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Organic–inorganic hybrid melting gels

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Abstract Melting gels are a class of organically modified silica gels that are rigid at room temperature, flow at temperature T1 and consolidate at temperature T2 (T2 > T1), when crosslinking is complete. The process of (a) softening, (b) becoming rigid and (c) re-softening can be repeated many times. Mixtures of mono-substituted alkoxysilanes and di-substituted alkoxysilanes have been studied in a systematic way to identify suitable melting gel compositions. The mixtures and the resulting melting gels have been characterized for their softening temperatures and consolidation temperatures. With an interest in using these materials for sealing microelectronics, their physical properties have been measured.

Keywords Melting gels · Polysiloxanes · Organic–inorganic hybrids · Glass transition temperature · Low-k dielectric

1 Introduction

1.1 Introduction to "melting gels"

Ordinarily, the outcome of the sol–gel process with the precursor tetraethylorthosilicate (TEOS) is a 3-dimensional network. By hydrolysis and poly-condensation, the TEOS, with 4 identical groups attached to Si, undergoes reactions according to pH and steric effects. However, the 4 identical groups can be changed to, for example, 3 identical groups and one group with a direct Si–C bond. While the ethoxy groups are hydrolytically reactive, the substituted group, for example, methyl, does not hydrolyze.

Figure 1 is a schematic of the number of reactive groups (NRG), as the ethoxy group on TEOS is substituted once by methyl, and twice by methyl. Substituting groups, which have been studied, include methyl, ethyl, phenyl, vinyl and many others [1]. Vinyl groups have been used because it is possible to polymerize the vinyl groups with UV irradiation.

In one of the cases, which will be described in detail, it is possible to prepare silica-based hybrid gels that are rigid at room temperature, but soften and flow repeatedly around 110°C. While the softening behavior has been called melting, it is not melting in a thermodynamic sense [2]. At the same time, it is not thixotropic behavior either, because the material cannot be caused to flow by shearing. Instead, the ability to flow is an indication that the material is not sufficiently cross-linked. In fact, some of the hybrid glasses show glass transition behavior at temperatures below 0°C. However, once these so-called melting gels have been consolidated at around 160°C, they no longer show the ability to soften. The consolidation treatment increases the degree of cross-linking in the gel to a point where the network is permanently rigid [3–5].

Mixtures of di-substituted and mono-substituted alkoxysilanes can produce so-called melting gels with a range of softening behaviors and a range of temperatures where the gel flows. As mentioned, the substituted groups can be methyl groups or phenyl groups, as well as others. The size and polarity of the groups influences the properties. The properties of these mixtures are the subject of this review.

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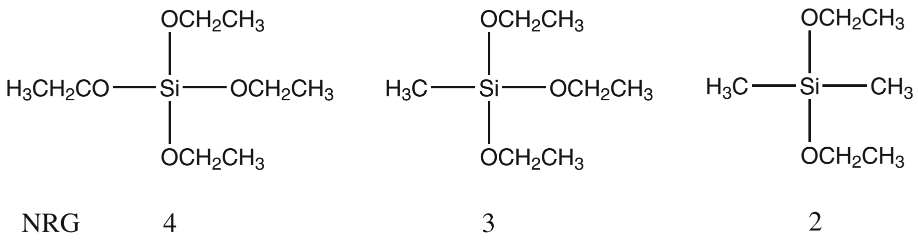

Fig. 1 Schematics showing number of reactive groups (NRG)

1.2 Property requirements for low k materials in integrated circuits

Many of the desired characteristics of so-called “low k materials” in microelectronics can be satisfied by melting gels [6]. For simple metal-oxide semiconductor field effect transistors (MOSFET), the low-k materials should be structurally uniform, have low dielectric constant ($k \sim 2$), low dielectric loss, high hardness, high adhesion strength, thermal stability, and low moisture absorption [7]. Because of the network structure in organically modified silica melting gels, the structural uniformity and hardness can be achieved. Also, the fact that SiO_2 has a low k by itself means that the dielectric constant of the melting gel can be close to 2 with the proper amount of organic and possibly some closed porosity [8]. In addition, the silica content of the hybrid gives the low k material thermal stability. Melting gels have low viscosity at their softening temperature, so they can be applied by spin coating. The coatings show good adhesion to silicon substrates. In the limited testing so far, the melting gels show very low vapor transport values [3]. For all of these reasons, melting gels are interesting materials to consider for multilevel interconnect structures. Further work is needed to characterize electrical properties, such as leakage current, and chemical properties, such as etch selectivity.

