Polymers as microsensors: Fabrication of electrically conducting Interpenetrating Polymer Networks for temperature sensors

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Abstract

We report on a novel approach to the fabrication of electrically conductive polymer micro sensors, combining direct ultraviolet (UV) laser lithography with an interpenetrating polymer network (IPN). From a combination of Novolak and Terthiophene doped with Copper(II) perchlorate, we manufactured electrically conductive microscopic paths on a glass substrate using a micro pattern generator. We then assessed the structures' impedances at frequencies from 0 to 100 kHz for differently dimensioned cross sections. To evaluate their use as a thermistor, we furthermore investigated the temperature dependence of the impedance in a range of 20 to 100 °C. We suggest such polymers and our approach may be of interest for the fabrication of temperature micro sensors and other applications, particularly when only a limited number of highly specialized sensors is required, e.g. in fire safety infrastructure.

1 Introduction

The production of micro sensors is usually limited to high volumes: Only when the quantity is large enough, production becomes economically feasible. However, some applications require only a few specialized miniature sensors at still reasonable costs. One such example is fire safety infrastructure. Equipped with network-integrated sensors, it can act as a cyber physical system, monitor its operating conditions and provide this information remotely. Yet retrofitting already installed hardware requires almost single-unit production. Therefore, there is a need to develop and produce sensors which can be miniaturized for integration into new and existing infrastructure elements, can be equipped with wireless communication, and can enable cost-efficient small-scale production. A long-term goal is to find novel methods to directly integrate such micro-scale sensor elements with 3D-printing or other fabrication methods like roll-to-roll processing. In addition, we aim to later implement such elements and structures as wireless systems and to combine them with acceleration sensors, gyroscopes and others, to monitor fire protection equipment.

In this paper, we report on our approach to this challenge with polymers and photolithography. We explore a solution to utilize a polymer that is both electrically conductive and can be structured with ultraviolet (UV) light. We have tested it by using a micro pattern generator to manufacture conductive paths and temperature-dependent resistances.

Flexibility and versatility for sensor design and production can be achieved through the use of polymers. They also offer a great potential for micro sensors. Particularly electrically conductive polymers are of interest both to perhaps replace common metal and semiconductor type sensors and for possibly totally new features. [1, 2, 3] Such polymers can provide high flexibility in mechanical properties and allow for optical as well as electro-magnetic functional features. For polymer micro sensors, production technologies like lithography, known, for example, from integrated circuits and micro-electromechanical systems (MEMS), micro 3D printing or micro injection molding offer a large variety of production capabilities. [3, 4] Especially direct UV lithography is a fast and adaptable method to economically fabricate micro elements on a limited scale, making it particularly interesting for prototyping and small-scale production.

Lithography of electrically conductive polymers is a topic of ongoing research. It requires a material which has both electrical properties and polymerizes (or de-polymerizes) under UV radiation. [5] and [6] give in-depth overviews of the current state of the art in functional polymers and photoresists. Some polymers with electrical properties are already in use, some show great promise for future application. Major approaches at the moment use electrically conductive filler materials, for example metals or carbon nanotubes [5, 7, 8]. For the latter, particularly electrically conductive hydrogels have emerged as a topic of interest [9]. In general, the use of such nanocomposite materials, as well as metals or semiconductors, is more complex and requires more extensive fabrication infrastructure. A simpler solution would be of advantage for the small-scale production that we aim at.

An alternative to these nanocomposite materials are interpenetrating polymer networks (IPNs), where two or more different polymers form chemically distinct, yet intermeshed networks. In our case, the goal is to combine the electric conductivity of one polymer and the photolithographic qualities of another. [10] and [11] explored how IPNs can be used as non-insulating photoresists for electron beam lithography. Further investigation into the materials' properties and their optimization was published by [12]. More recently, the idea has been picked up by [13], who are developing thermoelectric devices with IPNs.

