

Fig. 4. Schematic of the basis for water displacement between the polyacrylic acid and polyacrylamide. Injection of hydrogen ions from the positive electrode causes the polyacrylic acid layers to shrink and force water into the polyacrylamide. At the same time the stiffer polyacrylic acid layers cause the whole stack to contract along the directions parallel to the interface between the gels.

polyacrylamide was reduced to about half that of the polyacrylic acid in order to allow it to take up more of the water displaced from the polyacrylic acid.

This is not yet the ideal muscle system. The current drives the shape change through a pH gradient which arises from electrolysis of water, which cannot be reversible in a closed system. The gas formed also causes instabilities in our system. Other workers have experimented with the release of calcium ions from polypyrrole as an alternative system for swelling and deswelling the gels without electrolysis of water.^[10] The gels are also mechanically weak, but much stronger gels can be made by combining polyvinylalcohol with polyacrylic acid.^[11]

As outlined above, an ideal muscle should show an overall expansion or contraction along one axis in response to an applied field, with no overall volume change. This cannot be achieved with a single centrosymmetric material but is possible with an asymmetric series of layers. We have shown that stacked combinations of gels can be made to give linear contraction in response to applied electric field. In essence the asymmetry of gel stack balances the asymmetry of the applied field to allow a symmetric response. Other swollen polymer combinations should be capable of similar responses.

Experimental

Gels were made from solutions of acrylamide or acrylic acid at 200–400 g/L of water. The cross-linking agent was methylenebisacrylamide at levels from 20–50 g/L. For the acrylamide, the initiator was potassium persulfate, 0.25 g/L and the accelerator was tetramethylethylenediamine (TEMED) 3.6 g/L. For the acrylic acid, the catalyst system was a potassium persulfate (1.14 g)-potassium metabisulfite (0.94 g) redox couple. Fumed silica (210 g/L) was added as a physical gelling agent and the pH adjusted to 3.8–4.0.

Gel stacks were made by extrusion freeform fabrication. Acrylic monomer, water and catalyst is extruded from a syringe through a fine (0.2–1 mm diameter) nozzle which writes on a heated substrate. The composition of the gel can be changed by swapping syringes or by using a Y-junction between two syringe feeds. To prevent the monomer solution from flowing off the

substrate before curing, 8 wt.-% of fumed silica is added to the solution, to give it a toothpaste-like rheology. The solution cures to cross-linked gel by thermally activated free radical polymerization within a few minutes of being deposited on the plate. 6-layer stacks were formed into bars 5 cm × 0.5 cm (wide) × 0.4 cm (thick), before swelling. A typical stack would have a polyacrylic acid face with 1–5 (x) layers and a polyacrylamide face of (6– x) layers with a combination of dense and open-mesh layers (written as a series of spaced lines). When used, wire electrodes were usually placed between layers 1 and 2, and between 5 and 6.

This system allows interdiffusion and bonding between layers, which provides good stress transfer during the swelling processes. The early onset of gelation and the physical gelling agent prevent extensive mixing between layers. This was shown by cutting apart multilayer stacks and measuring the response of individual layers to acid and base.

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Low Dielectric Constant Mesoporous Silica Films Through Molecularly Templated Synthesis**

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The semiconductor industry is currently targeting new intermetal dielectric films with dielectric constant $k < 2.5$, and it is anticipated that as the packing density of metal lines on the semiconductors continues to increase, interleaved dielectric films with $k < 2.0$ will soon be required. Porous silica films with nanometer-scale porosity are potentially useful as low dielectric constant intermetal materials in advanced semiconductor devices. Nanoporous silica films can be synthesized from solution precursors in two ways: 1) by an “aerogel or xerogel” process^[1–4] in which random

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porosity is introduced by controlled gelation and removal of an alcohol-type solvent or co-solvent, and where the pore size is typically much larger than 5 nm; and 2) by a surfactant-templating process^[5-7] in which the pores are formed in a spin-coated^[8-11] or dip-coated film^[12,13] by removal of a surfactant. In this paper, we report on the synthesis and properties of highly porous silica films with low dielectric constants in the range of ≈ 1.8 to ≈ 2.5 , prepared using a polyoxyethylene ether surfactant to template nanometer-scale porosity. A mesoporous film with a dielectric constant less than ≈ 2.2 with stable dielectric response in ambient testing conditions over several days is described. This molecularly templated synthesis approach allows rational control of the porosity, pore size (less than 5 nm) and shape, and film texture and thickness, and results in good mechanical properties in the film. The deposition process does not require careful atmospheric control, and is potentially scalable to large (≥ 200 mm) wafers.

