Highly Condensed Fluorinated Methacrylate Hybrid Material for Transparent Low-k Passivation Layer in LCD-TFT

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ABSTRACT Photocurable and highly condensed fluorinated methacrylate oligosiloxane, with a low dielectric constant ($k = 2.54$), was prepared by a nonhydrolytic sol–gel condensation reaction. The oligosiloxane resin was then spin-coated, photocured, and thermally baked in order to fabricate a fluorinated methacrylate hybrid material (FM hybrimer) thin film. This study investigated the application of this FM hybrimer film as a low-k passivation layer in LCD-based thin film transistors (TFT). It was found that a dielectric constant as low as $k = 2.54$ could be obtained, without introducing pores in the dense FM hybrimer films. This study compares FM hybrimer film characteristics with those required for passivation layers in LCD-TFTs, including thermal stability, optical transmittance, hydrophobicity, gap fill, and planarization effects as well as electrical insulation.

KEYWORDS: LCD-TFT passivation layer • low $k$ • high transparency • solution-based process • organic–inorganic hybrid material

INTRODUCTION

As well as improving the visual display performance, the passivation layer in an LCD-TFT is important for protecting the film against its environment (water and air). Until recently, plasma enhanced chemical vapor deposition (PECVD) of SiO$_2$ or SiNx has been used for these passivation layers in a-Si TFT flat panel displays. Although SiO$_2$ and SiNx provide good protection against the environment, they introduce relatively high dielectric constants, 3.9 and 7, respectively, making them unsuitable for high-quality and large-sized TFT-LCDs. In a traditional TFT-LCD, the indium tin oxide (ITO) pixel electrodes cannot be extended in size. This is due to the capacitive coupling introduced when the high dielectric constant SiO$_2$ or SiNx material is placed adjacent to the gate and source lines. TFT-LCDs that use low-$k$ passivation layers, on the other hand, decrease this capacitive coupling and allow for extended ITO pixel electrodes above the gate. This allows for an increased aperture ratio, resulting in a large size, high brightness and high contrast ratio active matrix LCD (AMLCD). PECVD SiO$_2$ and SiNx layers also create high production costs and are technically difficult to produce, especially for large area LCD-TFTs. For these reasons, low-cost solution-based coating methods are preferred for the creation of low-$k$ materials, with $k < 3$, to be introduced as passivation layers in the production of LCD-TFTs (1–3).

Low-$k$ solution-based coating materials have been predominantly investigated for their use as the inter/intra level dielectric (ILD) in integrated circuits (IC) due to their ability to decrease capacitive coupling, RC time delay, and power dissipation. RC time is product of resistance of metal wire by capacitance of dielectric. RC time delay decreases switching speed and efficiency of entire device, so might be an obstacle for miniaturization and high integration. Therefore, the problem can be solved by use of low-$k$ material (4–6). Although many different low-$k$ materials have been trialed as the ILD in ICs, they are often not suitable for low-$k$ passivation layers in LCD-TFTs. Of note, SilK (trademark of The Dow Chemical Company, typical organic polymer which was developed to enable the fabrication of faster, smaller, and higher performance integrated circuits) cannot be used as the passivation layer of an LCD-TFT because of its low transparency and high temperature annealing requirement, up to 500 °C (7). For low-$k$ materials to be used as passivation layers in LCD-TFTs they must be broadly transparent and suitable for low temperature processing, less than 300 °C. It has been reported that low-$k$ organic solution-based materials possess these key properties (8, 9). For example, commercially available benzocyclobutene (BCB) and poly-silsesquioxanes like hydrogensilsesquioxane (HSQ) or methylsilsesquioxane (MSQ) display low dielectric constants (2.6–3.0), high thermal stability, and high transmittance. Organic–inorganic hybrid materials (hybrimers) which are based on sol–gel derived oligosiloxane have been studied for a diverse range of optical applications including optical waveguides and micro lenses. By combining both inorganic and organic characteristics, these materials exhibit high transparency, good thermal stability, and low optical loss/birefringence, as well as being simple to process (10, 11). Moreover, by varying the specific organic and inorganic composition, we can easily control the material character-
istics such as the dielectric constant and refractive index, making these films interesting for both electronics and optics. However, their use is currently limited to optical applications only, since the low condensation degree (CD) of oligosiloxane (<70%) in these hybrimers inhibits their use as insulators in electronics (12). The low condensation degree (CD) of oligosiloxane in the hybrimers might give rise to the insufficient number of siloxane bond in organic–inorganic materials. Therefore, the insulators made from the resin cause electric loss such as high leakage current and loss tangent. Thus, the synthesis of oligosiloxane that is highly condensed is required before these hybrimers can be used as dielectric coating layers in electronic applications. In this study, we have successfully fabricated highly condensed FM hybrimer (CD over 90%), as an engineered low-\(k\) material for application as the passivation layer in an LCD-TFT. This highly condensed FM hybrimer was controllably synthesized, and its composition was optimized to produce films with a low dielectric constant. Importantly, this hybrimer is photopatternable, because of its high photosensitivity, and is curable at a low temperature of only 150 \(^\circ\)C. These characteristics enable the FM hybrimer to be used as a passivation layer in LCD-TFTs without any additional etching requirements, and at temperatures compatible with general LCD processes.

