Effects of Sol-Gel Organic-Inorganic Hybrid Passivation on Stability of Solution-Processed Zinc Tin Oxide Thin Film Transistors

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We fabricated solution-processed zinc tin oxide (ZTO) TFTs with sol-gel organic-inorganic hybrid passivation layers owing to their solution-processibility and good water and oxygen barrier property. The sol-gel organic-inorganic hybrid passivation layers reduce hysteresis of the TFTs without deterioration of performance. The gate bias stability and the environmental stability under high temperature and relative humidity are also improved compared to unpassivated and poly(methyl methacrylate) (PMMA) passivated TFTs.

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Metal oxide semiconductors have attracted considerable attention as the channel layer for thin film transistor (TFT) in displays.1 Owing to their high electron mobility, good uniformity, and high transparency, oxide TFTs are considered the most promising devices for high performance and large area displays. However, for practical applications, the stability under long term bias stress should be guaranteed. The bias instability of oxide TFTs is attributed to not only charge trapping at the semiconductor/insulator interface but also the external molecules in the ambient atmosphere.2–5 In particular, the adsorption/desorption of water and oxygen molecules on the back channel surface is the main reason for the bias instability of common devices with an inverted staggered structure.

Oxide TFTs with various passivation layers such as SiOx, SiNx, AlOx, and poly(methyl methacrylate) (PMMA) exhibited improved bias stability due to effective protection from external molecules.5–9 While inorganic passivation layers have excellent gas barrier properties, they are generally deposited on the oxide channel layer using sputtering, plasma enhanced chemical vapor deposition (PECVD), or e-beam evaporation, which accompany some notable disadvantages. Specially, transistor performance may be degraded by surface damage during film growth and high fabrication costs are inevitable. On the other hand, polymer passivation layers have advantages of a simple and low-cost solution process, but suffer from high permeability to gases. As an alternative, organic-inorganic hybrid materials synthesized by a sol-gel reaction are potentially good passivation layer candidates.10,11 These materials offer solution-processibility and higher water and oxygen barrier properties than commercially available polymers, since they contain a highly condensed inorganic network with UV and/or thermal polymerizable organic functional groups. In particular, organic-inorganic hybrid materials realized via a non-hydrolytic sol-gel process, where inorganic networks are formed by a condensation reaction without water, can be easily synthesized and exhibit controllable characteristics with a suitable selection of precursors and optimization of processing parameters.12–16 Moreover, the absence of water molecules and hydroxyl groups in non-hydrolytic sol-gel derived materials can provide higher thermal and chemical stability relative to hydrolytic sol-gel derived materials. Exploiting these advantages, Jung et al. reported high performance barrier coating layers using non-hydrolytic sol-gel synthesized hybrid materials (hybrimers).17 The hybrimer layers showed low permeability values of up to 0.68 g m⁻² day⁻¹ per mil, and organic light emitting devices (OLEDs) encapsulated using the hybrimer layers displayed extended lifetime.

In the present work, we report the effects of hybrimer passivation layers on the stability of solution-processed zinc tin oxide TFTs. The hybrimer passivation layers were fabricated by UV polymerization of non-hydrolytic sol-gel synthesized methacrylate or epoxy oligosiloxane resins. Gate bias and environmental stabilities of hybrimer passivated TFTs are investigated in comparison with bare and PMMA passivated TFTs.

The sol-gel solution for fabricating ZTO thin films was prepared using zinc acetate (Zn(CH₃COO)₂, Aldrich) and tin chloride (SnCl₂, Aldrich). The details of the synthesis process can be found in a previous report.18 For the fabrication of bottom gate/top contact structured TFTs, the ZTO solution was deposited by spin-coating on top of a thermally grown 100 nm SiO₂ layer on heavily boron (p⁺) doped silicon wafers. The deposited films were then annealed at...
500°C for 1 h in ambient air. The ZTO layers were patterned by a wet-etching process using diluted HF (HF: H₂O = 1:100). Aluminium source and drain electrodes of 100 nm thickness were deposited by e-beam evaporation on the ZTO films, and were subsequently patterned by a lift-off process. The channel length and width of the ZTO TFTs were 100 and 1000 μm, respectively.

