Effects of Hydroxyl Groups in Gate Dielectrics on the Hysteresis of Organic Thin Film Transistors

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The position of hydroxyl groups in organic-inorganic hybrid gate dielectrics was varied by altering the processing conditions and its effect on the organic thin film transistor (OTFT) was investigated. Although the hysteresis in OTFTs depends on both the hydroxyl groups on the surface and in the bulk of the gate dielectric, the hydroxyl groups on the surface had a greater effect on the OTFT performance. The reduced hysteresis was achieved by the elimination of the hydroxyl groups on the surface by hexamethyldisilazane surface treatment.

Organic thin film transistors (OTFTs) have been paid a great deal of attention and their performance has subsequently improved. OTFTs can be easily incorporated into cheap electronic devices such as integrated circuits and driving circuits for active matrix displays,[1,2] sensors,[3] and radio frequency identification devices.[4] The application of solution processable organic gate dielectrics such as polymers is an important step in developing an all-organic transistor. Various organic dielectrics have been used as gate dielectrics in OTFTs.[5] However, some hydrophilic and polar organic dielectrics cause a significant hysteresis problem of the OTFT.[6-9] The large hysteresis prohibits the OTFTs from applying to a circuit and a switch device for active matrix displays.

There have been many attempts to understand the mechanism responsible for the observed hysteresis in OTFTs, but the exact origin is not yet fully understood. The hysteresis of the OTFTs with organic gate dielectrics could be caused by slow polarization,[6] a result of the dipole, charge injection, movement, and storage in the gate dielectric[7] and/or mobile ion charges.[10] In many explanations of the hysteresis, the hydroxyl groups in organic dielectrics are considered to be the origin of the hysteresis because hydroxyl groups act as electron trap sites.[9,11] In addition, the electrons trapped at hydroxyl groups in the gate dielectrics require an extra drain current to balance it and cause the drain current not to saturate in the saturation regime.[6] Thus it can be seen that hydroxyl groups in the organic dielectrics play an important role in the performance of OTFTs. Hydroxyl groups can be located in the bulk and/or on the surface of the gate dielectrics. However, it has not been confirmed whether the hysteresis depends on the hydroxyl groups in the bulk or on the surface.

The sol-gel derived siloxane based organic-inorganic hybrid materials (hybrimers), in which inorganic and organic components are intimately linked at the molecular scale by a covalent bond, have been widely studied with respect to new dielectric materials for applications in optics and electronics.[12,13] Such materials combine the characteristics of both glass and polymers, and they improve the thermal and mechanical properties of the final materials to be applied. By a suitable selection of precursors and optimization of processing parameters, we can easily control the properties of hybrimers such as dielectric constant, thermal stability, refractive index, surface roughness, and hydrophobicity.[12,14] Recently, a number of attempts have been made to use hybrimers as gate dielectrics for OTFTs. Bao et al.[15] and Jeong et al.[16] reported that silsesquioxane- or organoalkoxysilane-based hybrids are potential candidates for gate dielectrics in low cost and low process temperature OTFTs. Haas et al.[17] reported on ormocers (organically modified ceramics), which are polymerizable organoalkoxysilane-based hybrimers that

show excellent electrical and surface properties. OTFTs with directly patternable zirconium-doped ormocer gate dielectrics also showed a high mobility of ~ 1 cm^2/V s.

Since the hybrimers were fabricated by sol-gel reaction consisting of hydrolysis and condensation reaction, the contents and the location of hydroxyl groups in hybrimers can be easily controlled by manipulation of water during synthesis of solution and heat treatment of films. In this article, we used a titanium-doped organic-inorganic hybrid material (MDT) as a gate dielectric to control the contents and the location of hydroxyl groups in a gate dielectric by the process condition. We investigated the dependency of performance of the OTFT on the location of the hydroxyl groups in the gate dielectric.

