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Moisture-Insensitive Polycarbosilane Films with Superior Mechanical Properties

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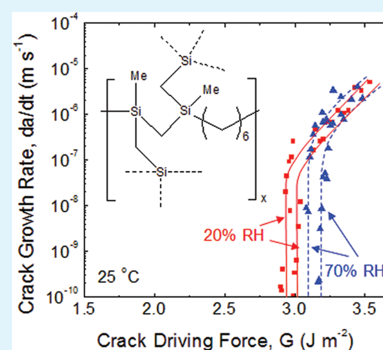
ABSTRACT: We report cross-linked polycarbosilane (CLPCS) films with superior mechanical properties and insensitivity to moisture. CLPCS are prepared by spin-coating and thermal curing of hexylene-bridged disilacyclobutane (DSCB) rings. The resulting films are siloxane-free and hydrophobic, and present good thermal stability and a low dielectric constant of $k = 2.5$ without the presence of supermicropores and mesopores. The elastic stiffness and fracture resistance of the films substantially exceed those of traditional porous organosilicate glasses because of their unique molecular structure. Moreover, the films show a remarkable insensitivity to moisture attack, which cannot be achieved by traditional organosilicate glasses containing siloxane bonds. These advantages make the films promising candidates for replacing traditional organosilicate glasses currently used in numerous applications, and for use in emerging nanoscience and energy applications that need protection from moisture and harsh environments.



KEYWORDS: *structure–property relationship, mechanical properties, moisture-sensitivity, dielectrics, hybrid material, and thin films*

1. INTRODUCTION

Porous organosilicate and silica-derived glasses are found in numerous industrial applications from membranes[1] to low-*k* dielectric materials.[2,3] Historically, the design of low-*k* dielectric materials for advanced technology nodes has been based on the chemical and structural modification of the silica network. Decreasing the dielectric constant has been achieved by introducing carbon, free volume, and more recently, porosity using sacrificial organic second phases.[2,3] Unfortunately, these materials not only suffer from poor mechanical properties due to the inherently mechanically fragile nature of silica and reduced glass network connectivity with the reduction of density, but they are also highly sensitive to "moisture-assisted cracking". This phenomenon occurs at loads well below fracture resistance because of a stress-enhanced reaction between water and moisture-sensitive siloxane bonds at the crack tip.[4−9]

The moisture-sensitivity of the silicates and organosilicate glasses therefore results in a deterioration of their mechanical properties and seriously limits their practical utility, particularly, in the microelectronics industry.[4,9−12] From a manufacturing point of view, moisture-assisted cracking is a difficult challenge to address because a small defect could slowly grow over time leading to a catastrophic failure of the device. Moreover, the additional porosity in organosilicate glasses to obtain low-dielectric constant offers a convenient pathway for reactive molecules, and therefore exacerbates this issue. To address the issue, nonsilicon containing organic polymers have been considered as potential low-*k* materials, but none of them has been successfully implemented.[2,3]

The moisture-sensitivity of organosilicate and silicate-based glasses therefore accentuates the need for new silicon-based materials without siloxane bonds, which mimic the three-dimensional molecular framework of the silicates and organosilicates. In addition, they should be easily processed and mechanically robust. Interestingly, siloxane-free organic polymers, such as silazanes (Si−N−Si bonds) and carbosilanes (Si−C−Si bonds), have been studied to address the issue of moisture-sensitivity of siloxane bonds.[13] Although silazanes are less prone to nucleophilic attack due to the less polar nature of Si−N−Si bonds than that of Si−O−Si bonds, they still display some property degradation in contact with moisture.[13] Carbosilane-based materials are not well explored for their mechanical properties (except for high temperature ceramics and barrier layers, e.g. SiC, SiCN, etc.) or moisture-assisted cracking behavior due to their general lack of solution processability and a suitable cross-linking mechanism.[13] Until now, the search for siloxane-free low-*k* dielectrics has been unsuccessful.