Fluorinated methacrylate oligosiloxane is synthesized by the nonhydrolytic sol–gel condensation reaction of 3-(trimethoxysilyl) propyl methacrylate (MPTS), (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (PFAS), and dipenylsilandiol (DPSD), as shown in Scheme 1a. The methoxy groups (\(-\text{OCH}_3\)) of MPTS and PFAS react with silanol groups (\(-\text{OH}\)) from DPSD by alcohol condensation to form a siloxane bond, with methanol as a byproduct. The synthesized resin is stable at room temperature because it contains no solvents, water or alcohol. The fluorinated methacrylate oligosiloxane includes both organic components, such as methacrylate and perfluoroalkyl chains, as well as inorganic parts, like polysiloxanes. The condensation reaction is known to continue until all the silanol groups of DPSD are eliminated (13). To produce highly condensed and highly insulating fluorinated methacrylate oligosiloxane, we optimized the composition and synthesis procedure and compared it with previously reported fluorinated methacrylate oligosiloxane (11). As a result, the CD of fluorinated methacrylate oligosiloxane increased from around 70 to more than 90%.

In this study, highly condensed FM hybrimer films were made by spin-coating the oligosiloxane resin onto substrates, followed by a process of photocuring and thermal-baking at 150 \(^\circ\)C. Scheme 1b represents the fabrication of an FM
hybrimer film from fluorinated methacrylate oligosiloxane with this photocuring procedure. By modifying the rotational speed and amount of solvent used, the thickness of each film was controlled, allowing the various characteristics of each FM hybrimer film to be examined and compared with the requirements for low-k passivation layers in LCD-TFTs.

EXPERIMENTAL SECTION

Synthesis and Characterization of Highly Condensed Fluorinated Methacrylate Oligosiloxane Resin. 3-(Trimethoxysilyl) propyl methacrylate (MPTS, Aldrich), (Heptadecafluorodecyl)trimethoxysilane (PFAS, Gelest), and diphenylsilandiol (DPSD, Gelest) were used as precursor molecules, and barium hydroxidemonohydrate (Ba(OH)2 · H2O, Aldrich) was added as a catalyst to accelerate condensation reaction among precursors. MPTS, PFAS, and Ba(OH)2 · H2O were mixed at 80 °C for 2 h, and DPSD was added uniformly divided in 10 times during the 2 h to prevent phase separation and self-condensation of DPSD. The solution was kept at 80 °C for extra 2 h to promote condensation reaction. This reaction was practiced in nitrogen purging condition to extract methanol, which is byproduct of condensation reaction. The content of experimented MPTS, PFAS, and DPSD was 20, 20, and 60 mol % of entire precursor, and the amount of Ba(OH)2 · H2O was 0.1 mol % of entire precursor. The molar ratio of MPTS and PFAS to DPSD was decided to 2:3 in order to make highly condensed materials. This ratio was chosen to react with functionalities of MPTS, PFAS, and DPSD that take part in condensed materials. This ratio was chosen to react with functionalities of MPTS, PFAS, and DPSD that take part in condensation reaction as much as possible. The resin was cooled to room temperature after the reaction for 4 h. Afterward, it was filtered through a 0.45 µm Teflon filter to remove the catalyst, Ba(OH)2 · H2O, and impurities. The resin can be made by nonhydrolytic sol–gel condensation reaction without solvent because of its stable reaction.

