Organic-Functionalized Pure-Silica-Zeolite MFI Low-*k* Films

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For all of the inorganic porous spin-on low-*k* films being developed today, a post-spin-on hydrophobic treatment is needed to reduce their moisture sensitivity. In the present work, we demonstrate that, for pure-silica-zeolite MFI spin-on low-*k* films, this extra hydrophobic treatment step can be potentially eliminated by using organic-functionalized pure-silica-zeolite MFI (OF PSZ MFI) nanoparticle suspension. Specifically, methyltrimethoxysilane was simply added to the synthesis solution for a PSZ MFI nanoparticle suspension that contains tetraethyl orthosilicate, tetrapropylammonium hydroxide, ethanol, and water. This approach takes advantage of the hydrophobic methyl groups in the zeolite nanocrystal framework as well as in amorphous silica in the low-*k* film. The improvement of the hydrophobicity of the spin-on film from this OF PSZ MFI nanoparticle suspension was demonstrated by the higher water contact angle of the film and less moisture sensitivity of the *k* value in an ambient atmosphere.

Introduction

The development of low-dielectric-constant (low-*k*) materials has become one of the main technology challenges for the semiconductor industry due to the continuing shrinkage of the feature size in microprocessors.[1−3] Of the many demanding requirements of a low-*k* material, mechanical strength is the top concern.[4] Maintaining high mechanical strength has been especially challenging for ultra-low-*k* materials which can only be achieved by embracing the concept of porosity.[2,3] For example, nanoporous organosilicate materials were prepared by removing microphase-separated thermally labile block copolymer in a thermally stable organosilicate matrix. A *k* value as low as 1.5 can be achieved; however, the elastic modulus of the film decreases to ∼0.6 GPa, which is much lower than the generally accepted threshold value for commercially viable low-*k* dielectrics (i.e., 6 GPa).[5] Pure-silica-zeolite (PSZ) thin films have been reported as low-*k* materials. A key advantage of zeolite low-*k* materials is that they allow for a decrease of the *k* value while maintaining a much higher mechanical strength than other amorphous porous low-*k* materials of comparable *k* value.[6,7] In our previous studies, PSZ MFI films were prepared by spin-on of a zeolite nanoparticle suspension as well as in situ crystallization from a clear synthesis solution.[6,7] The spin-on film has a bimodal pore size distribution (i.e., micropores and mesopores). We have also successfully introduced cyclodextrin to the zeolite nanoparticle suspension as a pore-generating molecule (porogen) to increase the mesoporosity of the spin-on films, and films with a *k* value of 1.8 and an elastic modulus of 14.3 GPa were obtained.[8]

Given the involvement of porosity in ultra-low-*k* materials, adsorption of moisture inside the pores is a serious concern. Adsorption of moisture can result in a significant increase of the dielectric constant because water has a very high *k* value ($k = 80-90$). Hence, it is important to make the silica material more hydrophobic so that it is less influenced by water vapor adsorption. Large PSZ MFI crystals (e.g., micrometer-sized) are known for their hydrophobicity.[9] However, our previous study showed that there are surface hydroxyl groups on small zeolite crystals, especially zeolite nanocrystals (diameter <100 nm), making the as-spin-on films from a nanoparticle suspension hydrophilic.[10] The moisture adsorption has been reflected by a significant increase of the *k* value of PSZ MFI spin-on films within 1 h of exposure in ambient air.[6] Amorphous-silica-based low-*k* films have a strong affinity for moisture even at high temperature (e.g., >100 °C).[11] To achieve a more stable *k* in an ambient atmosphere, an extra post-spin-on treatment step (i.e., vapor-phase silylation using chlorotrimethylsilane or hexamethyldisilazane) has been carried out to increase the hydrophobicity of the film.[6,12,13] Since the pore size of MFI is small (0.55 nm), the chlorotrimethylsilane molecules may encounter diffusion limitations, and therefore, they may