It is well established that conductive micro elements can be structured lithographically with a combination of photosensitive and conductive polymers in an IPN. The conductivity of such an IPN is likely to be temperature dependent. We conclude the following hypothesis: IPNs offer means to realize temperature sensors with conductive paths that

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can be flexibly miniaturized and fabricated in a small-scale production with a micro pattern generator. In this contribution, we report on our results of testing this hypothesis. Building on [11], we used Novolak to define the micro structure geometry and Terthiophene (3T) doped with Copper(II) perchlorate hexahydrate for conductivity. With these polymers and a HEIDELBERG INSTRUMENTS µPG101 we produced different test structures to investigate their photolithographic and general electric behavior, their impedance spectra up to 100 kHz, and the relation of resistance and temperature up to 100 °C. Here we present and discuss our first experimental results.

2 Methods and Materials

Experimental procedures were conducted at the Clausthal Centre of Material Technology (CZM) micro systems lab, Clausthal University of Technology.

2.1 Fabrication of IPN structures

For fabrication of the conducting polymer structures, we prepared a monomer solution adopting the method introduced by [11]. 2,2′:5′,2″-Terthiophene (3T), $M_w = 248.39\,\mathrm{g/mol}$, Copper(II) perchlorate hexahydrate ($Cu(ClO_4)_2 \cdot 6H_2O$), $M_w = 370.539\,\mathrm{g/mol}$, and 1-Methoxy-2-propylacetate (MPA or PGMEA), $\rho = 0.98\,\mathrm{g/mL}$, were purchased from SIGMA-ALDRICH. We used Novolak in form of the photoresist ma-N 1405 and ma-D 533/S as the developer (aqueous tetramethyl-ammonium hydroxide (TMAH)-based), both from MICRO RESIST TECHNOLOGY GMBH.

[10, 11, 12] thoroughly describe the relation of chemical compositions and conductivity in this IPN. Drawing from their results, as a start, we chose a mixture of similar proportions to what they suggest as an optimum. For this, we assume all solvents, specifically MPA, and other components from the ma-N 1405 evaporate or react completely, hence we do not consider them in the final product. Respectively, we infer the final micro structures are solely comprised of polymerized Novolak and Terthiophene, the oxidizer and their reaction products. We furthermore assume the ma-N 1405 contains 13.5 wt% (weight percent) Novolak (as stated by the manufacturer).

ma-N 1405 was mixed at a 1:1 mass ratio with a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ and 3T in MPA. The molar ratio of $Cu(ClO_4)_2 \cdot 6H_2O$ to 3T was set to be 1.5. The mass of ma-N 1405 was calculated so that the resulting micro structures would contain the desired wt% of 3T in relation to the total mass of 3T, $Cu(ClO_4)_2 \cdot 6H_2O$ and Novolak. The solutions were stirred with a magnetic stirrer. (Ultrasonic stirring does not work, as the mixture shows a tendency for ultrasonic polymerization).

Regular microscope objective slides (soda-lime glass) were cut to length and used as a substrate. We prepared them by first cleaning them with acetone, then 2-propanol, before holding them at 200 °C for 20 min on a hot plate to desorb H_2O and OH. After this and all other temperature treatments, the samples were left to cool down to room temperature (22 °C) before the subsequent step.

The resist solutions were spin-coated onto the substrates at 3000 rpm for 30 s. The samples were then baked at 45 °C for 120 s to remove the solvent. Next, the IPN films were exposed to UV light (375 nm) with a HEIDELBERG INSTRUMENTS µPG101 micro pattern generator at ca. 4178 mJ/cm^2.

Afterwards, polymerization was completed in a post exposure bake of 90 s at 50 °C. The structures were then developed by immersing the samples in ma-D 533/S for 10 s, then rinsing with de-ionized water and drying with compressed air. A final bake of 120 s at 140 °C was carried out for additional stabilization of the results.

As a test design we used a set of conductive paths with varying widths (5, 10, 50, 100, 500 and 1000 µm) with 1000 µm contacting plates at each end, shown in **Figure 1**.

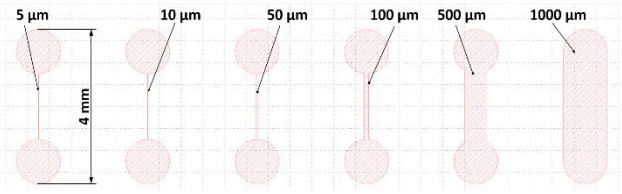

Figure 1 Micro structures as designed for the lithographic process. An array of structures with connecting paths of different widths was chosen to investigate both the photolithographic qualities of the IPN resist as well as its electrical behavior.

