Pure Silica Zeolites

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Mechanical and Dielectric Properties of Pure-Silica-Zeolite Low-*k* Materials**

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The continuing evolution of microprocessors requires the timely development of low-dielectric-constant (low-k) materials to replace dense silica, which with a k value of about 4 has been the dielectric insulator of choice since the inception of the semiconductor industry.[1–4] One leading approach to lower the k value to the ultralow-k range (i.e. $k < 2.2$) is to introduce porosity into the silica by taking advantage of the low k value of air ($k \approx 1$).[3,4] Amorphous porous silicas such as sol–gel silica[5,6] and organic-templated mesoporous silica[7–10] have been suggested as possible low-k materials. High thermal and chemical stability of porous silicas and their similarity to dense silica in terms of chemical composition are some of their attractive features over polymeric low-k materials.[3,4] Porous silicas can also offer generational extendibility within the ultralow-k range.[2] However, the introduction of porosity into amorphous silicas thus far has been generally accompanied by a dramatic reduction in mechanical strength (commonly manifested in lower values of the elastic modulus, E),[3,4] which makes their survivability during chemical mechanical processing (CMP) and packaging questionable. Germane to ultralow-k applications, pure-silica-zeolites (PSZs) offer several potential advantages over amorphous silicas, including crystalline structure, intrinsically uniform and small pore size, and hydrophobicity. Here we hypothesize that PSZs exhibit a higher E value for any given k value than their amorphous counterparts because of their crystalline nature and provide support for this postulate below.

We have been investigating PSZs as possible low-k materials and have developed two film-deposition processes: in situ crystallization and spin-on of a zeolite nanoparticle suspension.[11–16] The in situ films are pure zeolitic silica films that are useful for revealing the intrinsic properties of zeolites. The spin-on films are composites of PSZs and amorphous silica, and, as such, their properties are not necessarily the intrinsic properties of the pure zeolites. However, the spin-on films have the advantage of providing a k value in the ultralow-k range. Moreover, the spin-on deposition process is more viable for the manufacturing of integrated circuits (ICs).

To provide evidence for the hypothesis that crystallinity is important to the mechanical strength of silicas, experimental data from in situ and spin-on PSZ films and amorphous silicas were compared in an E versus k plot, which is one of the most revealing engineering plots for the evaluation of low-k materials. The amorphous silica data were obtained from the literature (Figure 1, open circles and solid data fitted line).[17] Clearly, the E value of amorphous silicas drastically declines as the value of k is lowered. A similar and much larger data set was also reported recently.[18] The rapid deterioration of E as k is lowered raises significant concerns for integrating amorphous porous low-k materials with a k value of less than 2.5 into conventional IC fabrication

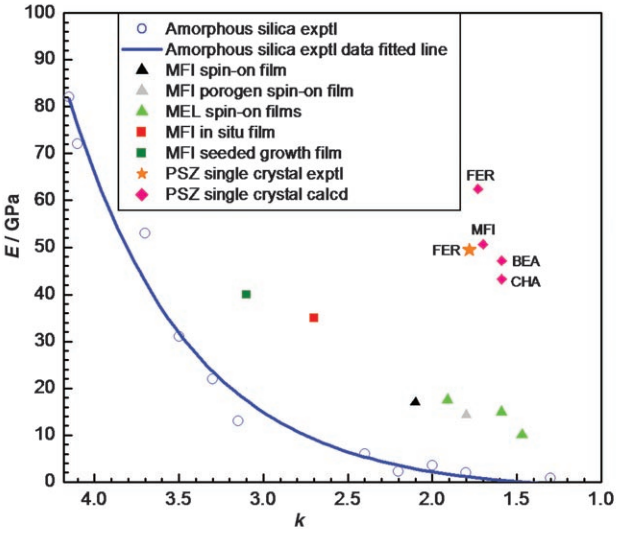

Figure 1. Elastic modulus (E) versus dielectric constant (k) for amorphous silicas and PSZs. The open circles and solid data fitted line correspond to experimental data taken from Xu et al.[17] Squares correspond to experimental data for polycrystalline PSZ MFI films; triangles correspond to experimental data for spin-on PSZ MFI and MEL films; diamonds correspond to calculations of PSZ single crystals; the star corresponds to experimental data for FER single crystals.

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processes because the E values fall in a range (e.g. $E < 6$ GPa) where CMP can be problematic and cracks can readily propagate during packaging.

