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Conducting interpenetrating polymer network sized to fabricate microactuators

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Interpenetrating polymer networks can become successful actuators in the field of microsystems providing they are compatible with microtechnologies. In this letter, we report on a material synthesized from poly(3,4-ethylenedioxythiophene) and polytetrahydrofuran/poly(ethylene oxide) and micro-sized by decreasing its thickness to 12 μm and patterning the lateral side using plasma etching at high etch rates and with vertical sidewalls. A chemical process and a “self degradation” are proposed to explain such etching rates. Preliminary actuation results show that microbeams can move with very large displacements. These micro-sized actuators are potential candidates in numerous applications, including microswitches, microvalves, microoptical instrumentation, and microrobotics. © 2011 American Institute of Physics. [doi:10.1063/1.3581893]

Integrating electronic conducting polymer (ECP) into microsystems is a challenge these days but difficulties can arise when it is necessary to microsize these polymers. To address this issue, different techniques have been considered and largely reviewed by Smela¹ and Holdcroft.² The first limiting factor for conducting polymer actuators operating in air is their thickness³ and the second is their robustness with respect to chemical and physical etching techniques.⁴ These actuators working in air are usually built in a trilayer configuration, where the internal layer is a solid polymer electrolyte (SPE) sandwiched between two ECP layers (ECP//SPE//ECP). The relative differential expansion between the conducting polymer layers results in bending (Fig. 1). We have previously demonstrated⁵ that with an interpenetrating polymer network (IPN) like poly(ethylene oxide)/polybutadiene (PEO/PB), the PEO component acts as tank for 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) ionic liquid, whereas the PB network ensures convenient mechanical properties. When an ECP such as poly(3,4-ethylenedioxythiophene) (PEDOT) is incorporated in such IPN, it can be turned into an actuator.⁶ The resulting 250 μm thick device was subjected to 3.5×10^6 cycles with no degradation and/or delamination.⁷ To reduce the thickness and make these materials compatible with microsystem technologies, an IPN matrix based on a polytetrahydrofuran (PTHF) derivative and PEO is proposed. These two polymers are independently crosslinked by two different chemical mechanisms yet in the presence of each other. When this reactive blend is introduced in a mold and pressed at 285 kg cm^{-2} at 50 °C for one hour then 80 °C for 30 min, a film of IPN matrix about 10 μm thick can be obtained. After incorporation of PEDOT, a thin conducting IPN (Ref. 8) is obtained. The actuator-synthetic pathway that we developed ensures a nonhomogeneous dispersion of PEDOT throughout the thickness of the IPN, i.e., its quantity decreases from the

outside toward the center of the film. Figure 2 shows a scanning electronic microscopy (SEM) image of a 12 μm thick conducting IPN which is smaller than a similar material of 250 μm thick previously published.⁷ On each face, a thickness of 3.5 μm of PEDOT electrode interpenetrated in the IPN matrix can be observed. Energy-dispersive x-ray spectroscopy (EDS) mapping was used to distinguish the sulfur content in PEDOT and shows that the diffusion of the conductive electrode in the matrix was perfectly controlled. It must now be proved that this material is compatible with microtechnologies. Patterning using photolithographic methods requires the thin films to be motionless and planar. First, actuators were fixed on silicon substrates with a poly(vinylalcohol) (PVA) adhesive layer and good planarization was obtained. An aqueous 300 g L^{-1} PVA solution ($M_w = 2000 \text{ g mol}^{-1}$ purchased from ACROS) was obtained by adding PVA to distilled water in a covered beaker and mixing for 24 h. Drops of this polymeric solution were then spin-coated on a silicon wafer. A 5.5 μm thick layer was obtained at 1500 rpm/750 rpm s^{-1} for 15 s. Then, the conducting IPN was pressed manually on the PVA layer while the latter was still moist. The PVA layer was then dried at 65 °C for 5 min. The Megaposit SPR 220 7.0 photoresist (Microchem corporation) was found to be useful in protecting the actuator

