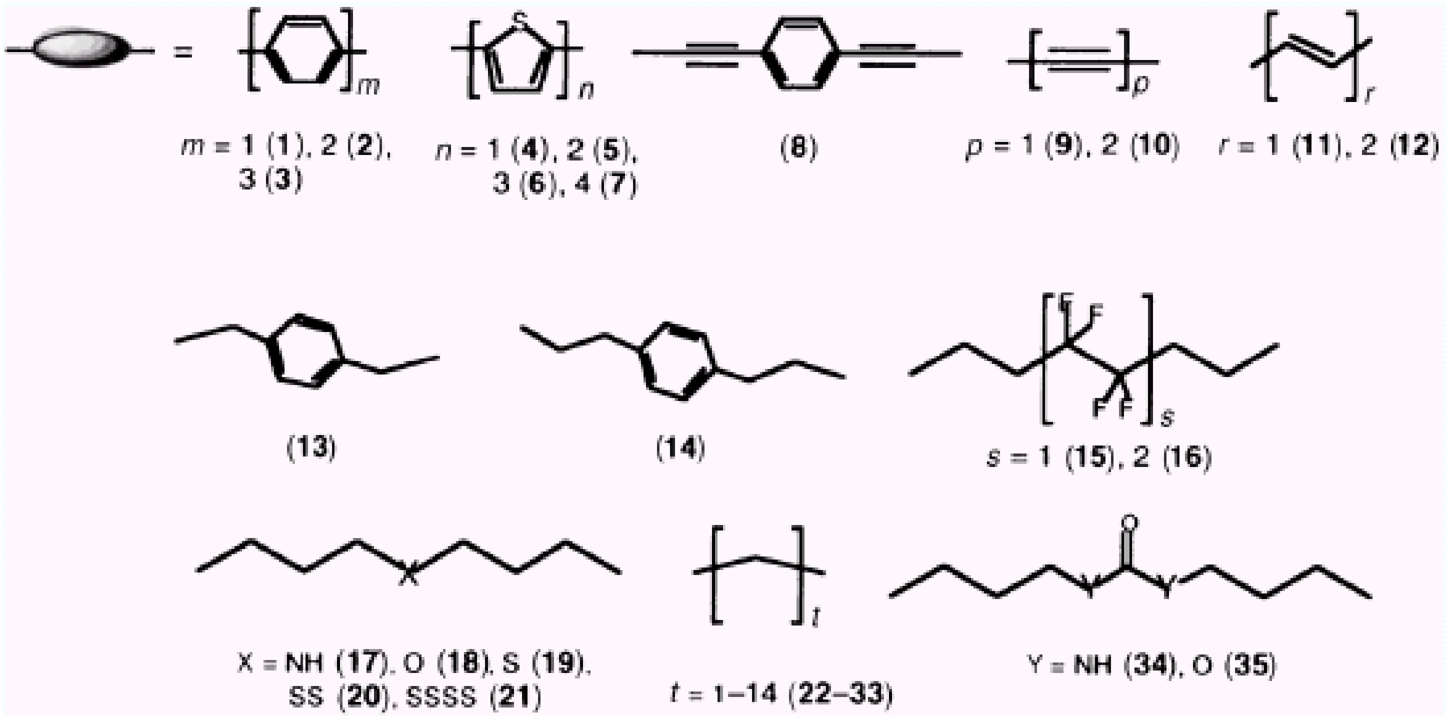


Chart 1. Bridging groups used in the synthesis of bridged polysilsesquioxanes.

Porosity Control

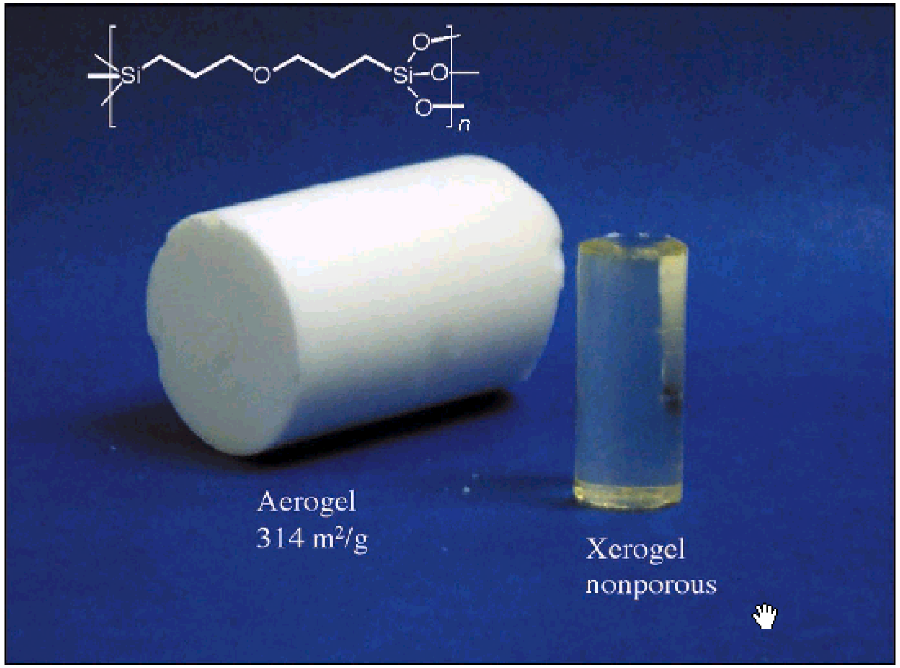


Figure 1. Dipropyl-ether-bridged polysils
acid-catalyzed sol-gel polymerization of
in EtOH with 2.4 M H_2O, 0.04 M HCl]. Th
supercritical carbon dioxide processing,
prepared by slow air-drying.

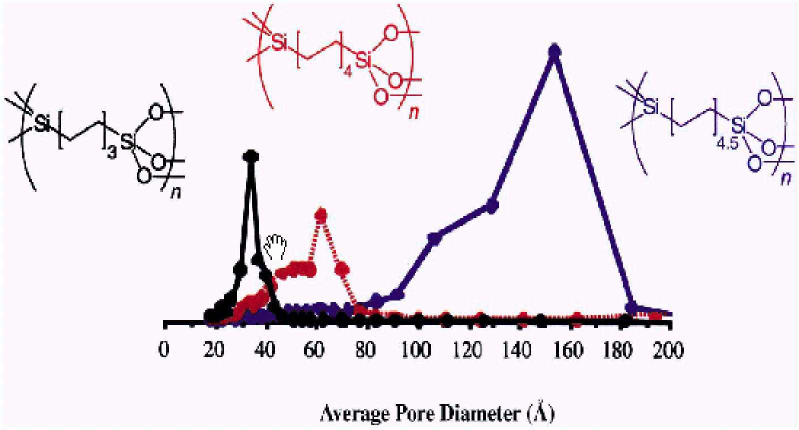


Figure 4. Change in pore-size distribution in alkylene-bridged polysilsesquioxane xerogels with increasing length of alkylene-bridging group.[17]

- **applications** : gas and liquid adsorbents, membranes, carriers for catalysts and enzymes, sensors, ion exchangers, enantiomer purification (molecular impression)…

Optical Property Control

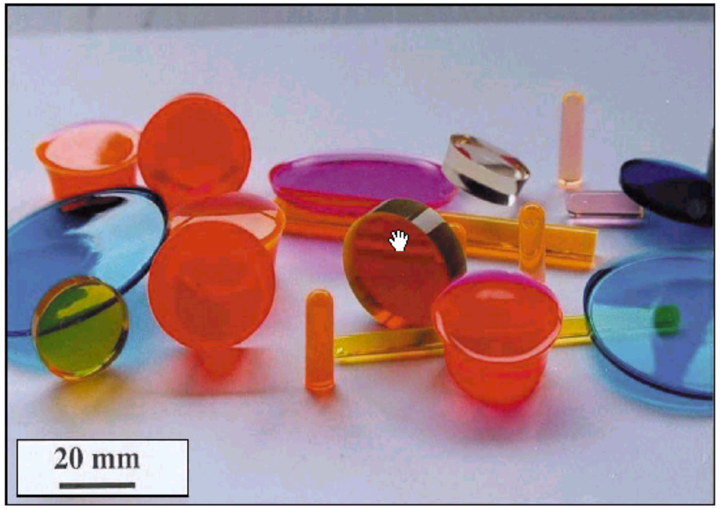


Figure 2. Hybrid organic–inorganic materials containing organic chromophores (courtesy of Dr. F. Chaput, École Polytechnique, Palaiseau).