1.3 Background of “ORMOSILs”

Hybrid organic–inorganic sol–gel materials containing silica were first called “ORMOSILs” in 1984 [9]. Since then the number of hybrid organic–inorganic combinations has increased rapidly [1]. Generally, organic–inorganic materials are classified in two broad categories: materials where the organic and inorganic components are embedded one within the other and display weak bonds (Class I), and materials where there are strong covalent bonds between the inorganic and organic components (Class II) [10]. In Class II, a common type of precursor is organoalkoxysilanes with general formula $R_n'–Si(OR)_{4-n}$. The result of hydrolysis and poly-condensation of these precursors are organo-polysiloxanes, which have desirable properties such as hydrophobicity, corrosion protection, low dielectric constants or good scratch resistance [11].

A common precursor for Class II hybrids is methyltriethoxysilane (MTES), $CH_3Si(OC_2H_5)_3$. MTES together with tetraethoxysilane (TEOS) leads to hybrid thin films [12]. When TEOS and MTES are mixed together and hydrolyzed with ammonia catalyst, it is found that condensation is faster than hydrolysis [13, 14]. The retention of the methyl groups in the films reduces tension and lessens cracking. Overall, the order of reactivity for the precursors increases from mono-substituted (MTES) to non-substituted (TEOS) to di-substituted (dimethyldiethoxysilane, DMDES) [15].

More complicated ORMOSILs are obtained by co-condensation of TEOS with MTES and vinyltriethoxysilane [16, 17] and 3 glycidoxy-propyltrimethoxysilane [17, 18]. Oxygen barrier coatings were achieved by using dielectric barrier discharge on vinyltriethoxysilane under ambient conditions [19]. Another approach to an oxygen barrier involved a hybrid layer with n-octyltriethoxysilane over an active layer that acts as an oxygen scavenger [20].

Other organic–inorganic coatings were developed for anti-graffiti, anti-adhesive and anti-static coatings, among others [21]. Since the refractive index and the thickness of hybrid coatings can be adjusted, waveguides based on phenyltriethoxysilane (PhTES), MTES and TEOS have been patterned by microfluidic lithography [22, 23]. Using a mixture of TEOS, MTES and DMDES, a planar integrated waveguide for water vapor sensing, was obtained by doping with Erytrosin B [24].

Another important feature of hybrid materials is the surface energy, which is reflected in its hydrophobicity or hydrophilicity. For example, a water-repelling surface has a contact angle greater than 90° because of surface chemistry and roughness, which increases the effective surface area [25, 26]. For silica-based hybrids, the affinity for water can be decreased by reducing the number of the vicinal OH groups [27]. Reducing the OH groups can be achieved by replacing them with hydrophobic groups such as methyl [28]. Fluorine is the most effective element for lowering the surface energy, resulting in decreasing contact angle in the order $–CF_3 > –CF_2H > –CF_2– > –CH_3 > –CH_2–$ [26].

The mechanical properties of hybrid materials are relevant when coatings are designed to protect glass [29] or polycarbonate [30]. Hybrid films containing TEOS and MTES showed a decrease in hardness from 1.75 to 0.35 GPa as the MTES content increased [31]. The nature of the organic group bonded to the silica network has a large effect on hardness, for example, hybrids with methyl groups are up to 4 times harder than hybrids with phenyl groups [32]. In addition, hardness varies with synthesis conditions, such as the type and amount of catalyst, the amount of the solvent, and the temperature of heat treatment [33].

