Wrocław University of Technology

Advanced microporous functional layer materials with extremely low dielectric constant

Mirosław Miller

Wrocław University of Technology, Poland

Collaboration

Katarzyna Broczkowska

Justyna Krzak-Roś

Wrocław University of Technology, Poland

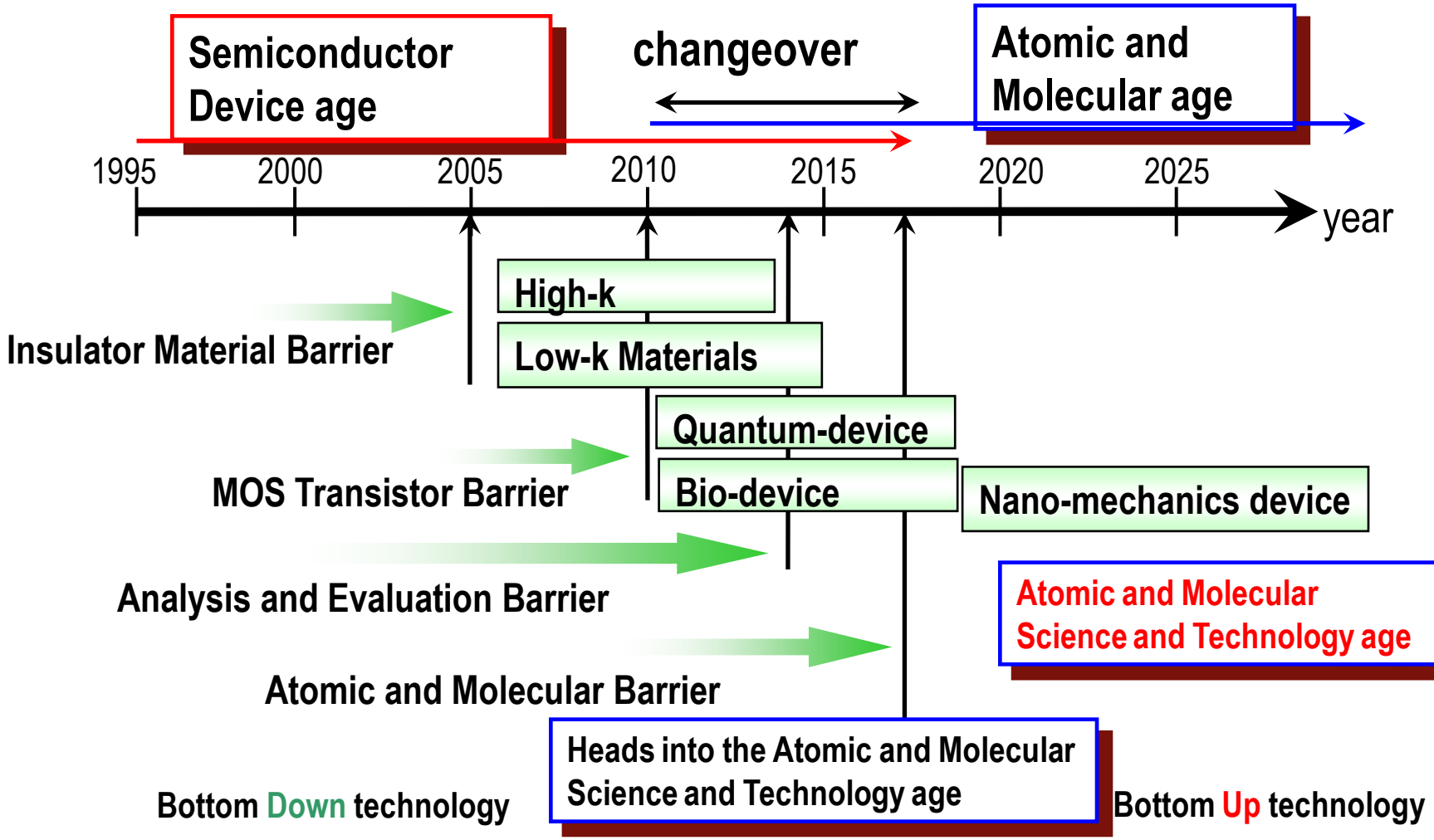
Adam Urbanowicz

IMEC, Bruxelles, Belgium

Outline

- **Why low-k materials ?**
- Materials in use after SiO_2
- Challenges in low-k technology
- Sol-gel method for porous thin layers
- Looking for breakthrough materials

Barriers for the micro-processing in the semiconductors



Interconnect delay of key importance

Al / SiO_2 → Cu / low-k

- Shrinking cross-section of wire: increase of resistance
- Bringing wires closer: increase of capacitance

Result: RC delay increase

Cu/low-k system for 32 nm technology

Strategy for reducing k-value of dielectrics

Decreased polarizability

- less polar bonds (Si-C, Si-F, C-C, C-H)

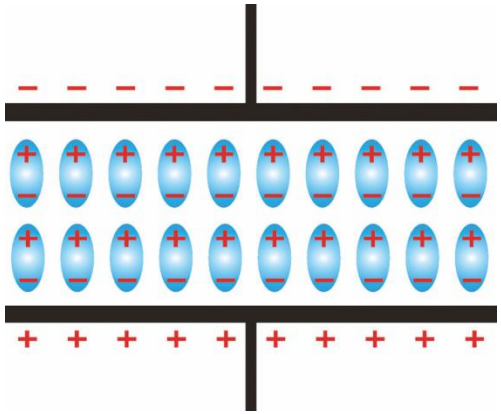
Decreased density

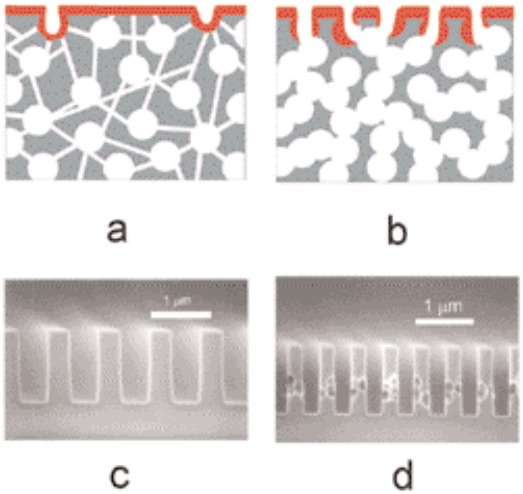
- constitutive porosity
- self-organized free volume

Subtractive porosity

- selectively removed material

New generation of materials





Outline

- Why low-k materials ?
- **Materials considered after SiO_2**
- Challenges in low-k technology
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Classification of low-k materials

Silica-based:

- Flourinated silicate glass SiOF (FSG)
- Organosilicate glass SiOCH (OSG)

Silsesquioxanes (organic-inorganic polymers R-$SiO_{3/2}$)

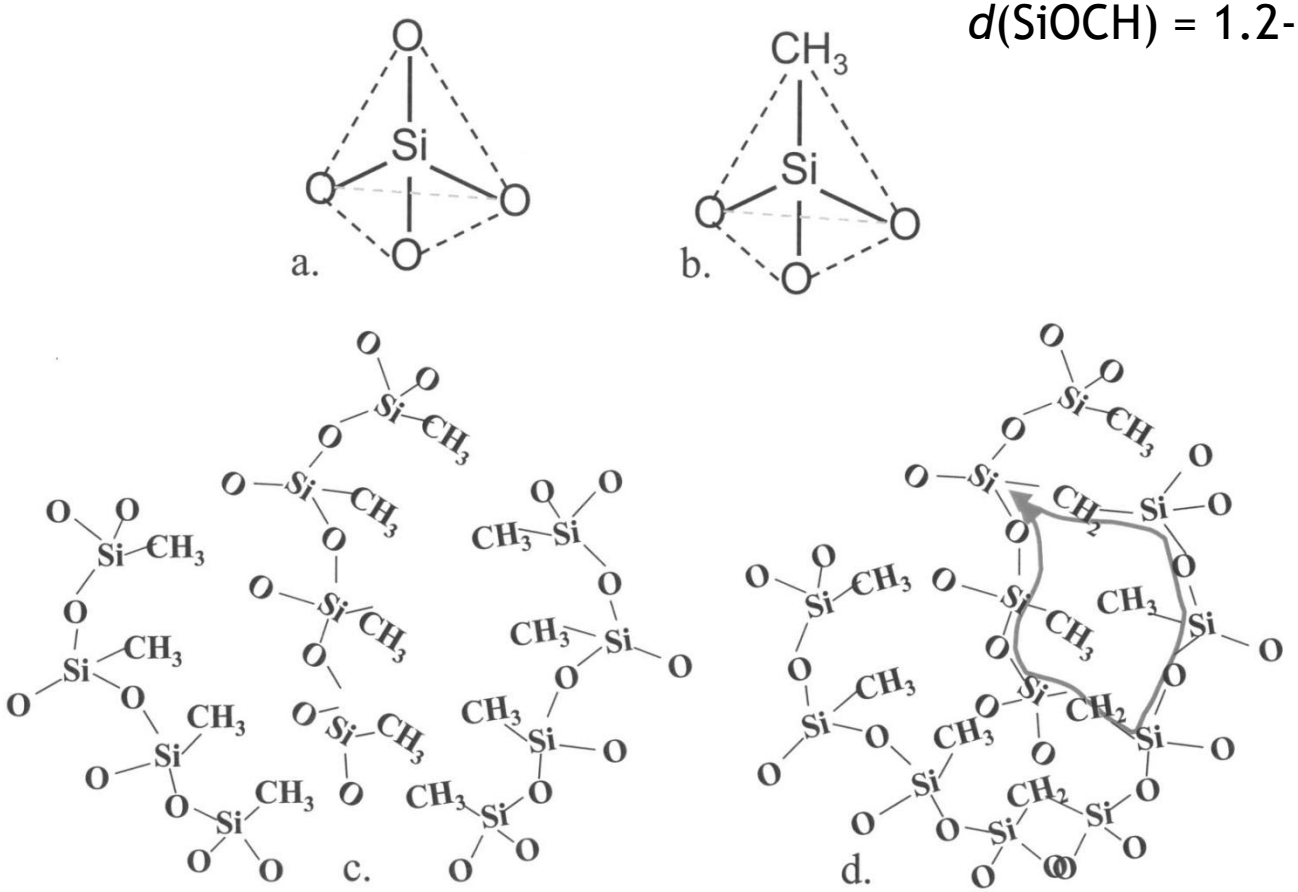
- H-$SiO_{3/2}$ (HSQ)
- CH_3-$SiO_{3/2}$(MSQ)

