Development of polypyrrole based solid-state on-chip microactuators using photolithography

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Abstract
There is a need for soft microactuators, especially for biomedical applications. We have developed a microfabrication process to create such soft, on-chip polymer based microactuators that can operate in air. The on-chip microactuators were fabricated using standard photolithographic techniques and wet etching, combined with special designed process to micropattern the electroactive polymer polypyrrole that drives the microactuators. By immobilizing a UV-patternable gel containing a liquid electrolyte on top of the electroactive polypyrrole layer, actuation in air was achieved although with reduced movement. Further optimization of the processing is currently on-going. The result shows the possibility to batch fabricate complex microsystems such as microrobotics and micromanipulators based on these solid-state on-chip microactuators using microfabrication methods including standard photolithographic processes.

Supplementary material for this article is available online

Keywords: microactuator, polypyrrole, gel electrolyte, microfabrication

(Some figures may appear in colour only in the online journal)

1. Introduction

There is a need for small, soft actuators in a wide range of applications such as micromanipulation of biological samples [1], for mechanical stimulation of single cells [2], to operate valves in microfluidics [3], or to drive micro-unmanned aerial vehicles [4]. Microactuators are actuators that can produce small force and motion in such small entities. They have been fabricated based on a variety of different physical principles, including thermal expansion [5], magnetism [6], and electrostatic forces [7]. Microactuators based on the reduction-oxidation reaction of the conjugated polymers (CPs) such as polypyrrole and poly(3,4-ethylenedioxythiophene) (PEDOT) have also been developed [8–10]. The reversible electrochemical reaction of polypyrrole and PEDOT is accompanied by a volume change caused by the doping and de-doping by ions and solvent exchange from the surrounding electrolyte [11–13]. Microactuators based on these CPs have many attractive features such as being electrically controlled, low activation voltage of 1 V or less, large strain and high strength and good biocompatibility and are of great interest for soft microrobotics [14]. Using these polypyrrole based microactuators, complex microsystems such as a microvial, self-assembling micrometer-sized boxes for cell biology and nanoliter chemistry, and microrobotics have been demonstrated [15–17]. Although these polypyrrole microactuators have been successfully operated in many interesting salt solutions, including blood plasma, urine, and cell culture medium, they are still limited to liquid environments. A solid-state microactuator system based on CPs, i.e. CP microactuators that can function in normal atmosphere without a...
liquid, is interesting because it will greatly expand the application areas of such CP microactuators.

To allow for operation in air solid polymer electrolytes (SPEs) are needed to replace the liquid electrolyte for solid-state microactuator fabrication. There are in principle two geometries to assemble the SPE in an actuator configuration: a sandwich construction or a parallel configuration (figure 1) [18]. The construction of microactuators adds another level of complexity since not only the active layers have to be patterned but also the SPE layer. There are several micropatterning techniques that can be used to pattern the solid polymer electrolyte such as reactive ion etching (RIE) or laser ablation. Maziz et al have demonstrated a conducting polymer microactuator operating in air showing kHz frequency actuation with RIE techniques [19]. They built the microactuator bottom up in a sandwich configuration, by sequential deposition of the CP, SPE and CP layers. Thereafter, they applied a photoresist pattern that defines the final actuator shape and used RIE to etch the unprotected areas. Similar sandwich PP-microactuators have been presented by Gaihre et al [10]. They deposited PPy on both sides of a thin polyvinylidene fluoride (PVDF) membrane and thereafter cut out a microactuator device using laser ablation. Although these methods do provide the resolution needed for microscale actuators and allow for batch fabrication, the obtained actuators are still simple, individual bending beam microactuators. Complex microdevices such as microrobots would comprise multiple and as well as articulated CP microactuators. Preferably the actuator unit is fabricated as a monolithic unit comprising individual addressable microactuators. More complex devices comprising several individually controllable milli- and microactuators based on CPs using photolithographic patterning have been demonstrated, but these methods are complex, require manual handling such as flipping the substrate, or cannot achieve microscale resolutions [20–22]. In addition, these methods typically allow only a single structural layer, typically only the SPE layer, and adding other structural elements is cumbersome. To achieve complex devices with multiple materials novel methods to pattern SPEs and fabricate conducting polymer microactuators are required. One interesting technique is standard photolithography as it enables a single-step process for precise micropatterning. As such, it has been widely used in the semiconductor industry for silicon based microelectronics. The motivation behind this project is to develop reliable and scalable microfabrication methods for individually controllable microactuators comprising SPEs by standard photolithography and thus to allow for more complex soft Microsystems that can be batch fabricated.