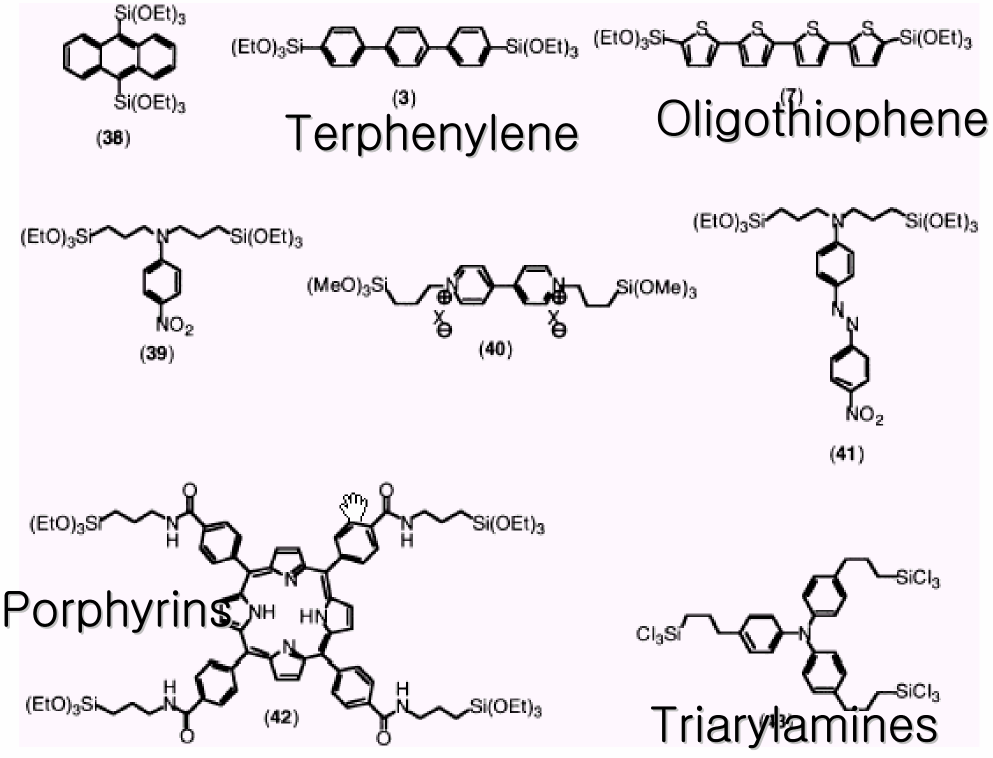


Chart 2. Bridged polysilsesquioxane monomers with chromophore bridging groups.

Mechanical Control

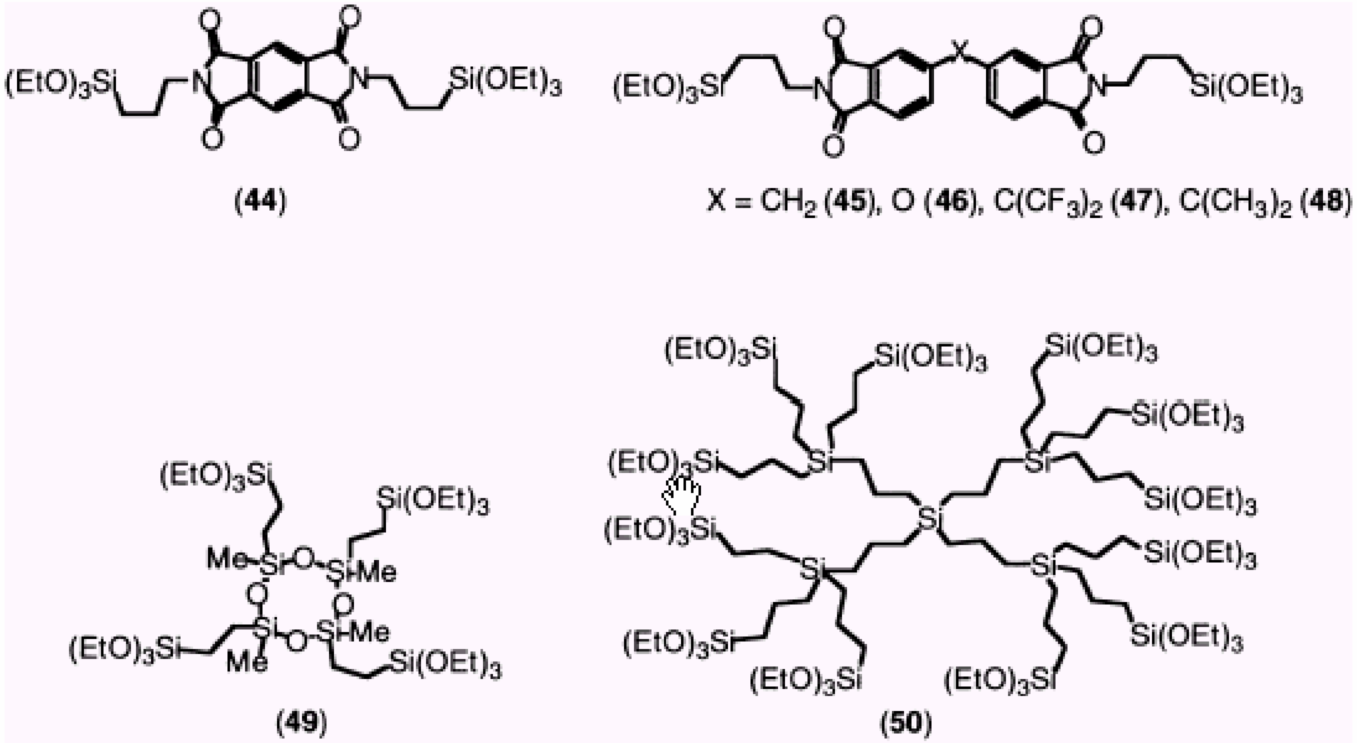


Chart 3. Arylimide-bridged monomers (**44–48**)[32] and monomers with dendritic bridging groups (**49, 50**).[34]

Metal bearing bridging group

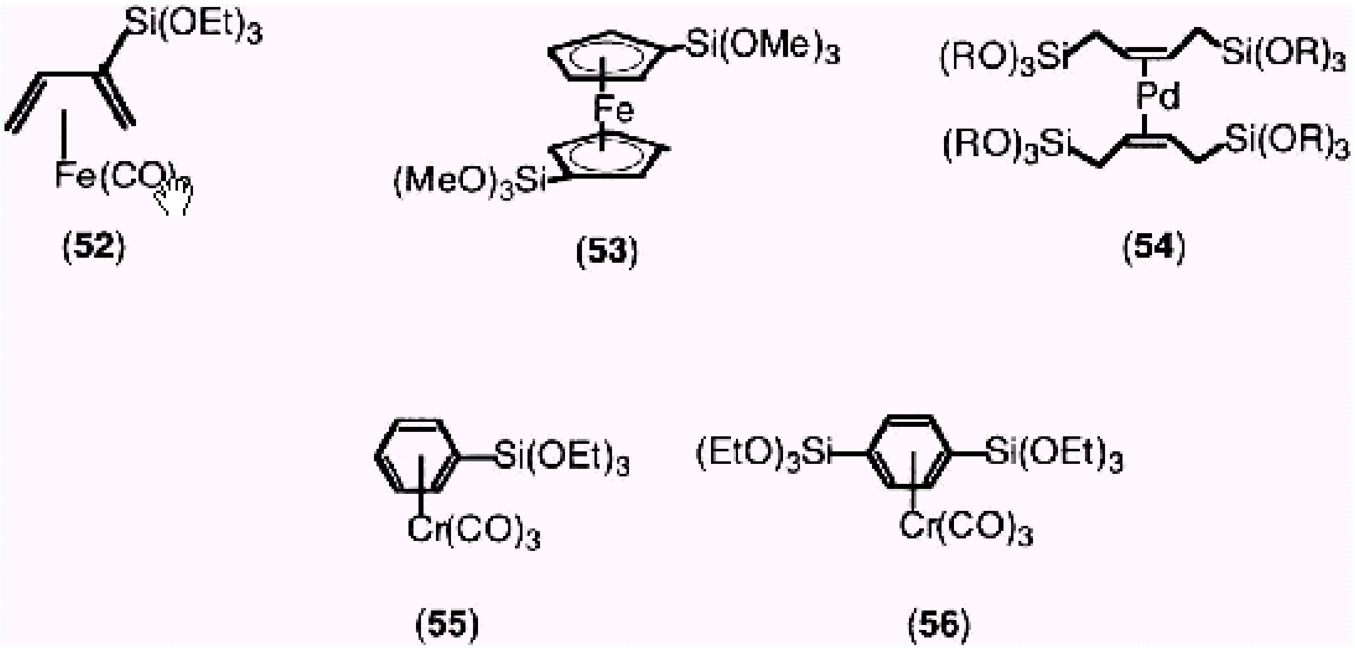
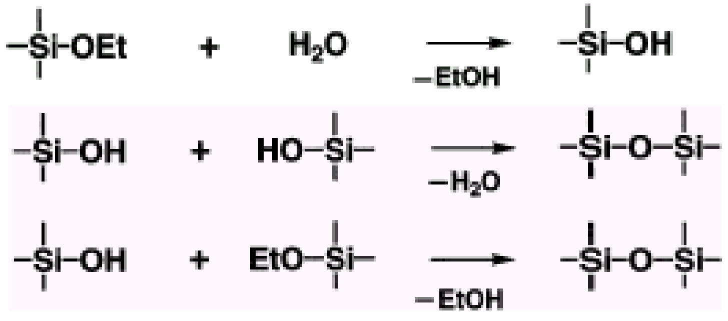
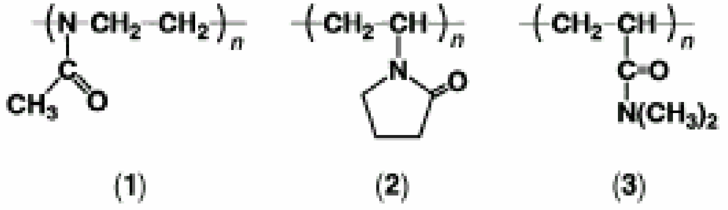


*Chart 4. Monomers with metal-bearing bridging groups. Monomers (**52**), (**53**), (**55**), and (**56**) are prepared and isolated before sol-gel processing; monomer (**54**) is thought to form* in situ *when the sol-gel is doped with palladium compounds.*

Heterogeneous System



Scheme I.



