

### Q1 Which types of chemical reactions involved Chemical Vapor Deposition processes do you know?

One reactand = precursor

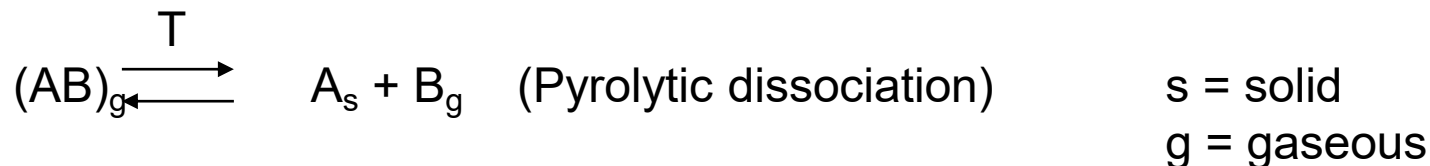
- 1) (thermal decomposition/) pyrolysis (one precursor)
- 2) Disproportionation (e.g. Cu precursor Cupraselect™)

Two reactands (two precursors or one precursor and one co-reactand) or more

- 1) Reduction (W-CVD: precursor WF<sub>6</sub>, co-reactand: Hydrogen H<sub>2</sub>)
- 2) Oxidation (formation of an oxide: two precursors)
- 3) Nitridation (TiN deposition using TiCl<sub>4</sub> + NH<sub>3</sub>, two precursors)

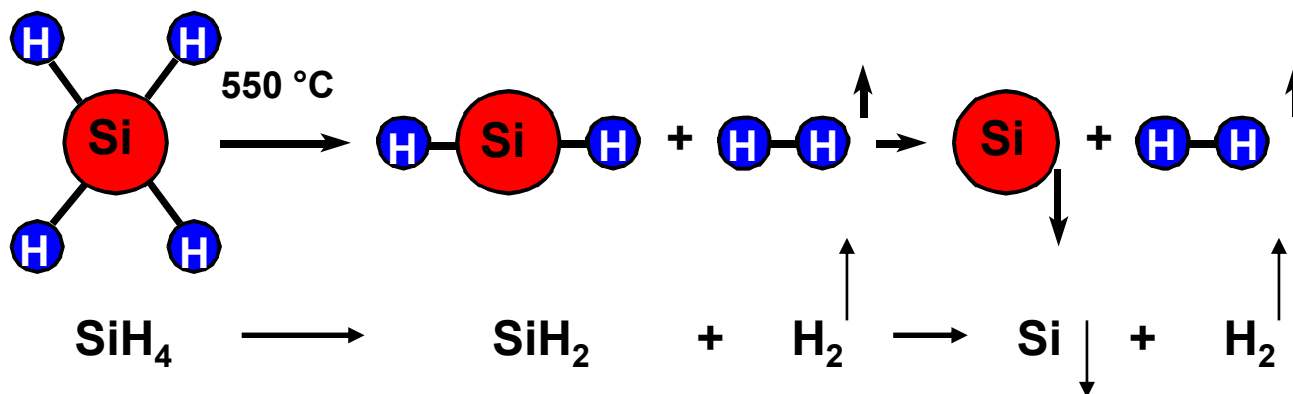
## Typical reaction types in CVD

### 1. Dissociation reaction

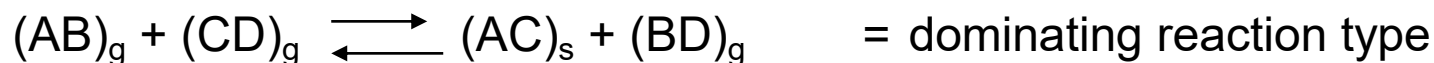


**Pyrolysis:** Thermal decomposition of gaseous species (hydrides, carbonyls, metal-organic compounds) on hot substrates

→ Example: *LPCVD of polycrystalline or amorphous silicon films*

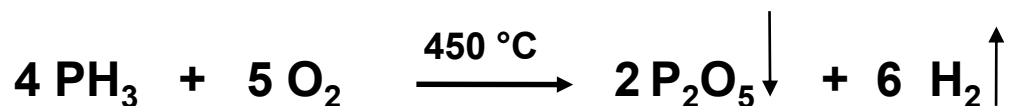
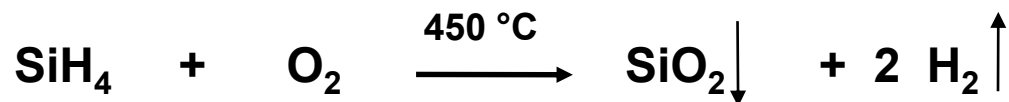


