Organic Electronics 15 (2014) 3306–3315

Contents lists available at ScienceDirect

Organic Electronics

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

Inkjet printed micropump actuator based on piezoelectric polymers: Device performance and morphology studies

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A R T I C L E   I N F O

Article history:
Received 8 July 2014
Received in revised form 8 September 2014
Accepted 9 September 2014
Available online 18 September 2014

Keywords:
P(VDF–TrFE)
Printed electronics
Piezoelectric actuators
Inkjet printing
Micropump
Lab-on-a-chip systems

A B S T R A C T

All inkjet printed piezoelectric actuators based on poly(vinylidene fluoride-*co*-trifluoroethylene) (P(VDF–TrFE)) for applications as pump actuators in microfluidic lab-on-a-chip systems (LOC) are manufactured and investigated in terms of their morphology and actuator performance. Furthermore, a pump demonstrator with an all-printed P(VDF–TrFE) actuator is characterized here for the first time. The actuators are manufactured in a fully additive and flexible way by successive inkjet printing of a P(VDF–TrFE) film sandwiched between two silver electrodes on a polyethylene terephthalate (PET) substrate. Different from most current micropumps where actuator elements are fabricated separately, no additional joining step is required in the manufacturing approach employed here. Actuator performance is investigated by measurements of piezoelectric d_{31} coefficients as well as remanent polarization P_{rem} for different thermal treatments of the as-printed P(VDF–TrFE) films. A strong dependence of the device performance on the annealing temperature is found with maximum values for d_{31} and P_{rem} of approximately 10 pm V^{-1} and 5.8 $\mu C\,cm^{-2}$, respectively. Morphology investigations of the printed films by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Atomic Force Microscopy (AFM) indicate an increased degree of crystallinity of the piezoelectric β-phase for samples annealed at temperatures above 110 °C, which coincides with improved device performance. A basic pumping function with pump rates of up to 130 $\mu L\,min^{-1}$ is demonstrated, which is promising for future applications in LOC. Furthermore, the process chain and characterization presented here can be employed to design and manufacture also other P(VDF–TrFE)-based devices and allows the combination with additional printed on-chip functionalities in future LOC.

1. Introduction

The fields of organic and printed electronics have attracted increased research interest within the past 15 years due to their abilities of cost-effective manufacturing and material deposition on large areas. Digital printing technologies, like drop-on-demand inkjet, do not require any masking and can realize fully additive, non-contact processing [1–3]. Manufacturing is compatible with low-cost flexible polymer substrates and can be performed either sheet-based or, in particular for large area printing also using roll-to-roll production lines [4,5]. Various functionalities have been realized using printing technologies, including radio-frequency

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http://dx.doi.org/10.1016/j.orgel.2014.09.007
1566-1199/

identification antennae, transistors, organic light-emitting diodes, organic photodiodes, organic photovoltaics and memory devices [6]. Furthermore, pyroelectric sensors [7] as well as piezoelectric pressure sensor networks [8] have been prepared using printing technologies.

Microfluidic lab-on-a-chip systems (LOC) are a promising field of application of organic and printed electronics. These systems are also termed miniaturized total analysis systems and integrate biological or chemical microreactions on compact chips [9]. Fluidic paths or channels are often structured into a glass or polymer substrate and sealed with a polymer cover foil. LOC are often designed as single-use, disposable chips to avoid contamination. Furthermore, the long-term stability requirements are relatively low in disposable LOC compared to systems that are designed for extended use. In order to keep the manufacturing costs low, the chips can be manufactured using polymer materials and cost-effective replication techniques [10]. When further on-chip functionalities are desired, low-cost manufacturing and low processing temperatures are essential, which hinders the use of conventional lithography-based electronics manufacturing techniques.