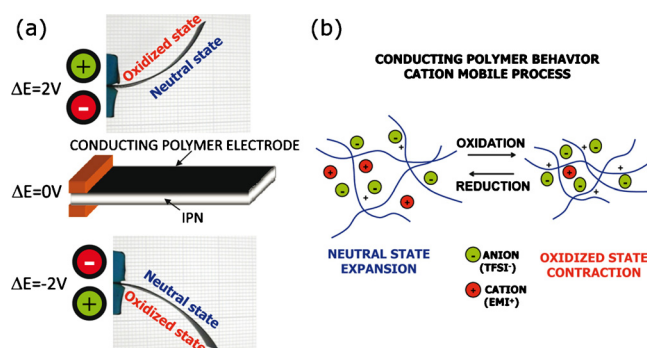


FIG. 1. (Color online) (a) Beam shaped IPN macroactuator ($\Delta E = \pm 2 \text{ V}$) (b) Oxido-reduction process of conducting polymer.

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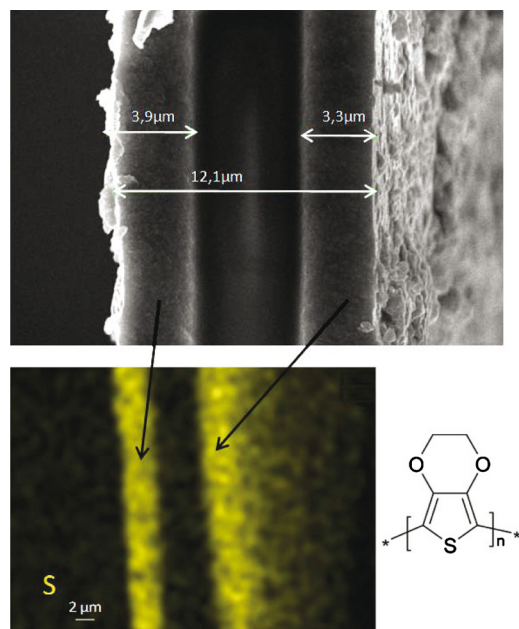


FIG. 2. (Color online) SEM image of the IPN cross section without ionic liquid. The host matrix and PEDOT electrodes are clearly distinguished by EDS mapping analysis on sulfur atoms. Chemical formula of PEDOT is given and sulfur atoms can be found only inside.

locally prior to dry etching, thus providing good resistance to the plasma. Layers $17 \mu\text{m}$ thick were obtained by spin coating at $750 \text{ rpm s}^{-1}/1000 \text{ rpm s}^{-1}$ for 40 s. No degradation of the actuator due to the photoresist was observed. No hard mask was considered because of the difficulty in growing thin metallic films on polymers. Afterward, the compatibility of conducting IPN with the photolithography techniques was demonstrated. Dry etching of conducting IPN was performed by reactive ion etching (RIE, OXFORD Plasmalab 80 plus) with O_2/CF_4 plasma at 300 W and 200 mT. Different etching recipes were used to improve the etch rate and the selectivity. These are reported in Fig. 3 as a function of the gas mixture. A high etch rate of $1.95 \mu\text{m min}^{-1}$ was measured for a 90/10 optimal mixture of O_2/CF_4 while the etching rate in pure oxygen plasma was lower ($0.25 \mu\text{m min}^{-1}$). The photoresist SPR 220 7.0 appears to be an interesting mask because of the good selectivity of 2.5 obtained (Fig. 3). The photoresist is preferentially etched by the oxygen plasma as demonstrated by its relative constant etch rate of $0.7 \mu\text{m min}^{-1}$ as a function of the gas ratio. Fluorine-containing gas had a signifi-

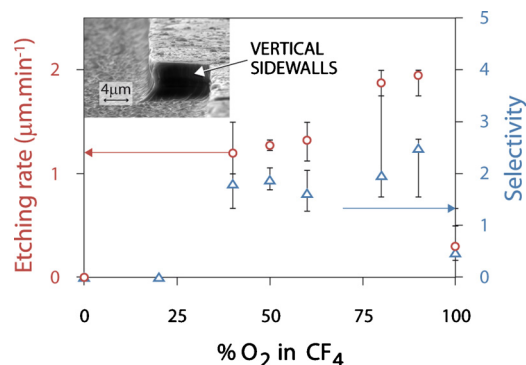


FIG. 3. (Color online) Etching rate at 300 W and 200 mTorr of microactuator precursor (O) and selectivity (Δ) vs percent of O_2 in CF_4 . An optimal ratio of 90/10 was found with selectivity of 2.5 (IPN etch rate/photoresist etch rate). In inset, the vertical sidewalls obtained after etching at 90/10.