## 2. Reaction of two gaseous substances on the surface



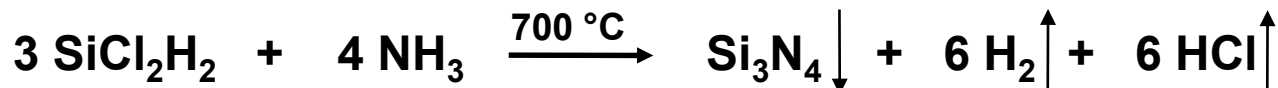
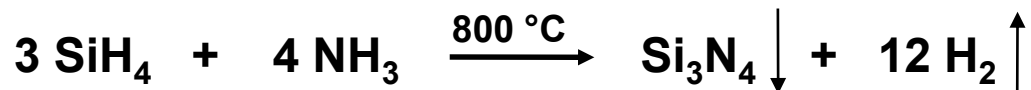
**Oxidation:** CVD of  $\text{SiO}_2$  and glasses by reaction of gaseous hydrides or halides of Si and dopants with oxygen or oxygen-containing compounds

→ Example: **LPCVD of PSG**



**Nitridation:**

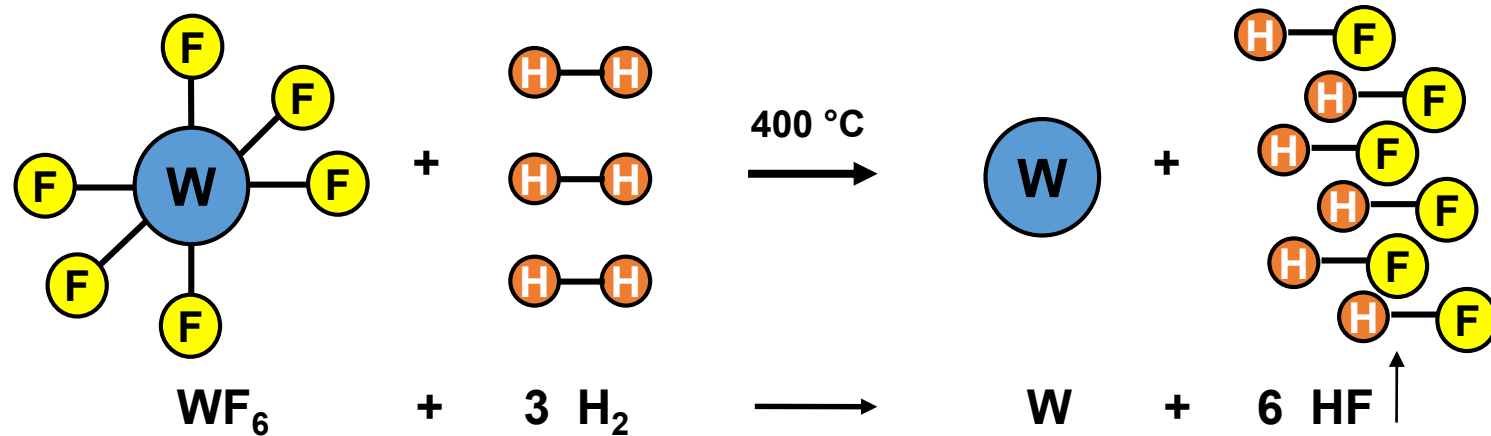
→ Examples: **LPCVD of silicon nitride**



**Reduction:** Reaction of halides or oxygen-containing compounds with hydrogen or hydrogen-containing compounds to generate solid deposits and gaseous byproducts

→ Examples:

LPCVD of Tungsten, blanket deposition



### Q2 What are requirements for diffusion barriers?

- very thin and very stable
  - thermodynamically stable (no reactions with adjacent films), no diffusion
  - high density
  - defect free (no pinholes)
- low resistivity (some 100  $\mu\text{Ohmcm}$ )
- good adhesion to the underground and also of layers on top of the barrier
- low mechanical stress
- ...