Structures **1**, **2**, *and* **3**.

- ◆ **Hydrogen bond Interaction**
- ◆ **π-π bond Interaction**
- ◆ **Ionic interaction**

POZO ; Poly(2-methyl-2-oxazoline)
PVP ; Poly(N-vinylpyrrolidone)
PDMAA; Poly(N,N-dimethylacrylamide)

Hydrogen Interaction

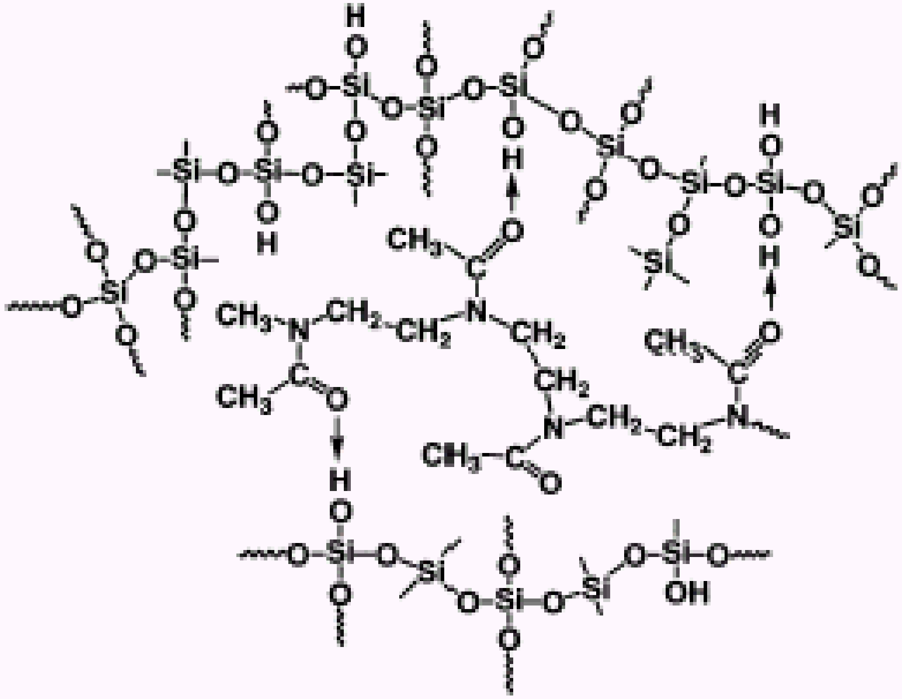
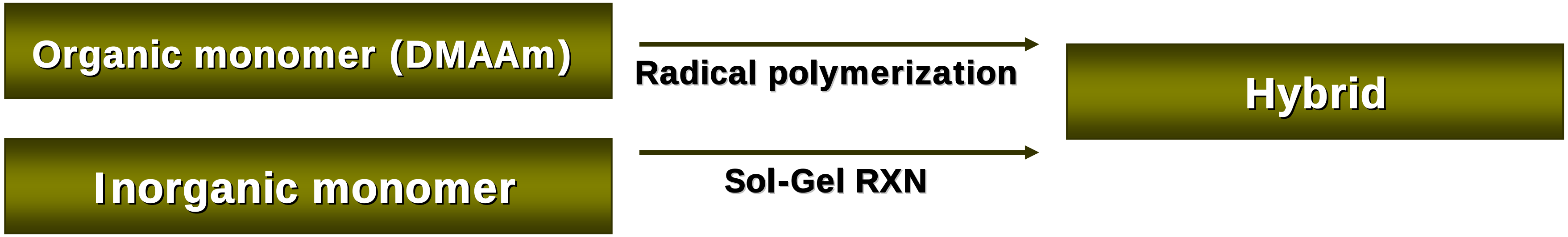


Figure 1. Schematic representation of hydrogen bonds in polymer hybrids.

Hybrid system

◆ **More homogenous system**


Organic monomer (DMAAm)

Radical polymerization

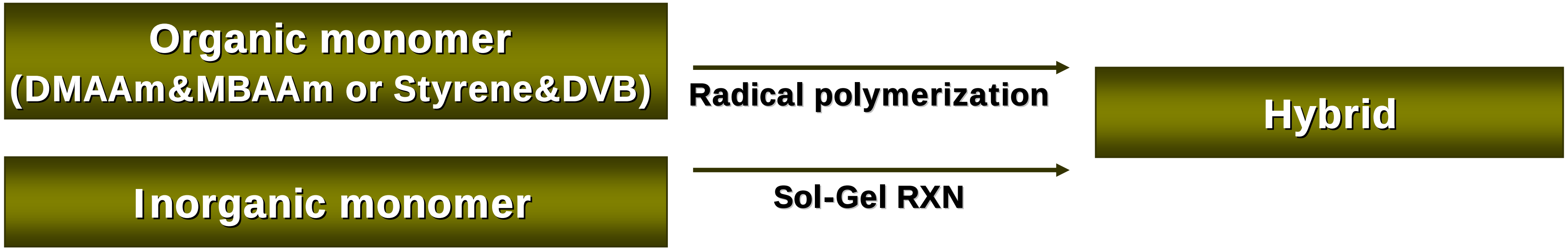
Inorganic monomer

Sol-Gel RXN

Hybrid

DMAAm; ($CH_2=CHCON(CH_3)_2$), MBAAm; ($(CH_2=CHCONH)_2CH_2$)

◆ **IPN system**


Organic monomer (DMAAm&MBAAm or Styrene&DVB)

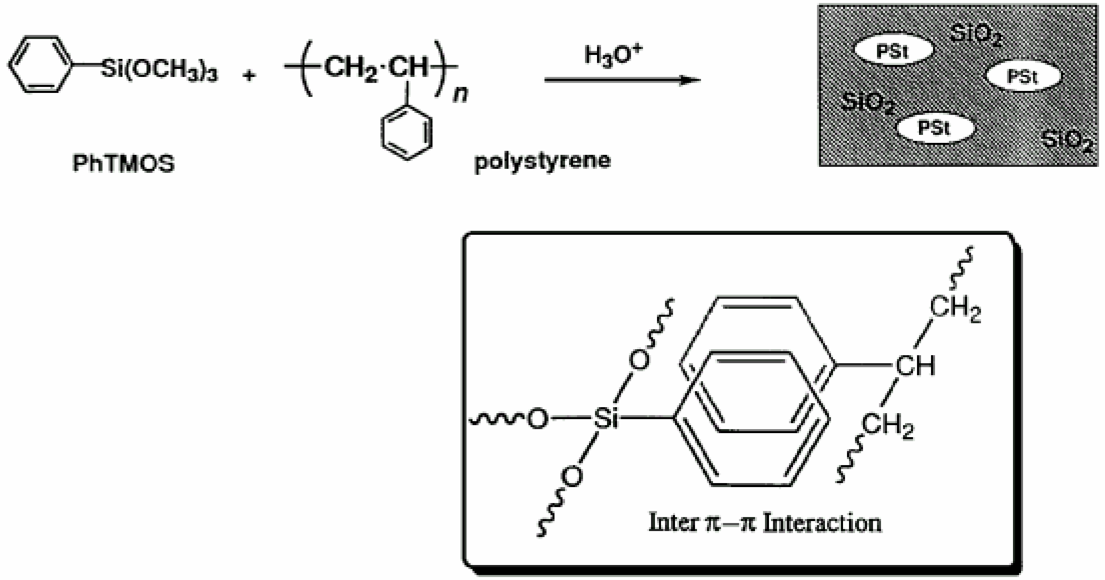
Radical polymerization

Inorganic monomer

Sol-Gel RXN

Hybrid

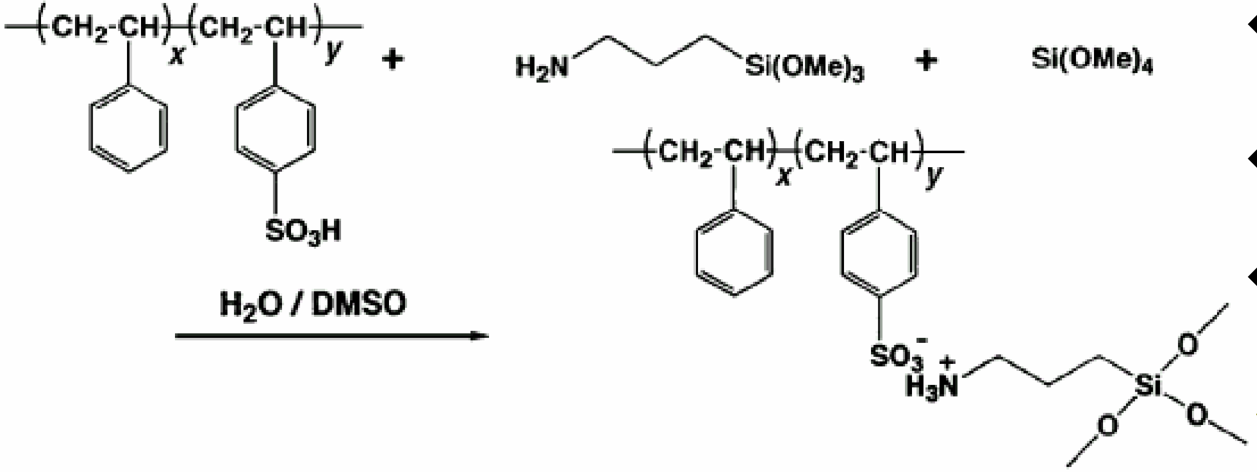
π-π bond Interaction



Scheme II.