We have recently developed cross-linked polycarbosilane (CLPCS) thin films that can form through the thermal ring-opening of embedded disilacyclobutane (DSCB) rings.[14−16] These polymers, which have the general formula, [-Si(CH_3)-(CH_2)$_2$Si(CH_3)-Y-]$_n$ where Y = -(CH_2)$_x$-, -C_6H_4-, etc. (Scheme 1), are readily soluble in common organic solvents and can be spin-coated onto Si and other substrates to yield uniform films

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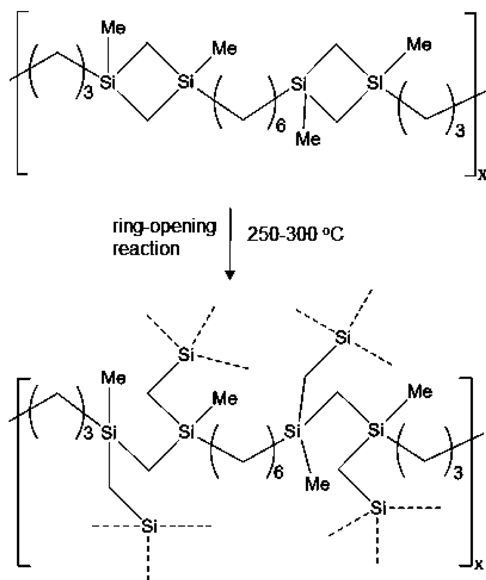
Scheme 1. Preparation of Cross-Linked Polycarbosilanes (CLPCS) Films through Ring-Opening Reaction of Disilacyclobutane (DSCB) Units



up to 1 μm in thickness. The DSCB rings open by curing at 300 °C to form a highly cross-linked polycarbosilane network that retains the uniformity and hydrophobicity of the original polymer film with minimal shrinkage and without cracking. The cured CLPCS film is completely insoluble, does not swell or react when in contact with organic solvents and all but the most aggressive aqueous reagents. Additionally, the CLPCS films have recently demonstrated excellent adhesion with SiO_2[17] and Cu[18] layers, both of which are currently employed in microelectronics devices. However, the mechanical properties of the CLPCS films including elastic constants, fracture resistance, and moisture-assisted cracking have not been studied.

In the present study, we focus on mechanical properties with emphasis on the moisture-sensitvity of siloxane-free CLPCS films generated by cross-linking of hexylene-bridged DCSB rings ($Y = (CH_2)_6$) without using a sacrificial organic phase. We first report the effect of curing conditions (200, 300, and 400 °C for 1 h) both on the degree of cross-linking and material properties of the CLPCS films. We then describe mechanical properties of the films cured at selected temperatures. We finally show the sensitivity of the films to moisture-assisted cracking. The films not only exhibit excellent mechanical properties but they are remarkably insensitive to moisture-assisted cracking. The crack growth rates at 25 °C and different humidities were identical, indicating an insensitivity to moisture-assisted cracking, which is in marked contrast to that of organosilicate glasses. We believe that CLPCS films are not only promising low-k candidates for microelectronics but also for emerging nanoscience applications where coatings that are resistant to moisture or harsh conditions are needed.

2. EXPERIMENTAL SECTION

Film thicknesses and refractive indices were measured using a Filmetrics F20 spectral reflectometer. Dielectric constants were determined using a capacitance bridge with an HP 4192A impedance analyzer using a metal insulator semiconductor (MIS) test structures. Young's modulus was obtained using surface acoustic wave spectroscopy (SAWS). SAWS studies were performed with a laser-acoustic thin film analyzer (LaWave, Fraunhofer USA) and acoustic waves were generated by a nitrogen pulse laser (wavelength 337 nm, pulse duration 0.5 ns). These were detected using a transducer employing a piezoelectric polymer film as a sensor. The measured surface wave velocity as a function of frequency was fitted with the theoretical dispersion curve to deduce Young's modulus (a value of 0.25 was assigned for Poisson's ratio). The measurements of Young's modulus were repeated 7 or 8 times.

Specular X-ray reflectivity measurements were used to determine samples density and these were performed using a diffractometer (X'Pert Pro MRD, Panalytical) with ceramic X-ray tube (wavelength = 0.154 nm) and high resolution horizontal goniometer (reproducibility ±0.0001°). The critical angles from the reflectivity data were obtained from the peak position of $Iq4$ vs q plots ($q = 4p/k$)sin h, where k is the wavelength and h is the grazing incident angle of the X-ray beam).

