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# Pure-Silica-Zeolite Low Dielectric Constant Films: Present and the Future

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The semiconductor industry has been evolving at an remarkable pace for the past four decades. To continue the evolution at this pace, new materials with unique combination of properties have to be introduced and incorporated, and one of them is low dielectric constant (low-k) materials. The material of choice for dielectric materials since the inception of the semiconductor industry has been dense silica that has a  $k=4.0$ . To reduce  $k$ , many materials have been studied and one major class is porous silica. Incorporation of air reduces  $k$  because air has a  $k$  of about 1. Here pure-silica-zeolite as a possible low- $k$  material is reviewed. Its major advantages over other porous silicas such as sol-gel silica and mesoporous silica are high mechanical strength, high thermal conductivity, and low hydrophilicity. The performance data and the deposition processes for zeolite low- $k$  materials are analyzed. The data available so far are promising, but more characterizations are needed and many technical issues are yet to be resolved. The future research needs for this technology are also discussed.

Keywords: zeolite, film, dielectric, silica, porous

## 1. The integrated circuit (IC) evolution

Since the first integrated circuit (IC) was invented in 1961 by Robert Noyce, the IC industry has been evolving at a remarkable pace and it has been exceptionally successful in delivering operating speed and affordability to its customers. This success is well reflected by the ever increasing popularity and capability of desktop, laptop and palmtop computers. The emphasis of this evolution so far has been the increase of density of transistors, the move to process larger silicon wafers (*e.g.*, 200 mm to 300 mm), and the stringent control of manufacturing processes to improve yield. Figure

1 shows the evolution of Intel microprocessors over the past three decades. The number of transistors on a single chip has grown from 2250 in the first generation 4004 Intel chip to a mind-boggling 55 million in Xeon. The corresponding clock speed has increased 5 orders of magnitude from  $6 \times 10^4$  Hz to  $2.8 \times 10^9$  Hz (2.8 GHz). The number of transistors on a single chip is predicted to reach 1 billion in 2007. Gordon Moore, the cofounder of Intel, made the observation in 1965 that the number of transistors on a single chip would double every 18 months, and the IC industry has been on track ever since (Figure 1).

## 2. The interconnect

To have the needed logic function of a microprocessor, the transistors need to be connected by metal wires. The wires have to be properly insulated. The combination of the metal wire and

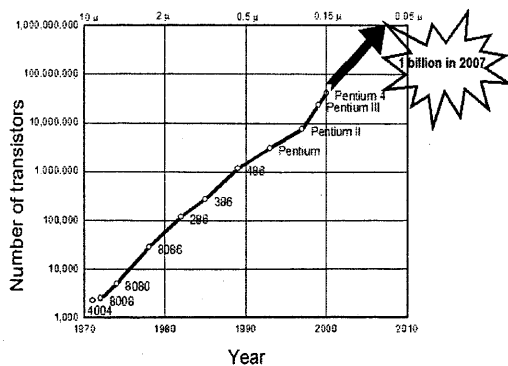


Fig.1 Number of transistors of Intel microprocessors versus the year of production and the feature size (data from www.intel.com).

the insulator is called interconnect. The insulator is also called inter layer dielectric (ILD). The materials of choice for interconnect have been Al/SiO<sub>2</sub> since the inception of the IC industry. Al has an electron conductivity of 3.0 μΩ-cm, and SiO<sub>2</sub> has a dielectric constant of 4 (k=4). To meet the continuing demand for speed, however, the density of transistors will increase and the feature size will continue to scale down, requiring that metal of higher electron conductivity and insulator with lower k (low-k) so that the RC delay (R for resistance and C for capacitance), crosstalk noise and power dissipation can be reduced. A new Damascene process has been adopted which allows a new metal, Cu (electron conductivity = 1.7 μΩ-cm), to replace Al. In contrast, despite the intensive worldwide effort, a suitable low-k material that has the proper k and can meet the integration and reliability requirements remains elusive. Figure 2 shows the k values for the recent past and current chips and the predicted k values for the future chips according to their technology nodes (i.e., the feature size). The year of production is also presented. Clearly, a low-k material with a k = 1.6 will be needed by 2010. And there are no known manufacturable solutions.

