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THIN FILM CONDUCTIVE POLYMER FOR MICROACTUATOR AND
MICROMUSCLE APPLICATIONS

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ABSTRACT

Conductive polymer/polyimide bimorphic microcantilevers have been actuated vertically
(out-of-plane) upon the volumetric changes induced by electrochemical doping of the polymer.
The microcantilevers that are 200-500 µm in length and 50-100 µm in width can be fully extended
from a circularly-curled geometry, and thus generate more than 100 µm displacement. Dynamically
the microcantilevers have been driven as fast as 1.2 Hz and the polymer was stable for over
a week stored in air and light. Residual stresses in the polymer film is estimated to be as high as
254 MPa, and actuation stresses are as high as 50 MPa.

INTRODUCTION

The work of J.W. Gibbs in the nineteenth century showed that chemical energy can be con-
verted into mechanical energy. But it was not until the 1960s that mechano-chemical engines have
been of interest to researchers (Wasserman, 1960, Katchalsky and Oplatka, 1971). In fact, the main
method of energy conversion practiced by all living creatures is an isothermal and direct conver-
sion of metabolic energy into mechanical motility, which functions by quick movements of ions in
and out of muscle fibers. Probably through this inspiration, recently there has been a strong interest
in the field of building artificial muscles (Bobbio et al, 1993, Yamaguchi et al, 1993, Hunter and
of actuation mechanisms can be built by learning from biological systems.

Conductive polymers are plastic materials which can be rendered electrically conductive
when oxidized or reduced by suitable reagents. For the past 17 years, the unique electrical, optical,
chemical properties of conductive polymers have attracted substantial research and development
attention (Salaneck et al., 1993, Reynolds et al., 1989). Not only do some conductive polymers
have electroluminescence properties, but the electrical conductivity can approach that of copper
and the mechanical properties are comparable to steel (Heeger 1993). Applications of conductive
polymers have been developed into LED flat panel displays, batteries, chemical and biochemical
sensors, corrosion-resistant materials, etc. Many more applications of conductive polymers, pol-

cermels, and their combinations are possible as material and process improvements are made.

The recent discovery of conductive polymers provide the most similar actuation to the mus-
cle contractions. A review was reported on the mechanical actuation potential of conductive polym-

ers upon electrochemical doping of donors or acceptors, along with many design ideas in

applying this type of material for microactuators (Baughman et al. 1991). Yoshini (1993) reported
a macro bimorph cantilever that was actuated by solvent composition changes and electrochemical
doping. There has also been a report combining polypyrrole with microfabrication to demonstrate actuation, although process problems had prevented any quantitative results from being generated (Smela et al. 1993).

Several researchers have actuated polyimide microcantilevers by methods including thermal bimorphs (Ataka et al. 1993) and RF heating (Rashidian and Allen 1993). This paper presents the complete design, fabrication, and testing of microfabricated polyimide cantilevers coated with polypyrrole, solving many of the processing problems experienced in reference [2]. Further improvements are necessary to make conductive polymer a practical actuator material, and some suggestions are made in this paper. The low voltage and large strains available make it advantageous over many existing microactuation schemes. Combined with the chemical and biosensing abilities of conductive polymers, "smart" systems that sense as well as actuate are possible (De Rossi et al. 1994, Yoshini 1993, Aizawa 1994). Other possible applications include liquid-based microactuators such as micropumps, microvalves, microtweezers, and in vivo microtools.

**CONDUCTIVE POLYMER AS A MICROACTUATOR**

To fully describe the principle of polypyrrole as a microactuator, it is necessary to describe the deposition and doping process pertaining to the structural formation and changes. The structure and morphology of a conductive polymer depend heavily on the type of polymer, preparation method and synthesis conditions (concentrations, electrolyte, dopant, temperature, voltage applied, solvent, to name a few). The properties which are affected include kinetics of dopant diffusion into and out of the polymer network, reversibility of the doping process, mechanical and electrical properties. Conductive polymers can be prepared in micron dimensions by electrochemical, chemical or photochemical method. For sub-micron thin films or structures, they can be fabricated by the Langmuir-Blodgett technique. Only the electrochemical deposition process will be described in this paper. First of all, a solution is made by mixing monopyrrole and an electrolyte in an organic solvent. Then by supplying a voltage between the cathode (film deposition surface) electrode and anode electrode (generally Pt), the pi electron on the pyrrole ring is prone to be consumed by the cathode and cause the positively charged pyrrole to adhere to the cathode surface. Layers are sequentially deposited and the dopant is bonded to the polymer backbone as the conductive polymer is forming. Explain how the dopant comes in and the backbone concept.