Cohesive fracture energy characterization: Blanket films (400 nm) capped with metal layers were bonded to blank silicon wafers with epoxy adhesives, which were then diced by a high-speed wafer saw to fabricate DCB geometry specimens with appropriate dimensions. The DCB specimens were loaded in pure mode I, and displacement was measured to determine cohesive fracture energy, G_c, in a laboratory air test environment at ∼25 °C and ∼40% RH with a Delaminator Test System (DTS, Menlo Park, CA). The measurements of G_c were conducted 15 times. The method for calculating G_c is detailed elsewhere.[19] After testing, X-ray photoelectron spectroscopy (XPS, VersaProbe, Physical Electronics) was used to determine the fracture path.

To characterize sensitivity to moisture-assisted cracking of the CLPCS films, we measured the crack growth rate, da/dt, with the DCB technique at 25 °C in 20 and 70% RH. DCB specimens were loaded at a constant loading rate (2 μm s^{-1}) to a predetermined load at which the displacement was fixed. Then automated analysis of the load relaxation with increasing compliance of the specimens determined the crack growth rate over the range of $\sim 1 \times 10^{-10}$ to $\sim 1 \times 10^{-4}$ m s^{-1} as a function of applied strain energy release rate, G. General methods of crack growth measurements are described elsewhere.[4]

3. RESULTS AND DISCUSSION

3.1. CLPCS Synthesis and Materials Characterization.

The degree of cross-linking through the opening of the strained DSCB rings was followed by monitoring the sharp C−H bending vibrations at 930 cm^{-1} in the FT-IR spectra, which upon ring-opening shifts to a broad band centered around 1050 cm^{-1}. The measurements of the C−H bending vibration intensity in the FT-IR spectra at 200, 300, and 400 °C revealed an increasing cross-linking when temperature increases, as expected (Figure 1a−c). However, the films cured at 400 °C exhibit a Si−H peak centered around 2100 cm^{-1} that was absent for the films cured at lower temperatures. The formation of the Si−H species during the curing of organosilicon polymers at high temperatures generally suggests involvement of radical species and indicates that some organic groups have been degraded. Additional shrinkage was observed for the film cured at 400 °C, but it is minimal (Table 1).

For the CLPCS films cured at 300 and 400 °C, the dielectric constant was around $k = 2.5$ (Table 1). Such a low dielectric constant results from a combination of low material polarity with the presence of free volume. Further characterization of the material intrinsic porosity by ellipsometric porosimetry indicated that the pore size should be below 7−8 Å as no adsorption was detected with toluene. This is advantageous regarding both processing damage, and diffusion of water molecules and chemical species within the film as the presence of supermicropores and mesopores usually aggravates these phenomena. Moreover, RBS/ERD detected a very small amount of oxygen atoms in the CLPCS films (Table 1),