To use this micropatterning technique, a solid polymer electrolyte photopatternable by UV light like a commercial photoresist must be developed. In this work, gel electrolytes synthesized from bisphenol A ethoxylate dimethacrylate (BEMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA) monomers via a photopolymerization in the presence of liquid electrolyte were prepared and tested as the SPEs in the fabrication of microactuators. The focus lies on the design of photopatternable solid polymer electrolyte and the use of standard photolithography in solid-state CP microactuator fabrication to broaden the microfabrication toolbox.

2. Materials and methods

2.1. Materials

Bisphenol A ethoxylate dimethacrylate (BEMA, \( Mn = 1700 \text{ g mol}^{-1} \)), poly(ethylene glycol) methyl ether methacrylate (PEGMA, \( Mn = 500 \text{ g mol}^{-1} \)), propylene carbonate (PC), sodium perchlorate hydrate, pyrrole, and 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (Photoinitiator) were purchased from Sigma-Aldrich. Pyrrole was distilled before use and stored at \(-18^\circ\text{C}\). Other chemicals were used without further purification.

2.2. Preparation of micropatterns of solid polymer electrolyte

The following general procedure was used for the preparation of the micropatterns of the solid polymer electrolyte using standard lithographic processes. The monomer precursor mixture was first prepared by mixing BEMA, PEGMA, photoinitiator, and liquid electrolyte (0.5 M NaClO4 in PC) under a light-protected condition. Their weight percentage in the mixture was 50%, 10%, 1%, and 39%, respectively. The polymer electrolyte precursor solution was filtered and then spun onto a gold coated silicon wafer at 700 rpm with an acceleration of 500 rpm s\(^{-1}\) for 30 s. Patterned UV illumination was performed by using a mask aligner (MJB-3 SUSS MicroTec) with UV intensity of 3 mW cm\(^{-2}\) for 120 s and a Cr-photomask comprising the SPE pattern. Hard contact mode was used, and a thin spacer was put between photomask and wafer to prevent polymer gel electrolytes sticking to the photomask after photopolymerization. The uncured materials in the unexposed areas were removed using acetone as the development solvent. After that, samples were dried with compressed nitrogen.
2.3. Fabrication of solid-state polypyrrole microactuators

The fabrication process of solid-state polypyrrole microactuators is based on the combination of the microfabrication processes for PPy-microactuator and gel electrolytes micropatterns. The complete process flow is shown in the figure 2. We started with a clean silicon wafer on which thick silicon oxide had been thermally grown to insulate the surface. Thin layers of Cr (50 Å) and Au (200 Å) were thermally evaporated on the wafer. The chromium layer is necessary as an adhesion promoter, because the gold itself adheres poorly to the silicon substrate. This differential adhesion is used to release the working electrodes in the finished actuators [23] and the gold layer was in turn used to prevent oxidation of the chromium and to adhere a second, structural gold layer later in the procedure. Standard photolithographic process was performed on the gold coated wafer using positive photoresist S1818 and photomask 1. Cr and Au layers were etched to form windows (step 3 in figure 2), which are necessary for the final release step. After that, a thick structural layer of gold (1000 Å) was deposited by thermal evaporation. A small spacer between the working and counter electrodes was etched to isolate them using standard photolithographic techniques and wet etching (step 5 in figure 2). To define the moving working electrodes (the PPy microactuators) and fixed counter electrodes, we deposited the active layer of polypyrrole, which was patterned by partially covering the wafer with photoresist. The polypyrrole was electrochemically synthesized at the uncovered gold surface from a 0.1 M pyrrole, 0.1 M NaDBS solution at a voltage of 0.55 V versus Ag/AgCl with an Au counter electrode. During the growth, the large DBS\(^-\) anions are incorporated in the polymer film, by which the polypyrrole becomes doped. Subsequently, micropatterns of SPEs were patterned on top of the polypyrrole layer using photolithography as described previously. The last step was to remove the excess gold and underlying Cr to form the final device layout, including the contact pads, and to free the working electrodes using wet chemical etching in a KI/\textsubscript{1} solution. After the etching, the working electrodes are movable but still attached to the surface. Microactuators operating in liquid, i.e. without the as-prepared gel electrolytes, were also prepared by skipping the step of gel electrolyte micropatterning.

