Photo-Curable Sol-Gel Hybrid Film as a Dielectric Layer by a Thiol-ene Reaction in Air or N2 for Organic Thin Film Transistors

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Sol-gel derived oligosiloxane resins are cured under air or N2 by a photo-initiated thiol-ene reaction. The cured film was fabricated as a dielectric layer for use in an organic thin film transistor, and offers a higher dielectric constant (4.13) than silicon dioxide (3.9). We investigated the effects of the curing conditions of a thiol-ene reaction on the TFT performance depending on air or N2. In the N2 conditions, hydroperoxide group (−OOH) free films were generated and they showed low leakage current density and hysteresis free behavior with higher mobility than those fabricated in air.

Organic thin film transistors (OTFTs) are being explored for low-cost alternative to typical inorganic based TFTs in many practical applications.1 With the recent increase in the interest in flexible electronics, in particular, OTFTs have increasingly been investigated to achieve the desired performance on flexible substrates. It might not be an overexaggeration to say that low cost and flexibility are the two most important driving factors to materialize OTFTs.2–4

In general, inorganic TFTs have benefited from the excellent insulating properties of thermally-grown SiO2 as the gate dielectric layer. However, a thermal oxidation process, which requires high temperature (700 ~ 1300 °C) to form SiO2, cannot be employed in the process of fabricating OTFTs based on a flexible plastic substrate. Thus, the realization of a low temperature processable dielectric layer with an insulating property as good as SiO2 is a key agenda in making successful flexible OTFTs. Polymers such as PVA (polyvinylalcohol) could be regarded as a candidate for such SiO2 replacement due to their solution processable properties and low cost, but their inferior insulating property poses a limitation that must be overcome.5 In efforts to address this issue, organic-inorganic hybrid type materials are explored in this work for gate dielectrics with low leakage current density. One of the main factors causing the leakage current of the polymer based dielectric layer is the existence of a hydroxyl group on the dielectric layer.6–8 The hydroxyl group acts like mobile ions and causes breakdown of the insulating layer when high energy is imposed by an applied electric field.9,10 Also, it was reported that the hydroxyl group traps the carriers, resulting in hysteresis behavior of OTFTs. Thus, eliminating the hydroxyl group from the dielectric layer can be an effective way of addressing these issues. In addition, increasing cross-linking density by heat-treatment or by adding a cross-linking agent is also considered to alleviate these problems.9,10

In this work, thiol-ene reaction is introduced to cross-link the sol-gel derived oligosiloxane resins in an effort to develop a low-leakage, high-quality dielectric layer that can be processed from solution at a temperature compatible with some of the common flexible substrates. In particular, we investigate the insulating performance of a phenyl-sulfur-hybbrimer (PSH) that is cured by the thiol-ene reaction in air or N2 atmospheres and the characteristics of the dielectric layer are discussed. Our new approach is expected to provide several important advantages. First, the cross-linking density through the thiol-ene reaction can be higher than that attained with other photo-curing systems since the photo-initiated thiol-ene reaction is a form of click chemistry that offers rapid reaction time with a high degree of conversion.11,12 Also, the thiol-ene reaction has low oxygen inhibition and thus can be processed even in air. This easy procedure with high reactivity may provide an affordable and suitable method for application to a solution-based dielectric layer in OTFTs. Additionally, the dielectric constant of the PSH is relatively high (k = 4.13) compared to the SiO2 (k = 3.9). The dielectric constant of the polymers commonly researched as a dielectric layer for OTFTs such as PMMA (poly(methylmethacrylate), k = 3.2), PMPA (poly(4-methoxyphenylacrylate), k = 3.4), PPA (poly(phenylacrylate), k = 2.9) is approximately 3.13 In this perspective, the k of the PSH (4.13) is advantageous for transistor characteristics by increasing the capacitance of the dielectric layer.

The word hybrimer denotes an organic-inorganic hybrid and polymer based material.14 The phenyl-sulfur-hybbrimer (PSSH), for which the chemical structure is presented in Fig. 1c, has a siloxane backbone with phenyl and sulfur groups.15 To prepare the PSH, two oligosiloxane resins were synthesized by the sol-gel process. A precursor shown chemical structure in Fig. 1a is synthesized using 0.1 mol of vinyltrimethoxysilane (VTMS, Aldrich) and 0.15 mol of diphenylsilanediol (DPSD, Gelset) with p-Xylene under 0.1 mol% of barium hydroxide monohydrate (BHM, Aldrich) as a catalyst at 80 °C for 4 hours. The other precursor shown in Fig. 1b is prepared using 0.1 mol of mercaptopropyltrimethoxysilane (MPTMS, Aldrich) and 0.15 mol of DPSD without any solvent. The sol-gel process was performed between those two precursors. The synthesized resins were mixed in a 1:1 ratio of vinyl group (C = C) to thiol group (SH) with 1 mol% of 2, 2-dimethoxy-2-phenyl-acetophenone (BDK, Aldrich) as a photoinitiator. Propylene glycol methyl ether acetate (PGMEA, Aldrich) was added five times as much as blend resins for dilution.