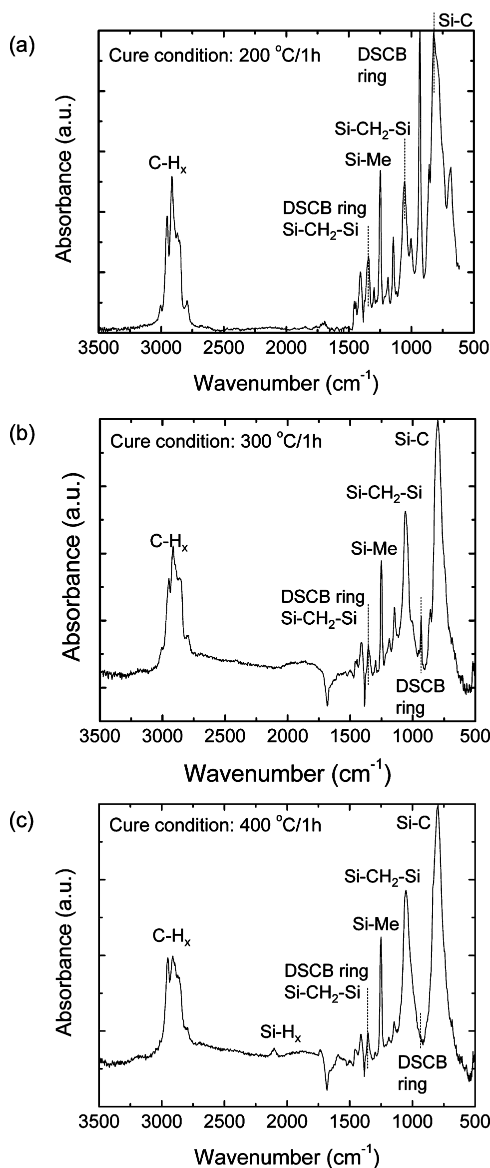


Figure 1. (a–c) FT-IR spectra of CLPCS films cured for 1 h at (a) 200, (b) 300, and (c) 400 °C.

Table 1. Material Properties and Chemical Composition of CLPCS Films and Traditional Porous Organosilicate Glasses with Similar Dielectric Constants

films	density, ρ (g cm^{-3})	dielectric constant, k	shrinkage (%)	RBS/ERD [Si]/[O]/[C]/[H] (at %)
CLPCS (300 °C)	1.058	2.5	6.7	6.5/0.7/27.1/65.7
CLPCS (400 °C)	1.074	2.5	12.9	7.1/1.2/23.7/67.9
MSSQ[20]	1.190	2.5–2.6		
CDO[21]	1.180	2.5		

indicating that there are very few Si–O–Si bonds susceptible to moisture-assisted cracking.

2.2. Mechanical Properties and Sensitivity to Moisture-Assisted Cracking.

We examined the Young's modulus, cohesive fracture energy, and sensitivity to moisture-assisted cracking of the CLPCS films cured at 300 and 400 °C. Films cured at 200 °C were excluded because of their low degree of cross-linking (Figure 1 (a)). The mechanical properties were compared with those of commercially available porous methylsilsesquioxane (MSSQ) and carbon doped oxide (CDO) organosilicate glasses with similar dielectric constants.

The Young's modulus, E, was measured by surface acoustic wave spectroscopy (SAWS). As shown in Figure 2, the films cured at 300 and 400 °C exhibited Young's modulus of 9.2 and 7.3 GPa, respectively. These measured values are superior to that of MSSQ (E = 4.8 GPa[20]) (Figure 2). The value for the films cured at 300 °C is even higher than that of CDO glasses (E = 8.1 GPa[21]) (Figure 2). These high Young's modulus, particularly for the films cured at 300 °C, is significant considering the presence of flexible sp^3 carbon chains and the lower materials density because Young's modulus depends on both bond stiffness and glass density. We believe that this observation results from two unique characteristics of the films. First, despite the lower density the glass network connectivity of the films can be greater than those of MSSQ and CDO glasses. It is known that cage and cyclic structures commonly formed in MSSQ and CDO glasses lead to reduced glass network connectivity.[22] However, such structures cannot form through the present cross-linking mechanism (scheme 1). Second, network forming Si–C bonds in the films can be stiffer than Si–O bonds in MSSQ and CDO glasses. Bond stiffness, S, for both Si–C and Si–O bonds may be estimated to first order from $S = E/r$ where r is a characteristic molecular bond distance. r may be approximated by $r = (M/n\rho N_A)^{1/3}$, where M is the molecular weight of structural unit, n is the number of bonds per repeating structural unit, ρ is the material density, and N_A is Avogadro's number. Using materials properties of both crystalline silicon carbide ($E \approx 400$ GPa, $\rho \approx 3.21$ g cm^{-3}) and fused silica ($E \approx 73$ GPa, $\rho \approx 2.2$–2.3 g cm^{-3}), the bond stiffness of Si–C bonds was estimated to be ~69.2 N m^{-1}, which is significantly greater than that of Si–O bonds ~16.8 N m^{-1}. The higher value for the Si–C bonds compensates for the flexible sp^3 C–C bonds, thereby resulting in a higher Young's modulus of the CLPCS films.