A special category of hybrid gels constitutes the so-called "melting gels" [2–4]. These hybrids have been developed to replace low melting temperature sealing glasses that melt around 600°C. This temperature is too high for most electronic packaging, especially newer devices such as organic light emitting diodes (OLED). An early approach to "melting gels" involved preparing poly(benzyl-silsesquioxane) particles, which were deposited onto an indium-tin oxide (ITO) coated substrate by electrophoretic deposition. After heat treatment at very low temperatures, continuous thick transparent films were obtained [2]. Using a different approach with PhTES and DPhDES (diphenyldiethoxysilane), polysilsesquioxanes were obtained that showed a low softening point. The first step involved hydrochloric acid, followed by a second step with ammonia to encourage condensation. Using a variety of analytical techniques, it was shown that the resulting molecular structure was three-dimensional, with the organic groups having weak bonds between molecular chains [33–35]. PhTES-DPhDES hybrids could be formed with or without ethanol as monodisperse particles, and the glass transition temperature of these hybrids varied with ratio of PhTES and DPhDES [36, 37].

2 Experimental

2.1 Precursors for melting gels

While the catalog of alkoxysilanes is almost limitless, the typical precursors are listed in Table 1. These include 4 pairs of mono-substituted and di-substituted alkoxysilanes, with the substitution being either methyl or phenyl, and the alkoxy group being ethoxy or methoxy. All of the precursors are readily available from catalogs such as Gelest (Morrisville, PA) and Sigma–Aldrich (Milwaukee, WI). Note that all of the precursors are liquids at room temperature, and all are described as reacting slowly with water at room temperature. Vinyltriethoxysilane and the unsubstituted precursors tetraethylorthosilicate and tetramethylorthosilicate are included for comparison.

Table 2 lists the same precursors by their abbreviations, indicating that those starting with D are the di-substituted alkoxysilane. The number of reactive groups is indicated, along with the SiO_2 content. In those cases with methyl substitutions, the SiO_2 content is higher in the di-substituted alkoxysilane, while the SiO_2 content is higher in the mono-substituted alkoxysilanes with the phenyl substitutions.

Table 2 Silica content and number of reactive groups for precursors

Precursor	Molecular weight	% SiO_2	Number of reactive groups
DMDES	148.28	40.5	2
MTES	178.30	33.7	3
DMDMS	120.22	50.0	2
MTMS	136.22	44.1	3
DPhDES	272.42	22.1	2
PhTES	240.37	25.0	3
DPhDMS	244.36	24.6	2
PhTMS	198.29	30.3	3
VTES	161.49	37.2	3
TEOS	208.33	28.8	4
TMOS	152.22	39.5	4

Table 1 Precursors investigated for melting gels

Chemical name	Formula	Molecular weight	Melting point °C	Boiling point °C	Specific gravity
Dimethyldiethoxysilane (DMDES)	$C_6H_{16}O_2Si$	148.28	−97	114	0.865
Methyltriethoxysilane (MTES)	$C_7H_{18}O_3Si$	178.30	–	142	0.895
Dimethyldimethoxysilane (DMDMS)	$C_4H_{12}O_2Si$	120.22	−80	82	0.880
Methyltrimethoxysilane (MTMS)	$C_4H_{12}O_3Si$	136.22	−78	102	0.955
Diphenyldiethoxysilane (DPhDES)	$C_{16}H_{20}O_2Si$	272.42	15	167	1.033
Phenyltriethoxysilane (PhTES)	$C_{12}H_{20}O_3Si$	240.37	10	112	0.996
Diphenydimethoxysilane (DPhDMS)	$C_{14}H_{16}O_2Si$	244.36	15	161	1.077
Phenyltrimethoxysilane (PhTMS)	$C_9H_{14}O_3Si$	198.29	−25	211	1.064
Vinyltriethoxysilane (VTES)	$C_8H_{18}O_3Si$	161.49	–	160	0.903
Tetraethoxysilane (TEOS)	$C_8H_{20}O_4Si$	208.33	−77	169	0.9335
Tetramethoxysilane (TMOS)	$C_4H_{12}O_4Si$	152.22	4	121	1.032