- ◆ Hydrogen bond Interaction
- ◆ π－π bond Interaction
- ◆ Ionic interaction

Ionic interaction



Scheme III.

- ◆ Hydrogen bond Interac
- ◆ π−π bond Interaction
- ◆ Ionic interaction

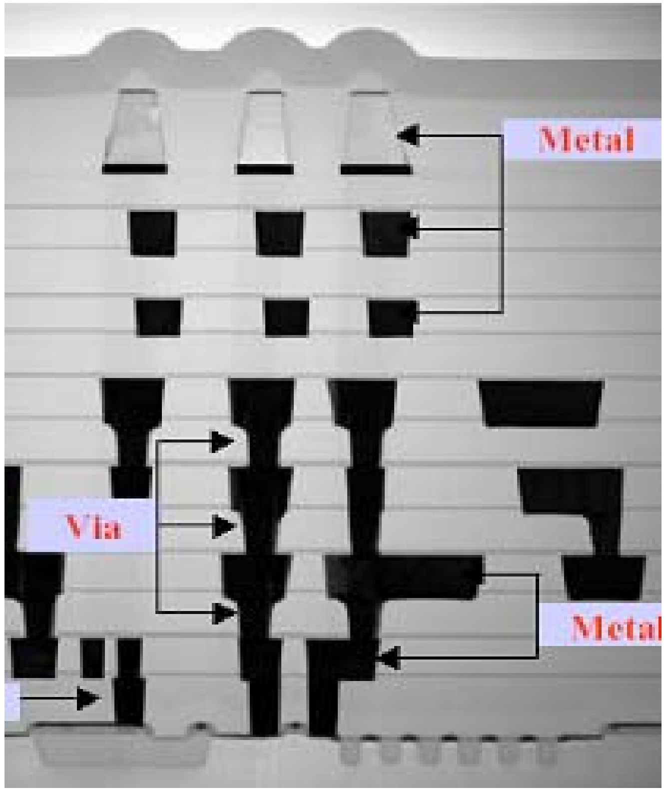
Semiconductor Insulating Materials

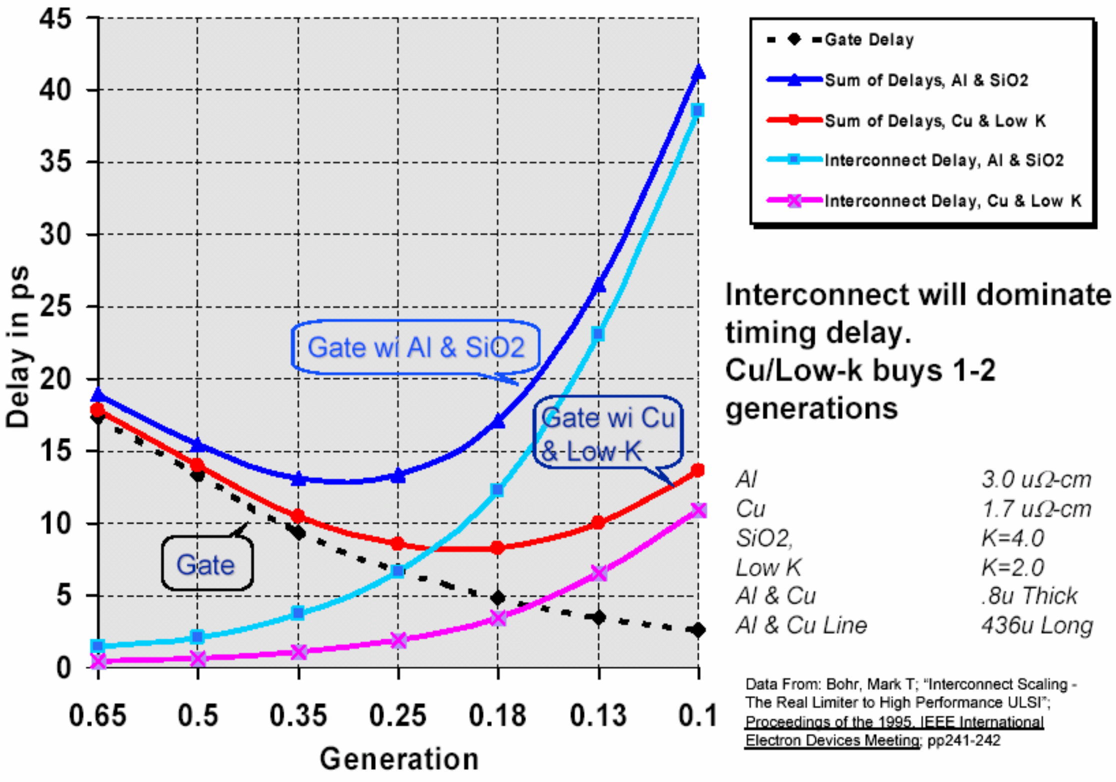
국립공주대학교
Kongju National University

Prof. Jin-Heong Yim

Semiconductor Insulating Materials

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





Interconnect will dominate timing delay.
Cu/Low-k buys 1-2 generations

Al	*3.0 uΩ-cm*
Cu	*1.7 uΩ-cm*
SiO2,	*K=4.0*
Low K	*K=2.0*
Al & Cu	*.8u Thick*
Al & Cu Line	*436u Long*

Data From: Bohr, Mark T; "Interconnect Scaling - The Real Limiter to High Performance ULSI"; Proceedings of the 1995 IEEE International Electron Devices Meeting; pp241-242

ITRS Roadmap

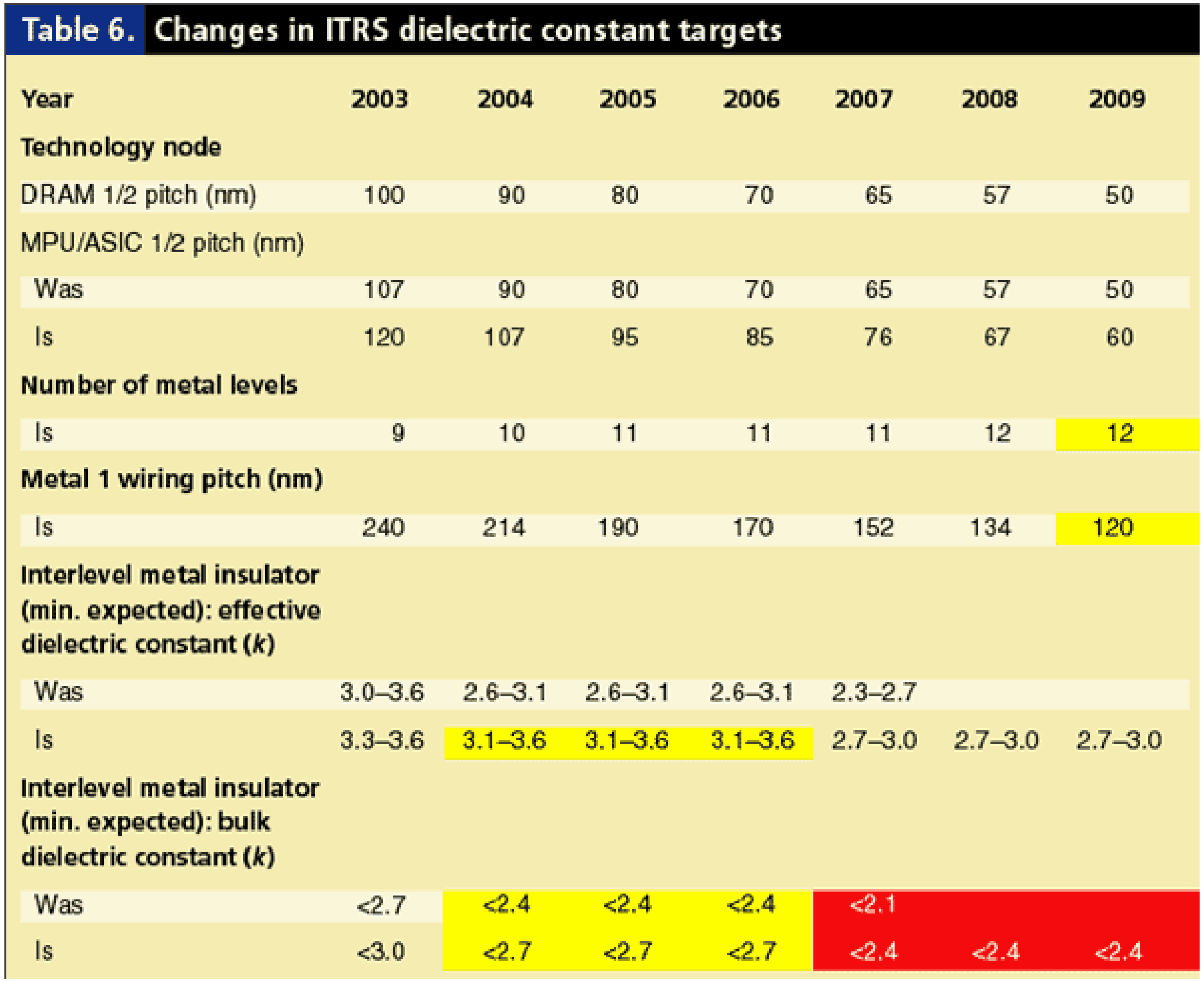
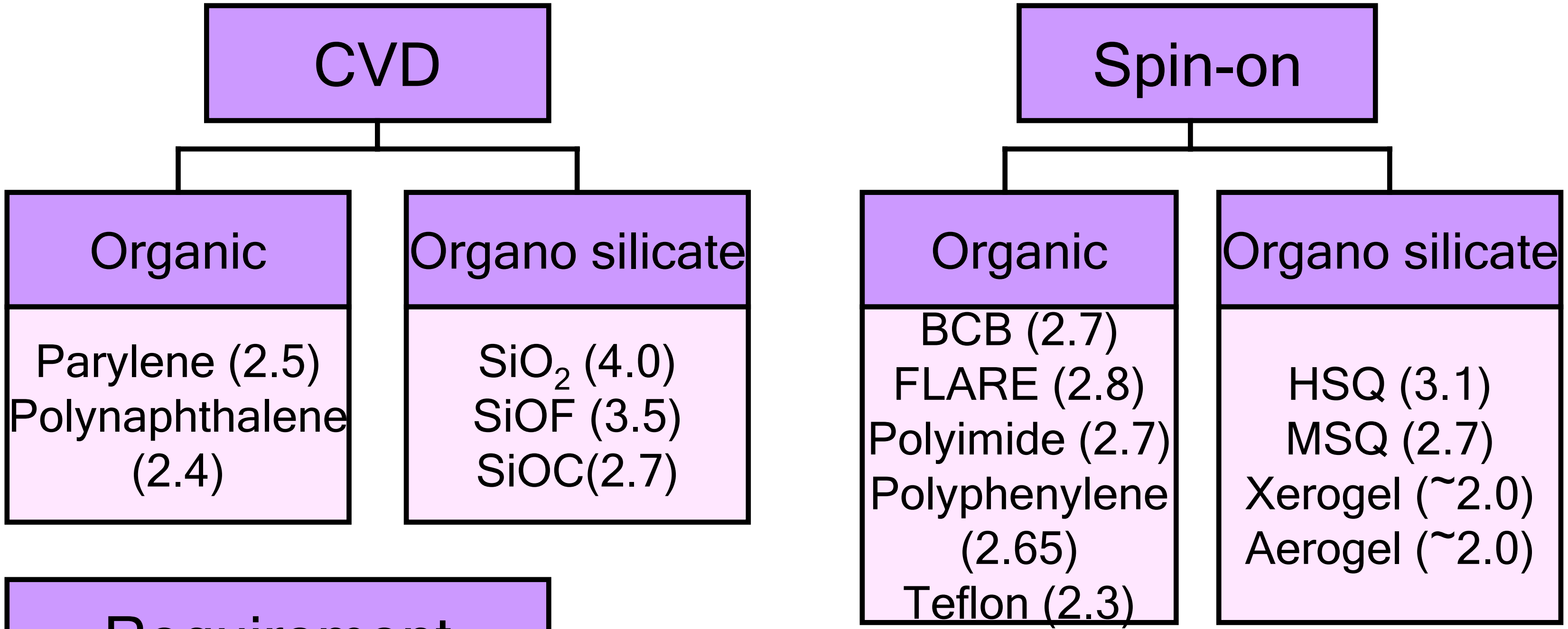


