Organic Electronics 14 (2013) 3070–3082

Contents lists available at ScienceDirect

Organic Electronics

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

High performance p-type organic thin film transistors with an intrinsically photopatternable, ultrathin polymer dielectric layer [☆]

Andreas Petritz [a,*], Archim Wolfberger [b], Alexander Fian [a], Joachim R. Krenn [c], Thomas Griesser [b], Barbara Stadlober [a]

[a] Materials-Institute for Surface Technologies and Photonics, Franz-Pichler Straße 30, Weiz A-8160, Austria
[b] Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, Leoben A-8700, Austria
[c] Institute of Physics, Universitätsplatz 5, Graz A-8010, Austria

ARTICLE INFO

Article history:
Received 12 April 2013
Received in revised form 8 July 2013
Accepted 12 July 2013
Available online 31 July 2013

Keywords:
Dielectrics
Thin films
Organic field effect transistor
Organic electronics
Photochemistry

ABSTRACT

A high-performing bottom-gate top-contact pentacene-based oTFT technology with an ultrathin (25–48 nm) and electrically dense photopatternable polymeric gate dielectric layer is reported. The photosensitive polymer poly((±)endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, diphenylester) (PNDPE) is patterned directly by UV-exposure ($\lambda = 254$ nm) at a dose typical for conventionally used negative photoresists without the need for any additional photoinitiator. The polymer itself undergoes a photo-Fries rearrangement reaction under UV illumination, which is accompanied by a selective cross-linking of the macromolecules, leading to a change in solubility in organic solvents. This crosslinking reaction and the negative photoresist behavior are investigated by means of sol–gel analysis. The resulting transistors show a field-effect mobility up to 0.8 $cm^2\,V^{-1}\,s^{-1}$ at an operation voltage as low as -4.5 V. The ultra-low subthreshold swing in the order of 0.1 V dec^{-1} as well as the completely hysteresis-free transistor characteristics are indicating a very low interface trap density. It can be shown that the device performance is completely stable upon UV-irradiation and development according to a very robust chemical rearrangement. The excellent interface properties, the high stability and the small thickness make the PNDPE gate dielectric a promising candidate for fast organic electronic circuits.

1. Introduction

The direct integration of disposable organic electronics could make everyday things "smarter", thus opening a wide field of novel applications such as flexible RFID tags [1], electronic paper [2], intelligent textiles [3] or bioelectronics [4]. In the context of ambient intelligence, the simplicity of processing is one of the key issues for true low-cost fabrication of organic circuits [5]. Only then the compatibility with a variety of substrate materials like plastics foils, textiles or even paper is ensured. Usage of an intrinsic photopatternable gate dielectric in organic thin film transistors (oTFT) – one of the basic elements for any organic logic circuit-clearly simplifies the fabrication of via holes and therefore the design of circuits. However, the electronic performance of the oTFTs has to fulfill the requirements of practical life. One important issue here is the achievement of a low oTFT supply voltage so that the organic electronic circuit can be powered by household batteries [6].

[☆] This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

[*] Corresponding author. Tel.: +43 316 876 3105; fax: +43 316 876 3010.
E-mail address: andreas.petritz@joanneum.at (A. Petritz).

http://dx.doi.org/10.1016/j.orgel.2013.07.014

The charge separation and, accordingly, the charge carrier density in the source–drain channel of an oTFT (Fig. 1a) are induced by the vertical electric field that is established between the gate-electrode and the semiconductor layer and drops over the gate dielectric. High charge carrier densities at low gate voltage and thus full transistor operation can be achieved only for high capacitive dielectrics with low leakage currents. In previous works, different approaches for high capacitive gate dielectrics were reported: one is the usage of ultra-thin close packed organic layers with a thickness of only a few nanometers, built up by self-assembling monolayers (SAMs) [6] or polyelectrolytes [7].

In a second approach high-k-dielectrics like titanium oxide (TiO_2), hafnia (HfO_2), tantalum oxide (Ta_2O_3), alumina (Al_2O_3) or zirconia (ZrO_2) fabricated by atomic layer deposition [8] and in a third approach also oxide/polymer bilayers and nanocomposites were utilized [9]. The applicability of ultrathin high-k polymer dielectric layers for low voltage organic thin film transistors (but without photostructuring) was shown in [10,11].