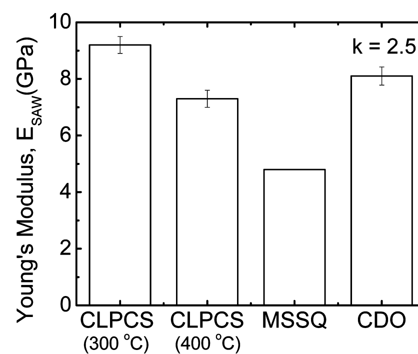


Figure 2. Young's modulus of CLPCS films cured at 300 and 400 °C for 1 h and traditional porous organosilicate glasses. All of the materials have dielectric constants ~2.5. Error bars represent one standard deviation.

On the other hand, a decrease in the Young's modulus with increasing cure temperature can be explained by film decomposition as indicated by the FT-IR peak corresponding to Si–H$_x$ group only in the films cured at 400 °C (Figure 1c). This is because the formation of Si–H$_x$ group reduces the glass network connectivity, thereby decreasing the Young's modulus of the films.[23,24] Typically, back-end-of-line (BEOL) processes involve thermal excursion at 400 °C, but recently new BEOL protection integration schemes that require maximum exposure

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to only 350 °C have been developed,[25] which will metigate the deterioration in the Young's modulus.

The cohesive fracture energy, G_c, of films cured at 300 °C was measured by double cantilever beam (DCB) testing.[19] The fracture path characterized by X-ray photoelectron spectroscopy was close to the silicon substrate, but within the films, indicating cohesive fracture. As shown in Figure 3, the cohesive

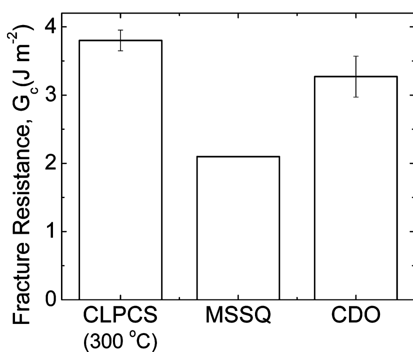

Figure 3. Cohesive fracture resistance of CLPCS films cured at 300 °C for 1 h and traditional porous organosilicate glasses. All of the materials have dielectric constants ~2.5. Error bars represent one standard deviation.

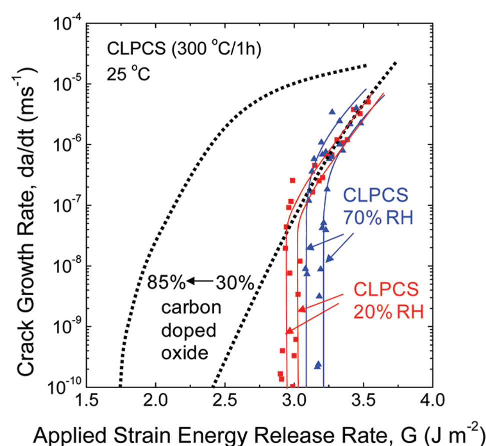

Figure 4. Crack growth rates of CLPCS films cured at 300 °C for 1 h as a function of applied strain energy release rate in 20 and 70% RH. Dotted curves represent crack growth rates of carbon-doped oxide organosilicate glasses at 30% and 85% RH. The crack growth behavior of CLPCS films is insensitive to humidity change, demonstrating a remarkable resistance of the films to moisture attack as opposed to CDO organosilicate glasses.

fracture energy of the films was 3.8 J m^{-2}, a value superior to those of MSSQ (2.1 J m^{-2}[26]) and CDO (3.2 J m^{-2}[21]) glasses. This higher value of cohesive fracture energy is due primarily to the insensitivity of Si−C and sp^3 C−C bonds to moisture attack. The cohesive fracture energy of silica measured in air environments tends to be lower than that measured in vacuum environments because of nucleophilic susceptibility of strained Si−O−Si bonds to water molecules.[6]