The formation of siloxane bonds and condensation reaction of precursors were characterized by 29Si NMR spectroscopy. (Bruker FT 600 MHz) The sample was made by dissolving 30 vol % of the resin in chloroform-d and adding 30 mg L−1 of chromium(III) acetylacetonate as a relaxation agent of silicon. Fourier transform infrared (FT-IR) spectroscopy (JASCO FT-IR 680 plus) was measured with a resolution of 4 cm−1 in the wavenumber range 400 to 4000 cm−1 in order to identify existence of various functional chains of the resin (12).

Fabrication and Characterization of Highly Condensed Fluorinated Methacrylate Hybrimer Dielectric Coating Film. The obtained resin was mixed with a photoinitiator, 2,2-dimethoxy-2-phenyl-acetophenone (BDK, Aldrich) for the photo polymerization of the methacrylate groups. The content of the added BDK was 10 mol % of the entire polymerizable methacrylate groups. The resin was diluted with an unreactive solvent, propylene glycol monomethyl ether acetate (PGMEA, Aldrich, purity 99 %), in a 1:1 weight ratio. The indium tin oxide (ITO) coated glass was cleansed with acetone, isopropylalcohol (IPA), and pure water in ultrasonic and was placed to oxygen plasma for 5 min at 200 W to eliminate organic contamination and to improve the coating characteristic of film. The diluted resin was spin-coated on an ITO coated glass 5000 rpm for 30 s, and then the resin-coated film was irradiated by an ultraviolet (UV) lamp (500W Hg Lamp, 365 nm, Ortel) in a N2 atmosphere. The photocured resin was used to examine and compared with the requirements for low-k passivation layers in LCD-TFTs.

RESULTS AND DISCUSSION

Formation of Highly Condensed Fluorinated Methacrylate Oligosiloxane Resin. The NMR spectrum of highly condensed fluorinated methacrylate oligosiloxane resin is represented in Figure 1. Species represented in the NMR spectrum data are only D0 or Tn species. The Dn species are notation of Si from DPSD and the Tn species are one of MPTS or PFAS. The subscript “n” means the number of siloxane bond of Si atoms. The NMR spectrum data of the oligosiloxane resin shows D1, D2, D3, and T3 species (−36 to −38 ppm, −42 to −47 ppm, −57 to −61 ppm, and −65 to −69 ppm). These data also represent that the fabricated resin does not have any D0 (diphenyldimethoxysilane or diphenylethoxysilanol, −29 ppm), D0 (unreacted DPSD, −54 ppm), T1 (−49 to −51 ppm) species (15, 16). Diphenyldimethoxysilane is formed through esterification reaction which is the reaction that silanol group (Si–OH) in DPSD reacts with methanol, and changed to methoxy group (−OCH3) (17). Most portions of the entire species are D2 and T3 species. This means that the condensation reaction among precursors was mostly accomplished, and the highly condensed oligosiloxane resin was successfully synthesized. The degree of condensation reaction can be represented by condensation degree (CD), which is calculated using the following equation (18) (eq 1). The CD of the fluorinated methacrylate oligosiloxane resin is about 90 %, which means the resin includes many siloxane bonds with organic chains (19).
FT-IR was measured to confirm existence of expected chains, and the data support the results of the NMR spectrum. Figure 2 shows the spectrum of FT-IR. There are no bands from 3200 to 3600 cm\(^{-1}\), which represents silanol (Si–OH) bonds making the resin unstable. The peak in the range of from 1000 to 1100 cm\(^{-1}\) that represents siloxane (Si–O–Si) bonds is observed clearly. This agrees with the result of NMR spectrum that there are large amount of T3 and D2, meaning many formation of siloxane bonds. Organic functional chain’s peaks such as perfluoroalkyl chain (C–F) and methacrylate chain (C≡C) are shown at 1206 and 1640 cm\(^{-1}\), respectively (20).