The experimental data we have obtained thus far on PSZ films, in situ (Figure 1, red square) and spin-on (Figure 1, triangles), support the hypothesis that PSZ films have greater E values than amorphous silicas at comparable k values (Figure 1). However, several critical questions remain. First, the elastic modulus is measured by nanoindentation on thin films with a thickness of about or slightly less than 0.5 µm and could be influenced by the contributions from substrate effects. The substrate in these cases is a silicon wafer that has $E = 130$ GPa. Typically the indentation depth should be less than 10 % of the film thickness to eliminate substrate effects. Depending on the modulus of the film and the geometry of the indenter tip, a thickness of greater than 1 µm is usually required. Second, these in situ and spin-on films are either polycrystalline or composites with amorphous silica, and thus it would be helpful to examine the intrinsic limiting values of k and E for PSZs from both experimental and theoretical perspectives to provide guidance for the development of spin-on films. To address these two questions, we initiated efforts on the preparation, characterization, and calculation of thick PSZ films and PSZ single crystals.

We synthesized polycrystalline PSZ MFI films with a thickness greater than 6 µm on silicon wafers by a seeded growth method.[19] Images corresponding to the top and cross-sectional views of a typical seeded growth film are shown in Figure 2 A and B. Unlike the polycrystalline *b*-oriented PSZ MFI films synthesized previously by in situ crystallization,[13] the seeded growth film has a majority of its crystals *c*-oriented.[19] After polishing, the film has a smooth surface free from cracks or delamination (Figure 2 A, inset), demonstrating the strong adhesion between the film and substrate. An image showing the cross-sectional view of the polished film (Figure 2 B) reveals that the film is dense without pinholes or microcracks between the individual crystals. The thickness is uniform over the entire substrate. The E value of the seeded growth PSZ MFI film is 41.8 GPa as measured by nanoindentation. Substrate effects can be neglected because the deepest indent is less than 200 nm, which is less than 3 % of the film thickness. The k value of the film is 3.10. Note that the E value for the seeded growth film (Figure 1, green square) is well above the amorphous silica line, again supporting the hypothesis that PSZs are mechanically stronger than amorphous silicas.

We synthesized single crystals of PSZ FER with the largest dimension over 1 mm (Figure 2 C and E) following a published procedure.[20] These are the largest FER single crystals ever synthesized. The FER crystals have a thin-plate geometry, which is crucial for measurements of k values. The plates are not perfectly flat but have a flattened four-sided pyramidal shape on both sides of the thin plate (Figure 2 C). The orientations of three edges of the FER crystals are parallel to the respective directions of the crystallographic a, b, and c axes (Figure 2 E).[21] The crystals were indented along the c axis (i.e. [001] direction). The results obtained for the elastic modulus and the hardness of one typical FER crystal are shown in Figure 2 D. Many crystals were tested, each with numerous indents, and consistent results were obtained. The E value and the hardness of the FER single crystals are 49.4 and 7.2 GPa, respectively. A 3D image of an indent with an indentation depth of 250 nm is shown in Figure 2 F. Note that there are no cracks or pile-ups around the indents.