The mesoporous silica films were deposited by a spin-on sol-gel process^[9-11] as described previously. The deposition solution was prepared by combining tetraethyl orthosilicate (1 M), deionized water (3–7 M), ethanol (4–5 M), hydrochloric acid (0.05 M), and a polyoxyethylene ether surfactant (0.05–0.30 M), with all chemicals being obtained from Sigma–Aldrich (St. Louis, MO). The solution mixture was aged for 20 h at room temperature. The aged solution was spin-coated with a Bidtec SP 1000 spinner in a class 1000 cleanroom on 4 inch $\langle 100 \rangle$ boron-doped silicon. A 1-s spreading cycle at 100 rpm with an acceleration rate of 100 rpm/s was followed by a 30 s coating cycle at 2000 rpm with an acceleration rate of 20 000 rpm/s. After spin-coating, the film was kept at 115 °C for 1 h. Subsequently, the film was heat-treated at 475 °C for 5 h in a furnace in static air.

Film porosity was inferred from the total number of Si and O atoms in the film, which were determined by Rutherford backscattering spectrometry (RBS), and by the $^{16}\text{O}(\text{d},\text{p}_0)^{17}\text{O}$ nuclear reaction analysis.^[14] Film porosity with the surfactant-templated material was measured to be $\approx 55\%$ by both RBS and the nuclear reaction analysis method. Low-angle X-ray diffraction of the films showed no evidence of pore ordering. A transmission electron microscopy (TEM) image of a section of the film in Figure 1 indicates that the pores are disordered with an isotropic nanoporous structure. Pore sizes were estimated to be less than 3 nm from TEM micrographs, and from nitrogen adsorption/desorption analysis on powders prepared from similar solutions by a rapid spray-drying process.

After calcination, the films were subjected to one or more of the following dehydroxylation treatments:^[15,16]

- Immersion in a stirred solution of hexamethyldisilazane (HMDS, $(\text{CH}_3)_3\text{Si-NH-Si}(\text{CH}_3)_3$) in toluene for 20–24 h.
- Heat treatment at 400 °C in flowing 2 % H_2 –98 % N_2 forming gas.
- Heat treatment at 400 °C in flowing argon.
- Spin-coating with pure HMDS at 2000 rpm.

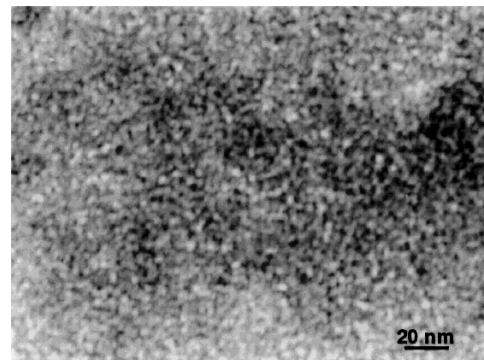


Fig. 1. Transmission electron micrograph showing microstructure of surfactant-templated mesoporous silica film.

For capacitance measurement, backsides of the coated wafer pieces were scratched and etched with buffered hydrofluoric acid. Within several minutes after etching, a layer of gold was sputter-deposited on the exposed silicon surface. On the top film side, an array of gold dots, each approximately 1000 Å thick and 2.8 mm in diameter, was formed by sputtering using an aluminum shadow mask. The gold dots were always applied after the final HMDS dehydroxylation treatment, and prior to the final heat treatment in argon or forming gas.

Capacitance measurements were performed with an HP 4284A precision LCR meter. The frequency and the oscillation level were 1 MHz and 100 mV, respectively. The dielectric constant was calculated from the capacitance, the film thickness corresponding to the specific dot location on the wafer, and the electrode dot diameter. The film thickness was measured with an optical imaging profilometer (ZYGO New View 200). For selected films, the film thickness under the electrode dots was measured by scanning electron microscopy (SEM).

The dielectric constant as a function of aging time after the final dehydroxylation treatment is shown in Figure 2. Without any dehydroxylation treatment, the dielectric constant is consistently over 5.0 due to the significant number of polar hydroxyl groups. With repeated treatments in

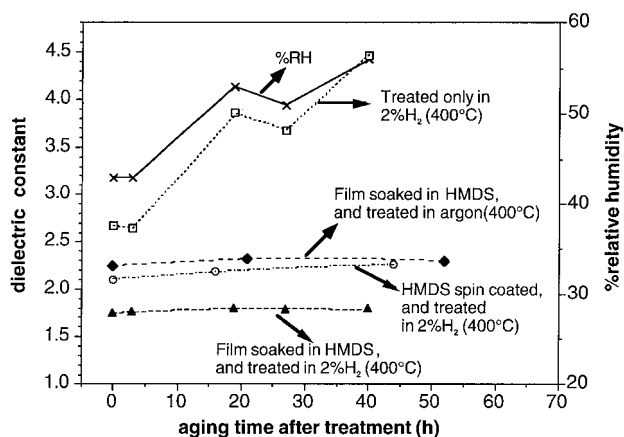


Fig. 2. Dielectric constant of mesoporous silica films and relative humidity as a function of aging time, after various dehydroxylation treatments.

