Doctoral Thesis

Experimental methods for evaluating the mechanical properties of thin layers of intrinsically conductive polymers

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Experimental Methods for Evaluating the Mechanical Properties of Thin Layers of Intrinsically Conductive Polymers

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presented by

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2008
Acknowledgments

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- my co-examiner Prof. Dr. Ralph Spolenak for very interesting and stimulating discussions especially on the AFM experiments.
- my co-examiner Dr. Andreas Elschner for taking the time to receive me at the H. C. Starck branch in Leverkusen on several occasions to thoroughly discuss morphological issues of PEDOT:PSS.
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- Dr. Elisabeth Müller from the EMEZ of ETH Zürich for running extensive TEM, HAADF-STEM and X-ray analysis on PEDOT:PSS thin films which allowed for a direct glance at the PEDOT:PSS morphology at a nanometer scale.
- Dr. Nicola Naujoks for AFM scans of fracture surfaces which allowed for the development of a micromechanical deformation model of PEDOT:PSS.
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  - Marcel Reichen was the first to experience my clean room drill. In his work he developed the process to fabricate freestanding polyimide specimens.
  - Fabian Risch could show the proof of concept for a biaxial microtensile test.
– Zoltán Nagy conducted FEM simulations on Si double fixed beams.
– Norman Juchler programmed a remote control script which allowed to access the microscope Zeiss LSM 5 from any other lab computer.
– Philipp Rüist developed a lift off process to structure PEDOT:PSS. Furthermore he designed a bulge test setup which allowed for the determination of the strain gauge factor of PEDOT:PSS and showed the sensor potential of the material.
– Last but not least Nina Wojtas and Tobias Süss who first worked on tensile tests with in situ AFM and then helped fabricate and tensile test single layer PI and bilayers of PI and PEDOT:PSS.


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Abstract

Organic electronic devices based on intrinsically conductive polymers and organic semiconductors have reached a mature status and are therefore starting to be introduced to the electronics consumer market, e.g. in flexible displays and radio frequency identification tags (RFID tags). A key property of these devices is their potential flexibility which raises the question of mechanical properties of these organic materials.

Hence, the main goal of this thesis is to provide a toolbox of different methods which allow for the determination of the most important mechanical properties such as Young’s modulus, tensile strength and yield strength and also electromechanical properties like the strain gauge factor of thin organic layers. The main challenge when testing thin layers of organic materials are their considerably lower Young’s moduli which are in the range of only a few GPa. For this reason sensitive measurement principles have to be developed. Additionally, thicknesses of functional layers in actual devices are in the range of micrometers and below. Freestanding organic test structures should therefore be in the same range which is a difficult microfabrication task. The methodologies presented in this thesis bear furthermore in mind that many different materials are used in organic electronics and therefore also the fabrication process flow and the testing approaches must be open for different organic materials. As a model material, in this thesis the intrinsically conductive polymer poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) is chosen. It is widely used in organic electronic devices and commercially available as an aqueous dispersion under the trade name Baytron P (H.C. Starck GmbH, Leverkusen, Germany).

Firstly a fabrication process based on laser-cutting to pattern freestanding 25 μm thick tensile specimens made of PEDOT:PSS is presented. Preliminary tensile tests then show that relative humidity strongly influences the mechanical behavior of the hygroscopic PEDOT:PSS. In a next step the tensile setup is installed in a climate chamber and the mechanical properties of PEDOT:PSS are subsequently systematically investigated in dependence of relative humidity. Thereafter a floating off process to yield freestanding 25 nm thick specimens for electron microscopy investigations is presented. Transmission electron microscopy (TEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) are then used to explore the morphology of the 25 nm thick film. The morphological model currently accepted in literature is based on particles with a mean size between 50 to 80 nm forming the layer. This model can be confirmed with the aforementioned methods. Additionally from high Na and Ca contents in the shell of the particles determined by energy dispersive X-ray analysis (EDX), a higher PSS content as compared to the core can be inferred. This is also in agreement with the currently accepted morphological model. In an additional step the fracture surfaces of 25 μm thick tensile specimens ruptured at different relative humidities are investigated. The AFM scans permit to develop a micromechanical model which explains the behavior under different relative humidities and is based on transgranular and intragranular fracture.

As functional layers in actual devices are in the range of hundreds of nanometers, thicknesses of tensile specimens should also be in the same range. In a first step, a microfabrication process to obtain freestanding 1 μm and 3 μm thick PI films is presented. Then this process is used to fabricate microtensile specimens which are connected at their ends to two double fixed beams. Upon exerting an external force on the first double fixed beam, the specimen and the second beam, the force sensing beam, are deformed. By using beam mechanics the force acting on the beam and the specimen can then be determined. These specimens are subsequently tested in a newly developed setup for in situ atomic force microscopy (AFM). First experiments with PI specimens with a single notch show that the crack propagation can be monitored with micrometer resolution and the force acting on the specimen can be determined with a resolution of about 0.012 N. Scanning electron microscopy
Abstract

(SEM) fractographs subsequently reveal the processes of brittle fracture in the crack area and of shear banding in its vicinity.

Then a microtensile specimen is presented which is based on the idea of testing bilayers composed of a polyimide (PI) substrate and a functional layer on top. PEDOT:PSS is chosen again as the model material and patterned by a lift-off process. To begin with, two microtensile tests are conducted on pure PI films of 3 μm thickness to obtain Young’s modulus of the substrate material. The strain and the force sensing beam deflection are evaluated by digital image correlation (DIC) of sample images taken by an optical microscope and a microscope camera. Young’s moduli of 2.4 GPa and 3.3 GPa can thus be derived. Further experiments then include a PEDOT:PSS layer with approx. 500 nm thickness on top of the PI substrate. By using a simple mechanical model which allows to differentiate between substrate and film the Young’s modulus of the PEDOT:PSS can be determined to be about 6 GPa. This is about twice as high as for 25 μm thick films, might be due to substrate or size effects and requires further experiments to confirm this value and to identify possible reasons.

In a last setup prototypes of pressure sensors made from a PI membrane and PEDOT:PSS stripes on top of it are proposed. First experiments show the proof of concept, i.e. defined changes of resistance upon defined pressure changes. By using membrane mechanics the strain gauge factor of PEDOT:PSS deposited on PI can then be determined to be in the order of about 0.8.

In summary, a toolbox of methods to comprehensively characterize the mechanical properties of intrinsically conductive polymers is presented. Future test series could be based on these methods and allow for the determination of statistically relevant data for mechanical properties.
Zusammenfassung

Elektronische Bauteile aus organischen Materialien, die auf intrinsisch leitfähigen Polymeren beruhen, haben die Marktübersicht erreicht und werden daher zunehmend in Produkten, wie z.B. Bildschirmen oder Funketiketten, eingesetzt. Ein entscheidendes Kriterium dieser Bauteile ist ihre potentielle Biegefähigkeit, die Fragen nach den mechanischen Eigenschaften der verwendeten organischen Materialien aufwirft.


Wie oben erwähnt befinden sich die Schichtdicken funktionaler Filme in tatsächlichen Bauteilen vorwiegend im Bereich weniger Hundert Nanometer. Mikrozugproben sollten daher ebenfalls diese Dicken aufweisen. In einem ersten Schritt in diese Richtung wird daher zunächst ein Mikrobefrakationsprozess präsentiert, der die Herstellung 1 und 3 μm dicker freistehender Polyimid (PI) Filme erlaubt. Dieser Prozess wird dann zur Fakturaion von Zugproben, die an ihren Enden mit Doppelballen verbunden sind, angewandt. Werden die Doppelbalken und die Zugprobe mit einer externen Zugkraft belastet, so werden die Balken und die Zugprobe deformiert. Mithilfe der Balkenmechanik lässt sich die Kraft, die diese Deformationen hervorgerufen hat, berechnen. Die Zugproben wer
Zusammenfassung


In einem letzten Aufbau werden Prototypen von Drucksensoren, die aus einer PI Membran und darauf abgeschiedenen PEDOT:PSS Streifen bestehen, vorgestellt. Erste Experimente bestätigen die Richtigkeit des Ansatzes, indem für definierte Druckwechsel auch definierte Änderungen der Streifenwiderstände gemessen werden können. Durch Anwendung von membranmechanischen Modellen lässt sich der piezoresistive Koeffizient von PEDOT:PSS in Höhe von etwa 0.8 bestimmen.

Zusammenfassend lässt sich sagen, dass die vorgestellten Methoden eine umfassende mechanische Charakterisierung intrinsisch leitfähiger Polymere erlauben. Zukünftige Experimente können darauf aufbauen und erlauben so eine statistisch abgesicherte Ermittlung mechanischer Eigenschaften.
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP</td>
<td>intrinsically conductive polymers</td>
</tr>
<tr>
<td>RFID</td>
<td>radio frequency identification</td>
</tr>
<tr>
<td>PI</td>
<td>polyimide</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>poly (3,4-ethylenedioxythiophene) poly (styrenesulfonate)</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>EDX analysis</td>
<td>energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light emitting diode</td>
</tr>
<tr>
<td>OTFT</td>
<td>organic thin film transistor</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>HAADF-STEM</td>
<td>high angle annular dark field (HAADF) scanning TEM</td>
</tr>
<tr>
<td>DIC</td>
<td>digital image correlation</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscopy</td>
</tr>
<tr>
<td>WLI</td>
<td>white light interferometer</td>
</tr>
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<table>
<thead>
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<th>Symbol</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>$r$</td>
<td>radius of gyration</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s constant</td>
</tr>
<tr>
<td>$M$</td>
<td>molecular weight of PEDOT:PSS</td>
</tr>
<tr>
<td>$y$</td>
<td>beam deflection</td>
</tr>
<tr>
<td>$h$</td>
<td>beam height</td>
</tr>
<tr>
<td>$L$</td>
<td>half length of double fixed beam</td>
</tr>
<tr>
<td>$P$</td>
<td>load</td>
</tr>
<tr>
<td>$N$</td>
<td>normal force</td>
</tr>
<tr>
<td>$E$</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>$I$</td>
<td>area moment of inertia</td>
</tr>
<tr>
<td>$M_b$</td>
<td>bending moment</td>
</tr>
<tr>
<td>$M_0$</td>
<td>bending moment at clamping</td>
</tr>
<tr>
<td>$A$</td>
<td>cross sectional area in general</td>
</tr>
<tr>
<td>$A_c$</td>
<td>beam cross sectional area</td>
</tr>
<tr>
<td>$f$</td>
<td>maximum beam deflection</td>
</tr>
<tr>
<td>$\Delta f_i$</td>
<td>beam deflections due to residual stresses</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>$F_{res}$</td>
<td>force due to residual stresses after dry etching</td>
</tr>
<tr>
<td>$F_{res, dep}$</td>
<td>force due to residual stresses after deposition</td>
</tr>
<tr>
<td>$F_{relief}$</td>
<td>reduction of force due to stress relief</td>
</tr>
<tr>
<td>$F_0$</td>
<td>force acting on substrate</td>
</tr>
<tr>
<td>$F_m$</td>
<td>measured force at $\varepsilon_0$</td>
</tr>
<tr>
<td>$l_0$</td>
<td>length of specimen after deposition</td>
</tr>
<tr>
<td>$l_1$</td>
<td>length of specimen after dry etching</td>
</tr>
<tr>
<td>$K_{IC}$</td>
<td>critical stress intensity factor</td>
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<tr>
<td>$x$</td>
<td>area fraction</td>
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<td>$p$</td>
<td>pressure</td>
</tr>
<tr>
<td>$w$</td>
<td>membrane deflection</td>
</tr>
<tr>
<td>$w_0$</td>
<td>membrane deflection at center of membrane</td>
</tr>
<tr>
<td>$t$</td>
<td>membrane thickness</td>
</tr>
<tr>
<td>$a$</td>
<td>membrane width</td>
</tr>
<tr>
<td>$b$</td>
<td>membrane length</td>
</tr>
<tr>
<td>$R$</td>
<td>resistance</td>
</tr>
<tr>
<td>$k$</td>
<td>strain gauge factor</td>
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<tr>
<td>$k_{PS}$</td>
<td>plane strain gauge factor</td>
</tr>
<tr>
<td>$V$</td>
<td>voltage</td>
</tr>
<tr>
<td>$V_0$</td>
<td>supply voltage</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of PEDOT:PSS</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>normal stress</td>
</tr>
<tr>
<td>$\sigma_{xx}$</td>
<td>normal stress in x direction</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>residual stress</td>
</tr>
<tr>
<td>$\sigma_{max}$</td>
<td>maximum normal stress</td>
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<tr>
<td>$\tau$</td>
<td>shear stress</td>
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<tr>
<td>$\tau_{max}$</td>
<td>maximum shear stress</td>
</tr>
<tr>
<td>$\tau_{crit}$</td>
<td>critical shear stress for plastic deformation</td>
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$\sigma_{res,dep}$</td>
<td>residual stress after deposition</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>strain</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>given strain for determination of film stress</td>
</tr>
<tr>
<td>$\varepsilon_{xx}$</td>
<td>strain in x direction</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson's ratio</td>
</tr>
<tr>
<td>$\beta$</td>
<td>change of resistive properties under strain</td>
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1 Introduction

In general polymers are non-conductive materials. However, in the end of the 1970s researchers succeeded in doping polyacetylene (polyethylene) with oxidants (iodine) which resulted in intrinsically conductive polyacetylene i.e. polyacetylene could conduct electrical current without any fillers such as silver or carbon particles. For this discovery Alan J. Heeger, Alan G MacDiarmid, and Hideki Shirakawa were awarded the Nobel prize in chemistry in 2000. Their work triggered the completely new field of research of intrinsically conductive polymers (ICP) and led to the development of organic electronic devices. Very promising examples of such devices are radio frequency identification tags (RFID tags) and organic displays. Fully organic RFID tags have been introduced in the market in fall 2007 by the company PolyIC (Erlangen, Germany). Figure 1.1 shows their fully organic electronic device. Another interesting device was announced in the end of 2007 by Philips Polymer Vision (Eindhoven, The Netherlands). The company developed a cell phone with an integrated rollable 5 inch display (see Figure 1.2). The two examples already show a key property and major advantage of these devices over inorganic devices: it is the possibility to fabricate them on flexible substrates. From an engineering point of view this raises the question of mechanical reliability. In this thesis a toolbox of methods to characterize the mechanical properties of ICPs is presented. The main challenge when testing thin layers of organic materials are their considerably lower Young’s moduli which are in the range of only a few GPa. For this reason sensitive measurement principles have to be developed. Additionally, thicknesses of functional layers in actual devices are in the range of micrometers and below. Freestanding organic test structures should therefore be in the same range which is a difficult microfabrication task. The methodologies are developed bearing furthermore in mind that many different materials are used in organic electronics and therefore also the fabrication process flow and the testing approaches must be open for different organic materials.

To begin with, in this chapter the fundamentals of conductance in organic materials are developed, followed by the presentation of the basic properties of the polymers under investigation in this thesis, the polyimide (PI) PI2723 (H.D. Microsystems Europe GmbH, Bad Homburg, Germany) and poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, H.C. Starck GmbH, Leverkusen, Germany). Chapter 2 then begins with the fabrication process of freestanding PEDOT:PSS tensile specimens with thicknesses in the range of 25 µm. Then a setup for tensile testing at different relative humidities and preliminary results of mechanical properties of PEDOT:PSS are presented. In the second part of the chapter the complete mechanical characterization in dependence of relative humidity is shown followed by comprehensive morphological studies. These studies lead to a deformation model which might fully explain the mechanical behavior of PEDOT:PSS. The following chapter 3 first contains a presentation of a wafer level process to fabricate freestanding specimens with thicknesses down to 1 µm. These samples made from polyimide PI2723 are then strained using a microtensile test with in situ atomic force microscopy (AFM) scans of the deformed surface. As the samples are fabricated with a notch on one side crack propagation in the material can be analyzed with micrometer resolution. In the second part of chapter 3 microtensile tests of thin PI samples and bilayers made of PI and PEDOT:PSS are presented. The contents of chapter 4 are firstly the development of a lift-off process for microstructuring of PEDOT:PSS. Secondly, based on this process, pressure sensors made from PEDOT:PSS on a PI membrane are presented and the strain gauge factor of PEDOT:PSS is derived.
1 Introduction

Figure 1.1: Fully organic printed RFID tag. Official press picture from PolyIC GmbH & Co.KG (2007, Erlangen, Germany)

Figure 1.2: Fully organic and flexible 5 inch gray-scale display. Official press picture from Philips Polymer Vision (2007, Eindhoven, The Netherlands)
1.1 Conductance in Polymeric Materials

The explanations in this section closely follow the outline of conductance in organic materials given in [1]. For further reading, a comprehensive and clear overview of this subject can also be found in [2]. In conductors (e.g., a metal) the conduction band is only partially filled (see Figure 1.3a) and electrons are therefore delocalized and highly mobile under an applied electrical field. In insulators however, there is a large bandgap between the valence and the conduction band. This bandgap is too large for thermal activation and thus no electrons from the valence band can enter the conduction band (see Figure 1.3b). Hence under an applied electrical field there is no current. Semiconductors do also have a bandgap but it is small enough for electrons to get into the conduction band by thermal activation. This is also true for polyacetylene which if pure is a semiconductor. This is based on the fact that its chain consists of conjugated bonds i.e. there are alternating single and double bonds (see Figure 1.4a). These conjugated bonds in a macromolecule form the valence band: in chemists' language the top of the band is called the HOMO or highest occupied molecular orbital. In a same way the bottom of the conduction band is called the LUMO or lowest unoccupied molecular orbital. In polyacetylene it corresponds to the delocalized electron system or metallic state along the chain. At room temperature pure polyacetylene is not in its metallic but semiconducting state due to the Peierls transition [2]. The whole situation changes fundamentally if a dopant such as $J_2$ is added. Iodine will remove an electron from the polyacetylene chain under forming of $J_1$ and a radical cation ("positive polaron") as shown in Figure 1.5. Due to Coulomb attraction between the iodide ion and the radical polaron the charge can not move freely along the chain but has very low mobility. It is therefore a localized defect. However, if the dopant concentration is high the mobility is increased as the defect could move from counterion to counterion. But doping leads to an additional effect: to states in the bandgap between valence and conductance band – to so called midgap states. Figure 1.3c) shows how for a positive polaron one midgap state is occupied by the dangling electron. Furthermore the higher the dopant concentration the more the number of midgap states. Figure 1.6 shows how then the lower states in the midgap are occupied. The arrow indicates how an electron could hop to an unoccupied state. The horizontal component of the arrow signifies the local distance between the two states while the vertical one represents the energetic distance. Thus energetic distance mostly is upward and hence assistance from phonons is necessary. Phonons are readily available at higher temperature which means that the whole hopping process is thermally activated. At lower temperatures the phonons freeze and the electrons have to do longer hops. This gave the model its name: variable range hopping. Electrons could not only hop on one chain (intra-chain conductivity) but could also get to midgap states on other chains (inter-chain conductivity). The sum of the two then yields the overall conductivity. This model explains the experimental data of conjugated polymers fairly well and is therefore commonly accepted.

