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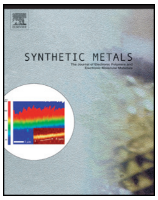

Temperature and layer thickness dependent *in situ* investigations on epindolidione organic thin-film transistors

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ABSTRACT

We report on *in situ* performance evaluations as a function of layer thickness and substrate temperature for bottom-gate, bottom-gold contact epindolidione organic thin-film transistors on various gate dielectrics. Experiments were carried out under ultra-high vacuum conditions, enabling quasi-simultaneous electrical and surface analysis. Auger electron spectroscopy and thermal desorption spectroscopy (TDS) were applied to characterize the quality of the substrate surface and the thermal stability of the organic films. *Ex situ* atomic force microscopy (AFM) was used to gain additional information on the layer formation and surface morphology of the hydrogen-bonded organic pigment. The examined gate dielectrics included SiO_2, in its untreated and sputtered forms, as well as the spin-coated organic capping layers poly(vinyl-cinnamate) (PVCi) and poly(($\pm$)*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, diphenylester) (PNDPE, from the class of polynorbornenes). TDS and AFM revealed Volmer-Weber island growth dominated film formation with no evidence of a subjacent wetting layer. This growth mode is responsible for the comparably high coverage required for transistor behavior at 90–95% of a monolayer composed of standing molecules. Surface sputtering and an increased sample temperature during epindolidione deposition augmented the surface diffusion of adsorbing molecules and therefore led to a lower number of better-ordered islands. Consequently, while the onset of charge transport was delayed, higher saturation mobility was obtained. The highest, bottom-contact configuration, mobilities of approximately $2.5 \times 10^{-3}\,cm^2/Vs$ were found for high coverages (50 nm) on sputtered samples. The coverage dependence of the mobility showed very different characteristics for the different gate dielectrics, while the change of the threshold voltage with coverage was approximately the same for all systems. An apparent decrease of the mobility with increasing coverage on the less polar PNDPE was attributed to a change in molecular orientation from upright standing in the thin-film phase to tilted in the bulk phase. From temperature-dependent mobility measurements we calculated activation barriers for the charge transport between 110 meV and 160 meV, depending on the dielectric configuration.

1. Introduction

The successful integration of organic materials into established inorganic semiconductor systems and technologies has proven to be one of the largest driving forces in research and development for the last decade [1]. The field of organic electronics remains highly relevant for the future of our electronic world, as it offers the possibility to utilize highly advantageous organic material properties for present-day and prospective applications. Characteristics, such as biodegradability and biocompatibility [2,3], low material cost and weight, room temperature deposition, and patterning for flexible substrates, as well as economical large area fabrication techniques, can all be found in these materials [4,5]. The known disadvantages when it comes to attainable performance, air and water stability, and utilization on an industrial scale, still have to be addressed and solved. As one of the most basic building blocks of organic electronic devices, switches in the form of organic thin-film transistors (OTFT) [6,7] are one of the pillars for technological success. Closely tied to the transistor

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performance, the growth, structure, and charge transport properties of the organic semiconducting layers have to be identified and controlled to suit the respective applications [8,9].

Following the pioneering success by Głowacki et al. [3,10–12], the organic pigment epindolidione ($C_{16}H_{10}N_2O_2$) (see inset in Fig. 1), a hydrogen-bonded analogue of the well-studied tetracene, has emerged as one of the most interesting candidates for the active layer in OTFTs [13,14]. As a structural isomer, the yellow to orange colored epindolidione is closely related to the industrially mass produced indigo, a blue organic dye with which it shares many advantageous properties. Epindolidione based OTFTs have shown excellent application potential, featuring very promising charge carrier mobility values of up to $1.5\,\mathrm{cm^2/Vs}$ for p-type conduction [10], electrode material and derivatization induced n-type behavior, high air, water and temperature stability, excellent biocompatibility, and stable operation in ionic solutions in a pH range of 3–10 [12].

We applied a specialized experimental setup [15,16] which enabled us to manufacture and then characterize both electrical and surface properties of epindolidione OTFTs *in situ* under ultra-high vacuum conditions. While inferior in terms of charge carrier injection and therefore maximum attainable mobility [7,17], the employed bottom-gate geometry allowed us to gain more insight into the correlation between semiconducting and growth properties. An investigation of the layer growth and transistor behavior of epindolidione as a function of the employed gate dielectric material, its surface treatment, i.e. sputtering, and of the sample temperature over a wide temperature range was performed. The *in situ* experiments were complimented by *ex situ* AFM measurements.