Non Si:

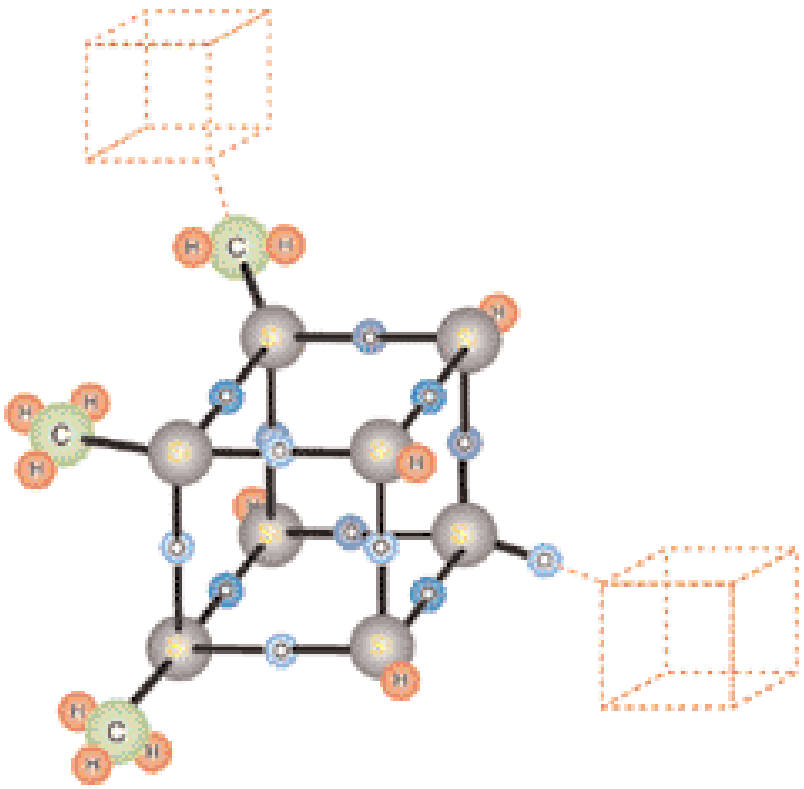
- Organic polymers
- Amorphous carbon (fluorinated, hydrogenated)
- Zeolites

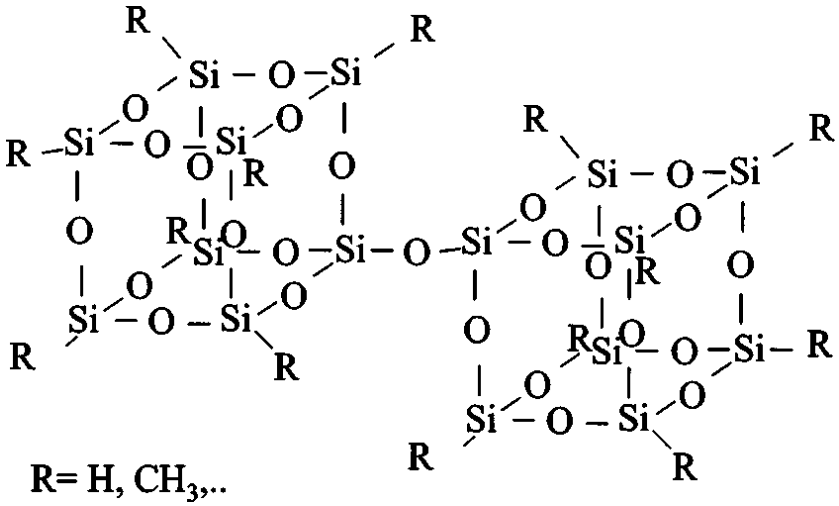
Elementary unit of: a) SiO_2, b) C doped silica glass

$d(SiO_2)$ = 2.1-2.3 g/cm^3
$d(SiOCH)$ = 1.2-1.4 g/cm^3)



Silsesquioxane unit (HSQ, MSQ)





R= H, CH_3,..

Low-k materials considered

5.0 - 3.9	**SiO_2**
3.7 - 3.0	SiOF (FSG)
3.9 - 2.9	Polyimides
3.0 - 3.2	Hydrogen silsesquioxane HSQ
2.8	Methyl silsesquioxane MSQ
2.8 – 2.4	SiOCH (OSG)
2.8 - 2.3	Fluorinated polyimides
2.7 - 2.3	Hydrocarbon polymers (polyethylene, polystyrene)
2.6 - 2.4	Fluorinate polyarylene ether (FLARE)
2.3	Parylene-F
2.2 - 1.8	Fluoropolymers (teflon)
1.7 - 1.3	Porous polymers (aero-gels, foams)
1.2 - 1.0	Air gaps
1.0	**Vacuum**

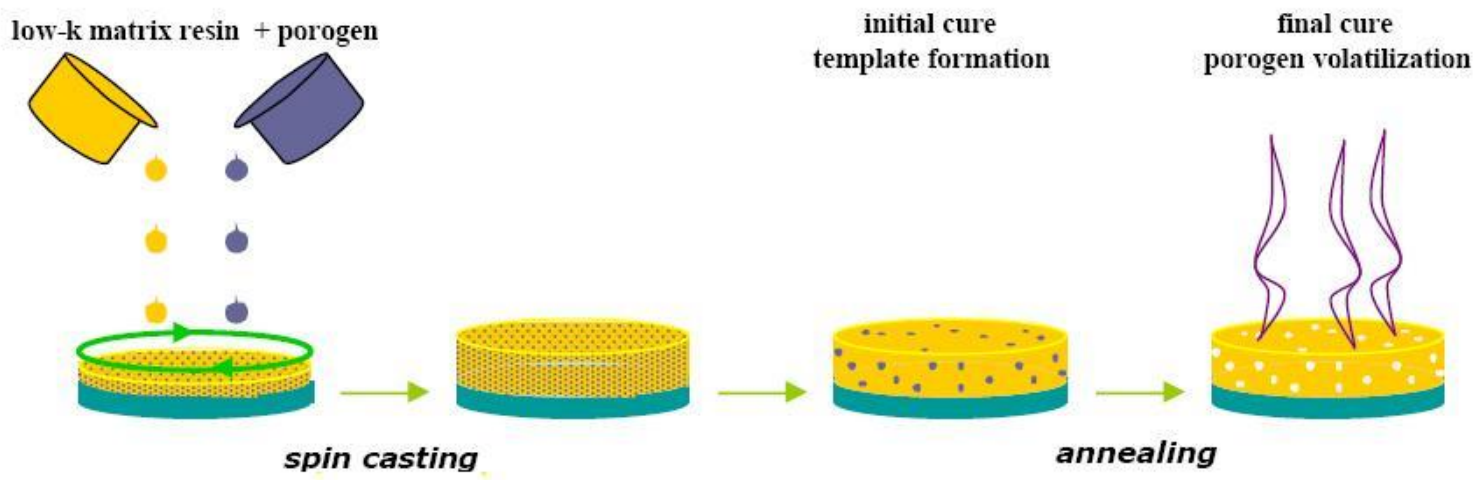
- **fluorine**
- **carbon**
- **porosity**

