

## Thiol-Ene Reaction Derived Sol-Gel Hybrid Dielectric Layer for Organic Thin Film Transistors

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Thiol-ene reaction derived dielectric layer, phenyl-sulfurhybrimer(PSH) was synthesized by mercaptopropyl-phenyl-oligosiloxane(MPO) and phenyl-vinyl-oligosiloxane(PVO). These oligosiloxane was synthesized by sol-gel process. MPO is a result of non-hydrolytic sol-gel condensation between (3-mercaptopropyl)trimethoxysilane and diphenylsilanediol, and PVO is a result of non-hydrolytic sol-gel condensation between vinyltrimethoxysilane and diphenylsilanediol. In this work, the thiol-ene derived dielectric layer is applied to OTFT for the first time. It has relatively high dielectric constant ( $k=4.1$ ) than silicon dioxide ( $k=3.9$ ) which is generally used for dielectric layer and shows hysteresis-free behavior.

### Introduction

The thiol-ene reaction is a kind of the photo-polymerization reactions that classified as click chemistry described by Sharpless et al. in 2001(1). The click chemistry stands for generating target chemical species quickly and reliably with high yields. The thiol-ene reaction is a step-growth free radical process between thiols and enes. Thiol-ene reaction can be processed even under air condition, but the final results are different as seen the chemical mechanism in Fig. 1.

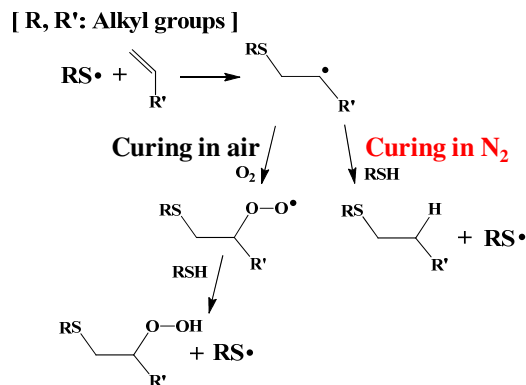


Figure 1. Chemical mechanism of a thiol-ene reaction depends on existence of the oxygen. The curing condition of air generates hydroperoxide groups (-OOH) while there is no hydroperoxide groups in the case of the PSH cured in inert condition (N<sub>2</sub>).

In this work, we applied the thiol-ene reaction derived thin film (300nm) to the dielectric layer in the organic thin film transistor (OTFT) for the first time. There have been many researches of polymer or metal oxide based dielectric materials for OTFTs. However, the low dielectric constant, low insulating property in polymers, and lack of flexibility, high processing temperature in metal oxides limit the performance of OTFTs. Our approach, using the thiol-ene system for dielectric materials, shows excellent insulating property with relatively high dielectric constant,  $k=4.13$ , than silicon dioxide which is generally used for dielectric layer.

We synthesized two types of oligosiloxane resins by non-hydrolytic sol-gel reaction for thiol-ene reaction. MPO for thiol functionalized groups and PVO for vinyl (ene) groups. These oligosiloxane resins bridge each other by a thiol-ene reaction through UV irradiation with photo-initiator resulting in the phenyl-sulfur hybrimer (PSH) as shown in Fig. 2(2).

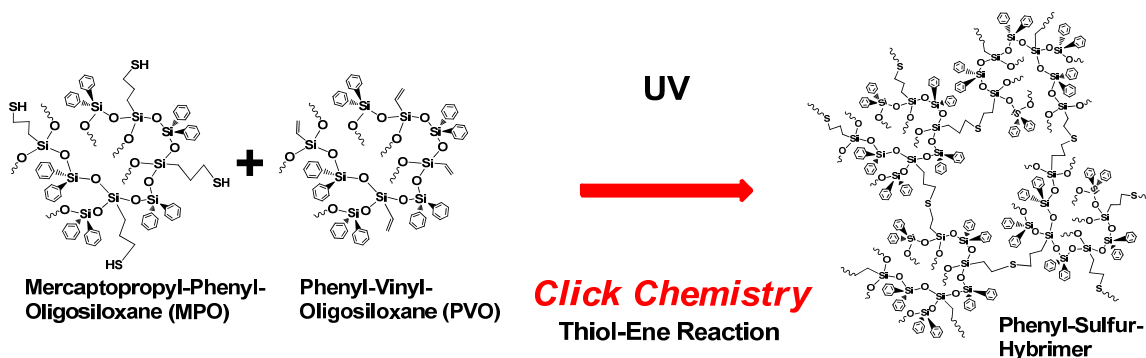


Figure 2. Sol-gel process derived oligosiloxane resins (MPO and PVO) are cross-linked by a thiol-ene reaction through UV irradiation. It results in the Phenyl-Sulfur-Hybrimer.

The hybrimer represents that the material contains inorganic components with chemically bonded organic groups. The PSH has inorganic siloxane backbone with organic phenyl and sulfur groups.

