CHALLENGES IN IMPLEMENTATION OF LOW-K DIELECTRICS IN ADVANCED ULSI INTERCONNECTS

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Outline

- Introduction
- Why low-k and why needed ?
- ITRS roadmap and available low-k materials
- Organosilicate glasses: PECVD and SOG.
- Low-k materials for 10 nm technology node and beyond
- Challenges of integration
- Barriers and conductors
- Innovative solutions for integration

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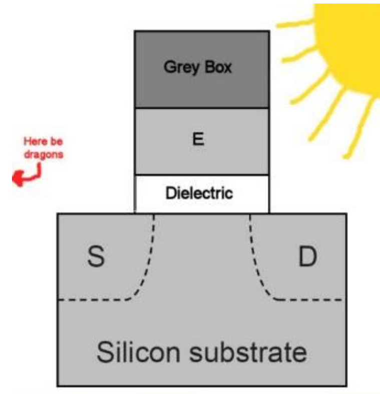
Two inventions that changed the modern world

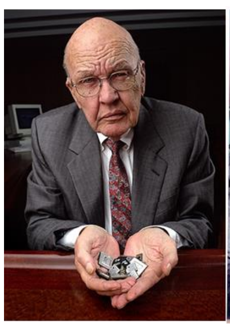
John Bardeen, William Shockley en Walter Brattain in Bell Labs, 1948.

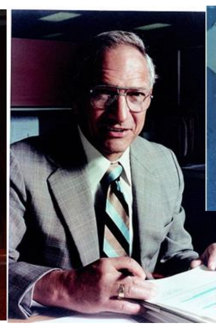
First transistor



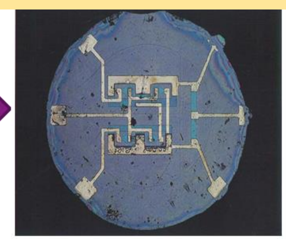
TRANSISTOR

More than 2 000 000 000 transistors in one chip

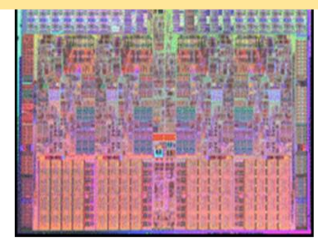




Kilby (TI), Noyce (Fairchild) 1958: "a body of semiconductor material ... wherein all the components of the electronic circuit are completely integrated."



1961
The First Planar IC, Fairchild

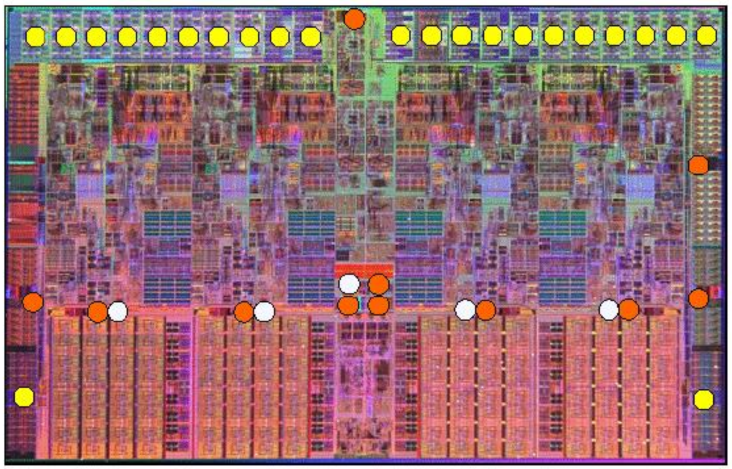


2008
INTEL NEHALEM

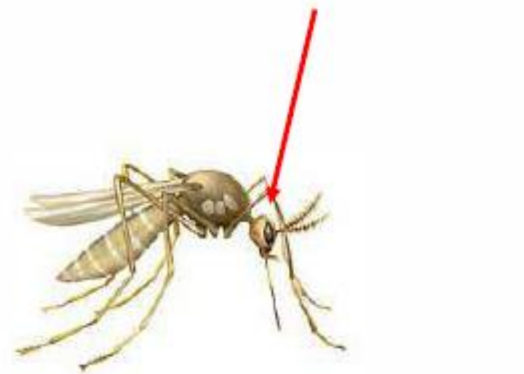
INTEGRATE
D
CIRCUIT

State-of-the-art of modern IC

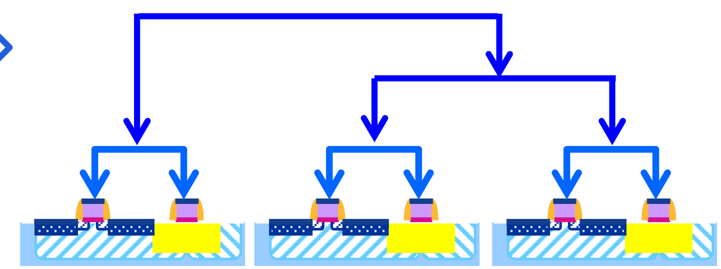
45 nm Nehalem CPU



The IC volume is close to
Mosquito's head ~ 0.5mm^3 ?



Transistor Count	731 million
Frequency	>3.6 GHz
# Cores	4
Cache Size	8 MB
I/O Peak Bandwidth	50 GB/sec



Billion transistors at IC bottom (in the area <1 cm^2) must be interconnected.

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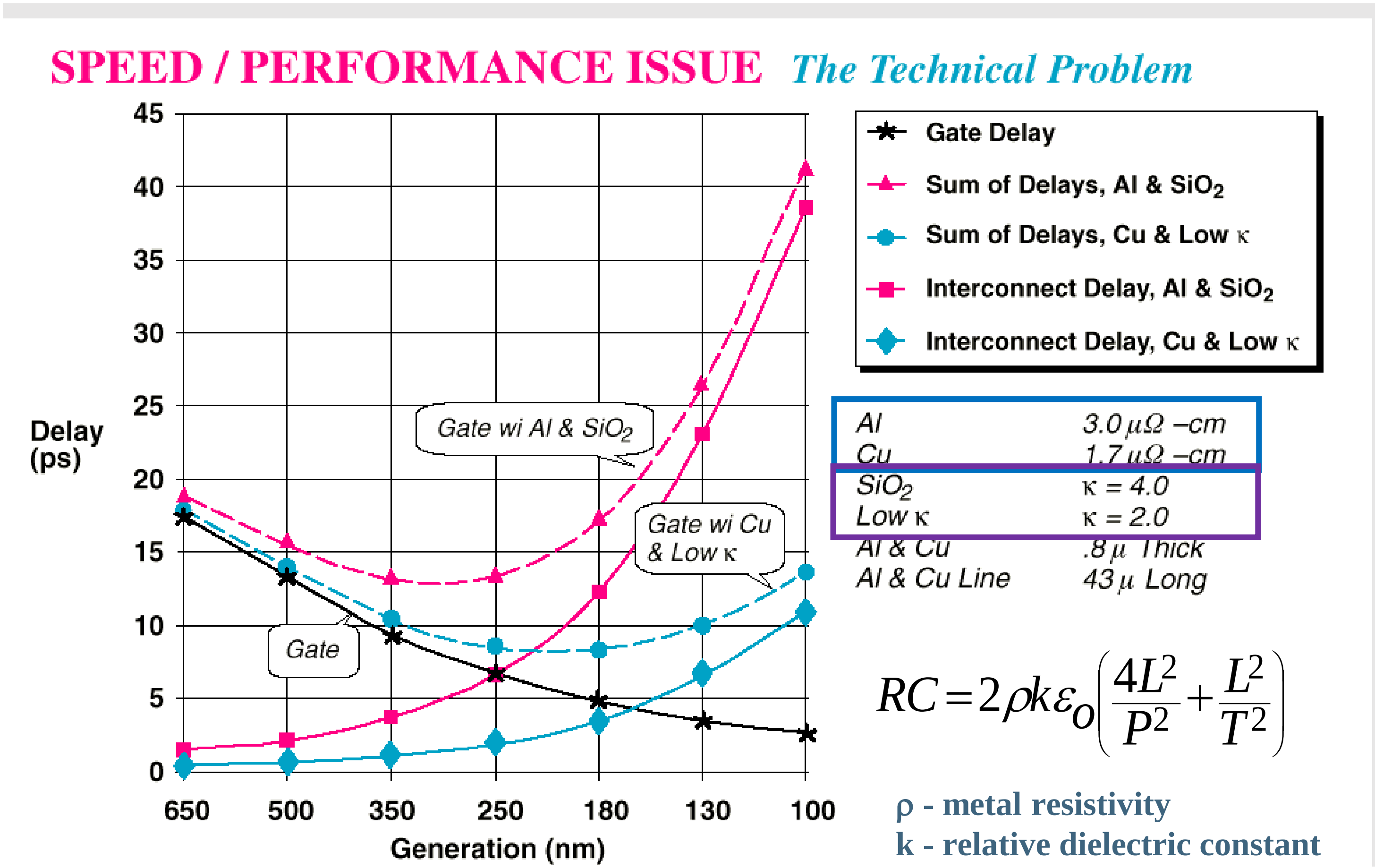
INTERCONNECT DELAY



ρ - metal resistivity
k - relative dielectric constant
L - line length; P - metal pitch
T - metal/dielectric thickness

Interconnects are needed in metals with low resistivity (Cu) and dielectrics with low dielectric constant (low-k).

Polarisability or porosity ?

(Clausius-Mossotti equation)

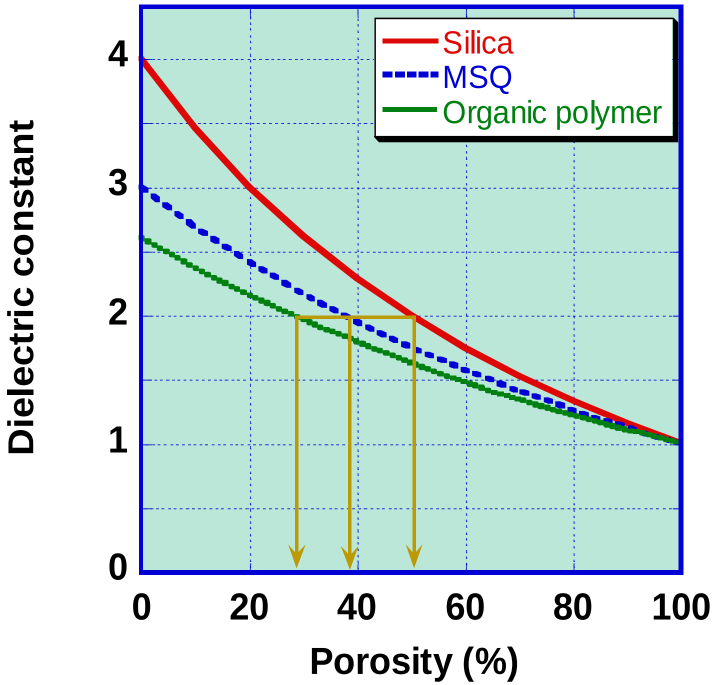
$$\frac{(k-1)}{(k+2)} = \frac{4\pi}{3} N\alpha$$

$$\frac{k_r - 1}{k_r + 2} = P \cdot \frac{(k_1 - 1)}{(k_1 + 2)} + (1 - P) \cdot \frac{(k_s - 1)}{(k_s + 2)}$$

- Dielectric constant $\boldsymbol{k = \varepsilon/\varepsilon_o}$ depends on molecular characteristics (polarisability α), and density (N).

- Molecular characteristics (**α**) allow changing the k-value in a limited range. Organic polymers have low frequency dispersion but hardly compatible with current ULSI technology.