### 3. Alternative low-k materials

The dielectric constant of a material depends

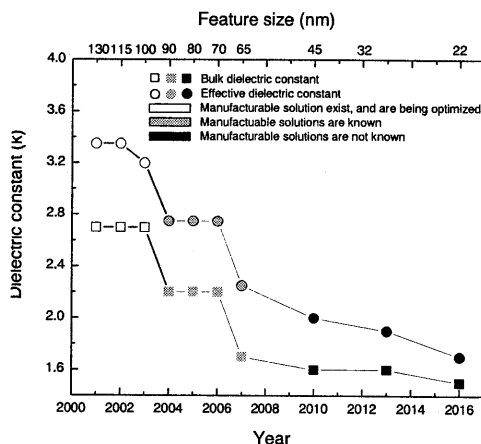


Fig.2 Dielectric constant of ILD required versus feature size and year of production of the microprocessors. The bulk k is the k for the pure ILD material while the effective k is after other layers such as capping layers surrounding the low-k material are considered (Data from International Technology Roadmap for Semiconductors 2001, www.sematech.org).

on the polarizability and the number density of its molecules. The polarizability has three contributions, namely, electronic polarizability, distortion (ionic) polarizability and orientation polarizability. Orientation polarizability is only applicable to molecules with permanent dipole moment whereas electronic polarizability and distortion polarizability are for both polar and nonpolar molecules. There is significant distortion polarizability contribution when ionic bonds are present in a material. Detailed discussion regarding the different polarizations is available in the literature<sup>1,2</sup>. Many materials have been studied as alternative low-k materials and three major classes are organic polymers, silsequioxane (SQ), and silica-based materials. Saturated organic polymers have low dielectric constant due to their low polarizability, but they are usually thermally unstable at temperature above 400 °C. By contrast, unsaturated polymers such as those aromatic rings are thermally stable, but they are highly polarizable, leading to large k value. Fluorine substitution can reduce k because it decreases the polarizability and the number density of chemical bonds. Most

of the organic polymers with sufficient thermal stability have a  $k$  value 2.6~2.8. Overall they face significant integration and reliability concerns due to their low mechanical strength and heat conductivity.

SQ materials are inorganic and organic hybrid polymers with an empirical formula  $(R-SiO_{3/2})_n$ <sup>3,4</sup>. The R- group is most commonly  $CH_3$ - or H- and the corresponding materials are called MSQ and HSQ (M for methyl and H for hydrogen). The substitution of C-Si or H-Si bonds for O-Si bonds lowers the polarizability and the bond density of the material, and therefore MSQ and HSQ have lower dielectric constant than  $SiO_2$ . MSQ usually has lower dielectric constant than HSQ (2.8 vs. 3.0~3.2) because C-Si bond is less polarizable than H-Si and MSQ is less dense than HSQ. Overall the dielectric constants of both materials are high.

Dense (nonporous) pure silica has been the material of choice as ILD since the beginning of the semiconductor industry and thus it is only natural that intensive research has been focused on silica-based low- $k$  materials. The doping of fluorine and carbon could lower the dielectric constant, but the reduction is limited<sup>5,6</sup>. For example, C-doped silica has  $k$  from 2.6~3.0.

Another important and promising approach is to introduce porosity into silica. Since air has  $k$  value of close to 1, incorporation of porosity into silica decreases  $k$  very effectively. There are three major classes of porous silica - sol-gel silica, surfactant templated mesoporous silica, and pure-silica-zeolite (PSZ). Sol-gel silica could have exceptionally high porosity and therefore extremely low  $k$  (e.g.,  $k=1.2$ ) if supercritical drying is used to generate the so-called aerogel<sup>7-9</sup>. However, sol-gel silica with extremely high porosity has low mechanical strength and low thermal conductivity. The significant shrinkage during drying is also of concern. Another drawback is that sol-gel silica has very wide pore size distribution and the randomly occurring large pores can cause electric breakdown (Figure 3). Sol-gel silica is also hydrophilic and

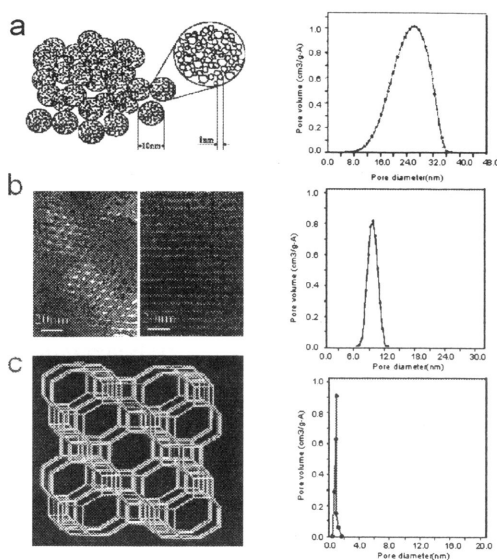


Fig.3 (a) Schematic representation of sol-gel silica structure, (b) transmission electron micrograph of mesoporous silica, and (c) atomic structure model of zeolite CHA. The corresponding typical pore size and pore size distribution are also included.