HMDS solution and treatment in forming gas (2 % H₂) at 400 °C, a film dielectric constant of less than 2.0 was obtained. The dielectric constant of the film that received a single treatment in 2 % H₂ at 400 °C increased significantly with aging time. During these measurements, the ambient relative humidity varied from 40 to 65 %. The change in relative humidity with aging time during this sample measurement is also shown in Figure 2. As the dielectric constant increased, the relative changes in dielectric constant during the long aging time appeared to parallel the changes in the ambient humidity.

The differences in surface chemistry after various dehydroxylation treatments were probed by X-ray photoelectron spectroscopy (XPS). The XPS data were collected on a Phi Quantum 2000 Scanning ESCA Microprobe with a focused monochromatic AlK α X-ray source for excitation and a spherical section analyzer. The carbon/silicon and oxygen/silicon atomic ratios determined from X-ray photoelectron

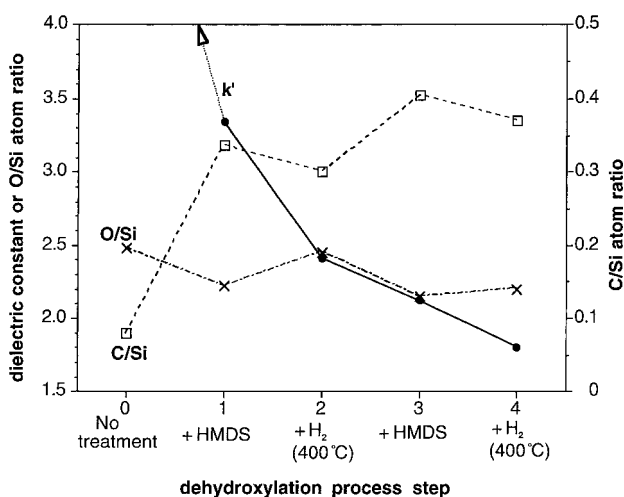


Fig. 3. Dielectric constant and elemental analysis of mesoporous silica films as a function of dehydroxylation treatment.

spectroscopy are plotted in Figure 3 as a function of dehydroxylation steps. The dielectric constant as a function of these dehydroxylation steps is also shown in Figure 3 for a set of film samples. The C/Si ratio increases significantly (to >0.3) after a single treatment in HMDS due to the methyl portion of the trimethylsilyl groups appended to the pore surfaces. Heat treatment at 400 °C in forming gas results in a decrease in the carbon content in the film due to the pyrolytic loss of hexamethylsiloxane. A second HMDS treatment results in increased carbon content in the film due to attachment of additional trimethylsilyl groups. Further heat treatment in forming gas again results in loss of some trimethylsilyl groups. The changes in surface chemistry with these dehydroxylation treatments also render the film substantially more hydrophobic. The water contact angle in the film was 12–16° before dehydroxylation treatments, and 70–78° after dehydroxylation treatments that included at least one treatment in HMDS. Further characterization by Fourier transform infrared spectroscopy is in progress.

Instead of using a long 20 h soak in HMDS solution, it is also possible to obtain low dielectric constant films by simply spin-coating HMDS on the film, followed by heat treatment in forming gas. As is shown in Figure 2, dielectric constants of <2.25 were obtained using HMDS spin-coating procedures and heat treatment in forming gas. Dielectric constants less than 2.25 were also obtained on films that had been subjected twice to a dehydroxylation sequence involving HMDS solution treatment and heat treatment in argon.

The mesoporous silica films templated by small non-ionic surfactants also show potential for meeting engineering requirements necessary for process integration and interconnect fabrication. Because of their fragility and potential contamination from polishing slurries, it appears unlikely that porous films will be directly planarized during interconnect fabrication using conventional chemical-mechanical-polishing (CMP) equipment. It is more likely that a dense “cap” layer of silica or another material on the porous low *k* film will be polished. However, even with a “cap” layer, the porous low *k* material must have adequate stiffness, as well as compressive and shear strengths, to withstand the stresses imposed during the CMP process.