- Therefore, more significant change of the k-value can be succeeded by changing density (pores)



- **The k-value depends on porosity and dielectric constant of skeleton.**
- **Low k-value of skeleton → low k-value of the film at lower porosity.**

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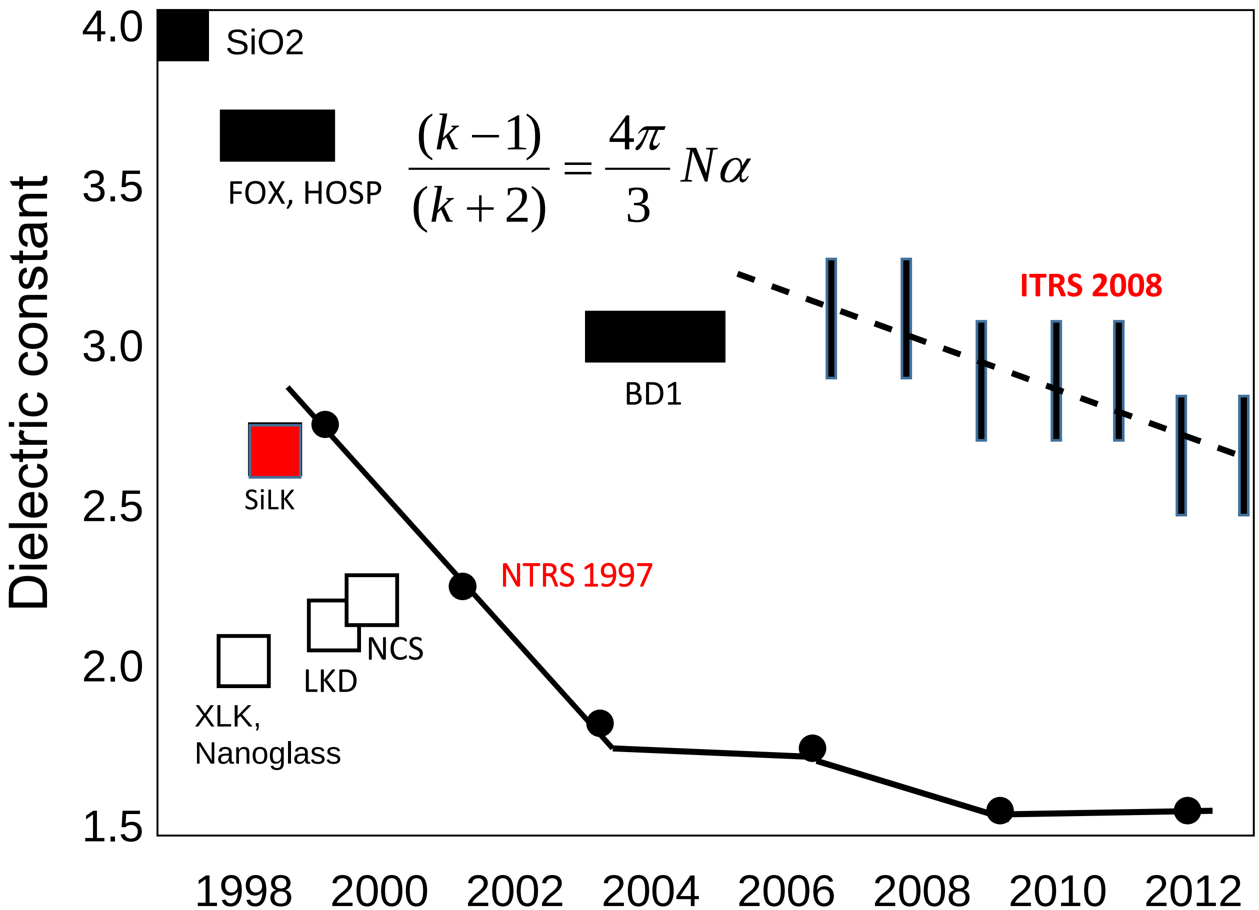
ITRS Roadmap



- K=2.7 in 2012 instead of predicted k=1.7 in 2003: huge delay ?

Low-k materials (past and present)

- Organic polymers
- **Organosilicate glasses**
- Silsesquioxanes
- *Zeolites*
- ***Boron carbonitrides***
- *Fullerene*
- ***MOFs***

Organosilicate glasses

Compatible with ULSI technology:

- **Properties similar to SiO2**
- **You can use traditional equipment**

- *Organic polymers: coefficient of thermal expansion*
- *Zeolites: intergranular voids*
- *Fullerenes: never shown reliable deposition (film formarion)*
- *Silsesquioxanes: might be interesting for subtractive approach. Young Modulus is a problem*

- *Boron carbonitrides are still candidates for non-porous version of ULK (M. Paquette)*
- *Metal-Organic Frameworks (MOFs) might be candidates for subtractive integration*

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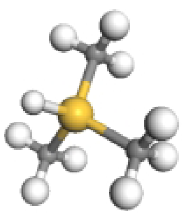
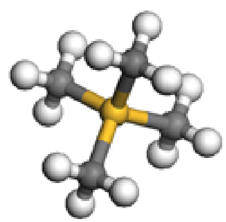
Precursors

SiO_2: $SiH_4 + O \rightarrow SiO_{4/2} + H_2O$
Low-k: $Si(CH_3)_4 + O \rightarrow (CH_3)SiO_{3/2} + H_2O$

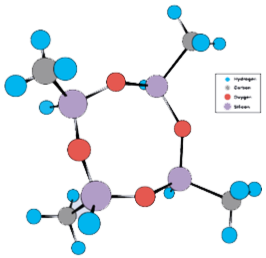
Matrix precursors are silane derivatives and siloxane derivatives and contain organic groups providing hydrophobicity of deposited films skeleton.



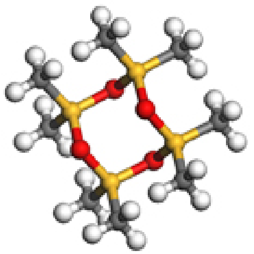
3-methylsilane



4-methylsilane



4-methylcyclotetrasiloxane (TMCTS)

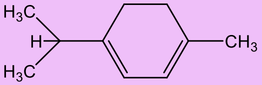


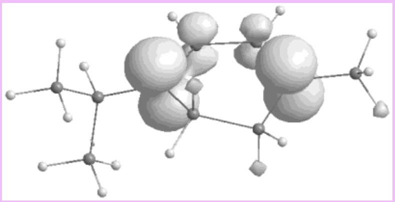
8-methylcyclotetrasiloxane (OMCTS)

Porogens are used to generate porosity.
A typical example of porogen is a-terpinen.
Porogen must be degradable at T < 450C and leave minimum amount of residue after removal.

A typical porogen molecule:

A-terpinen





Deposition of low-k materials

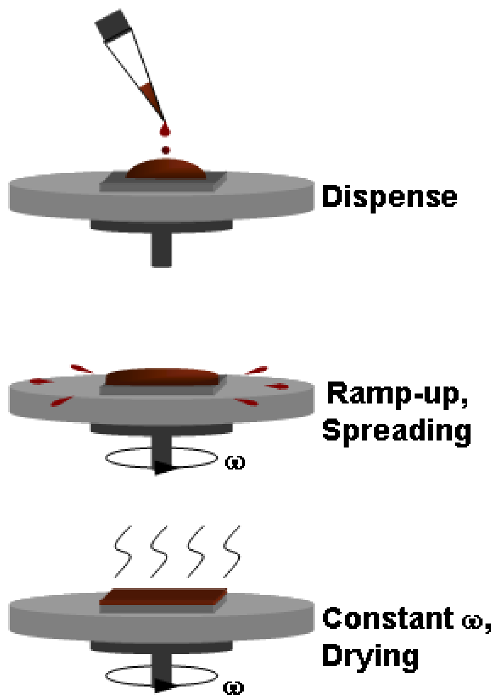
- Spin-on deposition
- CVD (PECVD) deposition

- porogen removal
- network formation

Curing

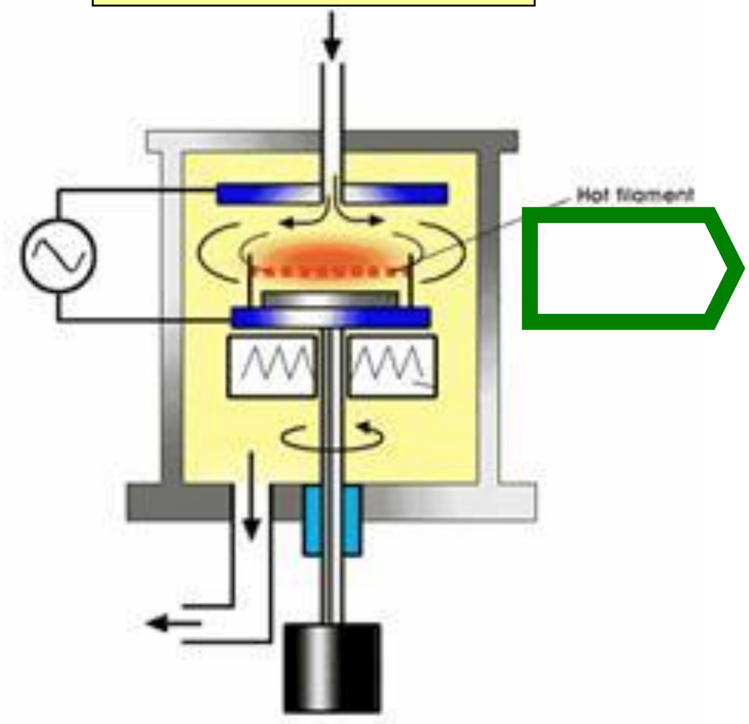
- thermal
- E-Beam
- UV

Spin-on



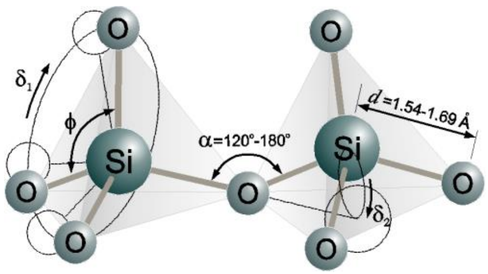
Aerogels/Xerogels, HSQ, MSQ (LKD JSR, NCS CCIC)

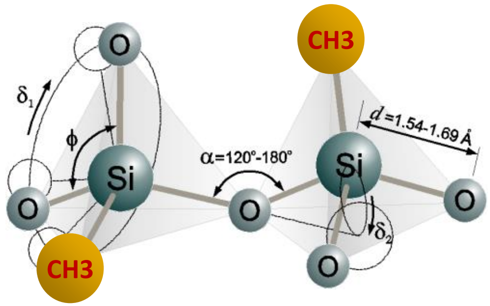
CVD/PECVD

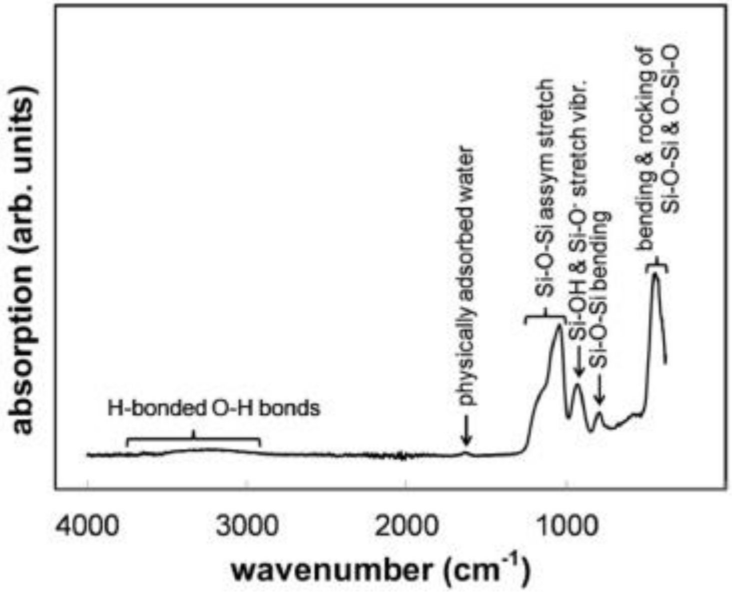


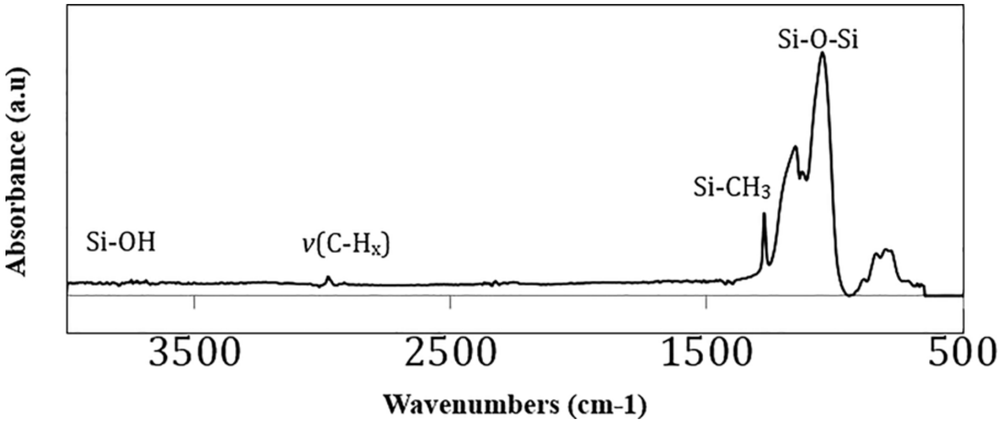
SiCOH (Black Diamond AMAT, Aurora ASM)