## Requirements for conducting CVD barriers (in copper interconnects)

- Ultrathin, but nevertheless very stable
  - High density / no or stuffed diffusion paths
  - Low defect level
  - Thermodynamically stable
- Good adhesion to underground and Cu
- Low stress
- Low resistivity
- Conformal or at least uniform sidewall coverage

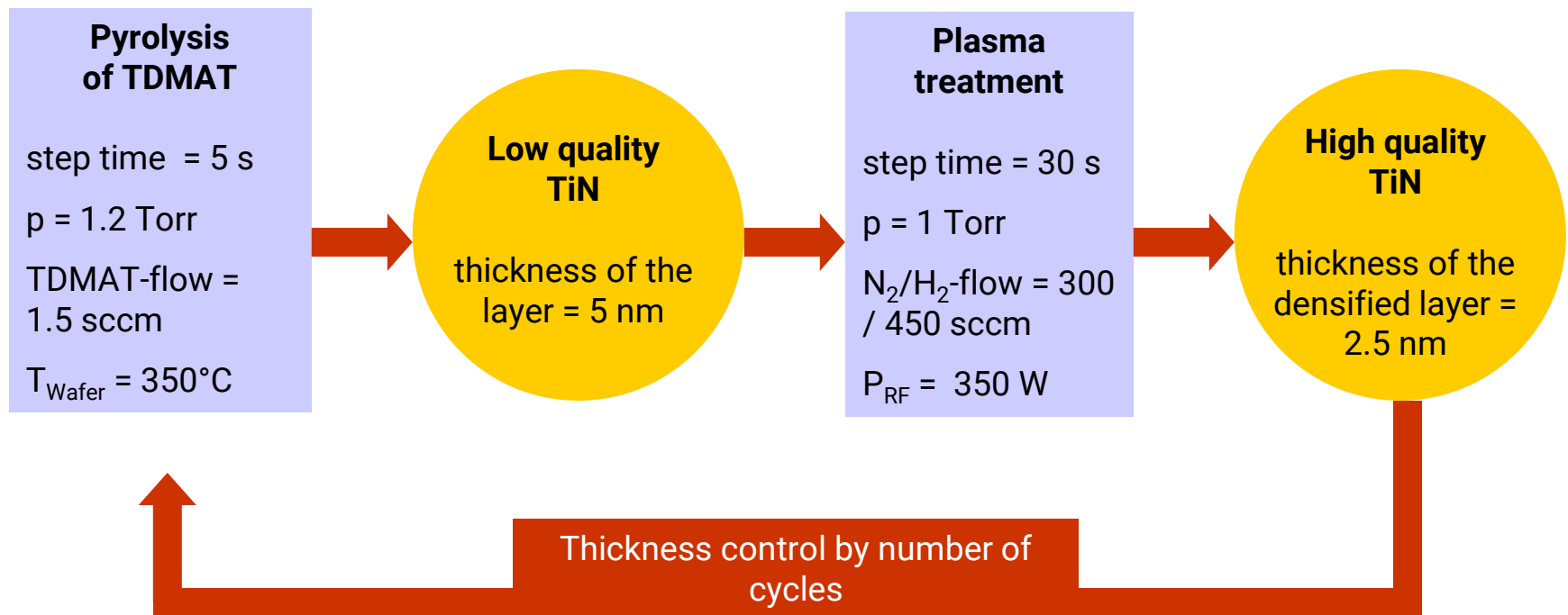
### **Q3 Please name the two steps in an MOCVD TiN deposition process using TDMAT precursor!**

- 1) deposition step: decomposition of TDMAT
- 2) post-treatment step: plasma treatment (N<sub>2</sub>/H<sub>2</sub>)

## CVD of Copper diffusion barriers: TiN by MOCVD from TDMAT

### Multistep process for high quality TiN

Method was introduced by  
M. Danek and coworkers (Applied Materials), 1995





## **Q4 What is the purpose of plasma post-treatment of MOCVD deposited TiN diffusion barrier films?**

- Film densification
- Lower resistivity (higher density, lower contamination level, lower oxygen uptake during air exposure)
- Amorphous → nanocrystalline film (nanocrystals embedded in an amorphous matrix)
- Decrease the contamination content in the film (C, O)
- Improvement in diffusion barrier properties

