Evaluation of Viscoelastic Materials for MEMS by Creep Compliance Analysis

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ETH ZURICH

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presented by

BERND MICHAEL SCHÖBERLE
Diplom Ingenieur, Albert Ludwigs Universität Freiburg

born 16.07.1976

accepted on the recommendation of
Prof. C. Hierold, examiner
Prof. P. Hauptmann, co-examiner

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Abstract

This thesis advances the current state-of-the-art in microscale material testing in two aspects. First, a new methodology is established to determine the long term creep compliance of non-linear viscoelastic thin films using fully clamped diaphragms under tensile stress. Second, the mechanical properties creep compliance, fracture strength and intrinsic in-plane stress of several photosensitive polymers are investigated and quantified with the introduced approach.

The measurement methodology employs the bulge test method, the resonant vibrometry test method and the uniaxial tensile test method. Theoretical models for non-linear viscoelastic behavior of membranes are established and experimentally verified. They include the influence of the specimens’ geometry as well as the complex loading conditions. The intrinsic tensile in-plane stress and strain of the polymeric thin films are integrated. Simulations support the model assumption of plain-strain conditions in the chosen geometry of the diaphragms.

A statistically firm experimental analysis of time-dependent mechanical behavior of MEMS-relevant polymers is performed under consideration of material constraints and the measurement technique. The materials are chosen on the basis of a physical property evaluation which reviews their suitability to serve in mechanically active microelectromechanical systems (MEMS). Three different negative photoresist formulations are thoroughly characterized. Experimental results are presented for the highly cross-linked epoxy resin SU-82002, the polyimide PI2737 and for GLM2060, a composite version of SU-8, filled with silica nanoparticles.

Based on a series of creep experiments, the isothermal long-term creep behavior of the polymeric thin films in their non-linear viscoelastic regime is extrapolated according to the time-stress superposition principle. Master creep compliance curves, predicting the creep compliance up to $t > 10^{10}$s are constructed. The shift factors of the individual creep compliance curves can be described by the Eyring theory of stress activated plastic flow for all experiments.

The fracture strengths are quantified and the von-Mises model is verified for the description of the latter under complex loading conditions for SU-8. Reference measurements of the fracture strength and the glassy modulus are taken on bone shaped SU-8 samples with an uniaxial tensile test setup. Furthermore, the time and temperature dependent characteristics of the intrinsic in-plane stress of SU-82002 membranes are investigated. Additionally, a fourth material is subject to experimental studies: GCM3060, a conductive SU-8 composite filled with silver microparticles. It is characterized in its mechanical short term behavior.

All experimentally obtained material properties are summarized in the following table.
Results: Compilation of the most important results of the tested materials. The products SU-2002 (epoxy) and PI2737 (polyimide) are unfilled negative photosensitive formulations. The composites GLM2060 and GCM3060 are based on the standard SU-8 formulation as matrix with silica nanoparticles and silver microparticles, respectively.

<table>
<thead>
<tr>
<th>Measurand / Parameter</th>
<th>SU-8_{2002}</th>
<th>PI2737</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial creep compliance $D_0$</td>
<td>0.251GPa$^{-1}$</td>
<td>0.101GPa$^{-1}$</td>
</tr>
<tr>
<td>Transient creep compliance $D_e$</td>
<td>0.310GPa$^{-1}$</td>
<td>0.187GPa$^{-1}$</td>
</tr>
<tr>
<td>Time constant $\tau$</td>
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<td>1.10·10^{10}s</td>
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<tr>
<td>Coupling parameter $m$</td>
<td>0.208</td>
<td>0.34</td>
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<td>Equivalent reference stress $\theta_{eq,ref}$</td>
<td>13.2MPa</td>
<td>13.8MPa</td>
</tr>
<tr>
<td>Fracture strength $\sigma_{f,eq}$</td>
<td>62.9MPa</td>
<td>100.1MPa</td>
</tr>
<tr>
<td>Initial in-plane strain $\epsilon_0$</td>
<td>0.0038</td>
<td>0.2% .. 0.19%</td>
</tr>
<tr>
<td>Initial in-plane stress $\sigma_0$</td>
<td>$\sim$ 21.4MPa</td>
<td>23.3MPa .. 21.6MPa</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measurand / Parameter</th>
<th>GLM2060</th>
<th>GCM3060</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial creep compliance $D_0$</td>
<td>0.199GPa$^{-1}$</td>
<td>0.175GPa$^{-1}$</td>
</tr>
<tr>
<td>Transient creep compliance $D_e$</td>
<td>0.234GPa$^{-1}$</td>
<td>not applicable</td>
</tr>
<tr>
<td>Time constant $\tau$</td>
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<td>Coupling parameter $m$</td>
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<tr>
<td>Equivalent reference stress $\theta_{eq,ref}$</td>
<td>21.5MPa</td>
<td>not applicable</td>
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<tr>
<td>Fracture strength $\sigma_{f,eq}$</td>
<td>80.1MPa</td>
<td>65.7MPa</td>
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<tr>
<td>Initial in-plane strain $\epsilon_0$</td>
<td>0.54% .. 0.48%</td>
<td>$\sim$ 0.27%</td>
</tr>
<tr>
<td>Initial in-plane stress $\sigma_0$</td>
<td>33.8MPa .. 30.4MPa</td>
<td>$\sim$ 22.2MPa</td>
</tr>
</tbody>
</table>
Zusammenfassung


Die Untersuchungen liefern neue Erkenntnisse über das mechanische Langzeitverhalten der untersuchten Dünnfilme, ihre Beanspruchungsgrenzen bei mehraxialen Belastungen sowie die zeit- und temperaturabhängigkeit der Vorspannung von
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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{thermal}$</td>
<td>Coefficient of thermal expansion (CTE)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Shape parameter</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Cantilever tip deflection</td>
</tr>
<tr>
<td>$\Delta F$</td>
<td>Maximum random error</td>
</tr>
<tr>
<td>$\Delta \bar{F}$</td>
<td>Mean error of function $F$</td>
</tr>
<tr>
<td>$\Delta_{rel}$</td>
<td>Relative error</td>
</tr>
<tr>
<td>$\Delta_{abs}$</td>
<td>Absolute error</td>
</tr>
<tr>
<td>$\Delta L$</td>
<td>Laplace operator</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Strain</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>Initial in-plane strain</td>
</tr>
<tr>
<td>$\epsilon_p$</td>
<td>Pressure induced strain</td>
</tr>
<tr>
<td>$\epsilon_{tot}$</td>
<td>Total strain</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Damping ratio</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Shear stress</td>
</tr>
<tr>
<td>$\theta_{eq,ref}$</td>
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</tr>
<tr>
<td>$\bar{\theta}_{eq,ref}$</td>
<td>Averaged equivalent reference stress</td>
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</tr>
<tr>
<td>$\nu$</td>
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<td>Stress</td>
</tr>
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<td>$\sigma_0$</td>
<td>Initial in-plane stress</td>
</tr>
<tr>
<td>$\sigma_{ij}^d$</td>
<td>Deviatoric stress</td>
</tr>
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<td>$\sigma_f$</td>
<td>Fracture strength</td>
</tr>
<tr>
<td>$\sigma_{f,eq}$</td>
<td>Equivalent uniaxial fracture stress</td>
</tr>
<tr>
<td>$\sigma_{ij}^h$</td>
<td>Hydrostatic stress</td>
</tr>
<tr>
<td>$\sigma_p$</td>
<td>Pressure induced stress</td>
</tr>
<tr>
<td>$\sigma_{tot}$</td>
<td>Total stress</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Time constant for creep</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
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List of symbols and abbreviations: Latin letters

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<thead>
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<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$a$</td>
<td>Dimensionless non-linearization factor</td>
</tr>
<tr>
<td>$b$</td>
<td>Weibull modulus</td>
</tr>
<tr>
<td>$c_{ijkl}$</td>
<td>Elastic modulus tensor</td>
</tr>
<tr>
<td>$d$</td>
<td>Damping coefficient</td>
</tr>
<tr>
<td>$D$</td>
<td>Creep compliance</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Initial creep compliance</td>
</tr>
<tr>
<td>$D_e$</td>
<td>Transient creep compliance</td>
</tr>
<tr>
<td>$D_{flex}$</td>
<td>Flexural rigidity</td>
</tr>
<tr>
<td>$E$</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>$E/(1-\nu^2)$</td>
<td>Plain strain modulus</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$G$</td>
<td>Shear modulus</td>
</tr>
<tr>
<td>$h$</td>
<td>Structure thickness</td>
</tr>
<tr>
<td>$H$</td>
<td>Potential energy</td>
</tr>
<tr>
<td>$I_1^\sigma$</td>
<td>First invariant of the stress tensor</td>
</tr>
<tr>
<td>$I_1^\epsilon$</td>
<td>First invariant of the strain tensor</td>
</tr>
<tr>
<td>$l_x, l_y$</td>
<td>Lateral extensions width and length</td>
</tr>
<tr>
<td>$K$</td>
<td>Bulk modulus</td>
</tr>
<tr>
<td>$m$</td>
<td>Coupling parameter</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of samples</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
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<tr>
<td>$P$</td>
<td>Probability</td>
</tr>
<tr>
<td>$Q$</td>
<td>Quality factor</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$s_{ijkl}$</td>
<td>Elastic compliance tensor</td>
</tr>
<tr>
<td>$s_x$</td>
<td>Uniaxial load</td>
</tr>
<tr>
<td>$s_0$</td>
<td>Non-linearity factor</td>
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</table>
List of symbols and abbreviations: Latin letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$t_{f,1-\alpha}$</td>
<td>Student’s t-distribution</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_W$</td>
<td>Weibull strength</td>
</tr>
<tr>
<td>$u, v, w$</td>
<td>Displacements in the x,y and z direction</td>
</tr>
<tr>
<td>$U$</td>
<td>Elastic potential</td>
</tr>
<tr>
<td>$U^h$</td>
<td>Hydrostatic potential</td>
</tr>
<tr>
<td>$U^d$</td>
<td>Distortion potential</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
</tr>
<tr>
<td>$V^*$</td>
<td>Activation volume</td>
</tr>
<tr>
<td>$W$</td>
<td>Elastic energy density</td>
</tr>
<tr>
<td>$\bar{x}$</td>
<td>Measured mean value</td>
</tr>
<tr>
<td>$x, y, z$</td>
<td>Cartesian coordinate axis</td>
</tr>
<tr>
<td>$Z_{\alpha/2}$</td>
<td>Confidence level</td>
</tr>
</tbody>
</table>
1 Introduction

This chapter first presents the motivation of this work. Then, the state-of-the-art in microtesting, the objectives and the methodology are introduced. Finally, the structure of this thesis is given.

1.1 Motivation

About two decades ago, the discipline of micro-electro-mechanical-systems (MEMS) emerged from the field of microelectronics by expanding the latter with the possibility to directly interact physically or chemically with the environment [1]. Due to the systems’ small size, the high integration factor, low power consumption, cheap unit price and high performance, this technology gained a remarkable share in the markets of automotive sensor systems, biomedical devices and optical applications. Certain sub-classes of MEMS devices require the employment of materials other than the traditional choices silicon or metal to be able to offer the expected characteristics. Optical systems usually employ materials which are transparent at wavelengths below infrared. Biomedical devices often have large lateral extensions compared to microelectronic chips. But since they are typically disposables, they have to be low priced at the same time. Other systems get in contact with aggressive chemical media and need to be inert. Hence, polymers are considered as materials of high potential in microsystems technology. They provide a broad variety of desirable properties. Many polymers are optically transparent at visible light. Some are biocompatible or even biodegradable. Most are electrically isolating and can still be actuated with the Kelvin–polarization force. Their mass density is low compared to semiconductors and metals. And the mechanical properties are adjustable, from brittle to hyperelastic. A further advantage is the comparatively low price of material and processing. The use of polymers as construction material has caused great excitement in recent years throughout the MEMS community. Increasing attention is drawn to fast and highly parallel processing techniques with photopolymers [2] and cheap replication methods, such as injection molding [3], reaction injection molding [4] and hot embossing [5]. However, most of the publications have been reporting on very simple, mechanically inactive polymer structures or with organic substrates. But since cost pressure is high and silicon is a relatively expensive feedstock, polymers become in-
creasingly popular even for more complex micromechanical structures [6, 7]. The vision within our group is, to partly replace the common materials for mechanically active structures in MEMS by carefully chosen, possibly designed and particularly well characterized polymers. This step though requires a deeper understanding of the employed materials’ mechanical behavior.

The applicability of data, obtained by macroscopic tests to microstructured devices is highly questionable due to the immense change of the surface-to-volume ratio, different processing, varying resin formulations and potential finite-size effects. Thus, for material characterization in small scales, an increasing number of different characterizations techniques are being conducted, boosted by surprising results, such as the extraordinary long life time of micro mirror hinges and their unexpected failure mechanism [8]. However, results of material property measurements in the microregime vary strongly [9–16], due to the immense influence of the fabrication methods and problems with accurate quantification of the measurands.

Also, the molecular structure of polymers can be eminently altered over time by internal physical processes and chemical reactions. These are particularly influenced by time and temperature during the process [17, 18]. Over the last years, great efforts have been spent on characterizing and establishing photosensitive polymers as structured, mechanically active materials in MEMS [10, 13, 14, 19–22]. However, their viscoelastic characteristics have not been investigated systematically for the case of microscaled structures. The viscoelastic nature of all polymers gives rise to time-dependent phenomena such as creep and stress relaxation. Creep in polymers can be significant, even at room temperature, and is rapidly accelerated by an increase in temperature or load. In particular, from the point of view of long-term performance of polymers for structural use in MEMS, creep has to be carefully accounted for in material selection issues.

All this results in an essential need to advance the investigation methods for micromachinable materials in the target dimensions of potential devices. Furthermore, the expected variations in outcome require a statistical approach for the interpretation. A discussion of possible systematic error sources and a compilation of mechanisms that are supposed to be randomly exerting influence on the measurements is needed.

### 1.2 State-of-the-art

This chapter gives an overview of the current state-of-the-art in the following research areas:

- Microscale testing of polymers used in MEMS
- Bulge testing of free-standing thin films
1.2 State-of-the-art

- Vibrational analysis of small viscoelastic diaphragms
- Alternative testing methods in the micrometer regime

For the reader’s convenience, table 1.1 compiles the mentioned test methods’ capabilities to determine mechanical material parameters in the microregime. Table 1.2 gives an overview of their general characteristics.

### Table 1.1: Experimental methods for mechanical measurements in the micrometer regime

<table>
<thead>
<tr>
<th>Property</th>
<th>Beam and plate bending</th>
<th>Bulge test</th>
<th>Nanoindentation</th>
<th>Pull-in test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prestress $\sigma_0$</td>
<td>Vlassak 1992</td>
<td>Xiang 2005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prestain $\varepsilon_0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stress gradient $d\sigma/dz$</td>
<td>Baek 2005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plain strain modulus $E(1+\nu)$</td>
<td>Hou 2004</td>
<td>Vlassak 1992</td>
<td>Li 2002</td>
<td></td>
</tr>
<tr>
<td>Poisson’s ratio $\nu$</td>
<td>Vlassak 1992</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strength $\sigma$</td>
<td>Hollman 1995</td>
<td>Xiang 2006</td>
<td>Li 2002</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coefficient $\alpha_{th}$</td>
<td>Ziebart 1998</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Creep</td>
<td>O’Connell 2005</td>
<td></td>
<td></td>
<td>Briscoe 1999</td>
</tr>
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</table>

### Table 1.2: General characteristics of the methods

<table>
<thead>
<tr>
<th>Property</th>
<th>Resonant structures</th>
<th>Surface acoustic wave test</th>
<th>Uniaxial tensile test</th>
<th>Wafer bow test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prestress $\sigma_0$</td>
<td>Baek 2005</td>
<td></td>
<td></td>
<td>Stoney 1999</td>
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<tr>
<td>Prestain $\varepsilon_0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stress gradient $d\sigma/dz$</td>
<td>Petersen 1978</td>
<td>Yu 2004</td>
<td></td>
<td>Sharpe 1997</td>
</tr>
<tr>
<td>Young’s modulus $E$</td>
<td>Tong 1994</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plain strain modulus $E(1+\nu)$</td>
<td>Tong 1994</td>
<td></td>
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<td>Sharpe 1997</td>
</tr>
<tr>
<td>Poisson’s ratio $\nu$</td>
<td></td>
<td></td>
<td></td>
<td>Sharpe 1997</td>
</tr>
<tr>
<td>Strength $\sigma$</td>
<td></td>
<td></td>
<td></td>
<td>Sharpe 1997</td>
</tr>
<tr>
<td>Thermal expansion coefficient $\alpha_{th}$</td>
<td></td>
<td></td>
<td></td>
<td>Lorenz 1998</td>
</tr>
<tr>
<td>Creep</td>
<td></td>
<td></td>
<td></td>
<td>Schapery 1969</td>
</tr>
</tbody>
</table>

1.2.1 Microscale testing of polymers used in MEMS

An increasing number of publications on the characterization of mechanical properties of polymers can be found in MEMS related literature. Various methods are applied: uniaxial tensile testing [10,12,13,54–56], beam and plate bending [14,21,57–60], resonant structures [12], surface acoustic wave tests [38], nanoindentation [61], wafer bow testing [16,62], and bulge testing [37,63–69].

The above tests employ common methods and models used for the evaluation of traditional MEMS materials (metals and semiconductors). Whereas the use of approved testing methods in the micrometer regime is reasonable, the employed models assume linear elastic behavior. Thus they are not suitable to describe the correlation between stress and strain of solid polymers.
1 Introduction

<table>
<thead>
<tr>
<th>Method</th>
<th>Materials</th>
<th>Geometry of specimen</th>
<th>Specimen preparation *</th>
<th>Preparation effort relative to other methods</th>
<th>Geometrical limitations</th>
<th>Effort for investigation under environmental influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam and plate bending</td>
<td>preferably brittle solids</td>
<td>cantilever [Hollman 1995]</td>
<td>structuring, release</td>
<td>high</td>
<td>medium size structures (&lt;µm²)</td>
<td>passive: low [Yi 1999]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>Materials</th>
<th>Geometry of specimen</th>
<th>Specimen preparation *</th>
<th>Preparation effort relative to other methods</th>
<th>Geometrical limitations</th>
<th>Effort for investigation under environmental influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface acoustic wave test</td>
<td>solids</td>
<td>thin film [Yu 2004]</td>
<td></td>
<td>low</td>
<td>medium surface area required (&lt;µm²)</td>
<td>low [Lorenz 1998]</td>
</tr>
</tbody>
</table>

* Presumed, the investigated thin film is already applied to a supporting surface

Table 1.2: General characteristics of the specified methodologies. The information are taken from the following publications: Beams 1955 [40], Biswas 1996 [41], Gerlach 1996 [42], Haque 2003 [43], Hollman 1995 [26], Hou 2004 [27], Jadaan 2003 [44], Kalkman 2003 [45], Kim 1999 [46], Lorenz 1998 [16], Lund 2004 [47], Osterberg 1997 [48], Paul 1999 [49], Petersen 1982 [1], Sharpe 2003 [50], Srikar 2003 [51], Stoney 1909 [33], Tabata 1989 [52], Yi 1999 [53] and Yu 2004 [38]. Statements without reference are either common sense or the opinion of the author.
1.2 State-of-the-art

Few investigations in the MEMS field report on polymer testing in consideration of viscoelastic behavior. Ruhmann [70] reported on the time dependence of the intrinsic in-plane stress in modified SU-8, Hossenlopp [22] investigated the dynamic response of SU-8, O’Connell studied the creep response of ultra-thin thermoplastic membranes [29], and we examined non-linear viscoelastic creep of SU-8\textsubscript{2002} [71]. The main groups, performing scientific work in the field of polymeric MEMS are: Prof. R. Farris (University of Massachusetts Amherst), Prof. C. Lexcellent (University de Franche-Comte), and Prof. P. Renaud (EPF Lausanne).

1.2.2 The bulge testing method

In 1915, Hencky [72] was the first to describe the deflection of a fully clamped circular membrane under an applied uniform pressure. Forty years later, Campbell [73] extended this model by adding a term which accounts for an intrinsic tensile in-plane stress. In the same decade, Beams et al. [74] were the first to report on mechanical testing of thin films with the bulge test method. In the beginning, the method suffered from a number of problems, such as sample preparation, handling and data acquisition. With the advent of silicon micro-machining, these difficulties could be overcome. In 1983 Bromley [75] published the first bulge tests with specimens of metal and SiN\textsubscript{x} which were fabricated with MEMS technology. The precise control of geometry and the repeatable and reduced specimen handling led to results with better precision. In the following, the models for circular specimen were improved to gain higher accuracy.

The analytical linear-elastic model for circular diaphragms was amended to account for large deflections and bending stress due to finite flexural rigidity [76–78] and was adjusted to finite element model simulation results [64, 79–81]. Circular diaphragms have been used to measure metals [80, 82, 83], ceramics [80, 84, 85], and polymers [29, 64, 66].

An analytical solution for deflected square and rectangular shaped diaphragms was available as early as 1949 [86]. However, Levy’s derivation was of academic value and far too complex for practical application. Allen [63] was the first to come up with an approximated linear-elastic solution, which he employed to evaluate micro-sized polyimide samples. Thereupon, a group of scientists extended and improved this approach [35, 52, 87, 88]. Square and rectangular diaphragms have been employed to measure metals [45, 89, 90], ceramics [88, 91–95], semi-conductors [96–98], polymers [37, 63–69] and multi-material, stacked layers [52], always assuming linear-elasticity.