Table 6. Changes in ITRS dielectric constant targets

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

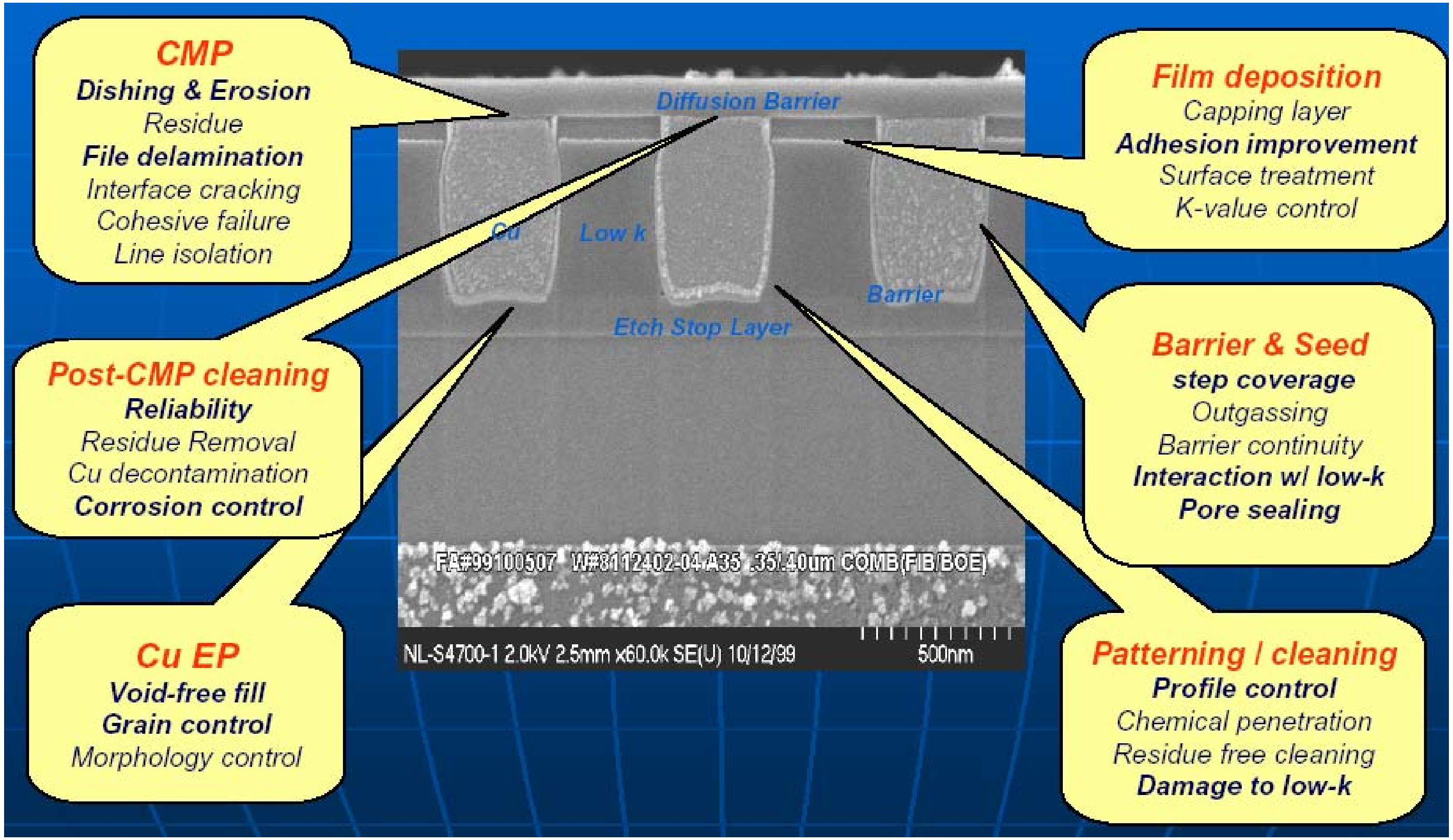


- CVD
  - Organic
    - Parylene (2.5)
    - Polynaphthalene (2.4)
  - Organo silicate
    - SiO_2 (4.0)
    - SiOF (3.5)
    - SiOC(2.7)
- Spin-on
  - Organic
    - BCB (2.7)
    - FLARE (2.8)
    - Polyimide (2.7)
    - Polyphenylene (2.65)
    - Teflon (2.3)
  - Organo silicate
    - HSQ (3.1)
  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

Requirement

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

Intergration Issues



CMP
Dishing & Erosion
Residue
File delamination
Interface cracking
Cohesive failure
Line isolation

Post-CMP cleaning
Reliability
Residue Removal
Cu decontamination
Corrosion control