Defined fluid transport represents a key issue in LOC and is often realized using external pumps. To avoid separate equipment, various micropumps that are suitable for on-chip integration have been demonstrated [11,12]. They are frequently designed as reciprocating membrane pumps, in which a periodic membrane movement creates a volume change that leads to a fluid flow in combination with inlet and outlet valves. Membranes are often actuated by piezoceramic lead zirconate titanate (PZT) actuators [13], but also electroactive polymer actuators have been employed, e.g. ionic polymer–metal composites [14] or piezoelectric polymers [15]. The actuators are typically mounted on the pump membrane in a separate joining step, which results in increased manufacturing costs.

In this contribution, all inkjet printed polymer actuators based on piezoelectric poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF–TrFE)) that are suitable for pump actuation in LOC are presented. The actuators are printed on a polyethylene terephthalate (PET) substrate and consist of a sandwich of two printed silver electrodes and a P(VDF–TrFE) film. After printing each layer, an annealing or sintering step is required. Compared to most current micropumps where an actuator is mounted on a pump membrane, this separate joining step is avoided in the all-printed manufacturing approach described here. In a previous publication we described the basic manufacturing process of the actuators and reported the piezoelectric d_{31} coefficient for inkjet printed P(VDF–TrFE) actuators for the first time. Moreover, studies of static and dynamic actuator deflection as well as the device stability were described [16]. However, a deeper insight into the underlying morphological changes within the P(VDF–TrFE) films during printing and subsequent annealing steps is crucial in order to control and improve the actuator behavior and, hence, the performance of the micropump.

It is well-known that an annealing step is required for solution-processed P(VDF–TrFE) films to reach a high degree of crystallinity of the piezoelectric β-phase, which is necessary for significant piezoelectric behavior [17–19]. Moreover, the influence of annealing, polymer composition and mechanical stretching on morphology has been widely studied [17]. The first investigations of screen-printed piezo- and pyroelectric P(VDF–TrFE) sensors were published by Zirkl et al. [7,8]. The first direct correlations between annealing temperature, film morphology and remanent polarization of P(VDF–TrFE) films were reported by Mao et al. [20,21]. The authors observed a high degree of crystallinity of the piezoelectric β-phase and large P_{rem} values for films that were annealed above the Curie temperature of approximately 110 °C, but below the melting temperature of P(VDF–TrFE) of approximately 150 °C. Annealing above the melting temperature lead to a degraded β-phase and reduced polarization. However, it should be noted that the films investigated by Mao et al. were processed by spin-coating, which is known to yield different morphologies compared to inkjet printing, as known from other polymeric systems [22]. Up to now, a detailed study on the relationship between morphology and the piezoelectric behavior of inkjet printed P(VDF–TrFE) films has not been reported.

Therefore, the influence of the thermal annealing of printed P(VDF–TrFE) films on the morphology and the resulting device performance is investigated in this contribution. For that purpose, P(VDF–TrFE) actuators are subjected to different thermal treatments. The electromechanical as well as electrical device performance is studied by actuator deflection measurements and ferroelectric hysteresis measurements, respectively. The influence of the thermal annealing on the piezoelectric d_{31} coefficient as well as the remanent polarization P_{rem} is extracted from those measurements. Results are compared to morphology investigations of the P(VDF–TrFE) films by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). Furthermore, a membrane pump with an inkjet printed P(VDF–TrFE) actuator is characterized here for the first time.

2. Experimental

2.1. Materials

The actuators were printed onto biaxially oriented PET substrates (Goodfellow GmbH, Germany, 125 μm thickness, upper working temperature 140 °C). A P(VDF–TrFE) film sandwiched between two silver electrodes was subsequently inkjet printed, leading to a unimorph actuator setup with one active layer on a passive substrate. Inkjet printing was performed using a 2 wt% solution of P(VDF–TrFE) (VDF:TrFE ratio of 70:30 wt%, Solvay Specialty Polymers Italy S.p.A.) dissolved in cyclopentanone. Bottom and top electrodes were printed using two commercial silver nanoparticle dispersions in tetradecane (NPS-JL, Harima Chemicals, Inc., Japan, solid content 55 wt%) and in a mixture of ethanol and ethylene glycol (CCI-300, Cabot Corp., USA, solid content 20 wt%), respectively. A detailed process description is provided in Ref. [16].