General requirements for a low-k material to be successfully integrated

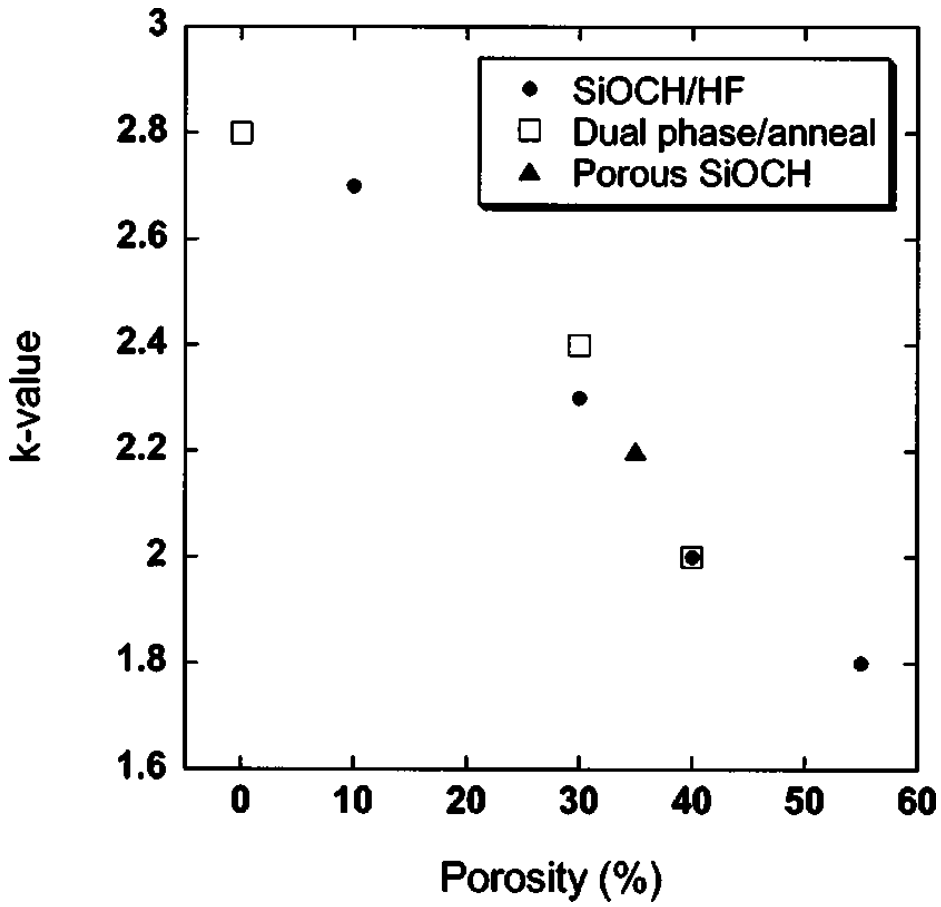
- Electrical:
  k<3 and isotropic, high breakdown voltage, low leakage current, high reliability
- Mechanical:
  good adhesion to metal or other dielectrics, stability (low brittleness, crack resistance), uniform thickness
- Thermal:
  low thermal expansion/shrinkage, high thermal stability, high thermal conductivity
- Chemical:
  no material change when exposed to standard chemistries, no metal corrosion, <1% moisture absorption, low solubility in water, low defect density
- General:
  environmentally safe, commercially available, low cost

Porous organics and inorganics

- Add closed cells of air to materials that show promising characteristics
- Dielectric constants below 2.0



The dielectric constant versus total porosity for SiOCH materials



K. Maexa, et al. IMEC,J. Appl. Phys., Vol. 93, No. 11, 1 June 2003

Disadvantages of porous materials in comparison to dense ones

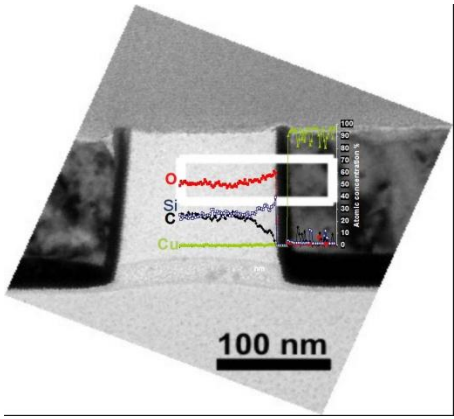
- decreased mechanical properties
- lower thermal conductivity
- narrow pore distribution to ensure dielectric constant is homogeneous and isotropic
- pores need to be closed cells to prevent crack propagation and moisture absorption
- need to add silica to seal surface pores

Chemical mechanical polish degradation and plasma treatment

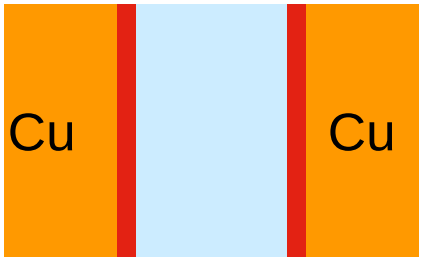
- Cracking due to mechanical weakness

  Parameters to be considered:

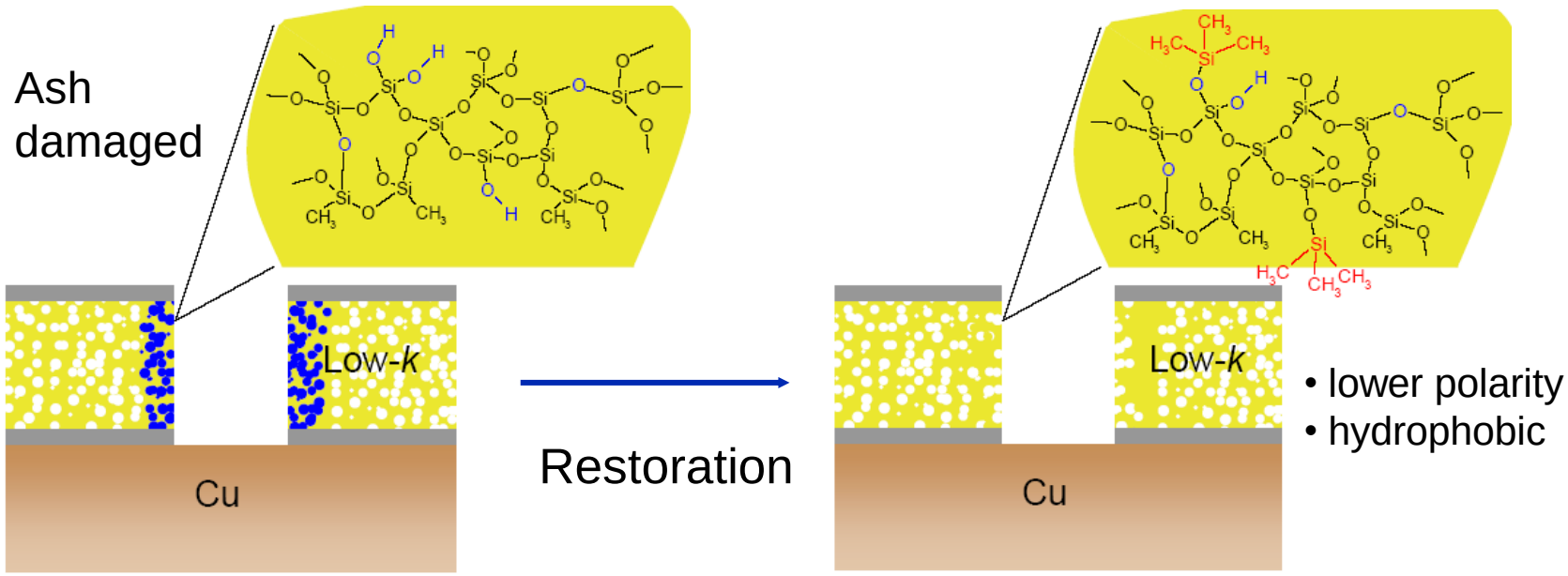
- Pressure (Down Force)
- Homogeneous Slurry
- Abrasive uniformity



- Carbon depletion due to chemical reaction with low-k
- Moisture up-take
- Plasma treatment: sidewall damage: Si-CH_3 to silanol Si-OH group or siloxane (Si-O-Si) bonds



Mechanisms for k-value restoration - silyation process



Through chemical reactions e.g.

$(CH_3)_3Si\text{-}NH\text{-}Si(CH_3)_3 + HO\text{-}Si \equiv_{(s)} \rightarrow (CH_3)_3 — Si — O — Si \equiv_{(s)} + NH_{3(g)}$

-CH_3 recovery: restores k-value; improves leakage property

D.Toma - SEMATECH / Low- K Symposium, 06-2004

Challange for low-k material

Porous SiCOH is the dielectric with the lowest k (k=2.4) implemented in the industry (IBM)

Goal 2015: k < 1.6

Outline

- Why low-k materials ?
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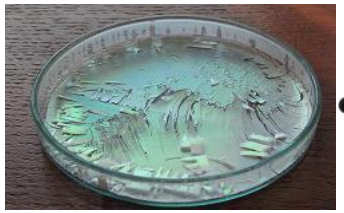
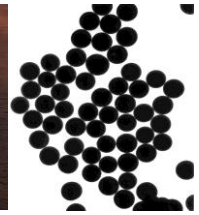
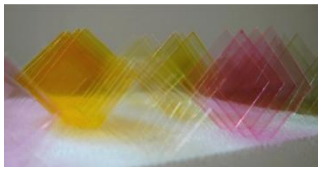
- Challenges in low-k technology
- **Sol-gel method for porous thin layers**
- Looking for breakthrough materials

