Synthesis and Evaluation of Pure-Silica-Zeolite BEA as Low Dielectric Constant Material for Microprocessors[†]

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Pure-silica-zeolite (PSZ) BEA film was prepared on stainless steel substrates by in situ crystallization at 130 °C for 14 days using a gel composition of 0.6:0.6:1:9.8 (TEA)OH–HF–SiO_2–H_2O. The film is polycrystalline, continuous, and about 15 μm thick. The film was characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), inductively coupled plasma–atomic emission spectrometry (ICP–AES), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). The as-synthesized film was also measured for the first time for dielectric constant (k), and a k value of 2.3 was obtained.

Introduction

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, functionality, and capability of desktop, laptop, and palmtop computers. One primary emphasis of this evolution so far has been the increase of density of transistors. For example, 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 Intel Xeon. The number of transistors on a single chip is predicted to reach 1 billion in 2007.

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 the insulator is called interconnect. Due to the extremely high density of transistors, multilayers of interconnects are needed. Thus the insulator is also called interlayer dielectric (ILD). The materials of choice for interconnect have been Al/SiO_2 since the inception of the IC industry. Al has an electron conductivity of 3.0 $\mu\Omega$ cm, and SiO_2 has a dielectric constant (k) of 4. To meet the continuing demand for speed, however, the density of transistors will continue to increase and the feature size will continue to scale down, requiring that a metal of higher electron conductivity and an 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.[1,2] A new Damascene process has been adopted which allows a new metal, Cu (electron conductivity = 1.7 $\mu\Omega$

cm), to replace Al. By 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. According to the most recent International Semiconductor Technology Road map (www.sematech.org), a low-k material with a k = 1.6 will be needed by 2010. And there are no known manufacturable solutions.

Dense (nonporous) pure silica has been the material of choice as dielectrics since the beginning of the semiconductor industry. An important and promising approach to reduce k 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 = 1.1–1.3) if supercritical drying is used to generate the so-called aerogel.[3–5] 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. Sol–gel silica is also hydrophilic and tends to adsorb water. Water has a k = 80–90, 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.[6–9] 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. However, it is 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.[10,11] Their pore size is extremely uniform. They could have high mechanical strength and heat conductivity due to their dense crystalline backbone. Although the aluminosilicate zeolites are hydrophilic, pure-silica zeo-

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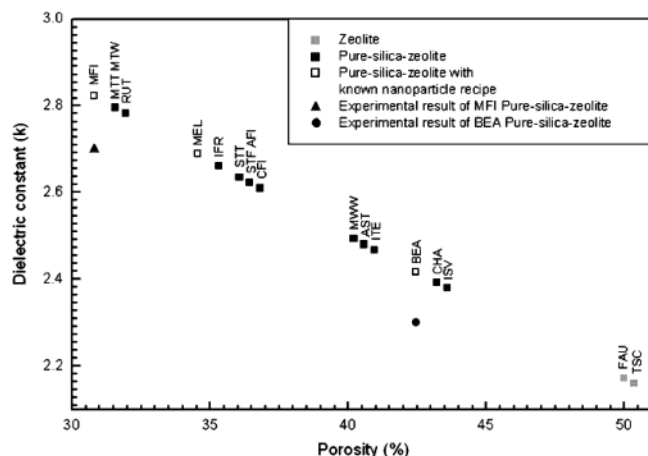
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Figure 1. Dielectric constant (k) versus microporosity of zeolites according to Bruggeman's effective media model.

lites (PSZ) are hydrophobic. This should help reduce water adsorption.