To fabricate hybrimer passivation layers, we synthesized methacrylate or epoxy oligosiloxane resins using a method described in a previous paper. The methacrylate oligosiloxane resin was synthesized by a non-hydrolytic sol-gel reaction between 3-(methacryloyloxy)propyltrimethoxysilane (MPTS, Aldrich) and diphenylsilanediol (DPSD, Gelest) at 80°C for 4 h under N₂ purging. The molar ratio of MPTS and DPSD was 2 to 3. Barium hydroxide monohydrate (Ba(OH)₂·H₂O, Aldrich) was added as a catalyst to promote the reaction. The epoxy oligosiloxane resin was synthesized using 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS, Gelest) and DPSD via the same procedures. To control the thickness of the coated film layer, a solvent, polyethylene glycol methyl ether acetate (PGMEA, Aldrich), was added to the resins. As a photo initiator, 2,2-dimethoxy-2-phenyl acetophenone (BDK, Aldrich) or mixed triarylsulfonium hexafluoroantimonate salt (Aldrich) was added to the methacrylate or epoxy oligosiloxane resins respectively. The resulting resins were spin-coated on the fabricated ZTO TFTs, and then photo-polymerized by UV irradiation using a Hg lamp (80 mW/cm², 365 nm, Oriel 97453). To promote polymerization and remove the remaining solvent, thermal curing was carried out at 150°C for 2 h under a vacuum condition. The thickness of the final hybrimer passivation layer was about 1.5 μm. Figure 1a describes the synthesis of the oligosiloxane resin by the non-hydrolytic sol-gel reaction, and the fabrication of hybrimers by photo-polymerization. PMMA (MicroChem C4) was also used as a passivation layer for the ZTO TFT as a reference polymer. A schematic illustration of the passivated ZTO TFT is shown in Fig. 1b. The transfer characteristics of the ZTO TFTs were measured with a HP 4155A semiconductor analyzer at room temperature in a dark room. For investigating the environmental stability, the passivated ZTO TFTs were stored at 85°C and 85% relative humidity (RH).

Figure 2 shows the transfer characteristics of the drain current (I_D) versus gate voltage (V_G) at a drain-to-source voltage (V_DS) of 40 V for the ZTO TFTs with or without passivation layers. All TFTs have similar saturation mobility (μₛ = 5 V), but shows different hysteresis and subthreshold swing (S) behaviors. Compared with the unpassivated ZTO TFT, the hysteresis of the methacrylate and epoxy hybrimer passivated TFTs was significantly reduced, and the S values of the latter were not degraded (~0.5 V/decade). These results indicate that the hybrimer layers effectively protect the back-surface of the ZTO TFTs without surface damage due to their highly condensed organic-inorganic network without charge inducing species such as water or residual solvent. In particular, non-hydrolytic sol-gel process and hydrophobic

![Figure 2](http://example.com/image.png)

Figure 2. (Color online) Transfer characteristics of (a) unpassivated, (b) methacrylate hybrimer passivated, (c) epoxy hybrimer passivated, and (d) PMMA passivated ZTO TFTs at V_DS = 5V (hollow dot) and 40 V (solid dot).
characteristics of oligosiloxane resin that originates from phenyl groups in DPSD minimize water incorporation in hybrimer passivation layer through fabrication process. However, the PMMA passivation cannot sufficiently suppress the hysteresis and deteriorates the subthreshold swing to 0.9 V/decade. It is generally known that H₂O molecules can act as electron trap centers on an oxide semiconductor surface. Thus, this observation can be attributed to the intake of H₂O molecules during fabrication of PMMA passivation layer in the ambient atmosphere.