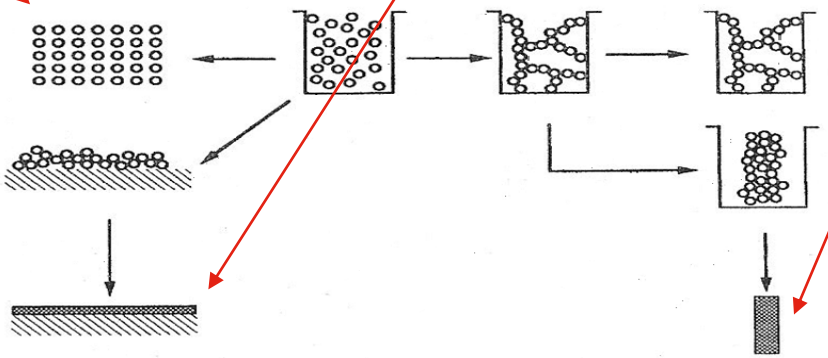
Sol-gel method for synthesis of subtractive porous materials

Powders

Layers

Blocks

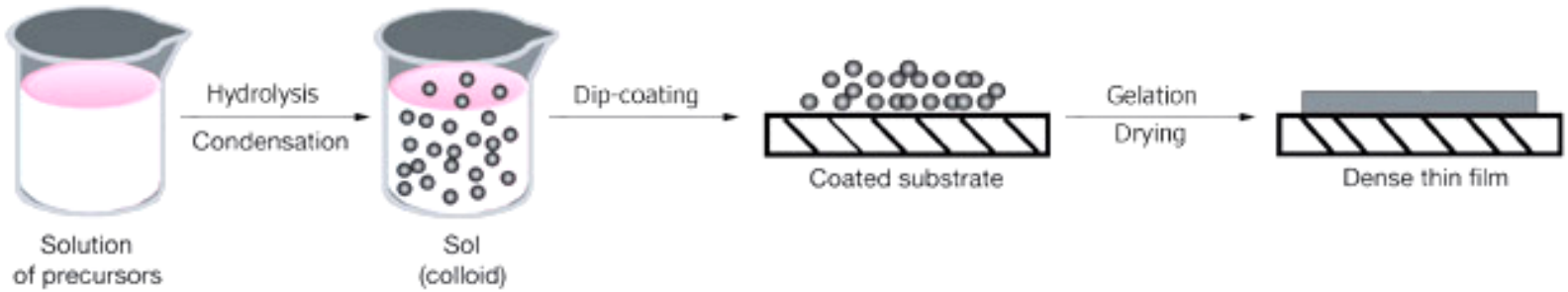


Parameters of sol-gel process:

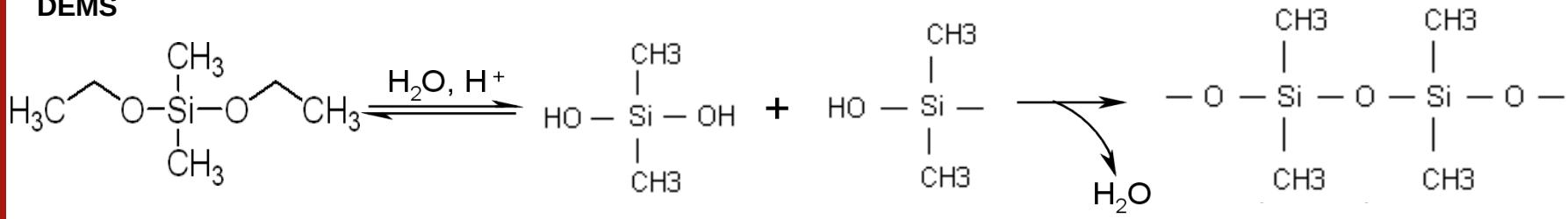
- chemical composition of hydrolyzate (precursors)
- pH (catalysis)
- drying process

Sol-gel method

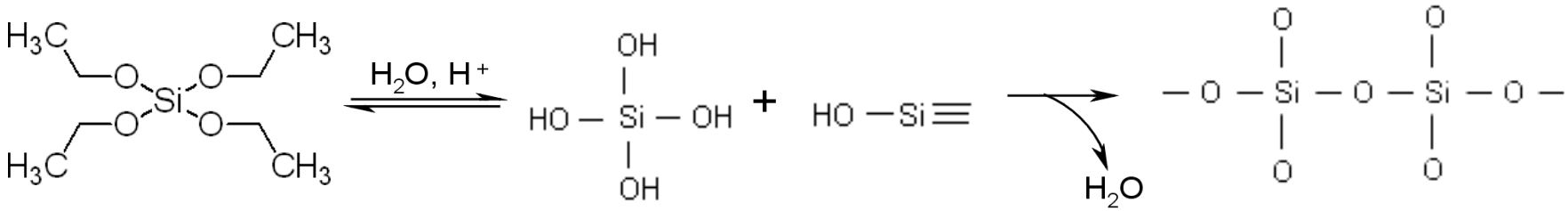
tetramethyl orthosilicate (TMOS) and diethoxydimethylsilane (DEMS)



DEMS



TMOS



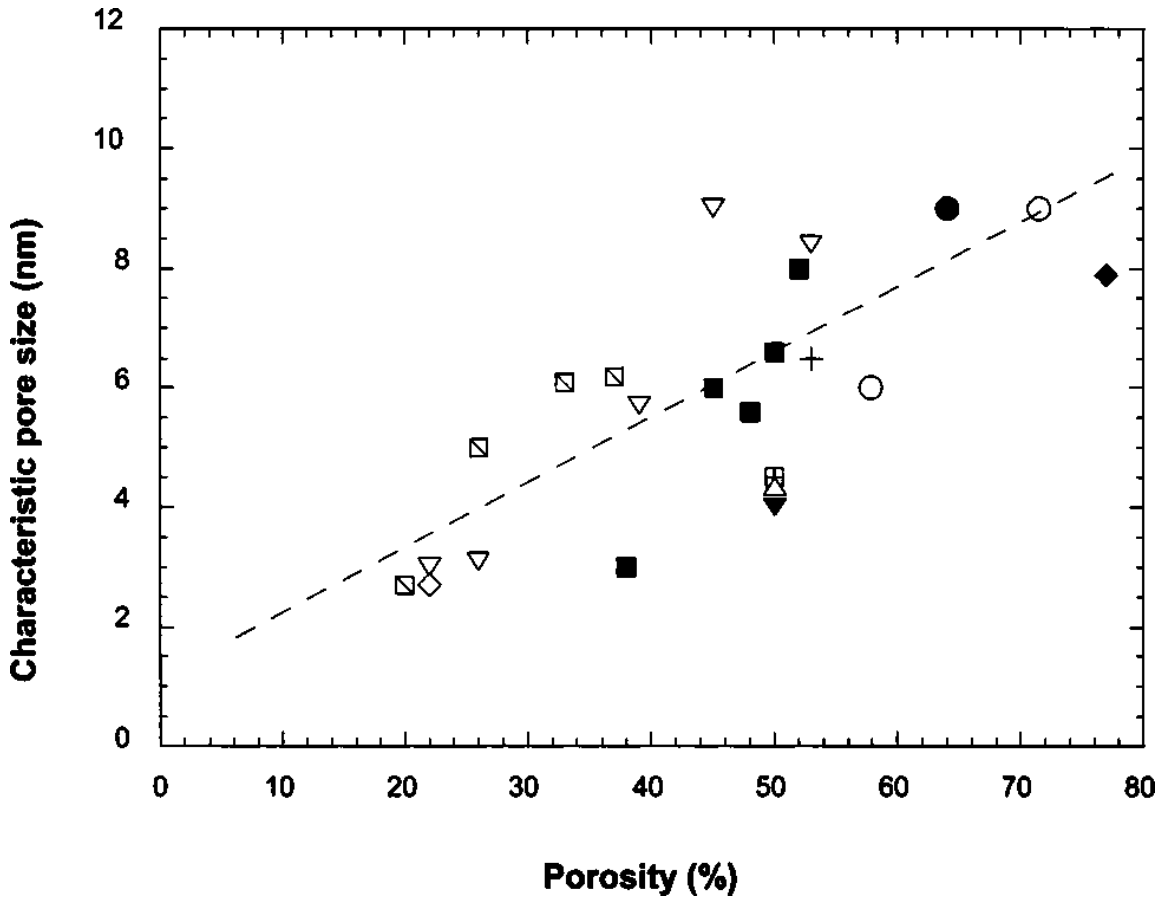
Parameters of sol-gel process

- mole fraction of precursors EtOH/TMOS /DEMS/H_2O/HCl:
  cross linking, porosity, density (thickness of layer)

- pH: hydrolysis speed (min at pH=7):
  powders → blocks → layers

- drying:
  density, porosity, C-content, cross-linking

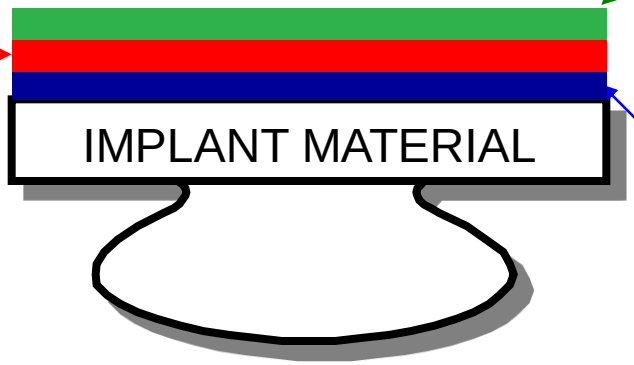
Average pore size vs total porosity for several sol-gel based materials



