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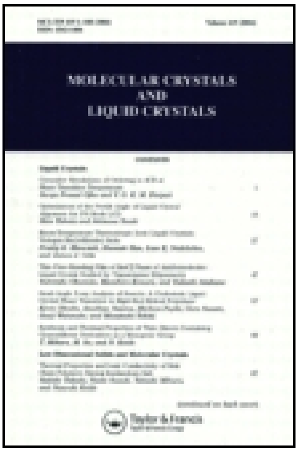

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Synthesis of a Photocurable Ladder-like Poly(phenyl-co-mercaptopropyl)silsesquioxane as Gate Dielectric Material

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Synthesis of a Photocurable Ladder-like Poly(phenyl-co-mercaptopropyl)silsesquioxane as Gate Dielectric Material

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A new photocurable ladder-like poly(phenyl-co-mercaptopropyl)silsesquioxane (LPPMPSQ) was synthesized in one pot via base catalyzed hydrolysis-polycondensation of a comonomer mixture of phenyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane. Obtained LPPMPSQ was characterized by ^{1}H NMR, FT-IR, ^{29}Si NMR, TGA, and the electrical ($k = 3.6$) and mechanical properties (surface modulus = 4.9 GPa) found to be suitable for application as a photocurable gate dielectric material.

Keywords silsesquioxane; ladder-like; gate dielectric; dielectric constant

Introduction

Over the past fifteen years or so, immense attention has been given to the field of organic electronics to supplant inorganic electronics in order to reduce high processing costs while offering aesthetic utility in being able to fabricate flexible devices [1]. For gate dielectric materials, SiO_2 has been the material of choice for many benchmark studies, as SiO_2 is known to have excellent thermal, mechanical, electrical, and dielectric properties [2–3]. But one of the downfalls of SiO_2-based dielectrics is that it is thermally deposited, a process unfavorable compared to solution processing. And as such, the use of solution processable polymers as gate dielectrics has been investigated as alternative means of fabricating OTFT devices [2].

Polysilsesquioxanes (PSQs) are a class of inorganic-organic hybrid materials with chemical formula $[SiO_{1.5}R]_n$ [4]. These materials exhibit a variety of thermal, mechanical, optical, and electrical properties, which can be tailored through its organic functional group –R [4–5]. There are three structural classes of silsesquioxanes of which include random branched, cage, and ladder-like [5–7]. Random branched structures contain a significant amount of uncondensed silanol groups, while cage and ladder-like structures offer a fully condensed siloxane structure. The amount of silanol groups is important because they act as defects in the interface between film layers and contribute to electron traps [2].

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Thus, a fully condensed siloxane structure with film uniformity is much to be desired. And while cages structures are fully condensed, their film properties have been limited compared to ladder-like polysilsesquioxanes due to poor solubility and low molecular weight [7]. Recently, our group has found the optimal conditions for the synthesis of ladder-like structured polysilsesquioxanes through hydrolysis-polycondensation in one pot under basic conditions, allowing for the synthesis of various ladder-like structured PSQs using conventional organotrimethoxysilane monomers [7–9]. While previous syntheses of ladder-like silsesquioxanes have been centered on templating polycondensation [10] and HPLC methods [11], our method has found to be more suitable for mass production.

In this study, a new photocurable ladder-like poly(phenyl-co-mercaptopropyl) silsesquioxane (LPPMPSQ) was synthesized in one pot via base catalyzed hydrolysis-polycondensation of a comonomer mixture of phenyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane. Obtained LPPMPSQ64 was characterized by ^{1}H NMR, FT-IR, ^{29}Si NMR, TGA, and the electrical and mechanical properties examined for possible application as gate dielectric material.

Experimental

Materials

Phenyltrimethoxysilane(Shin Etsu, 98%), 3-mercaptopropyltrimethoxysilane(Shin Etsu, 98%), and THF(J.T. Baker) were distilled over calcium hydride. Potassium carbonate (Dae-Jung) was dried in a vacuum oven overnight prior to use. All other solvents and reagents were used as received.

