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Synthesis of Polymetalloxanes and Their Properties as Gate Insulator for Organic Thin Film Transistors

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Abstract: We report here the synthesis and dielectric properties of polymetalloxane dielectric materials for organic field-effect transistor applications. The gate insulators were obtained from polymetalloxanes by condensation polymerization of metal chelates and silicic acid. The solution shows an appreciable stability to self-condensation and a good coating quality. A high dielectric constant 6.16-8.27 was obtained for the prepared films. Organic thin film transistors with this gate dielectric were found to exhibit high performances, including carrier mobility as large as 1.77 cm^2/Vs, on-off current ratios above 1×10^4, threshold voltages below -0.13 V, and subthreshold swing as low as 0.1 V/decade. In addition, the operating voltage ranges as low as 5 volts was obtained.

Keywords: organic thin film transistor (OTFTs), hybrid dielectrics, polymetalloxane, sol-gel process.

Introduction

Organic thin film transistor (OTFT) is an intensively pursued subject because it would play a key role in the promising era of organic and particularly flexible electronics.[1-5] A major goal in the development of OTFTs is to achieve higher carrier mobility so that higher current output can be obtained to drive other components in an organic electric device. There are many studies on the effect of structure of the gate dielectric on the mobility of a molecular film.[6] Materials of high capacitance have been used in the organic FETs to reduce the gate bias required to turn on the transistors.[7] One of the representative insulators with high dielectric constant is inorganic metal oxide such as TiO_2[8] and TaO_2.[9] However, inorganic insulators may be cracked when bent. In addition, the film preparation requires a high temperature vacuum process, which is not compatible with flexible substrates. To overcome these problems, polymeric materials are promising candidates as insulators in OTFTs.[10-12] Nevertheless, polymers, in general, exhibit relatively low dielectric constant (~3), which limits the OTFT performance. Therefore, it is necessary to design and develop a high capacitance film with economical and easy method.

To obtain non-breakable high dielectric material, metallosiloxane[13,14] composed of Si-O-M bond is one of the candidates. There has been many works on the synthesis and properties of metallosiloxane[14] which are expected to be a model compound for the inorganic polymers. It shows an excellent thermal stability since the typical linkage Si-O-M is similar to the backbone structures of silicate minerals. In this study, SiO_2-$M_xO_yR_2$ (M=Ti, Zr, R=acetylacetone) gels were synthesized by the condensation polymerization of silicic acid and acetylacetonate chelates of metals such as titanium and zirconium as shown in Scheme I, and used as gate dielectric layer by solution process. We also investigated the electric properties of polymetalloxane gate dielectrics and the performance of OTFTs.

Experimental

Materials. All reagents were analytical reagent. Silicic acid (SA) was prepared as 0.85M SA-THF solution according to the previous paper.[15] Aqueous hydrochloric acid (37%), 1-butanol (99.5%) and *n*-propanol were purchased from Duksan pure chemicals (Korea). Sodium metasilicate hydrate ($Na_2SiO_3\cdot9H_2O$), bis-(2,4-pentanedionato) titanium diisopropoxide (PTP), zirconium n-propoxide ($Zr(OPr^n)_4$) and ethacrylic acid were purchased from Sigma-Aldrich (U.S.A.). Tetrahydrofuran (THF) was purchased from J.T. Baker. Bis (2,4-pentanedionato) zirconium diisopropoxide (PZP) were synthesized by the method described in the literature.[16] All materials were used as received.