M. R. Baklanov, et al., Proceedings of IITC'2001, San Francisco, CA, 2001, 189

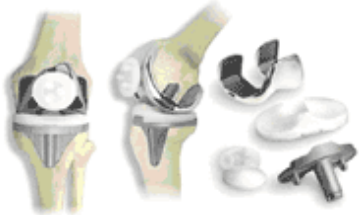
Implant silica and titania coatings

Insoluble coating (TiO_2) or partly soluble (TiO_2/SiO_2) or soluble (SiO_2), *containing drugs or organic grups as an option*



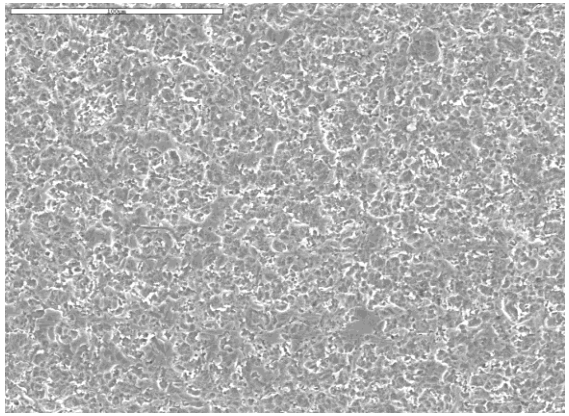
partly soluble (TiO_2/SiO_2) or soluble (SiO_2), the porosity and roughness ratio as demanded, TiO_2 + Ca or SiO_2 +Ca as osteostimulation factors

insoluble coating (TiO_2), isolate implant material from tissue environment

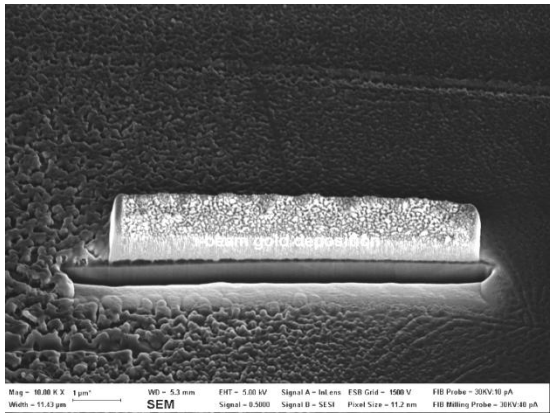


Sol-gel SiO_2/TiO_2 coatings characterization:

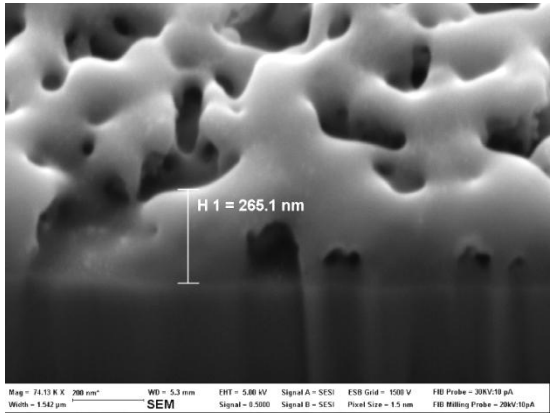
surface, porosity, Young's modulus, adhesion, biology



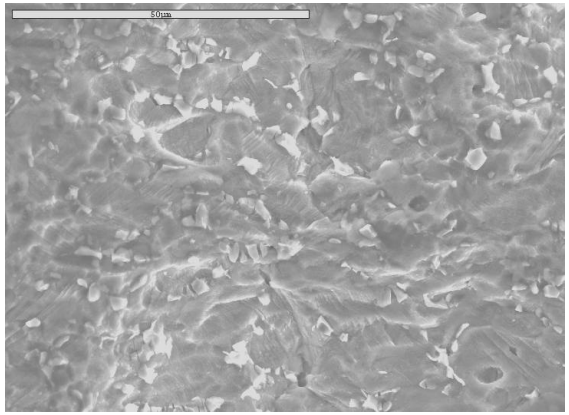
TiO_2 on 316L steel



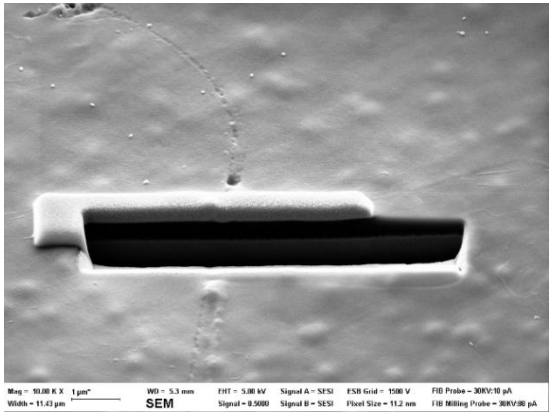
FIB 54° cross section



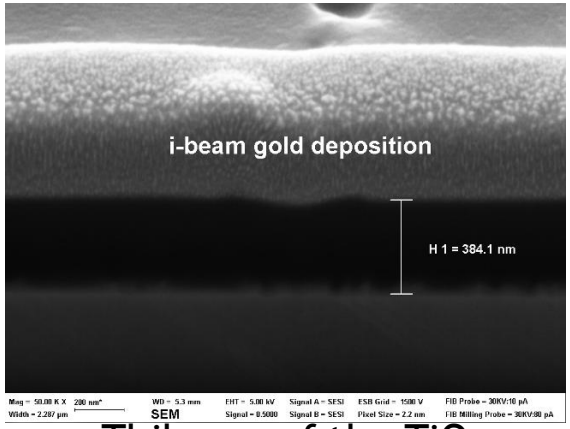
Thikness of the TiO_2 three-layer coating



SiO_2 on 316L steel



FIB 54° cross section



Thikness of the TiO_2 three-layer coating

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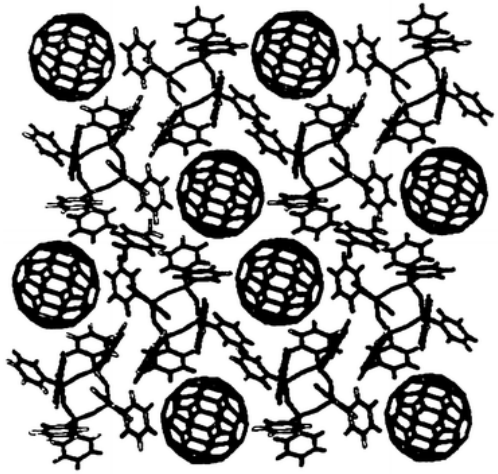
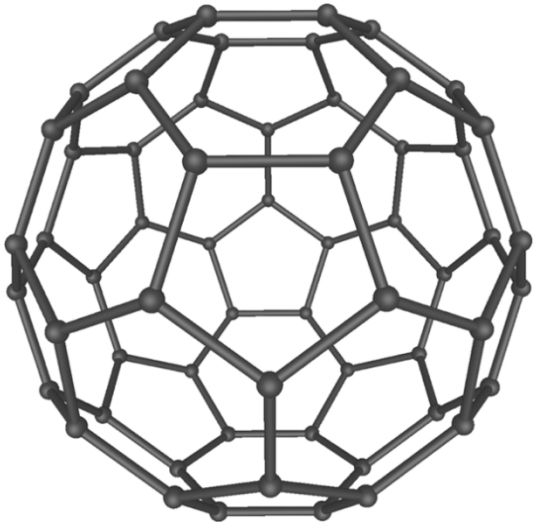
- Materials considered after SiO_2
- Challenges in low-k technology
- Sol-gel method for porous thin layers
- **Looking for breakthrough materials**

Fullerenes as low - k material component

Helmut Hermann, Institute for Solid State and Materials Research, Dresden: **k (C60) = 1.4 - 1.7**





Concept of $SiO_2 + C_{60}$

Is k value additive for hybrid materials ?

