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Dry growth of n-octylphosphonic acid monolayer for low-voltage organic thin-film transistors

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ABSTRACT

Dry method for monolayer deposition of n-octylphosphonic acid (C_8PA) on the surface of aluminium oxide (AlO_x) is presented. Vacuum thermal evaporation is employed to deposit initial thickness corresponding to several C_8PA monolayers, followed by a thermal desorption of the physisorbed C_8PA molecules. AlO_x functionalized with such C_8PA monolayer exhibits leakage current density of $\sim 10^{-7}$ A/cm^2 at 3 V, electric breakdown field of $\sim$6 MV/cm, and a root-mean-square surface roughness of 0.36 nm. The performance of low-voltage pentacene thin-film transistors that implement this dry AlO_x/C_8PA gate dielectric depends on C_8PA desorption time. When the desorption time rises from 25 to 210 min, the field-effect mobility increases from $\sim$0.02 to $\sim$0.04 cm^2/V s, threshold voltage rises from ~ -1.2 to ~ -1.4 V, sub-threshold slope decreases from $\sim$120 to $\sim$80 mV/decade, off-current decreases from $\sim 5 \times 10^{-12}$ to $\sim 1 \times 10^{-12}$ A, on/off current ratio rises from $\sim 3.8 \times 10^4$ to $\sim 2.5 \times 10^5$, and the transistor hysteresis decreases from 61 to 26 mV. These results collectively support a two stage model of the desorption process where the removal of the physisorbed C_8PA molecules is followed by the annealing of the defect sites in the remaining C_8PA monolayer.

1. Introduction

The use of organic thin-film transistors (OTFTs) in inverters [1–4], Braille displays [5], amplifiers and NAND or NOR digital gates [6] aims for reduction in their operating voltages. Low transistor operating voltage reduces power consumption in the electronic circuits and is one of the primary concerns of very large scale integrated devices. High capacitance of the gate dielectric is a key approach to low voltage transistor operation. High capacitance values can be achieved with high-k and/or ultra-thin dielectrics.

High capacitance has been obtained by using high-k dielectrics such as polymers ($k \sim 12.6$) [7] and metal oxides, e.g. HfLaO ($k \sim 15.3$) [8–10] $Ba_{1.2}Ti_{0.8}O_3$ ($k \sim 15.57$) [11], and $SrTiO_3$ ($k \sim 12.1$) [12]. Thick high-k dielectrics resulted in still high capacitance values while reducing the gate leakage current. However, with the exceptions of [10], such OTFTs typically exhibited high inverse sub-threshold slope [9,11] and low on/off current ratio [8,12]. OTFTs with moderate-k value dielectrics such as aluminium oxide ($k \sim 6.2$) [13,14] have achieved low operating voltages through reduction in thickness [15]. However, very thin aluminium oxide layers exhibit high leakage currents, e.g. >10^{-6} A/cm^2 at 2 V [15]. Hence, these ultra-thin dielectrics have their limitations in OTFTs.

To obtain low leakage current with aluminium oxide, the oxide surface has been modified with polymer layers [16–19] or self-assembled monolayers (SAMs) [20–26]. Along with low leakage current density, the polymer surface yielded very low surface roughness of $\leqslant$0.3 nm and transistor operating voltages of about 6–8 V. Further reduction in OTFT operating voltages down to 3 V was achieved with SAMs. Among SAMs the alkyl phosphonic acids are the most studied.

Longer-chain alkyl phosphonic acids are more explored [2]. The study of the alkyl chain length on OTFTs showed

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that alkyl phosphonic acids with fewer than ten carbon atoms, assembled from solutions, form disordered monolayers [21]. This is a result of weaker cohesive interaction between molecules leading to OTFTs with high gate leakage current, e.g. 10^{-9} A for n-hexylphosphonic acid. Similar study found poor insulating properties of n-hexylphosphonic acid (C_6PA) SAM and low transistor field-effect mobility for n-decylphosphonic acid (C_{10}PA) SAM [20]. Longer chain C_{18}PA and anthryl-alkyl-phosphonic acid SAMs were used to improve the insulating properties of the oxide layers [23,27].

To date the self-assembled monolayers based on alkyl phosphonic acids [20–27] have been obtained by solution process only. In this paper we present that such monolayers can be prepared by dry method as well. We use vacuum thermal evaporation to deposit monolayers of n-octylphosphonic acid (C_8PA). To our knowledge, this is the first demonstration of dry growth of C_8PA monolayer and its successful implementation in pentacene based OTFTs. (In the past, Halik et al. [28] and DiBenedetto et al. [29] used dry fabrication method for silane based monolayers and self-assembled nanodielectrics, respectively.) Pentacene was selected because it is the most understood organic semiconductor and its interface with solution-deposited alkyl phosphonic acids has been studied [20,21]. To grow a monolayer, the thickness corresponding to several C_8PA monolayers is deposited, followed by a thermal desorption of physisorbed C_8PA molecules. Only C_8PA molecules chemically bonded to the surface of aluminium oxide remain. The implementation of this procedure into OTFTs based on small molecule conjugated polymers opens up the possibility for completely dry OTFT fabrication process amenable to roll-to-roll processing.