We have demonstrated that PSZ MFI is a promising low-k material due to its superior mechanical strength, heat conductivity, and hydrophobicity originated from its crystallinity.[12–14] PSZ films have been deposited by two methods, in-situ crystallization and spin-on of zeolite nanoparticle suspensions. Although the in-situ crystallization process[15–17] has concerns as a commercial semiconductor manufacturing process, the continuous polycrystalline films produced could provide intrinsic k value and other intrinsic properties of zeolites. Thus, in-situ crystallized films could be an important research tool for understanding the structure−property relation of a zeolite as a low-k material. On the other hand, the spin-on process can potentially fit nicely into the current semiconductor processes and make zeolite low-k films attractive for practical use.[18] The spin-on films had two-level porosities involving zeolitic microporosity and mesoporosity and the mesoporosity offers a convenient way to adjust the film properties such as k value to meet practical requirements. The ultralow k value has been successfully achieved by incorporating γ-cyclodextrin as a porogen (pore generator) into PSZ MFI nanoparticle suspensions to increase the film mesoporosity.[19] However, increasing total porosity by using PSZ with higher microporosity will be a preferred route to reduce k because increase of mesoporosity tends to lead to higher moisture sensitivity and lower mechanical strength.

Currently there are more than 130 zeolites and zeolite-type materials available.[11] However, only 13 of them have been synthesized in pure-silica form and at the same time have a framework density lower than that of MFI (Figure 1). Framework density (FD) is defined as the number of the tetrahedron atoms (e.g., Si) in a 1000 Å^3 volume. Thus, lower FD means higher microporosity. Bruggeman effective medium model has been commonly used to predict k value from porosity for amorphous porous silicas.[2] Figure 1 shows the predicted k values for various pure-silica zeolites. Two highly porous zeolites FAU and TSC are also included although they are not presently available in pure-silica form. We have prepared PSZ MFI film and shown that this film has $k = 2.7$ (solid triangle). Clearly, moving from MFI to a zeolite with lower FD will decrease k. The primary goal of this article is to obtain the k value for PSZ BEA and to prove that PSZ BEA has k lower than PSZ MFI and thus could be an interesting low-k material. It is noted that our experimental data on PSZ

MFI is below the value predicted by the Bruggeman model, suggesting that the Bruggeman model may not be fully applicable to crystalline zeolite materials. Thus, it is fundamentally interesting to examine the experimental k value on PSZ BEA. Zeolite beta (BEA) is a large-pore zeolite with three sets of mutually perpendicular 12-member ring channels. The micropore volume of PSZ BEA is about 1.2−1.3 times higher than that of PSZ MFI. Although there are many reports on zeolite films (e.g., MFI), reports on zeolite BEA films are very limited. Only two studies on BEA films and coatings by in-situ crystallization have been reported, and in both cases, they are not pure-silica BEA.[20,21] Therefore, this study provides an important route to PSZ BEA films.

Experimental Section

PSZ BEA films were synthesized hydrothermally by using the starting materials including tetraethylammonium hydroxide ((TEA)OH) as structure-directing agent (SDA), fumed silica, HF, and deionized water. The synthesis gel was prepared as follows. First, fumed silica (99.8 wt %, Aldrich) was added slowly to an aqueous solution of (TEA)OH (35 wt % aqueous solution, Aldrich) in a polypropylene bottle under stirring at room temperature. Stirring continued until a semitransparent mixture was obtained. Aqueous HF (48 wt % aqueous solution, Aldrich) was added dropwise under vigorous stirring. Then a homogeneous gel was formed. The final gel molar composition was 0.6:0.6:1:9.8 TEAOH−HF−SiO$_2$−H$_2$O. The gel was then transferred to Teflon-lined (45 mL capacity) Parr acid digestion bombs for crystallization. To obtain PSZ BEA films, the substrate was fixed vertically inside the bomb and remained completely covered by the gel during the crystallization. The crystallization temperature was 130 °C for 14 days. The as-synthesized films were washed thoroughly with deionized water under ultrasonication. It is noted that PSZ BEA films were produced with fumed silica only, and efforts to produce PSZ BEA film with TEOS (tetraethyl orthosilicate, 98 wt % Aldrich) with similar gel composition were not successful.

Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D-500 diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) was performed at 20 kV, using a Philips XL-30 instrument. Thermogravimetric analysis (TGA) of as-synthesized and calcined pure-silica BEA powder was performed on a SDT 2960 simultaneous DSC−TGA instrument (TA Instruments) at a heating rate of 5 K/min under a flow of nitrogen (50 mL/min). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Equinox 55 in 375−7500 cm^{-1} range using KBr pellet method. The samples were mixed with nearly 100 times (by weight) of dry KBr, ground, and dried overnight at 403 K. Nitrogen adsorption−desorption measurements were performed at 77 K on a Micromeritics ASAP 2010. The calcined sample was evacuated overnight at 623 K and 1 μmHg. Microporosity was determined by the t-plot method, and the Horvath−Kawazoe (HK) method was used for the pore size determination.

For dielectric constant measurement, aluminum dots with a diameter of 1.62 mm and thickness of 1 μm were deposited on the film using thermal evaporation (Denton Vacuum DV-502) through a contact mask. The backside of the silicon wafer was also deposited with an aluminum layer. The capacitance of the aforementioned metal−insulator−metal structure was measured at a
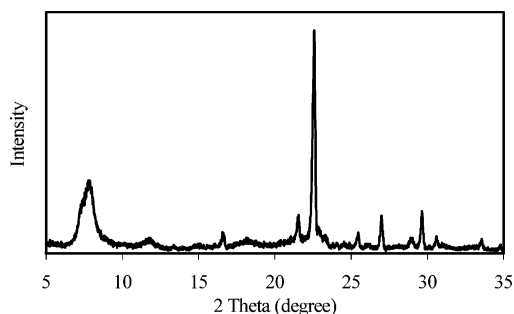
Figure 2. X-ray diffraction pattern of as-synthesized PSZ BEA film grown on stainless steel substrate.
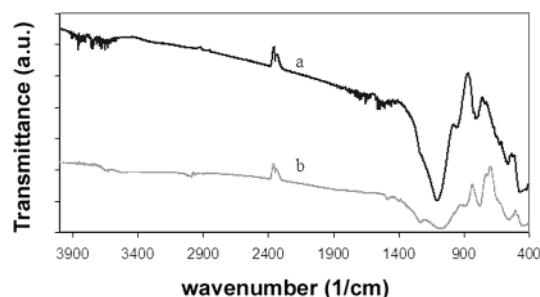

Figure 3. FT-IR spectra of PSZ BEA powder: (a) as-synthesized; (b) calcined.

frequency of 1 MHz on Solartron 1260 impedance analyzer combined with standard Signatone micorprobe station and micropositioner, and the dielectric constant of the film was then calculated. To minimize water adsorption, the film was dried at 120 °C overnight and then kept in a desiccator before capacitance measurement. A dry nitrogen blanket was usually applied during capacitance measurement. The capacitance was measured in several areas of the sample, and the k value reported here is an average.

Results and Discussion

High crystallinity and phase purity of the BEA film are evident from the XRD pattern (Figure 2). High crystallinity of the product was further confirmed by FT-IR spectroscopy that clearly showed characteristic framework vibrations of zeolite BEA at 450, 525, 780, 1016, and 1173 cm^{-1} (Figure 3).[22-24] The band around 450 cm^{-1} is the T-O-T bending vibration. The bands at 1016 and 1080 cm^{-1} probably are due to the splitting of the asymmetric T-O stretching band. ICP-AES analysis indicated a negligible amount of aluminum (Si/Al = 5575) in the framework of the as-synthesized PSZ BEA.