## **CVD of Copper diffusion barriers: TiN by MOCVD from TDMAT - Film properties**

	<b>without plasma treatment</b>	<b>multi step process with plasma treatment</b>
Spec. el. resistivity	$\approx 8000 \mu\Omega\text{cm}$	$170 \mu\Omega\text{cm}$
Stability of resistivity if exposed to air	increase $\approx 200\%$	increase $< 2\%$
Density (bulk value = $5.2 \text{ g/cm}^3$ )	$2.2 \text{ g/cm}^3$	$4.8 \text{ g/cm}^3$
Film stress (all compressive)	- 300 MPa (as dep.) - 500 MPa (after air exp.)	- 1400 MPa (as dep.), no change after air exp.
Microstructure	amorphous like	polycrystalline
Impurities	$\approx 25 \text{ at.}\% \text{ C}$ , $\approx 25 \text{ at.}\% \text{ O}$ if exposed to air	$6 \text{ at.}\% \text{ C}$ , $5 \text{ at.}\% \text{ O}$ if exposed to air
Barrier stability against copper diffusion (electrically tested with pn-diodes)	fails already at $350^\circ\text{C}$	stable up to $450^\circ\text{C}$

## **Q5 Please define the term “epitaxy” as a special type of CVD process!**

- Deposition (CVD) of a single crystalline film (high dep. T)
- On a single cryst. Substrate

## **Q6 What is the difference between “homoepitaxy” and “heteroepitaxy”?**

Homoepitaxy: identical material of substrate and growing film

Heteroepitaxy: different materials of substrate and film

**Epitaxy is the growth of single crystalline films upon the surface of a single crystal substrate.**

**Homoepitaxy**

identical

chemical composition of substrate and deposited film

**Heteroepitaxy**

different

**Examples:**

Si/Si  
SiGe

Ge/Si  
Si/Al<sub>2</sub>O<sub>3</sub> (Silicon on Sapphire)  
GaAlAs/GaAs (HEMT, HFET)

**Applications:**

- Bipolar: - Definition of transistor regions by vertical doping  
- SiGe structures heterojunction bipolar transistors (HBT)
- CMOS: - Minimization of the vertical "latch-up" effect (switching of a parasitic p-n-p-n thyristor) by deposition of lightly doped epi-Si on heavily doped substrates  
- Formation of strained Si on SiGe for higher electron mobility

**Techniques:**

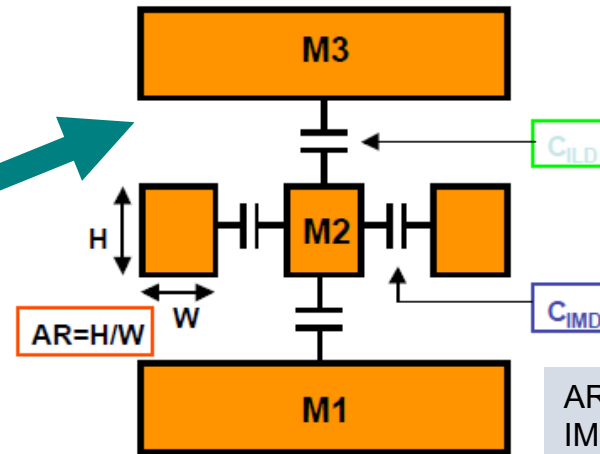
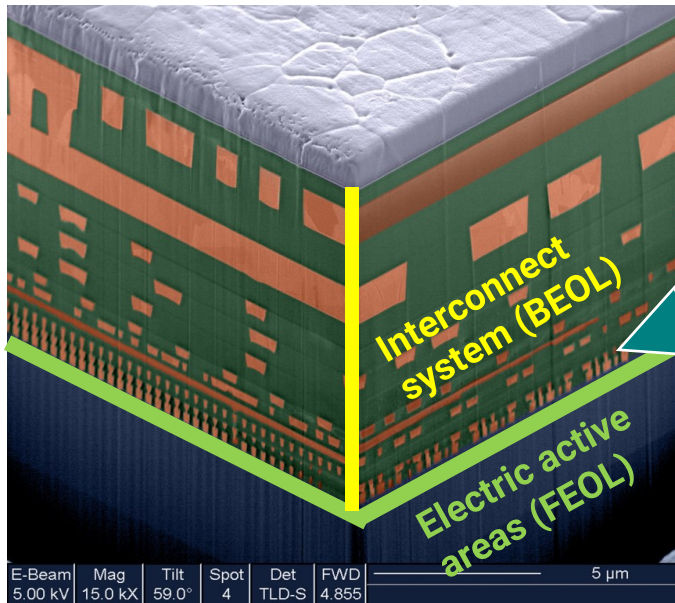
- **Vapor-phase epitaxy** (VPE, similar to CVD, dominating in Si processing)  
special case: Molecular Beam Epitaxy (MBE)
- Liquid-phase epitaxy (LPE, III-V compounds)
- Solid-phase epitaxy (SPE, annealing of amorphous layers)

**Q7** What is the motivation to use low-k dielectrics instead of conventional silicon dioxide as insulator/dielectric in on-chip interconnect systems?

