Low *k*, Porous Methyl Silsesquioxane and Spin-On-Glass

Abbe T. Kohl,[a] Richard Mimna,[b] Robert Shick,[b] Larry Rhodes,[b] Z. L. Wang,[c] and Paul A. Kohl[a],*,[z]

[a] School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100, USA
[b] BFGoodrich Company, Electronic Materials Division, Brecksville, Ohio 44141, USA
[c] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, USA

Low dielectric constant, porous silica was made from commercially available methyl silsesquioxane (MSQ) by the addition of a sacrificial polymer, substituted norbornene polymer containing triethoxysilyl groups (NB), to the MSQ. The silsesquioxane-NB polymer film mixture was thermally cured followed by decomposition of the NB at temperatures above 400°C. The dielectric constant of the MSQ was lowered from 2.7 to 2.3 by creating 70 nm pores in the MSQ. The voids created in the MSQ exhibited a closed-pore structure. The concentration of NB in the MSQ affected the number of pores but not their size. Porous films were also created in a methyl siloxane spin-on-glass and its dielectric constant was lowered from 3.1 to 2.7. Infrared spectroscopy was used to follow the curing of the MSQ and decomposition of the NB.

The development of low dielectric constant (low *k*) materials is critical to the fabrication of high-speed electrical interconnections for integrated circuits and electronic packaging. Methyl silsesquioxane (MSQ), $CH_3SiO_{1.5}$, is a spin-on-polymer with a ladder structure formed by the hydrolysis of methyl triethoxysilane.[1,2] Spin-on-glass (SOG) polymers belonging to the methyl siloxane family are also available, although their dielectric constants are sometimes not as low as that of MSQ. Hydrogen silsesquioxane (HSQ), the hydrogen analog of MSQ can also be used as a spin-on-glass dielectric.[3] Cross-linking (curing) takes place in MSQ and HSQ through reaction of the alkoxy silyl groups on the oligomers. Commercially available MSQ and SOG have dielectric constants of 2.7 and 3.1, respectively.[4,5] Cured MSQ films have low moisture content and show little sensitivity to humidity over the range of 40-80% relative humidity.

Recently, it has been shown that air gaps can be fabricated by using a family of polynorbornenes as sacrificial materials.[6] The polynorbornene was patterned and encapsulated in plasma-deposited silicon dioxide. The polynorbornene thermally decomposed at 400-425°C, and the decomposition products permeated the encapsulating silicon dioxide. Derivatives of norbornene polymer containing triethoxy silyl groups (NB) are particularly useful, as in MSQ and SOG, because of the reactivity of the alkoxy silyl groups, HSQ especially for adhesion to metal and oxide surfaces and cross-linking with other alkoxy silyl groups.

In this study, we demonstrate formation of nanoporous silsesquioxane foams by mixing NB with commercially available MSQ and SOG followed by curing of the MSQ/SOG and decomposition of the NB. The curing temperature of the MSQ, HSQ, and SOG is at or below the decomposition temperature of the NB so that stabilized silsesquioxane films can be fabricated which retain the porous nature of the films created by the NB decomposition. The critical issues are the permeation of the NB decomposition products through the silsesquioxane cage structures and distribution of the pores. It is thought that the alkoxy silyl groups on the NB will react with those of the uncured MSQ or SOG, or assist in dispersing the NB throughout the spin-on-dielectric and preventing agglomeration of the NB. This will hopefully lead to pores with uniform size and distribution.

Experimental

Dielectric measurements were performed by fabricating parallel plate capacitors on silicon (100) wafers. The bottom plate of the capacitors was a full-surface film of sputtered Ti/Au/Ti (300/4000/300 Å). The dielectric materials were spin-coated onto the substrate at 3000 rpm. Substituted norbornene polymer containing triethoxy silyl groups (BFGoodrich, Brecksville, OH) was used as the sacrificial polymer. The solvent for the MSQ, SOG, and NB

Table I. Summary of dielectric constants.