Work on general error analysis in bulge testing was conducted by Small and Mitchell [94, 99]. Ziebart and Vlassak quantified the error if the flexural rigidity is neglected.
1 Introduction

[39, 89]. Gerlach [42] investigated the behavior of clamping conditions with finite mechanical stiffness analytically and by means of FEM simulations and evaluated the influence on the bending of plates. Various mechanical properties of free-standing thin films with zero or tensile intrinsic in-plane stress can be quantified by means of the bulge testing method. From the pressure-deflection behavior and diaphragm’s shape, the stress and strain at any point within the structure can be determined. Hence, the intrinsic in-plane stress, Young’s modulus, Poisson’s ratio, as well as fracture stress and strain may be quantified for linear-elastic materials [100]. In recent years, the use of the bulge test has been extended: the influence of humidity on polymers was investigated [69] and time dependent effects, such as fatigue [101], accelerated life time testing [102], plastic deformation [36, 103], linear viscoelastic creep [29], and non-linear viscoelastic creep [71] were modeled and measured. The determination of time-dependent properties has mostly been circumvented due to the challenging problems in testing and modeling. However, an adequate evaluation of viscoelastic materials certainly requires this effort.

The fabricated specimens for bulge testing also qualify for point load or punch testing [81] and vibrational analysis (c.f. paragraph Vibrational analysis of small viscoelastic diaphragms below). In case of a material with compressive pre-stress, the measurements can be accomplished by expanding the single layer diaphragm to a multilayer diaphragm with a net tensile intrinsic in-plane stress [52]. Buckling in films with sufficiently high compressive in-plane stress are described in [39, 49, 104–106].

The main groups, performing scientific work in the field of microscaled bulge testing are: Prof. J. Vlassak (Harvard University, Cambridge). He has been publishing on this topic from the very beginning of MEMS based bulge testing. From 1990 onwards: Prof. O. Paul (Albert Ludwigs University, Freiburg). He first investigated compressively pre-stressed films and now works with Dr. Gaspar on a high-throughput measurement setup. Furtheron, the groups of Prof. D. Senturia (retired from MIT in 2002) and Prof. R. Nix (Stanford University) should be mentioned.

1.2.3 Vibrational analysis of small viscoelastic diaphragms

Vibrational analysis of diaphragms yields information on the sample’s resonant modes and their corresponding frequencies. Depending on their material, geometry and the intrinsic in-plane stress, flat diaphragms may act as membrane or thin plate. The resulting characteristics give information on the flexural rigidity with respect to the specific mass density for a thin plate or the intrinsic in-plane stress with respect to the specific mass density for a membrane [107, 108]. Usually, the specimens are designed in such a way, so that membrane behavior is achieved and the intrinsic in-
1.2 State-of-the-art

Plane stress can be determined - supposed that the specific mass density is known. An elegant way of observing the vibrational modes at resonant frequencies is the non-invasive measurement with Laser-Doppler-Vibrometry. **State-of-the-art systems** allow for three dimensional scans with beam diameters below 2 µm. This experimental technique has been applied successfully in MEMS testing to investigate the influence of humidity and temperature on material properties of polyimide and silver [109], and to determine the intrinsic in-plane stress of polydimethyl siloxane (PDMS) [110], aluminum [83], and anorganic multi-layers [41]. Elders [83] compared the results of vibrational analysis to bulge testing.

### 1.2.4 Alternative testing methods in the micrometer regime

The following material test methods in the micrometer regime can be found in MEMS related literature [100, 111] and review publications [50, 51, 112–115]. This summary provides a brief survey of common characterization techniques. Table 1.1 and 1.2 give an overview of the individual test methods’ capabilities to determine mechanical material parameters and their general characteristics, respectively.

The **tensile test** is the most common test used in material testing. It is often first choice for macroscopic samples, for which the testing conditions are standardized in ISO 527. The specimen is stretched uniaxially by defined forces, resulting in a measured elongation. Ideally, there is neither a stress gradient nor prestress. This test delivers the material characteristic stress-strain curve. Simple mathematical models can be established for the evaluation of the measured data. Hence, many micro material testing setups resemble their counterparts of the macro world [32, 116–120]. Although the applied force is relatively high and hence easy to measure, the elongation is fractional and hard to determine accurately, especially when using small sample specimen. Also, the repeatability of the alignment and clamping of the small specimen is difficult. Furtheron, this approach neglects the advantages and needs of micro structured probes: This testing method is not capable for parallel or high throughput creep measurements. And the value and influence of the intrinsic in-plane stress in the thin films can not be determined at all. But first of all, the specimen fabrication with brittle low-modulus materials (such as polymers at temperatures below their glass transition temperature $T_g$) is restricted to large thicknesses in order to allow for the required manual handling.

The **bending test** is preferably used with brittle materials. It provides information on the fracture strength and on Young’s modulus for cantilevers or the plain strain modulus for plate like specimen [121–123]. The microstructures and the setup are relatively simple. Problems arise from the difficulty to accurately determine the true size of the specimen’s cross section and the applied stress. If the structures’ geome-
try is measured without applied load, information on the stress gradient of the films is gained. Curled samples indicate an out-of-plane stress gradient in the structural layer [124, 125].

The **nanoindentation test** gives information on the material’s plain strain modulus, its strength, the hardness and indentation creep [126–128]. It is capable to evaluate viscoelastic thin films by applying a direct-contact vibration mode. High temperature measurements are possible, because there is no temperature coupling between sample and sensor. Unfortunately, the results can differ widely, though they are from the same specimen, due to the small sample area. Furthermore, intrinsic stress and a rough surface may alter the results drastically.

**Resonant structures** may be thin plates (A), membranes (B) or beam like (C) with various clamping conditions. They are capable to determine the intrinsic in-plane stress (B, C fully clamped), Young’s modulus (C single side clamped), the plain strain modulus (A), the coefficient of thermal expansion (B, C fully clamped), crack growth and fatigue (C), [46, 83, 129, 130]. The advantages are relatively simple actuation and test assembly. The structures usually require small space requirement and are easy to fabricate. Resonant structures are well integrable in an MEMS device and are suitable for non-destructive in-line process controlling. However, the exact geometry and density of the specimen have to be known.

The **pull-in test** is a static test method. The material under investigation forms a cantilever or bridge that is electrostatically pulled down. Only electrical contacts are required and the small structures are manufacturable in highly parallel processes. However, the structure has to be at least partly conductive [48, 131] or dielectric [6] and an elaborate mathematical model is necessary to explain the observed behavior for the case of static loading. Only thin structures can be evaluated due to the short ranging electrostatic forces and the inhomogeneity of the field which makes the modeling of the applied volume force difficult. Young’s modulus and residual stress can be quantified.

The **surface acoustic wave test** can be used to determine Young’s modulus of an elastic material or the storage and loss modulus of viscoelastic materials [22]. This measurement technique requires a large test area.

Further, a variety of **passive test methods** are available for the measurement of the intrinsic stress of thin films and micromachined structures. **Wafer bending** (or wafer bow) gives information on homogeneous tensile and compressive stress [16, 33, 132, 133]. It determines the overall stress of a thin film, which is attached to an underlying substrate. Furthermore, it can be used to determine the coefficient of thermal expansion. However, the error is large, compared to bulge testing or vibrational analysis, because the stress induced deflection is in the order of the original nonuniformities.
within the substrate [75]. Double side clamped buckled beams [114, 134, 135] and fully clamped buckled membranes [49, 106, 136] indicate compressive homogeneous stress in a structured thin layer.

1.3 Project objectives

The overall objective of this project is to establish a methodology for the determination of the creep compliance in microstructured, viscoelastic specimen. Due to its versatility and the apparent advantages in the reproducibility and geometrical flexibility of the sample fabrication, the bulge test is predefined as basis for the development of the new methodology. Procedures for the measurement of creep in viscoelastic materials with intrinsic in-plane stress are not yet introduced or systematically described for bulge testing. Therefore, mechanical models describing the expected response of the devices under the chosen test environment have to be established, which allow for the discrimination between the sought-after material properties, the influence of the device structure and the testing conditions. Arrays of testing sites need to be fabricated with common MEMS techniques. Because large variations have been observed in published measurements, multiple data sets are required. Thus, a fully automated test setup has to be constructed and characterized. After testing, the measured data require statistical evaluation. Potentially useful polymers for the application in MEMS devices have to be identified and characterized by means of the new methodology. Besides mechanical short term characteristics, fracture strength and creep compliance, their ability to store mechanical energy over a long period of time should be assessed.

1.4 Approach

The physical variables of state stress, strain and time are required to characterize the isothermal mechanical characteristics of viscoelastic materials. Since thin films usually feature intrinsic in-plane stress, the methodology has to account for the separability of the expected prestress from the induced stress by the test procedure. The investigated measurands and material properties are detailed in table 1.3. In order to incorporate the expected prestress within the thin films into the methodology and to be able to investigate other solid material classes in future works, fully clamped diaphragms are predetermined as specimen geometry and the use of the bulge test is specified a priori.

The quantities stress and strain are commonly derived from the accessible mea-
1 Introduction

Table 1.3: Compilation of the investigated measurands and material parameters.

<table>
<thead>
<tr>
<th>Measurand / Property</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stresses</strong></td>
<td></td>
</tr>
<tr>
<td>Total stress</td>
<td>$\sigma_{\text{tot}}$</td>
</tr>
<tr>
<td>Intrinsic in-plane stress</td>
<td>$\sigma_0$</td>
</tr>
<tr>
<td>Pressure induced stress</td>
<td>$\sigma_p = \sigma_{\text{tot}} - \sigma_0$</td>
</tr>
<tr>
<td><strong>Strains</strong></td>
<td></td>
</tr>
<tr>
<td>Total strain</td>
<td>$\epsilon_{\text{tot}}$</td>
</tr>
<tr>
<td>Intrinsic in-plane strain</td>
<td>$\epsilon_0$</td>
</tr>
<tr>
<td>Pressure induced strain</td>
<td>$\epsilon_p = \epsilon_{\text{tot}} - \epsilon_0$</td>
</tr>
<tr>
<td><strong>Fracture strength</strong></td>
<td></td>
</tr>
<tr>
<td>Equivalent uniaxial fracture stress</td>
<td>$\sigma_{f,\text{equivalent}}$</td>
</tr>
<tr>
<td><strong>Creep compliance</strong></td>
<td></td>
</tr>
<tr>
<td>Initial creep compliance</td>
<td>$D_0$</td>
</tr>
<tr>
<td>Transient creep compliance</td>
<td>$D_e$</td>
</tr>
<tr>
<td>Creep time constant</td>
<td>$\tau$</td>
</tr>
<tr>
<td>Creep coupling parameter</td>
<td>$m$</td>
</tr>
<tr>
<td>Equivalent reference stress</td>
<td>$\theta_{\text{eq,ref}}$</td>
</tr>
</tbody>
</table>

...surands pressure and displacement. The evaluation of the two latter is ideally non-invasive. The optical methods White Light Interferometry (WLI) and Laser Doppler Vibrometry (LDV) are chosen to conduct the required measurements. The WLI is employed in the bulge test and the LDV in resonant vibrometry. The time dependent correlation between stress and strain is measured with the bulge test method in short-term creep tests. The duration of these tests is in the range of hours. The intrinsic in-plane stress is monitored at discrete points in time with the resonant vibrometry method on the same samples.

Batch fabrication is the favored fabrication technique. It includes thin film spin coating of polymers and photolithography, as well as other MEMS methods, such as dry and wet etching or plasma enhanced chemical vapor deposition (PECVD). Free standing polymeric membranes are fabricated and tested with constant boundary conditions. Their lateral shape is a long rectangle, which allows for a reasonably accurate analytical modeling without the need of numerical fits.

Additionally, bone-shaped samples are fabricated and tested with an uniaxial tensile test setup, which is employed as a reference method. Furthermore, single side clamped beams are manufactured. They serve as indicators of a potential out-of-
1.5 Structure of this thesis

plane stress gradient in the thin film.
If the polymer’s behavior is non-linear viscoelastic according to the Eyring theory, the
time-stress superposition of the short-term creep tests from the bulge test allows to
determine the master creep compliance curve, which describes the creep compliance
over a long period of time, assuming a negligible influence of aging and degradation.
The fracture strength is derived from burst pressure tests with the bulge test method.

1.5 Structure of this thesis

The following chapter **Theory** presents the theoretical basis for the model based de-
scription of the creep compliance in solid viscoelastic bodies. An outline of the con-
stitutive equations of continuum mechanics is given and the description of linear and
non-linear viscoelasticity is treated. The implications on the evaluation of data from
biaxial testing is discussed and the the time-stress superposition is introduced, which
allows for an estimation of the material’s long term behavior under mechanical load.
Chapter three discusses the **Material Selection**. Therein, key parameters are defined
and applied. This leads to the nomination of the investigated polymers, which are
presented in detail.
Chapter four deals with **Experimental** topics. It describes the methodology of the
testing procedure elaborately, the individual test setups and the fabrication of the
polymer specimens. It concludes with an error analysis for the tested parameters.
The fifth chapter **Results and Discussion** is divided into two parts: first, short term
mechanical properties are presented and second, the results of long term mechanical
testing are discussed. The derived results are used to evaluate the ability of the ma-
terials under investigation to store mechanical energy over a long period of time.
Finally, the results are summarized in **Conclusions and Outlook** and possible trends
are suggested for future research.
2 Theory

This chapter presents the theory for the model based description and evaluation of the long term creep compliance in solid viscoelastic bodies. With respect to the goals of this work and the used measurement methods to investigate microstructured polymeric thin films, the following topics are addressed:

1. Qualitative description of the mechanical properties of polymers
2. Excerpt from the theory of elasticity
3. Models for the description of transient and dynamic deformations of linear-elastic diaphragms with tensile prestress
4. Models for the description of transient and dynamic deformations of viscoelastic diaphragms with tensile prestress
5. Statistics

Within item four, the description of linear and non-linear viscoelasticity is treated and the resulting implications on the evaluation of data from biaxial testing is discussed. The time-stress superposition principle is introduced as basis for the construction of a master creep compliance curve, which allows for an estimation of the material’s long term creep behavior under mechanical load. Furthermore, the influence of viscoelastic damping on the resonance frequency and descriptions of the mechanical energy in viscoelastic solids are presented.

2.1 The mechanical properties of polymers

Polymers are named viscoelastic materials, emphasizing their intermediate position between viscous liquids and elastic solids. Viscoelasticity of polymers is a molecular rearrangement of chains due to applied stress. This movement is called creep. However, the created internal stress in the material will cause the polymer to return to its original form when the external stress is taken away. Hence, the material shows creep (viscous), though it recovers fully (elastic), resulting in the term viscoelastic material. This material behavior excludes lasting plastic deformation (flow). Cross linked polymers generally allow for a description without plastic deformation [137, p.83].
Figure 2.1: At low experimental temperatures ($\ll T_g$), or high frequencies of actuation, polymers typically behave glass-like with relatively high moduli. The parameters of interest then depend on the testing procedure and are typically storage and loss modulus and glassy modulus and quality factor, respectively. Elevated experimental temperatures ($\gg T_g$) or low actuation frequencies are used to investigate the polymer’s rubber-like behavior with a lower modulus. The parameters of interest are dependent on the procedure of investigation. Typically, creep or relaxation is tested, yielding the time dependent information creep compliance or relaxation modulus. Measurement methods in microscale for each region are included in the drawing.

Depending on the conditions of testing (e.g. rate of load application, temperature, amount of strain, humidity, etc.), a polymer can show all features of a glassy brittle state, an elastic rubber or a viscous liquid (c.f. Fig. 2.1).

At temperatures well below the glass transition temperature ($T_g$), or high frequencies of actuation, polymers are typically glass-like with a Young’s modulus of $10^9 \text{Pa} - 10^{10} \text{Pa}$ and will break or flow at strains around 5%. At temperatures above $T_g$ or low actuation frequencies, the same polymer may be rubber-like with a distinctively lower modulus, withstanding large deformations. The experiments within this work are conducted at room temperature ($T \ll T_g$). The creep experiments have loading times in the range of hours, resulting in testing frequencies around $10^{-4} \text{s}^{-1}$. The
2.1 The mechanical properties of polymers

Resonant vibrometry tests

Short term tests

Long term tests

Temperature difference $T_{\text{exp}} - T_g$ [K]

$T_g = T_g$

Figure 2.2: The present work evaluates thin polymer films at room temperature. The abscissae is normalized with respect to the individual polymer’s glass transition temperature $T_g$. Hence, the symbols show the distance of the experimental temperature from $T_g$. On the ordinate, the testing frequency is plotted in logarithmic scale. The polymers SU-8$_{2002}$, SU-8$_{100}$, GLM2060 and GCM3060 are epoxies ($T_g \approx 210^\circ$C), whereas PI2737 is a polyimide ($T_g \geq 320^\circ$C). The investigated materials’ $T_g$ is well above the experimental temperature. The different characteristics of the polymers are explained in chapter 4.

short term experiments range at $10^{-2}$s$^{-1}$ and the resonant vibrational frequencies of the investigated diaphragms lay in the range of $10^5$s$^{-1}$. All testing conditions are depicted in figure 2.2.

The resulting different features of polymer behavior such as creep and recovery, brittle fracture, yielding, necking and cold-drawing are usually considered separately because different approaches and mathematical formalisms are adapted [17].

Comparison of polymers to elastic solids

An ideal elastic isotropic solid obeys Hooke’s law, relating the stress $\sigma$ to the strain $\epsilon$ for an unconstrained material deformation due to an uniaxial load:

$$\sigma = E \cdot \epsilon \quad (2.1)$$

where $E$ is Young’s modulus.

The mechanical behavior of polymers can deviate from the above model in five important ways:
2 Theory

1. The deformations induced by loading in a polymer are neither independent of the history nor of the rate of application of the load.

2. In general, the constitutive relations of polymers are non-linear.

3. Some polymers may show plastic deformation upon unloading.

4. Many polymers can be deformed to a large extent - however Hooke’s law is valid for small deformations only.

5. Certain polymers show anisotropic mechanical behavior and require a generalization of Hooke’s law.

The first two aspects are relevant to this work and are discussed in section 2.4.

2.2 Theory of elasticity

The theory of elasticity describes the mechanics of solid bodies. These continuous media show deformation upon the action of applied forces. The mathematical description of the deformation is outlined in the subsection State of strain, the tensorial representation of stress in the subsection State of stress. The interconnection between these two quantities is referred to in the subsequent paragraphs.

2.2.1 State of strain

In defining the strains, the deformation is described - that means the displacement of a point relative to adjacent points. Consider two points in a body which are very close to each other: their undisplaced positions have the coordinates $P_1(x, y, z)$ and $P_2(x + dx, y + dy, z + dz)$. On deformation, the points have the coordinates $P_1'(x + u, y + v, z + w)$ and $P_2'(x + dx + u + du, y + dy + v + dv, z + dz + w + dw)$, where $u, v$ and $w$ are displacements in parallel to the Cartesian coordinate axes $x, y$ and $z$. The quantities of interest are $du, dv$ and $dw$, the relative displacements [17].

With $dx, dy$ and $dz$ being sufficiently small (infinitesimal)

$$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy + \frac{\partial u}{\partial z}dz \quad (2.2)$$

$$dv = \frac{\partial v}{\partial x}dx + \frac{\partial v}{\partial y}dy + \frac{\partial v}{\partial z}dz \quad (2.3)$$

$$dw = \frac{\partial w}{\partial x}dx + \frac{\partial w}{\partial y}dy + \frac{\partial w}{\partial z}dz \quad (2.4)$$
2.2 Theory of elasticity

Thus, nine quantities need to be defined:

\( \frac{\partial u}{\partial x}, \frac{\partial u}{\partial y}, \text{etc...} \)

Regrouping these leads to the six components of engineering strain:

\[ e_{xx} = \frac{\partial u}{\partial x}, \ e_{yy} = \frac{\partial v}{\partial y}, \ e_{zz} = \frac{\partial w}{\partial z}, \]
\[ e_{yz} = \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}, \ e_{zx} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}, \ e_{xy} = \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \]

The first three quantities \( e_{xx}, e_{yy} \) and \( e_{zz} \) correspond to fractional expansions or contractions along the \( x, y \) and \( z \) axes. The second three \( e_{yz}, e_{zx} \) and \( e_{xy} \) correspond to the components of shear strain in the \( yz, zx \) and \( xy \) planes respectively.

In the tensor notation, the components of strain are defined as:

\[ \epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \]  

where \( i, j \) can take values 1, 2, 3 and all permutations are taken into account. With

\[ x_1 = x, \quad x_2 = y, \quad x_3 = z \]
\[ u_1 = u, \quad u_2 = v, \quad u_3 = w \]

the strain tensor becomes

\[ \epsilon_{ij} = \begin{pmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{pmatrix} = \begin{pmatrix} \frac{\partial u}{\partial x} & \frac{1}{2} \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) & \frac{1}{2} \left( \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right) \\ \frac{1}{2} \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) & \frac{\partial v}{\partial y} & \frac{1}{2} \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \\ \frac{1}{2} \left( \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right) & \frac{1}{2} \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) & \frac{\partial w}{\partial z} \end{pmatrix} \]  

The strain tensor in terms of engineering components is written as:

\[ \epsilon_{ij} = \begin{pmatrix} e_{xx} & \frac{1}{2} e_{xy} & \frac{1}{2} e_{xz} \\ \frac{1}{2} e_{yx} & e_{yy} & \frac{1}{2} e_{yz} \\ \frac{1}{2} e_{zx} & \frac{1}{2} e_{zy} & e_{zz} \end{pmatrix} \]  

2.2.2 State of stress

The components of stress are defined by six independent quantities \( \sigma_{xx}, \sigma_{yy}, \) and \( \sigma_{zz}, \) the normal stresses, and \( \sigma_{xy}, \sigma_{xz}, \) and \( \sigma_{yz}, \) the shear stresses. These form the stress tensor \( \sigma_{ij}: \)

\[ \sigma_{ij} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{pmatrix} \]  

Figure 2.3 shows the components of stress which act on an infinitesimal small cubical element. Its edges are parallel to the coordinate axes \( x, y \) and \( z. \)
2 Theory

Figure 2.3: The components of strain which act on an infinitesimal cubical element. Its edges are parallel with the coordinate axes $x$, $y$ and $z$.