After the polymer film is formed, it is immersed in a solution with only the electrolyte but without the pyrrole. Upon reversing the potentials of the electrodes, the electrolytes are electrically forced out of the polymer and in to the solution, resulting in undoping of the polymer. This causes the polymer backbones to be positively charged and repulsing forces cause the polymers to be stretched and aligned, creating an expansion force and strain. On the other hand, as the bias potential is returned to negative on the film, the polymer backbones are neutralized and entanglement of them cause the polymer to contract and produce a tensile strain. Upon doping and undoping, these polymers undergo large dimensional changes. Linear and volumetric changes by as much as 10% have been observed. These changes are one to two orders of magnitude larger than those of traditional piezoelectric materials (such as piezoelectric ceramics and polymers). Furthermore, the voltages needed to induce these changes are at least an order of magnitude less than those of piezoelectric or electrostatic actuators, usually only fractions of a volt. Researchers have found that the mechanical properties are related to anion size, with the larger organic atoms producing higher-quality films by increasing the order of the polymer chains during the polymerization and deposi-
tion process. Also stronger acids give higher conductivity (Reynolds et al. 1989).

When the conductive polymer is first electrochemically formed, the dopants are embedded in the polymer backbone and the material is conductive but neutrally charged as a whole. Electrons and holes are free to hop along the polymer backbones as well as between individual backbones. This will cause the lengthy polymer backbones to intertwine and the film to contract and generate tensile stress. On the other hand, if the dopants are driven out into the solution by reversing the potential, the dopant ions are forced out of the polymer and into the solution, the polymer backbones repulse each other electrostatically and become aligned. Thus a compressive stress is generated. By switching back and forth between these two states, a reversible actuation mechanism is formed.

DESIGN AND FABRICATION

Figures 1(a) and 1(b) demonstrate the fabrication sequence and the curling of the cantilever beam as result of the tensile residual stress in the polypyrrole. First a thin film of 500A Ti is evaporated onto the substrate as an adhesion layer for the polypyrrole to silicon. A 1 mm Al sacrificial layer is evaporated and patterned. A 2.2 mm polyimide structural layer (Du Pont PI2611) is then spun on and fully cured. This type of polyimide was selected due to its low thermal expansion coefficient (3x10^{-6}/°C). A Ti/Au layer is evaporated as the electrode for polypyrrole deposition and doping. A 500A Ni layer is then deposited as a masking layer for RIE of the polyimide. Then the sacrificial Al layer is etched away as well as the Ni mask. At this point the cantilever beams are free for conductive polymer deposition. This is done by preparing a deposition solution of 0.1M of pyrrole and 0.1M of p-toluenesulfonate (electrolyte) in an acetonitrile solvent. The pyrrole must be vacuum distilled and stored in a refrigerator. The polypyrrole is then deposited on a Bioanalytical System in the cyclic voltammogram (CV) mode. The positive electrode is applied to the microcantilevers and the counter electrode is a Pt coil. About 4 cycles between 0V to 1.1V grows approximately 2.2 mm. Figure 1(c) is an SEM micrograph of a 350 μm long, 100 μm wide microcantilever. The microcantilevers are 200-500 μm, with widths 50 μm and 100 μm. Figure 2(a) is an array of cantilevers that are 50 μm wide before being released from the substrate. Figure 2(b) shows the cantilevers after they are actuated for 50 cycles. The residue is the uncleansed acetonitrile solvent solution. It can be seen the longer the cantilevers the more curling the cantilevers are due to the residual stresses, and that the 500 mm long cantilevers can almost loop into a full circle.

Poor adhesion between Au and polypyrrole were reported by Smela et al. (1993), and there were two attempts to improve on the problem. One method was to deposit a thin layer of Ti (500 A) on the Au electrode to act as nucleation cites for the polypyrrole. Another method was to roughen the Au surface with plasma bombardment to increase the interface surface area.

EXPERIMENTAL TESTING AND RESULTS

The actuation testing was carried out on a Karl Suss probe station so that the motion could be recorded. Using a syringe, a few drops of electrolyte solution (0.1M of p-toluenesulfonate in acetonitrile) was applied to the testing area to immerse the structures. Contact of the probes to the electrodes must be assured before applying voltage to avoid vigorous bubbling from occurring. It was observed that to initiate the actuation of the beams it usually is necessary to dope and undope the polypyrrole a few cycles before more visible actuation takes place.