![Figure 1.3: Schematic of band states: a) conductive material, b) insulator, c) radical cation with midgap states. Each line represents an orbital which could be occupied by two electrons with opposite spin.](image-url)
1 Introduction

Figure 1.4: Polyaniline: a) in its semiconducting state with conjugated bonds, b) in its metallic state with delocalized electrons.

\[ J \]

Figure 1.5: Radical cation. The positive charge is localized due to Coulomb attraction from the iodide counterion.

1.2 Polymers under Investigation

1.2.1 PEDOT:PSS

In the 1990s, researchers at the Bayer AG (Leverkusen, Germany) developed a polythiophene derivative named poly(3,4-ethylenedioxythiophene), abbreviated PEDT or PEDOT. It exhibited very interesting properties: high conductivity (up to 300 S/cm), it was almost transparent as a thin film and was very stable in its oxidized state [3]. The major drawback was its insolvability. This problem could be solved with the water-soluble polyelectrolyte poly(styrene sulfonic acid), which acted as the charge balancing dopant during polymerization. This resulted in the ionic complex of PEDOT:PSS (see Figure 1.7). The PSS chain has a molecular weight (MW) of about 400,000 while the individual PEDOT segments do have a MW of about 1000-2500 which corresponds to 6-18 repeating units. The overall mass ratio for Baytron P is 1:2.5 for PEDOT to PSS. The oxidizing agent used in the synthesis of PEDOT:PSS is Na₂S₂O₈. This explains why Na could be found by EDX analysis in thin films of PEDOT:PSS (see section 2.2.5). Further details on the chemical synthesis can be found in [3, 4]. The reaction yields a dark blue dispersion which is commercially available from H.C. Starck GmbH (Leverkusen, Germany) under the tradename Baytron P. In recent years it has found numerous applications. Among these are antistatic coatings of photographic films to avoid electrostatic discharge, counter electrodes in electrolyte capacitors, conductive layers in all-organic thin film transistors or hole transport layers in organic light emitting diodes. An overview can be found in [4]. The general physical properties of Baytron P dispersion and solid PEDOT:PSS thin films are finally listed in Table 1.1.

Figure 1.6: Variable Range Hopping. Electrons can hop (tunnel) to others of the midgap states (arrow). The horizontal component of the arrow represents the distance and the vertical one indicates the energy necessary.
1.2 Polymers under Investigation

<table>
<thead>
<tr>
<th>State</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baytron P</td>
<td>Colour</td>
<td>dark blue</td>
</tr>
<tr>
<td></td>
<td>solid content</td>
<td>1.2 to 1.4%</td>
</tr>
<tr>
<td></td>
<td>Na content</td>
<td>500 ppm</td>
</tr>
<tr>
<td></td>
<td>mean size of water swollen gel-particles</td>
<td>≈ 80 nm</td>
</tr>
<tr>
<td></td>
<td>PEDOT:PSS ratio</td>
<td>1.25</td>
</tr>
<tr>
<td>solid PEDOT:PSS</td>
<td>conductivity</td>
<td>max. 10 S/cm</td>
</tr>
<tr>
<td></td>
<td>minimum surface resistance</td>
<td>300 ohms/square</td>
</tr>
<tr>
<td></td>
<td>refractive index</td>
<td>1.528 at 20°C</td>
</tr>
</tbody>
</table>

**Table 1.1:** Overview of the physical properties of Baytron P dispersion and solid PEDOT:PSS layers (from [4]).

![Primary structure](image1)

**Figure 1.7:** Primary, secondary and tertiary structure of the ionic complex of PEDOT:PSS (from [4]). The hydrophilic PSS has to fulfill two functions: firstly it serves as counterion for the hydrophobic PEDOT segments and secondly it enables PEDOT:PSS to become a stable microdispersion. The gel particles have a mean diameter of about 80 nm with the overall diameters ranging from about 20 to 200 nm.
1 Introduction

1.2.2 PI2723

Polyimides are widely used in microelectronics as passivation (i.e., protection) layers. They protect microelectronic circuits from moisture, corrosion, ion transport, and damage during packaging. Another field of application are stress buffer layers. Polyimide films absorb mechanical and thermal stresses imposed on silicon dies during packaging. As modern microelectronic chips are composed of several layers there is also a need for dielectrics which planarize surface irregularities for subsequent lithography steps. Polyimides are also well suited to fulfill this goal. In all of the aforementioned applications it is often necessary to pattern the polyimide layer. Conventional polyimides are microstructured by oxygen plasma which requires an additional photoresist layer as an etch mask. This can be circumvented by directly photodefinable polyimides which were introduced by HD Microsystems (Wilmington, USA) in the mid 1990s. The basic processing principle is that upon exposure photosensitive sidegroups of a soluble polyimide precursor crosslink and thus render exposed areas insoluble. After developing (i.e., dissolving unexposed areas) the remaining polyimide is then fully imidized by a thermal cure. A detailed description of these steps is given in [6]. There also values for physical properties of 10 μm thick PI2720 polyimides (PI2723 belongs to the PI2720 product family) on 500 μm thick silicon wafers are presented. Table 1.2 shows some of these properties that are of interest in this thesis.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>rupture strength</td>
<td>100 MPa</td>
</tr>
<tr>
<td>total strain at break</td>
<td>10%</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>2.7 GPa</td>
</tr>
<tr>
<td>residual stress</td>
<td>42 MPa</td>
</tr>
<tr>
<td>glass transition temperature</td>
<td>above 320°C</td>
</tr>
<tr>
<td>melting point</td>
<td>none</td>
</tr>
<tr>
<td>decomposition temperature</td>
<td>550°C</td>
</tr>
<tr>
<td>CTE</td>
<td>$5.7 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>thermal conductivity</td>
<td>$3.7 \cdot 10^{-5}$ cal/(cm·s·°C)</td>
</tr>
<tr>
<td>specific heat</td>
<td>0.36 cal/(g·°C)</td>
</tr>
</tbody>
</table>

Table 1.2: Physical Properties of the PI2720 product family (from [6]).
2 Tensile Testing of Freestanding PEDOT:PSS Films

2.1 Preliminary Results

2.1.1 Abstract

In recent years there have been vast efforts to establish organic electronic devices. A key property of such devices is the possibility to fabricate them on flexible substrates. As the layers are mechanically stressed during bending, the knowledge of mechanical properties of the materials used will become very important. In this research the mechanical properties of the intrinsically conductive and widely used polymer PEDOT/PSS were investigated using a micro tensile test setup. The tensile tests showed values for Young’s Modulus in the range from 1 GPa to 2.7 GPa, for the tensile strength in a range from 25 MPa to about 55 MPa and for the total strain at break between 3% and 5%, all of them depending on relative humidity.

2.1.2 Introduction

In recent years there have been vast efforts to establish electronic devices based on organic materials. A key property of such devices besides the easy and cheap fabrication is the possibility to fabricate them on flexible substrates. As the layers are mechanically stressed during bending, the knowledge of mechanical properties and reliability of the materials used will thus become very important. At the Center of Mechanics at ETH Zurich a tensile test set-up had already been established and applied to the experimental examination of mechanical properties of thin single crystal silicon specimen [8] and of size effects in thin copper foils [9,10]. It was decided to also use this set-up for the investigations presented in this paper. As there is a wide variety of materials used in polymer electronics, PEDOT/PSS was chosen due to its widespread applications such as in organic light emitting diodes (OLED) [11,12] and organic thin film transistors (OTFT) [13,14]. Furthermore it is readily commercially available from H.C. Starck GmbH & Co.KG in Leverkusen, Germany under the tradename Baytron P.

2.1.3 Methodology

The first step of the fabrication of the specimens was pipetting the dispersion on a substrate and letting it air dry at ambient conditions in a clean room (T=24°C, rH=50%). This resulted in a solid layer of about 25 μm thickness. As single layer specimens ought to be investigated, manual peeling off the specimens from the substrate was considered as the next step. As Baytron P is a waterborne dispersion, a hydrophobic substrate had to be used and polystyrene (PS) petri dishes were chosen. After letting air dry the dispersion the resulting solid film could be peeled off and was then glued at its borders to a glass wafer using scotch tape. Then laser cutting of the layers was used since it is a reproducible, exact and readily available technology. Furthermore it is a "dry" technique which prevents the layer from being altered in solvents or even dissolved in waterborne solutions. Figure 2.1 shows the sidewalls of a cut specimen. Even though it is not exactly straight but has indentations this is not a problem since they are evenly spread along the specimen. Hence the distribution of forces within the material is not disturbed and therefore no stress concentrations

---

1Reference [7]
have to be expected. The overall fabrication process with parameters is summarized in Figure 2.2. The shape of the specimen (Figure 2.3) was given in an international norm [15] and scaled down by a factor of 4 as allowed therein. The width of the specimen was measured using a Zeiss LSM 5 Pascal optical microscope with a resolution limited by the optical system (about 0.5 μm) and the thickness was determined by using a CaryCompas profilometer with a resolution of 0.1 μm. Details of the tensile test set-up are described in a previous paper [16] so here only a brief overview is given. One end of the specimen is attached to the stage which is actuated by a step motor while the other end is attached to a weight. This weight is on a precise balance (Precisa 1212 M) with a resolution of 1 mg. By actuating the step motor the weight is gradually lifted from the balance and therefore the mass measured by the balance is reduced. This reduction is a direct measure of the force acting on the specimen. As mentioned before the dimensions of the specimen are known and therefore the stress in the specimen can be calculated. The strain is measured using a CCD camera and an algorithm (least square template matching) with sub pixel resolution [8]. The experiments in [16] showed a strong dependency of the mechanical properties of PEDOT/PSS on relative humidity. Therefore for the experiments described in this paper the whole set-up was moved into climate chamber (CTS -40/200, Figure 2.4) and tests were conducted at different relative humidity (4 samples at 25% rH, 5 samples at 40% rH and 4 samples at 55% rH with all the samples from two different PEDOT/PSS foils) but constant temperature (22°C). Based on the results in [16] the specimens were conditioned under the respective relative humidity for 30 minutes prior to testing.

![sidewall roughness caused by lasercutting](image)

**Figure 2.1:** Image of side face of a specimen. Each indentation is caused by a single laser pulse.

<table>
<thead>
<tr>
<th>Step</th>
<th>Sketch</th>
<th>Description</th>
<th>Step</th>
<th>Sketch</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Sketch" /></td>
<td>• 15 ml of BAYTRON P were pipetted on the PS Petri dish</td>
<td>3</td>
<td><img src="image" alt="Sketch" /></td>
<td><img src="image" alt="Fabrication on a commercial laser type LASAG FLX 352" /></td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Sketch" /></td>
<td>• 24 hours drying time at ambient conditions in clean room (T=24°C, RH=50%) • Final thickness of solid layer is approx. 25 μm</td>
<td>4</td>
<td><img src="image" alt="Sketch" /></td>
<td><img src="image" alt="Fabrication on a commercial laser type LASAG FLX 352" /></td>
</tr>
</tbody>
</table>

**Figure 2.2:** Process flow for the fabrication of the tensile specimen.
2.1 Preliminary Results

Figure 2.3: Dimensions of specimen in mm as outlined in [15].

Figure 2.4: Tensile test setup in climate chamber.
2.1.4 Results

The preliminary results in [16] which showed that the mechanical properties of PEDOT/PSS strongly depend on relative humidity could be confirmed in this study. Firstly Figure 2.5 shows the results for Young’s Modulus. It is worthwhile mentioning that it drops by approximately two thirds when the relative humidity is increased from 25\% rH to 55\% rH. As can be seen from Figure 2.5 and 2.6 Young’s modulus and tensile strength exhibit the same tendency while the total strain at break increases as depicted in Figure 2.7. These results clearly indicate a loss of material coherence with increasing humidity. Taking into account the fact that Baytron P is a waterborne dispersion this is very plausible. With increasing humidity the material takes up moisture and approaches its original waterborne state and therefore the grain particles in the material become more and more independent of each other and so gain more degrees of freedom and will respond to an external force by slipping past each other. As can be seen in Figure 2.7 the standard deviation of the total strain at break also increases with increasing humidity. This might be attributed to inhomogeneities in the material that become more and more important with an increasing loss of material coherence.

![Young's modulus](image1.png)

**Figure 2.5:** Young’s modulus.

![Tensile strength](image2.png)

**Figure 2.6:** Tensile strength at break.

2.1.5 Summary

We presented a method to characterize the mechanical properties of thin polymer films under various environmental conditions. The polymer in focus in this research was the intrinsically conductive and in polymer electronics widely used PEDOT/PSS. The results show a strong dependency of mechanical properties on relative humidity. Therefore in actual applications of this polymer in flexible electronics these changes of properties have to be taken into account to avoid premature failure of devices due to mechanical overstraining.
2.1 Preliminary Results

![Graph](image)

**Figure 2.7:** Total strain at break.

**Acknowledgments**

The authors would like to thank Urs Notter and Harald Hediger from the mechanical workshop of the physics department of ETH Zurich for laser cutting of the specimen. We would also like to thank H.C. Starck GmbH & Co. KG for its support.
2.2 Systematical Tensile and Morphological Investigations

2.2.1 Abstract

By tensile testing we investigate the mechanical properties of poly(3,4-ethylenedioxythiophene)poly(styrene sulfonate) (PEDOT:PSS) under different relative humidities. Different electron microscopy studies are then used to explore the morphology of thin PEDOT:PSS films. Atomic force microscopy then reveals the topography of fracture surfaces. By combining the experimental findings a micromechanical model for the deformation behavior of PEDOT:PSS can be derived.

2.2.2 Introduction

In recent years there has been vast progress in research on electronic devices based on organic materials. Such devices could be organic thin film transistors, solar cells and organic light emitting diodes. They will be used in low-cost and high volume applications. A key property of organic devices is the possibility to fabricate them on flexible substrates. This allows for new applications like foldable displays but also cheap fabrication technologies like roll-to-roll production. Because layers are mechanically stressed during bending of the flexible substrate, the knowledge of mechanical properties of the applied thin films will thus become very important for reliability issues. A polymer with high conductivity widely used [4] in the aforementioned devices is the complex of the intrinsically conductive polymer poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate acid (PEDOT:PSS). It is commercially available as an aqueous dispersion (Baytron P, H.C. Starck GmbH, Leverkusen, Germany) and can be patterned for instance by lift-off [17,18], ink-jet printing [19] or laser ablation [16,20]. In this paper we fully explore the dependence of mechanical properties of PEDOT:PSS on relative humidity as the most influential factor and then conduct additional studies on morphology. By combining the two investigations we present a microscopic model to explain the mechanical behaviour of PEDOT:PSS.

2.2.3 Experimental

As single layer specimens ought to be investigated with tensile testing, manual peeling off the specimens from a substrate was considered as the first major fabrication step. Since Baytron P is a waterborne dispersion, a hydrophobic substrate had to be used and therefore polystyrene (PS) petri dishes were chosen. The first step of the fabrication of the samples was to pipette the dispersion on a substrate and to let it air dry at ambient conditions in a clean room (T=24°C, rH=50%). This resulted in a solid layer of about 25 μm thickness. The resulting solid circular film could be peeled off and was then attached at its borders to a glass wafer using scotch tape. Then laser cutting for patterning of the samples was used since it is a reproducible, exact and readily available technology. Furthermore it is a dry technique which prevents the layer from being damaged in waterborne solutions. The width of the specimen was then measured using a Zeiss LSM 5 Pascal optical microscope (Carl Zeiss AG, Oberkochen, Germany) with a resolution limited by the optical system (about 0.5 μm). The thickness was determined by using a Cary-Compar profiometer (Meseltron SA, Le Locle, Switzerland) with a resolution of 0.1 μm. The tensile test setup consisted of a lab view controlled stepper motor connected to a stage and a precise electronic balance Precisa 1212 M (Precisa Gravimetrics AG, Dietikon, Switzerland) with a resolution of 1 mg. One end of the sample was attached to this stage while the other end was attached to a weight of 400 g standing on the balance. By actuating the stepper motor the weight could gradually be lifted from the balance and therefore the mass measured by the balance was correspondingly reduced. This reduction was a direct measure of the force acting on the specimen. As mentioned before the dimensions of the specimen were known and therefore the stress in the specimen could be calculated. The strain measurement was obtained in real time by using a CCD microscope camera (microscope: Navitar, Rochester, USA; camera: Jai, Copenhagen, Denmark) and a real time image evaluation algorithm (least square template matching) with sub pixel resolution (0.1 pixel) [10]. Because of this, strain rate controlled experiments could be
conducted and the strain rate was set in the LabVIEW program to $\dot{\varepsilon} = 10^{-4}\text{s}^{-1}$. The whole setup was installed in a climate chamber (CTS-40/200, CTS GmbH, Hechingen, Germany) and tests were conducted at different relative humidities but constant temperature (22°C). The specimens were conditioned at the respective relative humidity for 30 minutes prior to testing. The SEM pictures were taken using a SEM LEO 1530 (Carl Zeiss SMT AG, Oberkochen, Germany). AFM scans of the fracture surface were conducted in tapping mode at a scan rate of 1 Hz under ambient conditions by using a Veeco Multimode with a Nanoscope IIIa controller (Veeco, Santa Barbara, USA). The samples for the TEM and HAADF-STEM investigations were prepared by spinning PEDOT:PSS at 3000 rpm on a 4 inch Si wafer coated with 10 μm of the photoresist AZ 4562. This resulted in a PEDOT:PSS layer of $\approx 25$ nm thickness. The wafer was then cut into pieces and the PEDOT:PSS film was floated off in a acetone bath and then put on a copper grid. The TEM pictures and EDX analysis were made with a Philips CM30 (Philips, Eindhoven, the Netherlands). A FEI Tecnai F30 FEG (FEI, Hillsboro, USA) was used for the HAADF-STEM investigations and the EDX analysis. Both TEMs were operated at 300 kV.