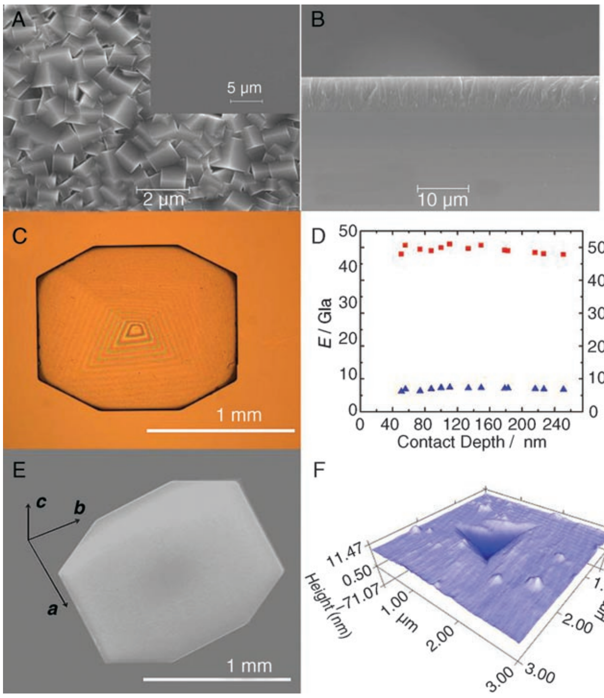

Figure 2. A) Top-view scanning electron microscopy (SEM) image of a seeded growth PSZ MFI film. The inset shows the surface of the film after polishing. B) Cross-sectional view of a polished film on a silicon substrate with a thickness of over 6 µm. C) Optical image of an FER single crystal. The rings seen in the image are light interference patterns showing the four-sided pyramidal shape on both sides of the thin-plate-shaped crystals. D) Nanoindentation results: red squares correspond to the elastic modulus (E), while blue triangles correspond to the hardness of PSZ FER crystals. E) SEM image of the FER crystal with the crystallographic orientation shown. F) Atomic force microscopy (AFM) 3D image of an indent scanned by the same Berkovich tip for indentation with a scan area of 3×3 µm^2.

Measurements of k on zeolite single crystals are not currently available. Although 1-mm FER single crystals are sufficiently large for measurements of E values by nanoindentation, they are still too small for measurements of k values using routine impedance analyzers. The small electrode area (≈ 1 mm^2) and the large thickness (≈ 30 µm) of the crystal lead to a capacitance that is beyond the limit of most of the commonly used impedance analyzers. Thus a time domain reflectometry (TDR) technique[22] was chosen to measure the capacitance of the FER crystals and a k value of 2.18 was obtained at 1 MHz. Note that this k value for FER was obtained from noncalcined crystals. After over 100 attempts, it became clear that cracking is inevitable during the calcination process for crystals of this size and that the cracks can lead to unreliable k values. We have previously shown that removal of the organic structure-directing agent leads to a reduced k value (e.g. 3.4 to 2.7 for polycrystalline PSZ MFI films[13]), and we believe that the FER crystals, once the organic structure-directing agent is removed, will yield a k value of 1.78, assuming a dependence on porosity similar to MFI.

All of the k values for the PSZ films and amorphous silicas reported in Figure 1 were obtained under ambient conditions at 1 MHz, which is the most commonly used measurement frequency for low-k materials. The E value for single-crystal FER (Figure 1, orange star) is well above the amorphous silica line, once again supporting the hypothesis that PSZs are mechanically stronger than amorphous silicas at similar k values.

We examined computationally the limiting values of k and E for PSZ single crystals. The elastic constants for each of the zeolites were determined with the MPDyn simulation code[23] and the BKS force field.[24] The bulk modulus, shear modulus, elastic modulus, and Poisson's ratio were determined by the Voigt–Reuss–Hill method.[25] Dielectric constants were calculated from energy-minimized structures using the GULP simulation package.[26] An ion-pair shell-model force field by Jackson and Catlow[27] was used to represent the interactions between atoms. The calculated E and k (infinite frequency) values for MFI, FER, BEA, and CHA are presented in Table 1. The Poisson's ratio and E value for randomly oriented polycrystalline samples are also listed. The values of E and the high-frequency k are used in the E versus k plot shown in Figure 1 and in Figure 3. Note that the calculated data points for MFI, FER, BEA, and CHA once again are above amorphous silicas in the E versus k plot (Figure 1). For comparison, experimental data for single-crystal MFI (E), CHA (E), FER (E and k), polycrystalline MFI (E and k), and BEA (k) are included in Table 1 and Figures 1 and 3. Because of the geometries (non-thin-plate), it was not possible to measure the k values of single-crystal MFI, BEA, and CHA. The fact that the polycrystalline films have a much higher k value than calculated values for single crystals (2.70–3.10 versus 1.70 for MFI, and 2.30 versus 1.6 for BEA) suggests that grain boundaries and crystal defects play a major role in controlling the k value.