Material	Dielectric constant	Standard deviation
Accuspin 418	2.71	0.05
Accuspin 418 with 20 wt % NB	2.31	0.09
Accuglass 512	3.1	0.1[4]
Accuglass 512 with 20 wt % NB	2.77	0.11

was 4-methyl-2-pentanone (Aldrich Chemical). The NB was dissolved in 4-methyl-2-pentanone, filtered, and mixed with the MSQ or SOG solution. The NB/MSQ and NB/SOG solutions were stirred for 1-2 h at room temperature, filtered, and spin-coated on the metallized silicon substrates. The MSQ, Accuspin 418, and SOG Accuglass 512, were obtained from Allied Signal (Santa Clara, CA). The cure schedule for the spin-coated materials consisted of soft baking in air at 180°C for 2 min, followed by curing in a nitrogen-purged, quartz tube oven. The temperature in the oven was ramped to the final temperature at a rate of 5°C/min. The final cure temperature, usually 425°C, was held for 30 min. The oven was allowed to cool slowly by natural convection to less than 150°C. The top electrode consisting of Ti/Au/Ti (100/4000/100 Å) was patterned by photolithography and wet etching. The area of the capacitors ranged from 0.025 to 1.1 cm^2. The capacitance and conductance were measured at 10 kHz. Only defect-free capacitors (see Results section) with low conductance, generally below 1 µS, and often below 0.01 µS, were used. Thus, the permittivity and dielectric constant are the same within the three significant figures reported. No correction was needed for fringing fields around the perimeter of the capacitors due to the high capacitor area-to-thickness ratio (>1000).[7]

Fourier transform infrared (FTIR) spectra (Nicolet 550) were obtained in transmission mode using low doped, double-sided polished silicon wafers. The transmission electron microscopy (TEM) sections were prepared in plane view by fracturing the film. Analysis was performed in a Hitachi HF-2000 microscope.

Results and Discussion

The capacitance and conductance of parallel plate capacitors on metallized silicon substrates were measured, and a summary of the dielectric constants is shown in Table I. The dielectric constant for 650 nm thick films of Accuspin 418 (methyl silsesquioxane) with a final cure temperature of 425°C was 2.71, with a standard deviation of 0.05. This value corresponds well to the published value of 2.7.[5] The capacitors were smooth, crack-free, and defect-free films.

A mixture of 20% NB (Molecular weight 158,000) and 80% MSQ (by weight) in 4-methyl-2-pentanone was made and spin-coated onto the metallized silicon substrates. The NB (20%)/MSQ (80%) capacitors were also defect-free (by optical microscopy) and slightly thinner (ca. 620 nm thick) than the MSQ-only samples. The amount of 4-methyl-2-pentanone solvent used in dilution of the NB was not tightly controlled. The cure schedule for the NB (20%)/MSQ (80%) capacitors was the same as for the MSQ-only samples. The dielectric constant for NB (20%)/MSQ (80%) heated to 425°C was 2.31 with a standard deviation of 0.09. Films of NB (40%)/MSQ (60%) and NB (60%)/MSQ (40%) were also prepared. The films were defect-free when spin coated; however, pinholes and voids formed during the curing step. The nature of these defects will be reported at a later time. Reliable capacitance values were not obtained due to the high conductivity of some of the films.

Capacitors were made from 20% NB in Accuglass 512 [NB (20%)/SOG (80%)] with a final cure temperature of 400°C. The average dielectric constant was 2.77 with a standard deviation of 0.11. The reported dielectric constant for Accuglass 512 is 3.1 ($\pm$ 0.1), although slightly higher values were obtained in this study (e.g., 3.3-3.5). The films were visually pinhole and defect-free.

The decrease in the dielectric constant with the addition of NB to the MSQ or SOG is due to the creation of nanometer-size voids in the cured film. Norbornene-based polymers have been shown to thermally decompose and produce volatile products that are able to permeate the encapsulating films.[6] It was shown that above 400°C, these polymers decompose and create air gaps when encapsulated by silicon dioxide. Thin sections of cured MSQ and MSQ/NB were prepared and examined by TEM. The micrographs for MSQ, NB (20%)/MSQ (80%), and NB (40%)/MSQ (60%) are shown in Fig. 1. No pores were observed in the cured MSQ (Fig. 1a), whereas pores could easily be identified in the MSQ/NB films. The pores observed in the 20% NB film (Fig. 1b) were approximately 70 nm in size and distributed throughout the film. The volume and shape of the norbornene chains with respect to the size of the pores formed in the MSQ is under investigation. The volume of the pores is greater than that expected from a single polymer chain, if the polymer was at its bulk density. As the weight percent of NB was increased, the number of pores increased but the size of the individual pores remained about the same. Figure 1 does not show the macroscopic pinholes observed by optical microscopy in the 40 and 60% NB films which prevented the capacitance measurements from being made.