Experimental

MDT was synthesized by sol-gel reaction using 3-(trimethoxysilyl)propyl methacrylate (MPTMS, Aldrich), diphenylsilanediol (DPSD, TCI), and titanium isopropoxide (TIP, Aldrich) chelated with acetylacetone (acac, Aldrich) with an equivalent molar ratio as precursors without further purification. The total proportion of MPTMS, TIP, and DPSD was 3:2:5 molar ratio. The sol-gel reaction was carried out in air or nitrogen to change the contents of the hydroxyl groups in the gate dielectric. MDT thin films were spin coated on the indium tin oxide coated glass from a 20 wt % solution in propylene glycol monomethyl ether acetate. Deposited films were exposed to UV light (500 W Hg lamp, $\lambda = 365$ nm, Oriel 97453) for 90 s and thermally cured at 150°C for 2 h either in air or under vacuum to control the location of the hydroxyl groups. The chemical structures of MDT thin films were observed by Fourier transform infrared (FTIR) spectrometer (FT/IR-680 Plus, Jasco).

OTFTs were fabricated by using a top contact geometry. A 50 nm thick pentacene film (polysis) was thermally evaporated on MDT dielectrics at a rate of 0.6–0.8 Å/s, at room temperature. Gold was thermally evaporated on the pentacene films through a shadow mask to form source and drain electrodes. The OTFTs had a channel length of 50 μm and channel width of 3000 μm. The electrical characteristics of the OTFTs were measured using an HP 4155A semiconductor parameter analyzer under ambient laboratory conditions.

Results and Discussion

Figure 1a shows the FTIR spectra of MDT resins synthesized in different atmospheres. The hydroxyl group is observed only for the MDT synthesized in air. Since MDT resin synthesized in nitrogen was synthesized via a condensation reaction between the silanol group of DPSD and the methoxy or propoxy group of MPTS and TIP without the hydrolysis, few hydroxyl groups exist in the MDT resin synthesized in nitrogen.[12] However, the MDT resin fabricated in air had a lot of hydroxyl groups because the water from the air hydrolyzed the MPTMS or TIP during the sol-gel reaction. Hydroxyl groups are located in the bulk since the hydroxyl groups have
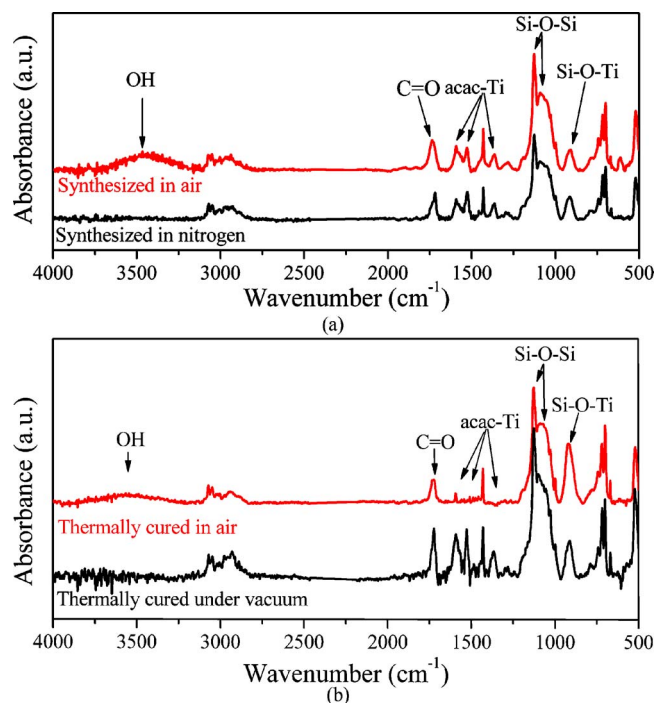
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Figure 1. (a) FTIR spectra of the MDT reins which were synthesized in nitrogen and in air and (b) FTIR spectra of the MDT thin films which were synthesized in nitrogen, and thermally cured in air and under vacuum.

a higher surface energy than phenyl or methyl groups. Figure 1b shows the FTIR spectra of MDT thin films which were synthesized in nitrogen and cured either in air or under vacuum. The peaks of chelating bond of acac and Ti disappear after being cured in air but remained after being cured under vacuum. Furthermore, the hydroxyl groups appear after being cured in air. This means the chelating bond between acac and Ti is broken and Ti is converted to Ti–OH during curing in air,[18] which is indicating the hydroxyl groups exist both on the surface and in the bulk.