The radius of curvature change due to residual stress in the polypyrrole films were mea-
Figure 1. (a) Fabrication cross-sectional layout of conductive polymer actuated microcantilever, (b) cross-section of microcantilever after sacrificial layer release, cantilever is curled up due to residual stress in the conductive polymer, and (c) SEM micrograph of a completed polyimide/polypyrrole microcantilever that is 500 μm long and 50 μm wide.
Figure 2. (a) An array of microcantilevers with lengths ranging from 200 to 500 μm, and widths 50 and 100 μm. (b) Microcantilevers after release from substrate; the beams curl upward due to residual tensile stress in the polypyrrole. IV curve upon doping and undoping of one array of microcantilevers.
sured by a Tencor FLX-2320 laser system. Ten sample dies were prepared to characterize the residual stress in the polypyrrole thin film. One test sample was simply a silicon die coated with the Ti/Au electrode film. Deposition of polypyrrole were then made with one, two and three cyclic voltammagrams, respectively. These samples provided stress data of as-deposited films. The test samples were then subjected to extensive doping and undoping to determine the relation between the residual dopants and the stress in the films. It must be pointed out that this is not a direct correlation to the actuation stress since diffusion of the dopants after the potential is removed would offset a lot of the stress. The residual stress were calculated from the wafer curvature using a modified Stoney’s equation (Hoffman 1966). Table 1 display the residual stresses ranging from 28MPa to 254MPa tensile. It is interesting to see that the more cyclic voltammagrams(CV) done (i.e., the thicker the film), the less residual stress there is. This may be due to the thicker the films, the more aligned become the polymer backbones, and thus generating more contractile tendency. Using the stress in the film and the radius of curvature as observed in Fig.1, the Young’s modulus of the conductive polymer was estimated to be 3 GPa by the amplitude of displacement during actuation.

Table 1:

<table>
<thead>
<tr>
<th>Residual Stress</th>
<th>MPa (4 CVs)</th>
<th>MPa (3CVs)</th>
<th>MPa (2CVs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>47</td>
<td>135</td>
<td>254</td>
</tr>
<tr>
<td>force doped</td>
<td>28</td>
<td>88</td>
<td>151</td>
</tr>
<tr>
<td>force undoped</td>
<td>142</td>
<td>88</td>
<td>87</td>
</tr>
</tbody>
</table>

The iv curve upon doping and undoping is shown in Figure 3 to illustrate the amount of power involved in the actuation since the current is in fact a function of time. Figure 4(a) and 4(b) illustrates the saturation of doping and undoping over time with a constant applied voltage of 1V. This demonstrates another similarity with muscle contractions that cannot sustain long periods of time. By applying bias voltages ranging from -3V to 3V, the radius of curvature of a 500 μm long beam can change from 150 μm to at least 320 μm. Using the Young’s modulus 3 GPa calculated above, the actuation stress is calculated to be 50 MPa.

The cantilevers were driven dynamically with an AC voltage with a frequency as high as 1.2 Hz and an observed amplitude of 50 μm. For maximum stroke movements, the response time is still between 1-2 secs/rev. One sample was actuated on and off for 1 week before it started to deteriorate, this being with no special preservation steps of the polypyrrole. It is reported that the material will slowly oxidize and affect it’s conducting properties. In the future it is suggested to be stored in a refrigerator and in an inert gas environment (e.g., argon). For thinner polypyrrole layers the electroluminescence property of the conductive polymer shows promise as a dynamic electro-optics device.

SUMMARY

Design, fabrication, and testing of polyimide microcantilevers powered by electrochemical doping was successfully achieved. The Young’s modulus was characterized to be 3 GPa, and the actuation stress generated was calculated to be 100 MPa. Voltages as low as 2-3 volts were applied to generate displacements larger than 100 μm. Since polymer gels can also be applied as
a wide variety of physical sensors, including chemical, biochemical, photonic, temperature, and radiation sensors, it is feasible to create smart microelectromechanical systems. These electromechanical properties make conductive polymers an excellent candidate for artificial micromuscles, since the actuation principle is that of muscle contraction.

Future work points toward using different electrolytes to actuate the conductive polymer to understand the dopant properties required to actuate.

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Figure 4. Time-current plot demonstrating the saturation of doping of electrolyte p-toluenesulfonate.

Figure 5. Time-current plot demonstrating the saturation of undoping of the polypyrrole with p-toluenesulfonate.
REFERENCES