TABLE I. Etching rate at 300 W and 200 mTorr with 90% O_2 in CF_4 of single polymers and microactuator precursor (N.M.: nonmeasurable). NBR is nitrile butadiene rubber.

Materials	Etching rate ($\mu\text{m min}^{-1}$)
PEO (saturated)	1
PTHF (unsaturated crosslinking functions)	N.M.
PEDOT (unsaturated, conjugated)	N.M.
NBR/PEDOT=IPN (without PEO)	N.M.
PEO/PTHF=IPN	0.4
PEO/PTHF/PEDOT=conducting IPN	1.95

cant influence on the activation of the etching as confirmed by the $2 \mu\text{m min}^{-1}$ etch rate measured with O_2/SF_6 (90/10) plasma. A pure Ar plasma produced a very low etch rate confirming that the chemical mechanisms override the physical mechanisms.

Atomic oxygen free radicals ($\text{O}\cdot$) usually initiate the polymer etching process. This has been demonstrated by the linear relationship between etching rates and either $\text{O}\cdot$ atom concentrations in the plasma⁹ or the amount of $\text{O}\cdot$ atoms consumed during polymer etching.¹⁰ It appears that the addition of fluorinated gas plays a major role in the increase in $\text{O}\cdot$ atom densities in the plasma by favoring an increase in the density and/or energy of the electrons in the plasma.¹¹ The gas composition which yields maximum rates exhibits also a strong dependence on polymer structure,^{12,13} specifically with the degree of unsaturation of the polymer. Indeed, the action of $\text{O}\cdot$ to destroy the double bonds requires more energy and additional reaction steps¹⁴ resulting in a low etch rate compared to saturated polymers (Table I). The PEDOT is an unsaturated polymer. Moreover, it is an aromatic system with a high conjugation length and an interchain stabilizing effect (Π -stacking). PTHF is a saturated polymer but the network behaves like an unsaturated polymer because of the presence of carbonyl bonds in the urethane functions of the crosslinker. Therefore, under the same plasma conditions, we obtain fast etching rate of PEO ($1 \mu\text{m min}^{-1}$) and we have large difficulties to etch PEDOT and PTHF (Table I), as expected. Atomic oxygen free radicals do not seem to affect also the photoresist as demonstrated by its relative constant etch rate of $0.7 \mu\text{m min}^{-1}$ as function of the gas ratio. Because of fluorine in the plasma, two types of reactions have to be considered. On the one hand, fluorine abstraction of hydrogen plays a role in generating reactive radical sites on saturated polymer surfaces (PEO) and on the other hand, etching of unsaturated polymers (PTHF, PEDOT) proceeds via a stable saturated radical intermediate resulting from addition reactions of fluorine atoms. Moreover, excessive amounts of fluorine in the plasma result in reduced etching rates and incorporation of fluorine and/or CF_x radicals into the polymer whatever his chemical nature. This can be explained on the basis of molecular orbital arguments which predict that the surfaces of unsaturated polymers have a higher affinity for atomic fluorine than saturated polymer surfaces.¹⁴ Indeed, this hypothesis confirms by EDS analysis performed on etched surfaces: fluorine binds to PEDOT and PTHF but not on PEO in our optimal condition of etching. The binding of fluorine on the surface of the material protects it against the plasma.