2. Experimental

2.1. Film preparation and surface characterization

The conducted experimental work is based on the characterization of 1 cm × 1 cm model OTFT devices *in situ* under a base pressure of approximately 2×10^{-8} mbar. In order to create these samples, highly p-doped silicon wafer pieces with a 150 nm thick dry-oxide layer were plasma etched for cleaning, before 60 nm thick gold contacts were deposited through a shadow mask. This yielded SiO_2 bottom-gate, gold bottom-contact transistor samples with a 4 mm wide (W) and 25 μm long (L) channel structure, which were then contacted *ex situ* and installed into the sample holder. The physical vapor deposition (PVD) of epindolidione from a Knudsen cell was performed through a 4.5 mm × 2.5 mm aluminium foil shadow mask in order to limit the deposition to the active channel area. The sublimation purified epindolidione material was synthesised following the procedure by Jaffe and Matrick [18] and considerations by Kemp et al. [19]. The high thermal stability and poor solubility of H-bonded organic semiconductors, attributed to the strong intermolecular interactions based on H-bonds and π–π stacking, limit the application of solution processed deposition and makes vacuum deposition the most applicable method [20–22].

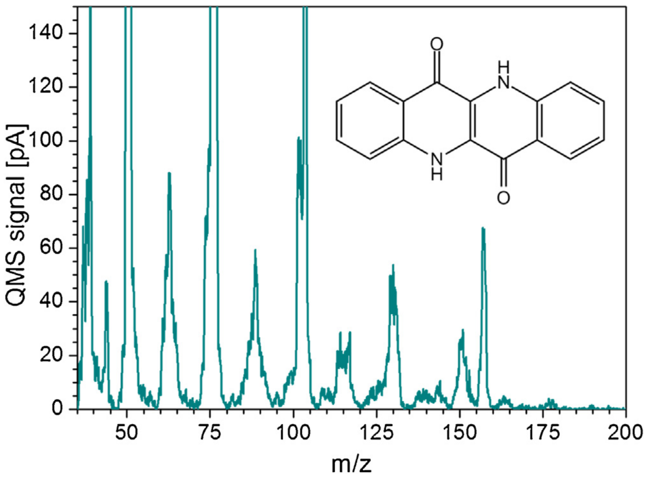

Fig. 1. Cracking pattern of epindolidione in our quadrupole mass spectrometer. In the inset, the molecular structure of epindolidione is shown.

One of the most important features of the experimental setup is the aforementioned capability to accurately control the sample temperature during semiconductor deposition and electrical evaluation. This can be done in-between a lower limit, set by the LN_2 cooling at about 120 K, and an upper limit of over 800 K, far exceeding the semiconductor desorption temperature. The wide temperature range attainable permits thermal desorption spectroscopy (TDS) and a subsequent re-deposition of new epindolidione layers for reproducibility evaluations. Argon ion sputtering has been used for sample surface cleaning and Auger electron spectroscopy (AES) allows analysis of the sample surface in-between cleaning and semiconductor deposition steps. A more in-depth description of the experimental setup, deposition system and sample mounting can be found in our previous work [15].

The parameters for the quartz microbalance controlled Knudsen cell deposition could not be found in literature and were approximated. A density of $\rho \approx 1.5\,\mathrm{g/cm^3}$ and long molecular axis length of 1.26 nm for epindolidione were assumed. These estimations could subsequently be verified by X-ray diffraction (XRD) and *ex situ* atomic force microscopy (AFM) investigations. On the quartz microbalance, which is covered by thick layers of epindolidione, a sticking probability of one can be assumed for impinging epindolidione molecules, resulting in a correlation of quartz resonance frequency change and nominal epindolidione layer thickness d of $1\,\mathrm{Hz} \approx 0.083\,\mathrm{nm}$. To attain sufficient precision for the deposition of thin layers a comparably low deposition rate of approximately 0.1 ML/min was employed throughout all experiments.

2.2. Dielectrics and electrical characterization

For organic electronic systems the choice of the gate dielectric is crucial for the attainable OTFT performance [11]. In particular, at the highly critical dielectric – semiconductor interface, the dielectric material fundamentally influences the electrical properties as well as the layer growth and molecular orientation, and thereby the intermolecular π–π stacking necessary for charge transport between molecules [23–26]. Głowacki et al. employed tetratetracontane (TTC)-capped AlO_x layers as the gate dielectric and reported the non-polarity and/or aliphatic nature of the dielectric to be vital in achieving optimal device performance [10–12]. In order to translate our expertise on coverage dependent *in situ* evaluations for pentacene [15,16] to H-bonded semiconductor systems and to gain more information on epindolidione performance on polar dielectrics we used SiO_2 in its untreated and sputtered form, which had previously been investigated for the related quinacridone molecules [27,28].

Additionally, we modified the SiO_2 surface with spin coated, more hydrophobic capping layers in the form of the, compared to SiO_2 less polar, organic dielectrics poly(vinyl-cinnamate) (PVCi) and poly((±)*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, diphenylester) (PNDPE, from the class of poly norbornenes) [29–31]. Subsequently, the gold source and drain contacts were deposited. The spin coated layer thicknesses were approximately 35 nm for PVCi and 15 nm for PNDPE, with relative permittivities ε_r of roughly 4.2 and 2.5, respectively, as obtained from capacitor structure measurements.