

Communications

Fluoropolymer-Based Polymer Gate Dielectrics for Organic Thin-Film Transistors

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Organic thin-film transistors (OTFTs) have gained huge recent interest in a number of applications.¹ To enable high driving speed and to reduce the charging time of gate capacitors in the device, a high electrical conductance is required. The electrical conductance of a TFT is determined by the product of charge carrier mobility (semiconductor property) and charge carrier density in the channel, governed by the capacitance of the gate dielectric. For organic semiconductors, great improvements have been reported within the last ten years, with carrier mobilities approaching that of amorphous silicon.² For gate dielectric, high dielectric capacitance for large electrical conductance of a TFT could be achieved by employing high-k dielectric and/or reducing the thickness of the dielectric film. Several classes of high-k materials have been reported as high capacitance gate dielectric.^{3,4} For organic gate dielectrics, ferroelectric polymers with high dielectric constant are representative examples.⁵ For instance, high performance ferroelectric TFTs have been demonstrated, employing poly(vinylidene fluoride/trifluoroethylene) ferroelectric copolymer as gate dielectric.⁶ Furthermore, low-voltage organic transistors and inverters have also been reported using ultrathin Cytop layer as gate dielectric.⁷ Although solution-processed fluoropolymer has shown promise as high capacitance gate dielectric for OTFTs, finding orthogonal solvents for solution-processed organic semiconductor to enable all solution-processed TFTs is of great challenge. To this end, we report the development of robust (insoluble), high-capacitance gate dielectric based on high-k fluoropolymer in this study.

Blending poly(4-vinyl)phenol (PVP) with silane-based crosslinker has been known to afford crosslinked polymer chain matrices as robust, adherent, pinhole-free, low-leakage gate dielectric materials.⁸ Therefore, blending high-k fluoropolymer with appropriate polymer-crosslinker combinations would afford strongly crosslinked gate dielectric with high capacitance. In this study, we used terpolymer, poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF_x-TrFE_y-CFE_{1-x-y})) (x = 59.23, y = 31.62), as high-k fluoropolymer.⁹ Furthermore, crosslinked polymer blend combination, PVP and acetoxysilane-based crosslinker

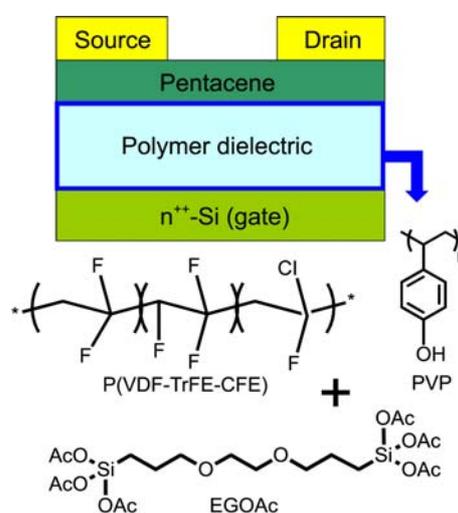


Figure 1. Bottom-gate/top-contact device structure and chemical structures of terpolymer P(VDF_x-TrFE_y-CFE_{1-x-y}), (x = 59.23, y = 31.62), PVP, and crosslinker (EGOAc) employed in this study.

(EGOAc), was used as reported in ref 8 (Figure 1).

To fabricate fluoropolymer-based gate dielectrics, PVP, crosslinker, and terpolymer were individually dissolved in ethyl acetate at a specific concentration, combined as a single solution, and spin-coated onto substrates. After curing at ~110 °C in a vacuum oven, these films are completely insoluble in the mother solvent, demonstrating strongly

Table 1. Gate dielectric deposition conditions – PVP:crosslinker: fluoropolymer ratio (mg:mg:mg), film thickness (*D*, nm), dielectric constant (ϵ) at 1 kHz, and pentacene TFT performance – carrier mobility (μ_{sat} , cm²/Vs), and current on/off ratio (I_{on}/I_{off})¹³

PVP:EGOAc: fluoropolymer Ratio	<i>D</i>	ϵ	Pentacene	
			μ_{sat}	I_{on}/I_{off}
40:40:0 ^a	120	4.9	0.50	10 ⁵
40:40:20 ^b	120-135	~6.7	0.08	10 ³
40:40:40 ^b	175-180	~7.2	0.02	10 ³
40:40:60 ^b	215-225	~9.3	0.01	10 ²

^{a,b}2 mL and 3 mL of EtOAc, respectively, was used as solvent.