Comparison of SiO2 and low-k materials



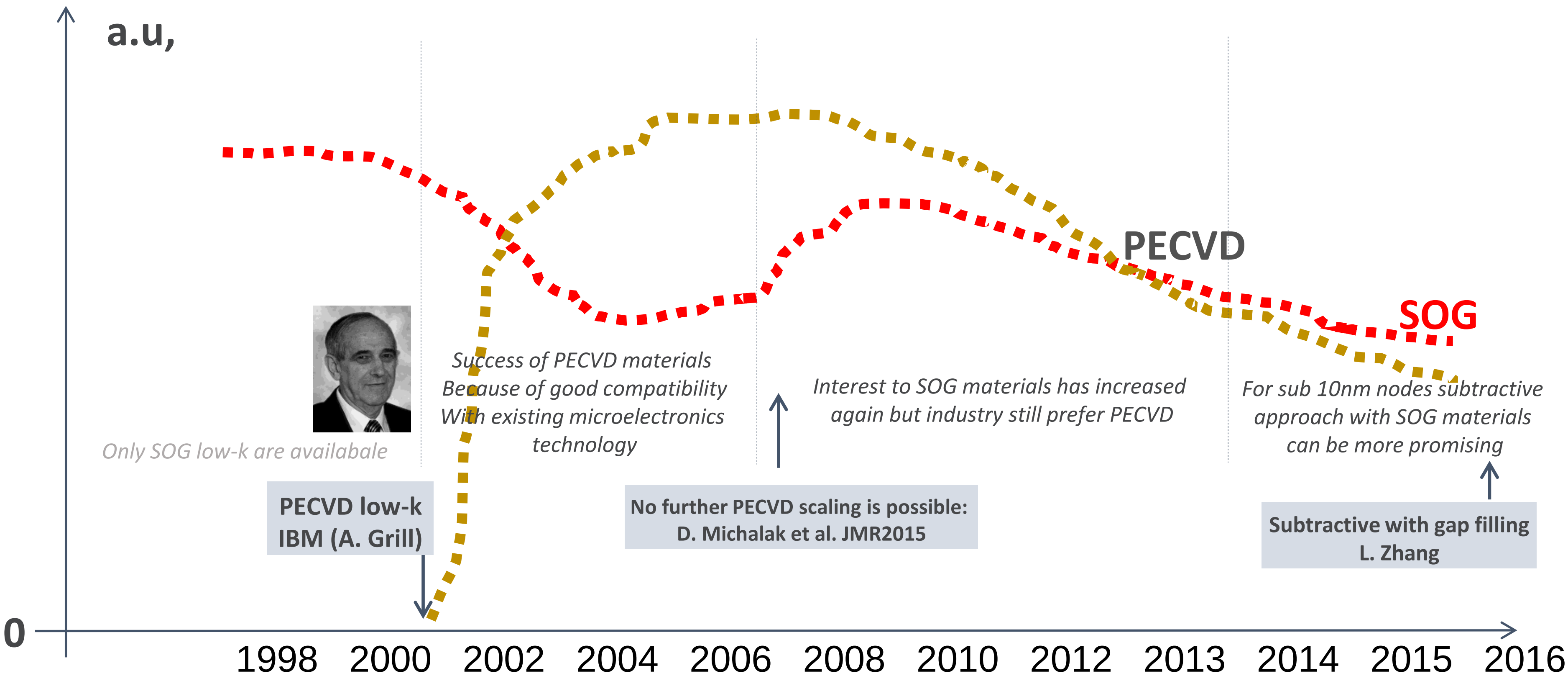






- ➢ **CH3 groups reduce polarizability and density, makes material hydrophobic.**

PECVD or Spin-on ?



- SOG materials historically were first low-k materials. PECVD materials became more popular when A. Grill developed low-k PECVD deposition.
- Interest to SOG increased again because of difficulty of PECVD further scaling.
- Possibility of subtractive integration requests the gap filling capability and it increases interest to SOG materials.

Problems of the k-value scaling

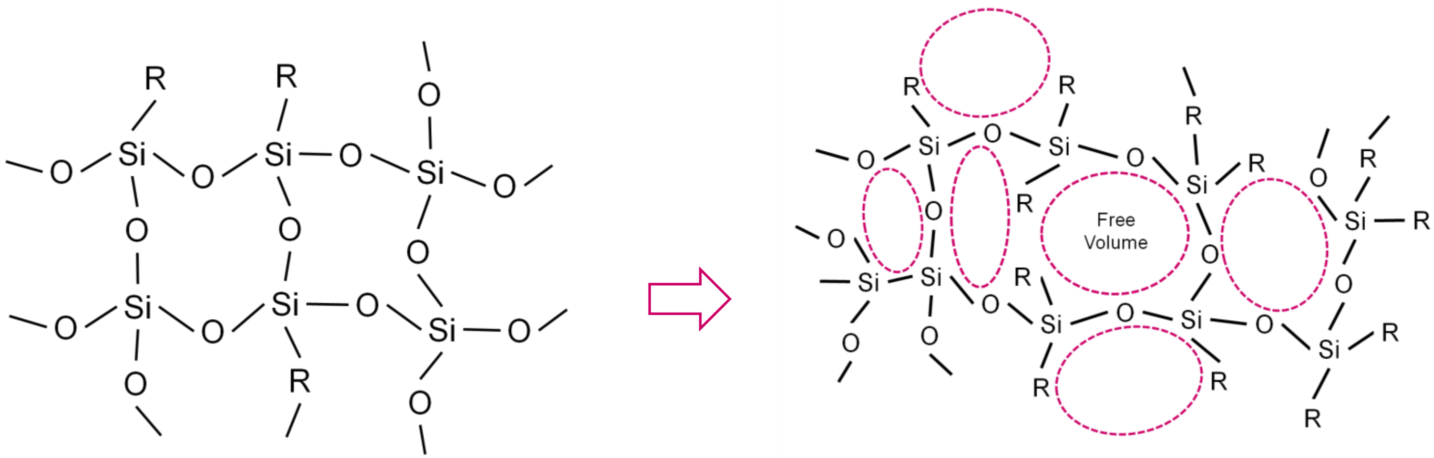
- Organosilicate glasses have matrix k-value close to SiO_2.
- Therefore only porosity introduction can reduce the k-value.
- **Effects of porosity and terminal carbon:**

- **Degradation of mechanical properties**
- **Compatibility with barriers deposition**
- **Plasma damage**
- **Degradation of dielectric characteristics**

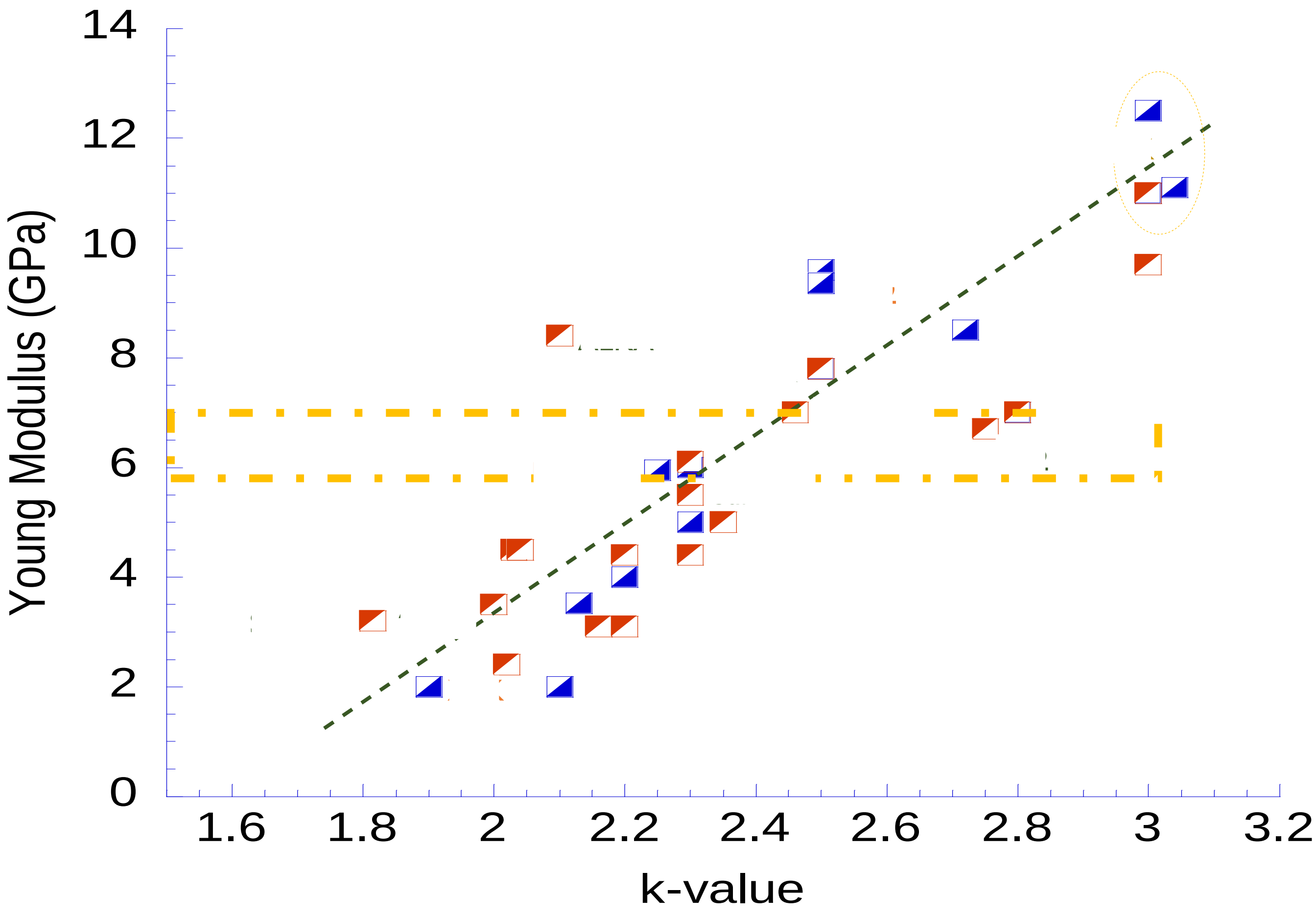
Effect of carbon

- Terminal ≡Si-CH_3 initiates hydrophobicity, increases plasma resistance reduces Cu diffusion but reduces Young Modulus.

- Non bonded residual carbon (porogen/template residue (sp2 Carbon, CH_x) may improve plasma resistance but deteriorate electrical properties.