tends to adsorb water. Water has a  $k=80\sim90$ , and thus minor adsorption of water could increase  $k$  drastically.

The recently discovered surfactant templated mesoporous silica has also been evaluated as potential low- $k$  materials<sup>10-12</sup>. Mesoporous silica could have high porosity and thus low- $k$ . Mesoporous silica also has much more regular and uniform pores than sol-gel silica, and thus it has better mechanical strength (Figure 3). However, it still amorphous by nature and could have similar concerns faced by sol-gel silica such as low mechanical strength and hydrophilicity. In addition, although mesoporous silica has ordered pores under the normal processing conditions, spin-on mesoporous silica has disordered pores.

Zeolites are inorganic microporous crystalline materials<sup>13,14</sup>. Their pore size is extremely uniform (Figure 3). They could have high mechanical strength and heat conductivity due to their dense crystalline backbone. Although the aluminosilicate zeolites are hydrophilic, pure-silica-zeolites (PSZ) are hydrophobic. This should help reduce water

adsorption. Based on these considerations, we have been working on development of zeolite low-k materials for the past several years<sup>15-17</sup>. Detailed discussion on the current state of this technology and the future research directions is the focus of this review and will be presented in the following sections.

#### 4. Pure-silica-zeolite (PSZ) low-k films

##### 4.1 PSZ MFI films by in situ crystallization

Although a promising material, zeolite low-k technology is still in its very early stage of research. At present, zeolites are commercially used as catalysts and separation media. For both applications, they are used in powder composite form such as pellets and granules. Recently, zeolite thin films have been developed for membrane and membrane reactor applications. Several reviews have been published on zeolite membranes<sup>18-21</sup>. Reviews on porous materials in general are also available in which novel applications of porous materials were discussed<sup>22,23</sup>. A review<sup>24</sup> covering a comprehensive list of applications for zeolite films and a collection of articles published on zeolite films is available recently. Specifically the applications included in the review are membranes<sup>25-31</sup>, membrane reactors<sup>32-37</sup>, adsorption, catalysis<sup>38-41</sup>, sensors<sup>42,43</sup>, heat pumps<sup>44</sup>, thermoelectrics<sup>45</sup>, hydrophilic coatings<sup>46</sup>, corrosion resistant coatings<sup>47,48</sup>, and zeolite low-k films<sup>16,17,49,50</sup>. New developments in zeolite films such as patterned films and fabrication of hierarchical porous structures by using zeolite nanoparticles as “building block” were also discussed<sup>51-54</sup>.

We began to work on zeolite low-k films in 1998. Our first effort was focused on PSZ MFI films by in situ crystallization. In situ crystallization was chosen because we were most familiar with in situ crystallization process, and in situ crystallization process can produce continuous zeolite films from which intrinsic properties of zeolites can be obtained. Intrinsic properties of zeolites were important for proof of concept and are still important to our current effort. In situ crystallization refers to a film deposition process where the substrate to

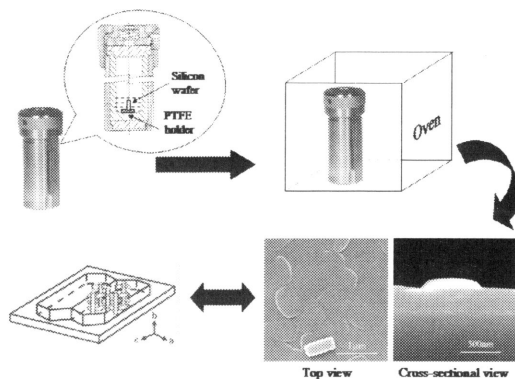


Fig.4 Process flow and results of preparation of PSZ b-oriented MFI low-k films by in situ crystallization.