Thermal decomposition of SDA and moisture adsorption of the samples were examined with TGA. The samples were heated from room temperature to 700 °C at a heating rate of 5 °C min^{-1} under a flow of nitrogen with a nitrogen flow rate of 50 mL/min. The as-synthesized sample dried at 100 °C for 24 h was used for studying the thermal decomposition of SDA, and a sample calcined at 550 °C for 12 h under air was used to measure the moisture adsorption. Before TGA analysis, both samples were exposed to the laboratory conditions for a couple of days. The TGA curves are shown in Figure 4. From Figure 4a, the SDA content was estimated to be about 16 wt % for PSZ BEA, which is greater than that of PSZ MFI (11.7 wt %).[25] This is consistent with higher microporosity of BEA as compared with MFI. Furthermore, TGA analysis provided
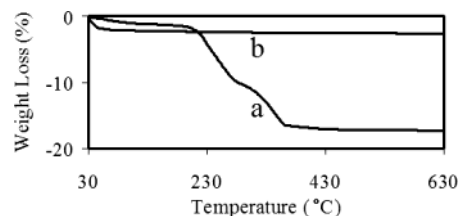
Figure 4. TG curves of PSZ BEA samples: (a) as-synthesized; (b) calcined.
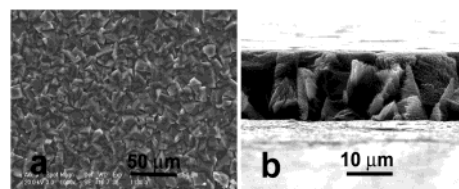
Figure 5. SEM images of as-synthesized PSZ BEA film on stainless steel substrate: (a) top view (before polishing); (b) cross-sectional view (after polishing).

valuable information on the hydrophilicity/hydrophobicity of the sample. It is known that moisture content has significant influence on the k value of the films. Water content of the as-synthesized sample was considerably low (<1.5 wt %) because the zeolite pores were occupied by the SDA. The calcined sample exhibited a very low moisture content of ~2 wt % (Figure 4b), and the moisture could be readily removed at a temperature lower than 60 °C, which suggests high hydrophobicity of PSZ BEA.

SEM images (Figure 5a) of the as-synthesized film reveal a well-intergrown, continuous, polycrystalline film of about 15 mm thick. No obvious defects such as intercrystal gaps and cracks were observed (Figure 5a,b).

To measure the k values of the films, the as-synthesized film surface was polished. The PSZ BEA films were first polished with sandpaper (4000-8000 grit) followed by fine polishing with 0.5 μm α-Al$_2$O$_3$ suspension using a Buehler polisher. Polishing did not cause delamination or cracking of the film. The films strongly adhered to the substrate. These indicate that PSZ BEA films have outstanding mechanical strength and adhesion with the substrate.

Dielectric constant of the as-synthesized zeolite beta film was measured, and an average k value of about 2.3 was obtained. It is not surprising that moisture has very little effect on the dielectric constant since the moisture content of the sample was low. It is noted that attempts to calcine the BEA film lead to cracking of the films probably because the film is relatively thick and there is a significant difference of thermal expansion coefficient between the film and the stainless steel substrate. In our previous study, the k value of in-situ crystallized PSZ MFI film was measured to be 3.4 for as-synthesized and 2.7 for calcined film, respectively.[13] It is clear that PSZ BEA is superior to PSZ MFI as a low-k dielectric material. It is likely that BEA film will have k less than 2.3 once it is calcined. The experimental k value for as-synthesized PSZ BEA film is presented in Figure 1 (solid triangle), and once again the k value falls below the Bruggeman line.

Summary

Although stainless steel substrate was used and the film was rather thick, the preliminary data presented

here suggest that PSZ BEA is a promising low-k material. Further effort is warranted to develop in-situ PSZ BEA films that can be synthesized from TEOS and safely calcined so that more reliable data on film properties can be obtained. A synthesis method for PSZ BEA nanoparticles with uniform particle size distribution has been recently developed.[26] The size of the BEA particle is still large but it still offers an exciting opportunity to develop spin-on PSZ BEA low-k films that could readily have $k < 2$. The preparation method reported in this study is also useful for preparing pure-silica BEA membranes, films, and coatings.

Acknowledgment

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