2.2.3 Generalized Hooke’s law

The most general, linear relationship is obtained by assuming that each tensor component of stress is linearly related to all the tensor components of strain and vice versa. Thus,

$$
\sigma_{ij} = \sum_{k=1}^{3} \sum_{l=1}^{3} c_{ijkl} \epsilon_{kl} \quad (2.9)
$$

and

$$
\epsilon_{ij} = \sum_{k=1}^{3} \sum_{l=1}^{3} s_{ijkl} \sigma_{kl} \quad (2.10)
$$

with $c_{ijkl}$ being the elastic modulus tensor and $s_{ijkl}$ being the elastic compliance tensor. With the usual Einstein summation convention in which repeated indices are summed over, eq.(2.9) and eq.(2.10) are written

$$
\sigma_{ij} = c_{ijkl} \epsilon_{kl} \quad (2.11)
$$

$$
\epsilon_{ij} = s_{ijkl} \sigma_{kl} \quad (2.12)
$$

These fourth rank tensors $c_{ijkl}$ and $s_{ijkl}$ consist of 81 components, but by taking into account the symmetry of the stress and strain tensors, just 36 of them are independent. Furthermore, strain energy considerations reduces this number to 21. Therefore, an abbreviated nomenclature is used, in which the generalized Hooke’s law relates the six independent components of stress to the six independent components
2.2 Theory of elasticity

of the engineering strains:

\[ \sigma_p = e_{pq} e_q \]
\[ e_p = s_{pq} \sigma_q \]

where

\[ \sigma_{p/q} \in \{ \sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{xy}, \sigma_{xz}, \sigma_{yz} \} \]
\[ e_{p/q} \in \{ e_{xx}, e_{yy}, e_{zz}, e_{xy}, e_{xz}, e_{yz} \} \]

The stiffness matrix is readily converted by substituting 1 for 11, 2 for 22, 3 for 33, 4 for 23, 5 for 13 and 6 for 12. Due to the factor-2 difference between the definition of the tensor shear strain components and the engineering shear strains, the compliance constants obey different rules for conversion:

\[ s_{ijkl} = s_{pq} \text{ when } p \text{ and } q \text{ are 1, 2 or 3} \]
\[ 2s_{ijkl} = s_{pq} \text{ when either } p \text{ or } q \text{ are 4, 5 or 6} \]
\[ 4s_{ijkl} = s_{pq} \text{ when } p \text{ and } q \text{ are 4, 5 or 6} \]

This is valid for both, isotropic and anisotropic solids. Depending on the material, the number of independent components reduces further.

An isotropic material, whose properties are independent of direction is describable by only two independent elastic constants, \( s_{11} \) and \( s_{12} \):

\[
\begin{pmatrix}
e_{xx} \\
e_{yy} \\
e_{zz} \\
e_{yz} \\
e_{xz} \\
e_{xy}
\end{pmatrix} =
\begin{pmatrix}
s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\
s_{12} & s_{11} & s_{12} & 0 & 0 & 0 \\
s_{12} & s_{12} & s_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & 2s_{11} - s_{12} & 0 & 0 \\
0 & 0 & 0 & 2s_{11} - s_{12} & 0 & 0 \\
0 & 0 & 0 & 2s_{11} - s_{12} & 0 & 0
\end{pmatrix}
\begin{pmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz} \\
\sigma_{yz} \\
\sigma_{xz} \\
\sigma_{xy}
\end{pmatrix}
\]

These constants \( s_{11} \) and \( s_{12} \) can be converted into two independent engineering constants Young’s modulus \( E \) and Poisson ratio \( \nu \). Alternatively, the quantities bulk modulus \( K \) or shear modulus \( G \) can be deduced.

**Young’s modulus** \( E \) relates stress and strain in uniaxial extension \( (\sigma_{yy} = \sigma_{zz} = 0) \) through

\[ \sigma_{xx} = E e_{xx} \]

Hence, Young’s modulus \( E \) is given by

\[ E = \frac{1}{s_{11}} \]
2 Theory

The Poisson’s ratio \( \nu \) gives the negative ratio of the lateral strain in y- (or z-) direction to the longitudinal extension in uniaxial extension in x-direction

\[
\nu = -\frac{\varepsilon_{yy}}{\varepsilon_{xx}} = -\frac{\varepsilon_{zz}}{\varepsilon_{xx}}
\]

(2.16)

This yields

\[
\nu = -\frac{s_{11}}{s_{12}}
\]

(2.17)

Since only two of the four constants, \( G, K, E \) and \( \nu \) are independent, they can be converted as follows:

\[
G = \frac{E}{2(1+\nu)}
\]

(2.18)

\[
K = \frac{E}{3(1-2\nu)}
\]

(2.19)

If the maximum elastic deformation is below 5%, the difference between the calculation with infinite and finite strain elasticity is negligible [137]. This is the case for all experimental results within this work.

2.2.4 Hydrostatic and deviatoric stress

The stress tensor \( \sigma_{ij} \) can be decomposed in a hydrostatic and the deviatoric fraction, \( \sigma^h_{ij} \) and \( \sigma^d_{ij} \), respectively. The hydrostatic fraction \( \sigma^h_{ij} \) causes a volume change, whereas the deviatoric part \( \sigma^d_{ij} \) is the reason for the change in shape [108].

\[
\sigma_{ij} = \sigma^h_{ij} + \sigma^d_{ij} = \frac{1}{3} \sigma^h \delta_{ij} + \sigma^d_{ij}.
\]

(2.20)

The mean normal stress is abbreviated with \( \sigma^h \) and \( \delta_{ij} \) is the Kronecker delta. The first invariant of the stress tensor \( I_1^\sigma = 3\sigma^h = \sigma_{xx} + \sigma_{yy} + \sigma_{zz} \) equals the addition of the three principal stresses. Hence, the deviatoric stress tensor can be written as

\[
\sigma^d_{ij} = \sigma_{ij} - \sigma^h \delta_{ij} = \begin{pmatrix}
\sigma_{xx} - \sigma^h & \sigma_{xy} & \sigma_{xz} \\
\sigma_{yx} & \sigma_{yy} - \sigma^h & \sigma_{yz} \\
\sigma_{zx} & \sigma_{zy} & \sigma_{zz} - \sigma^h
\end{pmatrix}
\]

(2.21)

Figure 2.4 outlines the hydrostatic and deviatoric strain responses in two dimensions. The hydrostatic and deviatoric fraction of the strain tensor are calculated identically to the stress.
2.2 Theory of elasticity

Figure 2.4: The strain reaction of an arbitrary two-dimensional rectangle to hydrostatic and deviatoric stress is schematically displayed. If the applied stress is purely hydrostatic, the ratio between the side lengths $\alpha$ and $\beta$ stays constant and the shape is preserved, while the area $A$ changes. The opposite is true for purely deviatoric stress. Then the area stays constant but the shape and the ratio between the side lengths change.

2.2.5 Mechanical energy in an ideal-elastic material

Through stress induced deformation, a certain amount of energy is transferred into a solid body. The elastic energy density $W$ in a Hookean material is equal to the specific elastic potential $U$ and is calculated with [108]:

$$W = U(\epsilon_{ij}) = \int_0^{\epsilon_{ij}} \sigma_{ij} d\epsilon_{ij} = E_{ijkl} \int_0^{\epsilon_{ij}} \varepsilon_{kl} d\epsilon_{ij} = \frac{1}{2} E_{ijkl} \varepsilon_{kl} \varepsilon_{ij} = \frac{1}{2} \sigma_{ij} \epsilon_{ij}$$

(2.22)

Equation 2.22 can be divided into two parts, the strain energy of uniform tension (hydrostatic part) $U^h$ and the distortion energy (deviatoric part) $U^d$:

$$U = \frac{1}{2} \left( \frac{1}{3} I_1^\sigma \delta_{ij} + \sigma_{ij}^d \right) \left( \frac{1}{3} I_1^\epsilon \delta_{ij} + \epsilon_{ij}^d \right) = \frac{1}{6} I_1^\sigma I_1^\epsilon + \frac{1}{2} \sigma_{ij}^d \epsilon_{ij}^d = U^h + U^d$$

(2.23)

with the first invariant of the stress tensor $I_1^\sigma$ and the first invariant of the strain tensor $I_1^\epsilon$ (cf. sections 2.2.4 and 2.2.6). For isotropic materials, Eq. 2.23 can be written as:

$$U = \frac{K}{2} I_1^\sigma I_1^\epsilon + G \epsilon_{ij}^d \epsilon_{ij}^d = \frac{1}{18K} I_1^\sigma I_1^\epsilon + \frac{1}{4G} \sigma_{ij}^d \sigma_{ij}^d = U^h + U^d$$

(2.24)

Hence, the maximum elastic energy density $W$ can be expressed by the material’s strength with the maximum elongation $\epsilon_f$ or rather maximum stress $\sigma_f$ at fracture, and two independent material properties out of Young’s modulus $E$, Poisson’s ratio $\nu$, bulk compression $K$ and shear modulus $G$. 
2 Theory

2.2.6 Yield strength: Von-Mises Criterion

The variety of testing methods and real applications with their different loads and specimen geometry, require a common criterion which describes the material’s inherent yield strength independently of the diverse stress fields. The Von-Mises criterion assumes that the deviatoric part $U^d$ of the strain energy density $U$ is decisive for yielding [138].

$$U^d = \frac{1}{4G} \sigma^d_{ij} \sigma^d_{ij}$$  \hspace{1cm} (2.25)

For an uniaxial load $\sigma_{xx} = s_x$, Eq. 2.25 becomes

$$U^d = \frac{1}{6G} s_x^2$$  \hspace{1cm} (2.26)

Inserting Eq. 2.26 in Eq. 2.25 yields

$$\sqrt{\frac{3}{2} \sigma^d_{ij} \sigma^d_{ij}} = s_x$$  \hspace{1cm} (2.27)

This means, an arbitrary state of stress $\sigma_{ij}$ can be compared to an uniaxial load $s_x$, if the material obeys the von Mises criterion.

If the relative load is pure shear $\theta_x$ in the $\sigma_1\sigma_2$-plain, Eq. 2.25 results in

$$U^d = \frac{1}{2G} \theta_x$$  \hspace{1cm} (2.28)

for $\theta_x = \sigma_{xy} = \sigma_{yx}$. Hence, an equivalent stress $\theta_{eq}$ can be stated from Eq. 2.25 and 2.28 as

$$\sqrt{\frac{1}{2} \sigma^d_{ij} \sigma^d_{ij}} = \theta_x = \theta_{eq}$$  \hspace{1cm} (2.29)

Equation 2.29 in an alternative form of the Von-Mises yield criterion and is used in the description of creep in viscoelastic materials [139].

2.3 Deformation of elastic diaphragms

This section deals with the transient and dynamic response of linear-elastic diaphragms to external loads. First, different subclasses of diaphragms are discussed, which allow for the constitution of valid models within the described boundary conditions. Subsequently, the models for static and dynamic deflections of thin plates and membranes are presented.

Depending on specimen geometry (cf. Fig. 2.5), material and load conditions (cf. Fig. 2.3), different models are applicable for the description of the deflection of diaphragms [108, 140–143]. The following terms are commonly used for the differentiation between modeled diaphragm behavior:
2.3 Deformation of elastic diaphragms

Figure 2.5: Sketch of a long, rectangular diaphragm. Its edges are parallel with the coordinate axes $x$, $y$ and $z$. The thickness is denoted $h$, the length of the transverse direction is abbreviated with $l_x$. The variable for the longitudinal side is $l_y$.

- Thin plates with small deflections
  Thin plates are flat structures with a small, constant thickness $h$, compared to their smallest lateral dimension $l_x$ ($8...10 \leq l_x/h \leq 80...100$ [141, p.3]). The applied loads are either forces which act orthogonal to the surface, or bending moments at the thin plate’s clamping sites. The maximum out-of-plane deflection $w_0$ due to the loads is much smaller than the thickness ($w_0/h \leq 0.2$ [141, p.3]). Hence, the in-plane deflection of the middle plane is assumed to be zero, it stays neutral during bending. The deformation energy is exclusively stored in bending moments. It is further assumed, that the transverse shear forces $\theta_{xz}$ and $\theta_{yz}$ are negligible (Kirchhoff Love Hypothesis), and that stresses in the direction of the normal to the diaphragm can be disregarded.

- Thin plates with large deflections
  Large deflections ($w_0/h \geq 0.3$ [141, p.3]) of clamped, thin plates result in in-plane strains which are not negligible any more. The applied load is then predominantly transmitted by tensile stress in the middle surface of the plate. This fraction is called the membrane action. The transmission though flexural rigidity (plate action) decreases with increasing out-of-plane deflection. If the maximum deflection $w_0$ is considerably greater than the thickness $h$ ($w_0/h \geq 5$ [141, p.3]),
### Theory

Table 2.1: Classification scheme for diaphragms with the geometrical dimensions: thickness $h$ and smallest lateral extension $l_x$. The maximum out-of-plane deflection is denoted $w_0$.

<table>
<thead>
<tr>
<th>Category</th>
<th>$l_x/h$ Conditions</th>
<th>$w_0/h$ Conditions</th>
<th>Initial Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thick plates</strong></td>
<td>$l_x/h \leq 8\ldots10$</td>
<td></td>
<td>Flat</td>
</tr>
<tr>
<td><strong>Thin plates with ...</strong></td>
<td>$8\ldots10 \leq l_x/h \leq 80\ldots100$</td>
<td>$w_0/h \leq 0.2$</td>
<td>Flat</td>
</tr>
<tr>
<td>... small deflections</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>... large deflections</td>
<td>$8\ldots10 \leq l_x/h \leq 80\ldots100$</td>
<td>$w_0/h \geq 0.3$</td>
<td>Flat</td>
</tr>
<tr>
<td><strong>Membranes</strong></td>
<td>$l_x/h \geq 80\ldots100$</td>
<td></td>
<td>Flat</td>
</tr>
<tr>
<td><strong>Shells</strong></td>
<td></td>
<td></td>
<td>Arbitrary</td>
</tr>
</tbody>
</table>

The flexural rigidity can be neglected compared with the membrane stress. The stress is then uniformly distributed over the plate thickness.

- **Membranes**
  A membrane is a flat, homogeneously prestressed structure. Its constant thickness $h$, which is very small compared to the smallest lateral dimension $l_x$ ($l_x/h \geq 80\ldots100$ [141, p.3]). It has no flexural rigidity, and transmits loads exclusively by tensile in-plane stresses to the supports. These stresses are assumed to be uniformly distributed over the thickness.

- **Shells**
  Shell structures are defined as arbitrarily shaped, two-dimensional structures capable of transmitting loads in more than two directions to supports. Compressive, tensile, and shear stresses can act in the in-plane direction of a shell.

- **Thick plates**
  Thick plates are diaphragms of considerable thickness ($l_x/h \leq 8\ldots10$ [141, p.3]). Their description requires to factor all components of stress, strain and displacements into the model.

Table 2.1 assists in classifying diaphragms under investigation, depending on geometry and displacement: In the following, the governing equations of thin plates with small deflections and membranes are presented and approximate or exact solutions for the relation between load and deflection are given. The following assumptions are established:

- The diaphragm has a rectangular shape.
- The diaphragm is initially flat.
- The thickness of the diaphragm is constant.
2.3 Deformation of elastic diaphragms

- The material is homogeneous, isotropic and behaves linear-elastically.
- The diaphragm is rigidly clamped on all four sides.
- All applied loads are uniformly distributed over the whole surface and act perpendicular.
- Shear forces are negligible.
- The influence of temperature is omitted.
- The geometrical space is described in cartesian coordinates.

2.3.1 Thin plates with small deflections

Thin plates with small deflections can be described by the inhomogeneous, bipotential equation [108]

$$\Delta^2 w = \frac{p}{D_{flex}} \quad (2.30)$$

known as the Kirchhoff’s plate model. The out-of-plane deflection is denoted $w$, the variable of the area load is $p$ and $D_{flex}$ is the flexural rigidity:

$$D_{flex} = \frac{Eh^3}{12(1-v^2)} \quad (2.31)$$

with Young’s modulus $E$, the plate thickness $h$ and Poisson’s ratio $v$. The Laplace operator is abbreviated with $\Delta_L$:

$$\Delta_L = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \quad (2.32)$$

The lateral coordinates are denoted $[x, y]$.

Static deflection of thin plates

The relationship between a static load $p$ and the maximum out-of-plane deflection $w_0$ in the center of a fully clamped, rectangular, thin plate without any prestress can only be computed numerically, as described by Timoshenko ([140, chapter 5]). The approximation for a plate with the width $l_x$ and the length $l_y$ (cf. Fig. 2.6) yields

$$w_0 = \alpha \frac{pl_y^4}{D_{flex}} \quad (2.33)$$

where $\alpha$ becomes 0.00254 for a plate with a lateral aspect-ratio of $l_y/l_x = 2$. For infinitely long, thin plates ($b/a = \infty$), $\alpha$ converges to 0.00260. For thin plates with a
Figure 2.6: Transverse cross section of the center of a deflected rectangular thin plate of thickness \( h \). The maximum deflection \( w_0 \) is exaggerated for the reader’s ease. Flexural rigidity is mainly responsible for the reaction to the constant area load \( p \). The plate width is denoted \( l_x \).

lateral aspect-ratio of \( l_y/l_x \geq 6 \), the solution for infinitely long plates is acceptable. The resulting systematic error is below 0.5% and therefore regarded as negligibly small.

Vibration of thin plates

For the derivation of the vibration model of thin plates, harmonic Eigenfrequencies are considered only. Kirchhoff’s plate theory (cf. Eq. 2.30) and d’Alemberts vis inertia lead to the following equation of motion [108]:

\[
\Delta_l^2 w + \frac{\rho h}{D_{\text{flex}}} \frac{\partial^2 w}{\partial t^2} = 0
\] (2.34)

The mass density is abbreviated with \( \rho \) and the time with \( t \). The angular Eigenfrequencies \( \omega_{mn} \) for thin plate like rectangular diaphragms are:

\[
\omega_{mn} = \left[ \left( \frac{m\pi}{l_x} \right)^2 + \left( \frac{n\pi}{l_y} \right)^2 \right] \sqrt{\frac{D_{\text{flex}}}{\rho h}}
\] (2.35)

with the width \( l_x \) and length \( l_y \) of the plate. A pair of non-zero positive integers \([m, n]\) is related to the different Eigenfrequencies \( \omega_{mn} \). The Eigenmodes for rectangular thin plates are:

\[
W_{mn} = F_{mn} \sin \left( \frac{m\pi x}{l_x} \right) \sin \left( \frac{n\pi y}{l_y} \right)
\] (2.36)

where \( F_{mn} \) is the amplitude of the resonant vibration.

2.3.2 Membranes

In the case of very thin diaphragms, which may have deflections many times larger than their thickness, the resistance to load is mainly determined by middle-surface
2.3 Deformation of elastic diaphragms

Figure 2.7: Transverse cross section of the center of a deflected rectangular membrane. The bending stiffness is negligible, hence its center cross section under constant area load $p$ is a circular arc. The values of interest are the maximum deflection $w_0$, the membrane width $a$, and the film thickness $h$.

Forces. The Lagrangian differential membrane equation links the applied pressure $p$, the membrane thickness $h$, and the induced stress $\sigma$ to the out-of-plane deflection $w$ [108]:

$$\Delta L^2 w + \frac{p}{h\sigma} = 0 \quad (2.37)$$

Static deflection of membranes

The extraction of stress dependent viscoelastic strains requires the assignability of stress and displacement. Hence, the creep experiments demand a constant stress field over the entire test length. Since this section stretches over the total width of the diaphragm, long rectangular membranes are favored. Provided they feature the characteristics of infinitely long membranes, the region in the geometrical middle provides a constant stress field with entries along the longitudinal and transversal axes only. Round [76] and square membranes [140] both show in-plane stress gradients and thus lack this requirement.

An exact analytical solution can be derived for the static deflection of a linear-elastic, infinitely long membrane. Since any plane of the film lying perpendicular to the longitudinal axis of the membrane is a mirror plane, the displacement $\epsilon_{yy}$ along this axis is zero, yielding $\sigma_{yy} = \nu\sigma_{xx}$ for an isotropic material. Neglecting the out-of-plane strain $\epsilon_{zz}$, this problem is reduced to plane strain conditions. In the presence of an intrinsic tensile in-plane stress $\sigma_0$, the analytical expression for the pressure-deflection curve is given by [89]:

$$p = \frac{64Eh}{3l_x^4(1 - \nu^2)}w_0^3 + \frac{8h\sigma_0}{l_x^2}w_0 \quad (2.38)$$

with the applied surface load $p$, the width of the membrane $l_x$ and the maximum deflection along the center of the membrane $w_0$ (cf. Fig. 2.7). The term $E/(1 - \nu^2)$ is re-
2 Theory

terred to as plane strain modulus, not to be confused with the biaxial modulus $E/(1-\nu)$. With the transition from membrane to thin plate regime, the bending stiffness increasingly influences the deflection and needs to be accounted for. Vlassak proposed to approximate this description to reality by adding a bending term to Eq. 2.38 ([140], chapter 5):

$$p = \frac{64Eh}{3l_x^4(1-\nu^2)} w_0^3 + \frac{8h\sigma_0}{l_x^2} w_0 + \frac{32Eh^3}{l_x^4(1-\nu)} w_0$$  \hspace{1cm} (2.39)

The importance of the bending stiffness for the description of diaphragms with intrinsic in-plane stress can be quantified with the ratio of the bending term to the term containing the intrinsic in-plane stress $\sigma_0$ with the ratio $\gamma$:

$$\gamma = \frac{4Eh^2}{\sigma_0 l_x^2(1-\nu)} \approx \frac{Eh^2}{\sigma_0 l_x^2}$$  \hspace{1cm} (2.40)

For values of $\gamma < 10^{-3}$, the influence of the flexural rigidity is negligible and Eq. 2.38 may be used as analytical solution for the load-deflection curve of infinitely long diaphragms.