2.2 Experimental setup

Since we explore a novel approach to IPN fabrication and similar studies of this material have not yet been published, we first conducted general investigations of its behavior. As a first experiment, we studied the general processability and electrical properties.

Geometric dimensions of the resulting micro elements were measured with a KEYENCE VK-X200K confocal laser scanning microscope (CLSM). After spin coating, structure heights are expected to be mainly a function of resist viscosity and spin coating parameters. However, we additionally observed what appears to be a correlation with structure width. For this reason, we measured each height and calculated the cross section for each conductive path individually.

The measuring setup to investigate electrical properties is depicted in **Figure 2**. Impedance measurements were carried out with a ZURICH INSTRUMENTS AG MFLI Lock-in Amplifier, refit as the MFIA Impedance Analyser with the MFITF Impedance Test Fixture. We adopt a 2-point-4-wire method, where we apply a voltage and measure the resulting current, however only use two contacting probes. For direct current (DC) measuring we used a 2-wire setup and a VOLTCRAFT VC 880 multimeter. Contacting was done directly with the polymer structures, using two gold-plated nickel contact probes with 1.02 mm diameter spherical contacting surfaces.

To investigate the relation of electrical properties and temperature, samples were heated thermoelectrically with a Peltier device which was in direct contact with the rear side of the substrate material, opposite of the sample structures. Structure temperatures were measured with the infrared pyrometer VOLTCRAFT IR 800-20C.

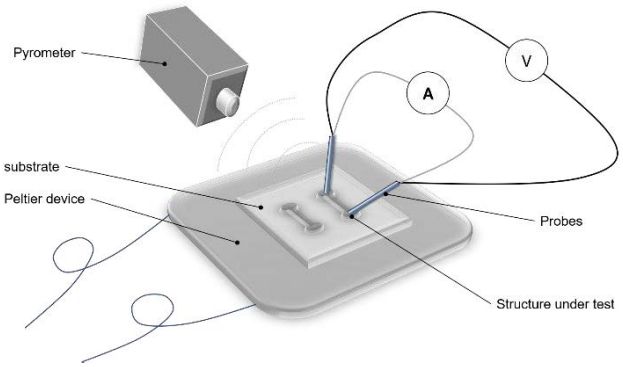

Figure 2 Measuring setup for the investigation of electrical properties of the IPN micro structures. Samples were heated with a Peltier device, temperatures measured with an infrared Pyrometer. Impedance measuring was conducted via a 2-point-4-wires approach, direct current (DC) measuring with 2 points and 2 wires.

We evaluate DC resistance R for different structures with cross sections A. To compare results with other materials and research results, electrical conductivity σ is calculated according to the relation in equation (1), where ℓ represents the distance of the probes, in our case 2.54 mm.

$$\sigma = \frac{1}{R}\frac{\ell}{A} \tag{1}$$

We furthermore investigated the DC resistance of elements under varying temperatures between 20 and 100 °C.
We then studied temperature influences on impedance in the alternating current (AC) frequency range of 500 Hz to 100 kHz, also at temperatures from 20 to 100 °C. The complex Impedance $\underline{Z}$ is calculated from the complex voltage $\underline{V}$ and complex current $\underline{I}$ as

$$\underline{Z} = \frac{\underline{V}}{\underline{I}} = \frac{|V|}{|\underline{I}|} \cdot e^{j(\varphi_V - \varphi_I)} = |Z| \cdot e^{j\varphi}, \tag{2}$$

where j represents the imaginary unit and φ_V and φ_I the phase angles of the sinusoidal voltage and current, respectively, making φ the phase difference of the two. In this publication, impedance spectra are shown in diagrams of $|Z|$ and φ over the frequency f of the impressed current.

3 Results and discussion

Test structures with varying concentrations of 3T and different geometric dimensions were manufactured. **Figure 3** shows one of the samples, IPNs with 11 wt% 3T on a glass substrate. We did observe that an increase of the 3T concentration decreases the solubility. For values below 20 wt%, the lithography seemed generally not strongly affected. However, this remains subject to further investigations.

