Thin Solid Films 649 (2018) 7–11

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Towards understanding the origin of the hysteresis effects and threshold voltage shift in organic field-effect transistors based on the electrochemically grown AlO_x dielectric

Lidiya I. Leshanskaya[a], Nadezhda N. Dremova[a], Sergey Yu. Luchkin[b], Ivan S. Zhidkov[c], Seif O. Cholakh[c], Ernst Z. Kurmaev[c,d], Keith J. Stevenson[b], Pavel A. Troshin[a,b,*]

[a] Institute for Problems of Chemical Physics of Russian Academy of Sciences, Semenov Prospect 1, Chernogolovka, Moscow region 142432, Russia
[b] Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Nobel St. 3, Moscow 143026, Russia
[c] Institute of Physics and Technology, Ural Federal University, Mira 19 Street, Yekaterinburg 620002, Russia
[d] M. N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, S. Kovalevskoi 18 Street, Yekaterinburg 620990, Russia

ARTICLE INFO

Keywords:
Organic field-effect transistor
Aluminum oxide
Dielectric, Hysteresis
Anodization

ABSTRACT

We show that the electrochemically grown aluminum oxide dielectric films always comprise some redox-active molecular species absorbed from the electrolyte. This contamination affects dramatically electrical performance of organic field-effect transistors (OFETs), particularly leading to the appearance of hysteresis in the current-voltage characteristics and positive shift of the threshold voltage. A strong suppression of the hysteresis was observed while reducing the concentration of the citric acid or replacing it with an alternative electrolyte based on the aminoacid (isoleucine) and its potassium salt.

1. Introduction

Poor long-term stability and reproducibility of organic field-effect transistors (OFETs) represents one of the serious obstacles for practical implementation of organic electronics [1]. In particular, an undesirable hysteresis frequently appears in the current-voltage characteristics of OFETs, affecting badly the electrical performance of single devices and logic circuits. Possible origins of such hysteresis have been intensively explored and discussed during the last decade [2–6]. The appearance of the hysteresis in OFETs can be induced by many different factors: charge trapping at the grain boundaries in the semiconductor films or at the semiconductor/dielectric interface, complicated electrochemical behavior of the materials, presence of mobile ions in the dielectric or even semiconductor layers and etc. [2–6]. Such diverse nature of the hysteresis effects in OFETs explains why there is no general and comprehensive understanding of this phenomenon elaborated by now in the field. Therefore, further research efforts are required in order to shed some light on the origins of the hysteresis and reveal possible routes for elimination of this parasitic effect in OFETs.

In this paper we address the origin of the hysteresis effects appearing in OFETs assembled using electrochemically grown aluminum oxide (AlO_x) dielectric. This material has a relatively high dielectric constant (~9) and can be easily grown on metallized plastic foils using a low-temperature well-controlled process [7]. Compatibility of AlO_x with the emerging flexible electronics technologies is one of the reasons why it is used so intensively in many research and industrial laboratories worldwide [8]. Generally, ultrathin aluminum oxide layer is passivated by applying a self-assembled monolayer (SAM) of a long-chain alkylphosphonic acid, thus forming a hybrid dielectric enabling low-voltage operation of OFETs [9]. Interface engineering between the dielectric and the organic semiconductor layers is the key issue in designing organic electronics devices.

2. Experimental details

2.1. Materials and instrumentation

Citric acid and isoleucine were purchased from Acros Organics and used as received. Tetradecylphosphonic acid was synthesized following the standard procedure [10].

NTEGRA PRIMA instrument (NT MDT, Russia) was used to obtain the AFM images. SEM images were obtained using Zeiss LEO SUPRA 25 instrument. Energy-dispersive X-ray spectroscopy (EDXS) analysis was carried out using Oxford Instruments Inco Energy unit integrated with the Zeiss SUPRA 25 microscope.

XPS spectra were measured by PHI XPS Versaprobe 5000

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[*] Corresponding author at: Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Nobel St. 3, Moscow 143026, Russia
E-mail address: p.troshin@skoltech.ru (P.A. Troshin).

https://doi.org/10.1016/j.tsf.2018.01.014
Received 3 May 2017; Received in revised form 28 December 2017; Accepted 9 January 2018

spectrometer with energy resolution of 0.5 eV.

Scanning Kelvin Probe Microscopy (SKPM) measurements were performed in the standard 2-pass amplitude modulation mode using Cypher EX AFM (Asylum Research, CA) under inert Ar atmosphere in a MBraun glovebox with $O_2 < 0.1$ ppm and $H_2O < 1$ ppm. Si cantilever with conductive W_2C front coating, about 70 kHz first resonance frequency, and about 3 N/m spring constant was used. The sample was grounded by conductive silver paint.

2.2. AlO_x anodization procedure

The gate electrodes were immersed in the appropriate electrolyte solution (see Table 2 in the Section 3.1) and anodized first in the amperostatic regime for 2 min at 100 μA and then in the potentiostatic regime at 10 V for 4 min. The current dropped below 1 μA at the end of the potentiostatic step. We were forced to use lower anodization potential of 6 V in the case of **CA3** electrolyte since performing the process at 10 V resulted in a severe degradation of the anode presumably due to reduced electrical conductivity of the electrolyte. Afterwards, the gate electrodes with the electrochemically grown AlO_x coatings were rinsed thoroughly with deionized water and dried at 60 °C for 20 min.