## Experiment

### Synthesis of Oligosiloxane Resin

Synthesis of MPO. MPO is synthesized using 0.1 mol of (3-mercaptopropyl) trimethoxysilane (MPTMS, Aldrich) and 0.15 mol of diphenylsilanediol (DPSD, Gelest) with 0.1mol% of barium hydroxide monohydrate (Aldrich) as a catalyst at 80°C for 4 hours under N<sub>2</sub> purging. The sol-gel reaction occurred between those two precursors.

Synthesis of PVO. PVO is synthesized using 0.1 mol of vinyltrimethoxysilane (VTMS, Aldrich) and 0.15 mol of diphenylsilanediol (DPSD, Gelest) with 0.1mol% of barium hydroxide monohydrate (Aldrich) as a catalyst and 20wt% of *p*-xylene as solvent at 80°C for 4 hours under N<sub>2</sub> purging. The sol-gel reaction occurred between those two precursors.

## Fabrication of Dielectric Film and OTFT

Fabrication of PSH Film. PSH is synthesized by thiol-ene reaction followed mixing MPO and PVO in 1:1 ratio of vinyl group ( $C = C$ ) to thiol group ( $-SH$ ) with 1mol% of 2, 2-dimethoxy-2-phenyl-acetophenone (BDK, Aldrich) as a photo initiator. Propylene glycol methyl ether acetate (PGMEA, Aldrich) was added five times as much as blended resins for dilution. The prepared solution was spin-coated at 5000 rpm for 30 seconds on ITO glass then exposed to UV light ( $80\text{mW}/\text{cm}^2$ , 365nm, Oriel 97453) in air or nitrogen atmosphere for 3 minutes. Heat treatment was performed at  $150^\circ\text{C}$  under vacuum for 2hours for further densification and to remove impurities or residual solvent, resulting in an approximately 300 nm thick PSH film. For MIM structure, Au was deposited on the coated PSH film by 35nm via thermal evaporation. HP 4156A semiconductor parameter analyzer is used for measuring the leakage current. Hydroperoxide groups ( $-OOH$ ) in PSH film generated by thiol-ene reaction in air were analyzed by X-ray photoelectron spectroscopy (XPS).

Fabrication of OTFT. Pentacene (60nm) was deposited on the PSH film coated on ITO glass by thermal evaporation to fabricate OTFT. For the top contact geometry, electrodes of tungsten oxide (20nm) with Al (50nm) for source and drain were deposited by thermal evaporation. The source/drain electrode pattern was defined by a shadow mask and the channel length (L) and width (W) were  $100\ \mu\text{m}$ , and  $980\ \mu\text{m}$ , respectively ( $W/L=9.8$ ). The OTFT performance was also measured by HP 4156A semiconductor parameter analyzer.

## **Result and Discussion**

Fig. 3(3) shows leakage current densities according to thickness of PSH films and applied electric fields. The leakage current density is almost unchanged up to film thickness 300nm. However, as films get thinner, comparing PSH film cured in air to that in  $\text{N}_2$  atmosphere, the leakage current density gets higher. This can be negative effect of hydroperoxide group ( $-OOH$ ) caused by thiol-ene photo-polymerization in air. On the other hands, PSH cured in  $\text{N}_2$  maintains low leakage current density as  $3.0\text{nA}/\text{cm}^2$  at  $1\text{MV}/\text{cm}$  for 70nm-thickness films which is almost 2-order lower than that cured in air.

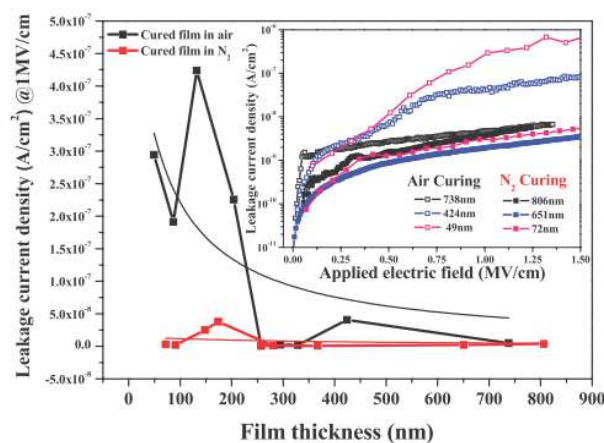


Figure 3. Leakage current density ( $A/cm^2$ ) at 1MV/cm of PSH depending on the film thickness and curing conditions (air or  $N_2$ ). The inserted graph is the leakage current density ( $A/cm^2$ ) spectra depending on the applied electric field (MV/cm) with various thicknesses of PSH and curing conditions (air or  $N_2$ ).

The higher leakage current density of PSH films cured in air than that cured in nitrogen atmosphere is caused by hydroperoxide groups (-OOH) as described in Fig. 1. The hydroperoxide groups and hydroxide groups have an effect to increasing leakage current density. Fig. 4 shows XPS analysis of surface of the PSH film. The 530.5eV peak indicates that existence of hydroperoxide groups (4). PSH films cured in air shows a weak peak at 530.5eV, but PSH films cured in  $N_2$  doesn't shows any peak at 530.5eV.