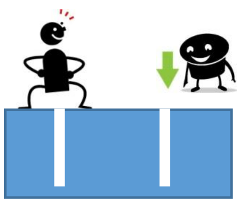


Young Modulus versus K-value

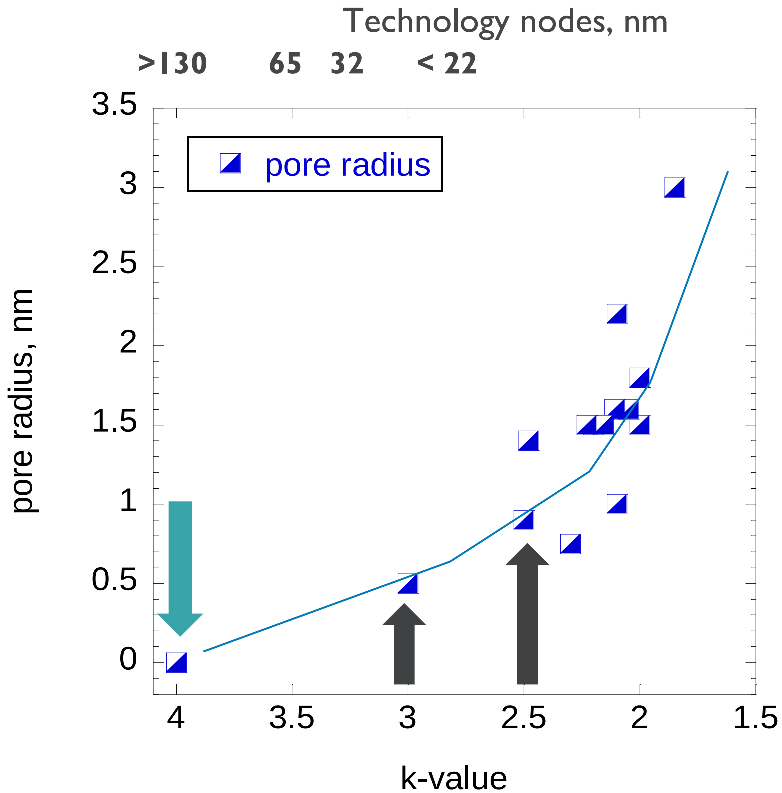


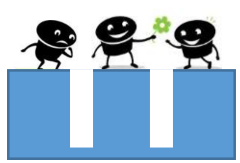
- ➢ Still OK for 14 -10 nm if to integrate k=2.5-2.6 materials

Pore size versus k-value. sealing



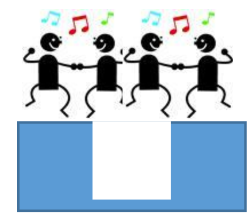
BD1, Aurora, Coral (k=3)





BD2, ELK HM (k=2.5)

ALK, SBA (k ≤ 2)



Molecular self-assembling:

M. Baklanov et al. J. APPL. PHYS. 113, 041101 (2013)

➢ **Pore sealing technology is becoming extremely important**

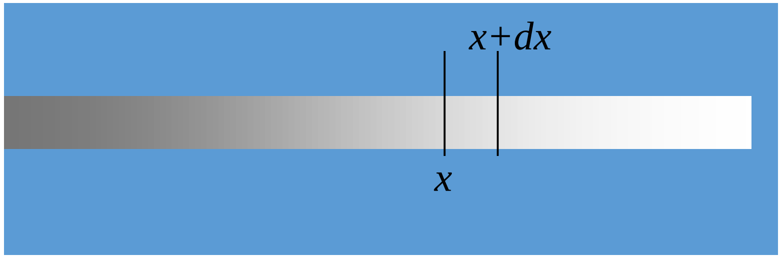
Diffusion of plasma species into pores

No gradient in gas phase:

$C_A = C_{As}$

No [A] at a certain depth

$C_{Al} = 0$



$$\frac{\pi d_p^2}{4} D_A \left(\frac{dC_A}{dx}\right)_x - \frac{\pi d_p^2}{4} D_A \left(\frac{dC_A}{dx}\right)_{x+dx} - \pi d_p dx C_A \left(\gamma_{reac} + \gamma_{recomb}\right) = 0$$

Flux in **Flux out** **1st order reaction**

γ_r

$\gamma_{reaction}$: A (O)+ Si-CH3 ⍰ SiOH--H2O + CO

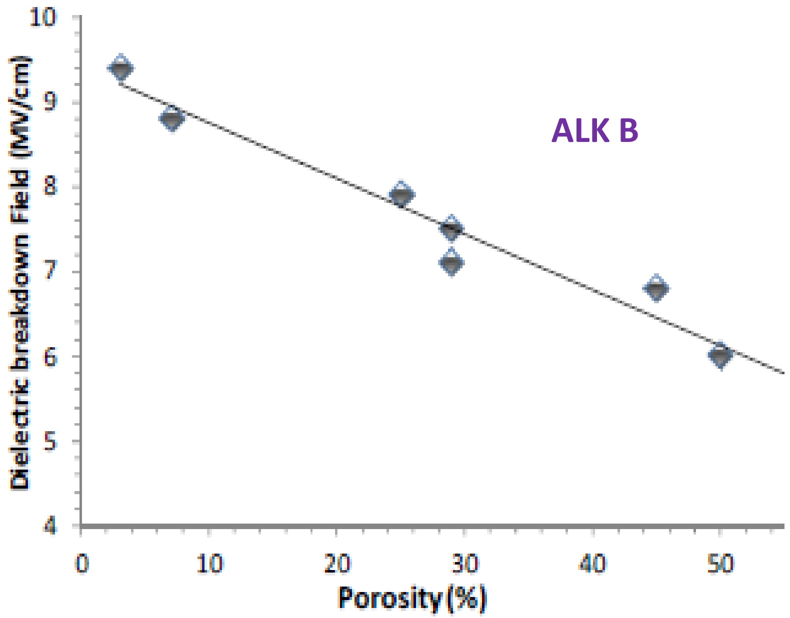
γ_{recomb}: A+A+M⍰ A_2

T. V. Rakhimova et.al., " IEEE Trans. Plasma Sci. 37(9), 1697 (2009).
M. Baklanov et al. J. APPL. PHYS. 113, 041101 (2013)

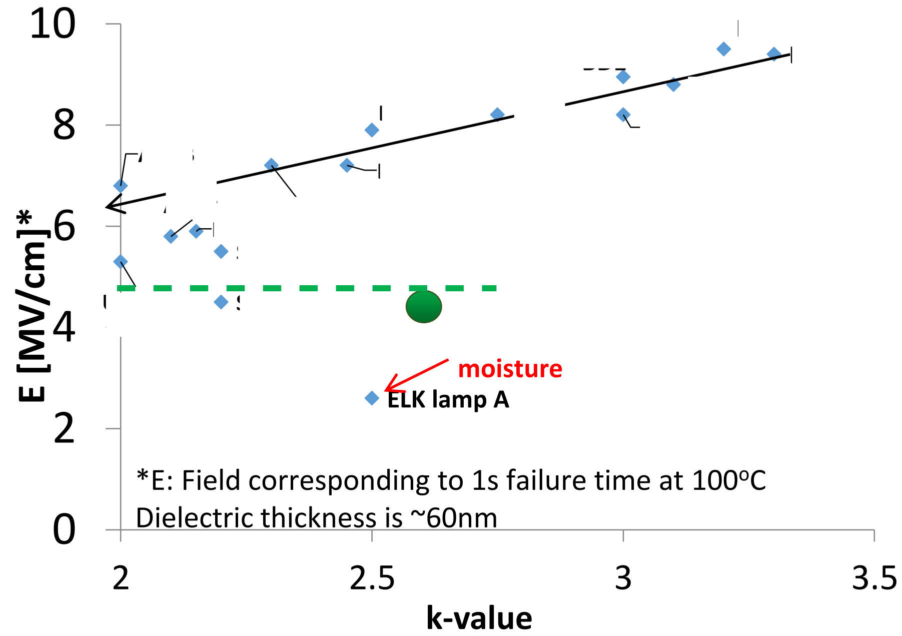
➢ **Pore size increases with porosity, therefore plasma damage is becoming stronger**

Breakdown field versus porosity and k-value

Same material with different porosity



Different materials



- **Porosity is of primary importance for breakdown.**
- **The chemical composition is also important: E is approaching to the values typical for organic polymers. Strong effect of adsorbed moisture.**

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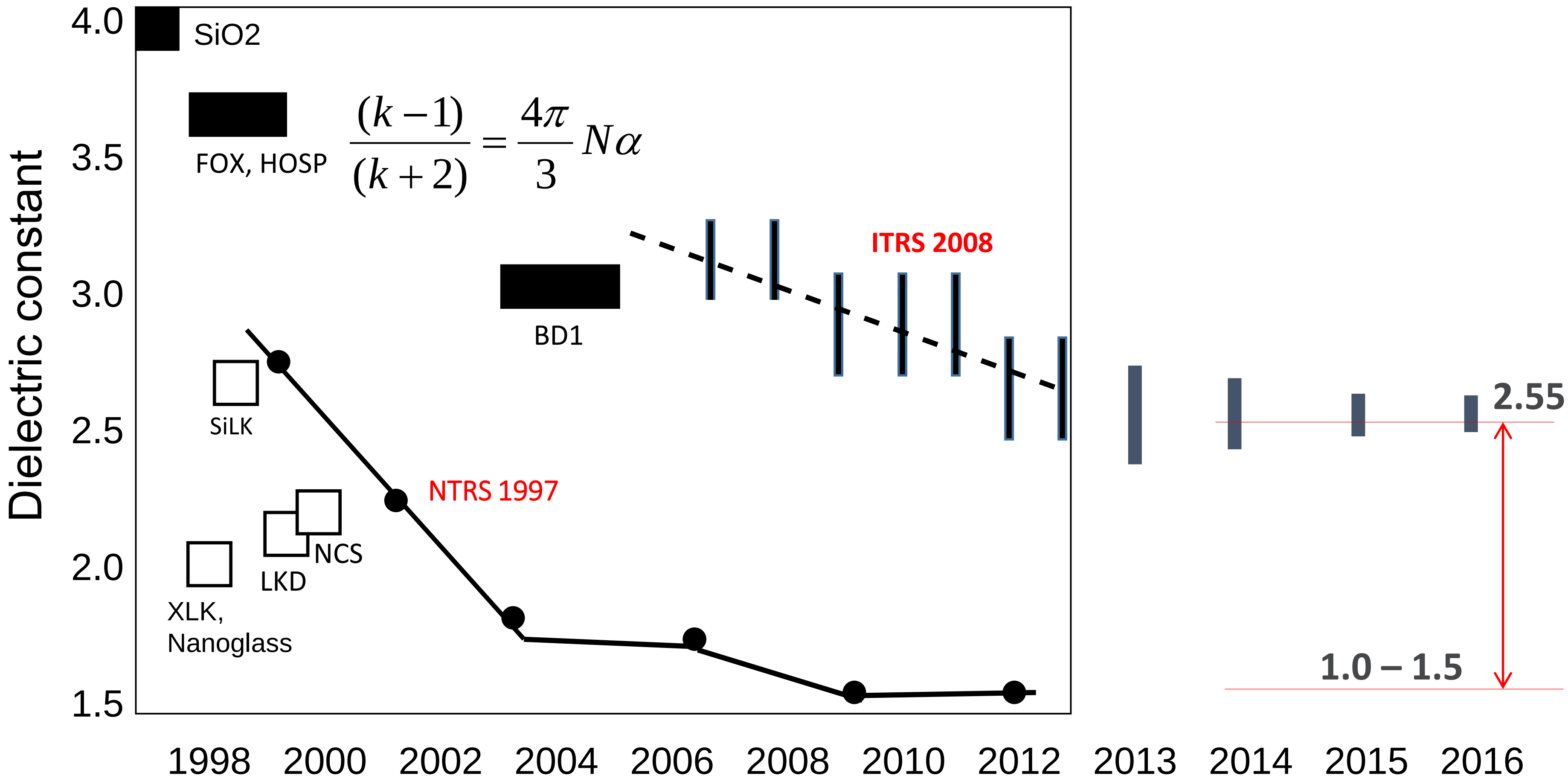
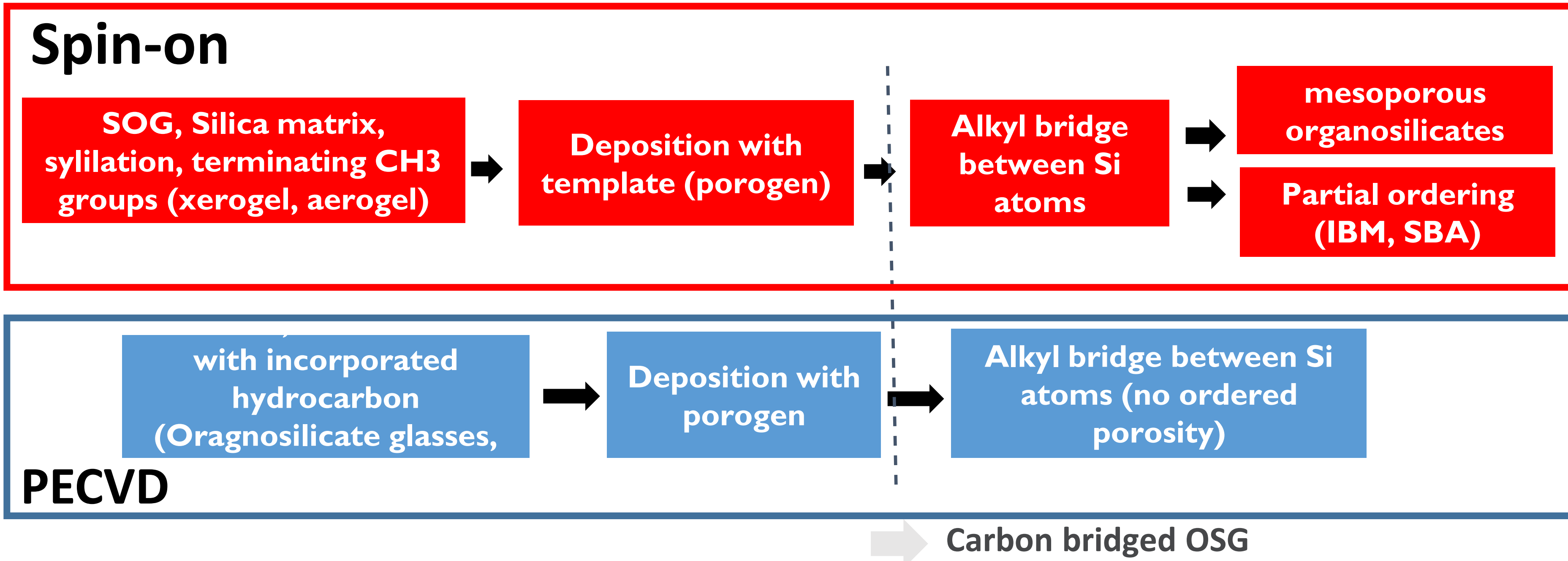
Roadmap and present selection