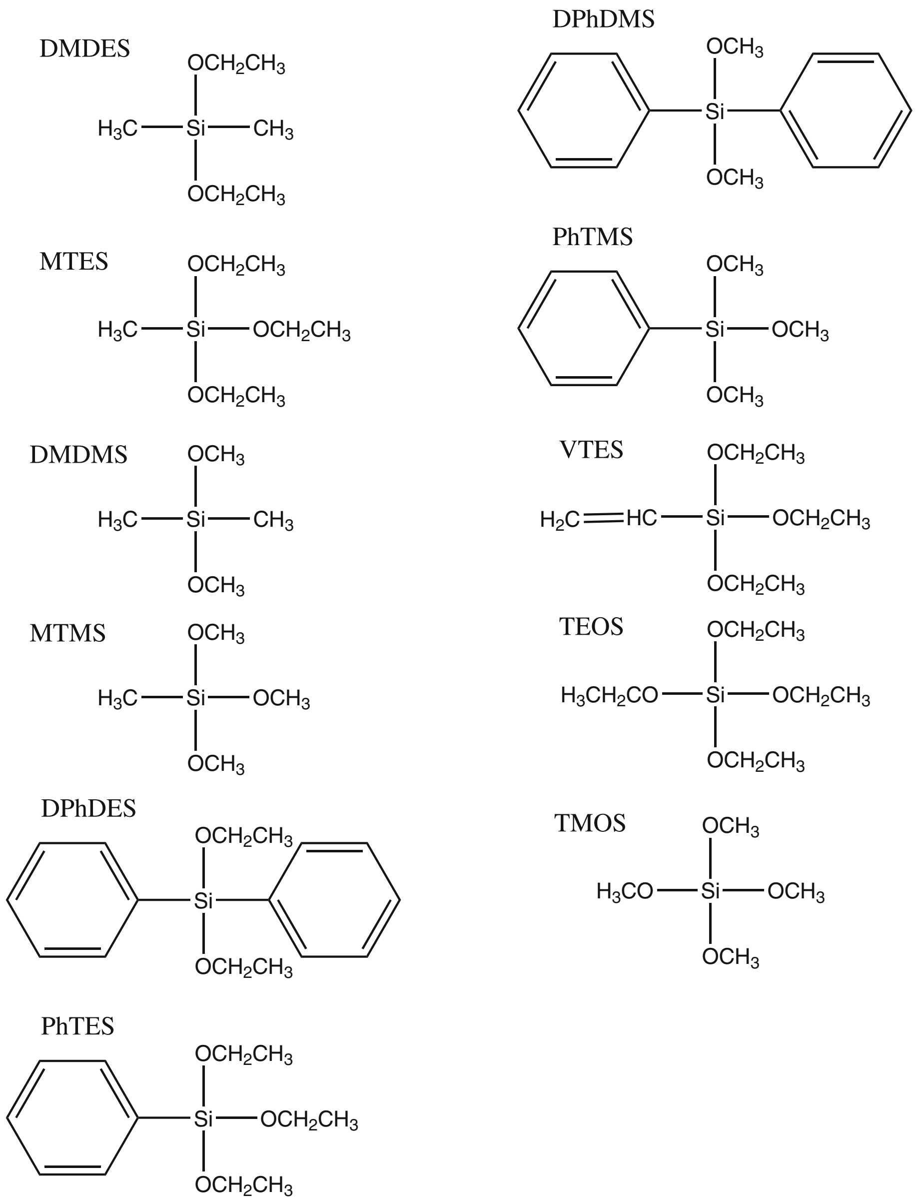

Fig. 2 Schematics of the melting gel precursors

Finally, Fig. 2 has the molecular structures of the precursors. This gives some perspective on the relative size of the substituting groups.

2.2 Synthesis of melting gels using mono-substituted and di-substituted alkoxysilanes

In a typical synthesis, the susbstituted alkoxysilanes are used without further purification. Hydrochloric acid and ammonia are used as catalysts. Anhydrous ethanol or methanol is the solvent. A total of 24 gels were prepared with the indicated mol% of mono-substituted and di-substituted alkoxysilanes shown in Fig. 2. As an example, the synthesis pathway for MTES-DMDES system is shown in the flowchart in Fig. 3, and described step-by-step.