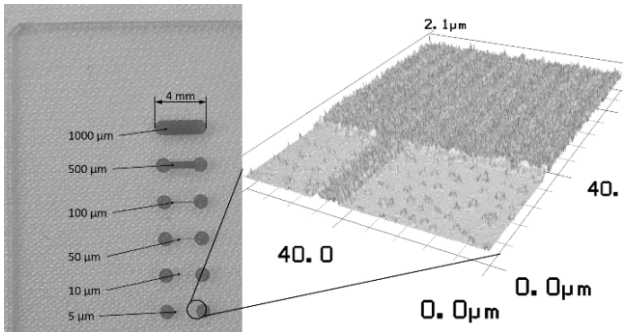

Figure 3 **Left**: Test structures fabricated on a glass substrate from an IPN resist with 11 wt% 3T. The structures very well match the intended design. **Right**: Confocal laser scanning microscope (CLSM) image of one of the structures. Structure height of the 5 µm path was measured to be approximately 174 nm.

[11] state that in their experiments the polymerization of 3T required baking after the UV exposure. They recommend temperatures above 100 °C. However, with our approach utilizing a laser for the UV exposure, which results in a much higher energy dose on the resist, we could show that electrical conductivity is already achieved after the exposure and before any additional baking steps. Assuming that for the IPN structures to be conductive, a network of the 3T is required, we infer the polymerization was in fact induced by the UV laser. Subsequent baking is still expected to improve the micro structures integrity. Nevertheless, this observation could provide an opportunity for streamlining the manufacturing process. What exactly causes the polymerization requires further investigation. Our current hypothesis is, this might be a case of "flash welding" as described by [14], where the laser energy is high enough to either induce polymerization directly, or to cause high enough temperatures on a nanoscopic level, which then in turn starts the polymerization.
CLSM measurements yield varying heights of the conducting path structures. Values were taken in at least 3 locations per structure and for several samples. The resulting averages are listed in **Table 1**.

Table 1 Geometric properties of fabricated test structures.

Structure #	Width in µm	Average Height in nm	Cross section in µm²
1	5	174	0,87
2	10	218	2,18
3	50	292	14,60
4	100	298	29,80
5	500	305	152,50
6	1000	307	307,00

Our IPNs and micro structures exhibit electrical conductivity. For an exemplary 3T content of 11 wt% and a basic, not

yet optimized, fabrication process, we achieved conductivities of 10^1 to 10^2 S/m, which is consistent with the results of [11].

The electrical resistance is a function of the structures' geometry. So far, we realized conductive paths from 1000 µm down to 5 µm (Table 1), the respective resistances range from 16 kΩ to 10 MΩ, see **Figure 4**.

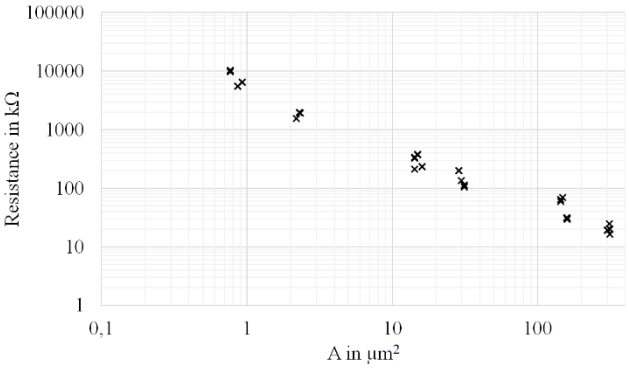

Figure 4 Measured electrical resistance (DC) as a function of the area cross section of IPN micro structures with 11 wt% 3T at 25 °C.

All of the tested samples exhibit clear ohmic behavior for the entire measuring range of excitation frequencies f, from 500 Hz to 100 kHz. As an example, **Figure 5** shows magnitude $|Z|$ and phase φ as functions of frequency for one sample at different temperatures. There is basically no phase difference between voltage and current and the impedance magnitude remains constant. At very high frequencies, the phase differences start to change slightly. We assume this is due to our measuring setup, most likely parasitic influences of cables and the measuring probes (see Figure 2 for setup). With rising temperature, the resistance decreases.