The location of the hydroxyl group in the MDT thin films is confirmed by the contact angle of water and diiodomethane using a contact angle analyzer (Phoenix 150, SEO). The MDT thin films cured under vacuum have higher contact angles and lower surface energies than the MDT thin films cured in air, as shown in Table I. This means that the hydroxyl groups are located on the surface of the MDT films cured in air. The location of the hydroxyl group in the MDT thin films with different process conditions is schematically illustrated in Fig. 2. When the MDT was synthesized in nitrogen and cured under vacuum (condition A), the hydroxyl groups during the sol-gel reaction are few and the chelating bonds between

the acac and Ti are not broken as shown in Fig. 2a. When the MDT was synthesized in nitrogen and cured in air (condition B), the hydroxyl groups from the sol-gel reaction are few and the hydroxyl groups from the broken chelating bonds between the acac and Ti are numerous. The hydroxyl groups are located on the surface and in the bulk as shown in Fig. 2b. When the MDT was synthesized in air and cured under vacuum (condition C), the hydroxyl groups from the sol-gel reaction were numerous and the chelating bonds between the acac and Ti were not broken. Almost all hydroxyl groups are located in the bulk as shown in Fig. 2c. When the MDT was synthesized in air and cured in air (condition D), the hydroxyl groups from the sol-gel reaction and from the broken chelating bonds between the acac and Ti are more numerous. The hydroxyl groups are located on the surface and in the bulk as shown in Fig. 2d.

The MDT thin films have smooth surfaces and their rms surface roughness is 3–4 Å measured by an atomic force microscope (XE/100, PSIA). The electrical properties of MDT thin films were measured using metal-insulator-metal capacitor structures. The thickness of the MDT thin films was controlled to have similar capacitance in the range of 300–350 nm and the capacitance of MDT gate dielectrics was ~ 11 nF/cm^2 at 100 kHz measured by a HP 4294A impedance analyzer. The leakage current densities at 1 MV/cm and dielectric strength measured at 10^{-6} A/cm^2 of the MDT thin film depending on the process conditions was 2.1×10^{-9} A/cm^2 and >3 MV/cm (condition A), 1.7×10^{-8} A/cm^2 and 2.3 MV/cm (condition B), and 8.2×10^{-8} A/cm^2 and 1.8 MV/cm (condition D), respectively. The leakage current density and the dielectric strength of the MDT thin films are much better than those of the commonly used solution-processable polymer gate dielectrics in OTFTs.[19-21] Polymer gate insulators were reported to have the relatively high leakage current density of $\sim 10^{-7}$ A/cm^2 at 1 MV/cm and the low dielectric strength of typically 0.1–1 MV/cm.[22]

Figure 3 shows the relationship of OTFTs with MDT gate dielectrics fabricated using different processing conditions. The gate voltage was swept continuously with a 0.5 V step, starting from +40 V, passing through −40 V, and finally returning to +40 V. The source-drain voltage (V_{DS}) was kept at −40 V. The electrical parameters are determined from the off-to-on sweep and are summarized in Table I. As shown in Fig. 3, the gate voltage is positively shifted to obtain the same drain current during the gate voltage, which indicates all OTFTs show electron trapping behavior in the gate dielectrics. The difference of the threshold voltage (ΔV_{th}) between off-to-on and on-to-off was taken as a measure of the extent of the hysteresis and ΔV_{th} is given in Table I. The OTFT with a MDT fabricated by condition A shows little hysteresis because the amount of hydroxyl groups is small. The OTFT with a MDT fabricated by condition D shows large hysteresis as it has the largest amount of hydroxyl groups in the gate dielectric. The OTFTs with a MDT fabricated by conditions B and C show a relatively small hysteresis. From these results, the hysteresis is dependent on the amount of the hydroxyl groups both on the surface and in the bulk. Comparing the

Table I. Summary of the contact angles of the MDT thin films prepared in different atmospheres and the device performance of pentacene OTFTs with MDT gate dielectrics fabricated in different atmospheres.