### 2.2.4 Mechanical Characterization

Despite the importance of this subject for practical applications so far only few studies on the mechanical properties of PEDOT:PSS have been published. For microspin fibres and cast films of PEDOT:PSS Young's modulus and tensile strength were determined at 25°C and 50% relative humidity [22]. In another study we presented the influence of ambient light and the large impact of relative humidity on mechanical stability [16]. Table 2.1 summarizes these results for the mechanical properties of PEDOT:PSS prior to the experiments presented in this paper.

<table>
<thead>
<tr>
<th>Mechanical property</th>
<th>Specimen</th>
<th>Dimension</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus</td>
<td>fibre</td>
<td>diameter 30 μm</td>
<td>1.1 ± 0.3 GPa</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>cast film</td>
<td>film thickness 30 μm</td>
<td>1.8 ± 0.2 GPa</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>pipetted film</td>
<td>film thickness 30 μm</td>
<td>2.2 ± 0.2 GPa</td>
<td>[16]</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>fibre</td>
<td>diameter 10 μm</td>
<td>17.2 ± 5.1 MPa</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>cast film</td>
<td>film thickness 30 μm</td>
<td>42.8 ± 9.2 MPa</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>pipetted film</td>
<td>film thickness 30 μm</td>
<td>35 ± 3 MPa</td>
<td>[16]</td>
</tr>
</tbody>
</table>

**Table 2.1:** Literature values for mechanical properties of PEDOT:PSS at 50% relative humidity.

The main insight gained from [16] was the strong dependence of the mechanical properties on relative humidity. Furthermore a considerable water uptake and swelling of the samples could be observed. This seems to be reasonable as PEDOT:PSS is known to be hygroscopic (e.g. in [23]). Based on this insight the first goal of the research presented in this paper was to conduct tensile tests on PEDOT:PSS samples in a climate chamber under controlled conditions to systematically investigate the mechanical properties at different relative humidities. The solid samples were made from the commercially available Baytron P from H.C. Starck. The geometry of the samples was according to an international tensile testing norm [15] for polymer sheets. The dependence on relative humidity can be seen in Figure 2.8, which shows typical stress strain curves obtained at different conditions. A comprehensive overview of the results is depicted in Figure 2.9 and summarized in Table 2.2. Most strikingly there is an almost linear drop for all mechanical characteristics between 23% rH and 40% rH and further to 55% rH. Especially at 23% rH the fracture behavior can be regarded as brittle while for higher relative humidities it becomes more and more plastic. This is a clear sign that the material loses its cohesion. Intuitively this is what should be expected as for 100% rH the original aqueous dispersion without any material strength would be obtained. Scanning electron microscopy (SEM) pictures (Figure 2.10) of the fracture surfaces justify this interpretation of fracture behavior. At a low relative humidity the fracture surface is fairly smooth which is a clear evidence for brittle rupture. At higher humidities the surface becomes rougher until even shear lips - a typical sign for pronounced plastic behavior - develop for samples tested at 55% rH.

---

2Reference [21]
**Figure 2.8:** Stress-strain diagrams for typical results obtained at different relative humidities.

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Mechanical property</th>
<th>Value</th>
<th>Number of specimens tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>23% rH</td>
<td>Young’s modulus</td>
<td>2.8 ± 0.5 GPa</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Poisson’s ratio</td>
<td>0.35 ± 0.03</td>
<td>3</td>
</tr>
<tr>
<td>40% rH</td>
<td>Tensile strength</td>
<td>53.2 ± 9.5 MPa</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Poisson’s ratio</td>
<td>0.34 ± 0.02</td>
<td>3</td>
</tr>
<tr>
<td>55% rH</td>
<td>Tensile strength</td>
<td>33.7 ± 10 MPa</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Young’s modulus</td>
<td>0.9 ± 0.2 GPa</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Poisson’s ratio</td>
<td>0.32 ± 0.0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Tensile strength</td>
<td>22.2 ± 4 MPa</td>
<td>7</td>
</tr>
</tbody>
</table>

**Table 2.2:** Overview of the most important properties for mechanical design. Please note that the experimental determination of Poisson’s ratio is most difficult and therefore fewer samples could be evaluated. For actual mechanical calculations we propose to use a value for Poisson’s ratio of 0.34 for all relative humidities between 23% and 55%.
2.2 Systematical Tensile and Morphological Investigations

Figure 2.9: Results of tensile tests: A) Young's modulus, B) Poisson's ratio, C) tensile strength, D) yield strength, E) total strain and F) elastic strain. From the diagrams it is obvious that the mechanical strength (i.e. Young’s modulus, yield and tensile strength) and therefore the cohesion within the material is reduced with increasing relative humidity and the material behaviour changes from brittle to plastic. This can be seen from the difference between total and elastic strain which increases markedly.
**Figure 2.10:** SEM pictures of fracture surfaces: A) for sample tested at 23% rH. The fracture surface is very smooth without any signs of plastic deformation. B) for sample tested at 40% rH. The increased surface roughness is a clear sign of increased ductile behaviour. C) for sample tested at 55% rH. A shear lip has developed which is an indication for distinct plastic behaviour.
2.2.5 Morphological Investigations\textsuperscript{3}

\textbf{Literature Review}

Starting from these observations the next goal was to derive a micromechanical deformation model for PEDOT:PSS based on morphology. The currently suggested model for the morphology of PEDOT:PSS solid films is that it consists of grains with a hydrophobic and highly conductive PEDOT rich core and a hydrophilic insulating PSS rich shell. \textsuperscript{25} The first investigations towards this model of PEDOT:PSS films were done by X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) \textsuperscript{25} and revealed a phase segregation of PEDOT and PSS. Further experiments by XPS and UPS then showed that individual grains consist of a PSS rich shell with a thickness of about 30-40 Å and a PEDOT rich core \textsuperscript{26,27}. These results could be confirmed by STM based spectroscopy \textsuperscript{28,29}. Additionally, in these publications a grain size diameter for PEDOT:PSS of about 10-20 nm depending on the manufacturer could be determined. This grain size diameter depends on the size of the gel particles in the dispersion and therefore on filtering processes during fabrication. For Baytron P from H.C. Starck GmbH the diameter ranges from 20 to about 200 nm in solution \textsuperscript{30} with the maximum number of particles in a range of about 5.5-100 nm. From these findings the manufacturer of Baytron P then assumed a morphological model of a pancake like structure \textsuperscript{31} (see Figure 2.11). In this model there is some lateral shrinkage during the drying process while the thickness of gel particles and therefore grains is considerably reduced resulting in the aforementioned pancake like morphology. It is further assumed that hydrogen bonds based on HSO\textsubscript{3} groups develop between the PSS rich shell as shown in Figure 2.11. The distribution of grain size of the top layer of a PEDOT:PSS film was confirmed by scanning probe microscopy (SPM) in several other publications (e.g. \textsuperscript{32-34}). Just recently new investigations on the morphology of spin coated PEDOT:PSS were published \textsuperscript{35}. These experiments further strengthened the aforementioned grain model and showed a vertical lasagne-like structure similar to the pancake model while in lateral directions the grains seemed not to be completely isolated from each other. The individual lamellar particles had a diameter of 20-25 nm and a thickness of 5-6 nm. Contrary to all these results there is one publication \textsuperscript{36} where no grain like structure is proposed but rather a sheet like morphology with alternating PEDOT and PSS layers. Table 2.3 summarizes these morphological investigations of PEDOT:PSS films.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Model of PEDOT:PSS solid film formation on a substrate e.g. glass: A) side views of model for pancake like morphology of PEDOT:PSS. Individual spherical gel particles are randomly distributed in the dispersion. Upon drying, a wet film is formed first before finally a solid dry film is obtained. During drying some lateral shrinkage and a considerable decrease in thickness takes place. This decrease in thickness is influenced by the substrate where PEDOT:PSS is deposited on and caused by adhesive effects.  B) It is assumed that hydrogen bonds develop between HSO\textsubscript{3} groups of the PSS rich outer shell of individual gel particles and therefore promote adhesion between individual PEDOT:PSS grains (with permission from \textsuperscript{31}).}
\end{figure}

\textsuperscript{3}Reference \textsuperscript{24}
2 Tensile Testing of Freestanding PEDOT:PSS Films

<table>
<thead>
<tr>
<th>Model</th>
<th>Preparation</th>
<th>Thickness</th>
<th>Method</th>
<th>Supplier</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>grains: diameter of ≈20 nm and a 30-40 Å thick PSS shell</td>
<td>PEDOT grains of ≈10 nm diameter separated by PSS</td>
<td>Spin coating on Si(100) substrate and annealing in vacuum at 120°C for 2 h</td>
<td>35-45 nm</td>
<td>XPS, UPS</td>
<td>H.C. Starck</td>
</tr>
<tr>
<td>lamellar grains with a diameter of ≈25 nm and a thickness of ≈5-6 nm</td>
<td>Spin coating on glass substrates and annealing at 200°C for 2 min</td>
<td>60 nm</td>
<td>STM, AFM</td>
<td>H.C. Starck</td>
<td>[35]</td>
</tr>
<tr>
<td>20-30 nm</td>
<td>Spincasting on quartz substrate and drying at room temperature</td>
<td>100 nm</td>
<td>AFM</td>
<td>Agfa</td>
<td>[34]</td>
</tr>
<tr>
<td>alternating PEDOT and PSS sheets with a step height of 3 nm</td>
<td>Solution casting on plastic-ITO substrate and annealing at 100°C for 1 h</td>
<td>1 µm</td>
<td>AFM</td>
<td>Agfa</td>
<td>[36]</td>
</tr>
</tbody>
</table>

Table 2.3: Overview of investigations on the morphology of PEDOT:PSS films made from commercially available dispersions.

Characterization by TEM and HAADF-STEM

In order to further explore the transition from brittle to plastic behaviour and to develop a micromechanical model for PEDOT:PSS thin films we first used a transmission electron microscope (TEM) to reveal the morphology of the PEDOT:PSS tested in our research. Thin films of PEDOT:PSS with a thickness of about 25 nm were investigated. Figure 2.12 shows typical results. The granular structure of PEDOT:PSS could be confirmed with an average grain diameter of about 30 to 50 nm. The distribution of grain diameters in the solid film seems to correspond fairly well to the one in the aqueous dispersion if some lateral shrinkage during drying of the film is assumed. These findings therefore support the pancake morphological model. Furthermore adverse effects of the organic solvent used to fabricate the films by a floating off process can therefore also presumably be excluded as the morphology is not fundamentally changed. In the next step high angle annular dark field (HAADF) scanning TEM (STEM) as another analytical method was used to enhance the contrast of grain boundaries. The HAADF-STEM method is based on the incoherent scattering of an electron beam comparable to Rutherford scattering. The image contrast shows a linear dependence on the sample thickness and nearly a square dependence on the atomic number z of the respective atomic species present in the sample. Figure 2.13 shows the clearly visible individual grains. The average grain diameter seems to be around 50 nm which confirms the results of the TEM pictures. Two observations are furthermore noteworthy: firstly the grains seem to be encircled by rings of enhanced contrast and secondly there are also agglomerates with grain diameters of about 200 nm. Even though most of the gel particles are in the range of about 50 nm it is still possible that a considerable amount of larger particles is present in the unfiltered Baytron P dispersion [30].

Characterization by EDX

In order to reveal the chemical composition of the films and to confirm the assumption that the agglomerates are made of PEDOT:PSS an energy dispersive X-ray (EDX) investigation was conducted. Figure 2.14 shows typical areas of the analysis and Table 2.4 tendencies for the relative atomic concentrations. From these results several conclusions can be drawn:

- the agglomerates and the film are made from the same elements and are therefore very proba-
2.2 Systematical Tensile and Morphological Investigations

by the same material and no contaminations from the fabrication process of the film.

- there are large differences in brightness between the film and the agglomerates. Because the elemental concentrations are principally the same for the film and the agglomerates these differences in brightness must stem from very different thicknesses. We therefore conclude that the agglomerates are on top of the film (see Figure 2.14B).

- the relative sodium and calcium concentrations in the contact areas of grains are significantly higher than in the rest of the film. As Na and Ca are relatively heavy elements an increase in relative concentrations will lead under the assumption of same thickness of contact and core areas to considerably brighter areas in HAADF-STEM images because the brightness depends quadratically on the atomic number $z$ as mentioned before. This could explain the bright rings around the PEDOT:PSS grains observed in the HAADF-STEM images (see Figure 2.13). Our assumption is that upon drying of the wet film the sodium and calcium ions and PSS build calcium and sodium polystyrene sulfonate (NaPSS and CaPSS). This would mean that the PSS concentration in the shell of the grains is significantly higher than in the core and would therefore further support the models of PEDOT:PSS depicted in Figure 2.11 and published by other researchers (Table 2.3).

- the relative sulfur atomic concentrations in the corresponding monomers are 1:13 for PEDOT and 1:20 for PSS. This means that higher PEDOT concentrations will lead to higher relative atomic concentrations of sulfur. Actually the EDX analysis shows that the relative sulfur concentration is higher in the core of the grains which hints at a higher PEDOT concentration as compared to the shell. This would also confirm the currently accepted morphological model of PEDOT:PSS.

- Na and Ca most likely stem from the fabrication process of Baytron P [37].

- The potassium concentrations are so small that they do not influence the brightness of the HAADF-STEM images significantly.

- The measurement of silicon can be most likely contributed to background signals from the TEM grid.

We then further investigated the rings around the grains. Figure 2.15 shows the intensity distribution of the HAADF-STEM signal across several grains. All grains show a laterally small but distinct peak of intensity right at the border. As explained before we contribute this effect mainly to a higher Na and Ca and therefore PSS concentration. An analysis of the width of the signal shows that the thickness is in the order of about 5-10 nm which corresponds very well to the thickness of the PSS rich shell determined in [25–27]. This is therefore a further direct proof of the currently accepted morphological model for PEDOT:PSS.

Radius of Gyration

Additionally, the PEDOT:PSS grains were also investigated at very high magnifications. Figure 2.16 show that even inside the grains a granular structure becomes visible. This granular structure seems to be composed of individual spots with a diameter of about 3-5 nm. As it is inherent to the HAADF-STEM method that only real material can cause a signal no artifacts but the actual structure inside a PEDOT:PSS grain of our particular film can be seen. In our study only one
Figure 2.12: Brightfield TEM picture showing the morphology of an approx. 25 nm thick PEDOT:PSS film. Circles have been added to emphasize the visibility of some of the grains. The grain size distribution resembles the one of the aqueous dispersion [4] under the assumption of some lateral shrinkage during drying.

Figure 2.13: HAADF-STEM image of a 25 nm thick PEDOT:PSS film. The individual grains are clearly visible with an average diameter of about 50 nm. The grains are surrounded by a thin bright ring. In the lower right corner an agglomerate of larger grains with a diameter of about 200 nm is partly visible. The bar represents 100 nm.
2.2 Systematical Tensile and Morphological Investigations

Figure 2.14: A) HAADF-STEM image of 25 nm thick solid PEDOT:PSS film with several agglomerates exemplarily showing different areas from which the EDX spectra of Table 2.4 were acquired. Area 1 represents contact areas between individual grains of an agglomerate, area 2 stands for cores of grains of an agglomerate and area 3 means that the measurement was acquired from the background i.e. the 25 nm thick PEDOT:PSS film. B) Schematic showing how agglomerates lie on top of the film.

<table>
<thead>
<tr>
<th>Area</th>
<th>Na [%]</th>
<th>Si [%]</th>
<th>S [%]</th>
<th>K [%]</th>
<th>Ca [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: contact area</td>
<td>15 - 20</td>
<td>0.4</td>
<td>≤0.6</td>
<td>2.6</td>
<td>0.11</td>
</tr>
<tr>
<td>2: core of grains</td>
<td>7.13</td>
<td>3.8</td>
<td>75.82</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>3: background</td>
<td>in principal the same as for core of grains</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4: Results of the EDX analysis: relative atom concentrations in different areas. The numbers of the EDX-quantification were deduced standardless with the sum of the composition being standardized to 100%. Therefore the absolute values should be regarded as arbitrary units, which only show tendencies. Furthermore the concentrations are averages over the whole area of the boxes and were obtained by several different measurements.

Figure 2.15: Linescan of signal intensity of the HAADF-STEM analysis (x-coordinate: length in nm, y-coordinate: signal intensity in arbitrary units). The width of the peaks (marked by arrows) is in the range of about 5-10 nm. We attribute these peaks to increased Na and Ca and therefore PSS concentration which therefore also confirms the findings shown in [26, 27]. The bar represents 100 nm.
sample was tested at these magnifications. Therefore at this point we do not claim that this is the final proof of PEDOT:PSS morphology at the nanometer scale but we would rather like to present assumptions that might explain the findings. These assumptions are based on the idea that in Figure 2.16 the spots are caused by individual spheroidal spaghetti-like tangles. These tangles are made of single PSS chains with adherent PEDOT polymers (see Figure 2.17 for a model of the structure of a PEDOT:PSS chain with corresponding molecular weights). As the weight ratio in Baytron P of PEDOT:PSS is 1:2.5 one can assume that the average molecular weight of that PEDOT:PSS chain is 160000 g·mol⁻¹ + 400000 g·mol⁻¹ = 560000 g·mol⁻¹. In another publication the mass density of PEDOT:PSS films was determined to be 1.45 g·cm⁻³ at 30% RH [38]. Under the assumption of a single chain with adherent segments forming a compact sphere and the density of the sphere being the same as for a solid film it is then possible to estimate a lower bound for the geometric radius of the macromolecule. The geometric radius can be calculated as follows [39]:

\[
r = \left( \frac{3}{4\pi \rho N_A} \right)^{1/3} M^{1/3}
\]

with \( \rho \) as the density of PEDOT:PSS, \( N_A \) Avogadro’s constant and \( M \) as the molecular weight of PEDOT:PSS. Plugging in the values given above yields a radius of \( r \approx 3 \text{ nm} \). Recent results from other researchers seem to confirm our estimation. In [40] single-angle X-ray scattering studies of pristine filtered Baytron P were conducted and showed that PEDOT:PSS assumes a globular shape (compact coil) in water. Moreover, their studies yielded a radius of gyration of about 38 Å. The geometric radius (i.e. not the radius of gyration but the radius of the outer bounds of the macromolecule) differs from the radius of gyration by a factor of \((3/5)^{1/2}\) [39]. Therefore the geometric radius is about 49 Å for the result obtained in [40]. The assumption for Equation (2.1) was a compact sphere. This is a lower bound for the estimated geometric radius of PEDOT:PSS while the experimental value obtained in [40] yields an upper bound due to swelling of the particles in a dispersion. The actual radius in a solid film therefore is somewhere in between. Comparing this estimation to the spot diameters observed in Figure 2.16 seems to justify the model of single PSS chains with adherent PEDOT segments forming spots with nanometer diameter. As shown in previous paragraphs, the PSS concentration is increased in the shell of the grains. This would be possible if the tangles in the shell of the grain adopted a form where the hydrophilic PSS was at the outside and those parts of the chains with hydrophobic PEDOT segments were in the core. Figure 2.18 finally summarizes these thoughts and shows a morphological model of individual PEDOT:PSS grains. It should be emphasized again that this model requires further discussion and additional experiments for confirmation and should therefore only give ideas on possible explanations of our experimental findings.