Preparation and Characterization of Films. A mixture of 0.02, 0.01, or 0.005 mol of PTP and 5 mL of methanol was dropped into a solution of 0.01 mol of 0.85 M SA-THF solution containing 5 mL methanol with stirring. Then, the mixture was refluxed for 20 min-1 h, and the solvents were distilled off in vacuum to give highly viscous solution of

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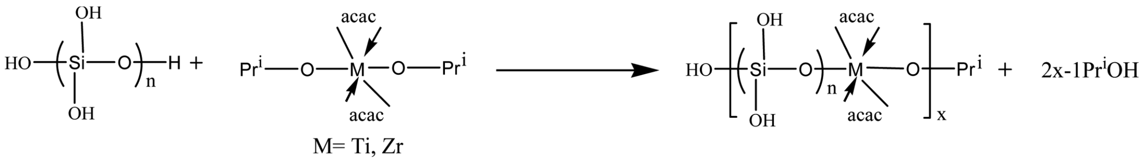


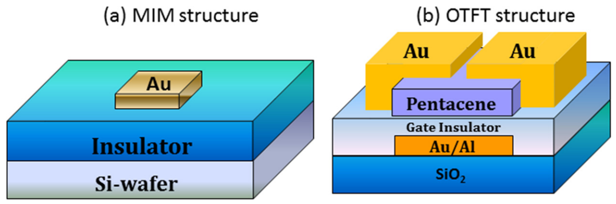
Scheme I. Synthesis of polymetalloxanes.

Table I. Sample Codes and Their Mole Ratios of Silicic Acid and Acetylacetonated Metals

Sample Code	Silicic Acid	$Ti(OPr^i)_2(acac)_2$	$Zr(OPr^n)_2(acac)_2$
PTS0.5	1	0.5	
PTS1	1	1	
PTS1.3	1	1.3	
PZS0.77	1.3		1
PZS1	1		1
PZS2	1		2

polytitanosiloxanes (PTS). Depending on the molar ratios of PTP/SA=0.5 and 1.0, these resulting products are abbreviated as PTS0.5 and PTS1. In the case of polyzirconasiloxanes (PZS), PZP was used instead of PTP. The remaining procedure and the abbreviation are the same as above. The sample codes were defined and given in Table I. In order to adjust the solution viscosity, the solution was further diluted with solvent and filtered through a 0.45 μm membrane filter. The coating solution was spin-coated on the Si or SiO_2 substrate.

Device Fabrication and Characterization. The schematic pictures of metal-insulator-metal (MIM) and OTFT structures are shown in Scheme II. For capacitance measurement, a solution of polymetalloxane/1-butanol as gate insulator was spin coated at 3,000 rpm on highly *p*-doped Si wafer as a substrate. The deposited film was pre-dried at 80 °C for 60 s on a hot plate, further dried at 180 °C for 2 h to remove organic residuals. Gold top contact as metal electrode was evaporated (0.65 mm^2 area and 100-150 nm thick) using a shadow mask at a rate of ~0.05 nm/s. In the case of OTFT, top contact geometry was used in the transistor devices as shown in Scheme II(b). Metal Au was deposited on SiO_2 substrate as a bottom gate electrode, and then Al electrode was deposited as a buffer layer through a shadow mask. Gate insulator film was deposited with the solution of polymetalloxane/1-butanol using a spin coater. After thermal treatment as described above procedure, pentacene was evaporated at ~0.01-0.02 nm/s (film thickness 75 nm), followed by gold top contacts (50 nm thick). All the vacuum deposition process were conducted at a pressure of ~1×10^{-3} Torr. FTIR measurement was performed using a FT/IR-4200 (JASCO, Japan) and Kosaka ET-3000 surface profilometer was used to measure film thickness. Thermal gravimetric analysis (TGA) was measured using TGA Q50 system analyzer. Phoenix300 equipment and atomic-force microscopy (N8 ARGOS, Bruker-Nano, Germany) were used to measure the contact angle of water and surface roughness on films. Capacitance measurements were made on an Agilent 4284A LCR meter. Thin film characterization was performed using a probe station equipped with HP4156C semiconductor parameter analyzer.



Scheme II. Schematic pictures of (a) metal-insulator-metal (MIM) and (b) OTFT structures.