2.4. Operation of the microactuators

The finished microactuators were individually addressed using micromanipulators (S-725PRM, Signatone) with Au tips to connect to the contact pads. In case of the PPy microactuators operating in liquid, the cut wafer sections were submerged in a 0.5 M NaClO\textsubscript{4} PC electrolyte solution. Cyclovoltammetry was used to operate the microactuators using an Ivium potentiotstat.

**Figure 2.** Overview of the fabrication steps for the solid-state polypyrrole microactuator. (1) Si substrate, (2) deposition of Cr Au layers, (3) etched Cr Au layers for the differential adhesion, (4) second, structural Au layer, (5) etched spacer between the actuator (WE) and CE, (6) patterned electropolymerized polypyrrole, (7) gel patterning, and (8) final Au Cr etching to form the finished devices including contact pads.
3. Results and discussion

3.1. Design of solid-state polypyrrole microactuator

The most common architecture of solid-state conducting polymer based actuators operating in air has the sandwich electrode configuration, in which solid polymer electrolyte is sandwiched between the working and counter electrodes, as shown in figure 1(a). In this ‘rocking chair’ configuration, ions in the solid electrolytes are shuttled between the working electrode and the counter electrode as the oxidation levels are changed. As mentioned, several microactuator systems have been presented in the literature based on this sandwich electrode configuration. The solid polymer electrolyte system used is based on an interpenetrating polymer network synthesized with thermal initiated polymerization techniques. As the IPN based solid electrolyte is not intrinsically patternable, microactuators are fabricated using RIE, rather than standard photolithography techniques. Instead of the conventional sandwich electrode configuration, we use a parallel electrode configuration for microactuator fabrication, in which the working and counter electrodes are put parallel on a substrate and covered with a layer of solid polymer electrolyte as in figure 1(b) [18]. Such electrode configuration has been used in other electrochemical devices such as electrochromic devices and batteries [24, 25], but not in conducting polymer based actuators. This parallel and on-chip configuration offers many advantages over the conventional sandwiched design. First, batch manufacturing using standard photolithography and microfabrication using additive methods only of the microactuator is achieved. Thousands of microactuators can be made at the same time on a single wafer. Secondly, it is possible to provide individual control to each single microactuator which is very cumbersome to achieve with the sandwich-type polymer microactuators [21]. For instance Maziz et al progressed the microfabrication of the sandwich-type CP microactuators, but it required complex patterned sacrificial layers and contacting the top and bottom electrodes could not be achieved on-chip, but required an external electrode contact [22]. Thirdly, it enables the integration of multiple materials thus enabling complex devices as shown for CP microactuators operating in liquids [15, 17]. Finally, it is possible to make the control electronics small using semiconductor technology and then integrate them with the microactuators on a chip. This integrated chip can be a building block for more advanced microsystems.