The elastic modulus of the mesoporous silica film measured with a Hysitron Picoindenter using a Berkovich diamond tip indicates potential for use in interconnects. The instrument and tip were first calibrated on a dense silica standard with a modulus of 70 GPa. A range of indentation loads (50–300 μN) and residence time (50–900 s) at maximum load were studied. For the measurement parameters used, indentation depths were less than 10 % of the film thickness. The modulus is in the range of 14–17 GPa for the highly porous film with a porosity of ≈55 %. The relative modulus of the porous silica film with respect to dense silica appears to be in reasonable agreement with calculations^[17,18] for porous solids, which were derived for closed pores in a continuous matrix. The data were also in good agreement with the open cell formulation developed by Gibson and Ashby^[19] and applied by Bellet et al.,^[20] to analyze their nanoindentation data on porous silica films.

The spin-coated mesoporous silica films can also meet other engineering requirements. Minimal striation-type surface texture was observed in these films prepared with a laboratory-scale spinner. Roughness is generally less than ±50 Å over length scales of tens of micrometers, and radial striations were not easily apparent by optical microscopy. Film thickness can be controlled between 0.5 and 1.2 μm by varying the spinning rate during deposition or by adjusting the relative concentrations of the components in the deposition solution.

In summary, low *k* mesoporous silica films with pore sizes of less than ≈5 nm have been synthesized using a spin-coating approach readily extendable to manufacturing. Dielectric constants of ≈1.8 to ≈2.5 were obtained in spin-coated films prepared using a surfactant to template the nanometer-scale porosity. Dielectric properties of films was

correlated with surface chemistry, characterized by X-ray photoelectron spectroscopy. The surface texture, thickness, and elastic modulus of the films indicate potential for integration in semiconductor interconnects.

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Experimental Evidence of a Giant Capacitance in Insulator–Conductor Composites at the Percolation Threshold**

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Ceramic–metal composites (cermets) are relatively widely used materials with important technological applications; however, many of their properties still remain undiscovered. In particular, the singular electrical properties of these materials, especially at concentrations close to the

percolation threshold, which can only be analyzed by percolation theory,^[1] have been widely studied in the past twenty years, but these properties are not yet totally understood. Moreover, at this concentration, the composite undergoes a metal–insulator transition, where the value of electrical conductivity changes by several orders of magnitude.^[1,2] In addition, due to the complex representation of the electrical properties, the capacitive term should also be considered in a conductor–insulator composite, because it has been shown that it becomes important at the percolation threshold.^[3–5] However, according to the theory, only in the neighborhood of the percolation threshold is the enhancement in capacitance very large, so that it is very difficult to experimentally observe this feature. Several experiments have been performed on insulator–metal systems^[6–8] but, until now, only a modest increase in capacitance (around 10 times) has been experimentally confirmed, which is much less than that predicted by the theory.^[4] These experiments were performed by using homogeneous monolithic conductor–insulator composites. This approach is strongly handicapped by the impossibility of preparing composites with homogeneous concentrations very close to the percolation threshold. In addition, the conductor–insulator ratio was optimized to study the conductivity gap, though not for the capacitance maximum because, in two of the cases, the matrix was an alkaline halide,^[6,7] while in the third case the conductor phase was carbon fiber.^[8]

In this work we want to show experimentally that at the percolation threshold of a metal–insulator graded composite (mullite/Mo functionally graded material, or FGM) there is a giant increase in capacitance at room temperature. This effect is similar to that observed in the metal–insulator transformation in semiconductors,^[9] though that occurs at a temperature of a few kelvin. The origin of such an increase in effective dielectric constant in the neighborhood of the percolation threshold is due to the fractal geometry of the infinite cluster at that concentration. Intuitively it can be explained by the existence of a large number of metal particles in parallel and in very close proximity, but blocked by thin barriers of dielectric material. According to theoretical predictions, this capacitance increase is not particular to a given chemical composition of the dielectric material, but depends only on the microstructure of the aggregate and on the ratio between the conductivities of the metallic and insulator phases. Such physical properties of composites, at this particular concentration, can be used to create new devices by using the exotic behavior of the dielectric constant at the percolation threshold, for example, high charge-storage capacitors. Some commercial devices known as BLCs^[10] (barrier layer capacitors) are based on a similar principle to that of percolation, although the topology of such systems does not strictly match that of an “infinite cluster”. Instead they use the enhancement of capacitance at the ceramic grain boundaries. Such devices, which are presently employed when large capacitors are needed in small places, only cov-

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