Figure 6 shows how the impedance of a micro structure changes for one cycle of heating to 100 °C and letting it cool back down to room temperature (example at $f = 1000$ Hz). For this case and in the shown range, the relation of temperature and resistance is almost linear. Sensitivity S, the ratio of change in resistance ΔR to change in temperature ΔT, is

$$S = \frac{\Delta R}{\Delta T} \approx -310 \frac{\Omega}{\mathrm{K}}. \quad (3)$$

This would already be sufficient to act as a temperature-sensing element.

In some cases, samples exhibit a significant shift of the impedance magnitude during successive heating and cooling cycles. An example of this is shown in **Figure 7**, where impedance values for each temperature vary from cycle to cycle. The cause of this needs to be investigated through additional experiments. An explanation might be, that some IPNs were not yet fully chemically inert. Heating them has then probably affected the molecular structure and thus the impedance. To prevent such effects, elements can possibly be brought to a stable and inert state via cyclic heating and cooling.

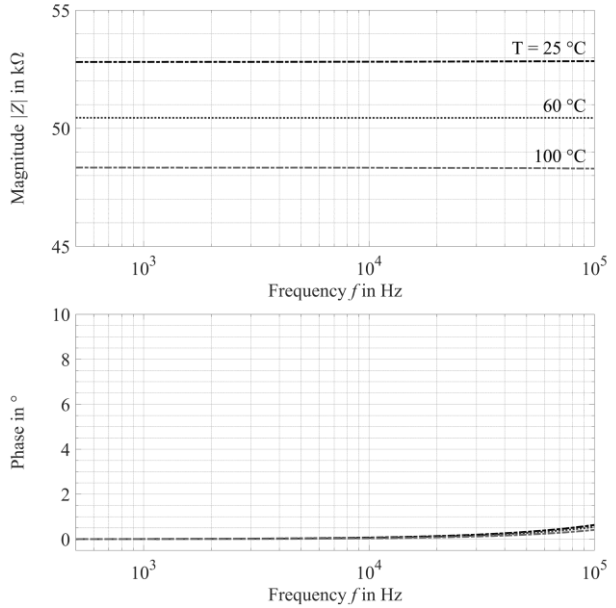

Figure 5 Impedance spectra of an IPN micro structure (11 wt% 3T, width 1000 µm) in the range of 500 Hz to 100 kHz for 25, 60 and 100 °C. The structure shows nearly ohmic behavior at all temperatures and frequencies. An increase in phase at high frequencies is attributed to the measuring setup.

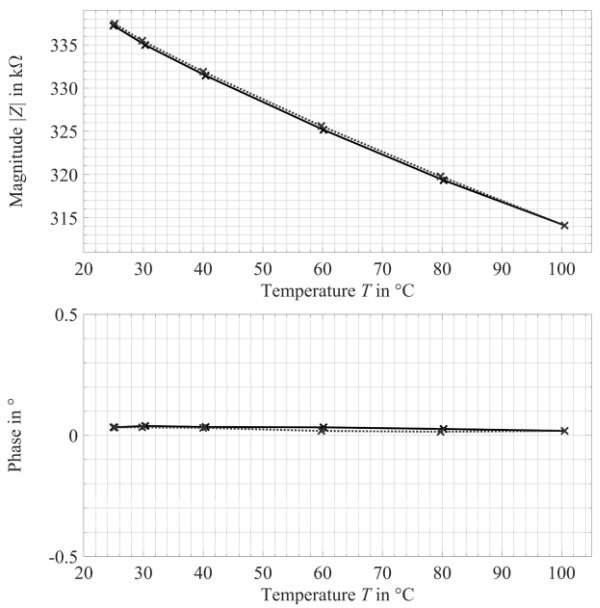

Figure 6 Impedance of an IPN micro structure (11 wt% 3T, width 100 µm) at 1000 Hz for varying temperatures. The phase remains negligible at all temperatures, so impedance is nearly ohmic. Occurring small phase differences are attributed to the measuring setup. Resistance shows a distinct dependence on temperature. The average resistance sensitivity of this sample is $S = -310\ \Omega/\mathrm{K}$.