2. Fabrication of metal–insulator–metal structures and OTFTs

Metal–insulator–metal (MIM) or capacitor structures were fabricated to study the properties of the gate dielectric. 20-nm-thick aluminium lines were deposited on a glass substrate (Eagle 2000). One end of the line was capped by gold layer to prevent its oxidation. AlO_x was prepared by exposing Al to UV/ozone in ambient atmosphere for 60 min. To prevent the contamination of the oxidizing surface, UVOCS UV/ozone cleaner was enclosed under a Hepa filter. AlO_x preparation by UV/ozone oxidation of thermally evaporated aluminium has been reported elsewhere [30]. Approximately 10-nm-thick (nine monolayers) C_8PA layer was thermally evaporated on top of AlO_x at room temperature. Afterwards the substrate temperature was set to 160 °C to remove all physisorbed C_8PA molecules at a pressure of $<10^{-6}$ mbar. Desorption times of 25, 60, 90, and 210 min were selected. Taking into account the temperature profile of the heated sample, we estimated that the 10-nm-thick C_8PA layer would completely evaporate in ~30 min. However, if chemical bonding occurs between C_8PA molecules and the AlO_x surface, the substrate temperature would not be high enough to break these bonds. Finally, 50-nm-thick gold contacts were evaporated to complete the MIM structures. Several MIM structures were fabricated for each C_8PA desorption time. In addition, AlO_x MIM structures with no C_8PA layer were prepared as reference.

Bottom-gate, top-contact OTFTs based on thermally evaporated pentacene followed the same fabrication procedure. After C_8PA desorption, a 50-nm-thick pentacene layer was deposited at a rate of 0.24 Å/s at room temperature. Vacuum sublimation pentacene purification was performed in a three-zone tube furnace at a pressure of $\sim 1 \times 10^{-5}$ mbar. Such four-time purified pentacene had previously provided OTFTs with higher field-effect mobility than a three-time purified pentacene from Sigma–Aldrich [31]. The transistors were completed by evaporating gold source and drain contacts and their cross-section is shown in Fig. 1. All fabrication steps were performed by using shadow masks. The fabricated transistors have channel lengths of 30, 50, 70, and 90 μm and a channel width of 1000 μm. The $W/L > 10$ to minimize the effect of extending electric field lines that could lead to an overestimate of the field-effect mobility [32]. Transistors and capacitors were fabricated side by side and all thermal evaporation steps were conducted in Minispectros (Kurt J. Lesker) high vacuum system ($\sim 10^{-7}$ mbar) enclosed in a N_2-filled glove box with O_2 and H_2O content less than 1 particle-per-million.

The capacitor and transistor measurements were performed with Agilent B1500A semiconductor device analyzer under ambient environmental conditions. The dielectric capacitance of MIM structures was measured between 1 kHz and 1 MHz. The MIM current density was measured between −3 and 3 V. In addition, the current–voltage measurement was extended to higher values to measure the dielectric breakdown voltage. We define the breakdown voltage as voltage at which the current through the MIM structure is 1 mA/cm^2. The transfer and output characteristics of the OTFTs were measured in a sweep mode. Transistor hysteresis was obtained by stepping the gate voltage from positive to negative values and back. Multiple MIM structures and transistors were measured for each C_8PA desorption time. Mean values and standard deviations were calculated for all parameters.

The surface topography of the gate dielectric and pentacene was studied by atomic force microscopy (AFM) using the tapping mode. The scanned images were of 1×1 μm^2 area. Water contact angle measurements of AlO_x and AlO_x/C_8PA surfaces were performed in ambient air with Krüss DSA30B goniometer.

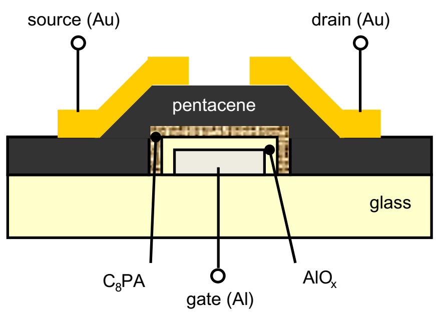

Fig. 1. OTFT cross-section.