Ziebart quantified the overall systematic modeling error in long, rectangular membranes on the complete right hand side of equation 2.39 if the flexural rigidity is neglected [39]. For strongly tensile prestressed diaphragms, the membrane model becomes a reasonable approximation and the relative error $\Delta_{rel}$ converges to:

$$\Delta_{rel} \approx 4 \sqrt{\frac{Eh^2}{12(1-\nu^2)l_x^2\sigma_0}}$$  \hspace{1cm} (2.41)

Vibration of membranes

For the derivation of the equations describing vibrational behavior of membranes, the following additional assumptions are made: the intrinsic in-plane stress is not affected by the deflection of the membrane and only the harmonic Eigenfrequencies are considered. Using d’Alembert’s vis inertia on Eq. 2.37, the two-dimensional wave equation results in [108]:

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} = \frac{\rho}{\sigma_0} \frac{\partial^2 w}{\partial t^2}$$  \hspace{1cm} (2.42)

The angular Eigenfrequency $\omega_{nm}$ of rectangular membranes is obtained by solving this differential equation with a homogeneous approach, yielding:

$$\omega_{nm} = \sqrt{\left(\frac{m\pi}{l_x}\right)^2 + \left(\frac{n\pi}{l_y}\right)^2} \sqrt{\frac{\sigma_0}{\rho}}$$  \hspace{1cm} (2.43)

The lateral dimensions of the membrane are length $l_x$ and width $l_y$. A pair of non-zero positive integers $[m, n]$ is related to the different Eigenfrequencies $\omega_{nm}$. The
characteristic Eigenmodes $W_{mn}$ of a rectangular membrane are

$$W_{mn} = F_{mn} \sin \left( \frac{m\pi x}{l_x} \right) \sin \left( \frac{n\pi y}{l_y} \right)$$  \hspace{1cm} (2.44)

where $F_{mn}$ is the amplitude of the resonant vibration. The time dependent out-of-plane deflection $w(x, y, t)$ is calculated as follows:

$$w(x, y, t) = F_{mn} \sin \left( \frac{m\pi x}{l_x} \right) \sin \left( \frac{n\pi y}{l_y} \right) \cos \omega t$$  \hspace{1cm} (2.45)

The above model assumes an ideal-elastic material and hence, does not reckon with intrinsic material damping. This influence is treated in paragraph 2.4.5.

Remark: The Eigenmodes are the same for plates and membranes. Hence, no differentiation between membrane and thin plate can be achieved by visualizing the shapes of the Eigenmodes. However, the relative change of the angular Eigenfrequencies of plates is faster with increasing $[m, n]$ than of membranes. This difference can be used to determine a diaphragm’s behavior.

2.4 Deformation of viscoelastic diaphragms

The investigated polymeric thin films are known to behave viscoelastic and to exhibit intrinsic tensile in-plane stress, which is induced during fabrication and is mainly due to thermal mismatch [16]. Thus, this section deals with the transient and dynamic response of viscoelastic diaphragms to external loads. First, the models describing stress and strain in an infinitely long diaphragm are presented. Then the constitutive equations for the interrelation of stress and strain in viscoelastic materials are given, Eyring’s theory of creep as activated process is introduced and the construction of interpolated long term creep curves from short term creep tests is presented. With this information, the constitutive equations of non-linear viscoelastic materials are established for bulge testing conditions. Thereafter, the effect of crosslinking and non-interacting, rigid fillers is described. Further, the theory of vibration of weakly damped viscoelastic diaphragms is shown. Finally, models are presented which describe the storage of mechanical energy storage in viscoelastic solids.

2.4.1 Stress and strain determined by bulge testing

In order to determine the time dependent stresses and strains in micromachined diaphragms, the bulge testing method is used. Therefore, fully clamped, long rectangular diaphragms are deflected by an applied differential pressure. This deflection is used to calculate stress and strain in transversal direction (along the x-axis in Fig. 2.5).
2 Theory

Infinitely long, plane-strained membranes are assumed. These assumptions are necessary and acceptable, considering the chosen material class and the geometrical dimensions: rectangular diaphragms with intrinsic in-plane tensile stress and small thickness-to-width ratio (< 1/200) leave the bending stiffness negligible and a sufficiently large length-to-width ratio (> 6) allows for the assumption of an infinitely long membrane [39, 141, 144] with the load induced strain being zero in y-direction. If the assumption of an infinitely long membrane can not be made, the resulting inhomogeneous stress field will make the evaluation of time dependent phenomena, such as creep, practically impossible.

The stress tensor $\sigma_{ij}$ of an infinitely long, rectangular membrane with an intrinsic in-plane stress $\sigma_0$ can be written in Cartesian coordinates as

$$\sigma_{ij}(t) = \begin{pmatrix} \sigma_{xx}(t) & 0 & 0 \\ 0 & \sigma_{yy}(t) & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \sigma_{xx,t}(t) + \sigma_0(t) & 0 & 0 \\ 0 & \nu \sigma_{xx,t}(t) + \sigma_0(t) & 0 \\ 0 & 0 & 0 \end{pmatrix}$$  \hspace{1cm} (2.46)

where the total stress $\sigma_{xx}$ in transversal direction consists of the intrinsic in-plane stress $\sigma_0$ and the pressure induced stress $\sigma_{xx,p}$ due to the applied pressure $p$. The load dependent stress in longitudinal direction $\sigma_{yy,p}$ may be written as $\nu \sigma_{xx,p}$ with the assumption of an infinitely long membrane. Little change ($< 5\%$) during measurement times of 0..10 hours is expected in the lateral contraction ratio $\nu$ (Poisson’s ratio for linear elastic materials) of highly crosslinked epoxies and polyimides [145, 146]. Hence, it is noted as time independent material property.

The equivalent stress $\theta_{eq}$ (cf. Eq. 2.29) becomes

$$\theta_{eq} = \sqrt{\sigma_0^2 + \sigma_{xx} \sigma_0 + \frac{1}{3} \left( 2\nu^2 \sigma_{xx} \sigma_0 + \sigma_{xx}^2 + \nu^2 \sigma_{xx}^2 + \nu^2 \sigma_0^2 - \nu \sigma_{xx}^2 - \nu \sigma_{xx} \sigma_0 \right)}$$  \hspace{1cm} (2.47)

As will be seen in the chapter results and discussion, the equivalent stress is of major importance for the evaluation of viscoelastic materials under complex loading conditions.

The strain tensor $\epsilon_{ij}$ has the following entries:

$$\epsilon_{ij}(t) = \begin{pmatrix} \epsilon_{xx}(t) & 0 & 0 \\ 0 & \epsilon_{0}(t) & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \epsilon_{xx,p}(t) + \epsilon_0(t) & 0 & 0 \\ 0 & \epsilon_0(t) & 0 \\ 0 & 0 & 0 \end{pmatrix}$$  \hspace{1cm} (2.48)

with the total strain $\epsilon_{xx}$ in transversal direction. The total strain is composed of the intrinsic in-plane strain $\epsilon_0$, and the pressure induced strain $\epsilon_{xx,p}$ due to the applied pressure $p$ during the bulge test. The strain in z-direction is existent but set to zero in order to reduce the calculations to a two-dimensional plane-strain problem. The resulting systematic error is negligible since the layer thickness is measured after
2.4 Deformation of viscoelastic diaphragms

the process induced shrinkage, leaving $\epsilon_{zz} = \nu \epsilon_{xx,p}$, which is well below the film thickness variation. Hence, the parameters $\sigma_{xx,p}$, $\sigma_0$, $\epsilon_{xx,p}$, $\epsilon_0$ and $\nu$ have to be quantified in order to fully describe stress and strain.

Measurement of strain

The maximum deflection $w_0$ along the center line of a deflected, rectangular membrane with the width $l_x$ (see Figs.2.5 and 2.7) may be used to calculate the pressure induced transversal strain $\epsilon_{xx,p}(t)$ purely geometrically [89]:

$$\epsilon_{xx,p}(t) = \left( \frac{w_0(t)}{l_x} + \frac{l_x}{4w_0(t)} \right) \cdot \arcsin \left( \frac{4l_x w_0(t)}{4w_0(t)^2 + l_x^2} \right) - 1 \quad (2.49)$$

Adding the intrinsic in-plane strain $\epsilon_0$ to Eq. 2.49 yields the total strain $\epsilon_{xx}(t)$ in the transversal direction:

$$\epsilon_{xx}(t) = \left[ \left( \frac{w_0(t)}{l_x} + \frac{l_x}{4w_0(t)} \right) \cdot \arcsin \left( \frac{4l_x w_0(t)}{4w_0(t)^2 + l_x^2} \right) - 1 \right] + \epsilon_0 \quad (2.50)$$

However, the intrinsic in-plane strain can not be measured directly. Hence, the experimental access with the bulge test method is limited to the pressure induced strain (Eq. 2.49).

Measurement of stress

The stress $\sigma_{xx}$ in the transversal direction may be calculated with the hoop stress formula for thin walled pressure vessels ([89]; [147], chapter 13). For the derivation, a long rectangular membrane is assumed which is clamped on all four edges. Its bending stiffness is negligible, hence its center cross section under constant area load can be assumed to be a circular arc. The area under observation is the transverse strip at the intersection of the diagonals. This region features a stress field without gradients. Theoretically, this assumption requires a membrane with infinite length-to-width ratio. However, with a lateral aspect ratio $l_y/l_x \geq 6$, this requirement is fulfilled. With the measurands pressure $p$, width $l_x$ and deflection $w_0$ (cf. Fig. 2.7), the analytical solution for the total transversal stress $\sigma_{xx}$ is:

$$\sigma_{xx}(t) = p \frac{l_x^2 + 4w_0(t)^2}{8hw_0(t)} \quad (2.51)$$

where $h$ is the layer thickness. Equation 2.51 is valid for vessels with a small ratio of wall thickness to curvature radius ratio. In the present work, the minimum ratio is 350.
2 Theory

The quantification of the intrinsic in-plane stress in viscoelastic thin films with the bulge test required a constant value of $\sigma_0$. Since this is not certain, $\sigma_0$ must be determined with an alternative measurement method. Vibrometry analysis is chosen to complete the measurement methodology.

Remark: The general expressions of strain (Eq. 2.49) and stress (Eq. 2.51) can be converted for linear elastic membranes into equation 2.38. Therefore, the first member of the Taylor series expansion of the strain equation is calculated, yielding

$$\epsilon'_{xx,p} = \frac{8 w_0^2}{3 l_x^2}$$

The Hoop stress equation may be truncated by eliminating $4w_0^2$, which is small compared to $l_x^2$, giving

$$\sigma'_{xx} = \frac{l_x^2}{8hw_0 p}$$

The resulting maximum errors for these simplifications with respect to the membrane samples used here are 0.5% and 2.5%, respectively. With the entries in the stress and strain tensors (Eqs. 2.46 and 2.48), a linear elastic relation (cf. Eq. 2.12) can be stated:

$$\epsilon_{xx,p} = \frac{1 - \nu^2}{E}(\sigma_{xx} - \sigma_0)$$

Inserting the simplified terms $\sigma'_{xx}$ and $\epsilon'_{xx,p}$ into the above equation and solving it for $p$ yields equation 2.38.

2.4.2 Constitutive Equations for viscoelastic membranes

This subsection presents the theoretical models to describe (non-) linear viscoelastic creep in infinitely long, prestressed membranes. Therefore, the theories of linear and non-linear viscoelasticity are outlined, interrelating stress and strain. The Eyring theory, which describes creep as an activated process is presented and the construction of the master creep compliance curve, predicting long term behavior from short term creep measurements is shown.

Linear viscoelastic deformation

Linear viscoelastic deformation at low stress levels and constant environmental conditions is usually described using linear response theory, which results in the well-known Boltzmann single integral [18]. For the exemplary description of viscoelastic material behavior, two types of testing methods are typically used: Creep tests, where the time dependent strain due to an applied constant load is measured (cf. Fig. 2.8)
2.4 Deformation of viscoelastic diaphragms

![Figure 2.8](image)

**Figure 2.8:** When subjected to a constant stress step, viscoelastic materials experience a time-dependent increase in strain, referred to as viscoelastic creep. At time zero, the viscoelastic material is loaded with a constant stress $\sigma$ which is maintained until time $t_1$. The material responds to the stress with an instant strain step $\epsilon_a$ and subsequently an increase of the total strain $\epsilon(t) = \epsilon_a + \epsilon_b(t)$ until the stress is removed at time $t_1$: the strain immediately decreases by $-\epsilon_a$ and then gradually converges zero strain at times $t \gg t_1$.

and stress relaxation tests, which observe the decay of stress in a specimen with constant strain.

For creep tests with prescribed stress $\sigma$, applied at time $t = 0$, the Boltzmann integral assumes the following form:

\[
\epsilon(t) = \int_{-\infty}^{t} D(t-\tau)d\sigma(\tau) = \sigma D_0 + \int_{-\infty}^{t} D(t-\tau)\dot{\sigma}(\tau)d\tau \quad (2.52)
\]

where $t$ is the time, and $D(t)$ is the creep compliance. The term on the right hand side of Eq. 2.52 splits the Boltzmann integral into the instant strain response $\sigma D_0$ and the viscous part, represented by the convolution integral. Creep is always a function of the entire loading history. In the linear-viscoelastic regime, each loading step makes an independent contribution.

Various empirical models are available for the description of viscoelastic behavior. The simplest model, which is capable of describing creep and relaxation is the Zener model (cf. Fig. 2.10), which is similar to the standard linear solid. In this arrangement, the two springs with the spring constants $E_1$ and $E_2$ and the dashpot with viscosity $\eta_0$ yield as time dependent strain $\epsilon(t)$

\[
\epsilon(t) = \frac{\sigma}{E_1} + \frac{\sigma}{E_2} \left[ 1 - \exp \left( -\frac{t}{\tau} \right) \right] \quad (2.53)
\]

when a constant stress $\sigma$ is applied. The retardation time $\tau$ is the ratio of viscosity and spring in parallel $\tau = \eta_0/E_2$. Hence, the creep compliance is:

\[
D(t) = \frac{\epsilon(t)}{\sigma} = \frac{1}{E_1} + \frac{1}{E_2} \left[ 1 - \exp \left( -\frac{t}{\tau} \right) \right] = D_1 + D_2 \left[ 1 - \exp \left( -\frac{t}{\tau} \right) \right] \quad (2.54)
\]
2 Theory

It has been shown by several authors [148–150], that short-term \( t < 10^5 \) s creep of chemically crosslinked, glassy polymers under constant load conditions can be described satisfactorily using a modified Zener model, which results in a time dependent creep compliance \( D(t) \):

\[
D(t) = \frac{\epsilon(t)}{\sigma_{\text{const.}}} = D_0 + (D_e - D_0) \left(1 - \exp \left[-\left(\frac{t}{\tau}\right)^m\right]\right)
\]  

(2.55)

Here, \( D_0 \) is the initial (glassy) value of the creep compliance at time \( t = 0 \). \( D_e \) is the transient (or equilibrium) creep compliance, a measure of energy storage in the crosslinked polymer in equilibrium, and \( \tau \) is the time constant for creep (cf. Fig. 2.9).

Ngai [151] proposed this model and attributed physical properties to the parameters: The coupling parameter \( m \) in the stretched exponential decay function describes the interaction between molecules. Hence, with an increased molecular mobility, the value of \( m \) increases as well. Values for \( m \) theoretically range from 0 to 1 although in practice, values of \( m \approx 0.3 \) are usually found. The stretched exponential function \( \exp[-(t/\tau)^m] \) is analogous to the Kohlrausch-Williams-Watts equation [152,153], which describes charge decay in amorphous polymer dielectrics.

**Non-linear viscoelastic deformation**

A material for which the creep compliance function \( D \) is a function of time and other parameters (such as stress or temperature) shows non-linear viscoelastic behavior (e.g. \( D = f(t, \sigma) \) or \( D = f(t, T) \)). The Boltzmann superposition principle can no longer be assumed to apply and the material behavior starts to deviate from the linear theory.

The rheological approach provides constitutive models for non-linear viscoelastic behavior using integral representations, which can be divided into multiple and single integral representations.

Multiple integral representations are essentially extensions of the Boltzmann single integral representation using higher order stress or strain terms to account for the nonlinear behavior [154]. However, the large number of necessary variables has limited the success of this approach so far.

Single integral representations are usually nonlinear variants of the Boltzmann integral. Hence, the starting point of single integral representations are a linear viscoelastic functional representation in which the separability of stress, strain and time is preserved. The Single integral functions can be further subdivided in representations based on factorizability (as proposed by Leaderman [155]) and representations based on reduced time [31]. The latter do not linearize stress or strain, but use stress and strain to non-linearize the time-scale by means of a strain or stress-reduced time (stress clock function [156]). This provides the possibility to treat the nonlinear stress-strain relation according to linear viscoelasticity. However, most of these approaches
2.4 Deformation of viscoelastic diaphragms

**Figure 2.9:** The creep compliance $D(t) = \varepsilon(t) / \sigma$ of a crosslinked polymer as a function of time $t$, plotted over a very long period of time. The immediate term $D_0$ is the time independent, initial or glassy compliance observed at the shortest experimentally accessible time. This value typically ranges for amorphous polymers at room temperature around $10^{-9} Pa^{-1}$. At very long time scales the compliance becomes independent of time again and is termed rubbery, transient or equilibrium creep compliance. At intermediate times the creep compliance $D(t)$ ranges between these two extrema and is time dependent. The characteristic time of this viscoelastic regime is denoted $\tau$ [17].

**Figure 2.10:** The Zener Model (similar to the standard linear solid) is a method of modeling the behavior of a viscoelastic material. It uses a combination of linear springs and dashpots to represent elastic and viscous components, respectively. It is capable to predict creep and relaxation.
are phenomenological and cannot be interpreted directly at the molecular level. Only a few representations are based on non-empirical theory: Schapery [31] used thermodynamic fundamentals for his models.

Besides the rheological approach, a constitutive model for non-linear viscoelastic behavior was established by Eyring et al. [157] (see the following paragraph), which modified the empirical model of the standard linear model by assuming that the time dependent movement of the dashpot can be described by a thermally activated process.

**The Eyring theory**

Eyring and colleagues [157] assumed that the non-linear viscoelastic response depends on an activated process. They modified the linear viscoelastic approach, modeled with a standard linear solid, by assuming that the load-response of the dashpot is not Newtonian but stress and temperature dependent. Hence, the deformation of a polymer could be described as a thermally activated rate process, in which segments of chain molecules have to surmount potential barriers when moving [17]. The parameters of this non-linear viscoelastic model include an activation energy and an activation volume which can be explained with the underlying molecular mechanisms.

It is assumed that deformation is based on either intermolecular (e.g. chain-sliding) or intramolecular (e.g. change in the conformation of a chain) processes. The frequency $f$ of these processes depends on the potential energy barrier of height $\Delta H$ between two possible states. At dynamic equilibrium (no load), an equal number of chain segments surmount the potential barrier in each direction at frequency

$$f = f_0 \cdot \exp \left( -\frac{\Delta H}{RT} \right)$$  \hspace{1cm} (2.56)

The gas constant is denoted $R$, the absolute temperature is abbreviated with $T$, and $f_0$ is a pre-exponential factor.

Due to an applied stress $\sigma$ the energy barriers are symmetrically shifted by $\zeta \sigma$ (cf. Fig. 2.11), where $\zeta$ has the dimension of volume. The increased frequency $f_1$ due to $\sigma$ from the higher to the lower potential is

$$f_1 = f_0 \cdot \exp \left( -\frac{\Delta H - \zeta \sigma}{RT} \right)$$  \hspace{1cm} (2.57)

and the decreased frequency $f_2$ thus becomes

$$f_2 = f_0 \cdot \exp \left( -\frac{\Delta H + \zeta \sigma}{RT} \right)$$  \hspace{1cm} (2.58)
2.4 Deformation of viscoelastic diaphragms

Net flow in direction of applied stress

Figure 2.11: According to the Eyring theory, the two equilibrium states separated by a potential energy barrier, are shifted symmetrically by the energy $|\zeta\sigma|$ when a stress $\sigma$ is applied. This changes the frequencies with which the potential barrier surmounted, resulting in a net flow in the direction of the applied stress.

Since the frequencies are understood as flows in their respective directions, a net flow $f_{\text{net}}$ in the direction of the applied stress results from Eqs.2.57 and 2.58:

$$f_{\text{net}} = f_1 - f_2 = f_0 \cdot \exp \left( -\frac{\Delta H}{RT} \right) \left[ \exp \left( \frac{\zeta\sigma}{RT} \right) - \exp \left( -\frac{\zeta\sigma}{RT} \right) \right]$$

(2.59)

With $2 \sinh(x) = (\exp(x) - \exp(-x))$, Eq. 2.59 becomes:

$$f_{\text{net}} = 2f_0 \cdot \exp \left( -\frac{\Delta H}{RT} \right) \cdot \sinh \left( \frac{\zeta\sigma}{RT} \right)$$

(2.60)

Assuming that the net flow is directly related to the change of strain $\dot{\epsilon}$, it can be stated:

$$\dot{\epsilon} = \frac{d\epsilon}{dt} = \epsilon_0 \exp \left( -\frac{\Delta H}{RT} \right) \cdot \sinh \left( \frac{V^*\sigma}{RT} \right)$$

(2.61)

with $\epsilon_0$ being a constant pre-exponential factor and $V^*$ the activation volume for the molecular event. Equation 2.61 can be understood as description of an activated viscosity, which may be used to non-linearize the model of a dashpot, stating

$$\dot{\epsilon} = \frac{\sigma}{\eta}$$

(2.62)

Inserting the result of Eq. 2.61 into Eq. 2.62 yields for the non-linear viscosity $\eta(\sigma, T)$:

$$\eta(\sigma, T) = \frac{\sigma}{\dot{\epsilon}} = \frac{\sigma}{\epsilon_0} \exp \left( \frac{\Delta H}{RT} \right) \left[ \sinh \left( \frac{V^*\sigma}{RT} \right) \right]^{-1}$$

(2.63)
Hence, the constitutive equation for linear viscoelastic behavior (cf. Eq. 2.55) can be converted to describe non-linear viscoelastic behavior by introducing the activated viscosity of Eyring’s theory. This changes the retardation time \( \tau \) in one dimension to:

\[
\tau = \frac{\eta(\sigma, T)}{E_2} = \left[ s_0 \exp \left( \frac{\Delta H}{RT} \right) \right] \cdot \left[ \frac{\sigma}{s_0 \sinh \left( \frac{\sigma}{s_0} \right) \varepsilon_0 E_2} \right] = \tau_0 \cdot a(\sigma) \tag{2.64}
\]

where \( a(\sigma) \) is a dimensionless non-linearization factor, the non-linearity factor is \( s_0 = RT/V^* \), and \( \tau_0 \) is the constant linear viscoelastic relaxation time in the limit of low stress, since \( \lim_{\sigma \to 0} a(\sigma) = 1 \). Hence, on a logarithmic time scale, \( a(\sigma) \) causes a linear shift.