The prepared solution was spin-coated at 5000 rpm for 30 seconds on ITO glass and was exposed to UV light (80 mW/cm2, 365 nm, Oriel 97453) in air or N2 atmosphere for 3 mins. Heat-treatment was performed at 150 °C under vacuum for 2 hours for further densification and to remove impurities or residual solvent, resulting in an approximately 300 nm thick PSSH film. Au (35 nm) was deposited on the coated film via thermal evaporation. A MIM (metal (ITO)/insulator (SH)/metal (Au)) structure was formed to measure the leakage current density using a HP 4156A semiconductor parameter analyzer. Pentacene (60 nm) was deposited on the PSSH coated ITO glass by thermal evaporation to fabricate OTFTs. For the top contact geometry, electrodes of tungsten oxide (20 nm) with Al (50 nm) for the source (S) and drain (D) were deposited by thermal evaporation. The Al/WO3 bilayer electrodes were previously shown to function as efficient hole injection S/D electrodes.16 The S/D electrode pattern was defined by the shadow mask and the channel length (L) and width (W) were 100 um, and 980 um, respectively (W/L = 9.8). The OTFT performance was also measured by a HP 4156A semiconductor parameter analyzer. Hydroperoxide groups (−OOH) in the PSSH film generated by thiol-ene reaction in air were analyzed by X-ray photoelectron spectroscopy (XPS).

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The cross-linking by the thiol-ene reaction can be processed in either air or inert atmosphere such as N₂. General radical polymerization in air is not possible, since oxygen absorbs the initiated radicals and terminates further reaction. However, as shown in Fig. 1d, the thiol-ene reaction is well processed even though oxygen affects the reaction, resulting in hydroperoxide groups, since the peroxyl radical (−O−O•) also absorbs the protons from the thiol groups, generating thiol radicals. This reduced oxygen inhibition behavior of the thiol-ene reaction has been well documented.¹¹

This different thiol-ene reaction mechanism is considered and discussed to investigate the consequent insulating performance depending on the curing atmosphere. The thiol-ene reaction for fabrication of PSH was performed only in air in our previous research.¹⁵ However, in order to apply the PSH as a dielectric layer in OTFTs, the curing atmosphere should be considered, since the hydroperoxide group contains a hydroxyl group and it critically affects the performance of the thiol-ene reaction.

The water contact angle represents the hydrophobicity of the films, and the PSH cured in N₂ shows a higher value of 86.3° compared to that cured in air (79.2°). This is due to the hydroperoxide groups generated on the PSH cured in air, based on the chemical mechanism shown in Fig. 1d.

There is also an apparent difference in the leakage current density between the PSH cured in air and that in N₂ atmosphere. In Fig. 2, the leakage current density (A/cm²) at 1 MV/cm for each PSH in the MIM structure is plotted as a function of the film thickness. Up to the thickness of approximately 300 nm, the leakage current behavior is almost unchanged, but as films get thinner, higher leakage current density is observed in the case where PSH is cured in air. This can be attributed to the negative effects of the hydroperoxide groups on the insulating property as the thickness is reduced. The leakage current density seriously increases for the PSHs cured in air with thickness under 300 nm. However, the PSH cured in N₂ maintains its insulating property; the leakage current density as low as 3.0 nA/cm² were detected at 1 MV/cm for 70 nm-thick films, whereas the PSH cured in air shows a value of 191.1 nA/cm², which is two orders higher than that from the PSH cured in N₂.

The different leakage current densities of the PSH films cured in air or N₂ is due to existence of the hydroperoxide groups (−OOH) as described chemical mechanism in Fig. 2. The hydroperoxide groups in the PSH cured in air are associated with increasing leakage current density. As shown XPS analysis of surfaces of the PSHs in Fig. 3, the peak at 530.5 eV of the PSH cured in air indicates the existence of the hydroperoxide group while no peak was detected at the same range in the case of the PSH cure in N₂.¹⁷

The observed insulating behavior correlates well with $I_{off}$ current in the transfer characteristics of the OTFTs shown in Fig. 4a. The OTFTs transfer characteristics were recorded while sweeping the gate voltage from +25 V to −25 V with the drain-source voltage ($V_{DS}$) set at −25 V. $I_{off}$ of the OTFT with air-cured PSH is approximately $5 \times 10^{-11}$ higher than that of the OTFT with N₂-cured PSH.

According to the inserted AFM images shown in the inset of Fig. 4a, the curing environment for PSH influences also the growth of the pentacene on the PSH. That is, the enhanced hydrophobicity of the PSH surface by the N₂-curing process results in lowered surface energy, and this prevents an increase of nucleation sites for pentacene on the surface.¹⁸ Thus, the pentacene preferentially agglomerates and forms larger size grains in the N₂-cured samples. The larger grain size of the pentacene then allowed the OTFTs with N₂-cured PSH to exhibit higher mobility (0.113 cm²/V s) than those with air-cured PSH (0.090 cm²/V s).

The comparison of forward and reverse sweep in transfer characteristics (Fig. 4b) indicates that there is virtually no hysteresis regardless of the curing method used for the PSH gate dielectrics. Recall that the existence of the hydroperoxide groups in the air-cured PSH could have contained hydroxyl group, which is known to cause hysteresis in the OTFT transfer characteristics, to some degree. Nevertheless, hysteresis-free behavior observed in both types of the OTFTs indicate that the thiol-ene reaction, classified as click chemistry, increases the cross-linking density of the PSH films with the high conversion yield, resulting in the observed hysteresis-free operation.
In summary, we presented our study on solution-processable low-leak dielectrics based on phenyl-sulfur-hybrimers (PSH) in which the sol-gel derived oligosiloxane resins are cross-linked through the thiol-ene reaction with a high conversion yield. Our study indicates that the PSH films can be cured well both in air and in N$_2$-environment yet the hydroperoxide group present in the PSH cured in air negatively affects its insulating property, resulting in higher off-current in the OTFTs with the air-cured PSH. The improvement in the mobility was observed in the OTFTs with N$_2$-cured PSH, and it was attributed to the enhanced hydrophobicity of the PSH cured in N$_2$, which promotes the larger growth of pentacene grains.

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