The nanometer-sized pores in the films seem to have a closed-pore structure. However, additional TEM analysis is required to support this conclusion since it is difficult to distinguish between interconnected pores and closed pores, which happen to occupy the same lateral (*x,y* direction) position, but different depths (*z* direction). Pore uniformity is an important parameter for porous silica films. The bonding of the polymer to the silica backbone, via hydrolysis of the -Si-O-C_2H_5 groups of the NB and the -Si-O-CH_3 groups of the MSQ followed by condensation during the soft baking or curing, appears to be important.

The infrared spectra of NB (20%)/MSQ (80%) is shown in Fig. 2. The solution was spin-coated onto a low-doped, double-sided polished silicon wafer. The wafer was quartered and heated to different temperatures. The uncoated silicon wafer was used for background subtraction. The spectrum for NB (20%)/MSQ (80%) after spin coating and soft baking at 180°C is shown in Fig. 2a, and samples baked at 400 and 425°C are shown in Fig. 2b and c, respectively. The moisture content of the film is lowered significantly by baking to 400 or 425°C. This can be seen by a decrease in the Si-OH peaks at ~3400 and at 870-950 cm^{-1}.[8] The condensation cross-linking reaction of the MSQ causes a decrease in the peaks at 1126 and 1026 cm^{-1}. A change in these peaks is observed between the soft baked sample (Fig. 2a) and the cured samples (Fig. 2b and c). The Si-C stretch is observed at 1273 cm^{-1}, which is not changed by curing the MSQ. There are only minor differences in these peaks between the samples cured at 400 and 425°C. The decomposition and removal of the NB
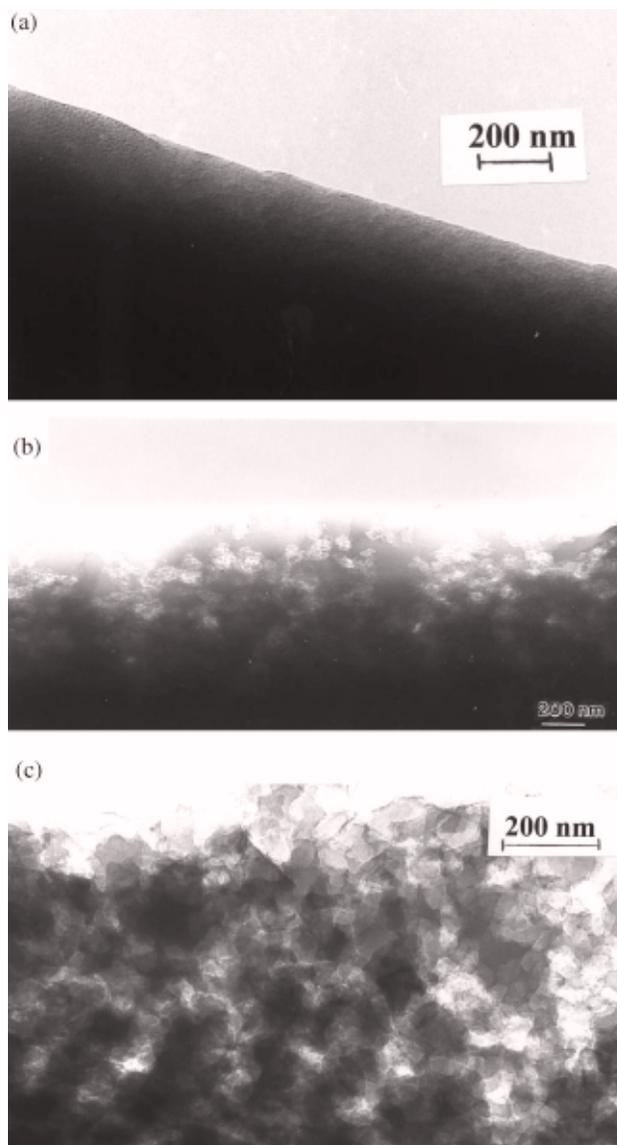

Figure 1. Transmission electron micrographs of (a) MSQ, (b) NB (20%)/MSQ (80%), and (c) NB (40%)/MSQ (60%) cured at 425°C for 30 min.

lowers the absorbance of the C-H_x stretching peaks between 2800 and 2980 cm^{-1}. A total of five peaks are expected in this region for the NB (20%)/MSQ (80%) mixture. There are two peaks each for C-H_2 and C-H_3 (symmetric and asymmetric stretches), and one peak for the C-H stretch. The MSQ contains only -CH_3 groups (two peaks), while the NB contains -CH_3, -CH_2, and -CH groups. The primary methyl peak for the MSQ is at 2873 cm^{-1}, however, the other C-H_x assignments have not been confirmed because of the unknown environment in the solid samples. Thus, the decomposition and evolution of NB should result in the disappearance of three small peaks, which was observed and is shown in the inset of Fig. 2.