3.2. Micropatterns of SPEs

As mentioned, to realize microactuators with a parallel and on-chip configuration, SPEs photopatternable like a photoresist used in standard photolithographic techniques are needed. Micropatterns of gel electrolytes were obtained by free radical polymerization from a mixture of BEMA monomers, PEGMA reactive diluents, a liquid electrolyte and a photoinitiator. The liquid electrolyte is confined in the solid polymer network resulting from copolymerizing BEMA and PEGMA under UV exposure. The use of radical photoinitiator enables to control the polymerization spatially and temporally, thus allowing for micropatterning with photolithographic techniques. However, the oxygen inhibition effect on free radical polymerization must be considered for thin film photopatterning, especially when the polymerization is performed in air and under low UV intensity as in our case. A photoinitiator with less oxygen inhibition effect was used in our photopolymerizable electrolyte solution and it allowed us to successfully pattern the electrolytes on the microscale. Polymer electrolyte solution was first spin coated on a gold coated silicon wafer to obtain uncured thin film. A UV exposure of the polymer electrolyte solution films was performed through a quartz chromium photomask using a mask aligner. After UV exposure, the development step was done by rinsing the irradiated polymer films in acetone to dissolve the non-crosslinked materials on the wafers where there was no UV illumination. The obtained micropatterns are shown in figure 3. Polymer patterns with lateral structure sizes down to 100 μm and thickness of around 6 μm were obtained. This clearly shows the good micropattermability of the BEMA gel SPE. The suitability of these gel electrolytes micropatterns for solid-state microactuator fabrication will be evaluated next.

3.3. Polypyrrole microactuators operating in liquid

Besides the micropatterns of solid polymer electrolyte, micropatterns of the actuating conducting polymer layer are also needed to fabricate microactuators. To obtain micropatterns of polypyrrole, gold coated wafers were first patterned with photoresist containing holes. During the following electropolymerization process, polypyrrole will only synthesize in the areas where there is no photoresist covered. However, the conventional solvent propylene carbonate often used to synthesize the acting material polypyrrole can only be synthesized from aqueous electrolytes solution when using this method. In our case we used propylene carbonate NaDBS aqueous solutions. Microactuators operating in liquid, that is without solid polymer electrolyte microactuators, were fabricated and tested in the propylene carbonate based electrolyte solutions. When LiTFSI propylene carbonate electrolyte solution was used, the microactuators showed an irreversible movement and a very small displacement of around 5° from the surface. A good actuation result was obtained when the PPy(DBS) microactuators were tested in NaClO4 propylene carbonate electrolytes as shown in figure 4. At the potential of −1 V, the working electrode of the microactuator lies flat on the wafer surface as seen in figure 4(a); when the potential changes to 0 V, the working electrode quickly bends away from the surface and rolls together within 10 s as seen in figure 4(b). The actuators were reversibly operated for 8 cycles during the test time of 160 s, although the bending angle decreased with each cycle from
180° to 15°. Since the fabricated PPy(DBS) microactuators showed a similar response to previous results [8], we continued to fabricate the solid-state version of these PPy microactuators.

3.4. Solid-state polypyrrole microactuators

Next, we combined the processes for the PPy-microactuator and gel electrolyte micropattern fabrication. Solid-state polypyrrole microactuators with the as-prepared SPEs were successfully prepared as shown in figures 5(a) and 6. Devices with lateral dimensions ranging from 1000 μm down to 100 μm were fabricated. The as-fabricated solid-state microactuators were tested under different conditions. Initially, no actuation was observed on the as-prepared microactuators. We contribute this to fact that the development solvent used in the micropattern development process had removed most of the ions in the thin film micropatterned gels. Thus, a small drop of the liquid electrolyte was placed on the microactuator to rehydrate the gel with the liquid electrolyte for 5 min and the excess liquid was removed with nitrogen gas. The soaking process was necessary for restoring the ion concentration in the solid polymer patterns [19], but this process may also potentially lead to delamination between micropatterned gel and the underlying actuating material layer as gel can swell too much in the liquid electrolyte. After restoring the electrolyte in the BEMA gel, the microactuators were operated by applying a square wave potential (+0.5 and −1.5 V) at 0.025 Hz. Some slow and irreversible movement could be detected. Typically, the tip of the actuator folded as seen in the figures 5(b), (c). In the initial cycles, the actuator folded much more inward than it folded backward during the reverse cycle resulting in a closure of the actuator as shown in figure 5(c). In addition to the bending of the tips of the actuator, a very clear and reversible electrochromism of the PPy (figures 5(d)–(g)) was visible, indicating that the polypyrrole is electrochemically active also using the patterned gel...
electrolytes. Complete bending like in the liquid electrolyte could not be achieved. We contribute this due to the relatively poor ionic conductivity of the micropatterned BEMA gel. The slow moving front in the electrochromism observed during the redox reaction of PPy (figures 5(d)–(g)) indicates the poor ionic conductivity of the SPE [26]. Although the Young’s modulus of the BEMA gel is relatively low ($E = 2.11$ MPa, figure S3 is available online at stacks.iop.org/SMS/27/074006/mmedia), the SPE layer may also add some increased bending stiffness.