Experimental conditions				Surface energy			Device performance		
Process condition	Synthesis atmosphere	Curing atmosphere	Surface treatment	Water contact angle (°)	DIM contact angle (°)	Surface energy (mJ/cm^2)	V_{th} (V)	Mobility (cm^2/V s)	ΔV_{th} (V)
A	Nitrogen	Vacuum	No	86.3	42.4	38.4	−9.08	0.24	0.9
B	Nitrogen	Air	No	79.2	36.1	41.9	−19.60	0.83	25.8
⋯	Nitrogen	Air	HMDS	93.9	47.8	35.7	−13.67	0.39	1.5
C	Air	Vacuum	No	84.1	39.9	39.7	−22.73	0.43	19.0
D	Air	Air	No	77.6	33.0	43.4	−27.04	6.82	42.1
⋯	Air	Air	HMDS	93.5	46.0	36.7	−22.49	0.46	13.1

Figure 2. Schematics of the location and contents of the hydroxyl groups in MDT thin films (a) synthesized in nitrogen and thermally cured under vacuum (condition A), (b) synthesized in nitrogen and thermally cured in air (condition B), (c) synthesized in air and thermally cured under vacuum (condition C), and (d) synthesized in air and thermally cured in air (condition D). The hydroxyl groups are located both on the surface and in the bulk of MDT gate dielectrics cured in air, but they are in the bulk of MDT gate dielectrics cured under vacuum.

hysteresis of conditions B and C, the large ΔV_{th} is observed when the MDT gate dielectric is fabricated using condition B. This result indicates that the hydroxyl groups on the surface of the gate dielectric have more important effect on the hysteresis of the OTFT than that in the bulk.

This degradation of the OTFT performance due to the existence of hydroxyl groups on the surface was confirmed by additional experiments using hexamethyldisilazane (HMDS) surface treatment of the MDT gate dielectric. HMDS changes an OH-terminated surface to a CH$_3$-terminated surface via a chemical reaction.[23] Figure 4 shows the transfer curves of OTFTs with the HMDS-treated MDT gate dielectrics. The hysteresis is dramatically reduced after HMDS

surface treatment, which indicates that the hydroxyl groups on the surface have an effect on the performance of OTFT. However, the hysteresis still remains after the HMDS treatment of the gate dielectrics, which indicates the hydroxyl groups in the bulk also affect the hysteresis. Thus, we conclude that although both the hydroxyl groups on the surface and in the bulk affect the hysteresis of the OTFTs, the hydroxyl groups on the surface of the MDT gate dielectric affect more effectively the hysteresis of the OTFTs.

The hydroxyl groups in gate dielectrics affect the OTFT performance, such as mobility and threshold voltage, as shown Table I. The OTFT with MDT gate dielectric prepared by condition D has higher mobility compared with that by other process conditions due to the high hydroxyl group contents in gate dielectrics. The hydroxyl groups are known to be the deep electron traps. The electrons

Figure 3. $(-I_D)^{1/2} - V_G$ characteristics of OTFTs with MDT gate dielectrics synthesized and thermally cured in different atmospheres. The drain-source voltage was kept at −40 V. The closed symbols represent the gate voltage sweep from +40 to −40 V and the open symbols represent the gate voltage sweep from −40 to +40 V.

Figure 4. $(-I_D) - V_G$ characteristics of OTFTs with HMDS-treated MDT gate dielectrics thermally cured in air.

trapped at hydroxyl groups in the gate dielectrics require extra drain currents to balance them and cause the drain current not to saturate in the saturation regime, which seems for OTFTs with high hydroxyl groups in gate dielectrics to have high field effect mobility.[6] Even though the mobility seems to be improved by increasing the number of hydroxyl groups in the gate dielectric, high mobility does not mean a true field-effect mobility. The OTFTs with a high hydroxyl group contents in gate dielectrics have more negative V_{th} compared with the OTFTs with a low hydroxyl group contents in gate dielectrics since the negatively charged species at the interface between the dielectric and semiconductor can modify the surface potential at the junction between the dielectric and semiconductor and develop an electric field, which induces a negative shift of the threshold voltage of OTFTs.[24]

Conclusion

We controlled the locations of the hydroxyl groups in the MDT gate dielectric by varying the process conditions, and investigated the dependency of the OTFT performance on the location of the hydroxyl groups in the gate dielectric. Even though the hydroxyl groups both on the surface and in the bulk of the gate dielectric affect the hysteresis and the saturation characteristics of the drain current of the OTFTs, the performance of the OTFT is more sensitive to hydroxyl groups on the surface of the gate dielectric than those in the bulk. The reduced hysteresis of the OTFT can be achieved by the elimination of the hydroxyl groups on the surface of dielectrics.

Acknowledgments

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