2.3. Fabrication and characterization of OFETs

Before depositing semiconductor AlO_x was passivated by self-assembled monolayer (SAM) of n-tetradecylphosphonic acid (TDPA) following the standard approach [11]. The semiconductor layer (100 nm) was grown by thermal evaporation of C_{60} fullerene in vacuum ($\sim 10^{-6}$ mbar). Finally, silver source and drain electrodes (80 nm) were deposited through a shadow mask, thus completing the OFET structure following the procedure provided in [12]. The device channel length (L) was 50 μm and the width was 2 mm.

Transistor characterization was carried out inside a nitrogen glove box with < 1 ppm O_2 and < 1 ppm H_2O. The transfer and output characteristics were recorded using Keithley 2612A instrument with LabTracer software. The charge carrier mobilities of organic field-effect transistors were calculated from transfer characteristics in a saturation regime according to a standard method [13].

2.4. Measuring the dielectric capacitance

The capacitances of the dielectrics were measured at 1–100 kHz frequency for the conventional MIM devices. The values obtained for the hybrid dielectric AlO_x/TDPA are listed in Table 1 as a function of the AlO_x growing conditions.

3. Results and discussion

3.1. Hysteresis in OFET characteristics depending on electrolyte composition

The OFET architecture used in this work is shown schematically in Fig. 1. Briefly, aluminum gate electrodes were prepared by thermal evaporation of metal on the soda lime glass substrates. Thin and compact dielectric layer of AlO_x (13 nm) was grown by anodic oxidation of aluminum first in a galvanostatic and then in a potentiostatic regime (10 V if not stated different). Details on the OFET fabrication and characterization are given in Section 2.2 below.

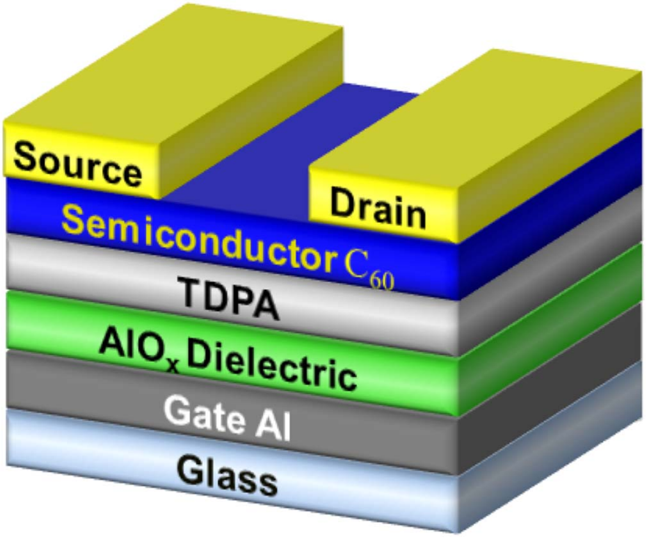

Fig. 1. A schematic layout of the bottom-gate top-contact OFET structure used in this work. TPDA represents a self-assembled monolayer of the tetradecylphosphonic acid.

Generally, the anodic oxidation of metals provides the cheapest and the highest quality oxide coatings compared to other techniques such as sol-gel deposition, sputtering or electron beam deposition [7]. However, the structure and performance of the resulting oxide film is strongly affected by the chemical nature and properties of the electrolyte. It is known from the literature that the perfectly dense non-porous aluminum oxide coatings (so-called barrier type oxide films) can be produced using almost neutral electrolyte solutions based on e.g., boric acid/sodium borate system with pH ~ 5.7 or some organic acids (e.g., citric, maleic or glycolic acids), which do not dissolve the resulting oxide [14]. Notably, citric acid or its combination with sodium citrate were extensively employed for production of AlO_x dielectric films used in OFETs, while other electrolyte formulations were neglected, presumably, due to historical reasons [7,11,15].

In this work we explored several electrolyte systems presented in Table 2.

While comparing the AlO_x dielectric films grown using different electrolyte solutions, we deposited TDPA self-assembled monolayer, semiconductor layer and top electrodes under exactly the same conditions (samples to be compared were processed in the same batch). The fabricated OFETs revealed rather diverse hysteresis in their current-voltage characteristics, which was strongly dependent on the used electrolyte composition. It should be emphasized that very strong differences in the electrical characteristics of the devices (as shown in Fig. 2) were observed regardless intense rinsing of the freshly prepared AlO_x films with the deionized water followed by the deposition of the TDPA passivation layer.

Visual examination of the transfer characteristics of the OFETs presented in Fig. 2 shows clearly that the concentrated solutions of citric acid (**CA1**) are not suitable for fabrication of high-quality OFETs due to strongly induced hysteresis. Surprisingly, this or similar

Table 1
Experimental values of the specific capacitances of the dielectrics grown under different conditions.

Electrolyte used for AlO_x growing	Anodization potential, V	Specific capacitance, nF/cm^2
CA1	10	370
CA2	10	365
CA3	6	440
Ile/K-Ile	10	238

Table 2
Composition of the electrolytes investigated in this work.

Electrolyte abbreviation	Composition
CA1	5000 mg of citric acid in 100 mL of H_2O
CA2	10 mg of citric acid in 100 mL of H_2O
CA3	3.2 mg of citric acid in 100 mL of H_2O
Ile/K-Ile	800 mg of isoleucine and 80 mg of isoleucine potassium salt in 100 mL of H_2O