**Characterization of Fracture Surfaces by AFM**

Based on this model for grain composition the next goal was to develop a model for the micromechanical deformation behaviour. The idea was to analyze fracture surfaces from samples tested at different relative humidities. This was done by scanning the fracture surface with an atomic force microscope (AFM). It is important to note that samples had a thickness of 25 μm and not 25 nm as for the TEM and STEM investigations. This means the morphology of the bulk and not only of the surface layer of the films could be determined and therefore a realistic picture of the structure of PEDOT:PSS films without major influences from the substrate could be obtained. Samples ruptured at 23% RH, 40% RH and 55% RH were analyzed. As could be expected from Figure 2.10 the fracture surface of the sample tested at 55% RH was very rough and it was therefore impossible to obtain any meaningful topography data. The results for samples tested at 23% RH and 40% RH are shown in Figure 2.19. For the sample tested at 23% RH the scans (Figure 2.19A) show a fairly smooth surface which corresponds well to the SEM pictures. Several additional observations could be made:

- on the height and amplitude scans striations with smooth surfaces are visible. We attribute these to brittle crack propagation.
2.2 Systematical Tensile and Morphological Investigations

Figure 2.16: HAADF-STEM picture. The film seems to be composed of individual spots in the range of about several nanometers. The bar represents 10 nm.

Figure 2.17: Part of PSS chain with PEDOT segments building ionic complexes (with permission from [31]). The respective molecular weights are also given. Along the whole chain the mass ratio of 1:2.5 for Baytron P has to be fulfilled.
2 Tensile Testing of Freestanding PEDOT:PSS Films

**Figure 2.18:** Hypothesis for the morphology of individual PEDOT:PSS grains. We propose that a grain is composed of numerous tangles. Each tangle is made of a single PSS chain with several PEDOT segments adherent to it. Inside the grain the tangles are shaped in a way that PEDOT segments are evenly distributed in space. In the outer layer of the grain the tangles arrange themselves in a way that mostly their hydrophilic PSS parts point towards the outside.

- nonetheless there are partly also grains visible which is an indication for some plastic deformation.

- in general, the phase scans depict differences in sample elasticity. Here it seems that flat particles (bright) are dispersed in matrix (dark). We assume that the dark areas are a matrix formed by the PSS rich shells. The bright lentil shaped areas are the PEDOT rich cores in this model. Comparing the results of this paper to the ones presented in [35] the grains within our samples seem not to be as flat. This might be attributed partly to the temperatures at which rupture took place (77K in [35] as opposed to room temperature here) and especially to the deposition method. Spin coating as used in [35] exerts centrifugal forces on the grains and therefore a more lasagne-like structure can be expected. Additionally the sample thickness differs considerably. Therefore in the samples tested here, effects from the substrate which might flatten grains due to adhesive forces, do not appear.

The sample tested at 40% rH yielded fairly different results for the AFM scans (see Figure 2.19B):

- the surface is considerably rougher as could be seen from the height scans.

- the particles do not have lentil shape any more but seem to be round with a diameter of about 30-50 nm. We therefore assume that the particles are individual PEDOT:PSS grains which have slide by each other during deformation. Because of this, grains in the sliding zone are not constrained geometrically any more by the solid film and could therefore resume a spherical shape like in the original dispersion.

**2.2.6 Micromechanical Model**

From the HAADF-STEM, EDX and AFM analysis and in agreement with the results in literature [26, 27, 35] we finally propose the following morphological and micromechanical model for PEDOT:PSS films:
Figure 2.19: A) AFM scans of a sample ruptured at 23% rH. The scan direction was perpendicular to the sample thickness. The topography image (top row) shows a fairly smooth fracture surface with some striations attributed to brittle fracture propagation. Partially individual grains are visible caused by some small plastic deformation. The phase images (bottom row) exhibit areas with different sample elasticity. It seems that particles (bright) are dispersed in a matrix (dark). We attribute the bright spots to areas with high PEDOT content and the dark areas to a PSS rich matrix. This would confirm the currently accepted model for PEDOT:PSS morphology. B) AFM scans of a sample ruptured at 40% rH. The scan direction was again perpendicular to the thickness direction. The surface (top row) is rougher than for the sample tested at 23% rH. We assume that individual grains could slide by each other during plastic deformation and then resume their original spherical shape. The phase images (bottom row) show again that particles are dispersed in a matrix. In all images no lamellar structures could be observed which suggests that bulk properties without any substrate effects were investigated.
2 Tensile Testing of Freestanding PEDOT:PSS Films

- PEDOT:PSS films are made from grains with an average diameter of about 30-50 nm which means that upon drying also the diameter slightly decreases. Occasionally PEDOT:PSS agglomerates with larger diameters for unfiltered Baytron P on top of the film can be found.

- upon drying the original sphere shape in the dispersion turns into a slight lentil shape under gravitational load

- the core of the grains is PEDOT rich while the shell is PSS rich. The coherence of the material is achieved by hydrogen bonds

- at low relative humidities these hydrogen bonds are very strong and therefore upon fracture the crack grows through individual grains (transgranular fracture) which results in brittle macroscopic fracture

- higher relative humidities lead to water uptake by the hydrophilic and hygroscopic PSS rich shell and thus to a swelling of the material and larger distances between grains. Larger distances between shells mean reduced cohesion and therefore reduced mechanical strength.

- upon tensile loading at higher relative humidities individual grains can slide by each other. This results in a rough surface and an intergranular fracture. Macroscopically plastic failure occurs.

Figure 2.20 summarizes the proposed morphological model and micromechanical failure mechanisms for PEDOT:PSS films found in this study. Even though pipetted films were investigated we still assume that these mechanisms are valid in general and could therefore also be applied to spin coated and inkjet printed PEDOT:PSS films as their morphology and hence their behavior under tensile load should be similar.

![Figure 2.20](image)

*Figure 2.20: Comprehensive schematic overview of the proposed models: A) PEDOT:PSS forms spherical gel particles in aqueous dispersions. Upon drying a solid film consisting of lentil-like shaped grains develops. B) At low relative humidities e.g. 23% RH the hydrogen bonds in the PSS rich shell are very strong and therefore external tensile forces lead to a transgranular brittle fracture and therefore smooth fracture surfaces. C) At higher relative humidities e.g. 40% RH the hygroscopic PSS takes up water which causes the hydrogen bonds to be weakened and also leads to a swelling of the film. Upon exertion of external tensile forces individual PEDOT:PSS grains can slide by each other and therefore intergranular plastic fracture takes place. The fracture surface is rough with rather spherical grains forming the outer layer.*

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2.2 Systematic Tensile and Morphological Investigations

2.2.7 Conclusions

In summary, by tensile testing we fully characterized the mechanical behaviour of PEDOT:PSS for a wide range of relative humidities. These data will be of help for the design of mechanically reliable organic devices. SEM, TEM and HAADF-STEM studies directly confirmed the currently accepted model of a PSS rich shell and PEDOT rich core. AFM scans of the fracture surfaces of samples tested at different humidities revealed the structure of pipetted PEDOT:PSS films. Generally the cohesion among grains is obtained by hydrogen bonds between PSS groups in the shells. At low relative humidities these hydrogen bonds are so strong that upon tensile loading transgranular i.e. brittle fracture through individual grains takes place. Increasing relative humidities lead to water uptake of the hydrophilic and hygroscopic PSS rich shell which results in a swelling of the samples and weakens the hydrogen bonds. Individual grains can thus even slide by each other and therefore intergranular plastic fracture i.e. fracture between individual grains is possible. We could therefore derive a microscopic model which could fully describe the mechanical behaviour of PEDOT:PSS films at different relative humidities.

Acknowledgements

The authors would like to thank Dr. Andreas Elschnir and Dr. Stefan Kirchmeyer from H.C. Starck GmbH in Leverkusen, Germany, for their support and very helpful discussions. We furthermore acknowledge Urs Notter from the mechanical workshop of the physics department of ETH Zurich for laser cutting of the specimens and Yu Higashigaito for conducting some of the tensile tests.
2 Tensile Testing of Freestanding PEDOT:PSS Films
3 Microtensile Tests

3.1 Fabrication of a Tensile Test for Polymer Micromechanics

3.1.1 Abstract
In recent years one could observe the advent of polymeric systems e.g. systems whose electronics are based on organic materials. The use of cheap organic materials and inexpensive technologies such as roll-to-roll fabrication and ink-jet printing promise a new kind of electronics and applications. Devices under investigation are RF tags and displays based on organic light emitting diodes (OLEDs). One major advantage that these devices have in common is the possible flexible substrate they are fabricated on. As devices on flexible substrates will be bent during operation the reliability and therefore the knowledge of the mechanical properties of the materials used is important. Typical dimensions of functional organic layers in actual devices are in the range of several hundreds of nanometers. Therefore also for mechanical testing typical dimensions of the test specimens should be in the same range. We propose a test setup which enables the investigation of mechanical properties of submicrometer thick organic layers. It consists of a 1 μm thick polyimide substrate and a deposited functional layer. In this paper we present the necessary fabrication process based on the Bosch deep etching process of silicon.

3.1.2 Introduction
Intrinsically conductive organic materials attract much attention as they promise new applications and cheap fabrication methods. For both a major advantage is the possible use of flexible substrates. This in turn raises questions about the reliability and therefore the mechanical properties of the materials used. As functional layers in actual devices are in the range of several hundreds of nanometers or a few micrometers test specimens should be in the same range. Haque and Saif [41] proposed a tensile test setup which allows tensile tests with thin layers and a precise force detection. We follow some of their ideas as this approach is very versatile and enables the investigation of many different kinds of materials. Furthermore, from a mechanical point of view the uniaxial tensile stress allows in theory the exact determination of Young’s modulus and tensile strength. Our approach is based on three major points (see also Figure 3.1):

- force detection by silicon beam deflection
- optical detection of strain in specimen by a least square template matching algorithm (LSM) developed at ETH Zurich [8]
- a bilayer tensile specimen consisting of a polyimide (PI) substrate and a functional organic layer

The difference between tensile tests with and without this functional layer will allow the determination of the mechanical properties of that layer. The functional layer could be applied either by spin coating or evaporation techniques which allows experiments with many different classes of polymeric materials. In this paper we present the fabrication process of the basic setup. The goal herein was to fabricate the freestanding PI substrate as this is the most difficult part of the fabrication process. PI was chosen because of its widespread application in microelectronics and the possibility of...
3 Microtensile Tests

photolithographic structuring. Furthermore in literature one could only find a few tensile tests with thin PI specimens [42] and therefore investigations of the mechanical properties of thin PI layers are of interest and can easily be conducted with this setup.

![Diagram](image_url)

**Figure 3.1:** Principle of tensile test: determination of F by measuring the deformation of the force sensing beam.

### 3.1.3 Experimental

In order to be able to measure the mechanical properties of submicrometer thick polymer layers the thickness of PI substrate needs to be in the same range. Furthermore, stress concentrations during testing should also be avoided which requires dog bone shaped substrates. We therefore chose the photosensitive Pyralin P12723 (HD Microsystems, Bad Homburg, Germany). It can be applied by spin coating with thicknesses down to 1 μm at 5000 rpm. As it shows major G-line absorption bands it can be structured using standard photolithographic equipment. This process is laid out in processing guidelines from the manufacturer [6]. As an example for a functional layer poly(3,4-ethylenedioxythiophene)poly(styrene sulfonate) (PEDOT:PSS, commercially available as an aqueous dispersion from H.C. Starck GmbH, Leverkusen, Germany) was chosen. It is widely used as a hole transport layer in OLEDs [11, 12] or as an electrode material in organic thin film transistors (OTFTs) [19]. It can be applied by spin coating [43] and structured by a lift-off process [44]. Furthermore, it showed good adhesion to polyimide Kapton tapes in preliminary tests. For the etching of the silicon substrate a dry deep etching Bosch process on an STS ICP system was used. It was soon realized that this standard process (see Figure 3.2) could not be used for the fabrication of thin freestanding PI specimens. This was due to the inhomogeneous etching behaviour at the bottom of the trenches (see process I in Figure 3.3) which resulted in prolonged exposure of polyimide in the center of trenches to the plasma and a subsequent premature rupture of the specimen during etching. Furthermore, perpendicular sidewalls are necessary for an exact application of beam mechanics on the force sensing beam. In order to avoid rounded corners we therefore developed a new deep etching recipe based on the original process. The final parameters of process II are also listed in Figure 3.3 along with the pictures of the resulting structures. In Figure 3.4 examples of different samples at different stages of the fabrication process are shown. The last picture with a 1 μm thick PI specimen with a 400 nm thin layer of PEDOT:PSS on top proofs the feasibility of the fabrication process described in this paper.
3.1 Fabrication of a Tensile Test for Polymer Micromechanics

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>A 1 µm thick layer of PE2723 (HD Microsystems, Bad Homburg, Germany) is structured photolithographically by a standard process [4].</td>
</tr>
<tr>
<td>PEDOT/PSS</td>
<td>AZ 4562</td>
</tr>
<tr>
<td>AZ 4562 10 µm</td>
<td>The lift off is conducted in an ultrasonically agitated acetone bath for 5 minutes.</td>
</tr>
<tr>
<td>Arencoc Crystallbond 555 Si support wafer</td>
<td>A 10 µm thick layer of AZ 4562 is patterned on the backside as a mask for the subsequent deep dry etching.</td>
</tr>
<tr>
<td></td>
<td>A second Si wafer is structured separately and then bonded to the first wafer using Arencoc crystallbond 555. This approach is necessary to protect both the thin PI and the functional layer.</td>
</tr>
<tr>
<td></td>
<td>Dry deep etching of the first wafer from the front side.</td>
</tr>
<tr>
<td></td>
<td>Removal of support wafer by heating of compound above approx. 54°C.</td>
</tr>
</tbody>
</table>

**Figure 3.2:** Process flow for the fabrication of the tensile test.

<table>
<thead>
<tr>
<th>Process Parameters</th>
<th>Sidview</th>
<th>Test Structure</th>
</tr>
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<tbody>
<tr>
<td><strong>I</strong></td>
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</tr>
<tr>
<td>Stamping:</td>
<td>SF = 130 sccm, O₂ = 13 sccm, C₄F₆ = 40 sccm</td>
<td>premature exposure of PI due to unhomogeneous etching at the bottom of the trenches</td>
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<tr>
<td>SF = 130 sccm, O₂ = 13 sccm, C₄F₆ = 40 sccm</td>
<td>thinning current</td>
<td>perpendicular sidewalls due to homogeneous etching at the bottom of the trenches</td>
</tr>
<tr>
<td>Col Power: 700 W</td>
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<tr>
<td>Patterning Power: 13 W</td>
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<tr>
<td>Passivation:</td>
<td>C₄F₆ = 100 sccm</td>
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<td>Col Power: 600 W</td>
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**Figure 3.3:** Development of etching recipe for perpendicular sidewalls.
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![Fabrication](image)

<table>
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<th>Fabrication</th>
<th>Fabrication</th>
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<tbody>
<tr>
<td>Tensile test setup with a 3 µm thick freestanding PI specimen still bonded to support wafer.</td>
<td>Tensile test setup with a 3 µm thick freestanding PI specimen after removal from support wafer.</td>
<td>Proof of concept: freestanding PI specimen (thickness 1 µm) with a layer of PEDOT:PSS (thickness 400 nm) on backside. This layer was structured using a lift-off process.</td>
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</table>

**Figure 3.4**: Pictures from different specimens at different stages of the fabrication process.

3.1.4 Discussion

We have shown a new idea for tensile testing in the micro and submicrometer range. It will be very versatile as different kinds of polymeric materials could be tested at high accuracy. The fabrication process itself might also be of high interest for other fields of applications. This is due to the ability of fabricating extremely thin freestanding PI layers. Additionally, we developed a new dry etching recipe which avoids rounded corners and therefore allows the fabrication of planar trenches.
3.2 Observing Crack Propagation in Polyimide Microtensile Specimens

3.2.1 Abstract

Due to their widespread application as stress buffer and planarization layers in microelectronics and as substrate material in polymer electronics and microelectromechanical systems (MEMS) the mechanical properties of polyimides are very important to know for reliability issues. In this paper a micro tensile test which allows the determination and observation of the fracture behaviour of thin polymer layers is presented. The setup consists of micromanipulators and piezo actuators for straining the sample while an atomic force microscope (AFM) is used for scanning the crack tip area with high lateral resolution. The stress in the specimen is determined by an optical microscope for observation of the deflection of a force sensing beam. The material under investigation is the amorphous and strongly entangled thermoplastic polyimide PI2723 which can be patterned photolithographically and is spin cast to form layers of 3 μm thickness. The results show the potential of the setup to measure crack growth, crack tip opening and nominal stress. The stress-crack length-diagram allows to determine different stages during crack propagation. Scanning electron microscopy (SEM) images of the fracture zone reveal brittle behavior for the crack and shear banding in its vicinity. In combination with the AFM scans a possible explanation of the fracture behavior is discussed.