### The master creep compliance curve

To extend the experimental short-term creep data of non-linear viscoelastic materials to long-time predictions up to several years, which is often required for the life-time specification of commercially available structural plastic parts, the well-known time-temperature superposition principle can be applied [150, 158–161]. This concept is based on the assumption that all retardation times depend in the same way on temperature. On a plot of the creep compliance versus the logarithm of time, individual creep curves of such a thermorheologically simple material (measured at different temperatures) can be arranged to form one continuous curve by shifting these short-term creep data onto a single master curve with respect to a certain reference temperature [156].

Assuming that all relaxation times depend also in the same way on stress, a time-stress superposition principle can be formulated, which implies that the nonlinear effect of stress is to alter the intrinsic time scale of the material. According to the Eyring theory of stress activated plastic flow ([157], [17] chapter 10), stress, like temperature, changes the rate of deformation, which results in a functional dependence of the retardation time \( \tau \) on stress (cf. Eq. 2.64). Similarly to the time-temperature superposition principle, the resulting time-stress superposition principle allows to shift each of the short-term experimental data, recorded at different stress levels, individually on a logarithmic time-scale to construct a master curve [31,139,155] with respect to a certain reference stress \( \sigma_{\text{Ref}} \) (see Fig. 2.12). According to the three dimensional formulation of the Eyring theory [139], the stress dependent retardation time \( \tau \) under isothermal conditions can be written as

\[
\tau(\theta_{eq}) = \tau_0 a(\theta_{eq}) \tag{2.65}
\]
2.4 Deformation of viscoelastic diaphragms

Figure 2.12: Schematics of the time-stress superposition principle: The individual short time creep compliance data, recorded at different stress levels (left), are shifted on a logarithmic time scale to construct the master creep compliance curve at the reference stress $\sigma_{\text{Ref}}$. The initial creep compliance $D_0$ is indicated by the intersection of the master curve with the ordinate, and the transient component $D_e$ equals the value of the plateau at infinite time.

with

$$a(\theta_{eq}) = \frac{\theta_{eq}}{s_0 \sinh \left( \frac{\theta_{eq}}{s_0} \right)} = \frac{V^* \theta_{eq}}{RT \sinh \left( \frac{V^* \theta_{eq}}{RT} \right)} \quad (2.66)$$

The equivalent stress $\theta_{eq}$ obeys the Von Mises stress criterion and is derived from Eq. 2.29. The function $a(\theta_{eq})$ is a dimensionless shift factor, and $\tau_0$ is the constant linear viscoelastic retardation time in the limit of low equivalent stress $\theta_{eq} \ll s_0$, where $s_0$ is a non-linearity parameter related to the activation volume $V^*$ of plastic flow as $s_0 = RT/V^*$. The temperature is denoted $T$, and $R$ is the gas constant. In the non-linear viscoelastic regime at higher equivalent stress, $\theta_{eq} > s_0$, the retardation time changes rapidly as described by Eqs. 2.65 and 2.66.

However, the creep behavior of glassy polymers is not only a function of temperature and load, but also a function of physical age [162, 163] and environmental exposure [150] during use. Thus, it must be emphasized that the creep compliance master curve constructed by shifts on the logarithmic time-scale of the short-term creep data is a virtual curve, which will deviate from an experimental creep test on this time scale.
2 Theory

Constitutive equations for the bulge test

The time dependent strain in transversal direction $\varepsilon_{xx}$ of an infinitely long membrane is composed of three parts:

$$\varepsilon_{xx}(t) = \varepsilon_{xx,\text{elastic}} + \varepsilon_{xx,\text{transient}}(t) + \varepsilon_0(t)$$  \hspace{1cm} (2.67)

The first term of Eq. 2.67 is the time-independent elastic response $\varepsilon_{\text{elastic}}$ at time zero when the load is applied and may be expressed as:

$$\varepsilon_{\text{elastic}} = D(t=0)(\sigma_{xx,p} - \nu(t=0)\sigma_{yy,p}) = D_0\sigma_{xx,p}(1 - \nu_0^2)$$  \hspace{1cm} (2.68)

The second term $\varepsilon_{xx,\text{transient}}(t)$ represents the time dependent, transient portion of the strain response in $x$-direction due to the applied load $p$ and may be written as:

$$\varepsilon_{xx,\text{transient}}(t) = [D_{t>0}(t) - D_{t=0}(t)] [\sigma_{xx,p} - \nu(t)\sigma_{yy,p}] = (D(t) - D_0)\sigma_{xx,p}(1 - \nu(t)^2)$$  \hspace{1cm} (2.69)

The lateral contraction ratio $\nu(t)$ due to an infinitesimal deformation is time dependent. However, it can be assumed, that the change of the intrinsic in-plane stress $\sigma_0$ during one measurement is negligible.

The third term of Eq. 2.67 stands for the intrinsic in-plane strain $\varepsilon_0(t)$. It can be calculated from the intrinsic in-plane stress $\sigma_0$, which is assumed to be constant during a single creep measurement. With $\sigma_0$ being equi-biaxial, $\varepsilon_0(t)$ may be determined as:

$$\varepsilon_0(t) = D(t)(\sigma_0 - \nu(t)\sigma_0) = D(t)\sigma_0(1 - \nu(t))$$  \hspace{1cm} (2.70)

As stated above, the lateral contraction ratio $\nu(t)$ due to an infinitesimal deformation in any real (i.e. viscoelastic) material is time-dependent [164]. However, if $\nu(t)$ can be assumed to be constant, Eq. 2.67 simplifies to:

$$\varepsilon_{xx}(t) = D(t)\left[\sigma_{xx,p}(1 - \nu^2) + \sigma_0(1 - \nu)\right] = D(t)\left[\sigma_{xx}(1 - \nu^2) + \sigma_0(\nu^2 - \nu)\right]$$  \hspace{1cm} (2.71)

2.4.3 Effect of crosslinking and fillers

The effect of crosslinking on glassy polymers is qualitatively depicted in the following. Furthermore, the influence of non-interacting, rigid particles as filler in a polymer matrix is described and a model based estimation of the influence on the glassy modulus of the composite is given.

Densely crosslinked glassy polymers

Densely cross linked polymers show little change in their glassy state and the onset of the transition phase, compared to uncured polymers. However, the onset and
shape of the plateau and terminal zones change dramatically. Increasing crosslink density reduces the free volume by bringing adjacent chains closer together. This raises the glass temperature $T_g$. The relaxation and retardation spectra (in dynamic measurements) broaden.

Very highly crosslinked polymers do not show a distinct glass temperature below their degradation temperature, because motions of extensive segments of the main chain are no more possible. The elastic energy then appears to be based largely on an entropy effect [17, 18].

Effect of non-interacting, rigid fillers

This paragraph deals with polymer-filler composites, where the polymer acts as matrix in which the non-interacting, rigid particles are evenly dispersed. These particles are non-soluble, hence forming a second phase. Their elastic modulus is considerably higher than the glassy modulus of the matrix. At moderate stress and temperature, the particle material exhibits negligible creep, compared to the polymer matrix. Common particle materials are silica (e.g. $SiO_2$ or $SiC$) or metals ($Al$, $Ag$). Fibres are known to have a more significant effect, especially on the creep and modulus. Nevertheless, particles are often used due to their lower price in purchase and processing [18].

The effect of these particles in polymer matrices is known to rise strength, wear resistance and stiffness with increasing volume fraction of the filler. The particle size does not seem to have an influence on the modulus. However decreasing particle sizes increase the tensile strength significantly [165]. The viscoelastic behavior of the composite as a whole depends on the stress experienced by the matrix.

The Hashin-Shtrikman model allows for an estimation of the upper and lower bounds of the expected glassy modulus $1/D_0$ of an isotropic composite [166]:

$$G_{\text{composite}} = G_2 + V_1 \cdot \left[ \frac{1}{G_1 - G_2} + \frac{6V_2(K_2 + 2G_2)}{5G_2(3K_2 + 4G_2)} \right]^{-1}$$

(2.72)

in which $K_i$, $G_i$, and $V_i$ are the bulk modulus, shear modulus, and volume fraction of phases $i = [1, 2]$, respectively. Interchanging the indices for the two materials yields the upper and lower bound.

Figure 2.13 demonstrates the effect of filler content on the glassy modulus of an epoxy matrix, composed of a matrix with a glassy modulus of $1/D_0 = 4.5GPa$ and silicon dioxide as particles with an elastic modulus of $E_{SiO_2} = 70GPa$. 

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Figure 2.13: Estimation of the glassy modulus $E_0 = 1/D_0$ for an isotropic composite, which is composed of an epoxy matrix with silica particles. The upper and lower bounds are calculated with the Hashin-Shtrikman model for composites. The glassy modulus for the epoxy matrix is assumed to be $1/D_{0,\text{epoxy}} = 4.5\text{GPa}$ and the elastic modulus for the $\text{SiO}_2$ particles $E_{\text{SiO}_2} = 70\text{GPa}$.

2.4.4 Aging

Lakes [166] defines aging as an autonomous change of material properties with time. Two different categories are discriminated: chemical and physical aging. While chemical aging changes the polymer irreversibly (e.g. proceeding curing process in an incompletely hardened thermoset, vulcanization or chain scission), physical aging is a thermoreversible process, which starts right after quenching the amorphous polymer from above the glass temperature $T_g$ to a temperature below $T_g$ [162]. It is attributed to a slowly decreasing free volume, which is identified with molecular packaging irregularities in the material. Since the free volume is directly linked to molecular mobility, the time effects of viscoelastic behavior will decrease as well. Properties which change drastically at the glass temperature $T_g$ are influenced by physical aging. The material becomes more and more glass-like, stiffer and more brittle, the damping and the retardation times decrease [17, 167].

Lee [168] describes the influence of crosslink density on physical aging. He found that the time needed to reach structural equilibrium is increased with rising crosslink
density of epoxy glasses. Hence, crosslinking reduces the influence of aging in a certain time-frame in which the material may be measured. The optimum starting position for each test would be identical probes. This could be achieved by using previously untested samples with the same (thermal) history or by quenching previously stressed specimens from a temperature \( T > T_g \) before each measurement. However, the first is not feasible due to time and costs. Quenching the samples from above \( T_g \) before each measurement is impossible for the materials used in this work, since highly crosslinked polymers do not show a glass temperature below their degradation temperature [18]. Further, the effect of rejuvenating the material by means of high stresses is doubtful [167,169].

### 2.4.5 Vibration of viscoelastic membranes

This paragraph deals with the influence of viscoelasticity on the dynamic behavior in order to quantify the systematic error if dynamic measurements of viscoelastic specimens are treated with linear elastic models. This approach is desired since analytical models describing viscoelastic behavior of membranes with acceptable simplicity are not available. In dynamic testing, the viscoelastic material damping shifts the resonant peaks towards lower frequencies. The resonant frequency \( \omega_r \) of a forced vibration of a mass-damper-spring model is [170]:

\[
\omega_r = \omega_0 \sqrt{1 - 2\zeta^2} \tag{2.73}
\]

where \( \omega_0 \) is the natural frequency without damping and \( \zeta \) is the damping ratio of the system:

\[
\zeta = \frac{d}{2m\omega_0} \tag{2.74}
\]

The damping coefficient is denoted \( d \) and the mass is abbreviated with \( m \). For slightly damped systems, i.e. for a small \( \zeta \), the resonant frequency is close to the natural frequency. In order to evaluate the damping ratio \( \zeta \) of vibrating diaphragms, the quality factor \( Q \) is measured. Using the physical definition, \( Q \) is the ratio between the total system energy at resonance and the energy loss in one cycle due to damping [170]:

\[
Q = 2\pi \frac{E}{\Delta E} = \frac{m\omega_r}{d} \tag{2.75}
\]

\( Q \) indicates the peak sharpness of a resonance peak. Combining Eq. 2.74 and Eq. 2.75 yields the relation between \( Q \) and \( \zeta \):

\[
Q = \frac{\sqrt{1 - 2\zeta^2}}{2\zeta} \tag{2.76}
\]
2 Theory

Hence, with decreasing $\zeta$ or increasing $Q$, the resonant frequency of the forced vibration $\omega_r$ converges to the natural vibration frequency $\omega_0$. For small damping ($Q \geq 20$), the quality factor $Q$ can be approximated by

$$Q \approx \frac{1}{2\zeta}$$

(2.77)

The resulting systematic error then remains below 0.1% and can be neglected. Thus, it is acceptable to describe the resonant behavior of a system with $Q \geq 20$ with linear elastic models.

2.4.6 Mechanical energy in viscoelastic solids

The storage of mechanical energy in solid bodies strongly depends on the material and loading pattern. Ideal-elastic materials react quasi instantly on the change of load (cf. paragraph 2.2.5). They do not dissipate energy during a closed strain path and hence, return the full quantity of the supplied energy. However, any real material dissipates energy as heat upon deformation. This may be observed as hysteresis in a closed strain path, with the area of the loop being equal to the dissipated energy. Viscoelastic materials show a distinct hysteresis, indicating the loss of energy when being deformed [18].

The storage of mechanical energy in viscoelastic materials, is described with the following items:

- Creep compliance and relaxation modulus
- Strength
- Time dependent lateral contraction ratio
- Range of elastic regime
- Degradation
- Aging
- Fatigue

The elastic regime is defined by the recoverability of strain at ambient temperature. Highly crosslinked polymers are not supposed to show non-recoverable plastic deformation without crazing [17]. The recovery times though vary widely dependent on the load conditions.

Degradation can be induced by chain scission or crosslinking due to high temperature, electromagnetic radiation, chemical reaction with environmental gases or moisture take-up. Fatigue forms due to crazes after cyclic loading and eventually leads to
2.4 Deformation of viscoelastic diaphragms

destruction. Both mechanisms are not part of the investigations and the probability of their occurrence during testing is kept as low as possible.
Aging is defined as processes that occur in a polymeric material during a specified period of time, and that usually result in changes of physical and/or chemical structure and therefore of material properties. The physical part is taken into account during the experimental procedure, as proposed by Ward [17, chapter 5]. Chemical degradation is avoided best possible.
The time dependent energy density \( W(t) \) for a viscoelastic material can be written as [166, page 20]:

\[
W(t') = \int_{-\infty}^{t'} \sigma_{ij}(t) \frac{d\varepsilon_{ij}(t)}{dt} dt
\]  
(2.78)

For relaxation testing in dilatation, the energy density \( W(t) \) of a linear viscoelastic material assumes the following form:

\[
W(t) = \frac{1}{2} \int_{-\infty}^{t} \int_{-\infty}^{t} E(2t - \tau_1 - \tau_2) \frac{e}{\tau_1} d\tau_1 d\tau_2
\]  
(2.79)

with \( \tau_1 \) and \( \tau_2 \) being time variables and the relaxation modulus \( E(t) \). For shear, \( e \) becomes the deviatoric strain \( \varepsilon_{ij}^{\text{dev}} \) and \( E \) becomes the shear relaxation modulus \( 2G(t) \).

**Energy storage and dissipation during a creep test**

For an uniaxial creep test, with constant stress \( \sigma \) applied at time \( t = 0 \), the total input of energy per volume \( W(t') \) into the system is given by:

\[
W(t') = \int_{-\infty}^{t'} \sigma(t) \frac{\varepsilon(t)}{dt} dt = \int_{0}^{t'} \sigma(t) \cdot \frac{D(t)}{dt} dt = \frac{D_0\sigma^2}{2} + \int_{0}^{t'} \frac{\sigma^2}{dt} \cdot \frac{D(t)}{dt} dt
\]  
(2.80)

The total energy density may be split into stored and dissipated energy per volume. For simple models, such as the Zener or standard linear solid (cf. Fig. 2.10) both parts can be calculated. The total energy density \( W(t') \) transferred into the elements of a Zener model configuration during a creep test with constant stress \( \sigma \) (applied at time \( t = 0 \)) is derived by inserting the modeled equation of the creep compliance \( D(t') \) [137] into Eq. 2.80, yielding:

\[
W(t') = \frac{\sigma^2}{2E_1} + \frac{\sigma^2}{E_2} \left( 1 - \exp \left( -\frac{t'}{\tau} \right) \right)
\]  
(2.81)

The dissipated part of this energy density equals the mechanical work done in the dashpot \( W_\eta \) during this creep process. This energy is converted into heat. To calculate this fraction, it is assumed, that the dashpot \( \eta_0 \) behaves like a Newtonian fluid, with the strain rate equal to the ratio of stress and viscosity \( \dot{\varepsilon} = \sigma / \eta_0 \) and the retardation time \( \tau = \eta_0 / E_2 \):

\[
W_\eta(t') = \int_{0}^{t'} \sigma_{\eta} d\varepsilon_{\text{Voigt}} = \frac{\tau \sigma^2}{2\eta} \left( 1 - \exp \left( -\frac{2t'}{\tau} \right) \right)
\]  
(2.82)
Figure 2.14: Mechanical energy storage and energy dissipation, modeled with a Zener configuration. Creep testing with constant stress, applied at time \( t = 0 \) is the boundary condition. The full line describes the total energy which is transferred into the system. Thereof, a certain fraction is dissipated as heat (pointed line), reducing the mechanically stored energy (dashed line).

Hence, the stored mechanical energy density \( W_{\text{stored}} \) during a creep test is the difference between total energy per volume \( W(t) \) and the dissipated energy density \( W_\eta(t) \):

\[
W_{\text{stored}}(t) = W(t) - W_\eta(t)
\]

\[
= \frac{\sigma^2}{2E_1} + \frac{\sigma^2}{E_2} \left( 1 - \exp \left( -\frac{t}{\tau} \right) \right) - \frac{\tau \sigma^2}{2\eta} \left( 1 - \exp \left( -\frac{2t}{\tau} \right) \right)
\]

\[
= \frac{\sigma^2}{2E_2} \cdot \left( 1 + \frac{E_2}{E_1} \exp \left( -\frac{t}{\tau} \right) + \exp \left( -\frac{2t}{\tau} \right) \right) \tag{2.83}
\]

Figure 2.14 demonstrates the different fractions of the energy in a Zener model during creep testing: the total energy density, which is put into the system until time \( t \), the dissipated energy per volume and the mechanically stored energy density.

For non-linear viscoelastic materials, the measured creep compliance \( D(t) \) must directly be inserted into Eq. 2.80. For the model used in this work (Eq. 2.55), the total assimilated energy density is obtained by:

\[
W(t) = \frac{D_0 \sigma^2}{2} + \sigma^2 \int_0^{t'} \frac{D_e - D_0}{t} m \left( \frac{t'}{\tau} \right)^m \exp \left[ - \left( \frac{t'}{\tau} \right)^m \right] dt' \tag{2.84}
\]
2.5 Statistics

The statistical evaluation of measurement results is defined in the norm DIN 53598 and is discussed in greater detail in [171,172]. Nevertheless, this section briefly recapitulates the basics for the Weibull distribution, the error propagation and the confidence level and interval.

2.5.1 Weibull distribution

The distribution of measured fracture stresses of glassy polymer specimens is usually asymmetric. Hence, it can not be described by the Gauss distribution with a mean value and a standard distribution. Rather, it may be evaluated with the Weibull distribution [173], which is a statistical distribution often used for the description of the strength of brittle materials. It is named after the Swedish physicist Waloddi Weibull (1887-1979).

For an infinite sample size, the cumulative distribution function $P(x)$ of the two-parameter Weibull distribution is:

$$P(x) = 1 - \exp\left( -\left(\frac{x}{\Theta}\right)^\beta \right)$$

(2.85)

with $\beta > 0$ the shape parameter (also called Weibull modulus) and $\Theta > 0$ the scale parameter (here Weibull strength), which is the value $x$ at 63.2% probability of the distribution. For the description of material strength, the function $P(x)$ determines the probability, that a specimen fractures before reaching the load level $x$.

For the evaluation of a finite sample size with $n$ specimens, the measured fracture strengths are sorted ascending and are numbered from $i = 1$ to $n$. Sample sizes below 30 specimens are called small sample size. For these, the failure probabilities $P_i$ can be assigned to each fracture strength as follows:

$$P_i = \frac{i - 0.5}{n}$$

(2.86)

For large sample sizes, Eq. 2.86 becomes $P_i = i/n$. The plot $P_i(x_i)$ is fitted with Eq. 2.85. Due to the finite sample size, the obtained scale and shape parameters are not the true values and are named $T_W$ and $b$, respectively.