Results and Discussion

Figure 1 shows the spectra of precursor polymers of PTS and PZS. The spectra of precursor polymers show characteristic absorption peaks due to silanol group (ν_{SiOH}=3400 cm^{-1}), 2,4-pentanedionato group (ν_{CO}=1580 and 1520 cm^{-1}), Si-O-Si linkage ($\nu_{Si\text{-}O\text{-}Si}$=1100-1000 cm^{-1}) and Si-O-Ti, Zr linkage ($\nu_{Si\text{-}O\text{-}Ti}$=940 cm^{-1}).[17] Consequently, the polymer back bones are constructed of Si-O-Si and Si-O-Ti linkage with 2,4-pentaedionato group as pendants. The spectrum of precursor polymer PTS1 is similar to that of PTS0.5 except that more distinct peaks with high intensity due to organic pen-

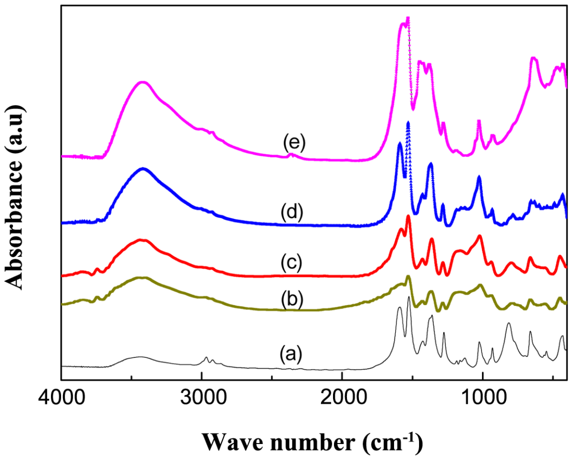


Figure 1. FTIR Spectra of (a) PTP precursor, (b) PTS0.5, (c) PTS1, (d) PZS2, and (e) 180 °C thermal treated PZS2 polymers.

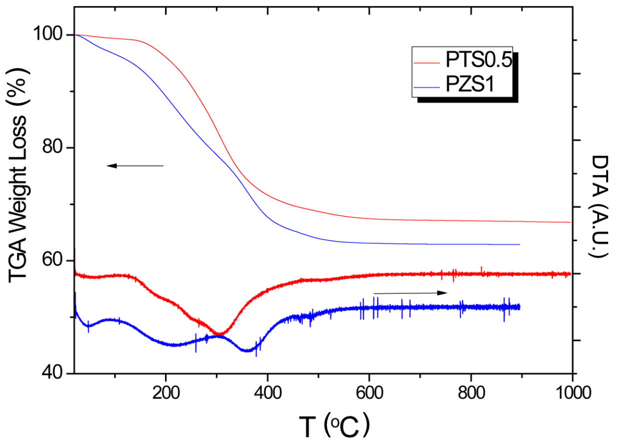


Figure 2. Thermogravimertric analysis (TGA) (left axis) and differential themo-analysis (right axis) graphs of the PTS0.5 and PZS2 at a heating rate of 10 °C min under N_2 atmosphere.

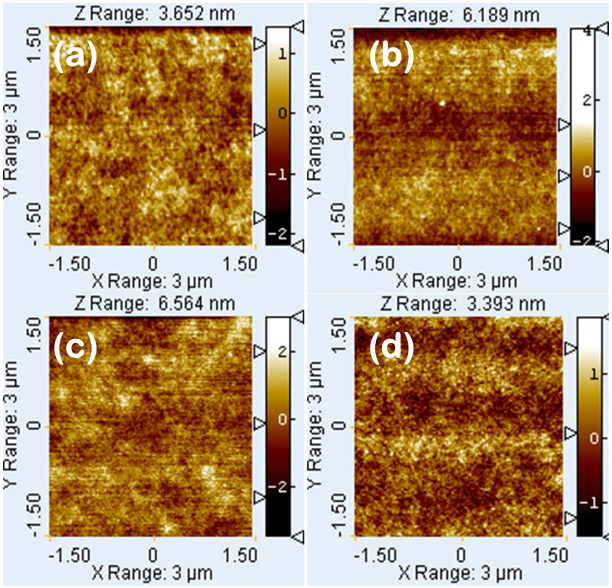


Figure 3. Atomic force microscopy (AFM) images with the polymetalloxane film. (a) PTS0.5 (b) PTS1.3 (c) PZS2, and (d) PZS1, having rms roughnesses of 0.426, 0.449, 0.62, and 0.438 nm, respectively.

