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Dielectric behavior of organically modified siloxane melting gels

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ABSTRACT

Hybrid melting gels were prepared by a sol–gel process, starting with a mono-substituted alkoxysilane and a di-substituted alkoxysilane, methyltriethoxysilane (MTES) together with dimethyldiethoxysilane (DMDES). Five gel compositions were prepared with concentrations between 50% MTES–50% DMDES and 75% MTES–25% DMDES (in mol%). The index of refraction was measured using a Becke line method. The index of refraction decreased slightly as the amount of mono-substituted alkoxysilane decreased. The dielectric constant was determined from impedance spectrometry that followed dielectric constant and dielectric loss as a function of frequency. The dielectric constant was lowest in the 50% MTES–50% DMDES composition at frequencies greater than 1 kHz, around 3.3. Since direct Si–C bonds are less polarizable than Si–O–Si, the di-substituted alkoxysilane component decreases the dielectric constant.

1. Introduction

Microelectronic fabrication techniques are becoming more sophisticated (e.g., see Ref. [1]) as devices shrink the processes for etching channels and depositing materials require greater precision. There is a drive for continuing the trend of Moore's law and, at the same time, for lowering the cost of the final product. A major change in the previous decade was to lower the resistance and capacitance (RC) signal delay in back end of the line (BEOL) interconnects. A more recent change has been the replacement of the insulator, silica with dielectric constant (k) around 3.9 to 4.2, with a porous organically modified silica insulator of a lower k value [2]. This has enabled a higher transistor density, which lowers cost but incorporates more complicated materials.

In general, plasma enhanced chemical vapor deposition (PECVD) is used to deposit these new insulating materials. For example, a matrix of methyltrimethoxysilane (MTMS) combined with various oxycarbosiloxanes is used commercially for interconnect layers in BEOL processing for the 32 nm node and below [3,4]. The oxycarbosiloxane precursor creates carbon bridges within the silica network to add strength to accommodate higher porosity. Problems occur when the porosity exceeds 30% of the volume [5]. Further studies show that MTMS with bis(trimethoxysilyl)ethane (BTMSE) lowers the dielectric constant as the percentage of MTMS is increased [6]. It is possible that with further combinations of alkoxysilanes and porosity, dielectric constants below 2 can be achieved.

A variety of sol–gel methods have been used to prepare hybrid organic–inorganic dielectric materials. The materials of interest all contain silanes and siloxanes. For example, mixtures of tetraethyl orthosilicate (TEOS), which has 4 hydrolyzable groups, and methyltriethoxysilane (MTES), which has 3 hydrolyzable groups and 1 non-hydrolyzable group, have been used to increase hydrophobicity and decrease dielectric constant [7]. In this case, the decrease in dielectric constant resulted from an increase in porosity, which compromised the hardness. Another formulation involved preparing porous silicate cages known as polyoctahydridosilsesquioxanes (POSS) and linking these together with linear dienes [8]. This mixture produced spin-coatings with small and consistent nanoporosity that decreased the dielectric constant. However, the films required a treatment with trimethylchlorosilane to decrease surface water.

In some cases, the emphasis has been on increasing the porosity without using hybrid gels. For example, pure silica films from TEOS have been prepared with pore fractions as high as 0.74. This was accomplished by introducing polymethyl methacrylate (PMMA) latex nanoparticles into the gels [9]. Below a pore fraction of 0.40, the pores were isolated, while above 0.40, the pores were percolated. The closed pore films exhibited an index of refraction of 1.29 at 600 nm. The latex was removed by combustion at 400–500 °C, without disrupting the pore structure.

The majority of low dielectric constant films have been hybrid compositions. Hybrid films with methylsilsesquioxane and benzylsilsesquioxane have been prepared by electrophoretic sol–gel deposition to increase film thickness [10]. In addition to methyl groups, TEOS has been modified with vinyl and γ-glycidoxypropyl groups, which increase the refractive index [11]. To repair the decrease in elastic modulus that accompanies increased porosity, a laser spike annealing (LSA) treatment has been used on organosilicate spin-on films prepared with TEOS and MTES [12]. Using a 110 W continuous wave CO_2 infrared laser with an output peak around 10.6 μm, it was

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possible to find an exposure that increased the modulus without increasing the dielectric constant.

While many other hybrid gels have been investigated, one last example of a hybrid gel designed for low-k dielectrics is one where TEOS and MTES are reacted in the presence of an ethyleneoxide–propyleneoxide–ethyleneoxide copolymer in multiple steps to produce an organo-functionalized mesoporous silica (OFM) and an organo-functionalized silicalite-1 (OFS), which are combined in different ratios [13].

While it is difficult to achieve the lowest values for dielectric constant without incorporating porosity, it is desirable to minimize porosity because of its negative effect on strength, hardness and vapor transport. Besides the sol–gel methods already described, melting gels are an approach to hybrid gels, where the carbon content can be adjusted. These so-called melting gels extend the range of SiCO(−H) compositions that presently are used in BEOL. In addition, sol–gel methods tend to be simpler than PECVD.