be coated is directly submerged in the synthesis mixture and the zeolite crystals are formed “in situ” on the substrate surface<sup>55,56</sup>. The term “in situ crystallization” originates from the fact that no preformed zeolite crystals are used in the synthesis. In situ crystallization could be considered a natural extension of the normal hydrothermal synthesis of zeolite powders. However, it is important to recognize that synthesis of a continuous zeolite film on a substrate could be fundamentally different from that of loose zeolite powder<sup>55</sup>. To form high quality zeolite films, the synthesis composition and crystallization conditions have to be conducive to good intergrowth among the zeolite crystals and good adhesion of the zeolite film to the substrate. This requirement makes composition optimization very often essential<sup>55,57</sup>. Many of the unsuccessful preparations for a functional zeolite membrane in the early days could be attributed to direct adaptation of a documented recipe for powder synthesis.

The first zeolite we attempted was PSZ MFI. Again this was a practical choice as we were most familiar with the synthesis of MFI and there were many synthesis protocols for MFI available in the literature. In addition, MFI has a reasonable level of porosity (~33%). The process flow of the in situ MFI film deposition process is illustrated in Figure 4. First, a synthesis solution is prepared with tetraethylorthosilicate (TEOS),

tetrapropylammonium hydroxide (TPAOH), and water. Alkaline metals that are routinely used for zeolite synthesis for catalysis and separation applications have to be avoided in the synthesis for low- $k$  films as they tend to cause many problems for semiconductors. A unique molecular composition is used<sup>49</sup>). The synthesis solution after proper aging is loaded in a Teflon® lined autoclave. The silicon wafer substrate is vertically fixed inside the solution (Figure 4). Then the sealed autoclave is placed into a convection oven preset at 165 °C. After about 2 hour 10 minutes to 2 hour 30 minutes, a monocrystal layer MFI film is formed. This crystallization can be shortened to within 10 ~ 15 minutes with microwave heating. The thickness of the film is about 400 ~ 450 nm and the film is clearly b-oriented, meaning that the b-axis of the MFI crystals is perpendicular to the substrate surface. This orientation is confirmed by x-ray diffraction<sup>57,58</sup>). Since there are straight channels in b-direction, and monocrystal film has no grain boundaries in the mass permeation direction, b-oriented monocrystal films are ideal as separation membranes<sup>59</sup>).

These films have a  $k$  value of 2.7 and are hydrophobic. The elastic modulus is 30 ~ 40 GPa by nanoindentation using a film of 0.43  $\mu\text{m}$  thick. This value is much higher than that of sol-gel silica or mesoporous silica films. Mechanical polishing experiments show that the film is strongly adhered to the silicon wafer and there is no cracking or delamination during the polishing. Low resistivity, high resistivity, oxide-covered, and nitride-covered wafers have been successfully coated with similar b-oriented films using the in situ crystallization method.

#### 4.2 PSZ MFI films by spin-on of zeolite nanoparticle

Although the films formed by in situ crystallization are strong mechanically, the  $k$  value is still high (see Figure 2) for future generation chips. Also the solution phase deposition under hydrothermal conditions is of concern to the

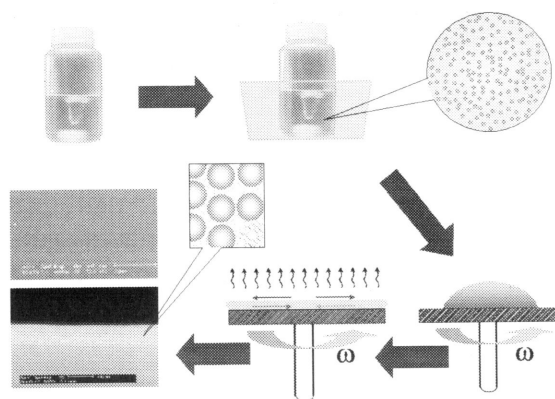


Fig.5 Process flow of deposition and typical scanning electron micrographs of PSZ MFI low- $k$  films by spin-on process.