The confidence interval for the Weibull modulus $b$ is then given by:

$$b \cdot \left( \frac{-0.78Z_{a/2}}{\sqrt{n}} \right) \leq \beta \leq b \cdot \left( \frac{+0.78Z_{a/2}}{\sqrt{n}} \right)$$

(2.87)

with the confidence level $Z_{a/2}$. Throughout this whole work, the confidence level is specified to be 95%, the corresponding values for $Z_{a/2}$ can be taken from table 2.2.
Table 2.2: Confidence levels

<table>
<thead>
<tr>
<th>Confidence Level</th>
<th>Z_{\alpha/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>99%</td>
<td>2.576</td>
</tr>
<tr>
<td>95%</td>
<td>1.960</td>
</tr>
<tr>
<td>90%</td>
<td>1.645</td>
</tr>
</tbody>
</table>

The confidence interval for the Weibull strength $T_W$ for a finite sample size is:

$$T_W \cdot \left( \frac{-1.05Z_{\alpha/2}}{b\sqrt{n}} \right) \leq \Theta \leq T_W \cdot \left( \frac{+1.05Z_{\alpha/2}}{b\sqrt{n}} \right)$$

(2.88)

For further information on the Weibull statistics, please refer to Kuehlmeyer and Staehel [171, 172].

Materials such as concrete typically have a Weibull modulus around $b \sim 5$, meaning that the measured strength of the specimens varies by up to ±30%. In state-of-the-art ceramics and pure silicon $b$ might be 10 – 15 and the variability in strength is approximately ±10%. Jadaan [44] gives an overview of MEMS based tests and results concerning fracture strength of silicon and silica materials used in MEMS. Test procedures for determining the Weibull modulus are specified in DIN EN 843-5 and DIN 51 110-3.

2.5.2 Error propagation

Indirect measurements of a certain quantity rely on a model based evaluation, which converts the direct measurands (e.g. pressure and deflection) into the required property (e.g. Young’s modulus or prestress). The introduced errors are random and systematic errors. All errors cumulate to an absolute value in respect to the required property.

If the measurands are independent and the distributions of their values are Gaussian, the absolute random error of the modeled property may be calculated with the Gaussian (quadratic) error distribution [172]. The mean error of the functional characteristics $\Delta F$ is calculated with the standard deviations of the individual measurands $\Delta x_1, \Delta x_2$, etc. [174]:

$$\Delta F = \sqrt{\left( \frac{\partial F}{\partial x_1} \Delta x_1 \right)^2 + \left( \frac{\partial F}{\partial x_2} \Delta x_2 \right)^2 + ...}$$

(2.89)

If the above assumption is not valid, Eq. 2.89 can not be applied. The maximum random error $\Delta F$ is then determined with the linear error propagation:

$$\Delta F = \left| \frac{\partial F}{\partial x_1} \right| \Delta x_1 + \left| \frac{\partial F}{\partial x_2} \right| \Delta x_2 + ...$$

(2.90)
Uncorrected, systematic errors (e.g. through deviation from an assumption) are then added linearly to the absolute random error.

### 2.5.3 Confidence level and interval

With an increasing number \( n \) of tests, the measured mean value \( \bar{x} \) of a Gaussian distribution converges to the sought-after true value \( \mu \). However, the discrepancy between \( \bar{x} \) and \( \mu \) can not be quantified exactly, but a *confidence interval* is given within which the true value is found with a probability of \( 1 - \alpha \). Thereby, \( 1 - \alpha \) is the *confidence level*, which is chosen throughout this work to be 95%.

The confidence interval for the true value \( \mu \) is given as:

\[
\bar{x} - t_{f,1-\alpha/2} \cdot \frac{\Delta \bar{x}}{\sqrt{n}} \leq \mu \leq \bar{x} + t_{f,1-\alpha/2} \cdot \frac{\Delta \bar{x}}{\sqrt{n}} \tag{2.91}
\]

with the value of Student’s t-distribution \( t_{f,1-\alpha/2} \) and with \( f = n - 1 \) degrees of freedom. The standard deviation is denominated \( \Delta \bar{x} \) [171].
3 Material Selection

All three polymer classes are subject to microstructuring: Thermosetting plastics [10, 46, 63, 66, 175, 176], thermoplastic resins [5], and elastomers [177]. The main emphasis lays on the first two, mainly because common photoresists are thermosets or thermoplastics and mold and hot embossing techniques mainly work with thermoplastics.

Photolithography is the most important method for microstructuring polymers and well understood with reproducible results. Different photoresists offer a minimum lateral feature size of less than 0.5\(\mu\)m and maximum thicknesses of more than 500\(\mu\)m. The structure transfer with photon energy from mask into material is parallel and fast [178].

Mold and hot embossing techniques are widely used in the production of microstructured polymeric devices due to the low piece cost. Additive and subtractive laser machining, micro drilling and precision milling are further processing techniques. They are feasible but due to their serial character relatively slow and therefore expensive in mass-production [178].

This chapter describes the initial material evaluation and the selected polymers for investigation: SU-8, an photosensitive epoxy resin which is available as original product in an unfilled state and as filled versions with silica nanoparticles and silver microparticles. Furthermore, a photodefinable polyimide is chosen for testing.

3.1 Material evaluation

The sought-after polymer is suitable to serve in mechanically active MEMS devices. Hence, the material ideally shows low creep, no plastic deformation, high fracture strength, high elastic range and little physical and chemical aging. Furthermore, it is obligatory that the material can be processed with common MEMS technologies. It should also be usable for thick film application to allow for an additional degree of freedom in the construction. The expense factor is included in the evaluation but subordinate. Table 3.1 compiles and assesses the most important specifications and evaluates the parameters molecular structure, crosslinking and non-interacting rigid fillers. The molecular structures of polymers are usually distinguished between semi-crystalline and amorphous. In average, amorphous polymers show lower creep rate, lower strength,


3 Material Selection

Table 3.1: Decision matrix for the evaluation of the material. The weighted criteria on the left are applied to variations in molecular structure and potential crosslinking density. Furthermore, non-interacting rigid fillers are considered. The evaluation indicates that the sought-after polymer is ideally amorphous, highly crosslinked with monomers containing ring structures. The addition of fillers appears feasible, though a significant influence on the main criteria creep is unlikely.

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Relative weight (1-10)</th>
<th>Influence (-1=negative, 0=zero or indefinite, 1=positive)</th>
<th>Fillers (rigid, non-interacting)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low creep rate</td>
<td>10</td>
<td>amorphous -1, semi-crystalline ring structures 1</td>
<td>0</td>
</tr>
<tr>
<td>Low plastic deformation</td>
<td>8</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>High strength</td>
<td>7</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>High elastic range</td>
<td>7</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>High glass transition temperature</td>
<td>7</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Low chemical degradation</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Low physical aging</td>
<td>6</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Low cost</td>
<td>3</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

*Sum* | 7 | -7 | 15 | 12 | 21 | 10 |

higher elastic range and higher cost, compared to semi-crystalline options [179–181]. The weighted comparison yields the amorphous polymers as the better suited alternative. Furthermore, ring structures are positively rated. They increase the glass transition temperature, lower the creep rate and hinder plastic deformation. However, at the same time they decrease the elastic range. The influence of crosslinking on the specifications is consistently positive, a high network density is favored. Highly crosslinked polymers show high fracture strength and low creep. There is practically no plastic deformation and the water uptake is usually low. Relatively little physical aging is observed in their glassy state and the chemical inertness is usually high, making them suitable for many environments. The ability to be processed with common MEMS technologies is excellent, given the fact that negative photoresists work with crosslinking to achieve differences in solubility. However, the fracture strain of densely crosslinked polymers is comparatively low. Yet this drawback can at least be partly compensated by intelligent system design. Non-interactive, rigid fillers result in higher strength as well as lower cost and are therefore considered as positive. Thus, the polymer of choice is ideally amorphous, highly crosslinked and its monomers contain ring structures. Compositions with non-interacting, rigid fillers are worth considering.

3.1.1 Potential polymers

Three classes of microstructurable, crosslinked photopolymers are available: *Single component systems* (no sensitizers), *positive and negative two-component systems* [178]. The first class can be crosslinked by deep UV radiation, electron beam, ion beam
3.1 Material evaluation

<table>
<thead>
<tr>
<th>Material</th>
<th>Epoxy</th>
<th>Polyimide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy modulus [GPa]</td>
<td>0.7–5</td>
<td>2.5–7.2</td>
</tr>
<tr>
<td>Yield strain [%]</td>
<td>~3</td>
<td>~3</td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>15–73</td>
<td>70–135</td>
</tr>
<tr>
<td>Glass Transition [°C]</td>
<td>&gt;200</td>
<td>290–350</td>
</tr>
<tr>
<td>Thermal Degradation [°C]</td>
<td>&gt;380</td>
<td>&gt;420</td>
</tr>
</tbody>
</table>

or X-ray lithography, yielding an almost insoluble resist. A material example is poly(glycidyl methacrylate) (PGMA) which crosslinks with X-ray energy [178, page 39]. However, the necessary processing is rather uncommon and expensive for a potential application in industrial fabrication. Hence, single component systems are omitted.

The positive two-component systems are mostly DQN resins, an abbreviation of the sensitizer material diazonaphthoquinone (DQ) and the matrix material novolac (N). The photoinduced reaction results in chain scission, rather than crosslinking. Hence, positive photoresists often show poor chemical resistance to organic solvents and the expected mechanical long term characteristics are unsatisfying. Furthermore, the positive formulations are available for layers up to 25µm maximum, since higher thickness ranges are challenging to formulate in a positive tone. It is very difficult to retain the necessary transparency for reasonable exposure doses with acceptable sidewall angles. And very thick positive novalak photoresists have the characteristic of popping or forming voids after exposure as a result of the nitrogen generation during exposure [182]. Hence, this option is dropped as well.

Negative photoresists on the other hand do not show the above mentioned drawbacks. They are very difficult to degrade due to their chemical composition, and are available in ultra-thick compositions (>200µm in a single spinning step). They yield a dense and stable network of highly crosslinked monomers. The most prominent representatives which meet the stated requirements are polyimides and epoxy resins. Their approximate mechanical properties at short times are compiled in table 3.2.

_Epoxy resins_ display high strength and modulus, wear resistance and cracking resistance, high temperature stability and good ageing properties. Many of these properties may be further enhanced using suitable fillers, for example metals, minerals and glass. Epoxy resins have good resistance to chemicals and good dimensional stability. The structure of the resins is based around the chemistry of the epoxy group, with the cured resin consisting of a prepolymer which becomes crosslinked with a curing agent. The mechanical properties of the cured resin depend on a number of
Material Selection

SU-8

- Epoxy resin
- Highest functionality
- High aspect ratio

Properties
- Negative tone photoresist
- Amorphous
- High functionality
- High fraction of ring structures
- No plastic deformation
- High strength
- Low elastic range
- High cost at small bundle size
- High glass transition temperature
- High chemical resistance

Composite
- SU-8 matrix
- 3.3 vol.% silica nanoparticles
- reduced friction and wear
- reduced friction and wear

GCM3060

- Composite
- SU-8 matrix
- 10.2 vol.% silver microclusters
- electrical conductivity (~$10^4$ S/m)

PI2737

- Polyimide
- Excellent temperature resistance
- Outstanding electrical properties
- Low water uptake

Figure 3.1: Short summary of the tested materials. Common properties are collected in the rectangular box, individual information are added below the specific product names.

Factors: the structure of the prepolymer, the curing agent, stoichiometry of resin and hardener, cure time and cure temperature. Subtle variation of any of these factors can have a profound effect on the properties of the cured resin. For MEMS applications, this thermosetting is sold under the brand name SU-8 [183]. Polyimides show good mechanical properties, including fatigue resistance, excellent high temperature performance (up to 450°C), high chemical resistance, and outstanding electrical properties, particularly dielectric strength [175]. Various products are available for thin film applications [184]. The upcoming sections explain the tested products in detail. Figure 3.1 presents a summary of the selected products.

3.2 SU-8

SU-8 is a near-UV, epoxy based negative-tone photoresist, developed at IBM Research [183]. It is prepared by mixing the photoacid generator triaryl sulfonium salt (CYRACURE UVI from Union Carbide), which is dissolved in propylene carbonate, with EPON SU-8 resin, which is also dissolved in an organic solvent. The monomer has the highest epoxide functionality commercially available and low molecular weight at the same time. Furthermore, it has a very high ratio of ring structures.
3.2 SU-8

Figure 3.2: Chemical structure of the SU-8 monomer on the left. Due to the eight epoxy groups in each monomer, the functionality of the monomer is eight, which explains the number in its name. The high ratio of binding sites to monomer size yields an extremely dense network. To the right, an epoxy group is shown.

compared to its weight and it is amorphous for temperatures below $T_g$. Its optical absorption in the near-UV is very low [185]. SU-8 monomers can be dissolved in a variety of organic solvents. The most common are propylene glycol methyl ether acetate (PGMEA), gamma butyrolacton (GBL), methyl iso-butyl ketone (MIBK) and cyclopentanone. The SU-8 dissolved with the latter solvent is called SU-8$_{2000}$ series. The ratio of solvent to solids determines the viscosity which determines the range of possible thicknesses of the resist layer when spun on a substrate. Solutions containing up to 85% solids by weight can be achieved.

These characteristics make this resist system very suitable for thick-film applications with the ability to obtain high aspect ratios.

The polymerization of SU-8 is based on chemical amplification, initiated upon UV-exposure (365 to 436nm) that starts a cascade of subsequent chemical reactions. An acid is generated (Lewis acid, [185]) which catalyzes the crosslinking formed among the epoxy groups. The chemical reactions are displayed in figure 3.3. The monomers with eight epoxy sites (cf. Fig. 3.2) yield a very dense, stable polymer after full curing. Standard formulations are offered from MicroChem covering a wide range of film thicknesses from $<1\mu m$ to $>200\mu m$. SU-8 has high functionality and high optical transparency. Images have an exceptionally high aspect ratio ($> 1:50$) and straight sidewalls [186–188]. Fully cured SU-8 is highly resistant to solvents, acids and bases and has excellent thermal stability, making it well suited for applications in which cured structures are a permanent part of the device. The glass transition temperature lies above 200°C [183]. The glassy modulus is high (around 4GPa), and compara-
3 Material Selection

Figure 3.3: The crosslinking of SU-8 is based on the reaction of an epoxy site with a second OH-Group. It is initiated in an acid-catalyzed deprotection mechanism. The catalytic species (Lewis acid $H^+SbF_6^-$) is generated by photolysis of a thermally stable onium salt (triaryl sulfonium).

ble with poly(methylmethacrylate) PMMA. The transient modulus is expected to be higher than for non-crosslinked glasses (cf. subsection 2.4.3). The uniaxial tensile strength reaches values around 70MPa.

3.2.1 SU-8$_{2002}$

The SU-8$_{2000}$ series from MicroChem is formulated in cyclopentanone and offers better adhesion, shorter drying and curing cycles than the original recipe. The product used in this work is named SU-8$_{2002}$, which offers film thicknesses between 2$\mu$m and 5$\mu$m after curing. The density at ambient pressure and room temperature is $\rho_{SU8} = 1220$kg/m$^3$ [13].

3.2.2 GLM2060 - Glass-filled SU-8

By combining the photosensitive SU-8 resin and silica nanoparticles MEK-ST from Nissan Chemical Industries, a negative tone composite photoresist is obtained, which can be used for the UV-LIGA application to microfabricate microscale structures with
reduced friction and wear [56, 62]. The silica particles have a mean particle size of 12nm (± 2nm) and a density of $\rho_{\text{glass}} = 2500 \text{ kg/m}^3$. The ratio is approximately 33:1, resulting in an overall density of $\rho_{\text{GLM2060}} \approx 1260 \text{ kg/m}^3$. The vendor Gersteltec sells this dispersion under the brand name GLM2060.

### 3.2.3 GCM3060 - Conductive SU-8

The inorganic-organic photoresist is obtained by dispersing silver microparticles (PUAG119 from Metalor) in the photosensitive SU-8 resin. The mean particle size of the Ag-clusters is 1.5 $\mu$m and the mass density of silver is 10500 $\text{ kg/m}^3$. With a relative volume fraction of 10.18%, the density of the cured film is calculated to be $\rho_{\text{GCM3060}} = 2165 \text{ kg/m}^3$. The photopolymerization, lateral resolution and the electrical properties were tested by Jiguet et al. [189,190]. The source of supply is Gersteltec, selling this filled resin under the brand name GCM3060.

### 3.3 Polyimide PI2737

The term *polyimide* is applied to a whole family of polymers which contains an imide group (cf. Fig. 3.4) as fundamental component [175]. The product PI2737 from HD Microsystems is a low stress photo-definable polyimide. It has originally been developed as a passivation layer for semiconductors and as an interlayer dielectric for high density interconnect applications. Its polyamic esters (starting substance) contain a photopackage making them sensitive to broadband exposure in the range of 350nm to 435nm. The basic crosslinking reaction of photosensitive amic ester is depicted in
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figure 3.5. The final product is amorphous below $T_g$ and its molecular structure is very stiff due to the ring structures and the imide groups. The material is supplied as low-viscous solution suitable for spin coating. Cured film thicknesses range between 2µm and 12µm. The resist is selfpriming, thus eliminating the need for an additional adhesion promoter. The cured polyimide film offers good mechanical properties, a low coefficient of thermal expansion and a low dielectric constant.

Both the glass and the decomposition temperatures are very high compared with other polyimides: >350°C and 500°C, respectively. And the water uptake is comparatively low: <1% at 50%RH. The density of the cured film is $\rho_{P_{12737}} = 1120\,kg/m^3$ [191].
Figure 3.5: The crosslinking reaction of amic esters with a photosensitive side-group leads to the final imide product over an insoluble intermediate. The initial crosslinking energy is supplied by photons (hν). The second stage which leads from the intermediate to the polyimide requires a large amount of energy (∆) which is supplied by high temperature over a certain period of time.
4 Experimental

This chapter describes the methodology of the testing procedure and the individual test setups. Included are experimental preparations and operational necessities for the measurement of viscoelastic materials. Further, the fabrication of polymer diaphragms and tensile test specimens is presented. Finally, an error analysis quantifies the expected uncertainties.

4.1 Methodology

The overall aim is the creation of a methodology to evaluate the polymeric materials’ creep compliance on micromachined diaphragms with the bulge test method. The resulting implications of this approach are discussed in the following.

As elaborated in the theory, six parameters are needed: pressure induced elastic and transient strain, intrinsic in-plane strain, absolute stress, Poisson’s ratio and the intrinsic in-plane stress. The absolute stress $\sigma_{xx}$ and the pressure dependent strains $\epsilon_{xx,\text{elastic}}$ and $\epsilon_{xx,\text{transient}}$ can be directly measured with the bulge test. However, the intrinsic in-plane stress $\sigma_0$ and the intrinsic in-plane strain $\epsilon_0$ can not be quantified with a static load right before or during a creep measurement without influencing the measurement of the viscoelastic material with its strain memory. Thus, resonant frequency analysis is used as complementary measurement technique to derive these parameters. Short term measurements on materials with high quality factor do practically not increase the specimen’s temperature and the deflections are so small, that the induced strain remains below $2 \cdot 10^{-7}$ and can therefore be assumed not to influence the strain history. Poisson’s ratio $\nu$ is measured with the uniaxial tensile test (SU-8_{100}) or taken from literature. Figure 4.1 summarizes the described circumstances.

The sequence of a complete experiment is predetermined:

1. Fabrication: The samples have to be chemically stable after the last process step. Further reactions, such as crosslinking, must not take place.

2. Dimensioning: Width, length and thickness are determined.
4 Experimental

\[ D(t) = \frac{\epsilon(t)}{\sigma_{\text{const.}}} = \frac{\epsilon_{xx,\text{elastic}}(t) + \epsilon_{xx,\text{transient}}(t) + \epsilon_0(t)}{\sigma_{xx}(1 - \nu^2) + \sigma_0(\nu^2 - \nu)} \]

**Figure 4.1:** Assigned measurement methods for the sought-after parameters of the creep compliance model. The pressure dependent elastic strain \( \epsilon_{xx,\text{elastic}} \), the pressure dependent transient strain \( \epsilon_{xx,\text{transient}} \) and the absolute stress \( \sigma_{xx} \) are derived with the bulge test method. The Poisson ratio \( \nu \) is quantified with the uniaxial tensile test or taken from literature. The resonant vibrometry test is used to measure the intrinsic in-plane stress \( \sigma_0 \) and, together with the bulge test, the intrinsic in-plane strain \( \epsilon_0 \).

3. **Creep conditioning:** In order to minimize aging effects and hence to have the same starting conditions for each creep measurement, the samples are cyclically conditioned at the highest stress and temperature of measurement until reproducibility is achieved. The conditioning stress is applied for the maximum period of loading during measurement. Subsequent relaxation periods of approximately 10 times the loading period ensure full recovery. This procedure ensures reproducible creep measurements. It was proposed by Leaderman [155] and is reproduced in [163] and [17, chapter 5].

4. **Membrane or plate behavior:** The main key figures can only be measured with diaphragms which behave membrane-like. The preliminary calculations (cf. Eq. 2.40) have to be verified by inspecting the ratio of the ascending resonance frequencies to the first resonant frequency as described in paragraph 2.3.2.

5. **Intrinsic in-plane stress:** This key parameter is determined with resonant frequency measurements. Constant prestress can not be assured a priori. Hence, this variable and has to be measured before every creep test.

6. **Zero deflection:** The shape and deflection of the membrane has to be measured with the white light interferometer before every bulge test to ensure complete strain recovery and equal starting conditions.
4.1 Methodology

7. Creep test: With the bulge testing method, a constant pressure (ideally stress) is applied for a short period, typically in the range of a few hours, and the deflection is measured at different times.

8. Recovery time: The recovery time after the individual creep tests should be approximately ten times the loading duration.

○ Repetition of items [5–8] at different pressure levels leads to multiple creep compliance curves. If the material behaves non-lineararily according to Eyring’s theory, those curves can be assembled to one long term master creep compliance curve.

9. Fracture test: Bulge testing with constantly increasing pressure (∼75Pa/s). The aim is to quantify the fracture strength at a strain rate of approximately $10^{-4}$ s$^{-1}$.

