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Low-voltage organic thin-film transistors with π-σ-phosphonic acid molecular dielectric monolayers

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Pentacene-based organic thin-film transistors (OTFTs) have been fabricated using π-σ-phosphonic acid self-assembled monolayers (SAMs) on top of aluminum oxide as the gate dielectrics. With ultrathin dielectrics, high capacitances up to 760 nF/cm^2 and low leakage current densities of 10^{-8} A/cm^2 at 2 V could be obtained, allowing operation of OTFTs within −3 V. Vast improvements in the gate leakage current (~2 orders), on/off current ratio (1 order), and subthreshold slope down to 85 mV/decade are achieved compared to control devices without SAMs. The OTFTs with pentacene vapor deposited at room temperature on SAM dielectrics-modified substrates exhibit mobilities of 0.14–0.30 cm^2/V s, on/off current ratios of 10^5, and threshold voltages of −(1.3–1.5) V.
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Organic thin-film transistors (OTFTs) based on π-conjugated materials are very attractive for a variety of large-area low-cost solution-processed/printed electronic applications,[1,2] such as logic circuits, displays, sensors, and electronic barcodes. It is critical to reduce the threshold voltage and the subthreshold slope of the devices for low voltage operation of OTFTs. However, current OTFT devices still require rather high operating voltages, often exceeding 20 V. This is due to the low capacitance of thick gate dielectrics (usually less than 15 nF/cm^2) and the high density of defect states in organic semiconductor films and at the interface between the gate dielectric and organic semiconductor. To produce low-voltage operating OTFTs, there have been numerous attempts to develop high capacitance gate dielectrics with reduced thickness, such as self-assembled molecular monolayers and multilayers[3,4] ultrathin polymer layers,[5] high dielectric constant (k) metal oxides (TiO_2,ZrO_2),[6,7] polymer electrolytes,[8] and high-k polymers.[9]

The use of self-assembled monolayer (SAM) gate dielectrics for OTFTs has been successfully demonstrated by several groups. Utilizing α-sexithiophene as the organic semiconductor and carboxyl-terminated n-alkyltrichlorosilane SAMs on top of native SiO_2/Si as the dielectric, Collet *et al.* have shown OTFTs operating at 2 V, with a subthreshold slope of 350 mV/decade and a gate current density of 10^{-6} A/cm^2.[10] Halik *et al.* used SAMs of 18-phenoxyoctadecyltrichlorosilane (PhO-OTS) with an aromatic end group to form a SAM that is resistant to molecular penetration. Utilizing pentacene as the organic semiconductor and PhO-OTS SAMs on native SiO_2/Si as the dielectric, they demonstrated OTFTs operating at 2 V, with a subthreshold slope of 100 mV/decade, and a leakage current density of 10^{-7} A/cm^2 at 2 V.[11] Compared to the conventional silane-based molecules, there are several advantages to use organophosphonic acids to form SAMs.[12–14] These include: (1) better stability to moisture, (2) less tendency to form homocondensation between the phosphonic acids, and (3) the reaction between organophosphonic acid and the metal oxide substrate is not limited by the content of surface hydroxyl groups. These advantages enable organophosphonic acids to form dense, robust, and structurally well-defined functional phosphonate monolayers on metal oxide surface which is ideal for their use as dielectrics in TFTs to ensure small leakage currents, operating voltages, and subthreshold slopes. Utilizing pentacene as the organic semiconductor and octadecylphosphonic acid (ODPA, σ-PA) SAM on AlO_x/Al as the dielectric, Klauk *et al.* recently demonstrated OTFTs operating within 3 V, with a subthreshold slope of 100 mV/decade and a leakage current density of 10^{-8} A/cm^2 at 2 V.[15] The leakage currents of the device are one order of magnitude lower than the one fabricated with octadecyltrichlorosilane (OTS) SAMs on AlO_x/Al. McDowell *et al.* also fabricated pentacene-based OTFTs using 9-anthrylphosphonic acid (π-PA) SAMs as a buffer between the silicon dioxide (100 nm) gate dielectric and the active pentacene channel region. A substantial decrease of the subthreshold slope (from 1500–1700 to 200 mV/decade) was observed compared to the control devices without using the SAM buffer.[16] In this paper, we introduce anthryl-alkylphosphonic acid (π-σ-PA) SAMs which combine the advantages of σ-PA dielectric with π-PA interfacial modification to further enhance the performance of OTFTs. By using pentacene as the organic semiconductor and π-σ-PA SAMs on AlO_x/Al as the dielectrics (Fig. 1), we have fabricated OTFTs operating within 3 V, with a subthreshold slope down to 85 mV/decade and a leakage current density of 10^{-8} A/cm^2 at 2 V.

