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Doping of TIPS-pentacene via Focused Ion Beam (FIB) exposure

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ABSTRACT

We report on the influence of Focused Ion Beam (FIB) exposure on TIPS-pentacene layers which are often used in solution-processable organic field-effect transistors (OFETs) and in many cases yield a field-effect mobility in the order of 1 $cm^2/V\,s$. We exposed TIPS-pentacene layers to a Ga^+ ion beam and measured the device characteristics of OFETs. We observed a strong influence of the FIB on *J–V* characteristics of TIPS-pentacene-based devices and determined an increase in the OFET mobility and on–off ratio and a decrease of the threshold voltage. To further investigate the underlying process we analyzed FIB-exposed and unexposed TIPS-pentacene samples via X-ray Photoelectron Spectroscopy (XPS). Exposed samples show a clear Ga XPS signature and the C1s peak shifts about 400 meV towards smaller binding energies which is an indicator for a Fermi energy shift closer to the valence states and hence p-doping of TIPS-pentacene. With Scanning Kelvin Probe Microscopy (SKPM) we could clearly distinguish FIB exposed areas from the unexposed areas. For exposed areas the work function increases about 200 meV which is consistent with XPS measurements and again displays that the implanted Ga^+ ions serve as p-dopants. Furthermore we took SKPM measurements on operating OFETs and could investigate a dramatic change in local conductance on FIB exposed areas. This demonstrates a novel way of nanopatterning conductive paths in organic semiconductors.

1. Introduction

Tuning the charge transport properties of electronic materials is one of the most important challenges in semiconductor technology. Doping of semiconductors circumvents problems generally associated with low intrinsic conductivity and inefficient charge injection [1]. Yet, there has been reported on various doping techniques in inorganic as well as in organic materials to manipulate charge carrier concentration and mobility. A common technique for doping of organic semiconductors is coevaporation of the organic host material with either organic molecules or inorganic species [1,2]. For inorganic materials, ion implantation via Focused Ion Beam (FIB) has been demonstrated to be a useful doping technique and has been successfully applied to various semiconductor systems such as GaAs [3] and doping of Ge nanowires [4]. Here we apply ion implantation with a Ga^+ FIB to organic thin films. We use 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) [5] to demonstrate ion implantation as it is widely employed for organic FETs. TIPS-pentacene or similar substituted pentacene derivatives regularly show mobilities in the range of 1 $cm^2/V\,s$ or above and thus is an often used material system. Another major advantage is the processability from solution which makes them a promising candidate for printing applications [6]. Therefore controlled manipulation of the charge transport characteristics is strongly required. Recently a method to n-dope TIPS-pentacene from solution has been demonstrated [7]. Here we will present local p-doping of TIPS-pentacene

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which might play an auspicious role in micropatterned electronics.

2. Experimental

To investigate the properties of FIB-induced doping, we used TIPS-pentacene field effect transistors in a bottom gate, bottom contact device architecture. Heavily n-doped silicon wafers with 200 nm of thermally grown SiO_2 served as a substrate and constitute the gate contact and gate dielectric of our TFTs. The drain-source pattern was defined by photolithography and deposited by thermal evaporation of 10 nm aluminum (adhesive layer) and 60 nm gold. The channel length and width was 4 μm and 160 μm, respectively. Such small structures had to be chosen to allow for further treatment with the FIB which is designed for sample manipulation in the nanometer and micrometer range. For the experiments which are summarized in Figs. 1 and 3–5. TIPS-pentacene was drop-casted from solution in toluene onto the electrode structure as this preparation method has been demonstrated before to enable a good performance with a mobility up to 0.2 $cm^2/V\,s$ [8]. Note that we did not treat the substrates with a self assembled monolayer (SAM) like octadecyltrichlorosilane (OTS) or hexamethyldisilazane (HMDS) to have a as simple and controllable system as possible. Therefore we gained lower field effect mobilities of about 10^{-4} $cm^2/V\,s$ which is consistent with the results of Anthony et al. [9]. For the conductance measurement in Fig. 2 the TIPS-pentacene was spin-coated to have better thickness and uniformity control. In these devices the layer thickness has been determined to be about 100 nm by FIB milling of the layer and afterwards SEM characterization of the milled edge.

