Design of a Nanoporous Ultra Low-Dielectric Constant Organosilicate

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Abstract

A new class of structured organosilicates has been developed with an ultra low-dielectric constant, k, of less than 2.0, and high dielectric breakdown strength (> 2 MV/cm). In this approach, a series of triblock polymers, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO), are used as sacrificial materials in poly(methyl silsesquioxane) (MSQ) to generate pores after heating to temperatures ≥ 400 ^{o}C. Small angle neutron scattering (SANS) shows that these materials have extremely small pores, on the order of 1 nm. Additionally, these low k materials exhibit high mechanical strength with a Young's modulus ≈ 3 GPa.

Introduction

As device features in integrated circuits (IC) continue to shrink to increase the microprocessor speed and the density of devices packed on circuits, more wires are needed to connect tightly packed individual devices. This in turn increases the RC delay, power consumption and wire cross-talk between multilevel interconnects. These signal delays tremendously limit chip performance and reliability[1]. The current inter- and intra-level dielectric material, silicon dioxide (dielectric constant, k, of ≈4.0), will no longer be suitable for next generation ICs. Therefore, new low dielectric constant materials need to be identified. In addition to a low k, the new material must have good thermal stability (above 400 ^{o}C), low coefficient of thermal expansion (CTE), low moisture uptake, high glass transition temperature (Tg), good mechanical properties, high dielectric breakdown field, and good adhesion to various substrates.

In the past few years new classes of low-k materials deposited by different methods have been explored[2]. Several groups have demonstrated k to less than 2 by introducing air (k=1) into the film[2-8]. Porous silica has been fabricated through sol-gel process as ultra low-k materials[4, 8]. However, more than 50% porosity is required to extend the k value to less than 2.0. These highly porous films may not have the mechanical properties needed to withstand chemical mechanical polishing (CMP) processing steps during circuit fabrication. In addition, hydrophilicity and sensitivity to moisture are issues that need to be addressed in porous silicas.

Another promising approach is to add sacrificial materials, such as hyper-branched polymers[5], high boiling point solvents[7] or organic spacers in an organic/inorganic hybrid silicate, such as poly(silsesquioxane), which have a relatively

low dielectric constant, k ≈ (2.6 to 3.0) and are hydrophobic. Only 30 % porosity is required to reach the ultra low-k region using these organosilicates as matrices. Low-k materials with closed nanopores will have the advantage of good electrical properties, strong mechanical strength, and resistance to metal diffusion.

Here, we report a new class of materials that can reach ultra low dielectric constants while maintaining good mechanical properties. In this general approach, amphiphilic triblock copolymers, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO) are used as sacrificial materials in poly(methyl silsesquioxane) (MSQ) to generate nanopores. These porous materials have dielectric constants of 2 and exhibit low I-V leakage. Small angle neutron scattering (SANS) revealed that these materials have extremely small pores, on the order of 1 nm. The Young's modulus and hardness of a film with a k value of 2.0 are ≈3 GPa and (0.5 to 0.6) GPa, respectively.

Experimental Section

Preparation of Ultra Low-k Materials. Solutions of block copolymers, Pluronic® F88 and P103 (BASF)[9] and MSQ precursor were spun on Si wafers coated with TiN (1000 Å). The films were then baked on a hotplate at 120 ^{o}C and placed in a tube furnace purged with N_2. After soaking in N_2 for more than 1 h, the furnace temperature was ramped up at a heating rate of 1.5 ^{o}C/min to 500 ^{o}C and held at this temperature for 2 h before being cooled down slowly. The final film thickness was (0.3-0.8) μm as measured by a Dektak^3-30 surface profiler.

Characterization. The morphology of the dielectric film was imaged from the cross-section TEM. The ultra-thin films (≈50 nm) were first cut by focused ion beam (FIB) milling[10]. They were then lifted-out and transported to a carbon coated copper grid for TEM analysis. The thermal decomposition of triblock copolymers was studied by a Perkin-Elmer thermogravimetric analyzer TGA 7 under nitrogen flow.

The capacitance of the film was measured between electrodes, Al (top) and TiN (bottom), at room temperature in air by a 4284A precision LCR meter with a frequency of 1 KHz. The capacitance measurement was averaged on 4 dots. The dielectric breakdown strength was measured on a 4145B Hewlett-Packard (HP) semiconductor parameter analyzer with the same sample setups.

Specular X-ray reflectivity (SXR) was measured using a θ-2θ configuration with a fine focus copper X-ray tube as the radiation source. The data was collected at grazing incident angles, ranging from 0.01 to 1.0 degrees to determine the density and thickness of the dielectric film[11]. The wall density of the pores and pore sizes were measured by SANS, which was conducted on the NG1 and NG3 instruments at the Center for Neutron Research at the National Institute of Standards and Technology (NIST)[11].