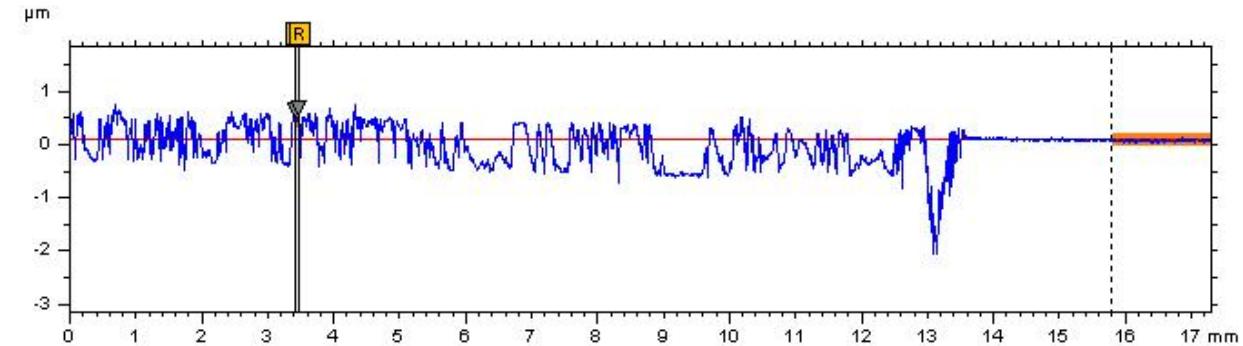
Sol – gel synthesis of SiO_2 / C_{60} layer

standard hydrolyzate

1. DEMS + TEOS + EtOH + HCl + C_{60} toluene solution
2. DEMS + TEOS + toluene + HCl + C_{60} toluene solution
3. PhTEOS + MeTMOS + EtOH + HCl + C_{60} toluene solution