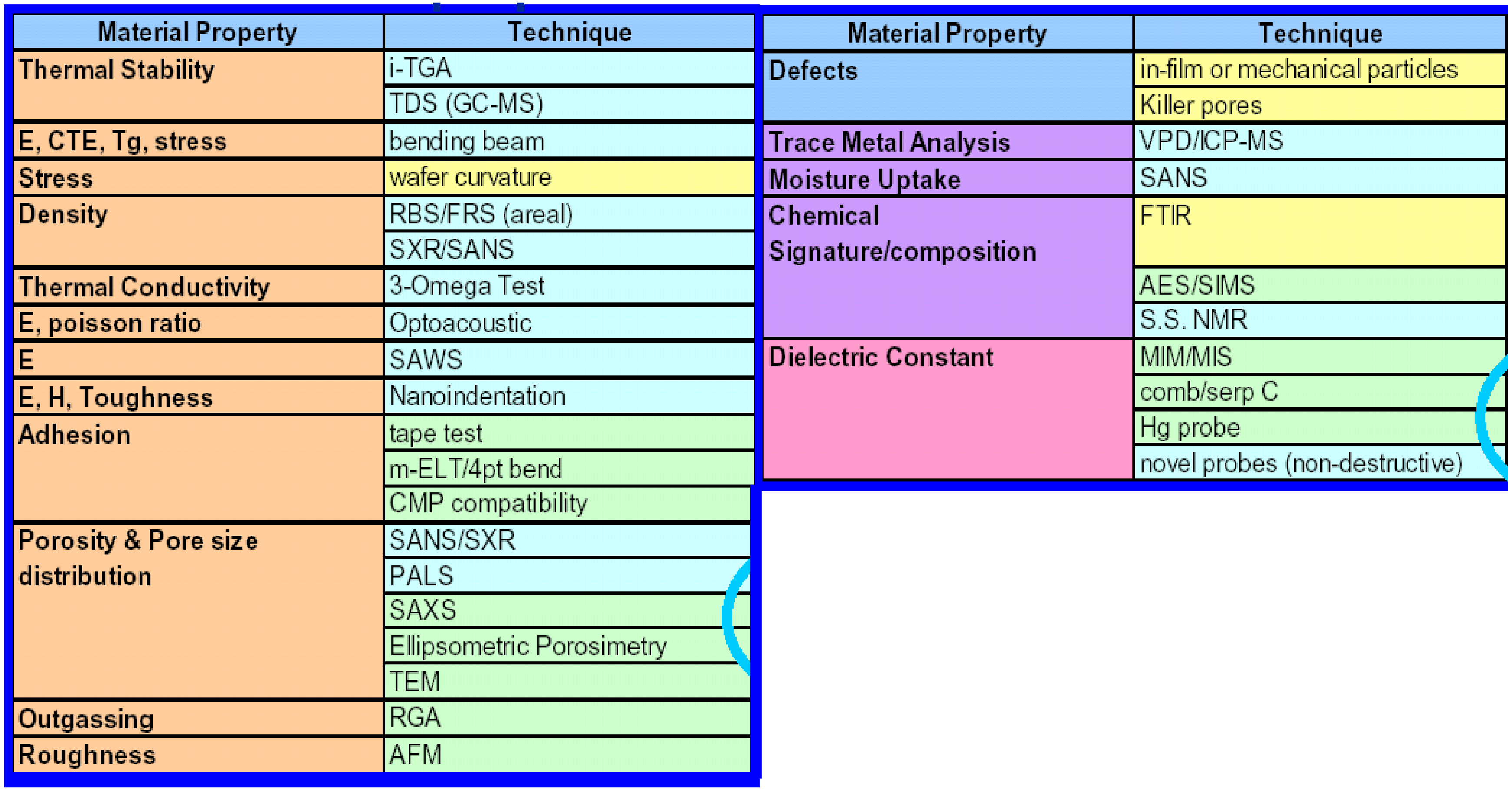
Cu EP
Void-free fill
Grain control
Morphology control

Film deposition
Capping layer
Adhesion improvement
Surface treatment
K-value control

Barrier & Seed
step coverage
Outgassing
Barrier continuity
Interaction w/ low-k
Pore sealing

Patterning / cleaning
Profile control
Chemical penetration
Residue free cleaning
Damage to low-k

Considering Parameters



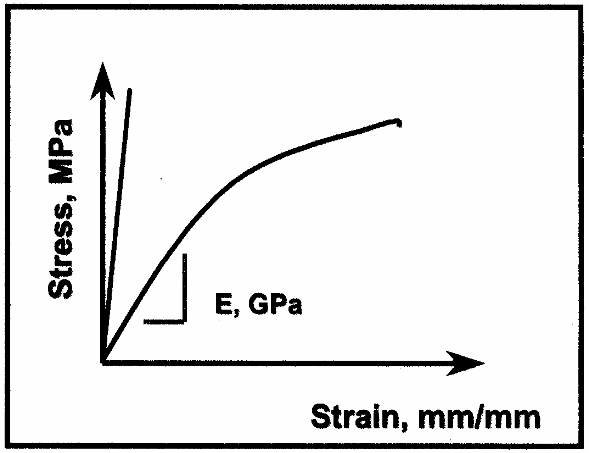
Material Property	Technique
Thermal Stability	i-TGA
	TDS (GC-MS)
E, CTE, Tg, stress	bending beam
Stress	wafer curvature
Density	RBS/FRS (areal)
	SXR/SANS
Thermal Conductivity	3-Omega Test
E, poisson ratio	Optoacoustic
E	SAWS
E, H, Toughness	Nanoindentation
Adhesion	tape test
	m-ELT/4pt bend
	CMP compatibility
Porosity & Pore size distribution	SANS/SXR
	PALS
	SAXS
	Ellipsometric Porosimetry
	TEM
Outgassing	RGA
Roughness	AFM

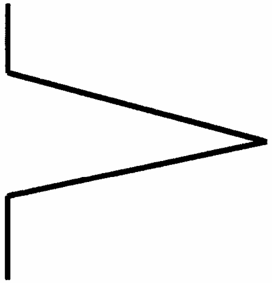
Material Property	Technique
Defects	in-film or mechanical particles
	Killer pores
Trace Metal Analysis	VPD/ICP-MS
Moisture Uptake	SANS
Chemical Signature/composition	FTIR
	AES/SIMS
	S.S. NMR
Dielectric Constant	MIM/MIS
	comb/serp C
	Hg probe
	novel probes (non-destructive)

Mechanical Properties

Measures of Mechanical Integrity

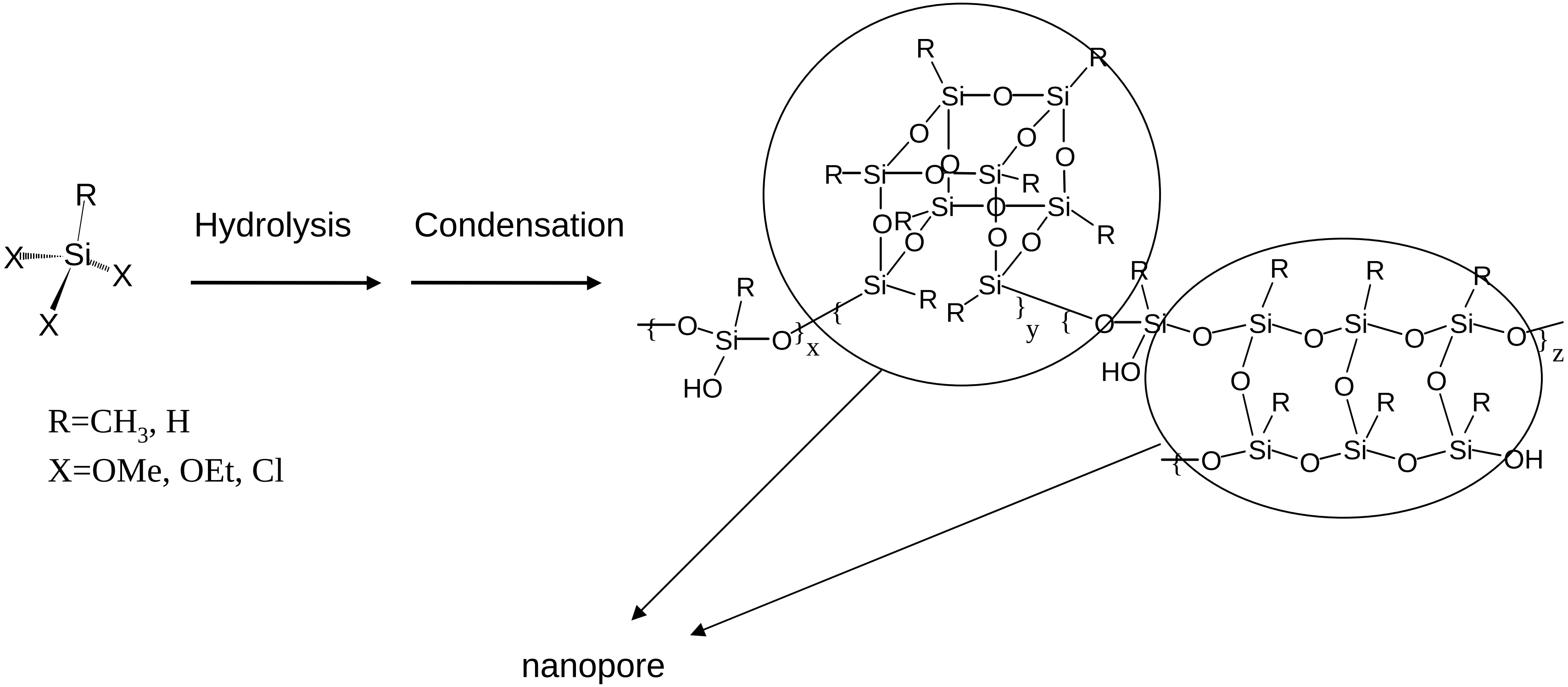
- **Young's Modulus**
  - Stiffness of the material
  - resistance to deformation
- **Strength**
  - Continuum approach
  - Compare to max. principal stress
- **Strain to failure or yield**
  - Maximum elongation
- **Hardness**
  - Function of modulus and strength
- **Toughness**
  - Resistance to crack initiation and propagation