Characterization

^{1}H-NMR, ^{29}Si NMR spectra 25°C on a Varian Unity INOVA (^{1}H: 300 MHz, ^{29}Si: 59.6MHz). FT-IR spectra were measured using Perkin-Elmer FT-IR system (Spectrum-GX) using solvent cast films on KBr pellets. Thermal gravimetric analysis (TGA) was performed by TA Instrument TGA 2950 under N_2. AFM images were taken using a Veeco Nanoscope V instrument in tapping mode. Dielectric constant measurements were conducted using a metal-insulator-metal (MIM) structure with film thickness of 500 nm. Nanoindentation measurements were made a Hysitron Inc. TriIndenter using a continuous stiffness measurement technique with the loading controlled such that the loading rate divided by the load was held constant at 0.5/s and the depth to be 50 nm at measurement termination. The film thickness for nanoindentation measurement was held constant at 500 nm to minimize substrate effects.

Synthesis of Ladder-like poly(phenyl-co-mercaptopropyl)Silsesquioxane (LPPMPSQ64)

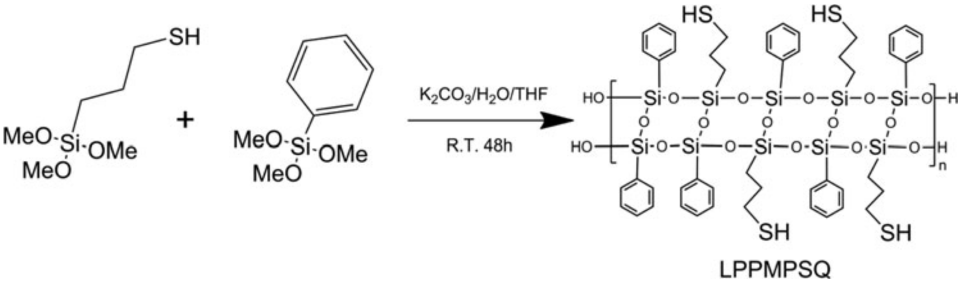
LPPMPSQ64, with phenyl:mercaptopropyl mol ratio of 6:4 was synthesized following a literature procedure [8]. Typically, in a 50 ml RB, potassium carbonate (40 mg, 0.30 mmol) was dissolved in deionized water (4.8 ml, 0.027 mol) with THF (8 g) as solvent. To this solution a 6:4 molar monomer mixture of phenyltrimethoxysilane (9.53 g, 48 mmol) and 3-mercaptopropyltrimethoxysilane (6.28 g, 32 mmol) was added dropwise under N_2 flow. After stirring for 48 hours, a white resinous material appeared. After decantation of the aqueous layer, the white resinous portion was dissolved in methylene chloride and extract with water several times. After drying over magnesium sulfate, filtering, and evaporating of the volatiles, LPPMPSQ64 was obtained in good yield (98%) as a white powder.

Photocuring of LPPMPSQ64

A solution of LPPMPSQ64 in toluene (5 wt%) with photoinitiator Igracure 184 (1 wt% with respect to LPPMPSQ64) was made and sonicated for 20 minutes. This solution was used for spin coating (1500 rpm, 30 sec) on precleaned Si wafers. After solvent annealing at 100°C for 2 hours, the films were photocured with total UV energy of 3 mJ/cm^2.

Results and Discussion

The synthesis of ladder-like polysilsesquioxanes adopted in this study follows a literature procedure [8], which allows for the facile, one pot synthesis of various ladder-like polysilsesquioxanes using conventional organotrimethoxysilane monomers and comonomers (Scheme 1).



Scheme 1. Synthesis of LPPMPSQ.

The ^{1}H NMR spectrum (Figure 1) of LPPMPSQ showed that all of the methoxy groups were hydrolyzed and condensed, as indicated by the lack of peaks at 3.55 ppm and 5.0 ppm, respectively. Moreover, the aromatic protons located at 6.8–8.0 ppm were

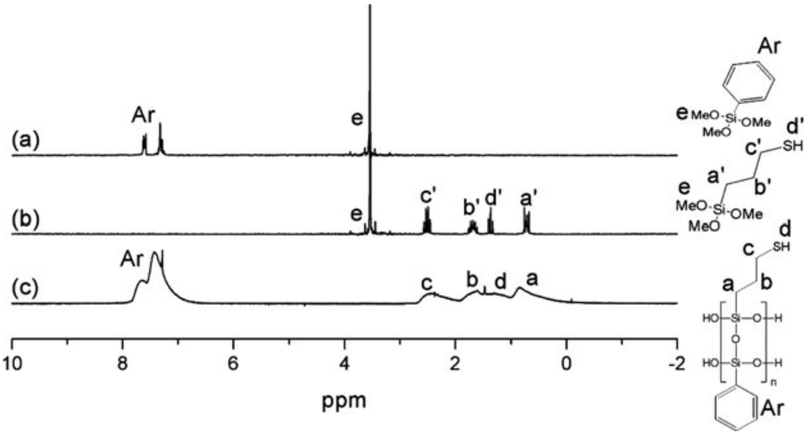


Figure 1. ^{1}H NMR spectra of (a) phenyltrimethoxysilane (b) 3-mercaptopropylsilane (c) LPPMPSQ.