➢ Low porosity of 2.55 OSG materials enables to minimize plasma damage and to achieve the smallest integrated k-value with reasonably good mechanical properties and reliability

Carbon bridged low-k films ?



- There is a clear interest to carbon bridged low-k materials in both PECVD and SOG because of expected improvement of mechanical properties.
- Some carbon bridged low-k materials form perfectly ordered pores (PMO). Successful examples are INTEL and some Universities.
- Some materials with carbon bridged materials form “no” or “limited” ordering with properties similar to PMO (A.Grill-PECVD, SBA Mat.-SOG, IBM Almaden-SOG)

SBA material

Preparation technique

Soft-bake at 150˚C for 2 minutes in air

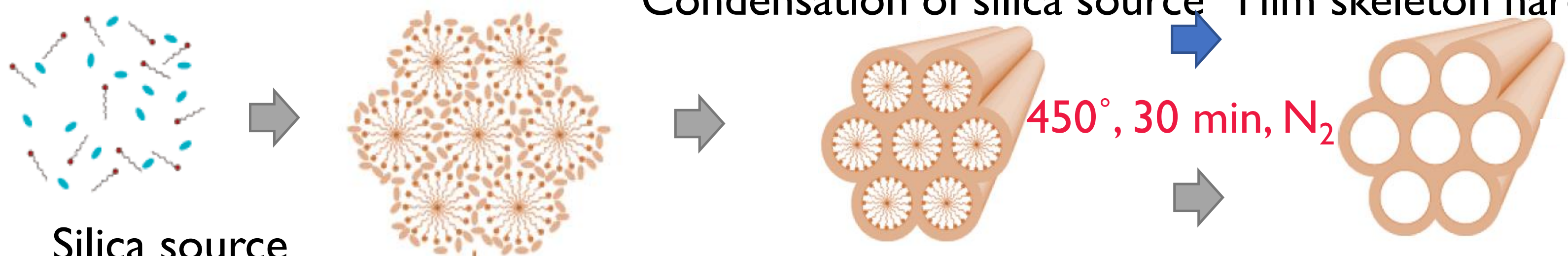
Self-assembly of surfactant

Curing

Removal of surfactant

Condensation of silica source

Film skeleton hardening



450˚, 30 min, N_2

UV, λ > 200 nm 400 ˚C

Silica source

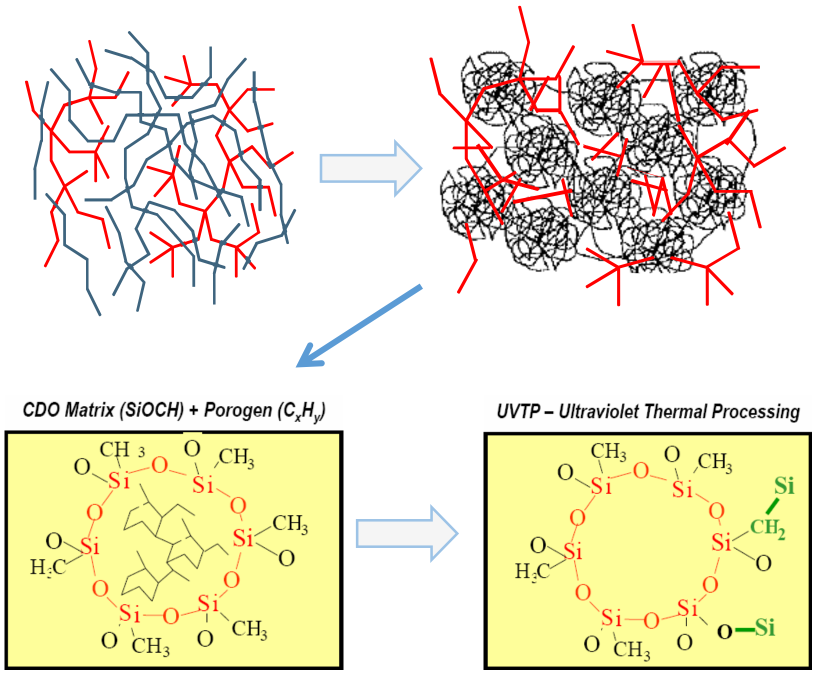
Surfactant

Silica source

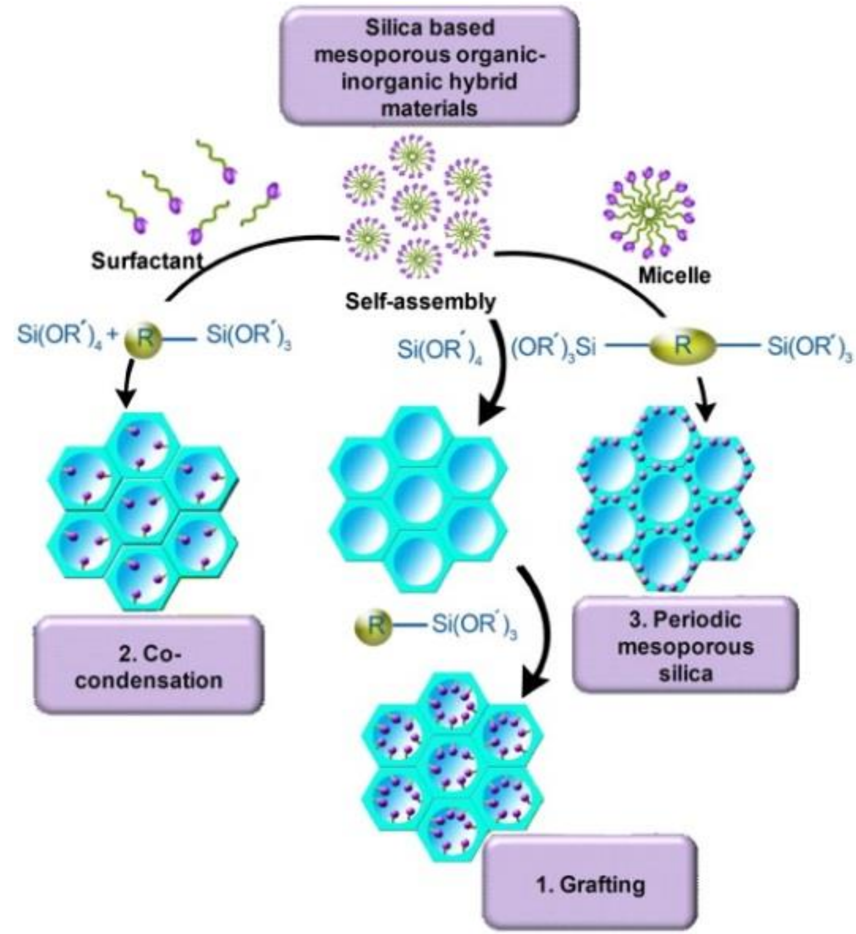
TEOS	Terminally alkylated silicate ester	Alkyl-bridged silicate
$Si(OC_2H_5)_3$	$Si(OC_nH_{2n-1})_x(C_nH_{2n-1})_{1-x}$	$\equiv Si - (C_nH_2)_n - Si \equiv$

PECVD versus self-assembling chemistry

PECVD



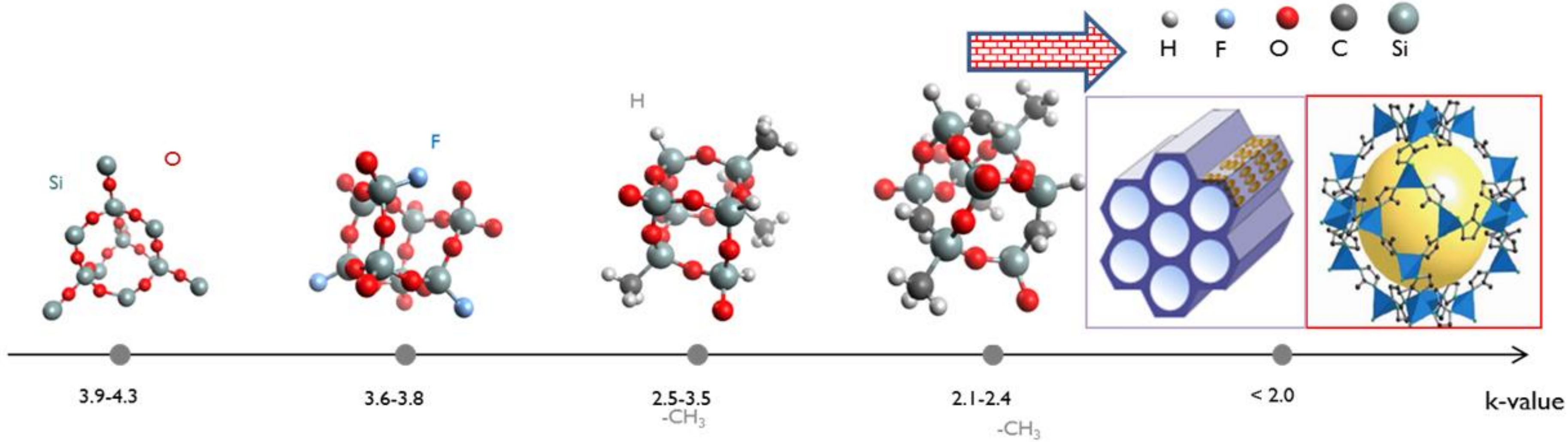
PMO



- Self-assembling chemistry (PMO) enables better control the pore and skeleton structure in comparison with PECVD materials.
- More attention to PMO ?