semiconductor industry. Adoption of hydrothermal process means significant deviation from current semiconductor processing schemes. To lower  $k$  and to develop a process that is more acceptable to the semiconductor industry, we developed a spin-on process. This was the first time that a spin-on process was used to form a direct functional zeolite film<sup>60</sup>). Spin-on process has been commonly used by the semiconductor manufacturers. Therefore the development of a spin-on process for zeolite low- $k$  film represents a significant step forward toward the potential integration of zeolite materials into microelectronic devices. The process flow of a spin-on process is illustrated in Figure 5. First we develop a synthesis composition that is able to produce zeolite MFI nanoparticles suspension. This is carried out under mild conditions in a plastic bottle. After crystallization, the suspension obtained goes through a brief low speed centrifugation (*e.g.*, 5000 rpm) to remove potential large particles. Then the suspension is directly used for spin-on. The suspension could be clear or slightly cloudy depending on the particle size and concentration. The suspension is stable for a long time (*e.g.*, several months). Important parameters that control the nanocrystal size and yield are the molecular composition, aging temperature and time, and crystallization temperature and time. The spin-on films with the normal one-stage synthesis have a

$k = 2.0 \sim 2.3$ . The films are mechanically strong and with excellent adhesion. Nanoindentation was performed on a  $0.42 \mu\text{m}$  thick film and the elastic modulus was  $16 \sim 18 \text{ GPa}$ . This is much lower than the modulus of the in situ zeolite MFI film ( $30 \sim 40 \text{ GPa}$ ). However, It is worth mentioning that a modulus of  $6 \text{ GPa}$  is usually considered to be the threshold value for industrially viable low- $k$  dielectrics<sup>60</sup>.

## 5. Future directions for PSZ low- $k$ research

### 5.1 Synthesis of small PSZ nanoparticles with high yield

The study of our first generation spin-on MFI films has revealed a significant technology barrier, the surface roughness. Although scanning electron microscopy (SEM) shows smooth surface on the large scale (*e.g.*,  $\mu\text{m} - \text{mm} - \text{cm}$ ), atomic force microscopy (AFM) at small scale (*e.g.*,  $5 \mu\text{m} \times 5 \mu\text{m}$ ) clearly establishes that the surface roughness could have a  $z$ -range of as high as  $40 \text{ nm}$ . This high roughness is undesirable. To reduce the roughness, a polishing step is an option, but it is preferable not to add another processing step. Spin-on of a smooth capping layer is also possible since a capping layer is required by most of the porous low- $k$  materials. It is believed that one important factor to improve the surface roughness is to control the particle size and particle size distribution. Figure 6 shows zeolite nanoparticle MFI Yield - Diameter curves for a normal one-stage hydrothermal synthesis and a hypothetical desirable synthesis. The yield is defined as the weight ratio of the crystalline nanocrystals obtained by centrifugation and the total silica weight. It is desirable to bend the Yield-Diameter curve upward so that the crystallinity of the film can be increased while maintaining low particle size and low surface roughness. High crystallinity of the film is expected to increase the mechanical strength and reduce the hydrophilicity of the spin-on films. It will also improve thermal conductivity. We are developing new synthesis processes that can produce small nanocrystals

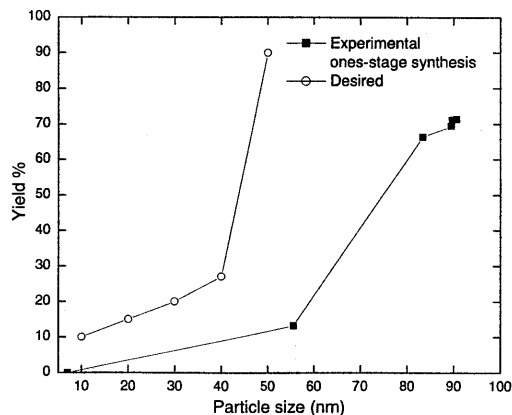


Fig.6 MFI nanoparticle Yield-Diameter curves for a one-stage synthesis and a hypothetical desirable synthesis.

with high yield. A two-stage nucleation/crystallization process appears to be promising. Our preliminary data also show that careful control of viscosity of the spin-on suspension by adding additives is also expected to be important to control the film uniformity and surface roughness.

### 5.2 Extendibility of $k$ to ultra low- $k$ range

The spin-on films have two levels of porosity – the intrinsic zeolitic microporosity and interparticle mesoporosity. Table 1 shows the pore size and porosity data of a typical spin-on MFI film. The film has a well defined bimodal pore size distribution. It is noted that the mesopore size is fairly small ( $2.7 \text{ nm}$ ). Small pores ( $< 5 \text{ nm}$ ) are preferred from the integration and reliability considerations. For any alternative low- $k$  material, it is important that its  $k$  can be extended to the ultra low- $k$  range ( $k \leq 2.0$ ) without significant change in the chemical composition of the film and the deposition processes. Clearly, there are two ways to reduce  $k$ . One is to increase mesoporosity and the other is to increase microporosity.