Although the performance was poor, i.e. only slow irreversible bending, the results are very promising and show that it is possible to batch fabricate many solid-state PPy microactuators on a single wafer using the parallel configuration (figure 6) and that the PPy microactuators are reversibly electrochemically active. Being able to pattern the SPE in the same manner as photoresists or photopatternable resins (polyimide, SU8, benzocyclobutane) as demonstrated here, is a great advantage. It enables an easy and straight forward way to fabricate individually controllable soft microactuators as shown here (figure 6) that can be mass produced on a single wafer. It will also enable complex devices comprising many individually controllable PPy microactuators, like a micro-robot [8, 27], but then working in air. However, to accomplish this the ionic conductivity of the patterned gel has to increase, preferably in the range of $10^{-2}$–$10^{-1}\text{s}\text{cm}\text{^{-1}}$ and the mechanical properties of the gel have to be enhanced. In order to not restrict the bending, the added gel layer should be very soft, preferably having a Young’s modulus lower than 1 MPa. A proper designed SPE layer will enable fast, in air operation of individual PPy microactuators as demonstrated for microactuators based on the sandwich construction that cannot be individually controlled [19].

4. Conclusion
In this work, we have successfully developed a batch microfabrication process for solid-state on-chip CP microactuators. BEMA gel micropatterns with sizes down to 100 $\mu$m could be fabricated. Solid-state PPy microactuators that could be individually controlled were fabricated in the range of 100–1000 $\mu$m. Electrochromism and some slow movement were detected indicating that the microdevices were electrochemically active and that CP microactuators that move in air and can be individually controlled are viable. However, the performance (speed of the actuation and bending angles) for the solid-state microactuators is much lower than that of the microactuators working in liquid electrolytes. This is most probably due to the fact that the ionic conductivity of the BEMA gel is low compared to that of the bulk liquid electrolytes. Also, although having a relatively low Young’s modulus ($E = 2.11$ MPa), the BEMA gel might add some increased bending stiffness. The bending is less than observed in the liquid state which we contribute to relatively high stiffness of the BEMA gel, impeding the movement. The result shows the possibility to fabricate solid-state on-chip CP microactuators which are necessary for complex microsystems fabrication. Smaller devices than presented here ($\sim 100\mu$m) are also feasible as the lateral sizes only depend on the features on the mask and resolution of the lithography process used. This new method will enable batch fabrication of microsystems in a monolithic unit comprising individual addressable microactuators. Further development is focused on designing new photopatternable SPEs with advanced polymerization techniques to combine high ionic conductivity and good mechanical properties. We have recently developed a novel ionogel that can be photopatterned and has good ionic conductivity and mechanical properties [28]. We will use this newly developed microfabrication process as presented here to integrate this ionogel and fabricate hopefully high performance, solid-state PPy microactuators.
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References