Typical SSQ Polymer

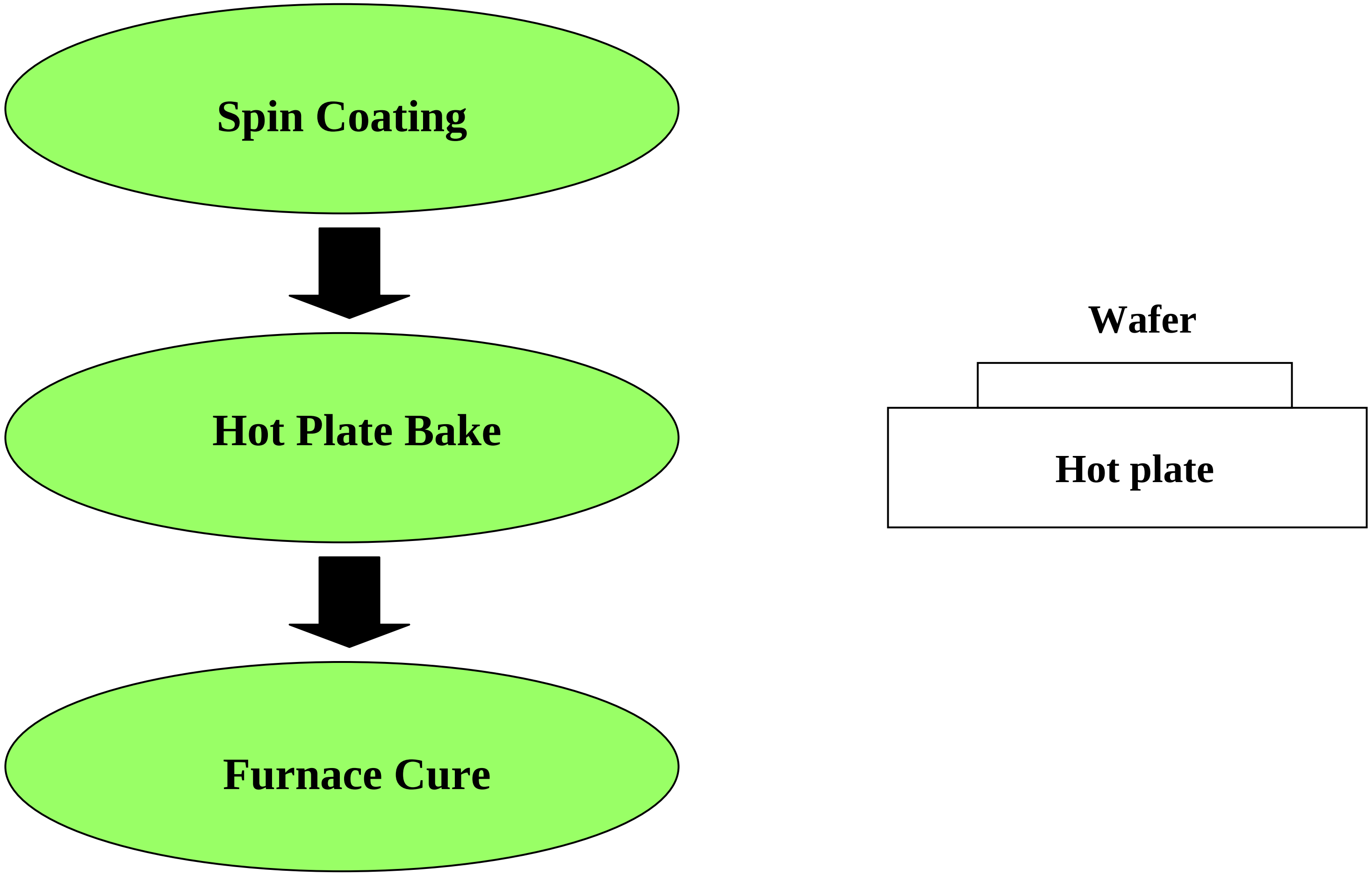
: as a precursor for sol-gel-drived polymer thin film



R=CH_3, H

X=OMe, OEt, Cl

Spin Coating Process



Spin Coating

↓

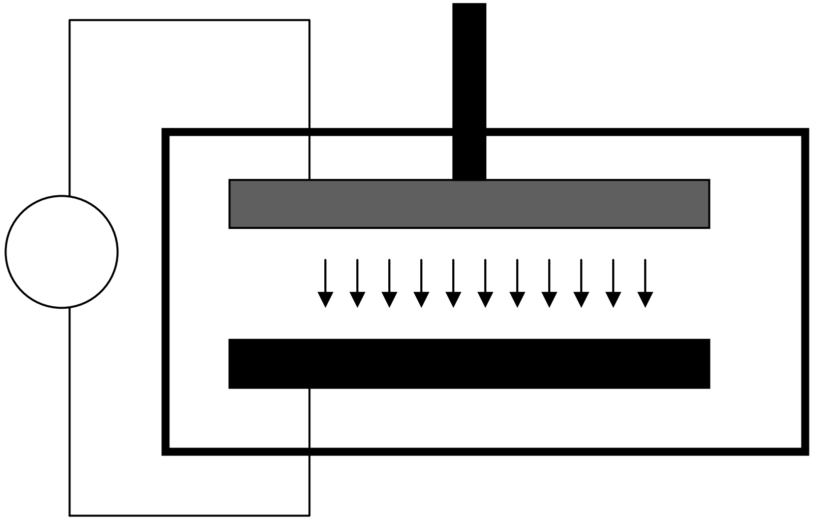
Hot Plate Bake

↓

Furnace Cure

CVD Deposition

Conventional (plasma type)



TEOS + CF4 ---> FSG

Sol-Gel Process (Aerogel, Xerogel)

Spin -coat (Sol)

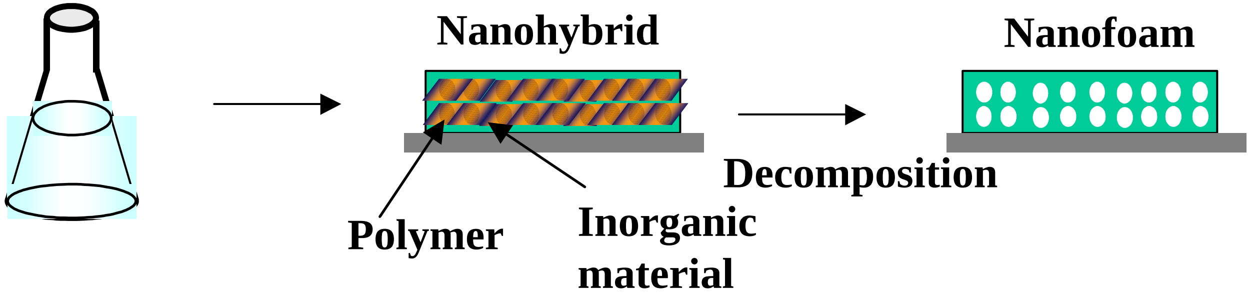
↓ **Aging**

Wet (Sol)

↓ **Drying**

Dried Film

Porogen-templated Approach



Nanohybrid

Nanofoam

Decomposition

Polymer

Inorganic material

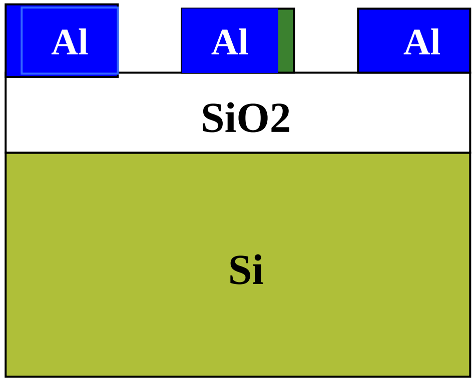
(as porogen) (as matrix)

$$\mathbf{k_{effective} = V_{matrix} \times k_{matrix} + V_{air} \times k_{air}\ (=1.0)}$$