Low-k materials: GENERAL roadmap

- Ultimate k value is that of air (k=1)
- Si-O bonds are replaced to less porous
- To achieve k-values < 2.8 artificial porosity needs to be introduced
- To improve mechanical properties cross linking is necessary



SiO2	F-SiO2	OSG	P-OSG	P-OSG, PMO	PMO, MOF...
K=4.0	K=3.5-3.7	K=2.7-3.0	K=2.5-2.7	K=2.0-2.5	K = (<2.0) -2.2
180 nm	130 nm	90, 65, 45 nm	45, 22, 10 nm	< 10 nm	< 7 nm

- Self assembling chemistry gives a benefit

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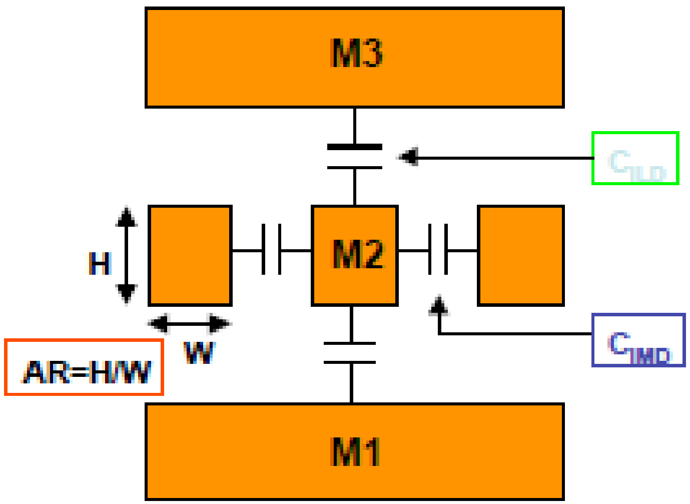
INTERCONNECT'S BASIC REQUIREMENTS



- Low R □ replace Al by Cu
- Low C: replace SiO2 by low-k

$$C_{inttot} = C_{ILD} + C_{IMD} = 2l\left(\frac{\varepsilon_{ILD}}{AR} + \varepsilon_{IMD} AR\right)$$

RC-Delay

$$\tau \propto RC_{inttot}$$

Power

$$P = \alpha C_{inttot} V^2 f \propto C_{inttot}$$

Crosstalk

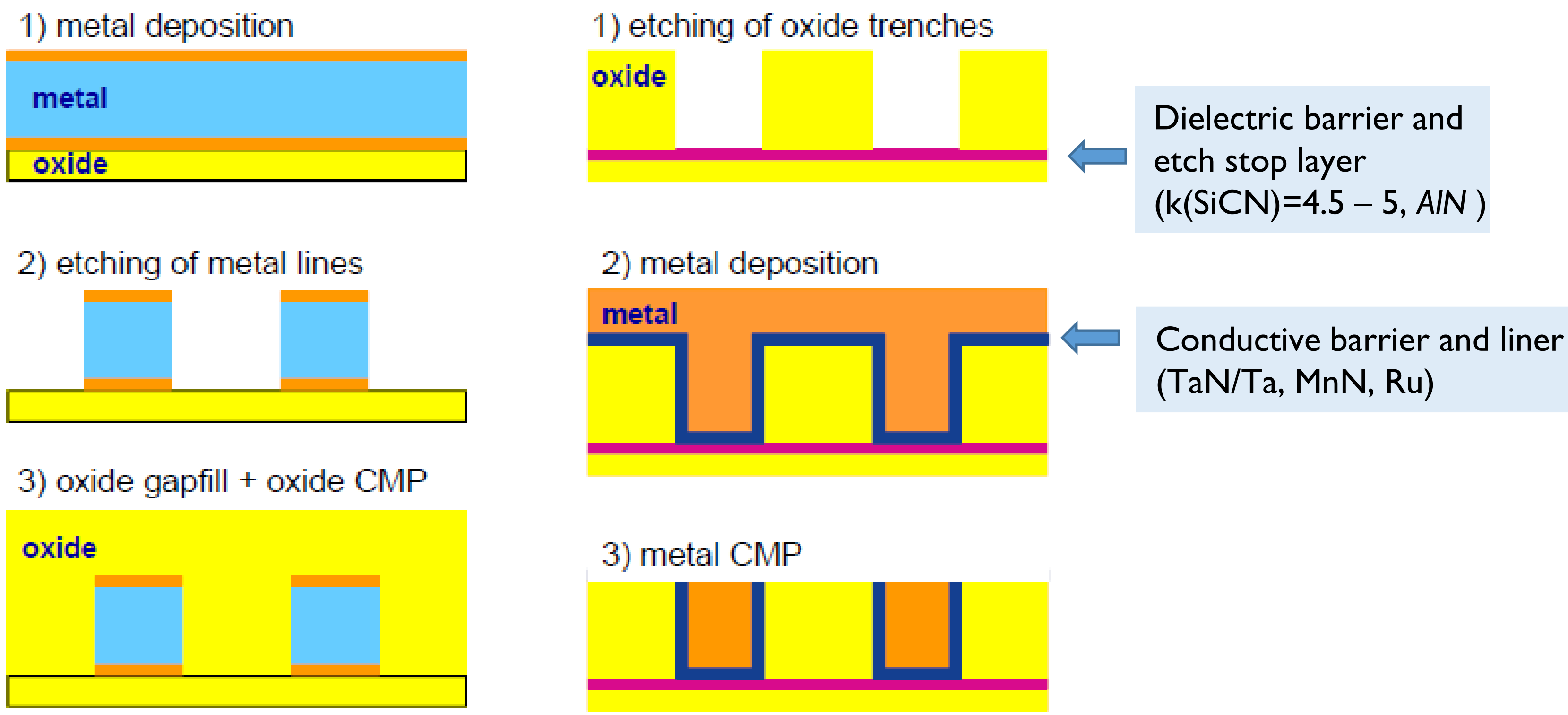
$$X_{talk} \propto \frac{C_{IMD}}{C_{inttot}} = \frac{1}{1 + \frac{\left(\varepsilon_{ILD}/\varepsilon_{IMD}\right)}{AR^2}}$$

Challenges:

- Plasma damage (etch strip, post CMP cleaning)
- Barrier thickness and deposition damage

(metal penetration into pores and N2 plasma)

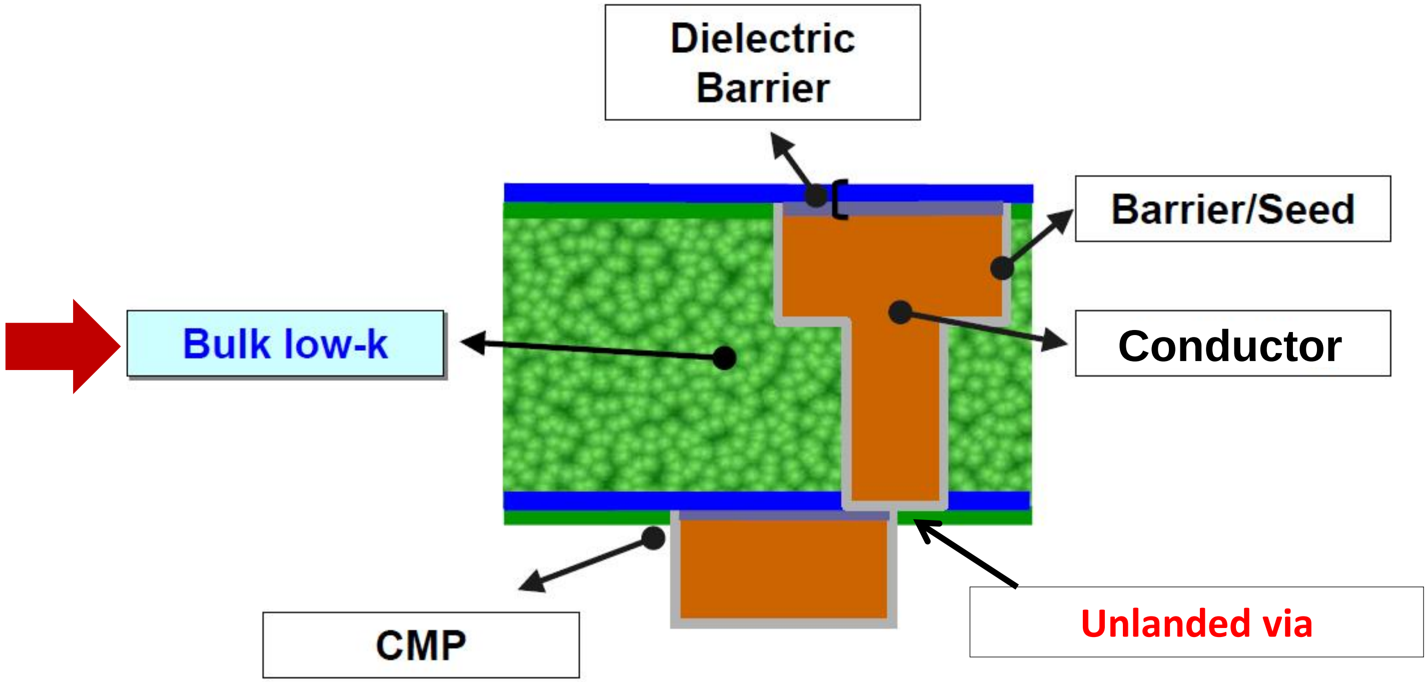
METAL ETCH VERSUS DAMASCENE



classical metallisation (Al) damascene metallisation (Cu)

- Introduction of damascene technology was related to replacement of Al by Cu since Al is patterned by RIE while all efforts to apply RIE to Cu failed.
- The barrier layers are becoming comparable with low-k thickness and “kills” the expected benefits. The pore size doesn’t allow efficient scaling of the barrier thickness

Large pore size and thin barriers are in conflict



- What is more important: OSG k-value or barrier thickness ?
- K = 2.55 for 10 and 7 nm technology nodes

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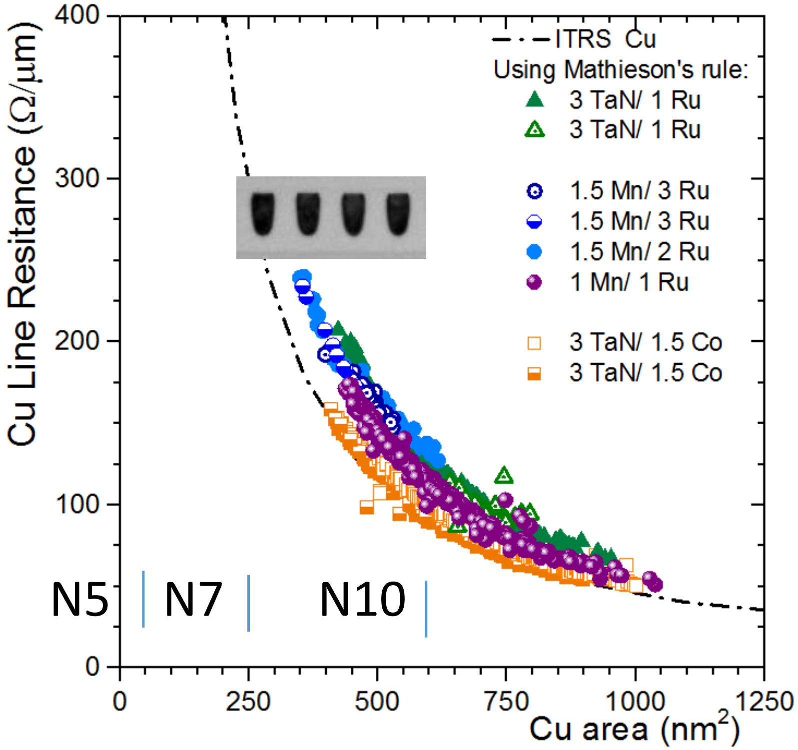
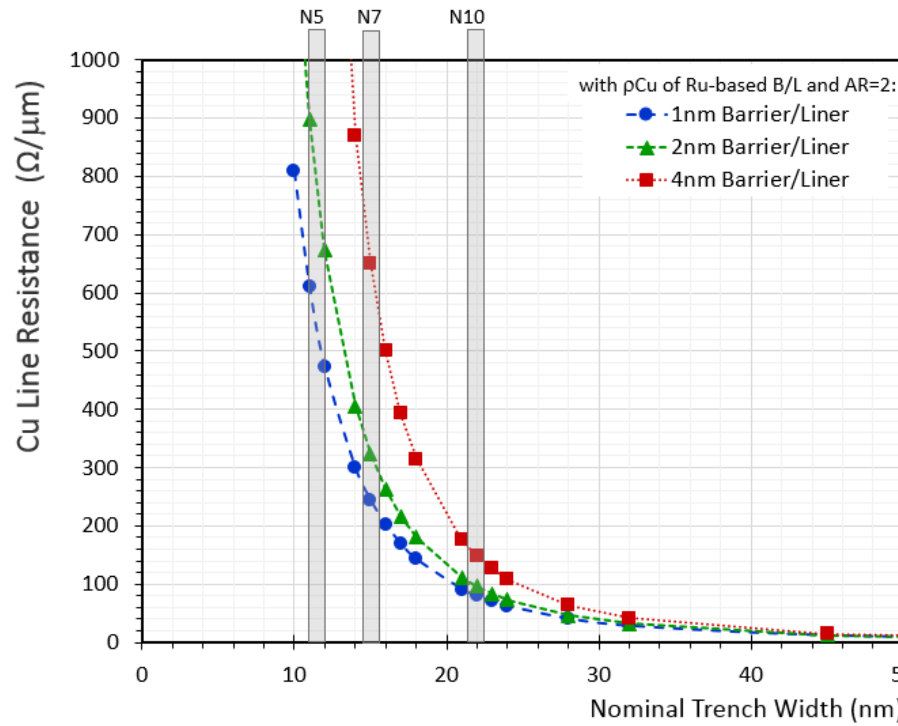
Metal: Wire resistance