- dip-coating
- open porosity 5-18 %

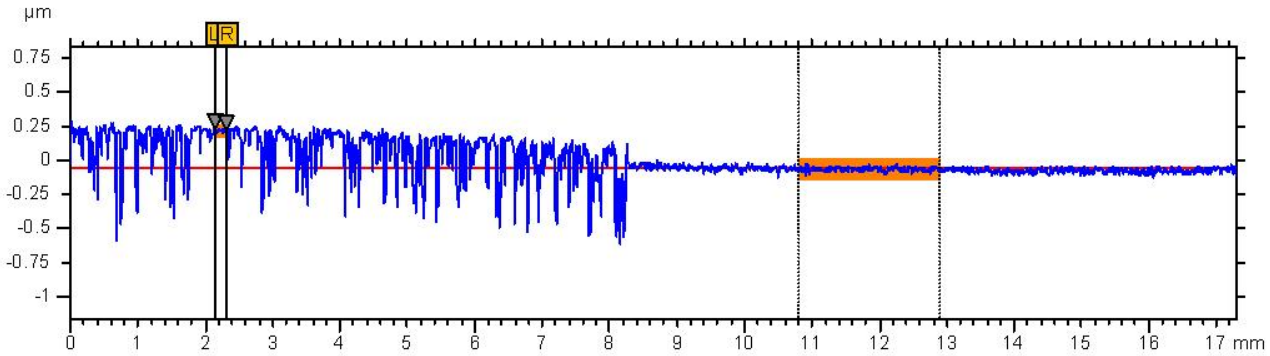
Thickness of dip-coated films



1

Maximum height	0.4481 µm
Mean height	0.4091 µm
Width	0.05896 mm

400 nm SiO_2 film

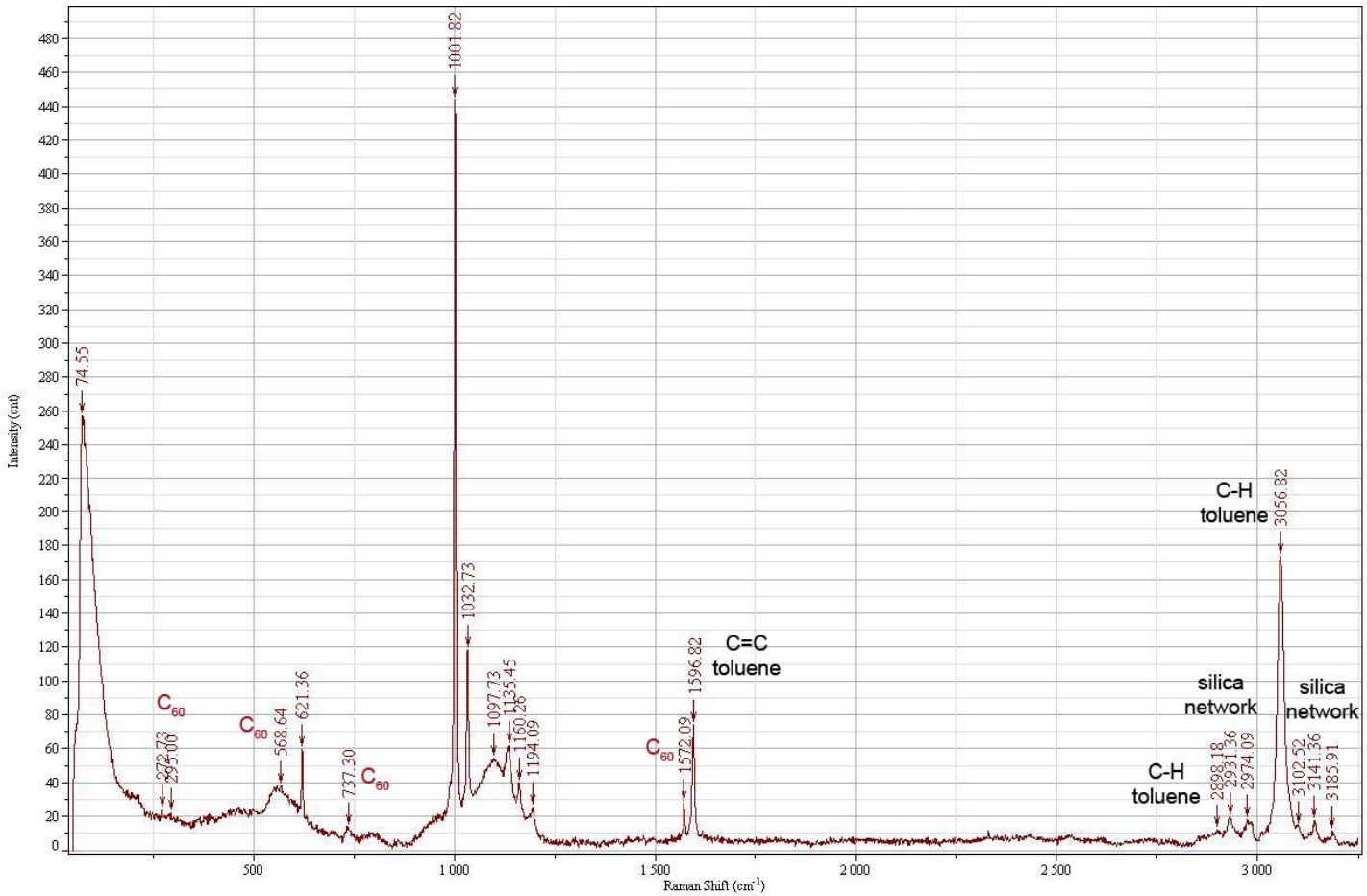


1

Maximum height	0.2941 µm
Mean height	0.2805 µm
Width	0.1703 mm

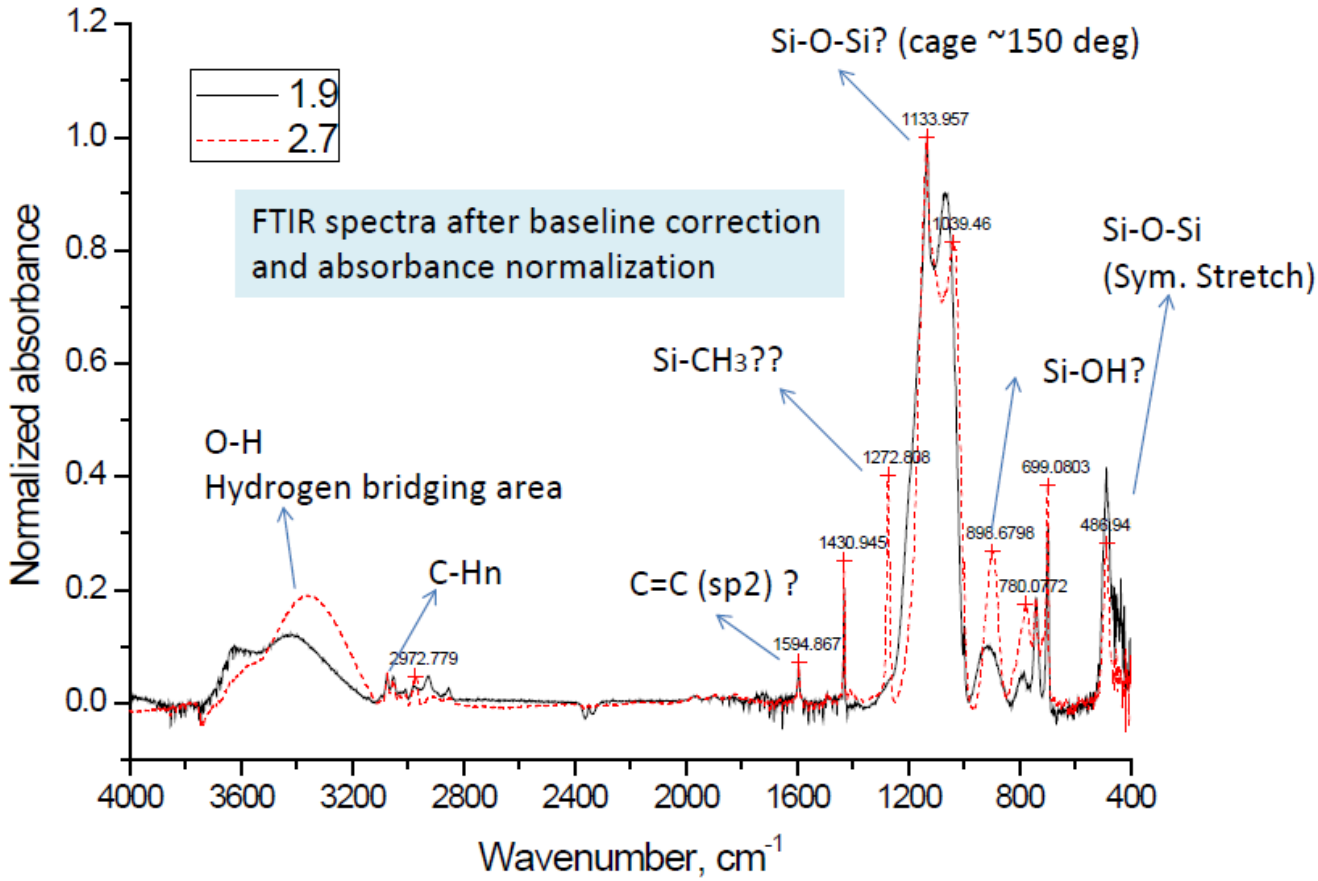
100 - 280 nm SiO_2/C_{60} film

Raman spectrum of C_{60} doped silica film



H. Kuzmany et al., Phil. Trans. Lond. A, 2004, 326, 2375

FT-IR spectra



*Normalization - absorbance is divided by the highest peak Absorbance

Preliminary evaluation of k value

Layer with Fullerene
30 nm SiO_2
Si(100) p-type

Layer without Fullerene
30 nm SiO_2
Si(100) p-type

Layer with Fullerene
Si(100) p-type

30 nm SiO_2
Si(100) p-type

k (SiO_2), 100 kHz = 3.9
k (SiO_2 / C60) = 2.0 - 2.3 ???

Advantages and disadvantages of SiO_2/ C_{60} materials

Advantages:

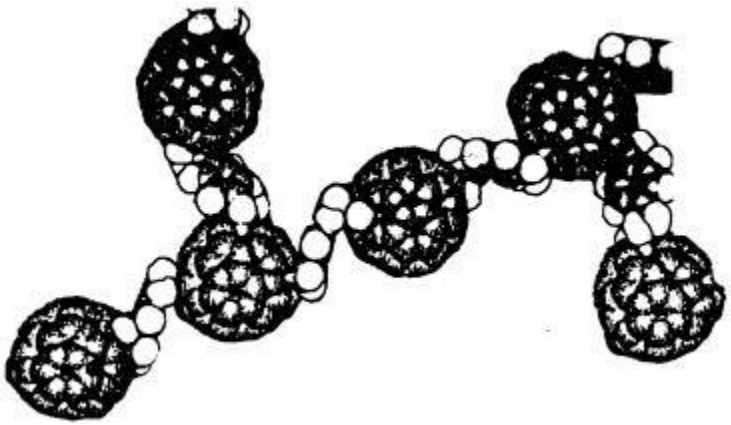
- good mechanical stability
- high quality of layers possible
- lower k value

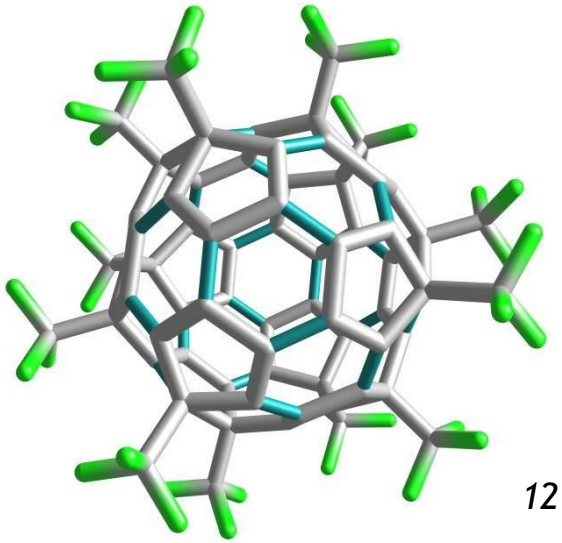
Disadvantages:

- small quantity of C60 incorporated (toluene-water emulsion)
- inhomogeneous distribution of C60 within a film
- handling of fullerenes difficult

Fullerene network ?

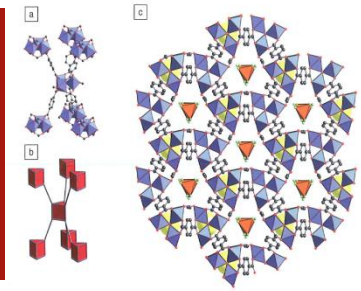
Polyfullerene ion synthesis of C_{60} with 2-methylazidrine
- United States Patent 5367051
- Polymer International, 1999, (48), 743-757



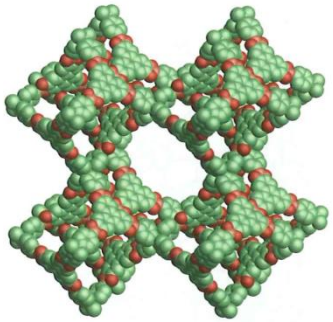


12 CF_3 groups attached, Prof. Schmeisser, BTU Cottbus

MOFs, COFs, ZIFs ????

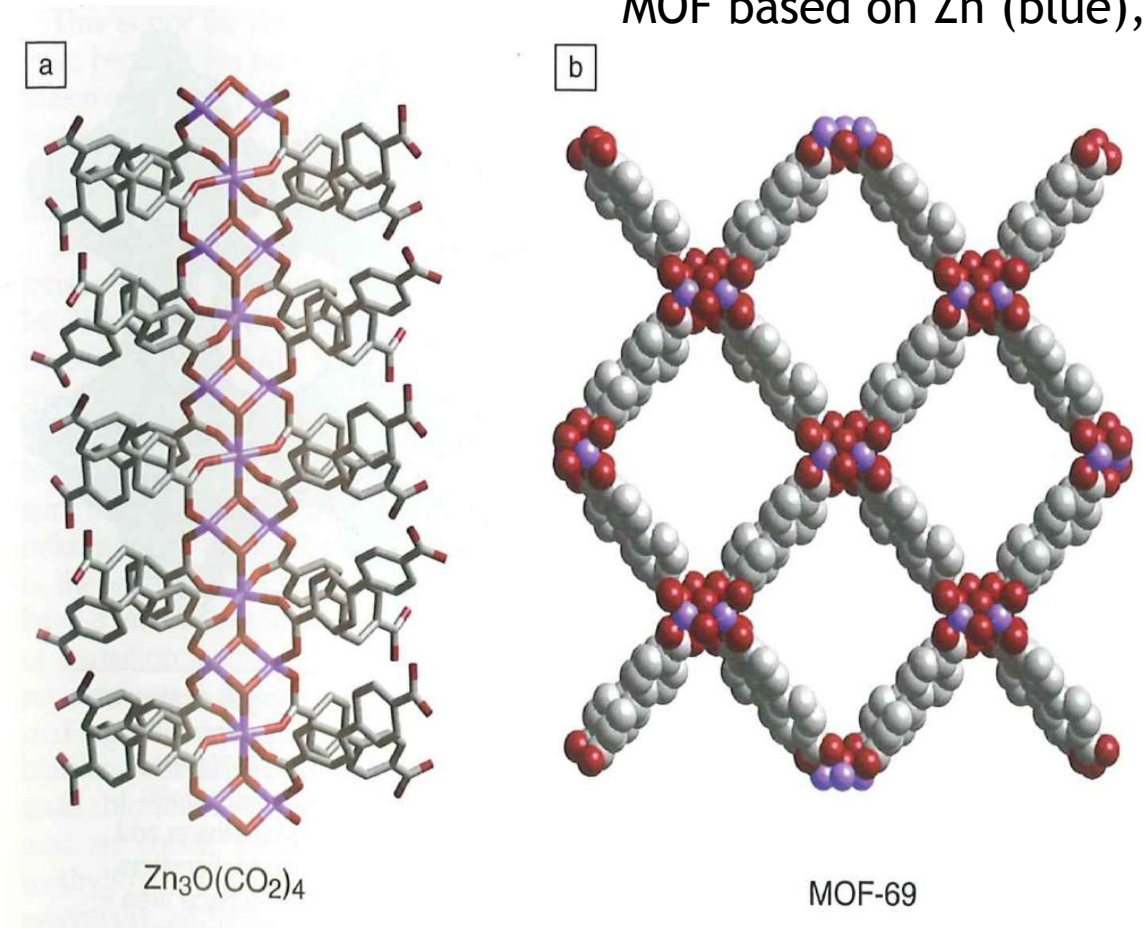


- „Net-like” chemistry: molecular building blocks are repeated and are held together by strong bonds
- Strong bonds of covalent characters (360 kJ/mol !)
- Robust materials useful for catalysts and storage materials (H_2, CO_2)
- Simple synthesis (1 atm, 25-200 ^oC)
- Thermal stability up do 500 ^oC
- Porosity: > 60% open space can be easily achieved (4 000 m^2/g)
- 5 500 m^2/cm^3 under vacuum ! (porous carbon – 1 500 m^2/g)
- Price already 4 $ / kg MOF