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have difficulty in accessing the silanol groups inside the zeolite micropores, leading to limited dehydroxylation effectiveness.[14] Even if this silylation step is effective, it is considered highly undesirable by the semiconductor industry because it is an extra processing step and is expected to increase the manufacturing cost. Previous sol−gel studies reported that by adapting a precursor solution with organosilanes such as methyltriethoxysilane, more hydrophobic amorphous silicas can be obtained even after 400 °C heat treatment in N_2.[14] Similarly, by adding phenethyltrimethoxysilane into the zeolite synthesis solution, phenethyl-functionalized zeolite crystals were synthesized. The phenethyl groups were subsequently converted to sulfonic acid groups, and the acid-functionalized zeolites were shown to be excellent shape-selective catalysts.[15,16] In the present work, we attempt to take advantage of the organic functionalization of zeolite crystals as well as amorphous silica during the synthesis of a zeolite nanoparticle suspension by adding methyltrimethoxysilane into the synthesis solution. We demonstrate for the first time that the spin-on film from this organic-functionalized nanoparticle suspension has improved hydrophobicity, making it possible to eliminate the post-spin-on hydrophobic treatment step.

Experimental Section

Preparation of an OF PSZ MFI Nanoparticle Suspension and a Spin-On Low-*k* Film. A typical synthesis procedure of an OF PSZ MFI nanoparticle suspension is as follows. A 0.5−1.2 g sample of methyltrimethoxysilane (MTMS; 98%, Aldrich) was added to a 250 mL polypropylene bottle that contained 32 g of tetraethyl orthosilicate (TEOS; 98%, Aldrich) and a stir bar. Then 30.47 g of ethanol (EtOH; 98%, Gold Shield Chemical Co.) and 32 g of doubly deionized (DDI) water were added. Finally, 25.6 g of tetrapropylammonium hydroxide solution (TPAOH; 40% aqueous solution, Sachem) was added to the mixture dropwise with strong agitation. The final molar composition of the synthesis solution was $1TPAOH{:}3SiO_2{:}(0.06{-}0.2)RSi{:}52.4H_2O{:}25.1EtOH$. The clear solution thus obtained was aged at room temperature for 3 days followed by a temperature increase to 80 °C. The solution was then maintained at 80 °C for 5 days. During the whole process, constant stirring was provided. For the convenience of discussion, we define two terms. We call the suspension obtained directly from the heating process without further separation processing a “nanoparticle suspension.” The nanoparticle suspension is used to prepare the spin-on low-*k* film. A centrifugation process can be performed on the nanoparticle suspension to collect discrete zeolite nanocrystals. Centrifugation is usually performed in a Beckman J2-HS centrifuge at 16000 rpm using a JA-21 rotor (centrifugal force of 29300*g*). We call these crystals “nanocrystals” and their corresponding suspension a “nanocrystal suspension.” The key difference between a nanoparticle suspension and a nanocrystal suspension is that the former has amorphous silica in addition to the nanocrystals. When a nanocrystal suspension is prepared, all of the zeolite nanocrystals are washed by three repetitions of centrifugation, decanting, and redispersion in H_2O under ultrasonication. Another useful term is the “yield of nanocrystals” in the nanoparticle suspension, which is a measure of the extent of crystallization. After separation, the nanocrystals are calcined to remove the organic structure-directing agent (SDA) and weighed (W_c). The total amount of SiO_2 in the suspension (W_{total}) is known, and the yield of the nanocrystals is defined as W_c/W_{total}. The nanocrystal yield of the zeolite nanoparticle suspension used in the present work is about 40%.

Before its use in the preparation of the spin-on films, the nanoparticle suspension was centrifuged at very low speed (5000 rpm for 20 min) and then filtered through a PTFE filter (0.2 μm pore size) to remove possible large particles. It was spun on Si wafers at 3300 rpm for 20 s at room temperature on a Laurell spin coater with an acceleration of 1275 rpm/s (model WS-400A-6NPP/LITE). Afterward, the film was prebaked in an oven at 80 °C overnight in stagnant air. It was then placed in a tubular furnace purged under N_2. The temperature of the furnace was then raised at a rate of 1 °C/min to 335−400 °C and held at this temperature for 9 h in a N_2 stream before slow cooling. The purpose of this heat treatment was to anneal the film and remove the SDA (i.e., TPAOH). For comparison, after heat treatment, some of the PSZ MFI films were subjected to a silylation treatment to make the film hydrophobic. Vapor-phase silylation was conducted at 320 °C for 4 h by flowing N_2 through a room temperature bubbler (chlorotrimethylsilane:toluene = 1:1).