We have recently developed a process that incorporates pore generating molecules or “porogens” into the zeolite nanoparticle suspension prior to spin-on. The organic porogens are later removed by calcination so that “extra” mesopores are generated.

Table 1 Porosity and pore size analysis of a typical spin-on MFI film.

Micropore size (nm)	0.55
Micropore volume [a][cm <sup>3</sup> /g]	0.17
Mesopore size (nm)	2.71
Mesopore volume [b][cm <sup>3</sup> /g]	0.18
Total porosity [c](%)	45
Theoretical k [d]	2.4
Measured k	2.3
Loss tangent	0.039

[a] The micropore volume was calculated by the t-plot method. [b] Mesopore volume = total volume – micropore volume. [c] Assuming that the density of the dense material is 2.3g/cm<sup>3</sup>. [d] According to Bruggeman's effective medium approximation.

When the porogens loading is 15 wt%, the k of the film is 1.7. This is significantly lower than the parent film (k = 2.3). There are many porogens that can be used. The important parameters to consider here are that they have reasonably high solubility in water as the zeolite nanoparticle suspension is aqueous based, and they are of an appropriate size (less than 5 nm pores are preferred). Cyclodextrin and dendrimers are good choices according to our experience<sup>50</sup>.

By increasing mesoporosity, mechanical strength of the film is decreased. The elastic modulus of the spin-on film after porogen use is 14 GPa while the parent film has an elastic modulus of 16~18 GPa. It is believed that reducing k by increasing microporosity is preferred as it may lead to smaller reduction in mechanical strength. To increase microporosity, a switch to zeolites with low framework density (FD) is needed. Figure 7 shows the framework density of all of the zeolites that have FD lower than MFI. Clearly, there are plenty of rooms to lower framework density starting from MFI. It is noted that the horizontal axis in Figure 7 is the size of the largest ring instead of the normal smallest ring as published in the zeolite community<sup>14</sup>. Small pore zeolites with high porosity are preferred for low-k applications. The gray squares are for zeolites without known

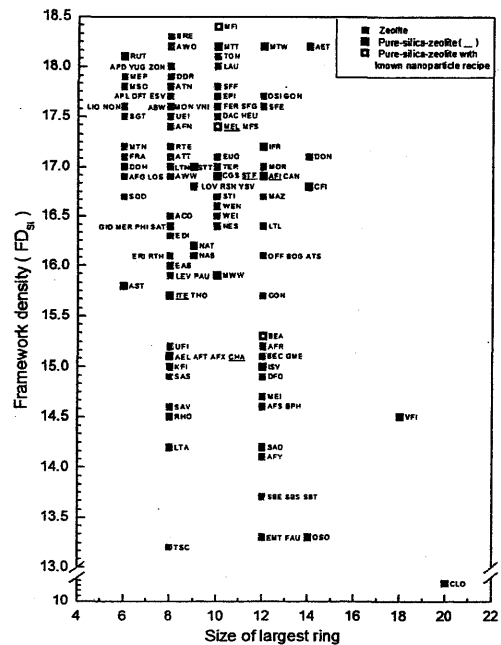


Fig.7 Framework density (FD) versus size of the largest ring of zeolite with FD lower than that of MFI.

pure-silica recipes, and black squares are for zeolites that have been synthesized in pure-silica form. The back squares that have open circles inside represent zeolites that have been synthesized in pure-silica nanocrystal form. Since it is nontrivial to synthesize a pure-silica-zeolite, CHA appears to be a good target in the near term among known PSZ's. Both in situ and spin-on CHA films would be useful. The benefits of in situ CHA films will be discussed in next Section. For the long term, zeolite TSC appears to be a very attractive target. PSZ BEA is also very interesting. PSZ BEA nanocrystals have been synthesized recently and low-k films were considered as their research goal<sup>61</sup>.