dant group are observed. After 2 h thermal annealing 180 °C as shown in Figure 1, minor changes on pentanedionato group were observed due to thermal induced condensation. In fact, the gate insulator film after thermal treatment was no longer soluble.

Figure 2 shows the thermal decomposition of PTS0.5 and PZS2 powder, respectively. In the TGA curves, the small weight loss at lower temperature below 200 °C is probably due to evaporation of residual alcohol and physically absorbed water. At the temperature of 200-600 °C, a sudden weight loss results from the decomposition of pendant organic groups, and the evaporation of by-product as the condensation reaction proceeds during TGA measurement. The weight loss observed for PTS0.5 is 33.2% at 1,000 °C, PZS2 is 37% at 900 °C, which may be explain since PZS2 has more organic residue. Beyond 600 °C, all organic residues are burned and the formed metallosiloxane is very stable as expected. However, in order to use this material as OTFT gate insulator, it requires organic residues to have good contact with organic semiconductor. Since our materials are relatively stable below 200 °C, it is possible to use as OTFT gate insulator.

The field-effect carrier mobility of the semiconductor is closely related to its microstructure and morphology, which in turn can be influenced by the interface between the semiconductor and the gate dielectrics.[18,19] In addition, the surface morphology of the hybrid thin films with film preparation condition may affect the domain growth of pentacene. Figure 3 shows the AFM images where gate insulator films were deposited on the Si film, and all the films gave homogeneous and smooth surfaces at nanometer scale with RMS roughness ranging from 0.426 to 0.62 nm. From this observation, concentration of Ti or Zr precursor did not make an effect on the surface morphology. Contact angle measurements were performed to compare the surface energies of the gate insulator layers. Table II shows the water contact angles on the thin films are ~100° indicating hydrophobic characters of films and are close to that of pentacene film, *i.e.* ~93°. It exhibits low surface energy due to the fact that the high *k* inorganic part is covalently with a low surface energy organic part. This increases the ordering of pentacene molecules. Since the silicic acid part is more hydrophilic than chelated metal part, it is expected that contact angle may depend on the compositions. However, contact angle measurements reveal that the water contact angle is only minimally affected by Ti, Zr concentration, suggesting minimal changes in surface energy for gate insulators. This observation may be explained by the local interactions between -Si-OH and the surface of Si or SiO_2. Since the surface of Si or SiO_2 may have abundant -Si-OH groups, this may interact with Si-OH group in metallosiloxane during thermal treatment. The silicic acid part of precursor polymer may go towards substrate and the remaining organo-metal parts may expose on the surface of gate insulator. This explanation is only a postulation and further experiment is beyond our scope.

Figure 4 displays the current density-electric field charac-

Table II. Water Contact Angles of Different Dielectric Materials Prepared on Si Substrate

Sample	PTS1.3	PTS1	PTS0.5	PZS2	PZS1	PZS0.77
Contact Angle	96°	97.9°	98.2°	99.5°	97.5°	99.9°