Since these approaches require complex photopatterning processes of the gate dielectric layer, which is essential to establish the electrical interconnection in electronic circuits, photoresists such as SU-8 were proposed as an alternative [12]. However, polymeric dielectric materials which contain photo-polymerizable units such as epoxy groups in SU-8 require photoinitiators for the light-induced curing. These photosensitive molecules lead to the formation of either reactive radicals or acidic groups initiating the polymerization and thus the crosslinking upon UV irradiation. In particular, residual ionic photoinitiators such as Crivello salts and also their cleavage products in the gate dielectric may cause hysteresis effects. It is well known that mobile ionic impurities can be responsible for the hysteresis in oTFTs and also decrease the long term stability of such devices [13]. Very often also an immediate deterioration of the oTFT characteristics was observed in photoinitiator containing polymer dielectrics that was caused by the UV-illumination step [14]. For the remaining reported photoinitiator-free UV-patternable dielectrics complex multistep cross-linking and curing processes of polymer blends had to be used to achieve thin and electrically dense gate dielectrics [15].

In this work, we explore the use of poly((±)endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, diphenylester) (PNDPE) as a directly photopatternable dielectric material for low voltage pentacene based oTFTs. This polymer bears aromatic ester groups which are capable of undergoing the photo-Fries rearrangement upon irradiation with UV-light.

The photo-Fries rearrangement, as first observed by Anderson and Reese [16] leads to a photolytic cleavage of the aryl ester moieties to acyl- and phenoxy radicals. The generated radicals can then recombine and form the corresponding ortho- and para-hydroxyketones. A schematic

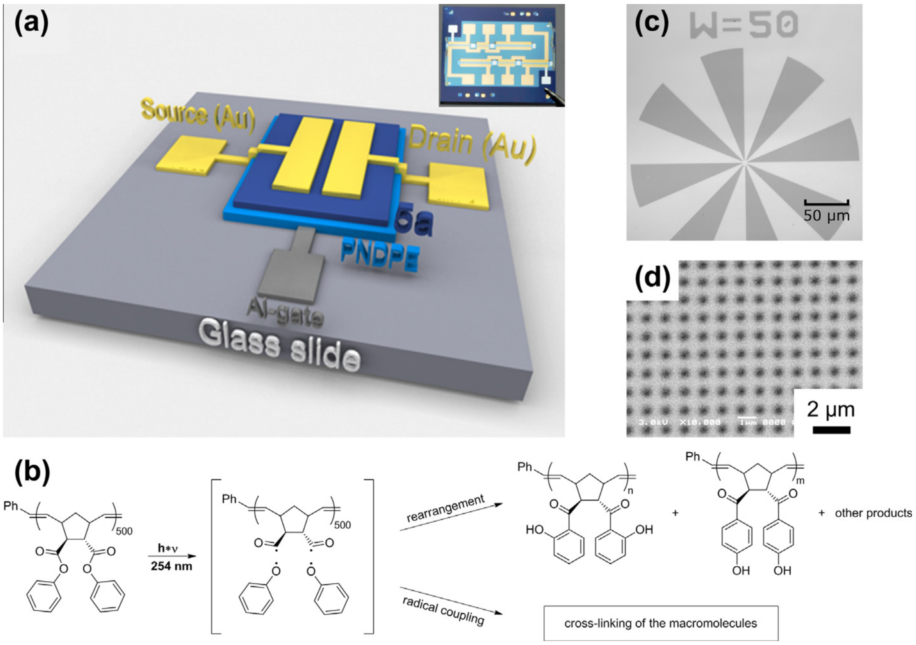

Fig. 1. (a) Schematic structure of the fabricated oTFTs, showing the glass substrate (light grey), aluminium gate electrode (dark grey), PNDPE dielectric (light blue), pentacene layer (dark blue) and Au source- and drain electrodes (yellow). The inset in Fig. 1a shows 6 oTFT's with a PNDPE layer photopatterned through a shadow mask in order to open the gate contact pad. A SiO_2 wafer is used here as a substrate for a clearer illustration of the patterned dielectric layer. (b) Schematic mechanism of photochemical reactions upon UV irradiation within PNPDE. Upon irradiation with UV light, photolysis leads to the cleavage of the aromatic ester in the polymer side chain, resulting in the formation of polymeric acyl radicals and phenoxy radicals. Recombination of these two radicals leads to the corresponding photo-Fries product, i.e. ortho-hydroxyketone (photo Fries rearrangement), whereas the radical coupling reaction of two polymeric acyl radicals results in crosslinking. (c) A micrograph of a photopatterned PNDPE polymer. The pattering is done under ambient condition and an exposure dose of 1.56 J cm^{-2} is used. (d) A scanning electron microscopy (SEM) image of a PNDPE dot array pattern structured by means of e-beam lithography. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)