The synthesis has three steps. First the water is mixed with hydrochloric acid and with half of the ethanol. The MTES is mixed with the other half of the ethanol separately. Then, the ethanol mixed with MTES is added dropwise to the water solution under continuous stirring. The beaker 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. The DMDES in ethanol mixture is added dropwise to the mixture from the first step. This solution is kept in a closed beaker at room temperature for another 2 h of stirring.

In the third step, ammonia is added to the reaction mixture and the solution is stirred for another hour in a closed beaker. Then the clear solution was stirred for 48 h

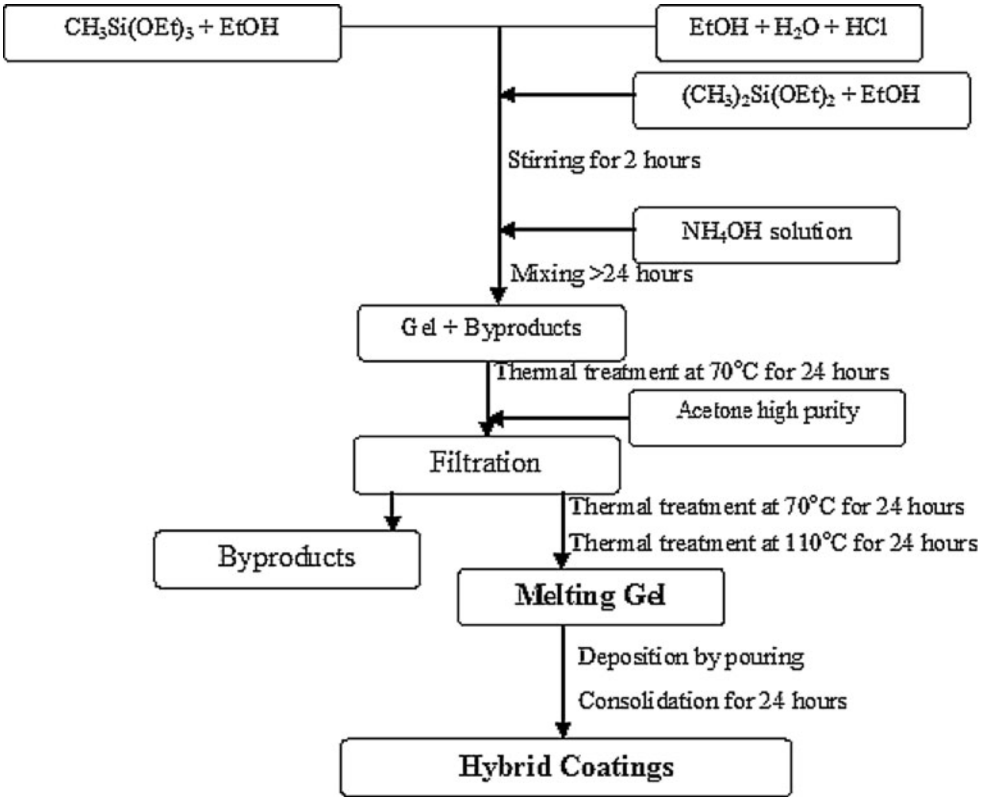

Fig. 3 Typical flowchart of the 3-step synthesis of melting gels

at room temperature in an open beaker until gelation occurs. The gels are heat treated at 70°C overnight in order to remove excess ethanol. During this process, a white powder of ammonium chloride forms on the gels. To remove the ammonium chloride, 10 ml of acetone are added to the samples, followed by removal by vacuum filtration. Again, the gels are heat treated at 70°C for 24 h, followed by a last heat treatment at 110°C for removal of un-reacted water.

After this heat treatment, the gels are rigid at room temperature. However, when heated above ~110°C, the gels soften and become fluid, in some cases as fluid as water. To locate the consolidation temperature, samples were subjected to heating and cooling cycles until the minimum temperature was found after which the gels could not be softened. Once the gel had been heated to the consolidation temperature, the behavior was no longer reversible. The consolidation temperatures are listed in Table 3.

