Fully printed, flexible, large Area Organic Optothermal Sensors for Human-Machine-Interfaces

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Abstract

Pyroelectric sensors presented in this work are based on polymers from the PVDF family which are comprised of a piezo- and/or pyroelectric polymer thin film capacitor integrated with either high performance organic thin film transistors (OTFTs) or electrochemical transistors (ECTs) acting as impedance converters, signal amplifiers and conditioners. For flexible integration with diverse electronic devices, large area processes such as screen printing applicable for industrial partners have been used for the fabrication of the sensors and ECT’s. With respect to the intended purpose for detection of human body radiation the absorbance of the impinging IR-light is dramatically increased by the application of printed carbon/Pedot to p-electrodes, hence meeting the requirements for low-cost large area processibility. Here we present good working integrated sensor devices based on two components, being an organic thin film transistor with a high-k-nanocomposite gate dielectric or a fully printed electrochemical transistor and a PVDF-copolymer based sensor.

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1. Introduction

The interest in the application of polymer ferroelectric thin films has continuously grown during the last decade, especially in terms of fabrication of non-volatile memory cells [1], high-performance organic thin film transistors [2], detectors for infrared radiation and temperature [3], and sensors for pressure and motion, pointing towards full organic actuators and artificial skin [4]. In the field of thermal imaging and pressure sensing, that usually is based on high-impedance capacitive sensor elements, a suitable read-out electronics for data representation and processing is highly recommended associated especially whit electronic skin and actuator applications.

Skin-like sensitivity, including the recognition and processing of touch and temperature is one of the essential features of future generations of robots. Requirements for electronic skin are high flexibility on large area, high

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pressure and temperature sensitivity and their realization on a three-dimensional surface. It has been shown recently, that conformable, flexible, large-area networks of thermal and pressure sensors based on organic semiconductors and a net-shaped structure of organic transistor-based electronic circuits can simultaneously detect various distributions of pressure and temperature [5].

In order to significantly facilitate the fabrication, to increase stability and improve reproducibility a direct integration of sensor elements and organic thin film transistor-based electronics on one flexible substrate would be highly recommendable. Further on, if the sensing material itself were temperature and pressure sensitive, which is the case for pyro- and piezoelectric PVDF-based polymers [6], the number of different elements could be dramatically reduced thus enabling a simultaneous detection of changes and modulations in temperature and pressure which is interesting for a large number of applications in robotics and human detection. In order to enable better discrimination between pyro- and piezoelectric response it could also be beneficial to use a sensor material with intrinsically decreased cross-sensitivity [7].

In this context we have developed an integrated, printed pyro- and piezoelectric sensor element on the basis of a PVDF-TrFE copolymer capacitor that is either combined with a high-performance low-voltage organic thin film transistor based on pentacene or a printed electrochemical transistor. This is the first application of OTFTs or ECTs in a pyroelectric polymer sensor operating as an opto-thermal light detector. We demonstrate that bottom gate OTFTs based on the organic semiconductor pentacene and high-k nanocomposite gate dielectrics directly integrated on the polymer sensor layer exhibit transistor performances with very low gate leakage currents, subthreshold swings close to the theoretical limit and low-voltage operation. Furthermore the direct integration of printed sensors and printed electrochemical transistors on flexible substrates has been realized.

2. Experimental

In the following the transistor, the temperature sensitive fluorinated polymer, their combination to an integrated circuit (Fig 1) and the application of this circuit as a thermal infrared sensor and as a switch that can be operated e.g. by a laser pointer is described. The circuit is composed of a capacitive sensor element with one electrode serving as the gate electrode of the transistor. The voltage output of the sensor controls the transistor.