3.2.2 Introduction

Crack initiation and growth are key issues when it comes to the mechanical reliability of microelectronic devices and microelectromechanical systems (MEMS). Especially in organic electronics where flexible substrates will play a major role these issues will become of utmost importance. It is therefore necessary to develop methods which allow the experimental investigation of fracture processes in thin organic layers as mechanical failure of devices is usually accompanied by crack propagation. Since polymers are often amorphous, non conductive and cannot withstand the electron beam of an electron microscopes for a long time the approach herein is therefore based on the use of an AFM to determine in situ crack propagation during straining of a polymer specimen. Similar setups have been used to examine silicon [45–51], thin metal films on polymer substrates [52–54] and for pure polymer samples [55–62]. In contrast to those approaches in the experiments presented here the force measurement is integrated in the microfabricated samples as presented by Haque and Saif in [41]. This allows to investigate thin samples with micrometer thickness and to measure forces in the range of millinewtons. By using an optical microscope the deformation of a silicon force sensing beam can be observed and by applying beam mechanics the force acting on the specimen can be determined (Figure 3.5). The tensile samples in this research are made from the polyimide PI2723 from HD Microsystems (Wilmington, DE, USA). Polyimide was chosen because it is widely used as a passivation layer to protect microelectronic devices from moisture and corrosion. Additionally polyimides are often used as stress buffer layers during packaging of dies [6]. Moreover, polyimides are promising candidates for flexible substrates in organic electronics [63,64] and in the MEMS community as a membrane material [65–67].

3.2.3 Experimental Specimens

The specimen itself consists of a freestanding 3 μm polyimide PI2723 tensile probe and a silicon frame. They are both shown in Figure 3.6 with dimensions. Connected to one of the silicon beams there is an extension rod which can be considered a rigid body. Due to this fact the deformation of the silicon force sensing beam is transferred directly to this extension rod. Therefore the deflection of the beam can be determined by measuring the distance between the extension beam and the rigid body.

Reference [63]
Figure 3.5: Principle of the setup: the specimen is strained between two silicon beams while crack growth is monitored in situ by an AFM. A photolithographically structured notch results in a locally well defined crack initiation. The deformation of a force sensing beam is determined by an optical microscope. The rigid extension rod is necessary because the actual force sensing beam is hidden underneath the AFM. The three pin holes in the Si frame are used for force transmission by small pins from the external piezo actuators and micromanipulators to the specimen.
3.2 Observing Crack Propagation in Polyimide Microtensile Specimens

silicon frame. This is necessary because the actual force sensing beam is hidden behind the AFM and can therefore not be monitored directly. The geometry of the PI tensile probe is based on an international norm on tensile tests of polymers [15] with an additional single notch on one side. The fabrication of the specimens is mainly based on the Bosch deep dry etching process and is explained in [68] in detail. Here only a brief overview of the process flow is given in Figure 3.7. The polyimide used in these experiments is PI2723 as mentioned before. It is photodefinition and can be applied by spin coating. It is therefore also very suitable for MEMS applications. Its morphology shows a very amorphous structure caused by a strong entanglement of the chains [69]. As its glass transition temperature is rather high (> 320 °C, [6]) and the tests are conducted at room temperature the thermoplastic will be in its glassy state and therefore one can expect a rather brittle and very limited viscoelastic behaviour [70-72]. This behaviour has already been shown in [73] for polyimide (Kapton) films. As PI2723 is even more entangled than Kapton tape [69] one could therefore assume that viscoelastic effects and the size of the plastic zone in front of the crack tip will be limited in size.

![Figure 3.6: Dimensions of setup: (a) shows the overall size of the specimen and of the extension rod (in mm), (b) shows the dimensions of the silicon force sensing beam (in mm) and its orientation on the wafer and (c) shows the dimensions (in µm) of the polyimide specimen including the notch. The thickness of the silicon (100) wafer is 525 µm. The thickness of the PI specimen is 3 µm.](image)

Atomic Force Microscope

An easyScan AFM (Nanoprobe AG, Liestal, Switzerland) was used in the experiments. Its main characteristics are a maximum scan range of 100 µm in x- and y- directions and of 20 µm in z-direction. Scans are taken in contact mode with a typical load of 11 nN and automatic z-offset adjustment. The cantilevers were of type Contr-16 (Nanoworld AG, Neuchâtel, Switzerland) and had a typical tip diameter of less than 10 µm and a tip height of about 10-15 µm. The picture analysis program Motic Images Plus 2.0 was used to measure the crack length. The AFM scans were thereby carefully analyzed by determining the distance from the bottom of the notch to the tip of the crack.

Detection of Forces

Mechanics of Force Sensing Beam The principle used here for measuring forces is based on the deformation of single crystal silicon double fixed beams and was first presented by Haque and Saif in [41]. As shown in Figure 3.5 the application of an external force on the first beam leads to the deformation of that beam, to the straining of the specimen and to the deformation of the second force sensing beam.

The calculation of a force causing large deflections of double fixed beams was first presented by Frisch-Fay [74] in detail. Here, a brief summary of his explanations only as far as necessary to understand the train of thought is given. The main idea is that when such a beam with two fixed
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<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
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<tbody>
<tr>
<td>PI</td>
<td>A 3 µm thick layer of PI2723 (HD Microsystems, Bad Homburg, Germany) is structured photolithographically with a standard process.</td>
</tr>
<tr>
<td>Si</td>
<td>A 10 µm thick layer of AZ 4562 is patterned on the backside as a mask for subsequent deep dry etching.</td>
</tr>
<tr>
<td>AZ 4562 10 µm</td>
<td>A second Si wafer is structured separately and then bonded to the first wafer using Arencor crystalbond 555. This approach is necessary to protect the thin PI layer.</td>
</tr>
<tr>
<td>Arencor Crystalbond 555 Si support wafer</td>
<td>Dry deep etching (Bosch process) of the first wafer from the backside. The flows during the etch cycles were 130 sccm for SF₆ and 13 sccm for O₂. During passivation the flow of C₆F₆ a was 100 sccm.</td>
</tr>
<tr>
<td>Removal of support wafer by heating of compound above approx. 50°C.</td>
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</table>

**Figure 3.7:** Process flow for the fabrication of thin freestanding polyimide tensile specimens [68].

**Figure 3.8:** Deformation of double fixed beam under a load of 2P and corresponding free body diagram.
ends undergoes a large deflection then also normal forces will develop in axial direction. It should be emphasized that large deflections in this context mean that normal forces develop in the beam but that the actual deflection in the middle is small compared to the overall length of the beam. Figure 3.8 shows a beam which is loaded with a force of $2P$ and the corresponding free body diagram. Contrary to first order theory, the equilibrium is derived from the deflected state. This leads to an additional moment $Ny$. Equilibrium of moments at an arbitrary point $x$ along the half of the beam therefore is:

$$
M_x = EI \frac{d^2y}{dx^2}
$$

$$
= Ny + M_0 - P(L - x)
$$

(3.1)

where $M_0$ is the bending moment at position $x$, $E$ is Young’s Modulus of the beam material and $I$ the moment of inertia of the beam for bending about the $z$-axis. The general solution of Eq. (3.1) is

$$
y = C_1 \cosh tx + C_2 \sinh tx + Ax + B
$$

(3.2)

where $C_1$ and $C_2$ have to be found from boundary conditions for a double fixed beam and from beam symmetry while $A = - P/N$, $B = (PL - M_0)/N$ and $t = \sqrt{(N/EI)}$ can then be found from comparing Eq. (3.2) to Eq. (3.1). Considering the axial extension of the beam caused by the constant normal force $N$ (for small slopes) and some additional calculus yields an equation for $N$:

$$
N^3 = \frac{A_c EP^2}{2} \left( \frac{3}{2} - \frac{1}{2} \tanh^2 u - \frac{3 \tanh u}{2u} \right)
$$

(3.3)

with $u = tL/2$ and $A_c$ the cross sectional area of the beam. Solving Eq. (3.3) for $P$ yields

$$
P = \sqrt{\frac{2N^3}{A_c \sqrt{E}}} \left( \frac{3}{2} - \frac{1}{2} \tanh^2 u - \frac{3 \tanh u}{2u} \right)^{-\frac{3}{2}}.
$$

(3.4)

Using Eq. (3.4) and Eq. (3.2) and calculating the value of $y(x)$ at $x = 0$ (middle of the beam) leads to

$$
f = 2 \sqrt{\frac{2L}{A_c}} (u - \tanh u) \left( \frac{3}{2} - \frac{1}{2} \tanh^2 u - \frac{3 \tanh u}{2u} \right)^{-\frac{3}{2}}.
$$

(3.5)

which is the desired relation between $P$ and the deflection $f$ at the middle of the beam. For $f$ given from the experiment, Eq. (3.5) is numerically solved for $u$. $P$ is then obtained from Eq. (3.4) using $u = tL/2$ and $t = \sqrt{(N/EI)}$. This calculation can be easily programmed with any computer algebra language e.g. Mathematica or Matlab. In these experiments a simple Matlab code was used to calculate $P$ from the measured deflection $f$. The maximum stress due to bending then develops at the fixed ends of the beam and is given by

$$
\sigma_{max} = \frac{1}{3} \left( \frac{h}{L} \right)^2 u^2 \left[ 1 + \sqrt{6} \tanh u \left( \frac{3}{2} - \frac{1}{2} \tanh^2 u - \frac{3 \tanh u}{2u} \right)^{-\frac{3}{2}} \right]
$$

(3.6)

where $h$ is the height of the beam, in this case 200 µm (see Figure 3.6). Assuming a yield strength of 7 GPa and a Young’s modulus of 169 GPa for silicon in $<110>$-direction [75], a theoretical maximum detectable force $P$ of $\approx 60$ N can be obtained from Eq. (3.4).
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**Measurement of Beam Deflection and Crack Growth** Measuring the actual displacement of the extension rod during experiments was done by an high magnification zoom lens (1x-12x) (Navitar Inc., Rochester, USA) with a 2 megapixel CCD camera (Moticam 2000, Motic Deutschland GmbH, Wetzlar, Germany) attached to it (see Figure 3.5). For every AFM scan also a picture of the extension rod was taken. The displacement was then determined by carefully measuring the distance between the rod and the frame using the analysis program Motic Images Plus 2.0. The optical system permits a resolve limit of ≈10 μm which yields with Equations (3.4) and (3.5) a force resolution of ≈0.012 N.

**Actuation and Control**

![Diagram of experimental setup](image)

**Figure 3.9:** Experimental setup. Two micromanipulators and two piezo actuators are used. They point pairwise into opposite directions which results in larger maximum displacements. Furthermore the notch area can thus be kept in a central position.

Figure 3.9 shows the actual setup. For the experiments the samples are put on the pins which transfer the motion generated by the micromanipulators and piezo actuators (model P-280, 100 μm range, PI GmbH, Karlsruhe, Germany) to the specimens. The micromanipulators are necessary to bring the pins in contact with the specimen to make sure that the whole range of the piezo actuators can be used for precisely straining the specimen. The actual experiment is conducted stepwise: the specimen is strained for approximately 5 μm then an AFM scan and a picture of the extension rod are taken. Then the specimen is strained for an additional 5 μm and again scans and pictures are taken and so forth until rupture of the sample. The whole experiment is therefore controlled by
actuator displacements. During manual actuation it might happen that the two micromanipulators are not actuated exactly the same way and thus the crack might be moved away from the central position of the AFM scan. This can then be accounted for in the AFM scan software by readjusting the scan area.

3.2.4 Results

Two experiments were conducted at 23°C and 25% relative humidity. The results are very similar for both of the tests as can be seen from Figure 3.10 which shows the nominal stress within the sample far enough away from the notch (i.e. the stress is calculated for a width of 185 μm) versus the crack length starting from the bottom of the notch. To relate the stress-crack length diagram to actual rupture processes different stages of the crack propagation through the sample are identified in Figure 3.11. For all of these different stages typical situations are shown in Figure 3.12 and are discussed now:

![Figure 3.10: Normal stress vs. crack length diagrams for the two conducted experiments. Both samples showed basically the same behaviour.](image)

![Figure 3.11: The different stages during crack propagation. The terms are used according to [76].](image)

- Initial Crack Length
  For both the samples there is an initial crack length even without external forces applied
Figure 3.12: Typical situations during crack propagation. Column I shows 2D scans with side lengths of 60 μm, column II are the corresponding 3D views and column III shows the stress-crack length diagrams. The AFM pictures always refer to the corresponding last data point of the diagrams. The stages of crack growth are: (a) initial crack length, (b) stationary state i.e. no crack propagation at increasing stress, (c) stable crack growth, (d) unstable crack growth i.e. without increase of nominal stress the crack grows for a considerable distance and (e) before failure the crack growth is stopped again and a final increase of stress is necessary to initiate rupture. Note the appearance of material at the bottom of the crack for the last data points. This is an indication for a crack growing vertically and laterally from the corner of the top middle of the notch into the specimen.
to the setup. In order to explain this phenomenon one has to take into consideration that during fabrication the compound of the silicon substrate and the polyimide layer is cooled down to room temperature after baking at 350°C. Due to the large mismatch in the coefficient of thermal expansion between the two materials high thermal tensile stresses develop in the polyimide layer. Furthermore, additional stress can develop in the surface layer due to solvent evaporation. After releasing the sample from the substrate during dry etching these residual stresses are partially relieved as the sample is free to contract, partially close the initial crack and deform the silicon beams (see below). If during the experiment the samples are strained the initial crack is opened again without applying any additional force. This explains why there is an apparent crack "growth" between the first two data points without any increase in external force and therefore nominal stresses. The fact why they initially amount only to a few MPa and not to the numbers given for residual stress by the manufacturer (42 MPa, [6]) can be contributed to the aforementioned stress relief in the polyimide layer after dry etching. As the sample is freestanding after the etch step it can contract and therefore reduce the residual stress until the residual force in the polyimide specimen is as large as the force necessary to deform the silicon beams to their initial position. Based on these thoughts in Figure 3.13 the basic idea to calculate the residual stresses is shown. The balance of forces yields:

\[
F_{\text{res}} = F_{\text{res,dep}} - F_{\text{relief}} = \sigma_{\text{res,dep}} A \frac{l_0 - l_1}{l_0} E_{P1} A
\]  

(3.7)

where \(F_{\text{res}}\) is the force due to residual stresses after dry etching, \(F_{\text{relief}}\) is the reduction of force due to stress relief by dry etching, \(F_{\text{res,dep}}\) is the force due to residual stresses after deposition and before dry etching. \(E_{P1}\) Young’s modulus of PI 2723, \(A\) is the cross sectional area of the specimen for calculating the nominal residual stress, \(l_0\) is the length of the specimen after deposition and \(l_1\) is the length of the specimen after dry etching. This initial length before the experiments can be calculated by

\[
l_1 = l_0 - \Delta f_1 - \Delta f_2
\]  

(3.8)

where \(\Delta f_i\) are the deflections of the silicon beams as defined in Figure 3.13. Assuming that \(F_{\text{res}}\) is small compared to forces during the experiments, \(\Delta f_1\) and \(\Delta f_2\) can be calculated by using linear beam mechanics:

\[
\Delta f_i = \frac{F_{\text{res}l_{S1,i}}}{24E_{S1}I}
\]  

(3.9)

where \(l_{S1,i}\) is the length of the respective silicon beam, \(E_{S1}\) is the Young’s modulus of silicon in <110> direction and \(I\) is the area moment of inertia for the silicon beams. Plugging in all known values into (3.7) and by using equations (3.8) and (3.9) a residual nominal stress \(\sigma_{\text{res}}\) of 4.5 MPa and a residual nominal stress after deposition \(\sigma_0\) of 43.6 MPa could be determined for experiment 1. This last value of \(\sigma_0\) is in very good agreement with the value of 42 MPa of residual stresses given by the manufacturer [6] for a 10 μm thick layer of PI 2720 after deposition on a silicon wafer. As the residual stress is known the stress state in the notch area can be estimated next. First the stress concentration factor for this particular situation has to be determined. As shown in Figure 3.6 the depth of the notch is 48 μm. On the mask used for the lithography the notch is perfectly sharp while in reality due to reflow of the polyimide during baking it will become rounded. Figure 3.14 suggests that the corresponding radius is about
3 Microtensile Tests

7.5 μm. This yields a ratio of notch radius to width of minimum cross section of 7.5 μm/143 μm ≈ 0.052. Assuming furthermore a hyperbolically shaped notch the stress concentration factor can be obtained from charts given in [77, 78] to be ≈ 2.8. The nominal stress in the smallest section of the specimen at the bottom of the notch is 43.6 MPa · 185 μm/143 μm ≈ 56.4 MPa. Multiplying this value with the stress concentration factor yields the stress in the bottom of the notch: 56.4 MPa · 2.8 ≈ 158 MPa. This is in the order of the rupture strength of 160 MPa given by the manufacturer [6] and therefore initial cracks after baking have to be expected.

- Stationary phase
The crack length remains stable while the external force is increased. The elastic energy stored in the material is not yet large enough to activate crack growth.

- Stable crack growth
The crack starts to grow and two very important observations can be made. Firstly during crack opening no crazes can be found and secondly material becomes visible at the bottom of the crack. This can also be seen in the three dimensional scans (Figure 3.12). Therefore the assumption is that a crack growing vertically and laterally from the corner of the top middle of the notch into the specimen could be seen. Such a crack will be from here on called a corner crack (for a geometrical description of a corner crack see e.g. [79]).

- Unstable crack growth
The crack propagates vastly into the material without almost any additional load.

- Pop-in
The unstable crack growth is stopped shortly before final failure of the sample. Such a behaviour is normally called pop-in for macroscopic samples. This term will also be used here. In order to be able to stop a propagating crack plastic deformations need to take place to dissipate energy. Only from the AFM pictures such plastic processes could not be determined.

In order to obtain additional information on the plastic behaviour of the polyimide PI2723 the samples were first sputtered with approximately 10 nm of Au and then investigated in a scanning electron microscope (SEM, LEO 1530). Figure 3.15 shows the fracture surface of the approximately first 40 μm of the crack. First of all it can be seen that the fracture surface is fairly smooth without any major shear lips. This is an indication of rather brittle fracture. In Figure 3.16 there is a close up of the region where the pop-in process took place. As can be seen in this area localized deformations appear on the surface of the sample and are from there on visible in a distance of about 2-3 μm away from the crack and are almost parallel to it. The overall appearance of these localized deformations justify the assumption that these are shear bands. Very similar results for the fracture surface and shear bands have already been reported in [80] which is a further hint that the observations made here are inherent polyimide properties.