(2-anthryl)undecoxycarbonyldecylphosphonic acid (π-σ-PA1) and (2-anthryl)undecoxycarbonyl-undecylphosphonic acid (π-σ-PA2) were synthesized by phosphonation of corresponding π-σ-Br with triethyl phosphite to provide diethyl π-σ-phosphonate. By reacting with bromot-

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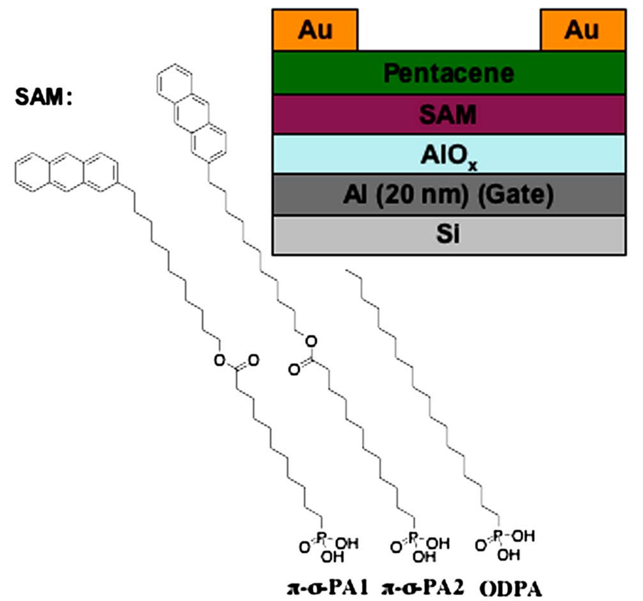

FIG. 1. (Color online) Schematic view of the pentacene TFTs with different phosphonic acid SAMs on AlO_x/Al as the dielectrics.

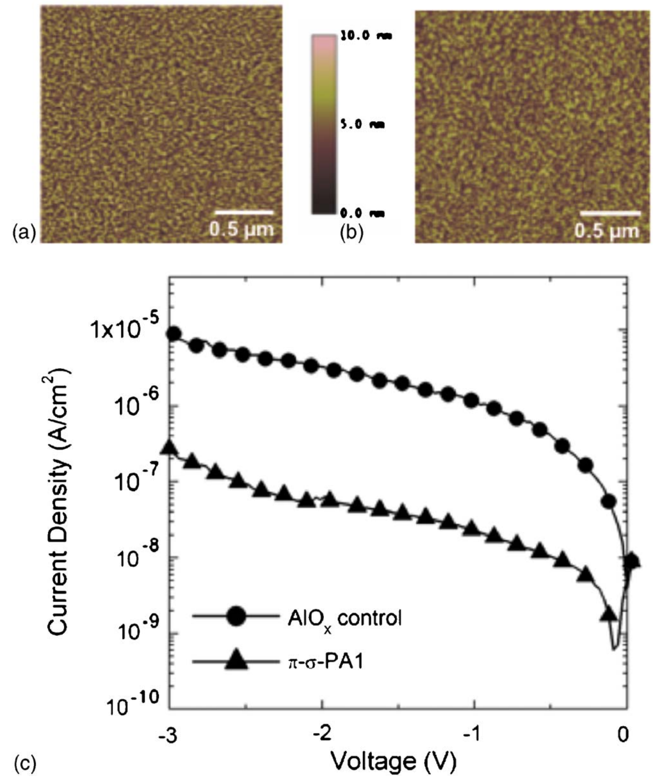

FIG. 2. (Color online) AFM height images of (a) bare AlO_x/Al (rms 0.84 nm) and (b) π-σ-PA1 SAM (rms 0.65 nm) on AlO_x/Al. (c) Leakage current density as a function of applied voltage. Each measurement was repeated on five junctions to evaluate the uniformity.