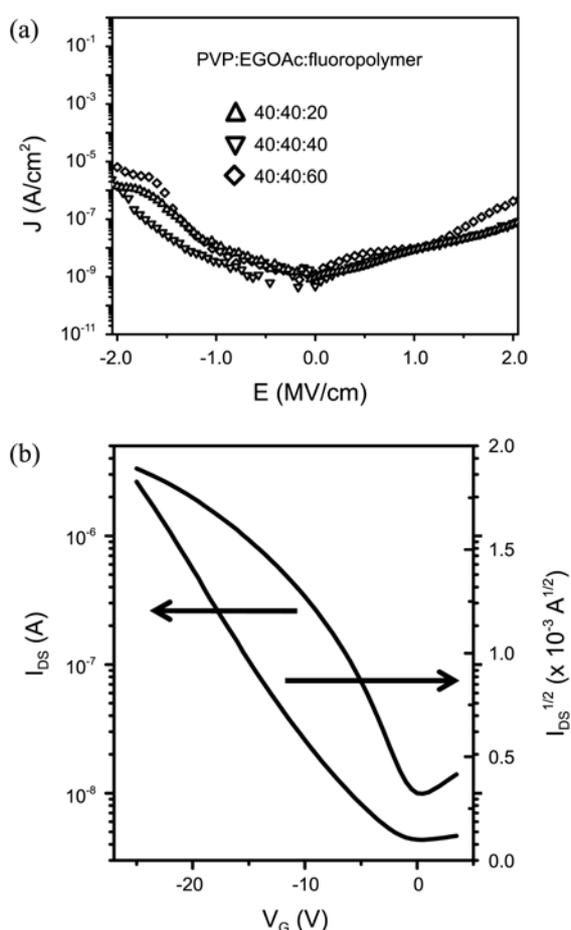


Figure 2. (a) Leakage current densities vs. electric field plot of fluoropolymer-based gate dielectric employed in this study (all three data shown in Table 1). (b) Transfer characteristics of pentacene TFT devices on gate dielectric (PVP:EGOAc:fluoropolymer ratio (mg:mg:mg in 3 mL of EtOAc) of 40:40:20 as in Table 1). Channel length and width are 100 and 500 μm , respectively.

crosslinked polymer matrices. To monitor the change of dielectric properties as a function of fluoropolymer content, stoichiometric ratio of each component was varied (Table 1). The areal capacitance values of each dielectric film were measured as a function of frequency (1-10³ kHz) and voltage on metal-insulator-semiconductor (MIS, M = Au, S = n⁺⁺-Si) structures. The formal dielectric constants of each gate dielectric were calculated at a frequency of 1 kHz using parallel plate capacitor model (Table 1). As shown, dielectric constant increased from 4.9 (without fluoropolymer) up to ~9.3, as the content of fluoropolymer increased, demonstrating ~100% increase in dielectric constant. Furthermore, leakage current density, insulating properties of gate dielectrics, was measured as a function of electric field. Pristine fluoropolymer films (without PVP and crosslinker) afforded leaky films ($J > 1 \times 10^{-5} \text{ A/cm}^2$ at 2 MV/cm, not shown). However, fluoropolymer-based crosslinked films all exhibited low

leakage current densities of $2 \times 10^{-8} - 6 \times 10^{-6} \text{ A/cm}^2$ at 2 MV/cm (Figure 2(a)).

The OTFTs were fabricated using fluoropolymer-based polymer films as the gate dielectric and pentacene as organic semiconductor (see Supporting Information for experimental details). The representative device characteristics are collected in Figure 2(b) and Table 1. As shown, OTFTs fabricated with fluoropolymer-based gate dielectric exhibited decent carrier mobilities of 0.01-0.08 cm^2/Vs and current on/off ratios of 10²-10³. Lower device performance with fluoropolymer-based gate dielectric compared to that of gate dielectric without fluoropolymer is possibly due to unoptimized, rough surface morphologies of the gate dielectric (Figure S1).¹¹

In conclusion, blending fluoropolymer with appropriate polymer (PVP) and acetoxysilane-based crosslinker afforded strongly crosslinked polymer matrices at low fabrication temperatures (~110 °C) with dielectric constant as high as ~9.3. These new gate dielectrics gave decent device performance for pentacene TFTs with carrier mobility as high as 0.08 cm^2/Vs . Further studies on the optimization of the surface morphologies of gate dielectric as well as the application of solution-processed organic semiconductor are under way.

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- P(VDF-TrFE-CFE), a high-k (> 40) dielectric, has been employed as high performance TFTs and energy density capacitor.
- Pristine fluoropolymer films were too leaky to be employed for working TFT device.
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