**Characteristics of Highly Condensed Fluorinated Methacrylate Hybrimer Dielectric Coating Film.** Thermal decomposition rates of the FM hybrimer were measured by thermogravimetric analysis (TGA) applied under an N\(_2\) atmosphere, as shown in Figure 3. The thermal decomposition temperature (5 wt % loss temperature) was found to be about 330 °C. A sudden decrease in weight is caused by the decomposition of unreacted methoxy groups and organic chains like methacrylate and perfluoroalkyl chains in the films. The thermal stability is enhanced by siloxane bonds (Si–O–Si) which are connected with organic functional chains. In addition perfluoroalkyl chains improve the thermal stability, because the C–F bond (117 kcal/mol) is stronger than a C–H bond (98 kcal/mol) (21). The optical transmittance in the visible region of the FM hybrimer film was measured using a UV–vis spectrometer as represented in Figure 4. The film is seen to be highly transparent with more than 95% transmittance across the entire visible region.

A hydrophobic surface on a low-k passivation layer is another requirement for combating moisture attack, which can become a source of leakage current (22). Contact angle measurements were used to investigate the water contact angle on our FM hybrimer films. This angle was seen to increase continuously as the amount of PFAS was increased because of the hydrophobicity of constituent perfluoroalkyl chains. However, past a certain point even with significant increases in the amount of PFAS, there is a limitation to the achievable increase in the contact angle (20). The contact angles for water on the FM hybrimers, from PFAS concentrations of about 1, 5, 10, and 20 mol %, were found to be 92, 104, 108, and 111°, respectively.

Low-k passivation layers, to be deemed useful for LCD TFTs, should display excellent gap fill effects and a high level of planarization. A good gap fill effect allows the passivation layer to show good adhesion with the metal which is used as a source or drain. Good planarization also enables ITO pixel electrodes to be coated flat above the passivation layer. This also allows for better reproducibility of the alignment layer rubbing process. Thus, to check the gap fill effect, we deposited the hybrimer onto an Al patterned Si substrate. The Al pattern had a dimension of 4 \(\mu\)m width and 1 \(\mu\)m height with a gap of 1.5 \(\mu\)m between patterns. Figure 5 shows the cross-sectional SEM micrograph of the coated sample. The FM hybrimer coating film covers well the Al patterns, forming a flat, uniform, and dense film. Thus, the FM hybrimer coating film shows a good gap fill effect and planarization characteristics. Therefore, this FM hybrimer, when used as a passivation layer, is expected to suitably fill the gaps among the electrodes in LCD TFTs, and the ITO pixel electrode above the passivation layer can also be coated flat and extensively.

**Electrical Properties of Highly Condensed Fluorinated Methacrylate Hybrimer Dielectric Coating Film.** The dielectric constant of each FM hybrimer film

\[
CD = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100
\]

(1)
was measured, and was also found to depend on the PFAS content in the precursor material. As the amount of PFAS increases from 1 to 20 mol %, the resulting dielectric constant decreases from 2.98 to 2.54, as measured at 1 MHz and listed in Table 1. The lowest dielectric constant seen here (2.54) is lower than that of BCB (2.65) and other polysilsesquioxane (2.6−3.0) coating films, which are the most represented candidates for low-k passivation layers at present.