10. Reference test: The uniaxial tensile test is used as reference. Bone shaped specimens are strained at a rate of $\dot{\epsilon} \simeq 10^{-4}$ s$^{-1}$ until fracture. The results are glassy modulus, Poisson’s ratio and fracture strength. However, the restrictions given in paragraph 1.2.4 apply.

11. Clamping sites: Destructive inspection of the clamping sites reveals a potential influence of their shape on the tests. However, adequate processing should be ensured before testing.

12. Data analysis 1: The slope of the stress-strain values taken at short times and different pressures can be used to calculate the initial plane strain compliance $1/[D_0(1 - \nu^2)]$, respectively the glassy plain strain modulus $E_0/(1 - \nu^2)$. Data have to be taken at short times only, where practically no creep can be observed.

13. Data analysis 2: With the initial plane strain compliance and the values of the intrinsic in-plane stress, the intrinsic in-plane strain $\epsilon_0$ can be quantified.

14. Data analysis 3: With the information on all key parameters, the creep compliance curves of the individual tests at constant pressure can be derived.

15. Data analysis 4: Fitting the creep compliance curves to equation 2.55 by shifting them on a logarithmic time scale yields the master creep compliance curve, with its fit parameters initial creep compliance $D_0$, transient creep compliance $D_e$, relaxation time $\tau$ and the exponential factor $m$. The permissibility of this non-linear viscoelastic approach is checked by fitting the shift parameters with their theoretical origin (Eq. 2.66). Thereby, the constant linear viscoelastic relaxation time $\tau_0$ and free volume $V^*$ are quantified.
4 Experimental

16. Data analysis 5: The fracture stresses are converted into equivalent stress values to allow for comparison between the bulge test results obtained under complex stress states and uniaxial tensile tests.

17. Data analysis 6: Evaluation of the material’s capability to store mechanical energy.

The chronological order of pressure application and the related measurements is shown in figures 4.2 and 4.3.

Figure 4.2: Chronological order of pressure application for a set of five membranes on the same substrate (wafer). The recovery time between the increasing pressure steps is much longer than shown. Three-fold black bars across zero-load periods indicate the leaps in time. The recurring measurements at each pressure level are exemplarily presented for the first pressure step (indicated by the round-cornered box) in figure 4.3.

4.2 Fabrication

The geometries of the investigated structures are designed to comply with the membrane model, which is capable to describe the expected phenomena and the sought-after parameters.

4.2.1 Fabrication of polymer diaphragms

The concept of microscale polymer layer testing is pursued on wafer-level, with a minimum effort for structuring. Rectangular membranes with different layer thick-
4.2 Fabrication

Figure 4.3: Sequence of the recurring measurements, exemplarily presented at an arbitrary pressure. First, the intrinsic in-plane stress is measured with the resonant vibrometry method. Then, the zero height (membrane height at zero pressure) is determined with the white light interferometer to ensure that the relaxation time was sufficient. Subsequently, pressure is applied and the individual membranes are consecutively measured with the bulge test method. The bulge test measurements are approximately repeated ten to twelve times. Here, only five repetitions are shown due to the confined space.

Figure 4.4: Fabrication steps of the silicon wafer with the membrane openings are the same for all specimens. As substrate, a double side polished SOI-wafer is used. It is supplied with a hard mask on both sides (bilayer of 200nm temperature grown SiO$_2$ and 300nm PECVD Si$_3$N$_4$) from Si-Mat Silicon Materials. The openings for the diaphragms are defined by standard photolithography with the positive photoresist Shipley 1813. The structures are transferred into the hardmask by means of highly anisotropic reactive ion etching. Then, the silicon bulk layer is anisotropically wet etched in potassium hydroxide (KOH) at 80°C until the trenches reach the buried oxide, which serves as etch stop layer. With approximate etch rates of 70µm/h, this step takes 7h20min. Alternatively, this step can be accomplished with the faster dry etching technique in a deep-reactive-ion-etching inductively-coupled-plasma (DRIE-ICP) system. Then, the processing time of this step reduces to 2h30min. However, this noticeably reduces the yield and the silicon edges of the membrane support become imperfect. This approach is used for the fabrication of the SU-8$_{2002}$ samples
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Figure 4.4: The process flow for clamped, fully released membranes consists of seven steps. On top, the basic substrate is shown. It is a double side polished SOI-wafer (Silicon-On-Insulator with 10\(\mu\)m device layer, 1\(\mu\)m SiO\(_2\) layer and 500\(\mu\)m bulk or handle layer), which is covered with a bilayer of 200\(\text{nm}\) temperature grown SiO\(_2\) and 300\(\text{nm}\) PECVD Si\(_3\)N\(_4\) on all sides, serving as hard mask. First, the opening for the diaphragm is defined with standard photolithography on the side of the handle layer [a]. In the second step, this structure is transferred into the hard-mask by means of highly anisotropic, reactive ion etching (RIE) [b]. Then, the silicon handle layer is anisotropically wet etched in potassium hydroxide (KOH) until the trench reaches the buried oxide, which serves as etch stop layer [c]. Alternatively, this step can be done with a highly anisotropic dry etching system. This reduces the processing time of this step drastically but also reduces the yield and produces imperfect silicon edges on the membrane support. The subsequent RIE step opens the SiO\(_2\) layer with minimal undercutting [d]. Subsequently, the SiO\(_2\) – Si\(_3\)N\(_4\) hard-mask is etched from the device layer side [e]. This process step leaves a clean and smooth surface, over which the polymer under investigation is coated [f]. The last dry etching step [g] uses both, anisotropic and isotropic etching to release the diaphragm without fabrication induced damage. Finally, the specimen is ready for testing [h].
4.2 Fabrication

<table>
<thead>
<tr>
<th>Polymeric thin film processing steps</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SU-8100</td>
</tr>
<tr>
<td>Spin coating Spread [rpm; s]</td>
<td>500; 3</td>
</tr>
<tr>
<td>Thinning [rpm; s]</td>
<td>1750; 30</td>
</tr>
<tr>
<td>Soft bake Hotplate [°C; s]</td>
<td>(65; 1200), (95; 3600)</td>
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<tr>
<td>Exposure $\lambda = 365\text{nm , [mJ/cm}^2\text{]}$</td>
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</tr>
<tr>
<td>Postexposure bake Hotplate [°C; s]</td>
<td>(65; 60), (95; 900)</td>
</tr>
<tr>
<td>Development light agitation [s] / solvent</td>
<td>240 / GBL; 390 / PGMEA; 30 / IPA</td>
</tr>
<tr>
<td>Postexposure bake Hotplate [°C; s]</td>
<td>(65; 120), (95; 300)</td>
</tr>
<tr>
<td>Hard bake Hotplate [°C; s]</td>
<td>200; 300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymeric thin film processing steps</th>
<th>GLM2060</th>
<th>GCM3060</th>
<th>PI2737</th>
</tr>
</thead>
<tbody>
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<td>500; 3</td>
<td>500; 3</td>
</tr>
<tr>
<td>Thinning [rpm; s]</td>
<td>5000; 30</td>
<td>4000; 30</td>
<td>5000; 30</td>
</tr>
<tr>
<td>Soft bake Hotplate [°C; s]</td>
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<td>(65; 600), (95; 3600)</td>
<td>90; 300</td>
</tr>
<tr>
<td>Exposure $\lambda = 365\text{nm , [mJ/cm}^2\text{]}$</td>
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<td>600</td>
<td>105</td>
</tr>
<tr>
<td>Postexposure bake Hotplate [°C; s]</td>
<td>(65; 300)</td>
<td>(65; 600)</td>
<td>(55; 180)</td>
</tr>
<tr>
<td>Development light agitation [s] / solvent</td>
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<td>no development</td>
<td>no development</td>
</tr>
<tr>
<td>Postexposure bake Hotplate [°C; s]</td>
<td>(95; 900)</td>
<td>(95; 360)</td>
<td>(200, 1800)</td>
</tr>
<tr>
<td>Hard bake Hotplate [°C; s]</td>
<td>(200, 1800)*</td>
<td>(200, 1800)*</td>
<td>(350, 3600)*</td>
</tr>
</tbody>
</table>

* To ensure full cross linking, the thin film is kept in an oven at 100°C for three days

Table 4.1: Compilation of the main processing steps for the individual polymeric thin films.

only.

The subsequent RIE step opens the $\text{SiO}_2$ layer with minimal undercutting. Finally, all remaining $\text{SiO}_2 - \text{Si}_2\text{N}_4$ on the front and back of the wafer is wet etched with 48% hydrofluoric acid (HF). After the application of the polymeric layer, as described in the subsections below and summarized in table 4.1, the remaining silicon device layer is removed with a two-fold dry etching step in a triode setup with inductively coupled plasma: first, the layer is thinned with an anisotropic process with little physical sputtering ("Bosch" process with accelerated ions). The final opening employs an isotropic dry etching step without physical etching at all. A good thermal connection to the cooled chuck is essential and is achieved with a handle wafer, which is bonded at 70°C in a vacuum oven with $\text{Crystal Bond 555}$, commonly referred to as $\text{white wax}$. This procedure yields diaphragms without fabrication induced damage. Figure 4.5 is a schematic drawing of a single membrane, seen from top.

The subsections below describe the application of the thin polymeric films.

Fabrication of SU-82002 layers

After dehydration (10min at 200°C), the support wafer is exposed to HMDS (adhesion promoter) for 30s. Then, the low-viscosity solution is spin-coated at 500rpm for 3s (spread) and at 2000rpm for 30s (thinning). After a relaxation phase, where the
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Figure 4.5: Top view drawing of a clamped polymer membrane with its lateral dimensions width $l_x$ and length $l_y$.

Figure 4.6: Transversal cross section of a GLM2060 membrane which is $920\mu m$ wide and $5\mu m$ thick. Picture A on the left shows the complete cross section of the diced sample. The bright polygons to the left and right are bulk silicon, the membrane stretches horizontally below. The supporting SOI (silicon on insulator) wafer has a buried silicon dioxide layer with a $10\mu m$ device. The bulk silicon flanks are etched anisotropically with KOH, yielding a perfect trench with side angles of $54.7^\circ$ between the slowest etching $<111>$ surface and the $<100>$ wafer top down to the $SiO_2$ layer. Picture B is the tilted and enlarged left support region, as indicated by the white box in (A). The cut membrane now runs from the middle left to the right bottom. The upper left reveals the different layers of the SOI wafer: bulk silicon layer on top ($500\mu m$), the sandwiched silicon dioxide ($1\mu m$) and the $10\mu m$ silicon device layer. The right part of (B) shows the released membrane with debris from dicing. Most important is the clamping region: due to the improved process using a SOI wafer, the etched silicon is neither receding nor projecting. This minimizes a possible influence of the clamping region as investigated in [49,125]
sample rests covered for 15min on a balanced tray, the polymer layer is soft baked on a hot plate at 65°C and 95°C, for 1min and 2min, respectively. After exposure by standard UV photolithography at a dose of 190mJ/cm², the thin film rests for another 15min. The post and hard bake are done in the same process step: starting at 65°C for 2 min, and then slowly ramping up to 95°C with 3.75°C/min. This temperature is kept for 3min. The following ramp with 2.3°C/min raises the temperature to 200°C. This value is maintained for 5min (square membranes for vibrometry tests), respectively 30 minutes (long rectangular membranes for long term tests). The cool-down step takes approximately 20min. To ensure full cross linking, all membranes for the bulge test are further kept in an oven at 100°C for three days. This processing yields a fully cross linked, ~ 2µm thick layer with minimal height differences (<20nm) measured at thirteen equally distributed positions on the wafer.

**Remark:** The bulk silicon of the SU-82002 membranes is etched with a deep-reactive-ion-etching inductively-coupled-plasma (DRIE-ICP) system. This results in a shorter processing time of 2h30min. However, the yield is considerably lower and the edges of the membranes are imperfect. Thus, this processing step is refined for and all subsequent support wafers, wet etching with KOH is used.

**Fabrication of conductive SU-8 layers**

The processing of conductive SU-8 with the brand name GCM3060 incorporates the suggestions provided by Gersteltec. After dehydration (10min at 200°C), the support wafer is exposed to HMDS (adhesion promoter) for 30s. Then, the high-viscosity solution is spin-coated at 500rpm for 3s (spread) and at 4000rpm for 30s (thinning). After a relaxation phase, where the sample rests covered for 10min on a balanced tray, the layer is soft baked on a hot plate at 65°C and 95°C, for 10min and 60min, respectively. After exposure by standard UV photolithography at a dose of 600mJ/cm², the thin film rests for another 15min. The post and hard bake are done in the same process step: starting at 65°C for 10min, and then slowly ramping up to 95°C with 2.0°C/min. This temperature is kept for 60min. The following ramp with 2.0°C/min raises the temperature to 200°C. This value is maintained for 30 minutes. The cooling-down to room temperature takes approximately 20min. To ensure full cross linking, the samples are further cured in an oven at 100°C for three days. This processing yields a fully cross linked, layer. However, the surface is rough. Measurements of thirteen equally distributed positions on the wafer yield a thickness raging from 7µm – 13µm. A SEM picture of a cross sectional cut (see Fig. 4.7) visualizes the large deviation in thickness and also reveals voids within the layer.
Fabrication of glass filled SU-8 layers

The processing of the glass filled SU-8 with the brand name GLM2060 follows the recipe provided by Gersteltec. After dehydration (10min at 200°C), the support wafer is exposed to HMDS (adhesion promoter) for 30s. Then, the medium-viscosity solution is spin-coated at 500rpm for 3s and at 5000rpm for 30s. After a relaxation phase, where the sample rests covered for 5min on a balanced tray, the layer is soft baked on a hot plate at 65°C and 95°C, for 5min at each temperature. After exposure by standard UV photolithography at a dose of 275mJ/cm², the thin film rests for another 15min. The post and hard bake are done in the same process step: starting at 65°C for 5min, and then slowly ramping up to 95°C with 2.0°C/min. This temperature is kept for 15min. The following ramp with 2.0°C/min raises the temperature to 200°C. This value is maintained for 30 minutes. The cooling-down to room temperature takes approximately 20min. To ensure full cross linking, the samples are further cured in an oven at 100°C for three days. This processing yields a fully cross linked, 5.7µm thick layer with minimal height differences (±12nm, measured at thirteen equally distributed positions on the wafer).

Fabrication of PI2737 layers

The polyimide layers are processed as recommended by the vendor. After dehydration (10min at 200°C), the low-viscosity solution is spin-coated onto the support
4.2 Fabrication

wafer at 500rpm for 5s (spread) and at 5000rpm for 30s (thinning). After a relaxation phase, where the sample rests covered for 10min on a balanced tray, the layer is soft baked on a hot plate at 90°C for 5min. After exposure by standard UV photolithography at a dose of 105mJ/cm², the thin film rests for another 10min. The curing step starts in air at 55°C for 3min, and is then ramped up to 200°C with 4.0°C/min. This temperature is kept for 30min. The following ramp requires nitrogen to avoid chemical degradation. It raises the temperature at a rate of 2.5°C/min to 350°C. This value is kept for 60 minutes. The subsequent cooling-down to room temperature is very slow and takes approximately 5 hours. The samples are further cured in an oven at 100°C for three days. This processing yields a fully cross linked, 865nm thick layer with minimal height differences (±7.7nm). The thickness measurements are taken at thirteen equally distributed positions on the wafer.

4.2.2 Fabrication of tensile test specimen

The tensile test specimens are made of SU-8₁₀₀, a formulation which uses gamma butyrolacton (GBL) as solvent, and yields thick layers. The support wafer is prepared with a 1.5μm thick LOR layer from Microchem. It serves as sacrificial layer for the later lift-off of the SU-8 samples. On top, the high-viscosity solution is spin-coated at 500rpm for 3s and at 1750rpm for 30s. After a relaxation phase, where the sample rests covered for 20min on a balanced tray, the polymer layer is soft baked on a hot plate at 65°C and 95°C, for 20min and 60min, respectively. After exposure by standard UV photolithography at a dose of 510mJ/cm², the thin film rests for another 15min. The post exposure bake is done at 65°C for 1min and at 95°C for 15min on a hotplate. The development is split in three parts: the pre-dip takes 4min in GBL, the development lasts for 5-6min and is done in propylene glycol methyl ether acetate (PGMEA), followed by rinsing for 1min in fresh PGMEA and finally 30sec in isopropyl alcohol. The hard bake starts at 65°C for 2 min, and is then ramped up to 95°C with 3.75°C/min. This temperature is kept for 5min. The following ramp with 2.3°C/min raises the temperature to 200°C. This value is maintained for 5 minutes. The cool-down step takes approximately 20min. The structured tensile test specimens (cf. Fig. 4.8) are released within 30min at room temperature in an acetone bath. This processing yields fully cross linked, ~170μm thick samples with testing areas of about 12mm length and approximately 470μm width.

4.2.3 Summary

Rectangular diaphragm probes for biaxial testing and bone-shaped specimen for uniaxial testing are fabricated. The designs for the diaphragms is chosen in a way to
achieve a homogeneous biaxial stress field over a certain stretch (middle part) of a membrane like structure. This ensures the descriptiveness of the correlation between time dependent stress and strain. One wafer per material and diaphragm geometry is tested successfully. Preliminary tests with round shaped and thicker \( h \geq 15\mu m \) diaphragms did not yield interpretable results due to the inhomogeneous stress fields in the in- and out-of-plane directions.

### 4.3 Bulge test setup

The bulge test allows for non-invasive measurements of the plane strain modulus, the Poisson’s ratio, the intrinsic in-plane stress and strain, the absolute stress, the pressure dependent strain, and fracture strain and stress in linear elastic materials [192]. The parameter extraction from visco-elastic materials permits the quantification of the absolute stress and the pressure dependent strain. For measurements at short time, the glassy plane strain modulus and the initial Poisson’s ratio are extractable from the stress-strain data.

The available setup is self-made and consists of three main parts: the pressure regulation and pressure measurement, the non-invasive, optical measurement of the displacement with a white light interferometer, and the controlling program (see Fig. 4.9).

The wafer with the diaphragms is clamped onto a cylindrical aluminium chamber with a lid. The pressure is applied with dry and filtered air by a digital flow controller (Bronkhorst P-602C) and is measured with an independent high-precision pressure...
4.4 Vibrometer test setup

The resonant frequency measurements are performed by applying a frequency chirp actuation to the specimen and measuring the frequency response with a Laser-Doppler-Vibrometer (Polytec MSA-400). The detected velocity signal is transformed from the time to the frequency domain by Fast Fourier Transformation. A miniature piezo actuator (PI-PL033.31, Dyneos AG) is clamped to the wafer with a lightweight clip. The transmitted signal has a frequency range from zero to 200 kHz. All measurements are performed under high vacuum (\(< 2 \times 10^{-7} \text{bar} = 0.2 \text{Pa}\)) to minimize air damping. Figure 4.11 shows a photograph of the measurement head and the vacuum chamber. A schematic of the measurement setup is illustrated in figure 4.12.

4.5 Tensile test setup

The tensile test setup is thoroughly described by Simons [193]. Recapitulatory, it measures the stress with a precision balance and the strain optically with a high-
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Figure 4.10: Photograph of the bulge test setup with the zygo labeled head and the attached objectives on top and the alumina chamber on the motorized $x - y$-table below. Attached to the chamber, which contains the silicon handle wafer with the polymer diaphragms, are the pressure, temperature and humidity sensors, as well as the tubing for pressure supply and drain.

resolution camera and appendant software. The stress is generated with a vertical translation stage (PI M-126.DG) which is connected to the upper handle site of the specimen. The lower part of the sample is connected to a weight on the balance (Precisa SuperBal 1212M), see figure 4.13). The balance has a weight resolution of 1mg corresponding to $10^{-5}$N. The images are acquired by a Jai CV-M1 CCD camera with a resolution of 6.7$\mu$m square pixels equipped with a Navitar UltraZoom 12X objective and a National Instruments IMAQ PCI-1408 framegrabber. The samples are glued with HBM X60, a two component adhesive. To reduce the influence of external vibrations the whole setup is mounted on an optical table. The whole experiment is computer controlled by LabView. It handles the images and weight values and actively regulates the strain rate.

4.6 Error analysis

The error analysis quantifies the expected random deviations from the mean values as well as systematic errors due to uncertainties and violations of assumptions and boundary conditions. The individual errors of the key values absolute stress, pressure induced strain, intrinsic in-plane stress and intrinsic in-plane strain lead to an overall er-
4.6 Error analysis

Figure 4.11: Photograph of the resonant frequency test. On top the head, mounted on a probe station with the vacuum chamber below.

Figure 4.12: Schematic of the resonant frequency test setup. The diaphragms are mechanically excited with a piezo actuator and are placed inside a vacuum chamber. The Laser Doppler Vibrometer detects the vibration spectra.
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Figure 4.13: Photograph of the uniaxial tensile test setup. The stress in the bone shaped specimen ($B$) is measured with a precision balance ($C$). The strain is quantified optically with a high-resolution camera ($D$) by grey correlation analysis. The strain is generated with a vertical translation stage ($A$) which is connected to the upper handle site of the specimen.
or on the creep compliance. All calculations are carried out conservatively, estimating maximum errors for each error source.

4.6.1 Error analysis of the absolute stress and the pressure induced strain

The measurands absolute stress $\sigma_{xx}$ and pressure induced strain $\epsilon_{xx,p}$ are quantified with the bulge test. Their total error is composed of random and systematic errors, which are both subdivided into instrumental, modeling, measurement, and geometrical errors. All errors of $\sigma_{xx}$ and $\epsilon_{xx,p}$ are compiled in table 4.2 for the reader’s ease.

All systematic instrumental uncertainties, such as hysteresis, drift or temperature dependence are included in the manufacturers’ information on mixed systematic and random measurement error. The systematic errors of the instruments are therefore incorporated in the random instrumental errors.