[1] Park J et al 2005 Design and fabrication of an integrated cell processor for single embryo cell manipulation Lab Chip 5 91–6
[2] Svennersten K et al 2011 Mechanical stimulation of epithelial cells using polypyrrole microactuators Lab Chip 11 3287–93
[3] Casadevall I Solvas X et al 2011 Micromixing and flow manipulation with polymer microactuators Microfluidics Nanofluidics 11 405–16
[4] Khaldi A et al 2011 Dry etching process on a conducting interpenetrating polymer network actuator for a flapping fly micro robot ASME 2011 International Mechanical Engineering Congress and Exposition (Denver, USA: IMECE) pp 755–7
[5] Miller C et al 2016 Thermal expansion as a precision actuator Proc. SPIE 9912 991269
[6] Cugat O, Delamare J and Reyne G 2003 Magnetic microactuators and systems (MAGMAS) IEEE Trans. Magn. 39 3607–12
[7] Conrad H et al 2015 A small-gap electrostatic micro-actuator for large deflections Nat. Commun. 6 10078
[8] Jager E W H, Smela E and Inganäs O 2000 Microfabricating conjugated polymer actuators Science 290 1540–5
[9] Khaldi A et al 2011 Conducting interpenetrating polymer network sized to fabricate microactuators Appl. Phys. Lett. 98 164101
[10] Gaihre B et al 2011 Effect of electrolyte storage layer on performance of PPy-PVDF-PPy microactuators Sensors Actuators B 155 810–6
[11] Pei Q and Inganäs O 1992 Electrochemical applications of the bending beam method: I. Mass transport and volume changes in polypyrrole during redox J. Phys. Chem. 96 10507–14
[12] Otero T F, Grande H and Rodriguez J 1996 Influence of the counterion size on the rate of electrochemical relaxation in polypyrrole Synth. Met. 83 205–8
[13] Jafeen M J M, Careem M A and Skaarup S 2010 Speed and strain of polypyrrole actuators: dependence on cation hydration number Ionics 16 1–6
[14] Smela E 2003 Conjugated polymer actuators for biomedical applications Adv. Mater. 15 481–94
[15] Smela E, Inganäs O and Lundström I 1995 Controlled folding of micrometer-size structures Science 268 1735–8
[16] Jager E W H, Inganäs O and Lundström I 2000 Microrobots for micrometer-size objects in aqueous media: potential tools for single cell manipulation Science 238 2335–8
[17] Jager E W H et al 2002 The cell clinic: closable microrivials for single cell studies Biomed. Microdevices 4 177–87
[18] Jager E W H, Smela E and Inganäs O 1999 On-chip microelectrodes for electrochemistry with moveable PPy bilayer actuators as working electrodes Sensors Actuators B 56 73–8
[19] Maziz A et al 2014 Demonstrating kHz frequency actuation for conducting polymer microactuators Adv. Funct. Mater. 24 4851–9
[20] Khaldi A et al 2016 Bottom-up microfabrication process for individually controlled conjugated polymer actuators Sensors Actuators B 230 818–24
[21] Jager E W H et al 2013 Patterning and electrical interfacing of individually controllable conducting polymer microactuators Sensors Actuators B 183 283–9
[22] Maziz A et al 2016 Top-down approach for the direct synthesis, patterning, and operation of artificial micromuscles on flexible substrates ACS Appl. Mater. Interfaces 8 1559–64
[23] Smela E, Inganäs O and Lundström I 1995 Differential adhesion method for microstructure release: an alternative to the sacrificial layer Transducers ’95 (Stockholm, Sweden) pp 218–9
[24] Brooke E et al 2017 Infrared electrochromic conducting polymer devices J. Mater. Chem. C 5 5824–30
[25] Gaikwad A M, Arias A C and Steingart D A 2015 Recent progress on printed flexible batteries: mechanical challenges, printing technologies, and future prospects Energy Technology 3 305–28
[26] Wang X, Shapiro B and Smela E 2004 Visualizing ion currents in conjugated polymers Adv. Mater. 16 1605–9
[27] Jager E W H, Inganäs O and Lundström I 2000 Microrobots for micrometer-size objects in aqueous media: potential tools for single-cell manipulation Science 288 2335–8
[28] Zhong Y et al Highly conductive, photolithographically patternable solid polymer electrolytes for flexible and stretchable electronic devices Unpublished