Characterization of an OF PSZ MFI Zeolite Nanocrystal, Nanoparticle, and Spin-On Film. Solid-state NMR spectroscopy was performed on a Bruker DSX-500 with operating frequencies of 500.23, 125.3, and 99.4 MHz for ^1H, ^{13}C, and ^{29}Si nuclei, respectively, using a Bruker 4 mm CPMAS probe. The typical spinning rates were 14, 6, and 8 kHz for ^1H, ^{13}C, and ^{29}Si, respectively. The chemical shifts were referred to the peak for tetramethylsilane (TMS) for all nuclei. All spectra were normalized to the number of scans and the sample weight used for the measurements so that a direct comparison could be made.

Nitrogen adsorption isotherms were collected at liquid nitrogen temperature (77 K) on a Micromeritics ASAP 2010 analyzer. TGA data were recorded with a Perkin-Elmer Instruments, Pyris Diamond TG/DTA instrument, with a heating rate of 15 K/min in air. IR data were collected on a Bruker Equinox 55 FTIR instrument with step scan (0.5 cm^{-1} resolution). Scanning electron microscopic (SEM) images were recorded on an XL-30 scanning electron microscope operating with an accelerating voltage of 20 kV. The contact angles of zeolite thin films were measured using the VCA-Optima (AST Products, Inc.).

Results and Discussion

The presence of organic functional groups (methyl groups) in the as-synthesized OF PSZ MFI zeolite nanoparticles was supported by IR results (Figure 1). Compared to the IR spectra of as-synthesized PSZ MFI nanoparticles, OF PSZ MFI nanoparticles show additional small peaks at ∼1276 cm^{-1} and in the range of 2850−3000 cm^{-1}, which can be assigned to the vibration of $Si-CH_3$ bonds and CH_3 bonds, respectively.[13,14]

^{29}Si CP-MAS NMR spectra of the OF PSZ MFI nanocrystals from synthesis solutions with different amounts of MTMS (i.e., CH_3Si/SiO_2) are shown in Figure 2. For all the samples, there are two peaks in the range of −90 to ∼−120 ppm, which are associated with Q_2, Q_3, and Q_4 (denotes $Si(OSi)_x(O^-)_{4-x}$). Compared to PSZ MFI nanocrystals (Figure 2a), OF PSZ MFI nanocrystals show a broad resonance in the range of 52−72 ppm (Figure 2b−d), which can be assigned to the Si−C bond.[17] Due to the broadening of this peak, we speculate there might be several chemical shifts

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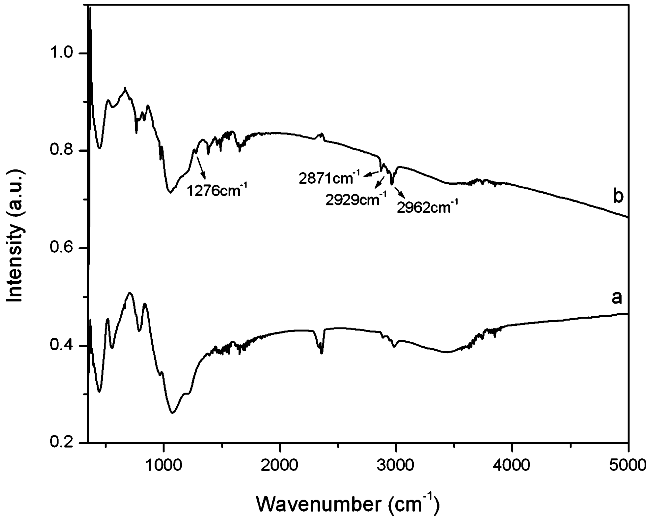

Figure 1. IR spectra of PSZ MFI (a) and OF PSZ MFI (b) nanoparticles.