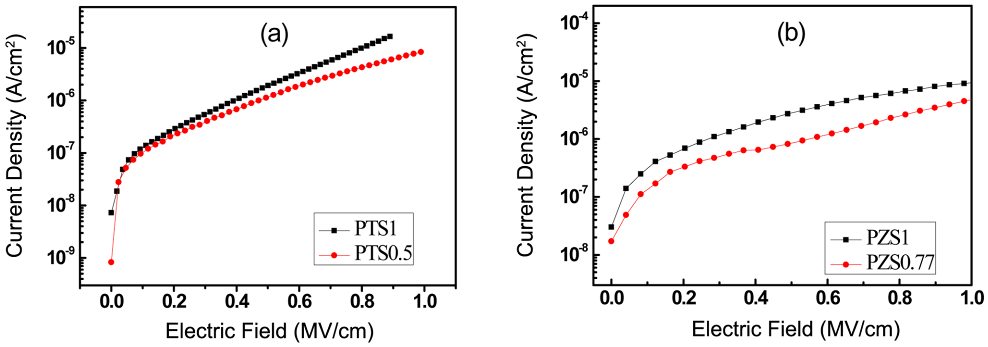


Figure 4. Current density-electric field (J-E) plot of the polymetalloxane film annealed at 180 °C. (a) PTS and (b) PZS.

teristics of Au/insulator/Si structures. PTS1 exhibits leakage current density in the range of 10^{-5}A/cm^2 at 0.8 MV/cm while PTS0.5 is 10^{-5}A/cm^2 at 1 MV/cm. The main contribution of leakage current may come from the OH group in silicic acid moiety. In addition, the relatively large leakage current density of PTS1 is attributed to the semiconducting character of TiO_2. Compare to the PTS, leakage of PZS1 is slightly decreased to 10^{-5} at 1 MV/cm whereas that of PZS0.77 is further decreased to 5×10^{-6} at 1 MV/cm. These results also indicates that leakage current depends on Ti(Zr)/Si molar ratio and increases with the concentration of Ti or Zr precursor. In general, PTS series exhibits larger leakage current density than PZS series, which may be explained by lower band gap of TiO_2 than that of ZrO_2.

To measure dielectric constants of gate insulators, metal-insulator-metal (MIM) structure with varying compositions of polymetalloxane was used. The measured capacitances per unit area (C_i) at 1 kHz for various dielectrics are listed in Table III. Using the capacitance-frequency result, the dielectric constant was calculated by the equation $C=k\varepsilon_0A/t$. The frequency dependence of dielectric constant is presented in Figure 5. The dielectric constants of PTS films are in the range of 6.16-8.18 at frequency of 1 kHz. It reveals the dielectric constant increased with the amount of Ti precursor in the gate insulators as expected. Compare to the PTS film, the dielectric constants of PZS films are in the range of 6.84-8.27 at 1 kHz, which are lower than those of PTS films at the same concentration. This is obvious because TiO_2 has

Table III. Summary of the Electrical Parameters for Pentacene TFTs

Gate Insulator	I_{on}/I_{off} ($\times10^4$)	Slope ($\times10^{-4}$)	SS (V/dec)	V_T (V)	Mobility (cm^2/Vs)	Insulator Permittivity (ε)	C_i (nF/cm^2)
PTS1.3	1.7	-2.0	0.09	-0.3	1.16	8.18	49.9
PTS1	5.94	-1.7	0.07	-0.49	0.8	8.0	57.0
PTS0.5	2.41	-2.14	0.1	-0.39	1.77	6.16	41.9
PZS2	3.5	-1.98	0.13	-0.6	1.3	8.27	73.2
PZS1	2.24	-2.36	0.07	-0.35	1.26	7.79	69.0
PZS0.77	7.5	-1.56	0.11	-0.9	1.02	6.84	60.5