Lowering parasitic capacitances, to lower or minimize:

- cross-talk between metal lines
- power consumption
- Signal delays

## Interconnect Challenges – Shrinking feature sizes



AR = aspect ratio  
IMD = intermetal dielectric  
ILD = interlevel dielectric  
 $\epsilon_r = k$

$$C = \epsilon_0 \epsilon_r \frac{A}{d}$$

### RC-Delay

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

### Power (consumption)

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

### Crosstalk

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

To  
minimize/  
decrease

Goal: lower parasitic capacitances in the interconnection system  
by integration of dielectric materials with lower permittivity (k-value)  
compared to standard SiO<sub>2</sub> (k=3.9...4.3)

**Q8** How can a lower k-value be achieved compared to  $\text{SiO}_2$ ?

(two different systematics: 1+2; A+B)

1) lower the material's density

- Introduce porosity via localized pores (0.5 – 2 nm size)
- Increase bond length
- Terminating groups

2) lower the polarizability: no dipoles, low pol. of bonds itself (e.g. Si-F, Si-C)

A) Change bond properties

- Higher bond length ( $\rightarrow$  lower density)
- Introduce elements (F) or groups ( $\text{CH}_3$ ) terminating properties – Si-F; Si-C(-H)<sub>3</sub>
- low pol. of bonds itself

B) Localized pores – introduce porosity

## How to build a low dielectric constant material?

### 1. Minimize polarizability

- Choose a nonpolar dielectric system: polarity is weak in materials with few polar chemical groups and with symmetry to cancel the dipoles of chemical bonds between dissimilar atoms
- Introduce elements with smaller electronic polarizability, e.g. C, F

Bond	C–C	C–F	C–O	C–H	O–H	C=O	C=C	C≡C	C≡N
Polarizability (Å )	0.53	0.56	0.58	0.65	0.71	1.02	1.64	2.04	2.24

(Source: K.J. Miller et al., Macromolecules, 23, 3855 (1990))

- Minimize the moisture content of the dielectric / design a dielectric with minimum hydrophilicity ( $k_{\text{water}} \approx 80 \rightarrow$  only small traces of water need to be absorbed before the low-k dielectric loses its permittivity advantage)



## How to build a low dielectric constant $k$ material?

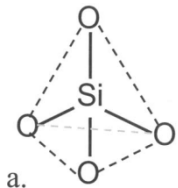
### 2. Increase the free volume $\rightarrow$ reduce $N_j$

#### Microscopic level:

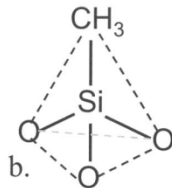
- $\rightarrow$  increase bonding length, bonding orientation, e.g. partially substitute Si-O (1.5097 Å) by Si-CH<sub>3</sub> (1.857 Å)
- $\rightarrow$  discontinue the network by inserting single bond atoms or groups in the backbone structure: adding F or CH<sub>3</sub> into SiO<sub>2</sub> network

#### Macroscopic level:

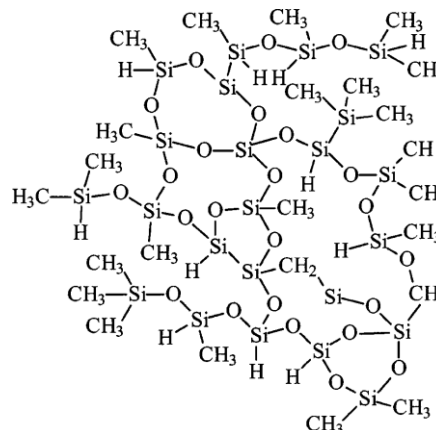
- $\rightarrow$  Add porosity ( $k_{\text{air}} = 1$ ): incorporation of a thermally degradable material (porogen) within a host matrix