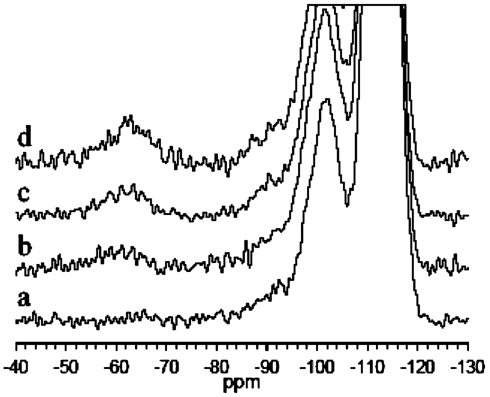

Figure 2. Si CP-MAS NMR spectra of OF PSZ MFI nanocrystals with different synthesis solution compositions of CH_3Si/SiO_2: (a) 0%; (b) 2%; (c)3.7%; (d) 5.5%.

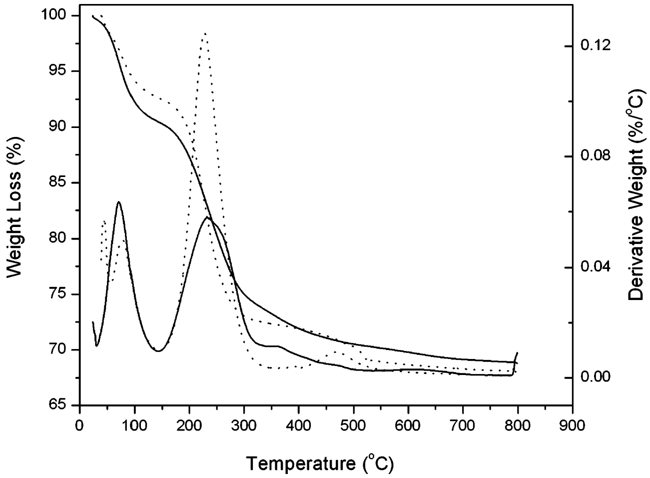

Figure 3. TGA results for PSZ MFI (solid) and OF PSZ MFI (dotted) nanoparticles in air (heating rate 15 K/min).

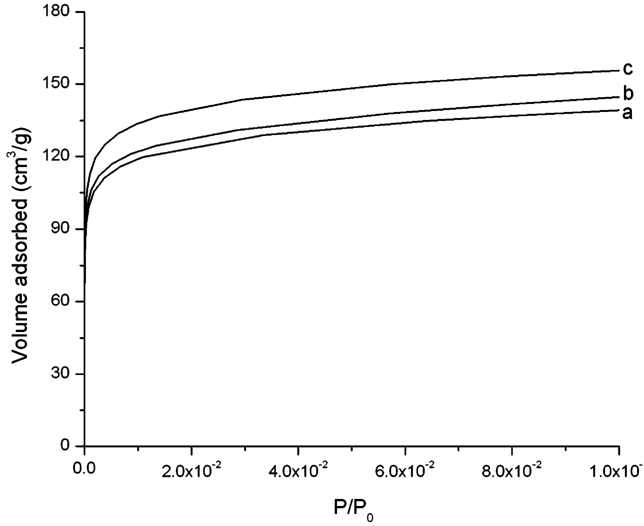

Figure 4. N_2 adsorption isotherms of OF PSZ MFI nanocrystals calcined in nitrogen at different temperatures: (a) 335 °C, $V_{micro} = 0.13$ cm^3/g; (b) 355 °C, $V_{micro} = 0.15$ cm^3/g; (c) 400 °C, $V_{micro} = 0.16$ cm^3/g.