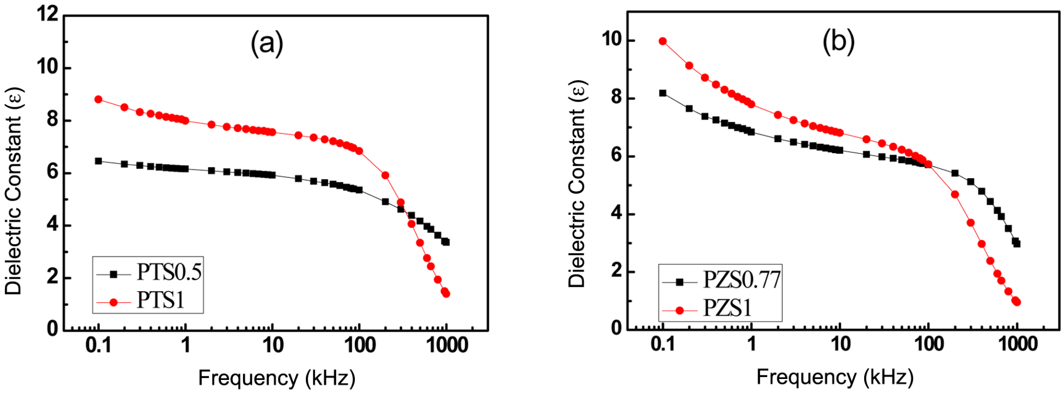


Figure 5. Dielectric constant *vs.* frequency plots of the polymetalloxane insulators. (a) PTS and (b) PZS.