In addition, secondary energy dissipation mechanisms contribute to the higher cohesive fracture energy. Secondary energy mechanisms consume energy in addition to one used for rupturing bonds during fracture, thus increasing the fracture resistance. Although absent in both MSSQ and CDO glasses, these mechanisms are active in our films due to the presence of both sp^3 carbon chains and Si−C bonds in the forms of molecular bridging,[20,27,28] bond trapping,[29,30] and plastic deformation. Molecular bridging involves the stretching of sp^3 carbon chains at the crack tip. Bond trapping is associated with phonon emissions that occur when stored energy in surrounding bonds are released as a result of fracturing dissimilar bonds. These two mechanisms have been reported to increase the cohesive fracture energy of bridged organosilicate glasses containing carbon bonds (CH_2[20,27]) and chains (C_2H_4[23,27,31]). Plastic deformation involves rearrangement of sp^3 carbon chains due to elevated stress fields from the crack tip. This mechanism has also been reported to increase the cohesive fracture energy of carbon-rich hydrogenated amorphous silicon carbide thin films, which have similar molecular structures to our films.[32]

We finally investigated the sensitivity to moisture-assisted cracking of the films cured at 300 °C. To examine the sensitivity, the crack growth rates from ~1×10^{-10} to ~1×10^{-4} m s^{-1} as a function of applied strain energy release rate, G, were measured using DCB testing combined with an automatic load relaxation technique.[4] The measurements were repeated twice using different specimens at 25 °C in 20 and 70% RH with repeatable results. As shown in Figure 4, the films exhibited time-dependent crack growth below the fracture resistance, G_c. However, there was very little difference in crack growth rates at different humidities. The crack growth rates were not accelerated by increasing humidity. Also, the crack growth was confined to a narrow range of G values (3.0−3.5 J m^{-2}), and reached a crack growth threshold, G_{th}, at ~2.9−3.2 J m^{-2}, below which crack growth is presumed to be dormant. These results clearly indicate the insensitivity of the films to moisture-assisted cracking, which is a marked contrast to organosilicate glasses. For comparison, the crack growth of CDO glasses with comparable G_c values[33] in humid environments are shown in Figure 4. The crack growth of the CDO glasses occurred in a much wider range of G values (1.7−3.5 J m^{-2}), and were significantly accelerated by increasing humidity. For example, the crack growth rate at G = 2.5 J m^{-2} increased by more than 3 orders of magnitude when the humidity was increased from 30 to 85% RH. Much lower G_{th} values of ~1.7 to 2.4 J m^{-2} were observed.

To the best of our knowledge, this is the first time that a low-k dielectric with $k \approx 2.5$ was found to exhibit an insensitivity to moisture-assisted cracking. This certainly could not be achieved in organosilicate glasses containing Si−O−Si bonds susceptible to moisture attack. The insensitivity of the films to moisture-assisted cracking is indeed consistent with our hypothesis, and thus would suppress moisture-assisted defect evolution and growth during BEOL process and in use that can negatively affect process yield and device reliability.

In spite of the absence of Si−O−Si bonds, however, time-dependent crack growth below G_c of the films was observed. A mechanism for the occurrence of such time-dependent crack growth is not related to moisture, but most likely due to the stress relaxation of flexible sp^3 carbon chains in the films. Flexible sp^3 carbon chains are known to exhibit stress relaxation near the crack tip resulting in time-dependent crack growth without any reaction to water molecules and other reactive species.[34−36] However, the time-dependent crack growth of the films was confined to a much narrower range of applied G than that of the CDO glasses, and therefore its impact on device reliability would be very limited.

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3. CONCLUSIONS

In summary, we have demonstrated that siloxane-free cross-linked polycarbosilane (CLPCS) films, prepared by spin-coating and thermal curing of disilacyclobutane (DCSB) rings, exhibit not only excellent mechanical properties but also a remarkable insensitivity to moisture attack. CLPCS films are hydrophobic, and present good thermal stability and a low dielectric constant $k = 2.5$ without using a sacrificial organic second phase. The absence of supermicropores and mesopores mitigates unwanted process damages and diffusion of moisture and chemical species. The elastic constant and fracture resistance of the films substantially exceed those of traditional porous organosilicate glasses because of the unique molecular structure of the films. Moreover, the films show a remarkable insensitivity to moisture-assisted cracking, which has never been achieved by traditional organosilicate glasses containing siloxane bonds susceptible to moisture-attack. Altogether, these advantages make CLPCS films promising candidates for replacing traditional silica-based organosilicate glasses, and for use in emerging nanoscience and energy applications that need protection from moisture and harsh environments.

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Notes

The authors declare no competing financial interest.

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