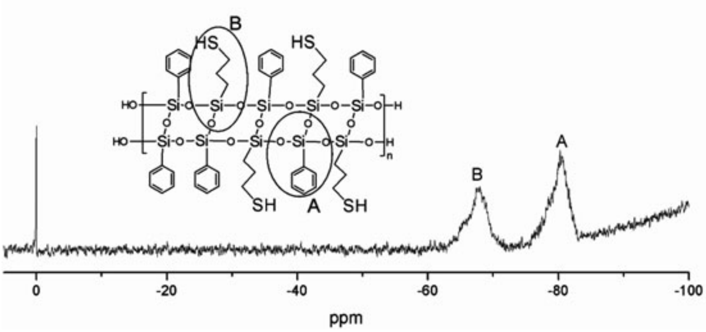


Figure 2. ^{29}Si NMR spectrum of LPPMPSQ.

attributed to phenyl groups, while as well the propylene protons arising from the mercaptopropyl moieties assigned at 0.8 ppm, 1.8 ppm, and 2.3 ppm. Also, the thiol proton at 1.6 ppm was found to remain intact under the basic conditions required of polycondensation. As shown, the broad proton peaks were attributed to the high molecular weight of LPPMPSQ64 (Mn ~12,000 g/mol).

The siloxane structure and degree of condensation were analyzed by ^{29}Si NMR (Figure 2). For polysilsesquioxanes, the characteristics peaks of T3 (Ph-Si(OSi-)$_3$) and T2 (Ph-Si(OSi-)$_2$OH) structures are centered at −77 and −70 ppm respectively, and the T3 (alkyl-Si(OSi-)$_3$) and T2 (alkyl-Si(OSi-)$_2$OH) for the mercaptopropyl-Si structures are centered at −68 and −58 ppm respectively [9]. As shown in Figure 2, only the T3 peaks of (Ph-Si(OSi-)$_3$) and (alkyl-Si(OSi-)$_3$) are shown, indicating that the siloxane structures were fully condensed (~99% T3). Moreover, the integrated ratio between T3 of (Ph-Si(OSi-)$_3$) and T3 (alkyl-Si(OSi-)$_3$) reflected the initial copolymerization molar feed ratio.

FT-IR has also been an excellent tool for the analysis of various polysilsesquioxanes. The siloxane Si-O-Si absorption peaks for all silsesquioxanes are found from

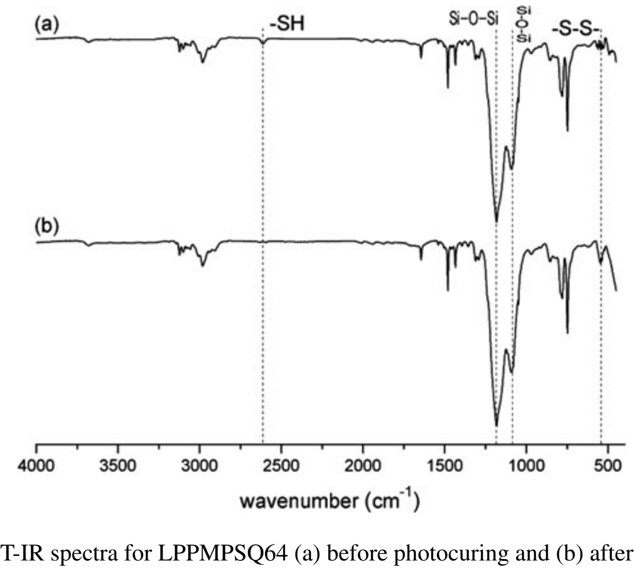


Figure 3. FT-IR spectra for LPPMPSQ64 (a) before photocuring and (b) after photocuring.