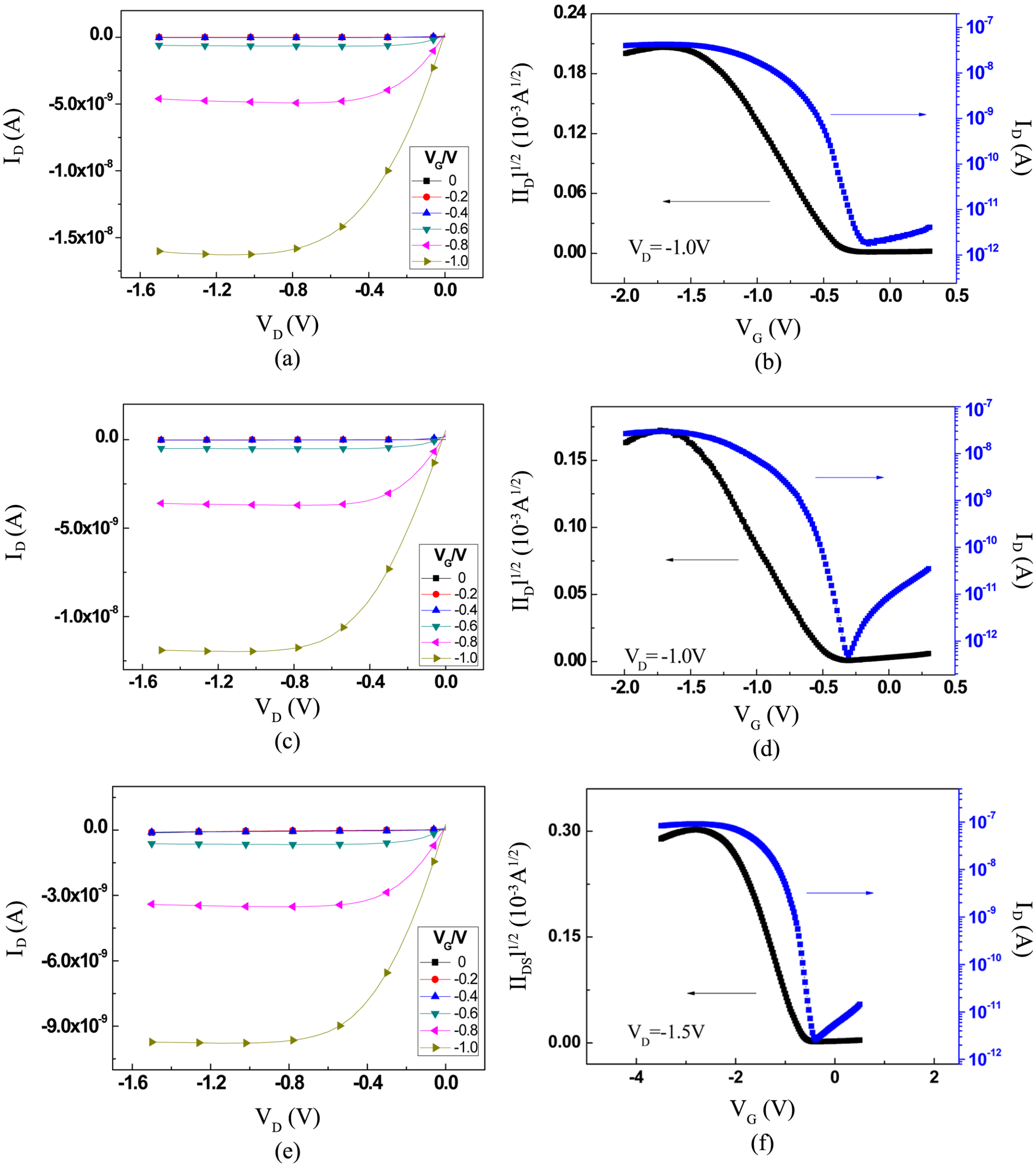


Figure 6. Electrical characteristics of the OTFTs: (a) I_D *vs.* V_D and (b) $I_D^{1/2}$ *vs.* V_G of the OTFT with PTS0.5 gate dielectric, (c) I_D *vs.* V_D, (d) $I_D^{1/2}$ *vs.* V_G of the OTFT with the PTS1 gate dielectric, (e) I_D *vs.* V_D, and (f) $I_D^{1/2}$ *vs.* V_G of the OTFT with the PZS2 gate dielectric.

higher dielectric constant than ZrO_2.

To further probe the correlation between the gate dielectric material and the carrier mobility, we have also fabricated pentacene OTFTs with hybrid gate dielectric layers. The output and transfer characteristics of OTFTs using hybrid dielectrics are given in Figure 6. The carrier mobility μ was calculated in the saturation regime using the following equations: $I_D = WC_i\mu(V_G - V_T)^2/2L$, where W and L are channel width and length, C_i is the capacitance per unit area of the insulating layer, and V_G and V_T are an applied gate voltage and a threshold voltage. Details of electrical properties of polymetalloxane are listed in Table III. PTS1-based pentacene OTFT shows a good saturation output at as low as -1V and exhibits a saturation carrier mobility μ_{sat} of 0.8 cm^2/Vs, a current on/off ratio of 5.94×10^4, and a V_T of -0.49 V. In contrast, with PTS0.5 gate dielectric, μ_{sat}, on/off ratio and V_T are determined to be 1.77 cm^2/Vs, 2.41×10^4, and -0.39 V, respectively. The higher field-effect mobility for PTS1.3 with higher dielectric constants may be due to their enhanced polarization, which increases the number of hole-carriers at the interface. Conclusively, it is believed that the good surface morphology and the matching surface energy of the PTS0.5 film had a positive influence on the crystallization of the pentacene molecules, which improved the electrical performance of the pentacene TFTs. Pentacene fabricated on PZS2 thin film also showed well saturated output characteristics at low driving voltages of -1 V. Because the field-induced current is proportional to the field-induced charge density, high k materials can afford greater surface charge density at the semiconductor-dielectric interface. The OTFT of PZS2 has the performance with the threshold voltage of -0.6 V, the mobility of 1.3 cm^2/Vs, subthreshold swing of 0.13 V/dec, and I_{on}/I_{off} of 3.5×10^4. These OTFTs operate at low threshold voltage, and exhibit reasonably high mobility. This suggests that the structure of our dielectric films is compatible with pentacene film growth and adhesion. However, it showed slightly low on/off current ratio mainly due to relatively high off current coming from leakage current density.

Conclusions

High dielectric materials for OTFT insulator have been synthesized successfully using polysilicic acid and organometalics. These materials offer a feasible and economic way to tune gate insulators for OTFTs with high capacitance. Furthermore, our experimental data demonstrates that obtained dielectric materials are good gate insulators for pentacene-based OTFT device requiring low-voltage operation.

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