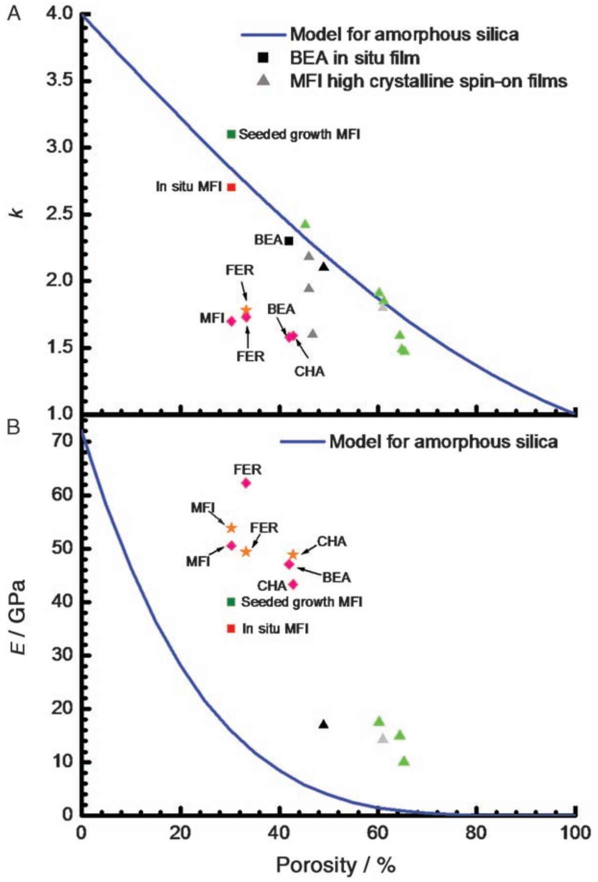

Figure 3. Dielectric constant (k) and elastic modulus (E) of PSZs versus porosity. A) k versus porosity; the solid line refers to a model for amorphous silica.[28] B) E versus porosity; the solid line corresponds to a model for amorphous silica.[29] Squares correspond to experimental data for polycrystalline PSZ MFI films; triangles correspond to experimental data for spin-on PSZ MFI and MEL films; diamonds correspond to calculations of PSZ single crystals; the stars correspond to experimental data for single crystals.

From the E versus k plot it is clear that zeolite materials significantly outperform amorphous porous silicas (Figure 1). Both E and k values depend on the porosity, and, it is fundamentally interesting and practically instructive to examine k versus porosity (Figure 3 A) and E versus porosity (Figure 3 B) for PSZs and amorphous silicas. For k versus porosity (Figure 3 A), most of the spin-on films (triangles) deviate little from amorphous silica (solid line), which is understandable because these films are a composite of zeolite and amorphous silica and contain a significant amount of amorphous silica. By contrast, when the spin-on films have higher crystallinity[12] (two gray triangles straying much below the solid line), the k value becomes significantly lower than that for amorphous silica. This result is consistent with the observations that polycrystalline in situ MFI (red square) and BEA (black square) films are below amorphous silicas, and FER single crystal is even lower (orange star). The polycrystalline seeded growth MFI film (green square) is above the

Table 1: Calculated and measured k and E values for different frameworks.

Framework code	MFI (monoclinic)			FER (orthorhombic)			CHA (monoclinic)			BEA (tetragonal)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
k calcd (∞ MHz)	1.71	1.71	1.70	1.69	1.75	1.75	1.59	1.59	1.59	1.58	1.58	1.61
k exptl (1 MHz)	[a]	2.7[b]	3.1[c]	[a]	[a]	1.78	[a]	[a]	[a]	2.3[d]		
Poisson's ratio calcd		0.1666 ± 0.0080			0.1996 ± 0.0077			0.3845 ± 0.0012			0.3701 ± 0.0015	
E calcd [GPa]		50.6 ± 0.7			62.4 ± 0.7			43.3 ± 0.8			47.1 ± 0.6	
E exptl[e] [GPa]		53.9 ± 0.5			49.4 ± 1.1			48.9 ± 1.2[f]			[a]	

[a] Values not measurable due to experimental limitations. [b] Measured on in situ films. [c] Measured on seeded growth films. [d] Measured on randomly oriented films. [e] Measured on single crystals assuming a Poisson's ratio of 0.25. [f] Measured on boron chabazite single crystals.

amorphous silica line possibly because of its c orientation. For E versus porosity (Figure 3B), it is clear that that PSZ materials (spin-on, polycrystalline, and single crystals) are vastly superior to amorphous silicas. Overall, it is the higher E values of PSZs rather than their lower k values at a given porosity that positions the PSZs well above the amorphous silicas in the E versus k plot (Figure 1).

In summary, our experimental results provide definitive evidence for the hypothesis that PSZs offer a significantly superior elastic modulus to amorphous silicas at any given k value or porosity. The PSZ single crystals offer the exciting possibility to simultaneously achieve remarkably high E and low k values, as demonstrated by $E = 49.4$ GPa and $k = 1.78$ for PSZ FER. The results further suggest that improving crystallinity and decreasing crystal defects are critical for achieving a higher E value and lower k value for the spin-on film, a strategy that we have already started to explore.[12] Moreover, our theoretical calculations of PSZ single crystals validate our experimental results and further suggest that there is much room for improving both k and E values of PSZ low-k films.

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