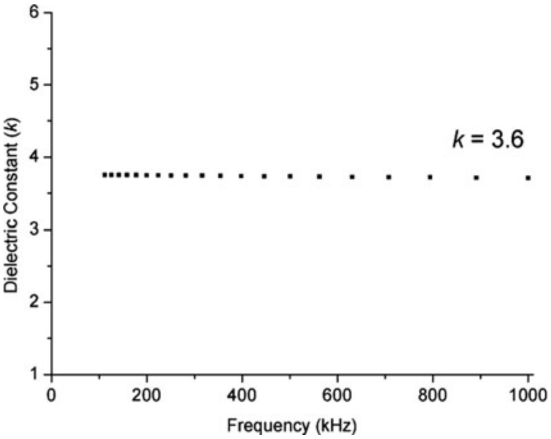


Figure 4. Dielectric constant of LPPMPSQ64 after photocuring.

1000–12000 cm^{-1}, but vary in shape depending on the structure [11]. Figure 3 shows the FT-IR spectrum for LPPMPSQ before and after photocuring. While cage PSQs exhibit one sharp siloxane peak at 1100 cm^{-1}, ladder-like silsesquioxanes show two sharp siloxane peaks at 1150 cm^{-1} and 1040 cm^{-1} assigned to the horizontal and vertical stretching modes of the siloxane bond [11]. This sharp splitting, coupled with minimal silanol content at 940 cm^{-1} and 3500 cm^{-1} suggests that the LPPMPSQ is mostly a ladder structure [7–9], [11]. Also, the weak, sharp absorption peak at 2550 cm^{-1} was assigned to the thiol moiety, which disappeared after photocuring to give a peak at 550 cm^{-1}, a characteristic peak for –S-S- disulfides functionalities.

The dielectric constant of photocured LPPMPSQ was measured using a standard metal-insulator-metal structure. As shown in Figure 4, the dielectric constant was found to be 3.6, a surprisingly high value considering the low dielectric constant of silsesquioxanes [4]. Moreover, low dielectric loss was observed, as the k value did not depreciate much with

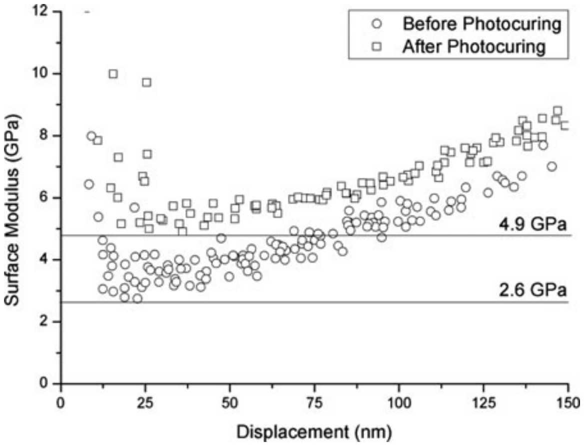


Figure 5. Surface modulus of LPPMPSQ64 before and after photocuring.

Table 1. Some physical, thermal, mechanical, and electrical properties of LPPMPSQ64

Mn[a]	12,000 g/mol
Td[c] (°C)	380°C
Dielectric Constant (k)	3.6
Surface Modulus (GPa)	4.8 GPa
R_a[d] (nm)	0.36 nm

[a] Number average molecular weight from SEC (THF)
[b] Degradation temperature derived from TGA (0.1wt% loss)
[c] R_a values from contact mode AFM.

increasing frequency, again confirming the superior dielectric properties of silsesquioxane based materials.

Mechanical properties of LPPMPSQ64 were investigated using nanoindentation tests. As shown in Figure 5, the surface modulus of LPPMPSQ64 before photocuring was 2.6 GPa, and increased to over 4.9 GPa after photocuring. These excellent mechanical properties were in tune with previously reported ladder-like silsesquioxanes [9], but with improvements in film interface properties. As shown in Table 1, the film roughness of photocured LPPMPSQ was found to be 0.36 nm, indicating that the film was extremely smooth giving an excellent interface.

Conclusion

A novel photocurable ladder-like structured poly(phenyl-co-mercaptopropyl)silsesquioxane (LPPMPSQ) was synthesized in one pot. Obtained LPPMPSQ was characterized as having ladder-like structure, with excellent thermal stability and good processability. Through photocuring of the thiol groups, smooth films with dielectric constant of 3.6, surface modulus of 4.9 GPa, and R_a value of 0.36 nm were obtained. These thermal, electrical, and mechanical properties may allow for possible application as gate dielectric layers.

Acknowledgments

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