Summary

Commercially available spin-on-dielectrics, methyl silsesquioxane (AlliedSignal Accuspin 418) and spin-on-glass (AlliedSignal Accuglass 512), have been modified by addition of a sacrificial polymer, substituted polynorbornene containing triethoxysilyl groups. The triethoxysilyl functionality of the norbornene is similar to that in the MSQ and SOG. After curing, the NB decomposed leaving closed pores in the MSQ. The addition of 20% by weight NB to MSQ lowers the dielectric constant from 2.7 to 2.3. Higher concen-
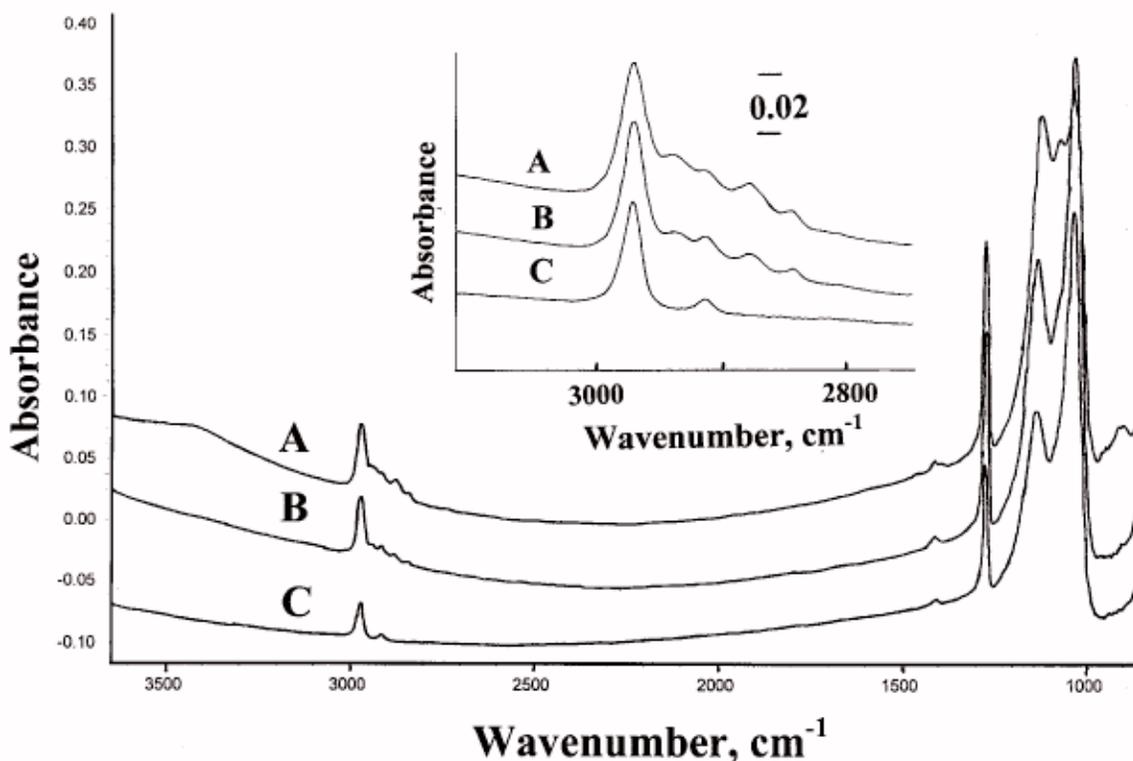
Figure 2. FTIR spectra of NB (20%)/MSQ (80%) (a) after soft baking at 180°C for 2 min, (b) curing at 400°C for 30 min, and (c) curing at 425°C for 30 min.

trations of NB in MSQ increase the number of pores, but not their size. FTIR analysis confirms the cross-linking of the MSQ during curing, the lowering of the moisture content, and the decomposition of the NB.

References

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