rimethylsilane, the diethyl π-σ-phosphonates were converted to ditrimethylsilyl π-σ-phosphonates and then hydrolyzed to afford π-σ-PA1 and π-σ-PA2. Heavily doped p-type Si(100) wafers were diced, cleaned in a piranha solution, washed with de-ionized water, and dried with a N_2 stream. To define the gate electrodes, a 20-nm aluminum film was deposited by thermal evaporation. Before self-assembly, the aluminum surface was briefly exposed to oxygen plasma (150 W, 15 s at 75 mTorr O_2 pressure). The plasma treatment increases the thickness of the native aluminum oxide layer and creates enough density of hydroxyl groups for molecular adsorption. After plasma treatment, the substrates were immediately placed in a flask containing either a 0.1 mM solution of π-σ-PA1, π-σ-PA2 in tetrahydrofuran/2-propanol (1:1) or ODPA in 2-propanol, and left to self-assemble under ambient conditions. After 16 h, the substrates were rinsed with 2-propanol, dried with a N_2 stream and annealed at 60 °C for 10 min under N_2. The topography of monolayer surface (Fig. 2) was examined by atomic force microscopy (Digital Instruments). The surface homogeneousness and smoothness of the SAMs were found to be comparable to those of $AlO_x/Al/Si$. The advancing water contact angles of the SAMs change dramatically before and after the SAM preparation (Table I), confirming the formation of hydrophobic monolayers.

To determine the leakage current densities and the capacitance densities (C_i) of dielectrics with different SAMs, Al–AlO_x-SAM-Au structures were prepared by evaporating gold dot contacts (1000 μm diameter) through a shadow mask directly onto the SAMs. Transistors were fabricated in a top-contact geometry, with interdigited gold source-drain contacts (50 nm) evaporated on top of the pentacene film (50 nm). Pentacene (Aldrich Chem. Co., without further purification) was deposited onto room temperature substrates at the rate of 0.05 nm/s by sublimation from a resistively heated quartz crucible boat at 2×10^{-6} Torr. Gold was deposited onto room temperature substrates at 0.1 nm/s through a shadow mask from a resistively heated molybdenum boat at 2×10^{-6} Torr. OTFT characterization was carried out in air using an Agilent 4155B semiconductor parameter analyzer. Figure 3 shows the typical output $I_{ds}-V_{ds}$ at various gate voltages (V_{gs}) and transfer $(-I_{ds})^{1/2}$-V_{gs}, $(-I_{ds})-V_{gs}$ characteristics for pentacene TFTs with π-σ-PA1 on AlO_x/Al as the dielectric, channel length (L) 90 μm and channel width (W) 9000 μm. From these data, the average field-effect mobility (μ) was calculated in the saturation regime ($V_{ds}=-1.5$ V) by plotting the square root of the drain current versus gate voltage [Fig. 3(b)] and fitting the data to the following equation: $I_{ds}=(WC_i/2L)\mu(V_{gs}-V_t)^2$.

A summary of the electrical parameters for pentacene TFTs with different SAMs on AlO_x/Al as the dielectrics is listed in Table I. The OTFTs using pentacene vapor deposition on room-temperature substrates with these SAM/AlO_x dielectrics exhibit mobilities of 0.14–0.30 cm^2/V s, on/off current ratios of 10^5, threshold voltages of $-(1.3-1.5)$ V and leakage current densities of 10^{-8} A/cm^2. With ultrathin SAM/AlO_x dielectrics, high capacitances up to 760 nF/cm^2 at 10 kHz have been obtained, allowing operation of OTFTs within -3 V. It is noteworthy that vast improvements in the gate leakage current (~2 orders), on/off current ratio (1 order) and subthreshold slope down to 85 mV/decade are achieved compared to the control devices without SAMs. This is the best subthreshold slope reported so far for an organic transistor, and close to the theoretical room-temperature minimum of ~58 mV/decade [$kT/q\ \ln(10)$]. It is very encouraging that improvements of device parameters in leakage current densities, capacitance densities, and subthreshold slopes could be simultaneously achieved for π-σ-PA1 and π-σ-PA2 SAM modified AlO_x dielectrics compared to the ODPA (σ-PA) SAM/AlO_x dielectrics. The π-σ-PA1 and π-σ-PA2 SAMs are thicker than ODPA SAM so their leakage current densities also decrease.