Metal organic framework (MOF)

MOF based on Zn (blue), O (red), and C (grey)

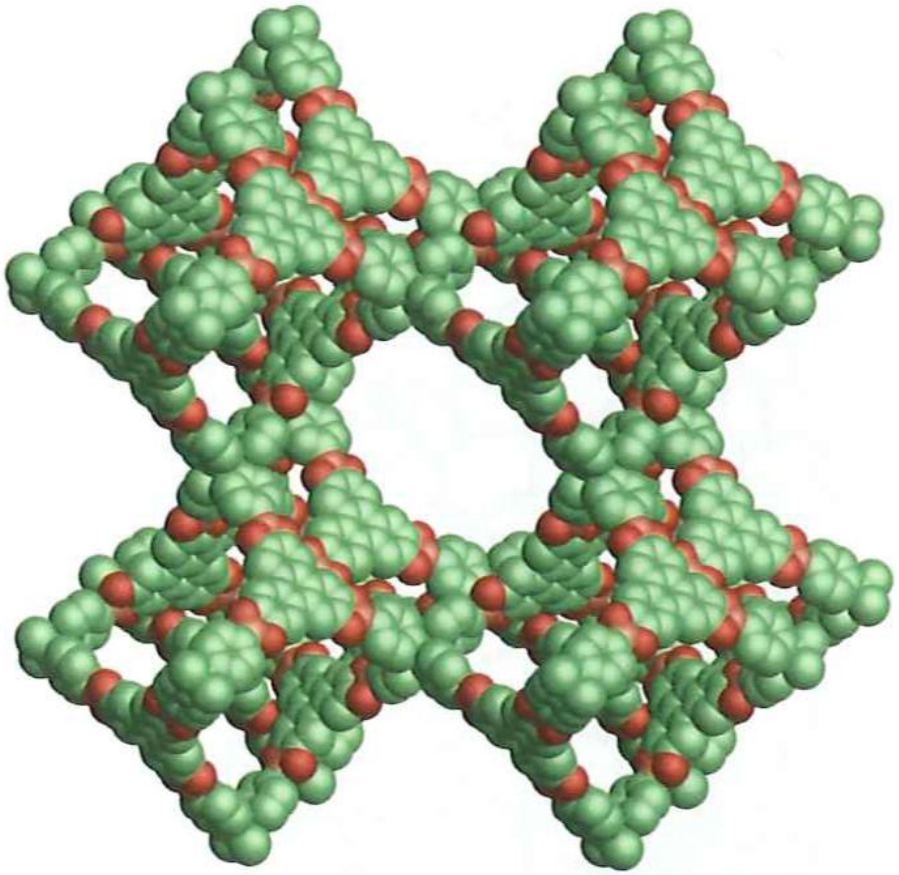


Omar M. Yaghi and Qiaowei Li, MRS Bull. 34 (2009)

Covalent organic frameworks (COFs)

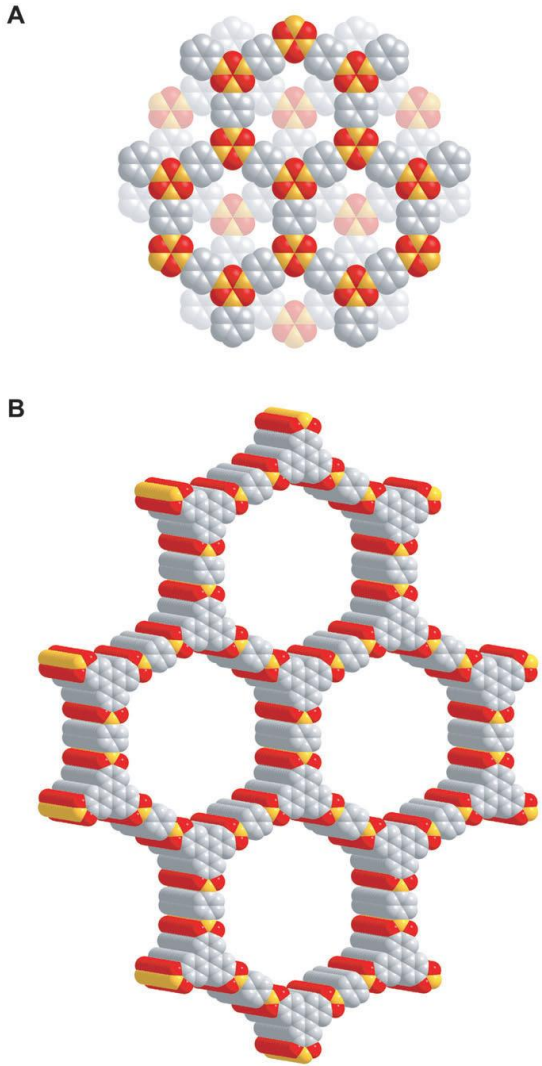
density 0.17 g/cm^3, surface area 4 700 m^2/g

COF-108 based on C (green), B (brown), and O (pink)



Omar M. Yaghi and Qiaowei Li, MRS Bull. 34 (2009)

COF-1, COF-5 based on C, B, and O



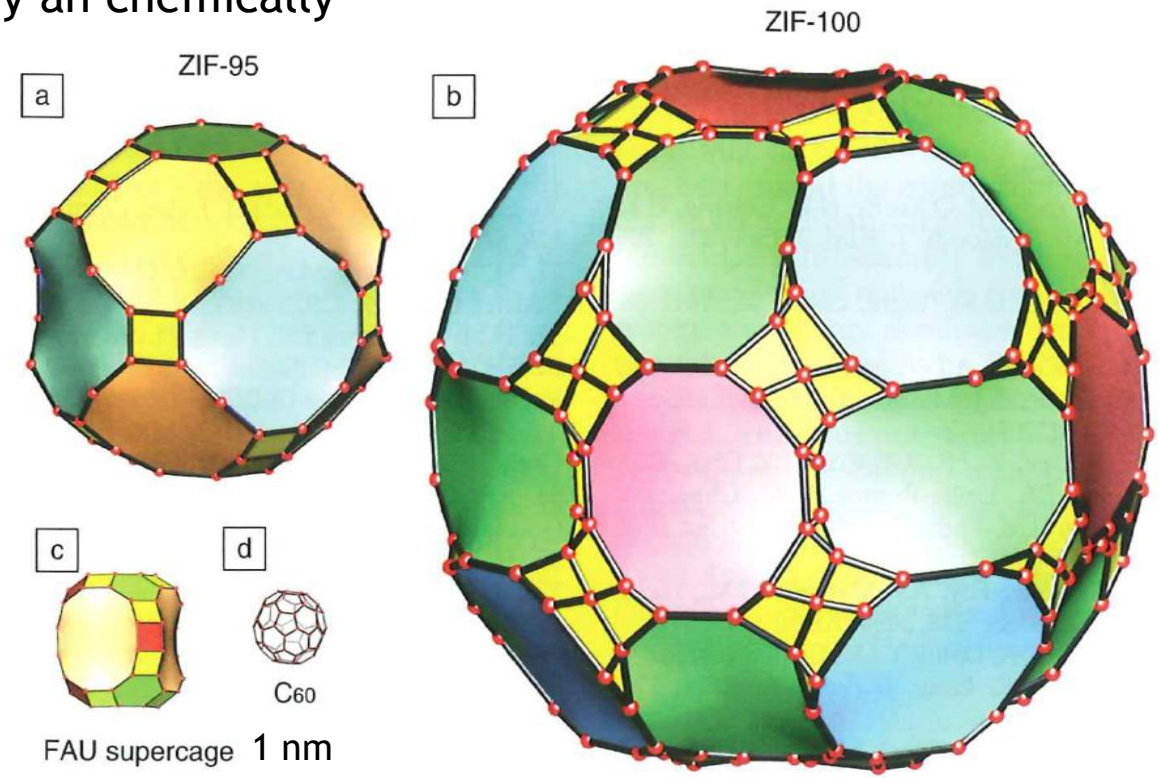
(A) COF-1 and (B) COF-5.
Carbon (grey), boron (orange), and oxygen (red)

Adrien P. Côté, et al., Science 310, 1166 (2005);

Zeolitic imidazolate frameworks (ZIFs)

- SiO_2 network
- Si replaced for Zn, Co (red)
- O replaced for imidazolate
- Very stable thermally an chemically

BASF: AU Czaja et al., Chem.Soc.Rev. 38 (2009) 1284



Conclusions

- Introduction of low-*k* dielectric is needed in order to continue to downscale technology
- Due to the high degree of porosity needed for ultra-low dielectric constant, mechanical stability of the materials will be an issue in integrating these films
- To scale the existing processes for 45nm, many adjustments are required (new techniques to reduce sidewall damage, new concepts of pore sealing etc.)
- New „stiff porous" materials (MOFs, COFs, ZIFs) should be tested in pure form or as a hybrid low-k component
- **Any low k proposal must demonstrate individual films plus how to integrate them**

Wrocław University of Technology

Thank you !