2.1. P(VDF-TrFE) Sensors

P(VDF-TrFE) copolymers have become very attractive as functional materials for high-tech applications due to a number of excellent inherent physical properties. Apart from the usage as high-k gate dielectrics in logic gates based on miniaturized organic thin film transistors, a remnant polarization charge of more than 100 nC/m² qualifies these copolymers as charge storage dielectrics in non-volatile memory elements [1], and high piezo- and pyroelectric coefficients (up to 40 μC/Km²) [8] make them attractive for sensor- and transducer based organic devices. However, no efforts have been undertaken until now to integrate P(VDF-TrFE) based pyroelectric sensors and OTFTs/ECTs, thus comprising a flexible, integrated organic sensor device.
For realizing such a sensor device, varying sensor stripes have been fabricated in a first step. These sensors were based on different solutions, electrodes and substrates and been extensively evaluated with respect to their electric properties. The PVDF-TrFE copolymer pellets with a composition of 70mol% PVDF and 30mol% TrFE purchased by Solvay Solexis turned out to be the most suitable precursor for our requirements. The standard Sol-Gel process used for the fabrication of solution based PVDF-TrFE layers for IR-sensors is published elsewhere [9]. The obtained solutions are suitable for spin-coating, bar-coating and screen printing. The fabrication of the sensor element starts with screen printing of PEDOT SV3 (HC Starck) bottom electrodes. In the second step the PVDF-TrFE solution is screen printed resulting in homogeneous films with a standard thickness of 5 μm. Finally top electrodes are screen printed using either PEDOT SV3 or Carbon paste 7102 (DuPont).

2.2. Transistors

As mentioned before, two different types of transistors have been used. OTFTs have been fabricated by lab-scale methods and ECTs have been fabricated by large area printing techniques. Both fabrication routines are described below.

2.2.1. OTFTs

The gate electrode is formed by thermal evaporation of 50 nm Al through shadow masks on a flexible substrate or directly onto the (PVDF-TrFE) layer of the sensor. A 50-65 nm thick high-k metal oxide layer is fabricated by reactive oxygen sputtering of Zr under high vacuum conditions thus forming club-shaped ZrO₂ grains [10],[11]. Afterwards a thin layer of PVCi (poly-vinyl-cinnamate) is spin-coated on the metal oxide layer to form a dense metal oxide polymer nano-composite. On the nanocomposite gate dielectric a 50 nm thick pentacene layer is thermally evaporated via a shadow mask at a rate of 0.1 nm min⁻¹. The devices are finalized by e-beam evaporation of gold source and drain electrodes on top of the semiconductor.

2.2.2. ECTs

The ECTs shown in Fig 1 are having a lateral design as described elsewhere [12]. The carbon electrodes are screen printed (black) in the first step followed by screen printing of the PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)) channel (blue) and the isolating lacquer (brown). In the last step the electrolyte (yellow) is inkjet printed on top of the channel.

3. Results

The superior performance of pentacene transistors with high-k nanocomposite gate dielectrics is clearly indicated in the output and transfer characteristics shown in Fig 2(a). The output characteristics are virtually hysteresis free.

![Fig. 2. (a) Output and Transfer characteristics of an OTFT; (b) Output and Transfer characteristics of a screen printed, lateral ECT.](image-url)
Fig. 3. (a) Sensor output (left top) and drain current modulation (left bottom) of an integrated OTFT sensor during a long time measurement. The blue arrow indicates the gate voltage supplied by the sensor when being exited with a power of 70 mW at a wavelength of 808 nm; (b) Sensor output (left top) and drain current modulation (left bottom) of an integrated ECT. The sensor was excited at a wavelength of 808 nm and an intensity of 70 mW.

and Fig 2(a) demonstrates that the OTFT can be operated at gate voltages below 2 V. Moreover, the charge carrier mobility is reasonably high (0.2 cm²/Vs) and the swing is substantially smaller than 1 V/dec (0.75 V/dec). The gate leakage currents are around 10 nA/cm². The high performance of these devices is remarkable since the organic thin film transistors having an ultra-thin (70-85 nm) gate dielectric are directly integrated on the rather rough PVDF-TrFE layer (rms = 10 nm).