TABLE I. Summary of the electrical parameters for pentacene TFTs with different SAMs on AlO_x/Al as the dielectrics. rms, root-mean-square roughness of the gate dielectrics; J, leakage current density; C_i, capacitance density at 10 kHz; μ, field-effect mobility; V_t, threshold voltage; S, sub-threshold slope; and I_{on}/I_{off}, on/off current ratio.

	rms (nm)	Contact angle (°)	J at 2 V (A/cm^2)	C_i (nF/cm^2)	μ ($cm^2/V\,s$)	V_t (V)	S (mV/dec)	I_{on}/I_{off}
π-σ-PA1/AlO_x	0.65	83	5×10^{-8}	760	0.18	−1.3	85	10^5
π-σ-PA2/AlO_x	0.75	84	5×10^{-8}	700	0.14	−1.4	85	10^5
ODPA/AlO_x	0.75	107	8×10^{-8}	600	0.30	−1.5	110	10^5
AlO_x	0.84	<10	2×10^{-6}	950	0.30	−1.7	200	10^4

The π-conjugated anthracene terminal group is more polarizable than methyl terminal group so thicker π-σ-PA1 and π-σ-PA2 SAMs still possess larger capacitance densities than ODPA SAM ($C_i=k\varepsilon_0/t$, where t and k are the thickness and relative permittivity of the dielectric, respectively). The π-σ-PA1 and π-σ-PA2 SAMs may also efficiently passivate the hydroxy groups on AlO_x/Al surface and provide a favorable anthracene interface with similar chemical structure yet still a larger bandgap than pentacene. Compared to the ODPA SAM, the lower subthreshold slopes for devices made from π-σ-PA1 and π-σ-PA2 SAMs could be due to smaller density of charge trapping states (surface hydroxyl groups and interaction-induced trapping states[17]) at the semiconductor-dielectric interface. We believe that the morphology of pentacene on the different dielectric surfaces is governed by a combination of the surface energy, chemical functionality and roughness. Through anthracene template-induced ordering of organic semiconductor layer, the mobilities of pentacene TFTs with π-σ-PA SAMs could be increased by assembling these SAMs on smoother substrates and/or by changing the organic semiconductor investigation.

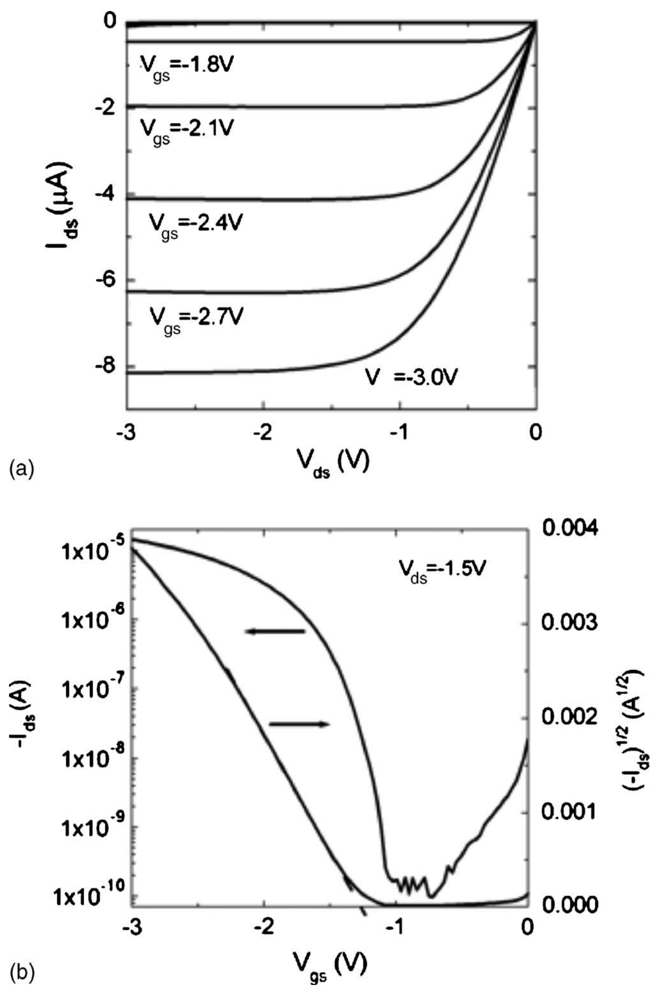

FIG. 3. (a) Typical output current-voltage characteristics of a 90 μm channel length and 9000 μm width pentacene TFT with π-σ-PA1 SAM on AlO_x/Al as the dielectric. (b) Transfer characteristics ($-I_{ds}$ vs V_{gs} at V_{ds}=−1.5 V) and $[(-I_{ds})^{1/2}$ vs V_{gs} at V_{ds}=−1.5 V].

We thus conclude that our π-σ-PA SAMs are quite promising candidates as gate dielectrics for low-voltage driven OTFTs with small leakage current densities and subthreshold slopes.

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