merged together including the $CH_3Si(OSi)_3$ in the MFI framework and contributions of nonframework $CH_3SiO_3^-$ trapped in the pores of MFI.[17] An asymmetric shape of this peak (in the range of $-65\sim-72$ ppm) was observed for the $[CH_3Si/SiO_2] = 5.5\%$ sample (Figure 2d), and it confirms the existence of $CH_3Si(OSi)_3$ in the MFI framework. By integrating the peak area, the total amount of methyl groups incorporated into the PSZ MFI nanocrystals can be estimated quantitatively. For sample d with $[CH_3Si/SiO_2] = 5.5\%$ in the synthesis solution, it is estimated that ~3.1% organosilane was incorporated into the zeolite nanocrystals. This suggests that, during the hydrothermal synthesis, about 2% CH_3Si was not incorporated into the zeolite crystals and remained in the amorphous silica in the zeolite nanoparticle suspension. In all of the following experiments, sample d was used.

For the spin-on film using a nanoparticle suspension, the SDA molecules (i.e., TPAOH) are occluded in the micropores of the zeolite nanocrystals and also buried in intercrystal mesopores. To take full advantage of the porosity of the spin-on film to achieve a low *k* value, the SDA molecules trapped in the micropores of the nanocrystals and in the intercrystal mesopores should be completely removed. To remove the SDA, the spin-on film was subjected to heat treatment in nitrogen, during which the organic functional groups (i.e., $-CH_3$) are also at the risk of decomposition. To examine the thermal stability of the methyl groups, TGA in air was performed on PSZ MFI and OF PSZ MFI nanoparticles (Figure 3). For both samples, there is a large weight loss from 150 to 350 °C, which is due to the combustion of the TPA species both occluded in the micropores of the MFI crystals and buried in the intercrystal mesopores. However, OF PSZ MFI nanoparticles have an additional weight loss at about 470 °C, which is believed to be associated with the combustion of methyl groups.[14] TGA results suggest that it is possible to remove the TPA species in zeolite nanoparticles by calcination at 350−400 °C without loss of the methyl groups.

To determine an appropriate annealing temperature that can effectively remove SDA molecules in both micropores and mesopores, nitrogen adsorption was performed. Since it is harder to remove the SDA molecules trapped inside the micropores than those buried in the intercrystal mesopores, we focused on the effect of temperature on microporosity generation in nanocrystals during calcination in nitrogen (Figure 4). Calcination at 335 °C of OF PSZ MFI nanocrystals gives a micropore volume of about 0.13 cm^3/g, which is much lower than the micropore volume normally observed for nonfunctionalized MFI. This indicates that the removal of TPA is still incomplete after calcination at 335 °C. By

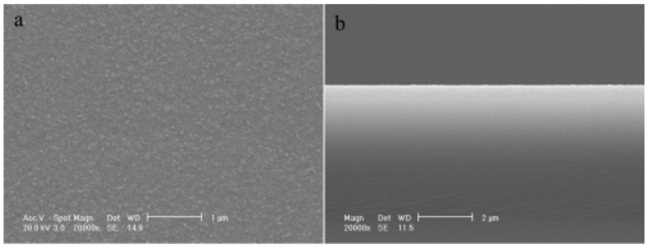

Figure 5. SEM of OF PSZ MFI films: (a) top view; (b) cross-sectional view.

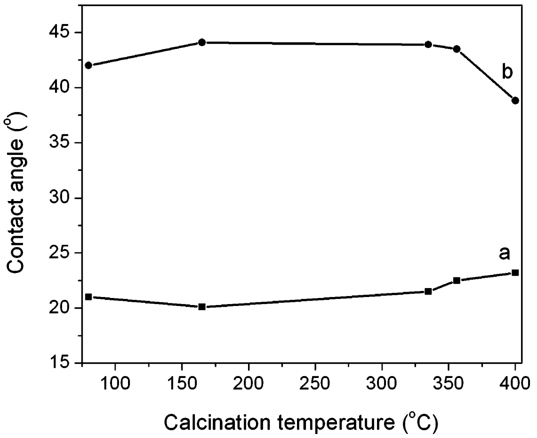

Figure 6. Water contact angles of (a) a PSZ MFI film and (b) an OF PSZ MFI film.

increasing the calcination temperature to 400 °C, a micropore volume of 0.16 cm^3/g was obtained, indicating an almost complete removal of SDA molecules.