3.2.5 Discussion
In the previous section the experimental findings have been described. In this section a possible explanation for the fracture behaviour of the PI 2723 with brittle fracture surfaces and shear bands in close vicinity is presented. In general surface and corner cracks cause a multiaxial (three dimensional) and complicated stress state underneath the bottom of the crack [81, 82]. Due to constraints on the contraction of material also a plane strain state is to be expected. Therefore even for a very thin sample the corner crack causes considerable out-of-plane stresses (from here on σz) in the notch area. Only further away from the crack tip the out-of-plane stress diminishes and therefore plane stress dominates (see Figure 3.17). At room temperature and therefore far below T_g the strongly entangled polymer chains prevent individual chains from reptating. Therefore void formation necessary for crazing is hindered and shear banding is favored [83, 84]. Furthermore, if there is a high three dimensional stress level chains are constrained by stresses in all directions and therefore brittle
3.2 Observing Crack Propagation in Polyimide Microtensile Specimens

Figure 3.13: Determination of residual stresses: (a) after dry etching the residual stresses in the specimen are partially relieved but cause a deflection of the silicon beams, (b) free body diagram: the same force acts on the specimen and on the beams. To determine the force it is sufficient to measure the initial deflection $\Delta f_2$ of the force sensing beam, (c) $\Delta f_2$ can be determined by comparing the position of the force sensing beam before conducting the experiments and after rupture. In the sketches the lower beam is the force sensing beam while dashed lines show the initial position determined by photolithography.

Figure 3.14: Notch bottom radius after fabrication and before applying external loads, taken from an AFM scan.
Figure 3.15: SEM image of the fracture surface of the specimen of experiment 2 with approximate areas of different stages of crack growth.

Figure 3.16: A magnification of the area where the pop-in took place reveals that shear bands on the surface of the specimen developed.
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failure could occur [85]. It is therefore assumed herein that chain scission in the area of plane strain is the failure mechanism. For the further discussion one needs to remember the failure hypotheses that are proposed for glassy polymers. An overview can be found in [86]. Most theories are in principle either based on the assumption of failure caused by the maximum shear stress (Tresca criterion), maximum shear and maximum normal stress causing internal friction (Mohr's criterion), only maximum normal stress or by a distortion strain energy hypothesis (von Mises criterion). Some of these principal ideas are depicted in Figure 3.18 which shows Mohr's plane $(\sigma - \tau)$ and the borders beyond which failure occurs. Additionally Mohr's circles for three dimensional and plane stress are shown. From this sketch it is also obvious that a triaxial stress state can lead to brittle rupture while plane stress favours shear failure. This also strengthens the idea of rather brittle behaviour at the crack tip while away from it shear banding could occur. If this was true the shear bands must appear under an angle of about $45^\circ$ between the maximum principal stress and the minimum principal stress. The minimum principle stress is the out-of-plane stress $(\sigma_3)$ which equals zero away from the tip. The direction of the maximum principal stress $\sigma_1$ is difficult to determine due to the complicated stress state around the crack. Nonetheless it is reasonable to assume that it does not deviate much from the direction of the nominal stress along the longitudinal axis of the specimen. By assuming this it can be seen that the shear bands are more or less orthogonal to these stresses. In Figure 3.19 an explanation for this is shown: through thickness shear banding under an angle of about $45^\circ$ relative to the $e_1$ and $e_3$ directions. Similar processes have also been proposed by [85, 87] for thin specimens. This would also explain why there are no shear bands close to the notch: only when the crack has reached a critical length then the maximum principal stress reaches a critical value due to reduced cross sectional area. Therefore also $\tau_{max}$ will then reach $\tau_{crit}$. In Figure 3.20 the shear bands of the second specimen at the opposite side of the notch are shown. The angle between maximum principal stress and the shear bands is not always perfectly perpendicular which might be contributed to surface roughness and material inhomogeneities that could locally slightly alter stress states. As another interesting observation in Figure 3.20, one could clearly see how the width of the sheared region increases with increasing crack length because all stresses around the crack tip grow because of decreasing cross sectional area of the specimen. This is schematically illustrated in Figure 3.21. This also explains why there is a considerable strain at break of about 10 percent [6]: the deformation in P12723 is localized in a small shear band region while other areas of the specimen do not yield. In summary, chain scission takes place in a complex three dimensional stress state and therefore in the bottom of the crack and shear banding is favoured in plane stress condition in adjacent areas. Molecular models for both processes based on ideas presented in [88] are sketched in Figure 3.22.

3.2.6 Outlook

While in these experiments only the crack length was determined the application of digital image correlation (DIC) software could greatly enhance the possibilities of the setup. Figure 3.23 shows the results obtained by the DIC software package VEDDAC (Chemnitzer Werkstoffmechanik GmbH, Chemnitz, Germany). Not only could the crack tip opening displacement be observed but also the displacement field ahead of the tip could in principle be analyzed. Both informations would be of great use in the application of fracture mechanics theories to the results and have partly already been reported in the literature for a resin polymer compact tension (CT) specimen [90]. Other examples in the literature on the determination of the displacement field around crack tips were based on AFM [90] or scanning tunneling microscopy (STM) [91] but without measurement of forces and stresses. Further improvements of the experiments seem to be possible by changing the layout of the P1 specimens by applying rules set by Feddersen [92]. Instead of single notched specimens as used in this study, middle tension specimens with a defined ratio of notch length to specimen width would be used. This would allow for a simplified quantitative determination of $K_{IC}$. 

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Figure 3.17: Sketch showing the stress states in the vicinity of the corner crack. Underneath the bottom of the crack a multiaxial three dimensional stress state and plane strain are to be expected while further away from the crack plane stress dominates.

Figure 3.18: Schematic of Tresca and Mohr criteria in Mohr’s plane. Additionally, Mohr’s circles for plane stress and three dimensional stress are depicted. The schematic shows that a multiaxial three dimensional stress state favors brittle rupture associated with e.g. the maximum principal stress criterion. In contrast material subjected to plane stress fails under maximum shear stress as predicted by e.g. the Tresca criterion [76,89].
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Figure 3.19: Sketched side view of the specimen with possible explanation of the shear bands: under an angle of 45° between the maximum principal stress ($\sigma_1$ in direction of $e_1$ i.e. the longitudinal axis of the sample) and the out-of-plane minimum principal stress ($\sigma_3$, outside the crack area this stress is zero).

Figure 3.20: SEM picture of the second specimen. It shows the area opposite of the notch (see inset). The shear banded area grows due to increasing stresses with decreasing remaining cross sectional area. The sputtered gold layer partially came off and revealed the underlying patterns on the polyimide surface.
3 Microtensile Tests

**Figure 3.21:** The size of the plane stress zone ahead of the crack grows with increasing crack length. Therefore also the width of the shear banding zone increases towards the right edge of the sample.

**Figure 3.22:** Molecular models of the failure behaviour. Depending on the stress state the polymer either fails by chain scission or shear banding (based on ideas in [76, 88]): the strong entanglement prevents chains from reptating which eventually leads to chain scission and therefore brittle fracture. Shear banding is still possible as under shear loads the chains could still slide by each other without disentanglement or chain scission.
3.2 Observing Crack Propagation in Polyimide Microtensile Specimens

![Image of a displacement field at a crack tip obtained with DIC software VEDDAC.](image)

**Figure 3.23:** Displacement field (white) at the crack tip obtained with the DIC software VEDDAC. It shows the state right before final rupture.

3.2.7 Conclusions

It was shown that the AFM could be used to observe crack propagation with micrometer resolution in polyimide microspecimens. By applying beam mechanics to the deformation of a double fixed silicon beam connected to the specimen forces in the range of millinewtons could be measured. This also allowed for the simple determination of residual nominal stresses. By combining the two data sets of nominal stresses and AFM scans the determination of stress-crack-length diagrams was possible. Different stages during crack growth could be identified. Combined with SEM pictures of the process zone it was then possible to characterize the fracture and deformation behaviour of very thin layers of PI2723. Future experiments could be done with different geometries and by using DIC software and might therefore allow a reliable quantitative determination of fracture toughness.

Acknowledgements

The authors would like to express their gratitude to Prof. Bharat Bhushan from the Ohio State University, Prof. Tahar Saif from the University of Illinois at Urbana-Champaign, Dr. Hans-Jakob Schindler from Mat-Tec AG (Winterthur, Switzerland), Dr. Pieter van Schendel from Nanosurf AG (Liestal, Switzerland), Dipl.-Ing. Bettina Seiler and Dr. Michael Dost from CWM GmbH (Chemnitz, Germany) and finally Dr. Nicola Naujoks from the Nanotechnology Group of ETH Zurich for very helpful discussions.
3 Microtensile Tests

3.3 Microtensile Testing of PI/PEDOT:PSS Bilayers

3.3.1 Introduction

In recent years one could observe the advent of polytronic systems e.g. systems whose electronics are based on organic materials. One major advantage that these devices have in common is their potential flexibility. As devices on flexible substrates will be bent during operation the knowledge of the mechanical properties of the materials in use is important. Typical dimensions of functional organic layers in actual devices are in the range of several hundreds of nanometers. Therefore also for mechanical testing typical dimensions of the test specimens should be in the same range. A test setup which enables the investigation of mechanical properties of submicrometer thick organic layers is proposed herein. In this study the methodology and preliminary results for testing of pure polyimide samples and of compounds made of poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate)(PEDOT:PSS) deposited on a polyimide (PI) substrate are presented. The experiments of single PI layers yield results for Young’s modulus of 2.4 GPa and 3.3 GPa. From the experimental results of testing of the bilayer the Young’s modulus of submicron thick PEDOT:PSS can be derived to be in the order of about 6 GPa.

3.3.2 Methodology

Experimental

The fabrication of the specimens is based on a wafer-level process to produce freestanding 1 µm or 3 µm thick PI723 films (HD Microsystems, Bad Homburg, Germany) by dry etching of silicon as presented in [68]. The PEDOT:PSS top layer (Baytron P, H.C. Starck GmbH, Leverkusen, Germany) with a thickness of about 500 nm is patterned by a lift-off process published in [18]. The determination of mechanical properties is based on an approach presented by Haque and Saif in [41]. Their main idea was to use the deformation of silicon double fixed beam as a force measure. Hence, the specimen is connected to two double clamped silicon beams. An external force is applied to the first beam which then transmits the force to the specimen and the force sensing beam. By applying beam mechanics as described in [93] the force can be calculated from the measured force sensing beam deflection. In the setup proposed here the external force can be imposed manually by micromanipulators (PI GmbH, Waldbronn, Germany) or by LabVIEW controlled piezo actuators (PI GmbH, Waldbronn, Germany) and is transmitted to the sample by three pins (see also Figure 3.24). For each of the two actuation methods two separate actuators are used which permits large stretching of the specimens. Furthermore, as the actuators point in opposite directions, the region of interest (force sensing beam and strain measurement area) remains almost at the same place. This enables a displacement field evaluation by digital image correlation (see below). An optical microscope with a 12 megapixel camera (both from Carl Zeiss AG, Oberkothen, Germany) is used to observe the deformation of the force sensing beam and of the strained specimen. For the tests an objective with 2.5x magnification was used which results in a sample resolution of 3.2 µm per pixel. A LabVIEW and a Visual Basic program running on the microscope PC control the acquisition of the sample pictures. Figure 3.24 shows the experimental setup with the geometry of pure PI samples. The dimensions for the bilayer specimens are shown in Figure 3.25. The geometry of the PEDOT:PSS stripe was chosen in a way that ensures that the force transfer from the substrate to the top layer via interface shearing occurs outside the strain measurement area. This means that the stripe is long enough to reach the shoulders of the sample which thus yields a homogeneous stress and strain field in the strain measurement area. The overall idea is shown in Figure 3.26. By using the commercial digital image correlation (DIC) software VEDDAC (CWM GmbH, Chemnitz, Germany) the displacements on the surface of the sample and of the force sensing beam can be evaluated with a resolution of 0.1 pixel i.e. 320 nm. This yields a force resolution of about 2.5 mN. In the study herein only every fifth image was used for the correlation in order to have displacements large enough for a reliable correlation. The calculated displacement field then allows for the determination of the strain in the sample as well as of the force sensing beam deflection. A result of a displacement evaluation is shown in Figure 3.27.
The experiments were generally conducted in two stages. First, the micromanipulators were used to bring the pins into contact with the specimen. Then the micromanipulators were used to strain the specimen for an overall range of 0.15 mm. This was achieved by applying stepwise displacements of 0.025 mm to each micromanipulator. After each step a picture with the optical microscope was taken automatically. After this stage, the piezo actuators were used to strain the specimen until final rupture. This stage was controlled by a LabVIEW program and the displacement rate of the piezo actuators was set to 1 μm per second and for each deformation step a picture was automatically taken by the microscope camera. After testing, the length of the force sensing beams was measured using the optical microscope and the image analysis software AxioVision (Carl Zeiss AG). Then the beams were deliberately ruptured and the cross section measured using again AxioVision. This ensured that only the individual actual dimensions were used for determining the forces.

**Figure 3.24**: Experimental setup of the microtensile test. Specimen geometry of pure PI samples (in μm) and of the force sensing beam (in mm) are also given. The thickness of the silicon wafer used herein was 500 μm.

**Theoretical**

The determination of the Young’s modulus of the top PEDOT:PSS layer is based on the following assumptions:

- the forces are transferred from the substrate to the top layer outside the strain measurement area. This results in a homogeneous stress and strain state in the region of interest
Figure 3.25: Dimensions of bilayer microtensile specimens (in mm). The rectangle indicates the PEDOT:PSS stripe which is deposited atop the PI substrate.

Figure 3.26: The PEDOT:PSS stripe is longer than the strain measurement area in the center of the sample. This means that the force transfer from substrate to layer occurs in the shoulder areas. Thus homogeneous stress and strain fields are obtained in the center of the sample.
**Figure 3.27:** Results of displacement evaluation by VEEDAC. The areas of strain evaluation and force sensing beam deformation are indicated.

- the difference in Young’s moduli between substrate and top layer materials is small and therefore any out of plane bending effects due to large differences in stiffness can be neglected
- differences in Poisson’s ratio can be neglected
- no interface effects in the region of interest
- only the elastic regime is analyzed
- both layers are exposed to the same strain
- the Young’s modulus of the substrate is known.

Figure 3.28 shows the fundamental idea to determine the Young’s modulus of the top layer: for the same strain $\varepsilon_0$ and same cross sectional area of the substrate any additional force will be borne by the top layer [94]. For the PI substrate the force $F_0$ can be calculated as follows:

$$F_0 = \varepsilon_0 \cdot A_{PI} \cdot E_{PI}$$

(3.10)

with $A_{PI}$ as the cross sectional area and $E_{PI}$ as the Young’s modulus of the PI substrate. Then the Young’s modulus of the top PEDOT:PSS layer is given by:

$$E_{PEDOT} = \frac{F_m - F_0}{A_{PEDOT} \cdot \varepsilon_0}$$

$$= \frac{\Delta F}{A_{PEDOT} \cdot \varepsilon_0}$$

(3.11)

with $F_m$ the total measured force at $\varepsilon_0$, $A_{PEDOT}$ the cross sectional area of the PEDOT:PSS layer and $F_0$ given by Equation (3.10).

If one introduces $x = A_{PEDOT} / (A_{PEDOT} + A_{PI})$ as the fraction of the cross sectional areas then after some calculus Equation (3.11) can be transformed to

$$E_m = x \cdot E_{PEDOT} + (1 - x) \cdot E_{PI}$$

(3.12)

with $E_m$ as the apparent Young’s modulus of the compound and to be directly derived from the measured values of strain and force.
Figure 3.28: Idea to determine Young’s modulus of a top layer. For a given strain $\varepsilon_0$ the total force $F_m$ is determined and the force $F_0$ acting on the substrate is calculated under the assumption of the knowledge of the substrate cross sectional area and the Young’s modulus of the substrate material. The next assumption then is that $\Delta F$ is completely borne by the top layer and can be thus used to calculate the stress acting on the top layer.

### 3.3.3 Results

Seven experiments were conducted at 24°C and 26% rH. Two of these experiments were done with pure PI samples, while five were conducted on bilayers with different PEDOT:PSS thicknesses. Figure 3.29 shows a typical result of a stress strain diagram obtained with the presented experimental method. Table 3.1 then gives an overview of the results of all the experiments.

![Stress-Strain for PI/PEDOT:PSS](image)

**Figure 3.29:** Stress-strain diagram for a bilayer of a 3 μm thick PI substrate and a 500 nm thick top layer of PEDOT:PSS.

### 3.3.4 Discussion

Figure 3.30 shows the Young’s moduli from Table 3.1 versus the area fraction $x$. From the added trendline it can be seen that the higher $x$, the higher is the measured apparent Young’s modulus $E_m$ of the bilayer. This shows that PEDOT:PSS seems to be stiffer than PI. The figure also shows the calculated modulus $E_{PEDOT}$. The values obtained here are two times the values measured in [24] for 25 μm thick freestanding PEDOT:PSS films. There are several possible effects that could explain this:
3.3 Microtensile Testing of PI/PEDOT:PSS Bilayers

<table>
<thead>
<tr>
<th>Exp.</th>
<th>( t_{PI} ) [( \mu \text{m} )]</th>
<th>( t_{PEDOT} ) [( \mu \text{m} )]</th>
<th>( x )</th>
<th>( E_m ) [GPa]</th>
<th>( E_{PEDOT27} ) [GPa]</th>
<th>( E_{PEDOT29} ) [GPa]</th>
</tr>
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<td>1</td>
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<td>0</td>
<td>2.45</td>
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</tr>
<tr>
<td>2</td>
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<td>0</td>
<td>3.31</td>
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</tr>
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<td>3.01</td>
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<td>0.12</td>
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<td>3.47</td>
<td>6.87</td>
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<tr>
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<td>0.95</td>
<td>0.64</td>
<td>0.66</td>
<td>4.09</td>
<td>6.16</td>
<td>5.92</td>
</tr>
</tbody>
</table>

Table 3.1: Results of microtensile testing of PI/PEDOT:PSS bilayers. \( E_{PEDOT27} \) was calculated using Equation (3.12) and a value of 2.7 GPa for \( E_{PI} \) as given in [6]. \( E_{PEDOT29} \) was determined the same way but for \( E_{PI}=2.9 \) GPa as the mean value of the two experiments with pure PI conducted in this study. The thicknesses \( t \) were obtained by a tactile profilometer.

- for the calculation of \( E_{PEDOT} \) the value of \( E_{PI} \) needs to be known as exactly as possible. The experiments showed values of 2.4 GPa and 3.3 GPa which is a large scatter. Therefore more experiments on PI samples with thicknesses in the range of 1-3 \( \mu \)m are necessary to reliably determine \( E_{PI} \).

- size effects of PEDOT:PSS. The layers tested here are about 50 times thinner than previously tested freestanding samples.