Resistance: Si-data



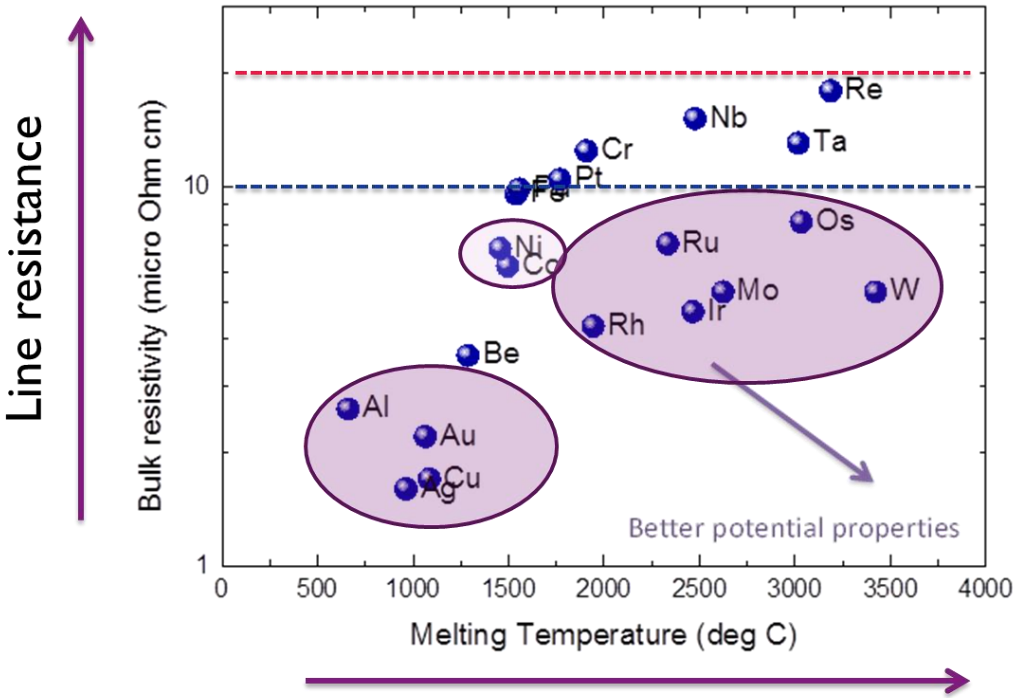
Resistance: model

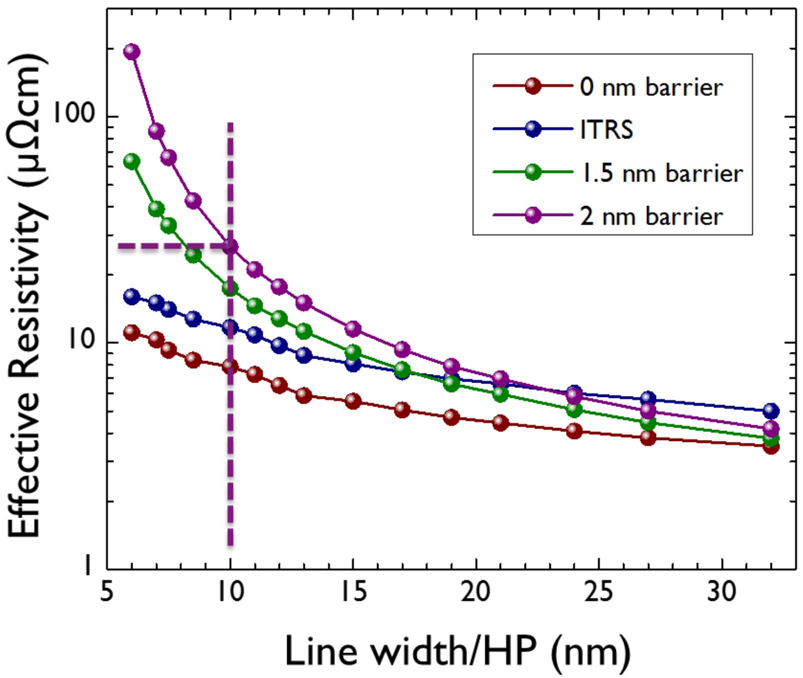


Zs. Tokei, Spring MRS 2015

➢ What is the pore size if low-k needs be sealed by 1 nm thick barriers ?

Alternative metals





At 10nm CD a resistivity of <25 μΩcm is competitive

Zs. Tokei. Spring MRS 2015

Intermediate conclusions

- The k-value scaling via porosity introduction degrades low-k properties: mechanical properties, plasma damage, barrier thickness and quality…

- The metal selection meets 2 contradictory problems:

- better R → worse EM
- Better EM → worse R

Prof. Iwai (ICSICT): Interconnect materials and methods are reaching the physical limit. Now approaches are needed

Outline

- Introduction
- Why low-k and why needed ?
- ITRS roadmap and available low-k materials
- Organosilicate glasses: PECVD and SOG.
- Low-k materials for 10 nm technology node and beyond
- **Challenges of integration**
- Barriers and conductors
- Innovative solutions for integration

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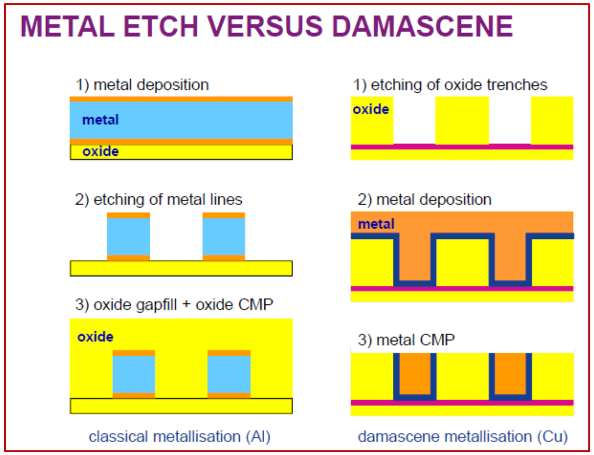
- **Innovative solutions for integration**

(pore stuffing, cryogenic etch, replacement low-k)

Routes for the integration technology



Present (damascene) technology

Damascene technology (dielectric etch)

What we need:

- Reduce pore size and porosity;
- Thin barriers compatible with porosity
- New metals
- Low damage patterning

130 nm – 3 nm technology node ?

Subtractive technology (metal patterning)

What we need:

- Patterned metal (Etch Al, Cu, select Ru)
- Low-k curing in narrow space

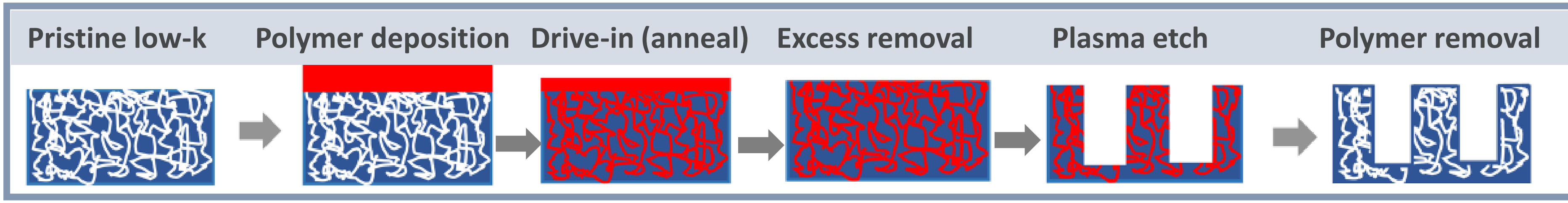
> 130 nm technology node

< 10 nm technology node ?

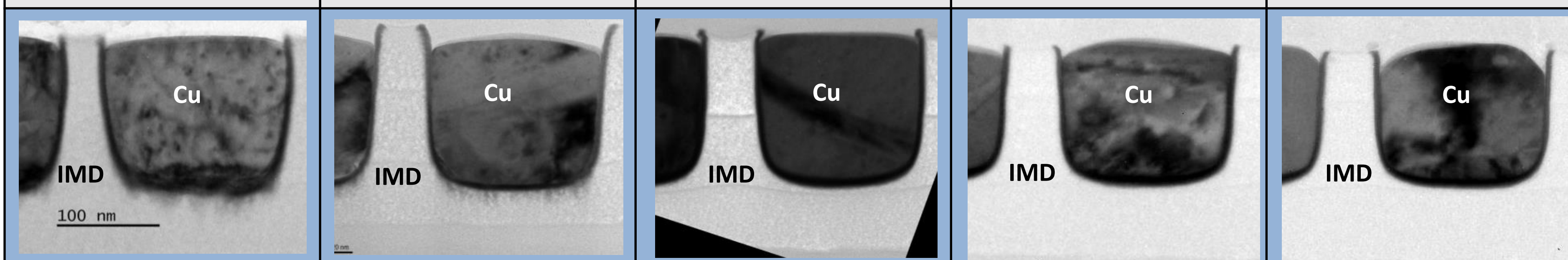
Pore stuffing by polymers (P4 approach)

T. Frot et al. US patent
T. Frot et al. (2011) Adv. Mater., ***23****(25), p. 2828.*
T. Frot et al. (2012) Adv. Funct. Mater., ***22****(14), p. 3043.*
M. Heyne et al. (2014) J. Vac. Sci. Technol. B., ***32****(6) p. 062202.*
L.Zhang et al. (2016) J. Physics D: Appl. Phys. In press

Pore stuffing by polymers (P4 approach)



No protection Reference process	PMMA protection Post etch de-stuffing	PMMA protection Post Metal de-stuffing	PMMA protection Post Metal de-stuffing	PMMA protection Post Metal de-stuffing
TA-420ºC-60min	TA-420ºC-60min	DSP-250ºC-540s	TA-420ºC-60min	UV-385ºC-60s
k_{eff}= 4.02 ± 0.35	k_{eff}= 3.04 ± 0.26	k_{eff}= 2.64 ± 0.20	k_{eff}= 2.56 ± 0.22	k_{eff}= 2.50 ± 0.22



- **Pristine k-value was 2.0**

M. Baklanov et al, AVS 62th Symp, Oct 2015

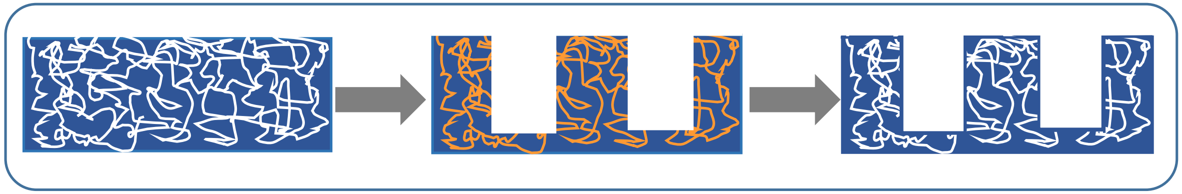
Cryogenic etch

M. Baklanov et al. EU, US and Japan patents
L. Zhang et al. (2013) *ECS Solid State Lett.*, **2**, 2, p. 5.
L. Zhang et al. (2013) *ECS Sol. St. Sci. & Technol.*, **2**(6), p. N131.