Young's modulus and hardness were measured by frequency specific depth-sensing indentation on Nanoindenter® XP as illustrated in the literature[12]. The data was obtained at the displacement depth of 75 nm of the films spun on Si wafers and averaging the results from 9 indents.

Results and Discussion

Block copolymers have unique amphiphilic characteristics and have been used as directing templates or surfactants[13]. When block copolymers are blended with another polymer or matrix, they may self-assemble into a spherical micellar structure with the miscible block as the shell and the immiscible block buried inside to minimize the interfacial energy. Given the ability to precisely control their functionalities and properties, block copolymers are used in our approach as sacrificial templates to mix with the MSQ precursor to generate homogeneous closed pores.

Before curing, the hydrophilic Si-OH groups and trace Si-OEt groups in the MSQ precursor are miscible with PEO blocks while the hydrophobic Si-CH_3 is compatible with PPO blocks. After curing, Si-OH/ Si-OEt groups are polycondensed to Si-O-Si and the film become hydrophobic due to the methyl groups in the crosslinked network.

Experiments were conducted with two types of PEO-b-PPO-b-PEO triblock copolymers, F88 and P103, which have molecular weights[14] of 11250 g/mol and 4950 g/mol, respectively and mass fractions of PEO blocks of (80 and 30) %, respectively (see Table 1). The spun film was then baked at 120 ^{o}C, followed by heating slowly to 500 ^{o}C and held at this temperature for 2 h in N_2 to generate pores. The dielectric constants (f = 1 KHz) decreased from (2.6 - 2.8) to 2.0 (see Figure 1) when F88 or P103 with a mass fraction of 30 % was added in MSQ.

Table 1. Comparison of properties of porous ultra low-k materials with polymer loadings mass fraction of 30 % to MSQ.

Properties	P103/MSQ, 30 %	F88/MSQ, 30 %	MSQ
Dielectric constant, κ	2.00	2.04	2.6-2.8
Density (g/cm^3)	0.86±0.02	0.88±0.02	1.3
Wall density (g/cm^3)	1.18±0.27	1.16±0.16	
Porosity	27±17	24± 9	0
Pore size (nm)	1.6±0.5	1.4±0.3	
Young's Modulus (GPa)	2.7±0.4	3.0±0.3	5.8±0.1
Hardness (GPa)	0.5±0.1	0.6±0.1	1.3±0.4

Electrical Properties. Because the dielectrics layers are thin, high dielectric breakdown strength becomes more important for low-k applications. The current-voltage (I-V) curves were measured for porous MSQ with different polymer loadings and compared to MSQ. As seen in Figure 2, the porous MSQ films have a very high breakdown field, >2 MV/cm. Although the dielectric constants have decreased to ≈ 2.0, the I-V curves are similar to that of cured MSQ (k ≈ 2.6-2.8) within experimental error. The I-V curves are very flat up to 100 volts. Because these films are not annealed before measurement or capped with a metal diffusion barrier, the high breakdown field indicates that these films may have either closed pores or very small pores.

Overall film density, pore size and wall density. The density of the overall film is important in understanding the mechanical strength of the dielectrics. Dielectric films are typically thin, ≈ 1 μm. The structure of a thin film may not be the same as that of a bulk material. By using high-resolution specular X-ray reflectivity (SXR), it is possible to monitor the thin film density directly on Si wafer after processing. Following the method

described by Wu et al.[11], the mass densities of films with k ≈2.0 are (0.88±0.02) g/cm^3 and (0.86±0.02) g/cm^3 for films from F88 and P103 respectively, compared to the density of MSQ matrix, 1.3 g/cm^3 (See Table 1). In addition to the material density, pore size, structure, and interconnectivity are very important parameters to determine electrical and mechanical properties of the films. The cross-section TEM of low-k films looked similar to that of MSQ; no visible pores were observed. To further understand the pore size and structure, small angle neutron scattering (SANS) was used in our study. SANS has the distinct advantage of measuring pore structures in thin films spun on the Si wafers because single crystal silicon wafers are essentially transparent to neutrons. By fitting the SANS data with the Debye model[15] and *assuming* the film has the elemental composition of the cured MSQ resin, the pore size, porosity and the pore wall density can be determined. The pore size (the average chord length of the two-phase material) is found to be extremely small, (1.4 ± 0.3) nm and (1.6 ± 0.5) nm for films from F88 and P103, respectively, with film porosities of (24 ± 9) % and (27 ± 17) %, respectively (see Table 1). The data from SXR and SANS are presented with the standard uncertainty of the measurements. These data are consistent with the results from TEM images and I-V measurements. The small pore size makes it very difficult for metals to diffuse into them so that the dielectrics would have very low leakage current.