The thermal behavior of the hybrid gels before consolidation was studied using differential thermal analysis (Perkin-Elmer DTA-7), thermogravimetric analysis (Perkin-Elmer TGA-7) and differential scanning calorimetry (DSC TA-Q-2000). DTA and TG were recorded at 5°C/min heating rate in the temperature range between 50 and 800°C under air flow (20 ml/min). The total weight loss was recorded and is listed in Table 3. The DSC analyses were recorded using a 5°C/min heating rate between −60 and 400°C in nitrogen flow. The glass transition temperatures were determined and are listed in Table 3.

In comparing the methyl substituted melting gels (MTES/DMDES and MTMS/DMDMS) and the phenyl-substituted melting gels (PhTES/DPhDES and PhTMS/DPhDMS), it is seen that the melting gels cannot be made in the same proportions. The methyl-substituted compositions have more even amounts of the mono- and di-substituted alkoxysilanes, while the phenyl-substituted compositions are a majority of the mono-substituted alkoxysilane, going so far as to have melting gels with 100% PhTES or PhTMS. When melting gels are made with PhTES and DMDES, the range of compositions is wider and the consolidation temperatures are the highest of any compositions.

3 Results and discussion

The weight loss for all gels occurred in two temperature ranges. At lower temperatures between about 150 and 300°C, the weight loss is attributed to the removal of the ethoxy, methoxy and hydroxyl groups. The second weight loss occurs between about 350 and 500°C due to the combustion of the methyl and phenyl groups. For all samples, the differential thermal analysis shows an exothermic peak accompanying the high temperature weight loss, indicating the combustion of the methyl and phenyl groups.

In all cases, the total weight loss increased with increasing amounts of the di-substituted alkoxysilane. Considering the silica content listed in Table 2, the total weight loss is expected to reflect the changes in silica content. Those mixtures with the lowest silica content would show the greatest total weight loss.

The consolidation temperatures listed in Table 3 decrease with a decrease of the amount of di-substituted alkoxysilane, for all systems. This decrease in the consolidation temperature is consistent with the fact that di-substituted alkoxysilanes have only two reactive sites available to create new bonds with the rest of the silica network, while mono-substituted alkoxysilanes have three. Without the mono-substituted alkoxysilane, the di-substituted alkoxysilanes remain liquids after hydrolysis and polycondensations reactions because only linear chains are formed. When mono-substituted alkoxysilanes are mixed with the di-substituted alkoxysilanes, the di-substituted alkoxysilanes act as bridges between the molecular species formed when the mono-substituted alkoxysilanes hydrolyze. In fact, both of the mono-substituted alkoxysilanes PhTES and PhTMS form gels by themselves. The substituted phenyl groups occupy a larger volume than the ethoxy or methoxy groups. When more di-substituted alkoxysilane is present, the high number of phenyl groups creates steric hindrance to the cross-linking process, which leads to an increase of the consolidation temperature. The highest consolidation temperature recorded was for the 50/50 mixture of PhTES and DMDES.

The glass transition temperatures listed in Table 3 show the opposite trend to the consolidation temperature. The T_g values increase with decreasing amount of di-substituted alkoxysilanes. The glass transition is generally thought of as the interval of transition between liquid states and glassy, amorphous states [35]. Put another way, the glass transition is associated with a temperature T_g, which is influenced by a number of macroscopic properties, such as

Table 3 Compositions investigated and glass transition (T_g) and consolidation temperature (T_{CON})

Mono-substituted (mol%)	Di-substituted (mol%)	T_g °C	T_{CON} °C	Total weight loss %
MTES/DMDES				
50	50	−56.7	160	45
60	40	−37.7	155	37
65	35	−18.8	150	35
70	30	−6.4	145	34
75	25	−0.3	135	30
MTMS/DMDMS				
50	50	−29.2	170	37
60	40	−24.7	160	34
65	35	−15.7	150	29
70	30	−5.4	145	26
PhTES/DPhDES				
80	20	0.4	150	65
83	17	7.9	140	64
87	13	27.7	135	61
91	9	33.9	130	60
100	0	33.1	130	57
PhTMS/DPhDMS				
80	20	2.6	180	65
83	17	5.0	170	65
87	13	26.1	150	61
91	9	25.4	145	60
100	0	56.6	130	57
PhTES/DMDES				
50	50	−61.0	205	65
57	43	−55.7	195	63
66	34	−29.6	180	58
74	26	5.6	160	53
80	20	2.1	150	55

