Sensors and Actuators B 229 (2016) 635–645

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Synergetic PEDOT degradation during a reactive ion etching process

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ARTICLE INFO

Article history:
Received 24 December 2015
Accepted 3 February 2016

Keywords:
Reactive ion etching
Degradation mechanisms
Polymer micro-actuator
Interpenetrating polymer network
Flexible electronics

ABSTRACT

Conjugated polymer etching is a key step in the integration of electro-chemical devices into microsystems, and one of the most important challenges for this type of material is to achieve fast etching with commercially available equipment. Conjugated polymer electrochemical devices are promising as they are used in different devices such as OLED, sensors, supercapacitors and actuators. The recent emergence of conducting interpenetrating polymer network actuators (IPN) based on poly(3,4-ethylenedioxythiophene) (PEDOT) has allowed operation frequencies of over 1 kHz to be attained, thus pushing the limits of the conjugated polymer technology. The plasma dry etching step of these PEDOT-based active mechanical devices, with high etching rates of around 2 μm min^{-1}, enables the production of these electrochemo-mechanical devices. To understand the high etching rate of these materials a systematic study of the chemical degradation mechanism of each polymer has been carried on. From the analysis of the etching of all the polymer actuator components, a chemical self-degradation mechanism is proposed to explain the surprisingly high etching rate obtained for PEDOT based materials. Finally, to conclude this study, the usefulness of this fast etching is demonstrated with the operation of standalone micro-beam actuators.

1. Introduction

Over the past decades, actuator materials used in microsystems have been getting increasingly smaller, resulting in a large number of publications on piezoelectric, magnetic and shape memory materials, and to a lesser extent, polymer-based actuators [1]. There is currently growing interest in the miniaturization of polymer actuators with mechanical properties close to those of mammalian skeletal muscles [2].

Among polymer mechanical transducer, electronic conducting polymers (ECP) actuators has been used to build prototypes of micrometric scale biomimetic devices. Moreover, ECP has already been widely micro-patterned for a number of interesting applications other than those of actuators. For example, these polymers can emit light in the visible region of the electromagnetic spectrum, and several microfabricated light emitting diodes (LEDs) have already been developed [3–9]. Electronic devices such as thin film transistors [10] and Schottky diodes [11–15] are another important class of applications, as well as chemical sensors [16–21]. Conjugated polymers are also used in supercapacitors [22] and batteries [23]. Poly3,4-ethylenedioxithiophene/poly(styrene sulfonate) (PEDOT/PSS) has found applications in organic electronics such as electrodes for plastic substrates. This material is also an interesting candidate for building neuronal electrodes in several bioMEMS (microelectromechanicalsystems) and neuroscience applications [24,25]. Due to its piezoresistive behavior, it has been used to build resonant MEMS structures [26], as well as strain gauges [27].

Abbreviations: ECP, electronic conducting polymers; LED, light emitting diodes; PEDOT/PSS, poly3,4-ethylenedioxithiophene/poly(styrene sulfonate); MEMS, microelectromechanicalsystems; PPy, polypyrrole; PDMS, polydimethylsiloxane; RIE, reactive ion etching; C-IPN, conducting interpenetrating polymer network; PEO/PTHF, polyethyleneoxide/polytetrahydrofurane; PEO/NBR, polyethyleneoxide/nitrile butadiene rubber; SPE, solid polymer electrolytes; DBTDL, dibutyltin dilaurate; PEGDM, poly(ethylene glycol) dimethacrylate; PEGM, poly(ethylene glycol) methyl ether methacrylate; EMITFSI, *N*-ethylmethylimidazolium bis(trifluoromethanesulfonyl)imide; AIBN, 2,2'-azobisisobutyronitrile; DCDP, dicyclohexylperoxidicarbonate; DCP, dicumyl peroxide; PVA, poly(vinylalcohol); SEM, scanning electronic microscopy; EDS, energy dispersion spectroscopy; U.P., unsaturated polymer; N.M., not measurable; Tos or Tosylate, para-toluensulfonate.

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http://dx.doi.org/10.1016/j.snb.2016.02.009
0925-4005/

Among ECPs, polypyrrole (PPy), polyaniline [28,29], polythiophenes [30,31] and PEDOT [32] have been already used to fabricate ionic polymer micro-actuators and are very promising [33–36] owing to their low driving voltage, light weight and stretchability [37]. However, to integrate these materials in Microsystems, the manufacturing processes must be compatible with microfabrication technologies. The process used must be adapted to the polymer and the remaining of the microfabrication sequence. The ECP patterning step is a key process enabling the use of polymer actuators in microsystems. The different ECP patterning methods have been extensively reviewed by Smela [39] and Holdcroft [38]. As shown, a considerable number of strategies can be used. Some polymers can be patterned directly under UV irradiation to locally cross-link poly(alkylthiophenes) [40], or with electron beam lithography to pattern poly(3-octylthiophene) films [41]. The same processes are also used on polymer precursor films to micropattern polyphenylene vinylene and polyaniline [5,42] where electron beam irradiation results in cross-linking. Alternatively, the addition of a photosensitizer to a solution of the monomer and an oxidant limits the chemical polymerization to the areas exposed to light. This approach has been used to deposit polypyrrole (PPy) [43]. Another approach use either photochemical generation of the oxidant to form PPy [44], or involves incorporating a photosensitive oxidant in a host polymer [45]. Additional methods for patterning conjugated polymers using photopolymerization and photocross-linking are reviewed in [46], and further examples of irradiation techniques can be found in references [5,47–52].