Options for cryogenic etch

GREMI: T < - 120C

1. Pristine material — 2. Plasma etch and **products condensation** — 3. Outgassing

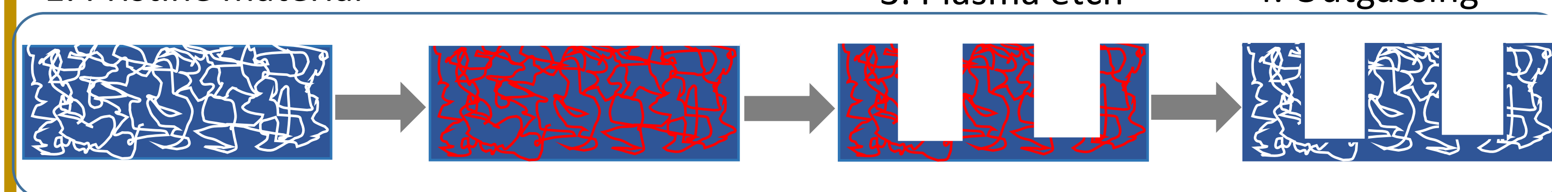


Challenges:

- ➢ not possible to control operation T. In the case of OSG etch, the products condense at -120C.
- ➢ Complicated products composition require high temperature annealing for unstuffing.

OINT: T < -80 C; TEL: T > -50C

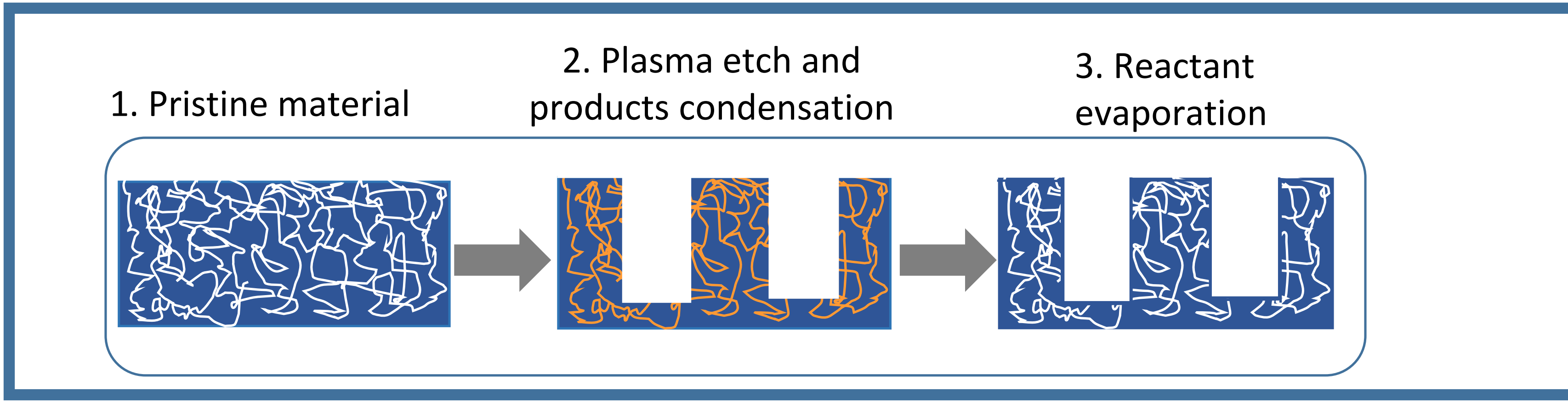
1. Pristine material — **2. Reactant condensation** — 3. Plasma etch — 4. Outgassing



Expected advantage:

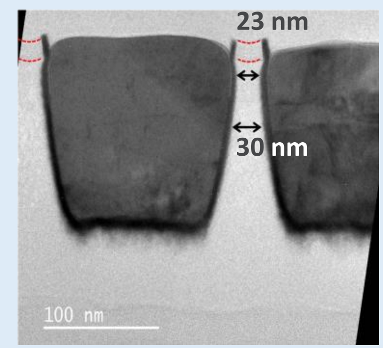
- ➢ Theoretically any temperature can be selected with appropriate choice of the etch chemistry.
- ➢ No fundamental difference with pore stuffing by polymers

M. Baklanov et al. EU, US and Jap. patents



1) $SiCH_3 + F$ (**SF6**) → $SiCH_2 + HF$	k~1e-12 cm^3/s
2) $SiCH_3 + O$ → $SiCH_2 + OH$	~1e-16 cm3/s
3) $SiCH_2 + O$ → $SiCH_2O$	fast
4) *$SiCH_2O + OH$ → $SiCH_2OH + O$*	~1e-17 cm3/s
5) *$SiCH_2 + OH$ → $SiCH_2OH$*	fast
6) $SiCH_2 + OH$ → $SiCH + H_2O$	~2.6e-11 cm3/s
7) *$SiCH + O_2$ → $SiC(H)=O + O$*	1e-13 cm3/s

Reactions products 4, 5 and 6 confirmed by FTIR analysis



K=2.38 at k=2.31 for pristine

M. Baklanov et al. Sol.St.Technol. 57, 5 (2014)

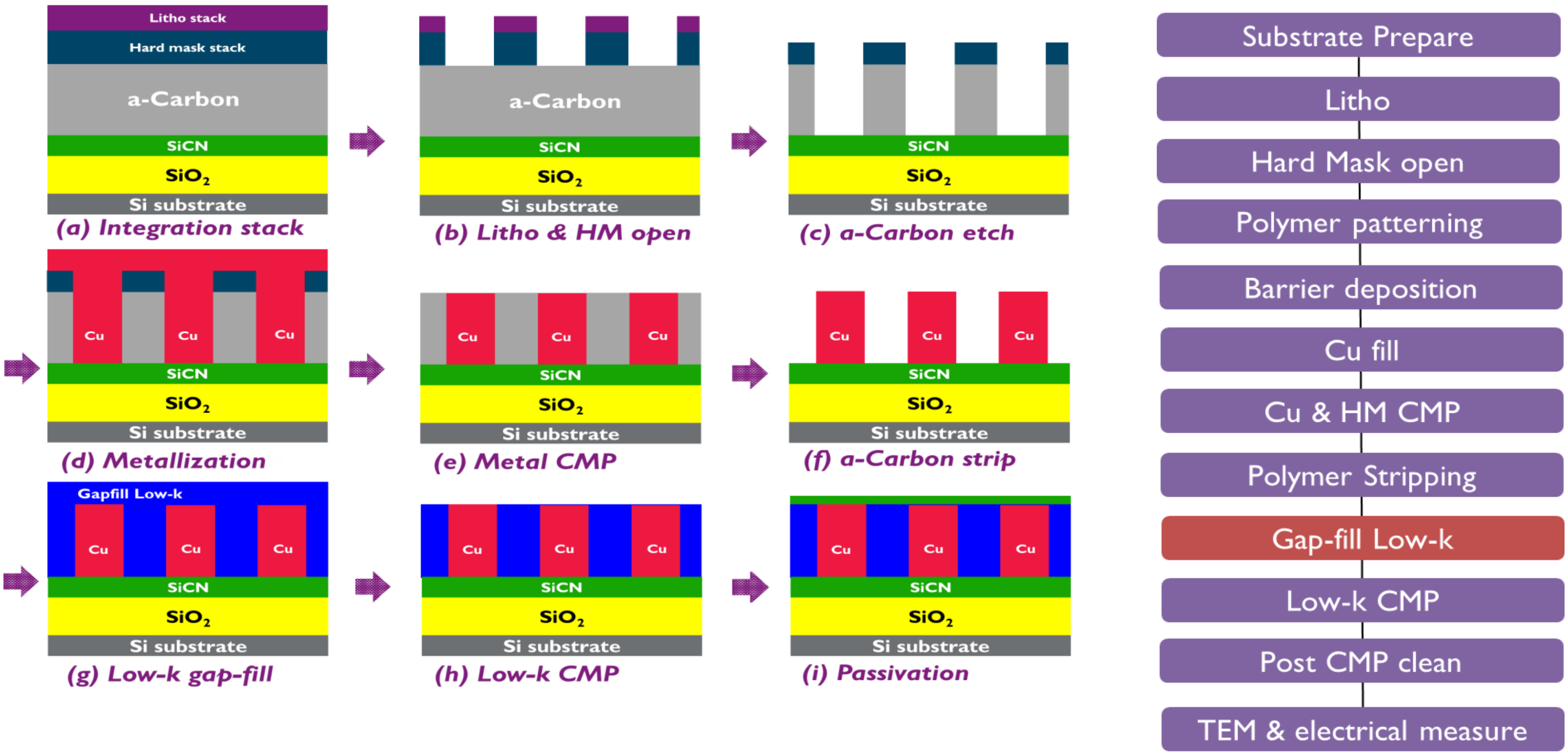
Challenges:

- The reaction products condense at T < -120C.
- No available industrial etch equipment operating at so low-k temperature

Replacement low-k

Replacement low-k

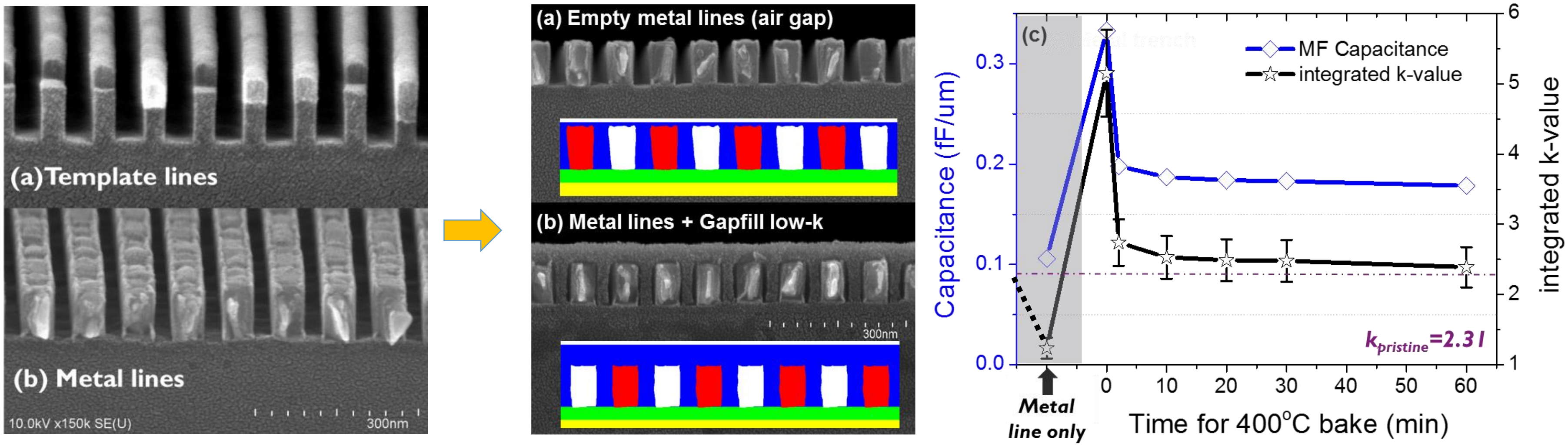
- Patterning template, Metallization, Template removal and Gap-fill low-k deposition.



- This approach does solve the two major challenges in conventional Cu/low damascene integration: ***low-k plasma damage*** and ***metal penetration during barrier deposition*** on porous structures.

L. Zhang et al., APPL. PHYS. LETT. 107, 092901 (2015)

Replacement low-k



- 1st integration lot, using **a-Carbon** as template and **Spin-on low-k** for gapfilling.
- Keff~2.39 is obtained on a 35nm gap. (integration Δk < 0.1 compared with pristine material.)

L. Zhang et al., APPL. PHYS. LETT. 107, 092901 (2015)

Conclusions

The key problem is large pore size of ultra low-k materials:

- Plasma damage -> huge degradation of dielectric constant and reliability
- Mechanical weakness -> do not survive during the packaging
- Electrical degradation -> leakage current, breakdown field, reliability
- Compatibility with barrier deposition
- Compatibility with damascene technology

Challenges and directions:

- Pore size and barrier thickness reduction -> selected for 10 and 7 nm technology nodes.
- Pore stuffing -> technology complication, limited protection against plasma damage, CTE…
- Cryogenic etch -> technology complication, barrier compatibility
- Pore sealing by SAM before metal barrier deposition and new barriers
- Subtractive integration: metal etch and low-k replacement: spin-on is important
- Selective deposition.