- substrate effects i.e. the PI substrate might influence the morphology of the PEDOT:PSS layer in a way that renders the PEDOT:PSS stiffer than if freestanding.

Future experiments will concentrate on the evaluation of these effects.

![Young's moduli](image)

Figure 3.30: Young’s moduli of \( E_m \) (squares), \( E_{PEDOT27} \) (circles) and \( E_{PEDOT29} \) (triangles) in dependence of area fraction \( x \). \( E_{PEDOT27} \) was calculated using Equation (3.12) and a value of 2.7 GPa for \( E_{PI} \) as given in [6]. \( E_{PEDOT29} \) was determined the same way but for \( E_{PI}=2.9 \) GPa as the mean value of the two experiments with pure PI conducted in this study. The figure shows that for increasing Young’s modulus of the substrate the calculated values \( E_{PEDOT} \) become smaller.

3.3.5 Outlook

Besides investigating the effects described in section 3.3.4, in the long run several extensions of the setup seem to be possible.

**Inkjet Printing of PEDOT:PSS Layers** In this study a lift-off process was used for patterning the PEDOT:PSS layer. In actual devices ink-jet printing is also used (e.g. in [19]). Therefore also ink-jet printed PEDOT:PSS stripes should be tested. A possible way to obtain such structures is the use of
the pipe-jet device developed at the University of Freiburg [95]. Figure 3.31 shows individual drops of PEDOT:PSS deposited with this technology. Further tests showed that stripes with thicknesses in the range of about 4 μm can be obtained. This would also enhance the range of tested area fractions x and could help close the gap of tested thicknesses of PEDOT:PSS.

![Figure 3.31: Drops of PEDOT:PSS deposited on a plastic foil by pipe-jet technology.](image)

**Electromechanical Testing** For some of the experiments also the resistance was measured. Figure 3.32 shows the result for experiment 7. It can clearly be seen that the resistance increases upon stretching. As the stripe was directly contacted with probe tips, the contact resistance might change and therefore lead to the steps in resistance. For future experiments therefore gold contacts as presented in [96] should be included to ensure reliable resistance evaluation. This would then allow to determine the strain gauge factor of PEDOT:PSS in dependence of layer thickness.

![Figure 3.32: Resistance of PEDOT:PSS stripe of experiment 7. With increasing strain the resistance also grows. The steps might have been caused by differences in contact resistance when touching the stripe with the probes.](image)

**Biaxial Microtensile Tests** The measurement principle can be extended to two axes. This would enable the evaluation of failure criteria in very thin layers. Not only organic layers on a PI substrate
could thus be tested but also thin metal layers. In a first study a biaxial test was designed and the geometry optimized in a way that possible bending moments acting on the arms of a cruciform specimen are minimized. Figure 3.33 shows the setup and the geometry of the specimen. First biaxial tests proofed the validity of the approach as the displacement field could be evaluated with VEDDAC.

**Viscoelastic Behavior** As the piezos can also be actuated at higher frequencies, tensile tests at higher frequencies to evaluate the viscoelastic behavior of thin organic specimens seem to possible. This would require to replace the current microscope camera with a highspeed camera. Then the phase shift between the deformation of the two silicon double fixed beams is a measure for the viscoelastic behavior.

**Microfabrication** In this study silicon test wafers with a thickness of about 500 μm were used. This leads to fairly long etching times. In a further step the microfabrication process should be adjusted to thinner wafers with thicknesses of 100 or 300 μm.

**Specimen Geometry** As the displacement resolution becomes better for higher optical magnifications, the specimens should be made smaller. In conjunction with the use of thinner wafers truly nanomechanical tensile tests i.e. specimens with overall thicknesses below 1 μm could thus be reached.

**Controlled Environment** As the mechanical properties of the organic materials also depend on relative humidity, an encapsulation of the setup in a micro climate chamber small enough to still fit underneath the microscope would allow for the complete mechanical characterization of thin organic layers.

### 3.3.6 Conclusions

A new idea for tensile testing in the micro and submicrometer range was presented. Preliminary results were obtained for pure PI specimens and for PI/PEDOT:PSS bilayers. It could be shown that for increasing area fractions \( x \) the bilayer becomes stiffer which means that \( E_{\text{PEDOT}} \) seems to be higher than \( E_{\text{PI}} \). For a reliable quantitative determination of \( E_{\text{PEDOT}} \) the value of \( E_{\text{PI}} \) needs to be known as precisely as possible and therefore requires additional future experiments on pure PI specimens. In section 3.3.5 possible extensions of the setup were presented which might enable new insights in many different fields ranging from electromechanical to failure criteria evaluation.
Figure 3.33: Biaxial microtensile testing: A) dimensions (in mm) of cruciform PI specimen with a thickness of 3 μm, B) Finite Element Method (FEM) optimization of the specimen to minimize the bending moments acting on the specimen. The left and the upper double fixed beams are force sensing beams for x and y direction. C) experimental setup. Four piezoactuators are used which transfer the force via pins to the specimen.
4 Application: Mechanical Sensors

4.1 Fabrication and Preliminary Testing of PEDOT:PSS Strain Gauges

4.1.1 Abstract

In recent years first commercial devices based on organic electronic materials entered the market. Recent market studies mention the necessity to include sensors in the design of organic electronic devices in order to broaden the range of applications. It is therefore essential to identify potential organic sensor materials and to develop processes and methods to structure and characterize them. Widely used in organic electronics is the complex of the intrinsically conductive polymer poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate acid (PEDOT:PSS). In this paper we first present a lift-off process for patterning thin PEDOT:PSS films. Crucial deposition parameters are systematically investigated and subsequently a reliable micropatterning process defined. Then a design for fully polymeric pressure sensors made from polyimide (PI) membranes and PEDOT:PSS strain sensors is proposed. Preliminary test results as proof-of-concept are finally shown.

4.1.2 Introduction

The most recent 2007 iNEMI (international electronics manufacturing initiative) roadmap [97] mentions the necessity to include sensors in the design of organic electronic devices. It is therefore essential to identify potential sensor materials and to develop processes and methods to structure and characterize them. First results on the piezoresistive properties of PEDOT have been presented in literature [98]. A similar material but more widely used in potential applications [4] is PEDOT:PSS. It is commercially available as an aqueous dispersion under the tradename Baytron P from H.C. Starck GmbH (Leverkusen, Germany). In this paper an idea to use it as a sensor material in mechanical transducers is presented. In the first part of the paper a lift-off process to pattern PEDOT:PSS is systematically developed and the structures obtained by this process are characterized. In the second part a bulge test setup is presented consisting of a silicon substrate with a deformable PI membrane and a PEDOT:PSS strain gauge on top. Preliminary tests finally allow to determine an approximate value for the strain gauge factor of PEDOT:PSS and therefore also show the potential of PEDOT:PSS as a material for polymeric mechanical sensors.

4.1.3 Experimental

Lift-off

In literature several techniques to pattern PEDOT:PSS have been proposed. Some approaches are based on ink-jet printing e.g. in [19]. Other possibilities include laser ablation [20,99] or lift-off processes [17,44,100]. The determination of piezoresistive properties requires a geometrically well-defined strain gauge. At the same time the patterning process should be straightforward so it could be easily integrated in mass scale fabrication. To achieve this a lift-off process (the principal steps are shown in Figure 4.1) was chosen in this study. It promises homogeneous thin film properties with well-defined dimensions. The following parameters were identified to be most important for the deposition of PEDOT:PSS by a lift-off process and were therefore closely investigated:

\textsuperscript{1}Reference [18]
4 Application: Mechanical Sensors

**Figure 4.1:** Steps during lift-off process: (a) a 3 μm thick layer of the polyimide PI2723 (HD Microsystems Ltd.) is spun on a silicon wafer, (b) a 10 μm thick layer of the photoresist AZ 4562 (Microresist GmbH) is patterned by standard photolithography, (c) Baytron P (H.C. Starck GmbH) is spin coated and then dried at 60 °C for one minute which results in a solid layer, (d) by agitating the wafer in acetone the photoresist and PEDOT:PSS on top of it are removed leaving the patterned PEDOT:PSS film behind.

- **width of lines**
  The width of PEDOT:PSS lines will influence initial resistance in strain gauge devices. It is therefore necessary to determine the fabrication restrictions. Experiments showed that for widths of less than 100 μm the PEDOT:PSS structures are lost in the acetone bath (see Figure 4.2 (a)).

**Figure 4.2:** Influence of lift-off parameters: (a) three crosses as alignment marks on mask layout (inset). The two smaller crosses were removed during lift-off, possibly due to insufficient adhesion caused by small contact area. The width of the bars of the largest cross is 100 μm. (b) If the spacing (here 100 μm) between individual lines of a meander-like structure is less than the minimum of 200 μm then the PEDOT:PSS layer remains intact over wide areas and lift-off is not possible. (c) With rounded corners as shown here the best results were obtained. The spacing between individual lines is 200 μm. (d) If the photoresist layer is too thin then its sidewalls are completely covered with PEDOT:PSS. This might be due to meniscus forces. It is therefore impossible for the acetone to dissolve the photoresist layer.

- **spacing between individual lines**
  The experiments showed that there is also a lower limit for the spacing between individual lines. Below this limit PEDOT:PSS tends to form a homogeneous layer and is subsequently completely removed in the acetone bath or large areas of PEDOT:PSS remain between the fingers (Figure 4.2 (b)). The results showed that a minimum spacing of about 200 μm is
necessary for reliable processing.

- rounded or rectangular corners
  The experiments showed that rounded corners are the preferable geometry (Figure 4.2 (c)). This is due to the same fact as before: For rectangular corners large areas of PEDOT:PSS remain in the corner which results in reduced yield.

- thickness of photoresist for lift-off
  A compromise has to be found as too thin of a resist layer renders it impossible to dissolve the photoresist in acetone due to coverage of the edges with PEDOT:PSS (see Figure 4.2 (d)) because of meniscus forces. However, if the photoresist layer is too thick this might lead to streaks during spin coating. The best results were obtained for a resist thickness of 10 μm.

- spin speed
  The most important parameter for spin coating of a given resist or dispersion is the spin speed as it determines the resulting film thickness. After patterning with the aforementioned lift-off process the resulting PEDOT:PSS structures on silicon substrates were measured using a Tencor P-10 profilometer. The results are shown in Figure 4.3. The exponent of -0.51 for the fitted curve agrees well with values for other conjugated polymers [101].

![Thickness PEDOT/PSS](image)

**Figure 4.3:** Thickness of spin coated PEDOT:PSS layers on silicon substrates in dependence of spin speed.

**Bulge Test**

In order to verify the strain sensor potential of PEDOT:PSS a bulge test was devised. The setup and the functional principle are shown in Figure 4.4. A pressure difference causes a deflection and therefore straining of the membrane. Simultaneous changes in resistance of the PEDOT:PSS strain sensor element are monitored by an electrometer (Keithley 6517A). The fabrication process for such freestanding PI membranes with 3 μm thickness and PEDOT:PSS structures on top has been shown in detail in [68]. For the proof-of-concept not meander-like PEDOT:PSS structures were designed but simple stripes were chosen (see Figure 4.4(a)).

**4.1.4 Results**

Figure 4.5 shows the results: for a pressure change from zero to 35.3 kPa and then to 48.2 kPa corresponding steps in resistance can clearly be seen. From membrane mechanics a strain gauge
4 Application: Mechanical Sensors

Figure 4.4: Bulge test: (a) actual setup for 36 membranes on a 4” wafer. The detailed view shows the dimensions of a specimen. (b) Functional principle of setup.

A factor of about 0.8 can be estimated [18]. Future work will concentrate on a systematic investigation of this effect in order to determine the strain gauge factor of PEDOT:PSS more precisely.

Figure 4.5: Proof-of-concept: defined steps in applied differential pressure cause defined steps in resistance.
4.1.5 Conclusions

Thorough investigations of a lift-off process to micropattern PEDOT:PSS films were presented. Design rules could be derived and will be of use in future sensor devices but could also be of help in other devices e.g. OLEDs or OTFTs. Then simple pressure sensors were designed whose main elements are fully made from polymers i.e. a polyimide membrane and a PEDOT:PSS strain sensor. Preliminary results show the proof-of-concept: defined pressure steps cause defined steps in resistance. From membrane mechanics an approximate value of 0.8 for the strain gauge factor could be derived. This clearly demonstrates the potential of PEDOT:PSS as a mechanical sensor material and might lead to completely organic MEMS [102].
4 Application: Mechanical Sensors

4.2 Towards Polymeric Pressure Sensors: Bulge Testing of PEDOT:PSS Strain Gauges

4.2.1 Abstract

Recent market studies mention the necessity to include sensors in the design of organic electronic devices in order to broaden the range of applications. It is therefore essential to identify potential organic sensor materials and to develop processes and methods to structure and characterize them. A material widely used in organic electronics is the complex of the intrinsically conductive polymer poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate acid (PEDOT:PSS). In this paper first the fabrication of a polyimide (PI) membrane with integrated PEDOT:PSS strain gauges is presented. Upon a pressure difference the membrane is deflected and the resulting changes in resistance of the sensor elements are recorded. By applying a membrane mechanics model the resistance changes could be linked to the strain in the membrane and then the plane strain gauge factor $k_{PS}$ for PEDOT:PSS of $0.48 \pm 0.07$ at $36.6 \pm 3\%$ could be determined.

4.2.2 Introduction

The most recent 2007 iNEMI (international electronics manufacturing initiative) roadmap [97] emphasizes the necessity to include sensors in the design of organic electronic devices. It is therefore essential to identify potential sensor materials and to develop processes and methods to structure and characterize their piezoresistive properties i.e. the strain gauge factor $k$. To the authors’ knowledge there are only few examples in the literature on intrinsically conductive polymers used as mechanical sensors. Several publications deal with fabrics coated with polypyrrole (PPy) [103–106], PEDOT [103] or PEDOT:PSS [107]. In other experiments an epoxy pellet coated with PEDOT:PSS was exposed to a compressive load and the resulting changes of resistance were recorded [108]. These publications show that there is a change of resistance under mechanical load for intrinsically conductive polymers. But because the intrinsically conductive polymer is deposited on fibers or fabrics it is loaded in a very complex mechanical stress state and the "true" piezoresistive properties can not be deduced from these results. In a next step it is therefore necessary to develop experimental setups which allow for a defined mechanical loading of the intrinsically conductive polymers in order to be able to derive quantitative relationships between load and resistance i.e. the determination of the strain gauge factor $k$. That was presented in [98] for spin coated PEDOT with a four point bending setup. Another possible candidate material for mechanical transducers is PEDOT:PSS. It is readily commercially available as an aqueous dispersion under the tradenname Baytron P from H.C. Starck GmbH (Leverkusen, Germany). So far it has been widely used in organic electronics e.g. as an electrode material in organic thin film transistors (OTFTs) or as a hole transport layer in organic light emitting diodes. A broad overview of these and other potential applications is given in [4]. In this research the idea to use it as a sensor material in mechanical transducers is presented. In order to obtain defined mechanical deformations a bulge test setup is chosen for these experiments. By applying a defined differential pressure it is possible to strain a membrane in a defined way. This method has therefore already been successfully used to determine mechanical properties of thin polymer layers [109–111]. As a substrate material PI is chosen as it has been widely used in micro machined membranes [66, 67, 112]. Based on recently published fabrication processes [18, 68] PI membranes with integrated PEDOT:PSS strain sensors are produced. Layouts for two different configurations are devised. The first one is a stripe across a rectangular PI membrane while the second one comprised four sensors in a half Wheatstone bridge. The two setups are then electro mechanically characterized in a bulge setup with a simultaneous two point recording of resistance and voltage, respectively. Based on a mechanical membrane model the piezoresistive properties of PEDOT:PSS characterized by the strain gauge factor $k$ can be derived from the experiments. This shows the potential of PEDOT:PSS as a mechanical sensor material.

Reference [98]

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4.2 Towards Polymeric Pressure Sensors: Bulge Testing of PEDOT:PSS Strain Gauges

4.2.3 Experimental

Layout

For the experiments two different layouts were used. The first approach was a stripe across a PI membrane. As principally shown in Figure 4.6 a deflection of the membrane causes a corresponding change in resistance which is directly measured by an electrometer (Keithley 6517A). The layout was accordingly straightforward with two gold pads added to ensure low contact resistance to the electrometer (see Figure 4.7). The second approach was based on a half Wheatstone bridge configuration. A full bridge was not possible due to the fact that all changes in resistance do have the same sign because all membranes deflect to the same side. Therefore in this case a half bridge gives a maximum voltage change across the bridge. The functional principle and the layout of the half bridge are shown in Figure 4.8.

![Figure 4.6: Bulge test experiment: A differential pressure causes the membrane to deflect outwards. Corresponding changes in resistance are measured simultaneously.](image1)

![Figure 4.7: Layout for stripe configuration. The PEDOT:PSS strain gauge is deposited on top of of the PI membrane. The Au contacts are added by e-beam evaporation for reliable contacts to the strain gauge.](image2)
Figure 4.8: Half bridge configuration: (a) principle, (b) actual layout. Two stripes are across PI membranes while the other two are deposited directly on the wafer. The stripes on the membranes are deflected upon a pressure difference and will therefore lead to a change in resistance. This causes a voltage change across the bridge. The dimensions of the individual strain gauges are the same as shown in Figure 4.7.
4.2 Towards Polymeric Pressure Sensors: Bulge Testing of PEDOT:PSS Strain Gauges

Fabrication Process

The fabrication process was published in detail elsewhere [18,68]. For this reason only a very brief summary with the most important steps is given here (see Figures 4.9). The final samples consisted of a 500 μm thick Si wafer with 3 μm thick PI membranes. The PEDOT:PSS strain gauges with a thickness of 150 nm were deposited on top of these membranes (see Figure 4.10).

![Fabrication Process Diagram](image)

**Figure 4.9**: Process flow for the fabrication of the samples: (a) a 3 μm thick layer of the polyimide PI2723 (HD Microsystems GmbH, Bad Homburg, Germany) is spun on a silicon wafer and imidized at 350°C for 10 minutes, (b) a 10 μm thick layer of the photoresist AZ 4562 (Microresist GmbH, Ulm, Germany) is patterned by standard photolithography, (c) Baytron P (H.C. Starck GmbH, Leverkusen, Germany) is spin coated and then dried at 60°C for one minute which results in a solid layer. By manually agitating the wafer in acetone the photoresist and PEDOT:PSS layers on top of it are dissolved leaving the patterned PEDOT:PSS film behind, (d) standard photolithography with a 10 μm thick layer of the photoresist AZ 4562 on the backside of the wafer, (e) gluing of the wafer to a support wafer for protection of the specimen and subsequent dry etching from the backside, (f) by removal of the support wafer the samples can be obtained.