The Bruggeman effective media model has been commonly used for predicting k for porous low-k materials<sup>2</sup>. It is unclear at this time if this model is applicable to zeolite materials. Nonetheless, Bruggeman model was applied and the predicted k values for all of the known PSZ's are shown in Figure 8. Two experimental data points with one for calcined in situ MFI and one for as-synthesized

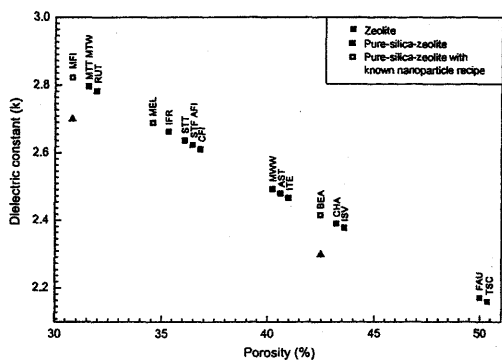


Fig.8 Dielectric constant ( $k$ ) versus microporosity of zeolites according to Bruggeman's effective media model.

in situ BEA films are also included (solid triangles). These two points fall under the Bruggeman's curve, suggesting that it is possible that Bruggeman's model may not be accurate for zeolite materials. Zeolite FAU and TSC are shown in Figure 8 although pure-silica form of these two zeolites are currently unavailable. An in situ TSC film could have a  $k < 2.2$  without any mesoporosity. Thus to reach ultra low- $k$ , very minor amount of mesoporosity will be needed for a spin-on TSC film and this is expected to lead to minimal reduction in mechanical strength and heat conductivity.

### 5.3 Synthesis of PSZ films with different framework density (FD) by in situ crystallization

Despite the fact that in situ crystallization is not preferred as a commercial process by the semiconductor industry, in situ films are still of great value to the zeolite low- $k$  research. They can serve as model systems to obtain intrinsic zeolite properties. For example, the intrinsic thermal conductivity of a zeolite can be readily obtained from its continuous in situ crystallized film. Thermal conductivity of zeolites has been experimentally measured using compressed pellet from zeolite powders. The value is only an estimate at best as the pellets contain large amount of interparticle voids. The effects of porosity on  $k$ , elastic modulus,

and thermal conductivity have been studied for sol-gel silicas. A fundamental question here is do zeolites behave similarly as sol-gel silicas? As mentioned in the previous Section, it is still unclear if Bruggeman's model is suitable for predicting  $k$  for zeolite materials. It has also been shown that both elastic modulus and thermal conductivity of a sol-gel silica decrease more than linear with porosity. Is this true for zeolites? Since zeolites are fully crystalline material with well defined microstructure at the atomic level, theoretical calculation and simulation may be useful and informative in terms of answering these fundamental questions.

### 5.4 Synthesis of nanoparticles of PSZ with extremely low framework density (FD)

To develop a commercially attractive zeolite low- $k$  film with ultra low- $k$  and maximum mechanical strength and thermal conductivity, it is desirable to use zeolite nanoparticles with low framework density. From Figure 7 and Figure 8, it is very attractive to synthesis PSZ TSC nanoparticles. It is noted that pure-silica form TSC is not currently available. In the near term, synthesis of PZS CHA nanoparticles is useful because PSZ CHA recipe is already available. It is also hoped that zeolites with framework density even lower than TSC and small pore size will be synthesized in the future.

## 6. Concluding remarks

Zeolites are mature commercial catalysts and separation media even though rooms for improvements exist. Zeolites in a thin film configuration promise to significantly improve catalysis and separation and open up numerous new applications such as corrosion resistant coatings, hydrophilic zeolite coatings, thermoelectrics, and heat pumps that have not been adequately explored before<sup>24</sup>). The PSZ low- $k$  research discussed in this review presents zeolites an exciting opportunity but admittedly it is still in its very early stage. Over the years, many pure-silica-zeolites have been



synthesized and these materials have not found serious commercial applications. Zeolite low-k technology may offer a good outlet for this type of materials. Zeolite design and synthesis has been mostly guided by catalysis and separation applications, and with zeolite low-k application in mind, it is possible that new zeolite structures will be discovered.

The data obtained so far for low-k applications have been encouraging. However, many technical issues have yet to be resolved. Integration of a new material into semiconductors has proved to be always extremely challenging and there is no exception for zeolites. The mechanical strength is perhaps the strongest attribute for zeolite low-k materials in comparison with other porous materials. More theoretical work on the effects of porosity on k, elastic modulus, and thermal conductivity seems warranted. The crystalline nature of zeolites presents a unique opportunity of theoretical work.

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## 8. Glossary

- FD – framework density
- ILD – inter layer dielectric
- k – dielectric constant
- Low-k – low dielectric constant
- PZS – pure-silica-zeolite

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