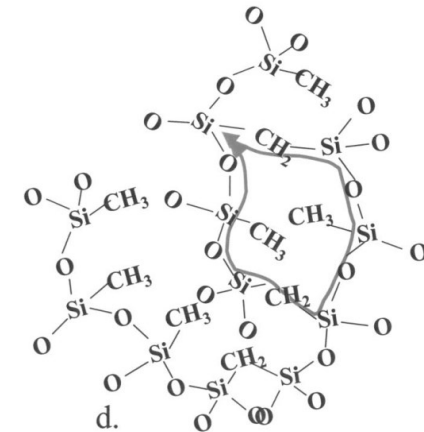
SiO<sub>2</sub>  
 $k \approx 4.0$



C-doped oxide  
 $k \approx 3.0$



Dense SiCOH  
(Precursor TMCTS)  
 $k \text{ min. } 2.6$

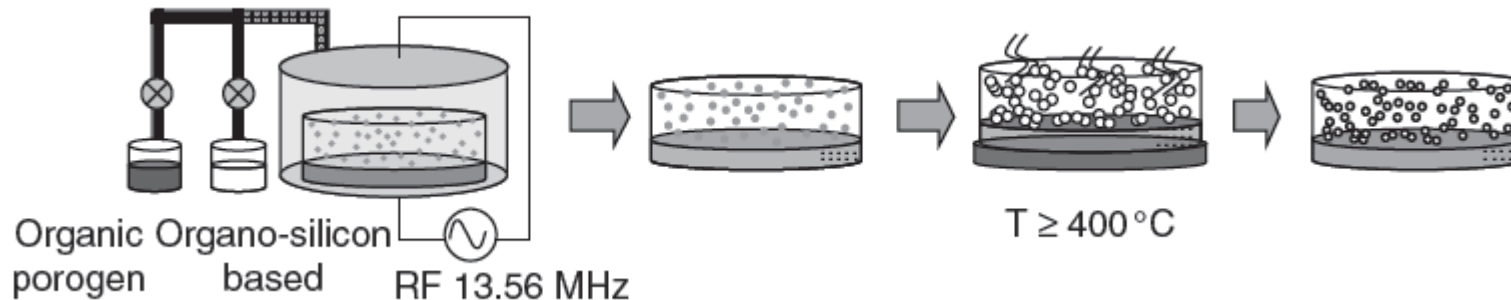


Porous SiCOH  
(Precursor TMCTS +  
Porogen)  
 $k \approx 2.1 - 2.5$

**Q9** Which types of processes can be used for low-k dielectric deposition?  
Which of those is *most frequently used* in IC production?

- 1) Spin-on process
- 2) *Plasma-enhanced CVD (PECVD)*

## Deposition of porous low-k dielectrics by PECVD



**PECVD porogen approach:** sacrificial process, currently performed in high-volume manufacturing for 32 / 28 nm technology nodes and below

- Deposition from the decomposition of (at least) two precursors in the plasma
  - Pure organic molecule (porogen)
  - Molecule consisting of silicon atoms and organic radicals (matrix precursor)
- Formation of a „hybrid“ film composed of organosilicate-based matrix enclosing organic inclusions

**Q10** Which type of post-deposition (curing) processes can be used to form porous low-k dielectrics?

What is the purpose of those curing processes and which film properties are affected?

- 1) Thermal annealing (T)
- 2) Thermal annealing (T) + UV radiation
- 3) Thermal annealing (T) + e-beam
- 4) Thermal annealing (T) + Plasma treatment by using H<sub>2</sub>
- 5) Supercritical CO<sub>2</sub> treatment

Purpose/affected properties:

- Removal of porogen (C-organic material)
- Porosity (higher) / density (lower)
- Shrinkage (film thickness reduction, needs to be minimized)
- Permittivity → lower k-value
- Increase of crosslinking in the matrix material → enhance mechanical properties
- Mechanical properties: hardness, Young's/elastic modulus decrease
- Thermal conductivity is lower

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### **Post-deposition treatment (curing)**

- thermal annealing, UV-assisted thermal annealing, e-beam assisted thermal annealing, H<sub>2</sub> plasma, supercritical treatment in CO<sub>2</sub>

### Purpose:

- removal of the organic phase, mostly consisting of porogen molecule fragments → Film becomes porous and has ultra low-k properties
- Improvement of mechanical properties of matrix network by additional cross-linking

### Affected film properties

- porosity/density
- mechanical stability (hardness, Elastic modulus)
- Thermal conductivity