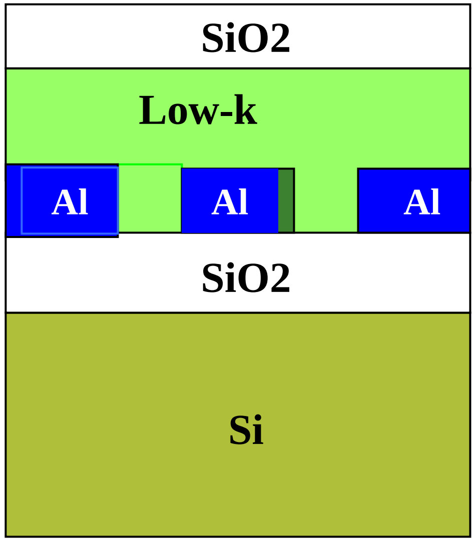
Porogen = Pore Generating Material

Integration Scheme : Al 배선 공정

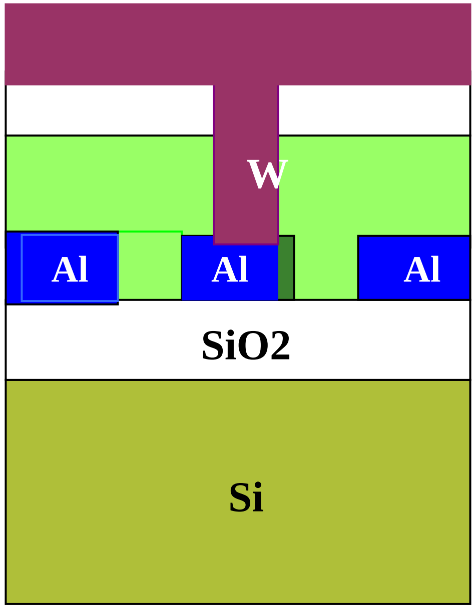
- Deposit Al
- Anneal Al
- Pattern Al



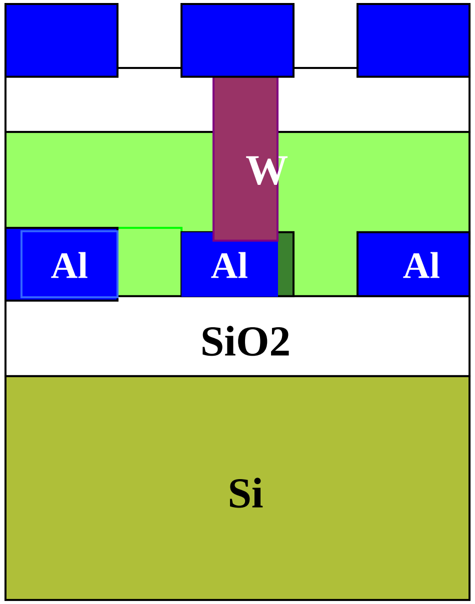
- Deposit & Cure Low-k
- Deposit cap



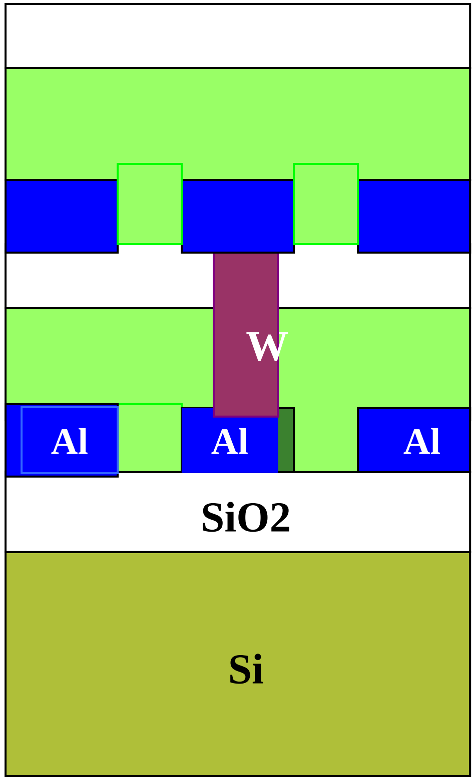
- Pattern Via
- Deposit W



Integration Scheme : Al 배선 공정



- CMP W
- Deposit Al
- Al anneal (>400 C)
- Pattern line



- Deposit and Cure Low-k
- Deposit Cap

Problems vs.Requirements

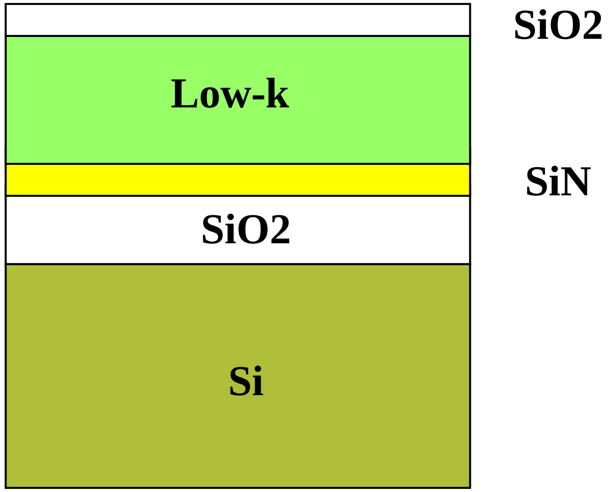
Problems	Property Requirements
- Inadequate gapfill	- Good gapfill Properties
- Cracking after thermal cycling	- Good thermal Stability/Good Crack resistance
- Delamination	- Good Adhesion/small CTE mismatch
- Deformation of low-k layer with compressive capping layers	- Good mechanical Strength/High Tg
- Outgassed Via	- Little outgassing

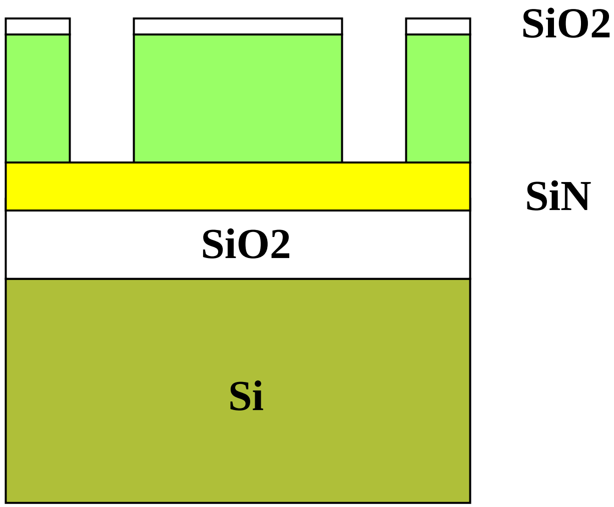
Integration Scheme : Damascene 공정

1. Deposit

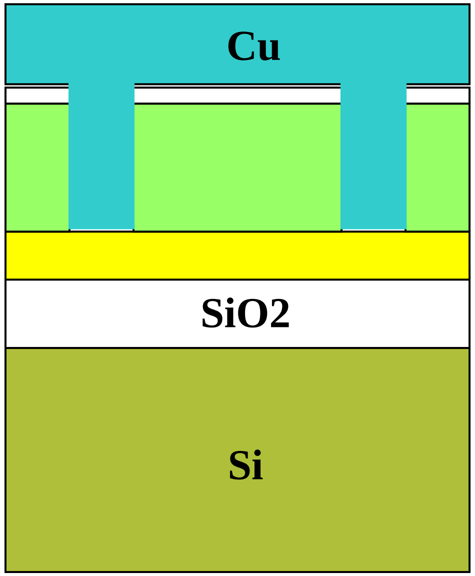
2. Deposit Cap

3. Pattern and etch low-k





Integration Scheme : Damascene 공정



4. Deposit barrier

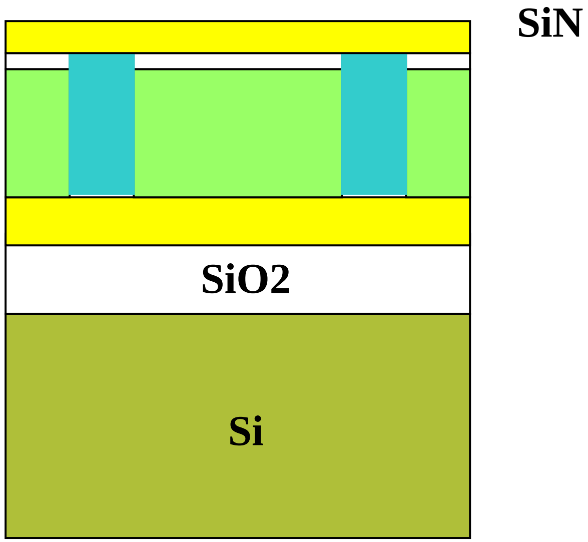
5. Deposit Cu Seed

6. Electroplated Cu

7. Cu anneal (250-350 C)

8. CMP

9. Deposit Cap



Problems vs.Requirements

Problems

-Delamination

- Etch Selectivity to Photoresist / PR strip / wet Cleans

- Outgassed in via

- Mechanical strength

- Dry etch issue in some low-k

Property Requirements

- No Gapfill needed

- Good thermal Stability

- Good Adhesion / small CTE mismatch

- Good mechanical Strength / High Tg

- Little outgassing

- Good crack resistance

Material Structure-Property Relationships

- Bond polarizability affect the dielectric constant and thermal stability

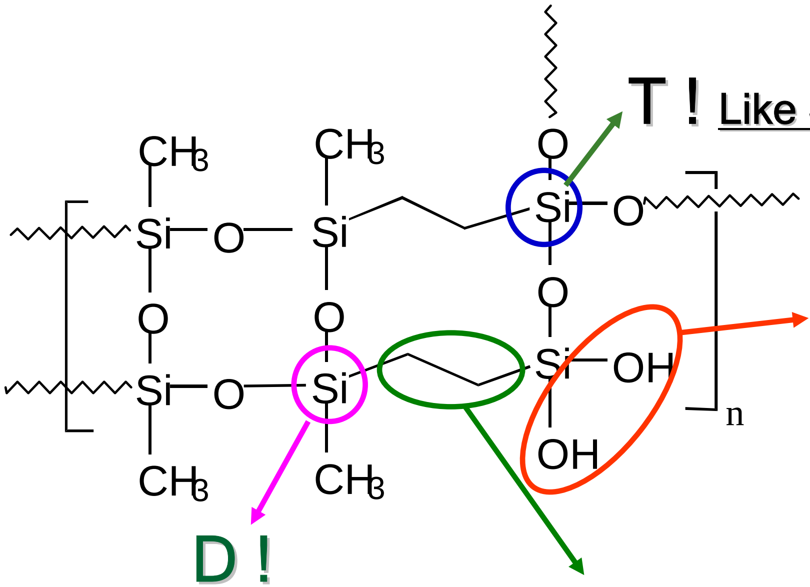
Bond	Polarizability (Å^3)	Bond Energy (kcal/mol)
C-C	0.531	83
C-F	0.555	116
C=O	1.020	176
C=C	1.643	146

- C-F bonds lower k.

  C=O and C=C bonds improve thermal stability, but both increases k.

- O-H bonds increase k, and faciliate moisture uptake which also increases k.

Example of SSQ precursor



T ! Like Silsesquioxane (Stability)

Si-OH group !

Compatibility with porogen
moisture absorption
Cross-Linking
Good Mechanical Properties

D !

As an Elastomer
(Increase Toughness & Modulus)

Alkyl bridge !

Increase molecular porosity (decrease k)
Good mechanical properties