An original interpretation is now proposed to explain the high etch rates ($1.95 \mu\text{m min}^{-1}$) obtained with these gases for the conducting IPN. Normally PEDOT, constituting the top electrode, would block the etching. However, in the conducting IPN, PEDOT interpenetrated the PEO/PTHF matrix. This matrix and in particular the PEO-rich phase remains accessible to the plasma. First, we demonstrated that PEDOT and PTHF are completely degraded in a piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$), a highly concentrated medium of radical species ($\text{O}\cdot$). This result indicates that the concentration is not enough in the generated plasma, and that only a high concentration of radical species is necessary to destroy the PTHF and PEDOT polymers. We, therefore, believe that the degradation of the PEO is the factor that triggers the etching of the other components of the conducting IPN. Within the matrix and PEDOT a high concentration of radical species ($\text{O}\cdot$, $\text{HO}\cdot$, $\text{C}\cdot$...) will be generated during the degradation phase of PEO. Previous works^{15,16} have shown that under thermo-oxidation conditions in open air, the formation of hydroxyl radicals $\text{HO}\cdot$ occurs by oxidation of PEO single network. Furthermore it has been also demonstrated that the $\text{HO}\cdot$ reacts with the PEDOT leading to the rupture of the Π -conjugation in the backbone, hence, to the loss of electroactivity.¹⁶ However, hydroxyl radical production is sensitive to temperature and increase particularly when it exceeds 80°C . The rise in temperature during the etching step is an additional factor in the formation of a high density of radical species. To summarize, we can describe the etching process as two coupled phenomena; the presence of fluorine modifies the reactivity of PEDOT and PTHF but increases the $\text{O}\cdot$ atom densities in the plasma, whereas the presence of oxygen (and in particular the concentration $\text{O}\cdot$) is principally responsible for the quick degradation of PEO. This degradation produces a large quantity and variety of reactive radicals that activate the decomposition of PTHF and PEDOT. In this case, the etching is done essentially by radical species produce directly inside the conducting IPN and the plasma has a secondary role. It is therefore a phenomenon of "self-etching." Another IPN (NBR/PEDOT; see Table I) without PEO was etched in the same conditions and no measurable steps were detected after etching. This confirms definitively that PEO presence is the predominant factor in the etching process. Synthesis process of IPNs allow therefore to adapt it by introducing a polymer of our choice which will be the source of a large concentration of radical species in the presence of a triggering factor, these radicals producing the destruction of the remaining material.

This plasma was used to pattern conducting IPN microbeams ($900 \times 300 \times 12 \mu\text{m}^3$). These microbeams were immersed in an N,N-1-ethyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide solution (EMITFSI from Solvionic was used as received) for 48 h to obtain an actuator. The EMITFSI content was measured on wider beam by swelling ratio at 150 wt %. EMITFSI content was determined by measuring the weight of a macrosample before and after swelling.

$$\text{EMITFSI uptake(\%)} = 100 \times (W_t - W_0)/W_0,$$

where W_0 is the initial weight of macrosample and W_t is the weight after swelling.

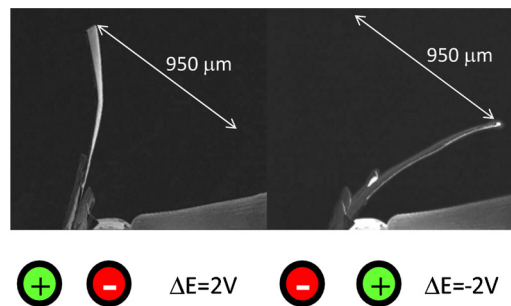


FIG. 4. (Color online) SEM image of microactuator ($900 \times 300 \times 17 \mu\text{m}^3$) at 10^{-4} mTorr operating at 5×10^{-2} Hz, ± 2 V.

The swollen material thickness increases to reach about $20 \mu\text{m}$. The actuator was electrically stimulated by a square input voltage of 4 V peak to peak at 0.05 Hz and the displacement response of the actuator was observed using SEM. Large amplitude of $950 \mu\text{m}$ was observed (Fig. 4) corresponding to a strain of 1.11%, a curvature of $1.045 \times 10^3 \text{ m}^{-1}$ and a bending angle of 63° .

In conclusion, we have proposed a patterning protocol for plasma dry etching of conducting IPN actuators operating in air. We have demonstrated that it is possible to pattern a $12 \mu\text{m}$ thick microbeam of conducting IPN, producing substantially vertical sidewalls (inset, Fig. 3). A mask of photoresist was used and a selectivity of 2.5 was obtained, demonstrating the compatibility with classical technology. The mechanisms of the dry etch rate in a mixture of O_2/CF_4 plasma are explained according to the particular interpenetrating structure of conducting IPN. Liftoff of microbeams was obtained and after immersion in EMITFSI electrolyte solution these beams were actuated. Amplitude and frequency obtained in low vacuum are remarkable and promising for Microsystems applications.

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