Mechanical Properties. Mechanical strength for dielectric materials is essential for the circuit integration process. The dielectrics must be compatible with chemical mechanical polishing (CMP) and etching processes. Compared to conventional dielectric material, SiO_2, all low-k materials are less dense, which dramatically decreases their mechanical strength. MSQ with extremely small pores makes it possible to have an ultra low dielectric constant while maintaining good mechanical properties. The Young's modulus and hardness of our ultra low-k materials have been measured by nanoindentation. To minimize errors associated with potential nanoscale variabilities, fused glass with a Young's modulus of 58 GPa and a hardness of 5.4 GPa was used as a reference. The Young's modulus and hardness of these ultra low-k materials (k ≈2.0) are ≈ 3 GPa and (0.5 - 0.6) Gpa, respectively, compared to 5.8 GPa and 1.3 Gpa, respectively, of the MSQ matrix (see Table 1).

Conclusions

A new class of ultra low-dielectric constant material has been designed to reach a k value of less than 2.0. The amphiphilic triblock copolymers, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO), are used as sacrificial materials in spin-on organosilicate matrices, poly(methyl silsesquioxane) (MSQ). TEM and SANS revealed that these pores are extremely small, on the order of 1 nm. These materials exhibited high electrical breakdown field (> 2MV/cm) and strong mechanical strength, Young's modulus of ≈ 3 GPa and hardness of (0.5 - 0.6) GPa.

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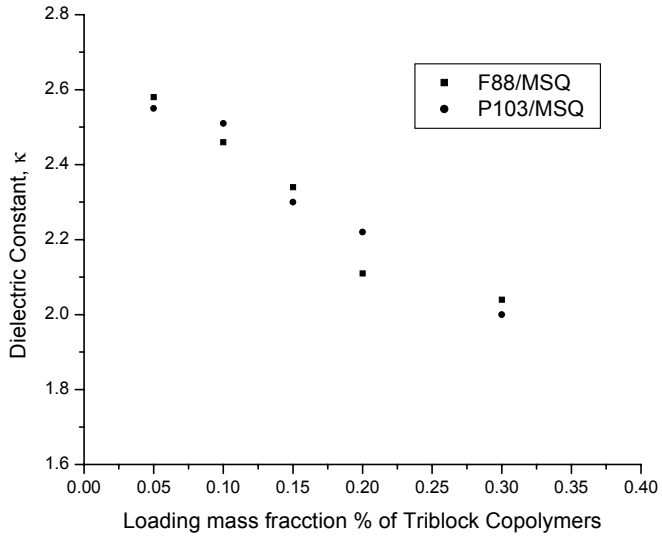

Figure 1. The relationship of dielectric constant versus loading mass fraction of triblock copolymers in MSQ.

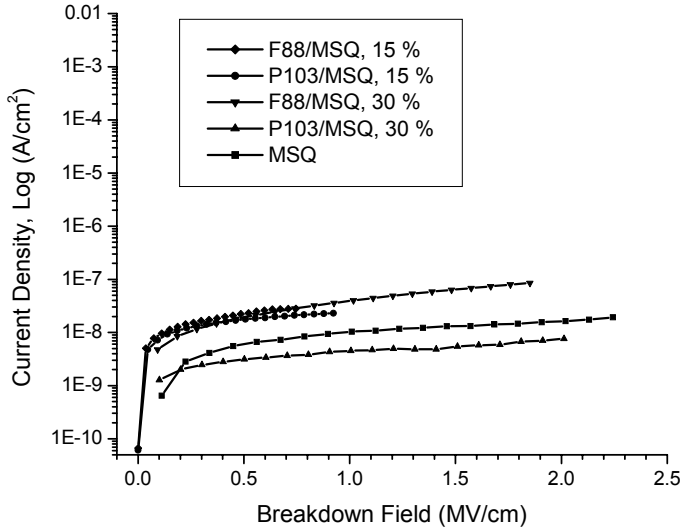

Figure 2. The dielectrical breakdown strength of low-k materials with different loading mass fractions of triblock copolymers.

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14) According to ISO 31-8, the term "molecular weight" has been replaced by "relative molecular mass," symbol M_r. Thus, if this nomenclature and notation were to be followed in this publication, one would write $M_{r,n}$ instead of the historically conventional M_n for the number average molecular weight, with similar changes for M_w, M_z, and M_v, and it would be called the "number average relative molecular mass." The conventional notation, rather than the ISO notation has been employed for this publication.
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