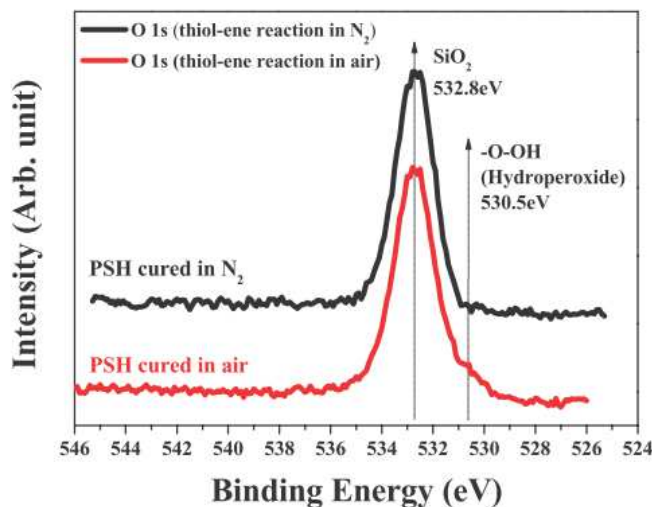


Figure 4. O 1s core level XPS for the Phenyl-Sulfur-Hybrimer film cured in air or  $N_2$ . The arrow at 532.8eV peak indicates that  $SiO_2$ , and the arrow at 530.5eV peak indicates that hydroperoxide groups.

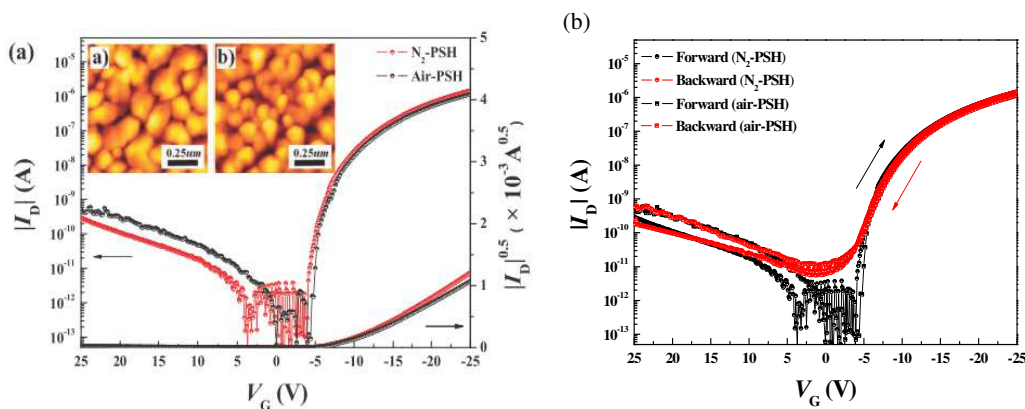


Figure 5. (a) Transfer curves and (b) hysteresis free behaviors of the OTFT with the PSH cured in air or  $N_2$ . Insets of AFM analysis indicates the grain morphology of pentacene on the PSH film cured in a)  $N_2$  b) air. In both cases, drain-source voltage ( $V_D$ ) was kept at  $-25V$ , and W/L ratio was 9.8.

The transfer curve of the fabricated OTFT with the PSH is shown in Fig. 5 (3). As shown AFM image in Fig. 5, the curing atmosphere of PSH film influences the growth of pentacene on PSH film. In other words, the higher hydrophobicity of the PSH by the  $N_2$ -curing process lower the surface energy of pentacene, so that decreasing nucleation site for pentacene growth on the PSH surface (5). The larger grain size of pentacene on the PSH cured in  $N_2$  represents higher mobility ( $0.113\text{cm}^2/\text{Vs}$ ) than that of cured in air ( $0.090\text{cm}^2/\text{Vs}$ ). The comparison of two transfer curve with forward and reverse sweep (Fig. 5(b)) indicates that there is almost no hysteresis in both curing conditions, even though the PSH film cured in air condition has hydroperoxide groups which contain hydroxyl group, which is one of the reasons for hysteresis in TFT characteristic. The high cross-linking density and high conversion yield of PSH film which is synthesized by thiol-ene reaction, results in hysteresis-free characteristic.

## Conclusion

We applied thiol-ene reaction derived thin film, Phenyl-Sulfur-Hybrimer, in which the oligosiloxane resins are cross-linked with high cross-linking density as a dielectric layer for OTFTs. The film is solution-processable, and has low-leakage current density. The PSH film can be cured both in air and in  $N_2$  atmosphere, but the hydroperoxide groups caused by air curing negatively affect its insulating properties, causing higher off-current than  $N_2$  curing one. Also, the higher hydrophobicity of  $N_2$  curing PSH film results in larger grain size of pentacene, which increase the mobility of the OTFT.

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