Furthermore we used a Carl Zeiss AURIGA cross beam microscope to expose well defined areas in the OFET channels with the FIB. We operated the FIB at an acceleration voltage of 30 kV and adjusted the beam characteristics well outside the to be exposed sample area, to prevent from uncontrolled exposure before the actual experiment. To regulate the ion dose we varied the FIB current (emitted ions per time) and the exposure time.

To observe the influence of FIB on transistor characteristics one transistor was exposed several times and transistor characteristics were recorded in situ in the microscope after every exposure step. The field effect mobility has been derived from the slope of the OFET transfer curve at a source-drain voltage of 20 V. Threshold voltage and on–off-ratio have been extracted from the transfer curve as well.

The conductance measurements shown in Fig. 2 were performed on transistor structures without contacting the gate such that two terminal devices were created and the resistances were derived from the linear parts of the *IV* curves.

The photoemission spectra were taken in a PHI VersaProbe 5000 multitechnique analysis system equipped with a monochromated Al-Kα X-ray source and a hemispherical photoelectron analyzer. The energy scale of the spectrometers was calibrated to the Fermi energy position of a clean silver foil. Using a pass energy of 11 eV the energetic resolution of the system is about 350 meV at the Fermi edge.

We used a BRR-upgrade (from the company DME) of the Zeiss crossbeam workstation to perform atomic force microscopy (AFM) and scanning Kelvin probe microscopy (SKPM). In this combined system FIB exposure as well as SEM imaging and scanning probe microscopy (SPM) measurements can be performed simultaneously so that in-situ preparation and characterization without breaking the vacuum is possible. SKPM is a scanning probe technique which maps the contact potential difference (CPD) between the tip of the microscope and the sample surface [10]. The measured CPD is a superposition of the difference of the local surface work function [11] and the applied voltage. SKPM is a powerful tool to analyze charge transport as it has a spatial resolution down to 20 nm and an electrical resolution down to 10 mV [12].

3. Results and discussion

3.1. Doping of TIPS-pentacene transistors

We first observed the doping effect of FIB exposure when milling OFETs to study buried interfaces with SKPM.

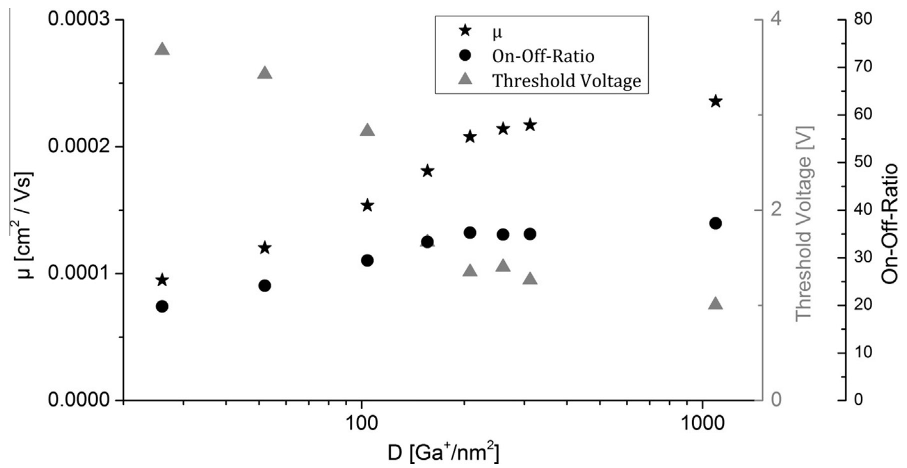

Fig. 1. Mobility, threshold voltage and on–off-ratio of a TIPS-pentacene OFET depending on the Ga^+ dose. The dose is given in Ga^+ ions per square nanometer.