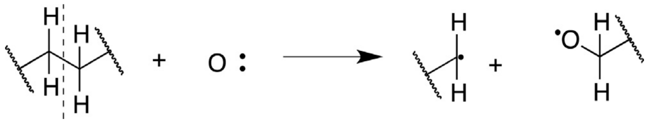
Patterned electrodes can be used also to determine the area on which a polymer is deposited by electropolymerization [53–55], or the local electrodeposition of the polymer can be achieved on an entire wafer covered by a metal film through a photoresist mask. A variation of this method is to use a micropatterned self-assembled monolayer to define areas favorable or unfavorable for polymer deposition, as shown in [56–62]. A pattern of alkanethiol (for use with PPy) or 12-amino-1-dodecanethiol (for polyaniline) was defined by microcontact printing on gold and then immersed in a solution containing short chain alkanathiols. The polymers were preferentially deposited on the regions covered by the short chain self-assembled monolayer.

Other industrial techniques have been developed also to locally deposit the material of interest and have also been used for ECPs. These techniques include ink jet printing where the polymer is dissolved in a volatile solvent and ejected dropwise onto a substrate [63,64], roll to roll printing [65], and soft lithography, for example casting PEDOT/PSS in a PDMS (polydimethylsiloxane) scaffold for integrating stretchable electrodes in a deformable substrate. ECP patterns can also be obtained by micro contact printing using a positive micropatterned PDMS stamp [66,67]. In addition to the low resolution obtained by each of the aforementioned methods, these approaches are limited by the insolubility of many conducting polymers. More recently, a high resolution PEDOT pattern of 60 nm was obtained with an oxidative chemical vapor deposition technique using a covalent grafting method [68,69].

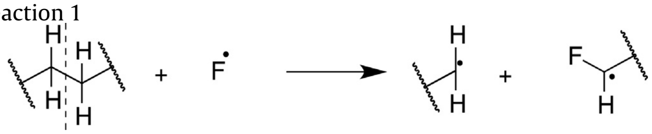
A bilayer structure is the minimum required to achieve a conducting polymer bending actuator, and in this structure, the actuator must operate in a liquid electrolyte medium. The techniques presented above can then be used insofar as the layer supporting the localized polymer participates in the actuator structure. These actuators are based on conjugated polymers that undergo volume changes during oxidation and reduction. One of the layers is a passive substrate, and under electrochemical oxidation and reduction, the change in volume dominated by ionic movement into and out of the second active layer forces the assembly to bend. These bilayer actuators have been already used in the fabrication of microactuators [39,70,71], and very successful demonstrators operating in liquid medium were achieved by Smela and co-workers [72–74] and Jager [75]. Smela and Jager used electrodeposition on rectangular electrodes or reactive ion etching (RIE) to pattern their conducting polymer layers.

The trilayer structure enables the actuator to work out of a liquid environment, opening up a new range of applications. Recently, conducting interpenetrating polymer network (C-IPN) microactuators operating in air have been successfully described with systems based on polyethyleneoxide/polytetrahydrofurane (PEO/PTHF) or polyethyleneoxide/nitrile butadiene rubber (PEO/NBR) as solid polymer electrolytes (SPE) interpenetrated with PEDOT [71,76]. Printing techniques such as inkjet, stamping or soft lithography become difficult to control for the successive deposition of several superimposed layers, and patterning of multilayer polymer devices becomes more challenging. In contrast, photolithography coupled with plasma is a widely applicable patterning method if plasmas allowing fast etching and good selectivity towards photoresist can be found. Photolithography has the added advantage of being the most developed patterning technology and the current patterning method of choice in the semiconductor industry. However, photolithography is not panacea as it may induce chemical deterioration of active organic materials upon exposure to UV light or to process solvents during development or lift-off of photoresists. Solvents can dissolve or at least swell the conjugated polymer films, but damages can often be avoided by using an appropriate process sequence. RIE coupled with photolithography can be used to pattern the three layers of the polymer actuators simultaneously. RIE is well controlled in the manufacturing of electronic components; it is well known for its high dimensional accuracy and the control of the depth etched, and it also allows high-throughput fabrication. The photolithography step can be avoided by using laser ablation [6,70,77–80], but the process can be long if a high surface area of material must be removed. However, today, industrial laser ablation devices can increase etching rates, but controlling the etching depth is still difficult.

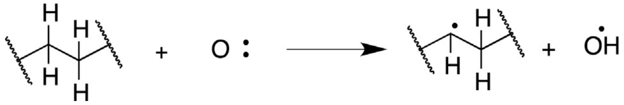
Smela has pointed out the difficulty of etching PEDOT (using RIE) with Cl^- or $ClO_4{}^-$ as counterions [39], and only a few papers report the ability to etch a PEDOT/PSS blend [81–83]. Surprisingly, even if PEDOT(Cl^-) is present at the surface of the material, C-IPN is etched at a very fast average rate of 1.75–1.95 μm/min with O_2/CF_4 plasma [71]. To understand the etching mechanisms of these C-IPNs, the chemical nature of the used polymers and the nature of the plasma must be considered. The main families of chemical reactions that can occur during RIE with the polymer partners of the C-IPN are presented below. They are direct scission by oxygenated (Reaction 1) or fluorinated radicals (Reaction 2), formation of radicals on polymers, hydroxyl radical formation (Reaction 3), and fluorine binding to the backbone of unsaturated polymers (Reactions 4 and 5). The detailed reactions that occur during O_2/CF_4 plasma etching are shown in the supplementary material.



Reaction 1



Reaction 2



Reaction 3