Melting gels are a class of organically modified silica gels that are rigid at room temperature, flow at temperature T_1 and consolidate at temperature T_2 ($T_2 > T_1$), when crosslinking is complete [14–16]. The process of (a) softening, (b) becoming rigid and (c) re-softening can be repeated many times. So-called melting gels were developed originally to replace low melting inorganic glasses [17,18]. Melting gels have been prepared with combinations of mono-substituted alkoxysilanes and di-substituted alkoxysilanes. The substituted group is either methyl or phenyl. The properties of melting gels that have been studied so far are their surface chemistry as indicated by water contact angle measurements and their gas transmission properties in hermetic seals. In evaluating the barrier properties, it was noted that melting gels have the potential to replace epoxy in a variety of electronic packages, and, therefore, the dielectric properties require careful investigation.

2. Experimental procedures

2.1. Sample preparation

The melting gels were prepared by using a mono-substituted and a di-substituted alkoxysilane. The mono-substituted component is methyltriethoxysilane (MTES) (Sigma-Aldrich), and the di-substituted component is dimethyldiethoxysilane (DMDES) (Fluka Chemicals). The chemical formula and calculated oxide content for the precursors are listed in Table 1. The substituted alkoxysilanes were used without further purification. Hydrochloric acid (Fisher Scientific) and ammonia (Sigma-Aldrich) were used as catalysts. Anhydrous ethanol (Sigma-Aldrich) was the solvent. Five gels were prepared with the indicated mol% of mono-substituted and di-substituted alkoxysilanes listed in Table 2.

Briefly, the synthesis, which has been described in detail elsewhere [15], has three steps. First, water is mixed with HCl and ethanol. Separately, MTES is mixed with ethanol. Then, the ethanol mixed with MTES is added dropwise to the water solution under continuous stirring. The container is covered tightly, and the mixture is stirred at room temperature for 3 h.

In the second step, the di-substituted alkoxysilane DMDES is diluted with ethanol, and then added dropwise to the first mixture. This solution is kept in a closed container at room temperature for two more hours of stirring.

Table 1
Molecular weight, formula, oxide content and functionality of precursors.

Precursor	Chemical formula	Molecular weight	% SiO_2	Number of reactive groups
DMDES	$C_6H_{16}O_2Si$	148.28	40.5	2
MTES	$C_7H_{18}O_3Si$	178.30	33.7	3

Table 2
Composition, consolidation temperature, thermal weight loss, sample thickness, density and contact angle for MTES–DMDES gels [19].

Composition		Consolidation temperature (°C)	Thermal weight loss (%)	Sample thickness (mm)	Density g/cm^3	Contact angle °
Mol% MTES	Mol% DMDES					
75	25	135	30	0.81	1.284	98
70	30	140	34	0.80	1.263	98
65	35	150	35	0.80	1.252	100
60	40	155	37	0.82	1.255	98
50	50	160	45	0.53	1.251	97

In the third step, ammonia is added to the mixture and stirred for 1 h in a closed container. Once this solution is clear, it is stirred for 24 h at room temperature in an open container until gelation occurs. If ammonium chloride forms during gelation, 10 ml of dry acetone is added, and the ammonium chloride and acetone are removed by vacuum filtration. This is followed by a heat treatment at 70 °C for 24 h to remove any remaining acetone and ethanol, followed by another heat treatment at 110 °C for removal of un-reacted water.

Samples were stored in closed vials. When it was time to prepare a film, the gels were warmed to their softening temperature, ~110 °C. The fluid gel was poured onto a substrate, typically muscovite mica, where it became a rigid film. The same amount of sample was poured each time to prepare films of approximately the same thickness. The film was heated to the consolidation temperature listed in Table 2, and held at this temperature for 24 h. Following the consolidation treatment, the samples no longer softened, and they were ready for measurement of dielectric properties. The sample thickness is given in Table 2 [17].

2.2. Property measurements

Dielectric properties were measured on melting gel samples that had received a consolidation treatment. Each sample was painted with circular areas of silver paint averaging 5.0 mm^2. The samples were placed between the copper wires of a GenRad 1689 Digibridge and measured with an alternating current. First, the samples were measured across the composition percentage of MTES–DMDES at the highest frequency the instrument would allow, which was 100 kHz. Next, the dielectric constant of each sample was measured at 1 kHz, 10 kHz, and 100 kHz. The dielectric constant of all the samples was shown to decrease with increasing frequency.

In addition, the dielectric constant was measured at temperatures between room temperature and 100 °C. The conductive areas painted on the samples that were heated were smaller and therefore gave a less reliable measured capacitance. The capacitance measured was only 1–10 pF, so experimental error in this case is large. Measurements were repeated on more than one film with the same composition, and it was found that the measured dielectric constant remained the same from sample to sample and over a period of days.

AC impedance measurements were performed on a Solartron 1260 Frequency Response Analyzer with an 1186 HP Electrochemical Interface. Ionically blocking electrodes were applied on the surface of the samples by coating with a silver paint. The measurements were carried out at room temperature (~25 °C) over the frequency range of 5 Hz to 65 kHz. The measurements from the Digibridge and the Frequency sweep were in good agreement.

Index of refraction was measured using a Becke line method. Small slivers of samples were immersed in matching index oils and viewed under a light microscope.

Preliminary measurements of the dielectric breakdown strength were measured on thin chips of gel. No polishing was performed before gold electrodes were sputtered onto the chip. A high voltage power supply was used to generate up to 10 kV at a rate of voltage