![Final Stripe Specimen](image)

**Figure 4.10**: Final stripe specimen.
Bulge Test Setup

The basic principle of a bulge test is to apply a defined pressure difference and record the resulting membrane deflection. The actual bulge test setup used in this research was applied in previous experiments [113] for the determination of creep in glassy polymer membranes and was described in detail there. Here, only a very brief overview of the setup is therefore given (see Figure 4.11). The pressure is adjusted by a flow controller (Bronkhorst) which is connected to a PC with a LabVIEW control and measurement program. The resulting deflections are measured by a white light interferometer (WLI) (Zygo New View 5000) and then processed by the measurement software MetroPro (Zygo). For the stripe configuration in this research the changes of resistance during deflection were determined by two point measurements with an electrometer (Keithley 6517A). For the half bridge configuration a constant voltage source (Keithley) and a digital multimeter (Keithley 2000) and were used to record the changes in bridge voltage (see Figure 4.12). The testing voltage was 40 V for the stripe configuration and the supply voltage was 10 V for the half bridge configuration. The connections from the Au contact pads of the specimen to the recording devices were made by isolated copper wires which were glued to the pads using a silver filled adhesive (Locitite 3888).

![Diagram of the bulge test setup](image)

*Figure 4.11:* Schematics of the bulge test setup. The main components are the digital flow controller (DFC) for pressure control and the white light interferometer (WLI) for measurement of the membrane deflection. Other parts are the pressure sensor (PS) and the current meter (CM).

4.2.4 Theory

Mechanical Model

In this section the theoretical background for the deflection of a rectangular membrane (see Figure 4.13 for the geometry) and the determination of the piezoresistive properties of the strain gauge material is developed. In the actual case the membrane is a bilayer of PI and PEDOT:PSS. In general this would have to be taken into account but here the Young’s moduli $E$ of PI and PEDOT:PSS are almost the same [6,7,16] and the thickness of the PEDOT:PSS layer $t_{PEDOT:PSS}$ is smaller than $t_{PI}$. Because of this, one can assume $t = t_{PI} + t_{PEDOT:PSS}$ for the membrane thickness and $E = E_{PI}$ for the Young’s modulus of the membrane.

Since the PI layer is very thin and strongly prestressed due to residual tensile stresses (imidization at 350°C versus testing at room temperature) a membrane stress state can be assumed and the elastic deformation of the membrane can then be described by [114,115]

$$-p \left[ 1 + \left( \frac{dw}{dx} \right)^2 \right]^{\frac{1}{2}} = \left( \sigma_{xx} + \sigma_0 \right) \frac{d^2 w}{dx^2} \tag{4.1}$$

where $p$ is the applied differential pressure, $w$ the displacement and $\sigma_0$ the residual stress. Using $d\sigma_{xx}/dx = 0$ (membrane state), small curvature for small slopes and $w(-a) = w(a) = 0$, equation (4.1) can be integrated and yields...
4.2 Towards Polymeric Pressure Sensors: Bulge Testing of PEDOT:PSS Strain Gauges

![Diagram](image)

**Figure 4.12:** Bulge test setup: (a) a 4" test wafer is clamped between a plate and the pressure chamber. The plate contains 36 windows for the measurement of membrane deflection and changes in resistance of the strain gauges, (b) electrical setup for stripe configuration, (c) electrical setup for half-bridge configuration.

**Figure 4.13:** Deflected rectangular membrane with length $2b$ and width $2a$. 

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\[ w(x) = \frac{p}{2l(\sigma_{xx} + \sigma_0)} (a^2 - x^2). \]  

(4.2)

Choosing \( x = 0 \) (center of membrane) in equation (4.2) yields

\[ w_0 = \frac{pa^2}{2l(\sigma_{xx} + \sigma_0)}. \]  

(4.3)

For long membranes (\( a < 5b \)) it was shown in [114] that the deflection in the center of the membrane approaches the plane strain solution. This also emphasizes why this approach is very useful for the determination of the piezoresistive properties: at small deflections and in the center and adjacent areas no disturbing strain along the long axis of the membrane is to be expected and the resulting change in resistance can clearly be attributed to a well defined strain quantity. For coated fibers or fabric in contrast a complex multiaxial strain state occurs and the resulting change in resistance is composed of several strain components which cannot be separated. Considering then the additional condition \( \sigma_{zz} = 0 \) (thin membrane) a condition for the uniaxial strain in \( x \) direction can be found:

\[ \varepsilon_{xx} = \frac{1 - \nu^2}{E} \sigma_{xx} \]  

(4.4)

with \( \nu \) and \( E \) Poisson’s ratio and Young’s modulus of the membrane. Some additional calculus [114] then yields an expression for \( \sigma_{xx} \):

\[ \sigma_{xx}(\sigma_{xx} + \sigma_0)^2 = \frac{p^2a^2E}{6l^2(1 - \nu^2)} \]  

(4.5)

By using equations (4.4) and (4.5) it is now possible to calculate \( \varepsilon_{xx} \) if the values for \( \sigma_0 \) and \( p \) are experimentally determined and the geometrical dimensions and material properties are known. For the experimental verification of the model presented in this section, equation (4.3) can be plugged into (4.5) which yields an expression that fully describes the deformation in the center of the membrane:

\[ p = \frac{2l\sigma_0}{a^2}w_0 + \frac{4Et}{3a^3(1 - \nu^2)}w_0^3. \]  

(4.6)

For a wire made from a given material the strain gauge factor \( k \) describes the resistive behaviour under mechanical strain and is defined by:

\[ \frac{\Delta R}{R_0} = \frac{\varepsilon_{\text{geometrical}}}{1 + 2\nu} + \sqrt{\frac{\beta}{\varepsilon_{\text{piezoresistive}}}} \]  

(4.7)

with \( \Delta R \) change of resistance and \( R_0 \) initial resistance. The strain gauge factor \( k \) is composed of a geometrical component which describes the change of dimensions due to mechanical load (2\( \nu \) due to contraction along the two axes perpendicular to the tensile loading direction) while \( \beta \) describes the change of the resistive material properties under strain. In the actual case it has to be taken into account that the strain gauge is loaded in plane strain. Therefore the relative change of resistance is given by
4.2 Towards Polymeric Pressure Sensors: Bulge Testing of PEDOT:PSS Strain Gauges

\[
\frac{\Delta R}{R_0} = (1 + \nu + \beta)\varepsilon
\]

= \frac{k_{PS}\varepsilon}{2}

(4.8)

where \(k_{PS}\) is the strain gauge factor under plane strain loading conditions. It can be determined by plugging the experimentally determined values of \(R_0\), \(\Delta R\) and \(\varepsilon_{xx} = \varepsilon\) into equation (4.8). It should finally be emphasized that \(k_{PS}\) in this study is smaller than the more general value of \(k\). The difference is the value of \(\nu\) which is in the order of 0.35 for most polymers [116] and therefore presumably also for PEDOT:PSS.

Resistance and Bridge Voltage Measurements

The determination of \(k_{PS}\) is straightforward for the case of two point recording of resistance changes by simply using equation (4.8). However, for the Wheatstone bridge configuration some additional considerations are necessary. The bridge voltage \(V\) (see also Figure 4.8) is given by

\[
V = V_0 \left( \frac{\Delta R}{2R_0 + \Delta R} \right).
\]

(4.9)

By assuming that \(\Delta R\) is much smaller than \(R_0\), equation (4.9) can be simplified:

\[
V \approx V_0 \left( \frac{\Delta R}{2R_0} \right).
\]

(4.10)

Rearranging (4.10) and using (4.7) yields the equation to determine \(k_{PS}\) in half bridge configuration:

\[
\frac{V}{V_0} = \frac{k_{PS}\varepsilon_{xx}}{2}.
\]

(4.11)

4.2.5 Results

Initial Properties

After fabrication and before actual bulge testing the initial properties of the specimen were determined. Measurements of initial resistance showed values of about 1.5 M\(\Omega\) which corresponds to 0.016 S/cm for conductivity. From these results it was concluded that the contact resistance between the gold pads and the PEDOT:PSS strain gauges was negligible because it was shown to be less than 1 k\(\Omega\) [117]. Therefore it was not considered further. Given the initial resistances of about 1.5 M\(\Omega\) for the PEDOT:PSS strain gauges currents of about 0.025 mA for the stripe configuration and of about 0.003 mA for the half bridge configuration were calculated at supply voltages of 40 V and 10 V, respectively. The resistance of Cu wires from the Au contact pads of the specimens to the electrometer or multimeter was in the range of about 5 \(\Omega\). Compared to the sensor resistances this resistance was also considered negligible. From wafer bow measurements directly after imidization of the PI layer a residual stress in the PI layer of about 40 MPa could be derived which agrees well with the value given by the manufacturer [6].

Stripe Configuration

Three samples with stripe configuration were tested. Each one was loaded with several differential pressure steps. A typical result is shown in Figure 4.14. From these experiments \(\Delta R\), \(R_0\), \(p\) and \(w(0)\) and therefore \(\varepsilon_{xx}\) could be obtained. By using equation (4.8) the strain gauge factor \(k_{PS}\) was determined. The experimental results are summarized in Table 4.1 which shows a final value of \(k_{PS} = 0.48 \pm 0.07\) at relative humidities of 36.6\%±3\%.
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<table>
<thead>
<tr>
<th>Sample</th>
<th>( k_{PS} ) [( \cdot )]</th>
<th>( t ) [( ^\circ \text{C} )]</th>
<th>( \text{rh} ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.46( \pm )0.07</td>
<td>27.0</td>
<td>32.4</td>
</tr>
<tr>
<td>2</td>
<td>0.46( \pm )0.01</td>
<td>26.0</td>
<td>38.7</td>
</tr>
<tr>
<td>3</td>
<td>0.52( \pm )0.02</td>
<td>26.0</td>
<td>38.7</td>
</tr>
<tr>
<td>average</td>
<td>0.48( \pm )0.07</td>
<td>26.3( \pm )0.8</td>
<td>36.6( \pm )3</td>
</tr>
</tbody>
</table>

Table 4.1: Results of experiments for stripe configuration and ambient conditions.

Figure 4.14: Typical result for a stripe configuration experiment. The differential pressure is increased in two steps from zero to 35.3 kPa and then to 48.2 kPa. The resistance changes correspondingly. The resistance peaks and therefore pressure peaks were caused by the opening and closing of the pressure control valve of the bulge test setup.

Half Bridge Configuration

In half bridge configuration one sample was tested. The bridge voltage \( \Delta V \) was recorded during pressure changes. A typical result for the bridge voltage is shown in Figure 4.15. The strain \( \varepsilon_{xx} \) was determined as outlined in the mechanical model. Together with the supply voltage of \( V_0 = 10 \text{V} \) and equation (4.11) the strain gauge factor \( k_{PS} \) could be calculated. From the experiments a value for \( k_{PS} \) of 0.32\( \pm \)0.02 could be obtained. The relative humidity during the experiments was 46.3%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( k_{PS} ) [( \cdot )]</th>
<th>( t ) [( ^\circ \text{C} )]</th>
<th>( \text{rh} ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.32( \pm )0.02</td>
<td>24.3</td>
<td>46.3</td>
</tr>
</tbody>
</table>

Table 4.2: Results of experiments for half bridge configuration and ambient conditions.
4.2 Towards Polymeric Pressure Sensors: Bulge Testing of PEDOT:PSS Strain Gauges

![Graph of Bridge voltage over time](image)

**Figure 4.15:** Bridge voltage for a pressure step from zero to 57.5 kPa and back to zero. As all strain gauges had a fixed initial resistance the bridge voltage could not be nulled. Therefore there is a residual bridge voltage of 2.11 V due to fabrication variations. The voltage peaks and therefore pressure peaks were caused by the opening and closing of the pressure control valve of the bulge test setup.

### 4.2.6 Discussion

Two fundamental observations can be made from the results. The first one is related to the definition of the strain gauge factor. As shown in equation (4.8) the strain gauge factor is composed of a geometrical and a piezoresistive part. Assuming a commonly accepted Poisson’s ratio of \( \nu = 0.35 \) for polymers [116] yields a value of 1.35 for the geometrical part. Since \( k_{PS} = 0.48 \) at 36% rH, the piezoresistive factor \( \beta \) is about -0.9 which means that under mechanical tensile load the morphology of PEDOT:PSS is changed in a way that reduces the resistance. This might be contributed to the granular structure of PEDOT:PSS: the contraction perpendicular to the tensile load might result in a denser packing of the grains and therefore enhanced electrical conduction between these grains. Additionally, inside the grains PSS chains might already get aligned in tensile direction. This would then also lead to a better conductivity between individual PEDOT segments. The second observation is the difference in \( k_{PS} \) for the stripe and the half bridge experiments. It was shown previously in [7, 16] that the mechanical properties of PEDOT:PSS strongly depend on relative humidity e.g. Young’s modulus drops distinctively between 25 and 40% rH. Even though only one sample was tested at 46.3% rH, one could still assume that the drop of \( k_{PS} \) from 0.48 to 0.32 is related to the same influence of humidity and therefore also piezoresistive properties strongly depend on relative humidity. For potential sensor applications this means that a PEDOT:PSS mechanical transducer should be encapsulated.

### 4.2.7 Conclusions

Microfabrication techniques were used to develop pressure sensors whose deformable parts were completely made from polymers. Two different layouts (stripe and half Wheatstone bridge) were presented and tested with a bulge setup. Based on membrane mechanics a model could be derived to determine the plane strain gauge factor \( k_{PS} \). From the experimental results it was possible to obtain values for \( k_{PS} \) of PEDOT:PSS in dependence of relative humidity: \( k_{PS} = 0.48 \pm 0.07 \) at approximately 36% rH and \( k_{PS} = 0.32 \pm 0.02 \) at approximately 46% rH. The corresponding values for \( k \) are obtained by adding the value of \( \nu \approx 0.35 \) which yields \( k = 0.83 \) and \( k = 0.67 \). These results show the proof-of-concept: defined pressure steps cause defined steps in resistance. This clearly demonstrates the potential of PEDOT:PSS as a mechanical sensor material and might lead to completely organic MEMS [102]. Additionally, this result will also be of use for the design of other flexible organic electronic devices (e.g. flexible displays) where integrated PEDOT:PSS elements will be bent during operation and might therefore change the performance of electric circuits.
4 Application: Mechanical Sensors
5 Conclusions and Outlook

In this thesis, methods to mechanically characterize thin organic layers were presented. This chapter shall give a brief overview of the findings and is separated into sections corresponding to the different research projects. Each section contains subsections covering fabrication details, summaries of the applied methodologies, results and outlooks.

5.1 Freestanding PEDOT:PSS Films

Fabrication Reliable fabrication of 25 µm thick freestanding tensile specimens.

Methodology Installation of experimental setup in a climate chamber and tensile tests under controlled environmental conditions. The morphology of the films was investigated by electron microscopy (HAADF-STEM, EDX and TEM) and atomic force microscopy.

Results The main insight gained was that with increasing humidity the material became weaker e.g. Young's modulus dropped from 2.8 GPa for 23% rH to about 0.9 GPa for 55% rH. Furthermore the fracture behavior turned from brittle to plastic. The morphological analysis showed that the films were composed of individual grains with a mean size in the range from about 50 nm to 80 nm with a PSS rich shell and a PEDOT rich core.

5.2 Microtensile Tests

Fabrication Development of a silicon dry etching process to fabricate microtensile specimens with polyimide substrate thicknesses down to 1 µm. Functional layers to be mechanically tested can be deposited and patterned atop the substrate by e.g. lift-off, shadow mask or inkjet printing.

Methodology The force measurement was based on the deflection of a double fixed force sensing beam and the application of beam mechanics to derive the force.

5.2.1 In Situ Atomic Force Microscopy

Methodology The geometry of the PI specimens included a single notch on one side. During straining, an AFM integrated into the setup was used to in situ monitor crack growth. SEM fractographs were used to investigate the fracture surface.

Results Stress-crack growth diagrams were obtained. The SEM images revealed that the fracture surfaces were smooth caused by brittle fracture while in the vicinity of the notch shear banding occurred.

Outlook DIC could be used to analyze crack tip opening displacement. This would allow to apply fracture mechanics theories.
5 Conclusions and Outlook

5.2.2 Testing of PI Films and of PI/PEDOT:PSS Bilayers

Methodology DIC was used to evaluate the strain in the specimen and the force sensing beam deflection. A mechanical model to derive the Young’s modulus of the top layer was presented.

Results The Young’s modulus of the PI samples was 2.4 GPa and 3.3 GPa. Bilayer samples exhibited an increasing stiffness for increasing area fractions \( x \). This showed that PEDOT:PSS was stiffer than PI.

Outlook Future tracks of research seem to be possible in the following fields:

- testing of bilayers with different area fractions \( x \) to investigate possible size effects
- testing of inkjet printed PEDOT:PSS structures
- biaxial microtensile tests
- investigations of viscoelastic behavior
- use of thinner Si wafers to speed up sample fabrication
- smaller samples to improve strain resolution
- determination of strain gauge factor in dependence of layer thickness
- use of small climate chambers to conduct experiments under controlled environments

5.3 PEDOT:PSS Pressure Sensor

Fabrication Development of a lift-off process to reliably pattern thin layers of PEDOT:PSS on PI substrates.

Methodology Membrane mechanics was used to derive a relationship between deflection of the membrane and strain in the PEDOT:PSS stripe. By measuring resistance changes caused by pressure differences the strain gauge factor could be derived. For measuring the resistance changes two different configurations were used: a stripe and a half bridge.

Results A plane strain gauge factor of 0.48 for stripe configuration and 36.6% rH could be derived. For the half bridge configuration and 46.3% rH the plane strain gauge factor was 0.32.

Outlook Next steps should include the integration of amplifiers made of organic materials to improve signal quality. In the long run, total polymer MEMS could be achieved.

In summary, methods to mechanically characterize organic films with thicknesses of about 500 nm and 25 \( \mu m \) were developed and their applicability proven by experimental results. Future test series could therefore be based on the presented methods and would allow for a statistically relevant determination of mechanical properties of industrially important intrinsically conductive polymers and organic semiconductors.
Bibliography


Bibliography


Bibliography


Bibliography


Bibliography


Bibliography
Curriculum vitae

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Education

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