The spin-on film from the OF PSZ MFI nanoparticles is fairly smooth, and no cracks were observed (Figure 5). The film thickness is in the range of 0.38−0.48 μm, which is similar to the thickness of a nonfunctionalized PSZ MFI film.

Although nanoindentation was not performed, the addition of methyl groups to a few percent of the framework silicon is not expected to lead to an OF MFI film with an elastic modulus significantly different from that of the MFI films without organic functionalization (16−18 GPa).[6]

Since the methyl groups tethered on PSZ MFI nanoparticles are expected to affect the hydrophobicity of the films, water contact angles on the zeolite film were measured. Figure 6 shows the water contact angle of both the OF PSZ MFI film and PSZ MFI film at different calcination temperatures. The contact angle of the OF PSZ MFI film is ∼20−25° higher than that of the PSZ MFI film, which is apparently due to the incorporation of methyl groups in the OF PSZ MFI nanoparticles. Moreover, a significant decrease of the contact angle was observed on the OF PSZ MFI film when the calcination temperature exceeded 355 °C. By contrast, there is no such change of contact angle in this temperature range for the non-organic-functionalized PSZ MFI film. The contact angle drop for the OF MFI film is most likely due to the loss of methyl groups in the amorphous silica in the spin-on film, as TGA shows that the loss of methyl groups occurs above 400 °C for nanocrystals.

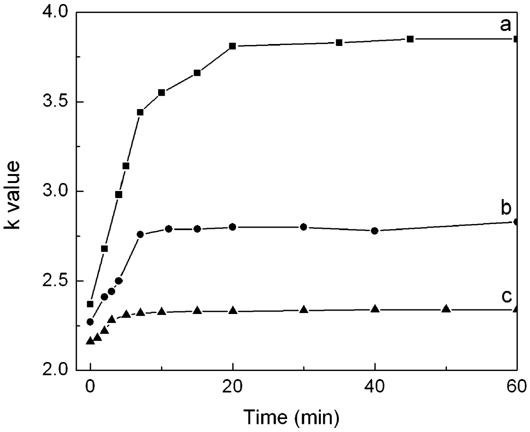

Figure 7. Dielectric constant (*k*) versus exposure time to air with 50−60% relative humidity: (a) nonsilylated PSZ MFI film; (b) OF PSZ MFI film calcined in nitrogen at 355 °C; (c) silylated PSZ MFI film.

Combining the N_2 adsorption results with the zeolite film contact angle measurement, we chose 355 °C in N_2 as the condition to calcine OF PSZ MFI films. At this temperature, a slight loss of micropore volume is expected, but the loss of methyl groups in mesopores can be avoided.

The above water contact angle measurement shows that the incorporation of organic functional groups into zeolite nanoparticles enhances the hydrophobicity of the zeolite film. This hydrophobicity improvement is expected to decrease the moisture adsorption and thus help stabilize the *k* value in an ambient atmosphere. The changes in *k* value of OF PSZ MFI and PSZ MFI films with and without silylation were monitored against the exposure time to ambient air (Figure 7). For the PSZ MFI zeolite film without silylation (Figure 7a), an increase of the *k* value from 2.3 to 3.9 (i.e., 70% increase) was observed within 1 h of exposure in ambient air. By contrast, the silylated PSZ MFI film only shows a slight increase (∼10%) in *k* value with the same exposure time (Figure 7c). The OF PSZ MFI film falls between these two curves with an increase of ∼20% in the *k* value (Figure 7b).

This result demonstrates that the introduction of a hydrophobic organic functional group into PSZ MFI nanoparticles can effectively enhance the hydrophobicity of spin-on low-*k* films, and thus decrease their moisture sensitivity. The OF PSZ MFI film is still not as hydrophobic as the silylated PSZ MFI film. Attempts to further improve the hydrophobicity of the spin-on film are under way.

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