If these low-voltage OTFTs are directly integrated on the pyroelectric sensors for an amplified, low-impedance read-out one has to account for the equivalent circuit of the whole configuration. The modulated incident laser light generates charge waves at the sensor electrodes and thus the sensor acts as a modulated current source. Via its intrinsic (very high) impedance the sensor can be operated in the voltage mode at least for frequencies higher than the cut-off frequency $f_{\text{co}}$. With realistic parameters of the input stage of the transistor (gate resistance $R_G = 1 \, \Omega$ and gate capacitance $C_G = 5 \, \text{nF}$) and of the output stage of the sensor (sensor impedance $R_{\text{sens}} > 10 \, \Omega$ and sensor capacitance $C_{\text{sens}} \approx 0.5 - 5 \, \text{nF}$) the cut-off is calculated to be about $f_{\text{co}} \approx 0.01 \, \text{Hz}$. For $f > 0.01 \, \text{Hz}$ which is the interesting regime, the sensor is working in the voltage mode.

The performance of printed ECTs can be derived from its output and transfer characteristics shown in Fig 2(b). The working principle of these chemical transistors is described in [12]. The switching current of ECTs shown in the transfer characteristics in Fig 2(b) must be treated analogous to the leakage current of OTFTs with respect to the equivalent circuit of the integrated sensor device described in the next paragraph. Due to the equivalent circuit the effective sensor output voltage is determined by the overall impedance that is summed over all resistances connected in parallel. If only the sensor is characterized by a parametric analyser ($R_{\text{meas}} = 10 \, \text{G} \Omega$) the overall impedance $R_{\text{tot}}$ is given by $1/R_{\text{tot}} = 1/R_{\text{meas}} + 1/R_{\text{sens}}$ with $R_{\text{meas}}$ and $R_{\text{sens}}$ being in the same order of magnitude whereas the overall impedance is $1/R_{\text{tot}} = 1/R_G + 1/R_{\text{sens}} \approx 1/R_G$ is mainly determined by the gate resistance if the transistor is connected in parallel to the high resistive sensor.

In case of integration with a transistor the sensor’s output voltage is equivalent to a gate voltage biasing the transistor. In Fig 3 it can be seen how the modulated sensor voltage (Fig 3 top) translates into a modulated output current of the transistor (Fig 3 bottom). For the OTFT a complete switching could be realized because of the good impedance matching as described before. The integrated sensor device shows a very stable behavior in long time experiments as shown in Fig 3(a). The integration with ECTs shows a reasonable drain current modulation but the sensor signal is reduced because of the current consumption of the electrochemical switching process thus not enabling a complete switching of the transistor Fig 3(b). The switching currents can be reduced by decreased channel sizes which will be realized by ink-jet printing of the next generation of ECTs. Preliminary experiments revealed that the impedance matching between sensor and ECT can be optimized by this way and a complete switching of the ECT can be expected.
4. Conclusion

In conclusion we have shown that ferroelectric capacitive sensors combined with organic field effect transistors on flexible substrates are suitable for versatile sensor applications. By direct integration of an OFET/ECT with a fluoropolymer sensor element, a pyroelectric sensor response is obtained, thereby demonstrating that organic pyroelectric sensor elements with organic signal processing electronics can be achieved.

A wet – chemical production process for obtaining ferroelectric thin films based on polyvinylidene fluoride and its copolymer trifluoroethylene has been developed by means of a sol – gel method. The solutions show good properties regarding different kinds of coating/printing processes. The obtained layers show good remnant polarizations and sufficient properties regarding the thermally induced voltage and current responses.

Moreover we managed the reduction of the threshold voltage and the subthreshold swing of organic thin film transistors for low voltage operation. Due to the low leakage current of these ZrO₂ – PVCi nanocomposite gate dielectric OTFTs a suitable impedance matching between the read out transistor and the biasing polymer-sensor could be achieved. Direct integration of these devices on a flexible polymer PET substrate and onto the pyroelectric sensor layer was performed successfully appearing as a complete on-off switching of the transistor due to light stimulation of the sensor.

Furthermore a fully printed sensor device could be combined with a fully printed electrochemical transistor on flexible substrates. The light stimulation of the sensor results in a reasonable drain current modulation of the ECT. Due to the required switching currents of the ECT the impedance matching between the capacitive sensor and the transistor is not yet optimized and the transistor could not be totally switched off. The next generation of printed ECTs will be fabricated by ink-jet printing resulting in thinner channels and reduced current consumption during the switching process thus enabling a complete switching of the transistor by the sensor signal.

References