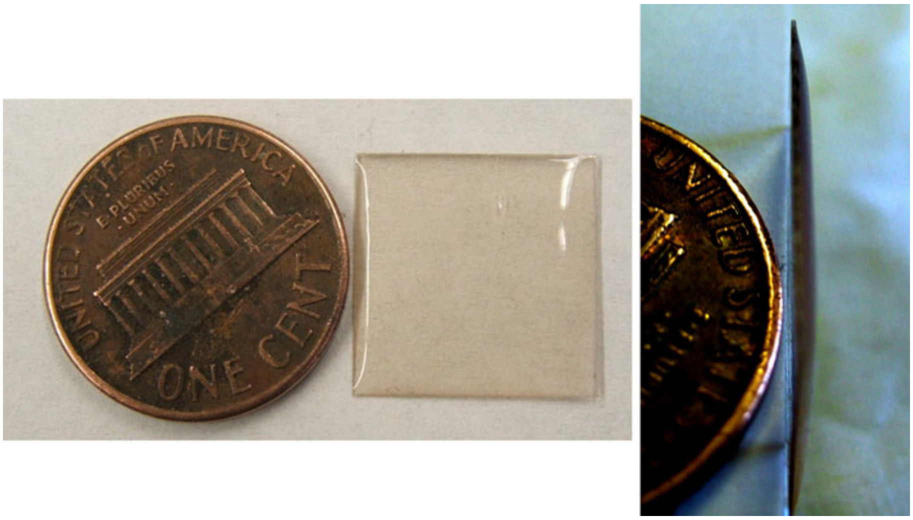

Fig. 4 Front and cross section images of the thick film prepared with 70% MTES–30% DMDES

viscosity, dielectric constant, and mechanical properties. Using the approach developed for traditional organic polymers and applied to inorganic silica-based polymers [22], the glass transition temperature is considered a measure of the degree of cross-linking in the silica network. In other words, the T_g increases with an increase in the number of oxygen bridges between silicon atoms. The highest T_g values are for samples with only mono-substituted alkoxysilanes, 41.6°C for PhTMS and 33.1°C for PhTES. The T_g values for the methoxy-substituted alkoxysilane are higher than the T_g values for the ethoxy-substituted alkoxysilane, given that the methoxy groups are more reactive and achieve a higher degree of polycondensation than for the samples, which contain ethoxy groups.

4 Conclusions

Melting gels containing mono-substituted and di-substituted alkoxysilanes were prepared in a three-step synthesis. The hydrochloric acid in the first step acts as a catalyst to allow formation of linear polymer chains. The ammonia in the third step serves to neutralize the hydrochloric acid and to catalyze further cross-linking between the polymer chains, which leads to gellation. The degree of cross-linking is reflected in the glass transition temperature T_g of the gels before consolidation.

After gellation and heat treatment to remove solvents and water, the gels are rigid. They can be softened by heating to a modest 110°C. Most of the combinations softened to a viscosity between water and syrup, making pouring easy. When the fluid gel was poured onto a variety of substrates, including glass, mica, silicon, copper and aluminum, the gel adhered well to all surfaces. The thick films were about 1 mm thick and relatively smooth. A sample is shown in Fig. 4. The films have better than 70% transmittance of visible light.

One composition that looks promising for low-k dielectrics is the 65% MTES—35% DMDES coating, which has a high value of the contact angle ($\theta = 100°$), negligible BET surface area (0.0138 m^2/g) and a low density (1.252 g/cm^3). It appears that this composition is a favorable combination of the mono-substituted and di-substituted alkoxysilanes, which gives a compact network with no accessible surface area. The hardness is about 50 MPa and does not vary with load. Most important, the dielectric constant is about 2.4 at 10 and 1.9 at 100 kHz. These values are preliminary data and they will be followed up to determine the suitability of these materials for multilevel interconnect structures.

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