We also investigated the effect of hybrimer passivation on the gate bias stability of the ZTO TFTs with stress voltage of V_G = 20 V and duration of 3600 s. Figure 3a shows the variation of the transfer curves for the unpassivated ZTO TFT after gate bias stress. The saturation mobilities and the S values do not change significantly; however, the V_th is positively shifted (ΔV_th = 5V) after the gate bias stress. The bias stability of the methacrylate or epoxy hybrimer passivated ZTO TFTs is shown in Figs. 3b and 3c. The hybrimer passivated TFTs exhibits substantially improved stability with only a small shift of V_th (ΔV_th < 0.5V). The larger ΔV_th of the unpassivated ZTO TFT originates from oxygen molecules adsorbed from the ambient atmosphere. The electric-field-induced adsorption of oxygen molecules can lead to the capture electrons from the backchannel, and consequently the resulting depletion layer causes a positive shift of V_th. In the case of the hybrimer passivated TFTs, the hybrimer layers prevent the adsorption of oxygen molecules based on their good gas barrier property. All TFTs with/without a passivation layer show almost unchanged S values after the bias stress. Thus, it is believed that the origin of the gate bias instability of the solution-processed ZTO TFTs is charge trapping at the semiconductor/insulator interface, rather than defect creation, which degrades the S value. Meanwhile, the PMMA passivated TFT doesn’t effectively suppress positive shift of V_th effectively, compared with the hybrimer passivated TFTs. This is attributed to desorption of positively charged H₂O species on the surface and/or the adsorption of diffused oxygen molecules, because the PMMA layer retains some H₂O molecules during fabrication and has a poor barrier property, thus allowing easy permeation of gases.

To investigate the effects of the hybrimer passivation layer on environmental stability, the ZTO TFTs were stored in a chamber with 85°C and 85% RH for 10 h. After exposure to harsh conditions, the unpassivated ZTO TFTs exhibit a significantly negatively shifted transfer curve and a degraded S value compared to the original curve (Fig. 4a). Under a high RH environment, H₂O molecules can be easily adsorbed on the backchannel surface of the ZTO TFT, and the adsorbed H₂O molecules act as electron donors. Thus, the ZTO TFT with excess electrons induced by H₂O molecules requires larger negative voltage for turn-off, and shows somewhat increased off current. As noted previously, H₂O adsorption also can create electron trap sites, and thus the S value is degraded after high RH exposure. On the contrary, the hybrimer passivated ZTO TFTs show fairly stable transfer characteristics in the environmental stability test. The V_th values of the methacrylate and epoxy hybrimer passivated TFTs are slightly shifted in the negative direction (ΔV_th ∼ 0.6 V) and their S values are almost unchanged. In comparison with

![Figure 3](http://www.ecsdl.org/terms_use.jsp)
the hybrimer passivated transistor, the PMMA passivated TFT is remarkably degraded after the test. The deterioration of the on-voltage and the S value (2.4 V/decade) mainly originate from diffusion of H2O molecules through the PMMA layer. In the case of the hybrimer passivated TFTs, the dense structure of the hybrimer results in improved environmental stability, because the hybrimers are composed of not only a highly condensed inorganic siloxane network, which effectively suppresses diffusion of gas molecules, but also an organic network with high crosslinking density. The latter characteristic originates from the unique molecular structure of oligosiloxanes that consists of siloxane core and organic functional groups. After polymerization of the organic groups, short organic chain segments are isolated by inorganic cores with 0.8 nm size.12,13 This structure provides a large amount of crosslinking points and consequently increases the crosslinking density compared to typical long chain organic polymers consist of main backbone and crosslinked side chain.20,21 These results indicate that hybrimers are good candidate materials for passivation layers of oxide TFTs.

In summary, we fabricated solution-processed ZTO TFTs with methacrylate and epoxy hybrimer passivation layers, which are synthesized by a simple non-hydrolytic sol-gel reaction. The hybrimer passivated ZTO TFTs exhibit similar transistor performance with minimized hysteresis. Under gate bias stress, the hybrimer passivated TFTs show improved stability compared to unpassivated and PMMA passivated TFTs. Hybrimer passivation also provides improved environmental stability under high temperature (85°C) and RH (85%). These results originate from the excellent H2O and gas barrier property of the hybrimers.

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References