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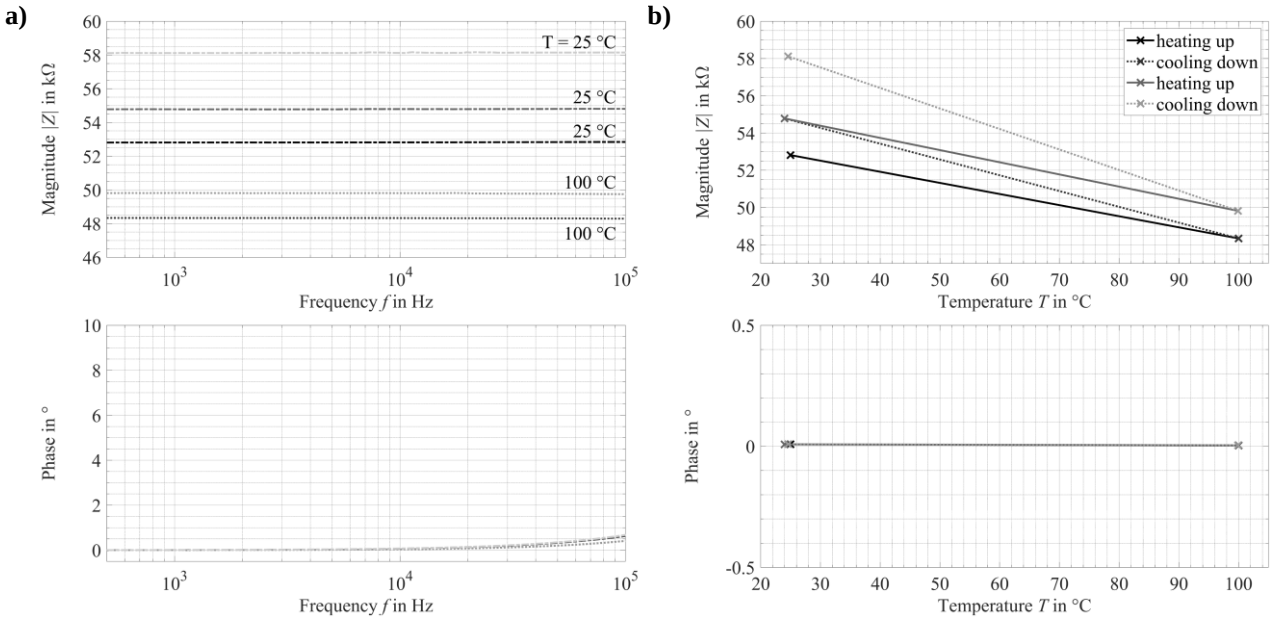

Figure 7 a) Impedance spectra of an IPN micro structure (11 wt% 3T; conductive path width 1000 µm) at different points of several cycles of successive heating and cooling. For this sample, the magnitude of the impedance undergoes a significant shift towards higher values. **b)** Impedance over temperature for the same sample at $f = 1000$ Hz.

4 Conclusions and perspectives

We successfully demonstrated the fabrication of electrically conductive polymer micro structures with direct laser lithography and interpenetrating polymer networks (IPNs). Our investigations show that IPNs from Novolak and Terthiophene exhibit a nearly ohmic behavior and their resistance has a significant reaction to changes in temperature, which makes them interesting for the use as temperature sensors. Samples with a content of ca. 11 wt% Terthiophene show conductivities of 10^1 to 10^2 S/m. A test structure of width 100 µm, height 298 nm and length 2.54 mm has a resistance sensitivity to temperature changes of ca. $-310\,\Omega/\mathrm{K}$.

We can reliably fabricate test samples with varying contents of 3T and different dimensions in the micro range. Additionally, the overall production process which we describe is fairly simple and does not require a lot of infrastructure, mainly a spin coater and a micro pattern generator in a relatively clean environment. It is furthermore very accessible to changes, for example, of the structures' design. Our research shows IPNs may be an integral part of future sensor designs and an important step towards our long-term goal of purpose-built integrated polymer micro sensors for cyber physical systems.

As a next step, we will work on optimizing the fabrication process and implementing our micro structures into geometrically matched housings to demonstrate the potential of combining direct laser lithography with 3D printing. Furthermore, we are going to explore the physical behavior of the IPNs and their long-term stability against aging. It will also be interesting to explore possible different sensor applications of the IPN material, where our main interest are optoelectronic devices for optical micro sensors.

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