This dielectric constant is provided by using the Clausius-Mossotti relation, representing the relationship between density, polarizability and dielectric constant (eq 2). The total polarizability ($\alpha_{tot}$) is composed of electronic polarization ($\alpha_e$), atomic polarization ($\alpha_a$), and dipole orientation polarization ($\alpha_o$) components (23).

$$\frac{e - 1}{\varepsilon} = \frac{N_A(\alpha_e + \alpha_a + \alpha_o)}{3\varepsilon_0}$$  

(2)

First, the symmetric configuration of phenyl groups in an FM hybrimer lowers the dielectric constant, despite the group’s high polarizability, because the symmetry of the structure decreases the overall polarization (24). Also, the addition of DPSD, which is a difunctional silane creates more Si–C than Si–O bonds. Each Si–C bond has a lower polarizability than the Si–O bonds, thus the lower dielectric constant of these films compared to general siloxane materials (25).

A high concentration of PFAS, which contains long perfluoroalkyl chains, also decreases the dielectric constant of the FM hybrimer films. This is explained first by the expansion of the free volume when occupied by long perfluoroalkyl chains, decreasing the density ($\rho$) and lowering the number of polarizable ions or dipoles per unit volume. Second, perfluoroalkyl chains reduce the electronic polarization thanks to the strong electron withdrawing inductive effects of the fluorine atom (26). Finally, C=O bonds in methacrylate chains provide a larger dipole orientation-induced polarization than the C–F bonds in perfluoroalkyl chains, because the dipole moment of C=O is higher than that of C–F (27). Therefore, the substitution of perfluoroalkyl chains for methacrylate chains, through the addition of more PFAS, reduces the total polarizability and results in the lower dielectric constant seen.

The dielectric constant can be simply calculated with Maxwell’s identity. (eq 3) Refractive indices of the FM hybrimer films were measured with a prism coupler allowing the dielectric constants to be obtained and listed in Table 1.

$$\varepsilon_e = n^2$$  

(3)

This simple calculation is solely applicable at the optical frequency (1 × 10^{15} Hz) where only electronic polarization exists among the total polarizations. The effect of atomic polarization and dipole orientation polarization become significant at around 1 × 10^{12} Hz and 1 × 10^{9} Hz, respectively (23). Comparing the dielectric constants calculated from the refractive index at 1 × 10^{15} Hz and those measured at 1 MHz, as represented in Figure 6, it can be seen that the measured values at 1 MHz are larger than those at 1 × 10^{15} Hz. The dielectric constant increases continually as the frequency decreases because of the increase in the number of contributing polarization terms.

Other important electrical properties for good passivation layers, in addition to the dielectric constant, are the leakage current and loss tangent. Figure 7 shows leakage current and loss tangents for FM hybrimer films with 20 mol % PFAS. Leakage currents represent the dissipated current in FM hybrimer passivation layers between the metal contacts (source or drain) and the ITO pixel electrodes. Leakage currents increase as the electric field increases, and the value of the FM hybrimer film at 1MV/cm is about 4 nA/cm². Loss tangents are closely connected with the leakage current. The loss tangent, which is also called the dissipation factor, is
the ratio of the conduction current and the displacement current. It increases as frequency increases, and in this case the value at 1 MHz is about 0.01 (28). These leakage current density and loss tangent values are small enough to be used in any dielectric layer in electronic devices. These suitably low values, as measured, are a direct result of the high CD of the oligosiloxane and the high cross-linking density of methacrylates in these FM hybrimers. It is because the high CD of the oligosiloxane forms lots of siloxane bonds (complete inorganic networks) and the high cross-linking density of methacrylates reduce the unreacted organic parts which cause of electric loss.

CONCLUSION

Highly condensed fluorinated methacrylate oligosiloxane was synthesized and FM hybrimer films were prepared by a process of spin-coating followed by photocuring and thermal baking at 150 °C. The high content of perfluoroalkyl chains and symmetric configuration of phenyl radicals in the FM hybrimer structure results in low dielectric constants, down to 2.54. High condensation of siloxanes as well as good cross-linking in the methacrylate networks cause the FM hybrimer films to have excellent insulating characteristics, with low leakage currents and loss tangents. Also, the coated films are highly transparent and thermally stable, and exhibit excellent gap fill effects and planarization on the patterned substrates. Therefore, we propose that FM hybrimer can be applied as a low-k passivation material when used in large area LCD-TFTs.

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