Systematic modeling uncertainties may arise from violations of model assumptions of the absolute stress and pressure induced strain. The models for the absolute stress $\sigma_{xx}$ and the pressure induced strain $\epsilon_{xx,p}$ assume plane strain conditions and negligible shear stresses within the diaphragm, an infinitely long cylinder or rectangular membrane, and uniformly applied load. The applied theory further assumes small strains. Since the maximum experimental strains lie in the order of a single digit ($<3\%$), this is acceptable. Hence, the neo-Hookean approach with finite strains is not required [17, chapter 3]. The uniformly applied load is inherent to the bulge testing method due to the gas pressure difference at the two sides of the diaphragm.
4.6 Error analysis

Table 4.2: Error sources and values for: a) the absolute stress $\sigma_{xx}$ and b) the pressure induced strain $\varepsilon_{xx,p}$

<table>
<thead>
<tr>
<th></th>
<th>Systematic</th>
<th>Random</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Instrumental</strong></td>
<td>Included in random</td>
<td>Included in random</td>
</tr>
<tr>
<td></td>
<td>instrumental error</td>
<td>measurement error</td>
</tr>
<tr>
<td><strong>Geometrical</strong></td>
<td>–</td>
<td>Included in random</td>
</tr>
<tr>
<td></td>
<td></td>
<td>measurement error</td>
</tr>
<tr>
<td><strong>Measurement</strong></td>
<td>–</td>
<td>a) 0.1 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) 10.2 %</td>
</tr>
<tr>
<td><strong>Modeling</strong></td>
<td>a) ± 4 %</td>
<td>b) ± 4 %</td>
</tr>
</tbody>
</table>

**Maximum relative error**

- Absolute stress: 4.1%
- Pressure induced strain: 14.2%

With Ziebart’s calculations (cf. paragraph 2.3.2), the systematic modeling error due to the neglected stiffness can be quantified. Since this error incorporates both error fractions of absolute stress and pressure induced strain (cf. Eq. 2.12), the quantification can be seen as upper boundary for the isolated view of the uncertainty of each individual model. The conservative evaluation of the systematic modeling error of the pressure $p$ for an infinitely long membrane with high tensile prestress $\sigma_0 = 30\text{MPa}$, Young’s modulus $E = 4.5\text{GPa}$, thickness $h = 2\mu m$ and diaphragm width $a = 1\text{mm}$ accounts to $\sim 3.0\%$. This error decreases with increasing out-of plane deflection, because the tensile intrinsic in-plane stress is further raised (cf. Eq. 2.40), and the influence of the flexural rigidity becomes even less important. This condition is taken into account during the analysis of the measured load-deflection curves. Hence, data of center deflections $w_0(p)$ are taken only if they are at least two times larger than the membrane thickness $h$.

Though the stress is calculated via the model for thin walled pressure vessels, the stress fields within the two structures are not identical due to the different clamping conditions. Thus, the error in transverse stress from finite stiffness is larger for a fully clamped diaphragm than for a cylindrical pressure vessel, with the latter featuring an error of $\leq 0.5\%$ for the above values [194,195].

The requirement of an infinitely long membrane is satisfied for a minimum length-to-width ratio of $R \geq 6$ [71]. It is supported by non-linear elastic finite element simulations with ANSYS of plates with different length-to-width ratios (see Fig. 4.14).

For the illustration of the simulation results, the ratio of the pressure induced stresses in $x$- and $y$-direction, $\sigma_{yy,p}/\sigma_{xx,p}$, is plotted against the length-to-width ratio of the diaphragms. The results show a distinct convergence of the simulated values to the
Figure 4.14: The variation of the ratio between pressure induced longitudinal stress ($\sigma_{yy,p} = \sigma_{yy} - \sigma_0$) and the pressure induced transverse stress ($\sigma_{xx,p} = \sigma_{xx} - \sigma_0$) is simulated with ANSYS. The ratio approximates the assumed lateral contraction ratio (Poisson’s ratio) at a length-to-width ratio of 6. This convergence is required for the description of the investigated structures as infinitely long, plain-strained membranes.

The predicted value of $\sigma_{yy,p}/\sigma_{xx,p} = \nu$ under plain-strain conditions at a length-to-width ratio of $\geq 6$. For $R = 6$, the simulated relative error accounts to 0.9% and for $R = 7$, it reduces to 0.3%. All fabricated membranes used in the bulge test have a length-to-width ratio above 6. Hence, this source of systematic error is conservatively accounted to 1%.

Further, the assumption of plane stress conditions is contradictory to the presumption of constant thickness and the assumption of plain strain. However, the change in thickness through load and creep is a factor 5 below the effective vertical measurement resolution and can be neglected.

**Systematic geometrical uncertainties** may arise through inhomogeneity in thickness or the influence of imperfect clamping sites. The homogeneity of the film thicknesses are sufficient for all polymer layers (roughness$_{rms} < 20$nm) to satisfy the assumptions, except for the conductive SU-8.

The clamping sites may influence the measurement by their mechanical compliance or detrimental shape. Previous research shows a negligible effect of elastic supports of silicon substrates on practical purposes in bulge testing [39, 100]. The influence of imperfect geometry of the clamping support is investigated with finite element mod-
4.6 Error analysis

<table>
<thead>
<tr>
<th>Measurand</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>± (0.1% + 395Pa)</td>
</tr>
<tr>
<td>Vertical displacement (white light interferometer)</td>
<td>&lt;1nm (however, $\Delta h_{film} \approx 20$nm)</td>
</tr>
<tr>
<td>&lt; 150 µm (piezo)</td>
<td>&lt;1nm</td>
</tr>
<tr>
<td>&gt; 150 µm (stepping motor)</td>
<td>±0.75%</td>
</tr>
<tr>
<td>Lateral resolution</td>
<td>±1µm</td>
</tr>
</tbody>
</table>

Table 4.3: Instrumental uncertainties

eling with COMSOL. Projecting silicon edges of the support are found to negatively influence the measurement [125]. Thus, the shape of the clamping sites are inspected after the testing. The good results (cf. Fig. 4.6) negate a potential systematic influence of the geometry.

**Systematic measurement uncertainties** may arise through a permanent mistake by the operator. Since all measurements are controlled and logged by a computer, the direct influence of the operator can be ruled out. An indirect influence could occur through a software bug. The well-developed program runs stable and no systematic software error is known. Hence this error is accounted for as zero.

There are no **random modeling errors**.

The **random instrumental uncertainties** originate from the system inherent errors of the pressure measuring chain, the vertical height measurement and the lateral measurement. These errors are listed in table 4.3.

The vertical resolution of the white light interferometer up to 150µm is theoretically better than 1nm. The lateral extension of the membranes is measured with a light microscope with back side illumination, since all polymers are transparent. The horizontal field of view is 2mm, resolved in 2048 pixels. Hence, the precision is approximately 1µm.

Because every measurement is influenced by random measurement errors as well, the random instrumental errors are incorporated in the paragraph about **random measurement uncertainties**.

The **random geometrical uncertainties** are a consequence of variations in the shape of the membranes. Lateral deviations up to 2µm and vertical deviations up to 20nm are observed for the membranes. However, the latter result does not apply for the conductive SU-8, which shows large thickness deviations. For the calculation of the random error, the random geometrical uncertainties are also added to the random measurement uncertainties, below.

The **random measurement uncertainties** originate from user error and pressure fluctuations during the measurements. Their determination is conducted with eighteen repeated measurements of four membranes for the vertical quantification and with
three membranes with different widths which are measured twenty times each for the lateral uncertainty. Of course, these results include the instrumental errors of pressure and vertical displacement measurement. With the normal parameter set for ordinary measurements, the vertical measurement yields a standard deviation of ±96nm and the lateral dimensioning is afflicted with a standard deviation of ±2.35µm. In conclusion, the total lateral deviation consists of the random instrumental, geometrical and measurement uncertainties, yielding a value of ±4.35µm.

With the quadratic error propagation analysis, the relative random error of the transversal absolute stress can be calculated to be below 0.1% for all deflections above 1µm. The total absolute random error of the pressure induced strain increases steadily with increasing deflection and can be approximated with a Taylor series to be

\[ \Delta \epsilon_{xx,p} \approx 3.64w + 21759 \times (w - 8 \cdot 10^{-5})^2 \]

For the geometries used in this study, the maximum relative random error of the pressure induced strain is 10.2% at the maximum deflection of 80µm. Hence, maximum errors of

\[ \Delta_{rel}(\sigma_{xx}) = 4.1\% \]
\[ \Delta_{rel}(\epsilon_{xx,p}) = 14.2\% \]

can be assigned to the values of absolute stress \(\sigma_{xx}\) and pressure induced strain \(\epsilon_{xx,p}\). These results are incorporated in the error analysis of the material properties below (cf. paragraph 4.6.4).

### 4.6.2 Error analysis of the intrinsic in-plane stress

The intrinsic in-plane stress \(\sigma_0\) is determined with resonant vibrometry measurements. For the error analysis of the calculation of the intrinsic stress in membranes, the measurement errors are divided in three categories: random instrumental errors, random geometric errors and the unknown systematic error from the uncertainty of the density.

Sources of instrumental errors are the Fast Fourier Transformation (FFT) of the signal from the Laser Doppler Vibrometer (LDV) and the resolution limits of the white light interferometer (WLI) or the light microscope for the determination of the geometrical extensions. The FFT uses 12800 FFT-lines over a bandwidth of 400kHz, resulting in an inaccuracy of 31.25 Hz. The random error of the WLI is <1nm in vertical and 2.72µm in lateral direction. The instrumental errors are summarized in table 4.4.

Random geometric and measurement errors derive from variation in thickness and width of the membrane. The thickness is measured with a standard deviation of <0.03µm. The maximum error in lateral dimensions is assessed to be 40µm for
Table 4.4: Combined systematic and random error sources for the vibrometry measurements

<table>
<thead>
<tr>
<th>Measurement equipment</th>
<th>Measured parameter</th>
<th>Error (absolute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polytec OFV-500</td>
<td>Frequency</td>
<td>±31.25Hz</td>
</tr>
<tr>
<td>Zygo WLI</td>
<td>Lateral dimension</td>
<td>±2.72µm</td>
</tr>
<tr>
<td>Zygo WLI</td>
<td>Vertical dimension</td>
<td>±0.1nm</td>
</tr>
</tbody>
</table>

square membranes and 4.35µm for long, rectangular membranes. The higher number for square membranes is a result of the different measurement technique (due to size differences) and imperfect edges. Concerning the measurement of the lateral dimensions of the square membranes, a stitching algorithm has to be used because the specimen’s extensions are larger than the field of view. By doing so, the precision is reduced.

Since direct measurements of the material’s density are not performed, an unknown systematic error from the uncertainty of the density is considered and defined as ±5%. This systematic error influences the measurement of the intrinsic in-plane stress linearly and is added to the total random error.

The absolute error of $\sigma_0$, measured with the vibrometry test, is calculated by adding the total random and systematic errors. The absolute random error is derived with the Gaussian formula for linear error propagation of (cf. section 2.5.2) from equation 2.43, which must be solved for $\sigma_0$. For square membranes, the error ranges from 0.79MPa to 1.34MPa and for long, rectangular membranes, the error lies between 1.64MPa and 1.83MPa ($\Delta_{rel}(\sigma_0) \approx 6.6\%$). These values refer to the first mode, which is used for the determination of the intrinsic in-plane stress.

4.6.3 Error analysis for the plane strain modulus, the intrinsic in-plane strain and the creep compliance

The plain-strain compliance $D_0(1 - \nu^2)$ is derived from the slope of the absolute stress and versus the pressure induced strain, taken at short times. Both measurands are inaccurate due to their estimated errors, hence the fit is subject to these uncertainties as well. As upper boundary, the addition of the total error values is taken:

$$\Delta_{rel} \left(D_0(1 - \nu^2)\right) = \Delta_{rel}(\sigma_{xx}) + \Delta_{rel}(\epsilon_{xx,p}) = 18.3\%$$

Commonly, the Poisson’s ratio is assumed to be an intrinsic material parameter. However, advanced continuum models of glassy polymers [139, 196] which show good agreement with experimental data, predict strain dependence of $\nu$. To account for this, we assume an average initial Poisson’s ratio which is slightly higher than sug-
Table 4.5: Maximum errors of the key parameters, the initial plain-strain creep compliance and the creep compliance

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total relative error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute stress $\sigma_{xx}$</td>
<td>4.1%</td>
</tr>
<tr>
<td>Intrinsic in-plane stress $\sigma_0$</td>
<td>6.6%</td>
</tr>
<tr>
<td>Pressure induced strain $\varepsilon_{xx,p}$</td>
<td>14.2%</td>
</tr>
<tr>
<td>Intrinsic in-plane strain $\varepsilon_0$</td>
<td>19.5%</td>
</tr>
<tr>
<td>Initial plain strain</td>
<td></td>
</tr>
<tr>
<td>creep compliance $D_0(1 - \nu^2)$</td>
<td>18.3%</td>
</tr>
<tr>
<td>Creep compliance $D(t)$</td>
<td>17.7%</td>
</tr>
</tbody>
</table>

gested in literature [55,144,146] and include an expected uncertainty: The change in the lateral contraction ratio (Poisson’s ratio for linear elastic materials) is estimated to be less than 5% [145] for the tested materials within the parameter set of the conducted measurements. Hence, the the fourth key parameter intrinsic in-plane strain $\varepsilon_0$ and its estimated error can be calculated according to equations 2.70 and 2.89, respectively. The total relative error of the intrinsic in-plane strain is estimated to be

$$\Delta_{\text{rel}}(\varepsilon_0) = 19.5\%$$

The creep compliance $D(t)$ is calculated from equation 2.71. Yet, the experimental condition of constant pressure does not yield a constant stress during the measurements (cf. Eq. 2.51) due to the creep induced increase in deflection $w(t)$ with time. The resulting systematic modeling error on $D(t)$ is estimated from the maximal change in stress at the highest stress level, which is approximately 4%, to be $\Delta_{\text{rel, creep}} \leq 5.0\%$. This value is added to the uncertainty, derived from the quadratic error propagation with the relative errors of the absolute stress (4.1%), the pressure induced strain (14.2%), the intrinsic in-plane strain (16.3%) and stress (6.6%), and the lateral contraction ratio (5%), yielding a maximum relative error of 12.7%. Hence, the estimated, relative error of the creep compliance is

$$\Delta_{\text{rel}}(D(t)) = 5\% + 12.7\% = 17.7\%$$

This result reflects the value in the working point of ~80MPa transversal stress. All total errors are listed in table 4.5.

4.6.4 Error analysis for the tensile test

Simons [193] conservatively estimates the maximum relative error in the longitudinal strain measurement of micro-tensile probes to be $\leq 4\%$. In lateral direction, the
4.6 Error analysis

The stress measurement directly relates to the quantification of the specimen’s cross section and the accuracy of the balance ($10^{-5}$N). The transversal dimensions of the beam are determined with the same light microscope as is used to determine the lateral dimensions of the diaphragms. Hence, a standard deviation of $\pm 4.35 \mu m$ is accounted for. With the quadratic error distribution (cf. section 2.5.2) and the fabricated cross-sectional dimensions height $\approx 150 \mu m$ and width $\approx 500 \mu m$, the error is $\leq 6\%$ for all stress levels $\geq 0.3$MPa. Lower stress measurements show a large deviation, but the range of interest stretches from 1MPa to 100MPa, giving results with good accuracy. The ratio of stress-to-strain yields the glassy modulus with a total error of $7.2\%$, derived by quadratic error propagation. The errors of the uniaxial tensile test are displayed in table 4.6.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain $\epsilon$</td>
<td>$\pm 4%$</td>
</tr>
<tr>
<td>Stress $\sigma \geq 0.3$MPa</td>
<td>$\pm 6%$</td>
</tr>
<tr>
<td>Glassy modulus $\sigma / \epsilon$</td>
<td>$\pm 7.2%$</td>
</tr>
</tbody>
</table>

4.6.5 Outlier management

Experimental results become unevaluable if the stated models do not apply any more. This may be case if assumptions are infringed or if an unexpected error occurs in the measurement chain. Reasons for outliers are for example diaphragms which do not behave membrane like, variations in thickness or width over an individual specimen or an inhomogeneous stress field in the investigated area (c.f. paragraph 4.2.3). Further, reflecting or light absorbing dust particles on a specimen, differing measurement points on the probe or an inclination of the specimen holder can lead to varying values.

In the majority of cases, this discrepancy is predictable by preliminary calculations or by optical inspection before testing. However, a certain number of specimen yield outlying results. The discrimination between a large variation and an outlier may be achieved by comparing the individual value of a potential outlier to the median of all data (random distribution of the data points) or to the trend of data and its parameters. If an outlier is determined, subsequent inspection is required in order to track down the reason for the nonconformity and to justify the exclusion of the data point.
4 Experimental

4.6.6 Summary

A comprehensive error analysis is conducted for the proposed new methodology, which employs the bulge and resonant vibrometry tests for the determination of the creep compliance.

The error calculations show the sensitive reaction of the methodology to uncertainties in the lateral dimensions. The expected total error values are mainly based on the difficulties to exactly determine the lateral dimensions. This measurement is influenced by the user (random error), the fabrication (random error) and the measurement technique (systematic and random error). Furthermore, the uncertainties in mass density and Poisson’s ratio add to the absolute error of the creep compliance parameters.

Future efforts should above all concentrate on the improvement of the lateral dimensioning. Beyond, the exact determination of the mass density of the thin films seems promising, rather then the attempt to measure a time dependent lateral contraction ratio in microscaled tests. Also the advanced fabrication technique barely leaves space for advancement.

The significance of further endeavors can be seen from direct comparison of the expected error of the proposed methodology to the reported error values of the uniaxial tensile test. The total error for the glassy modulus $1/D_0$ is more than two times higher.
5 Results and Discussion

This chapter is divided into two parts: first, short term mechanical properties are presented, which are derived from measurements at the shortest time possible. Second, the results of long term mechanical testing are discussed. The data are evaluated with non-linear viscoelastic models, as presented in section 2.4. Finally, the derived results are used to evaluate the ability of the materials under investigation to serve in mechanically active MEMS applications.

5.1 Short term mechanical properties

The polymeric materials are tested in their glassy regime with measurements taken at short times. Hence this sections deals with the viscoelastic properties, quantified for \( t \rightarrow 0 \). Besides initial modulus, intrinsic in-plane stress and fracture strength of all investigated polymers, the initial Poisson’s ratio of SU-8 is measured. The testing methods comprise bulge test, resonant vibrometry and tensile test.

5.1.1 Initial modulus and Poisson’s ratio

The initial (glassy) modulus is measured for \( SU-8_{2002}, GLM2060, GCM3060 \) and \( PI2737 \) with the bulge test. Therefore, short time stress-strain measurements are taken at discrete pressure levels. The slope is equivalent to the glassy plane strain modulus \( E_0/(1-\nu^2) \) and inversely proportional to the glassy plain strain compliance \( D_0(1-\nu^2) \). For the quantification of the glassy plain strain modulus, the very first measurement of each membrane in every creep test is taken (cf. Fig. 5.1). This is the value which is recorded closest to time zero. Between the creep tests, a recovery time of a least two times the loading time is allowed for complete relaxation. Assuming a constant intrinsic in-plane stress, \( E_0/(1-\nu^2) \) is derived from the slope of the graph of the total stress \( \sigma_{xx} \) over the pressure dependent strain \( \epsilon_{xx,p} \) (cf. Fig. 5.2). This approach is chosen for the evaluation of the unfilled \( SU-8_{2002} \). It also yields the intrinsic in-plane stress \( \sigma_0 \) from the intersection of the graph with the ordinate. However, subsequent tests of the time dependency of \( \sigma_0 \) show a distinct relaxation behavior (cf. section 5.1.2). Hence, the testing procedure for the SU-8 composites and the polyimide is improved: Before every creep test, the intrinsic in-plane stress is measured.
5 Results and Discussion

Figure 5.1: Chronological measurement procedure of one membrane: Before each creep test, a resonant vibrometry test (□) determines the actual intrinsic in-plane stress $\sigma_0(t)$ (this is not done for the measurements of SU-8$_{2002}$). The creep compliance tests are then conducted at a constant pressure $p_i$ for a period of time $t_{m,i}$. Approximately ten to twelve bulge test measurements (X) are taken during $t_{m,i}$ on each membrane on the tested wafer (see also figures 4.2 and 4.3). Up to 32 membranes per wafer allow for high throughput measurements of many samples. The measurements are sequential, meaning that all individual membranes are tested consecutively. Hence a total of up to $32 \cdot 12$ data points are taken during a single creep test at pressure $p_i$. Subsequent relaxation periods with times $\leq 2 \cdot t_{m,i}$ allow the specimens to recover their original state. For the evaluation of the short term properties, the very first data point of a membrane during the creep test is taken (bold X).

with the vibrometer. The quantification of the glassy plain strain modulus is then derived from plotting the pressure dependent stress $\sigma_{xx,p} = \sigma_{xx} - \sigma_0$ over the pressure dependent strain $\epsilon_{xx,p}$ (cf. Fig. 5.3). The slope equals $E_0/(1 - \nu^2)$ independently of the prestress. This graph intersects the origin.

Additionally, the glassy modulus of SU-8$_{100}$ is determined with a uniaxial tensile test setup. This measurement serves as reference measurement.

Short term bulge test results - glassy modulus of unfilled SU-8$_{2002}$

The glassy plane strain modulus of 23 SU-8$_{2002}$ membranes is measured. Evaluating all results yields a mean glassy plane strain modulus of $E_0/(1 - \nu^2) = 4.60$GPa (±0.59GPa), see figure 5.4. This measured error is clearly above the estimated maxi-
5.1 Short term mechanical properties

Figure 5.2: Stress-strain interrelations recorded at short times where practically no creep is expected. Assuming constant intrinsic in-plane stress $\sigma_0$, the slope of the total transversal stress $\sigma_{xx}$ vs. the pressure dependent transversal strain $\epsilon_{xx,p}$ equals the glassy plain strain modulus $E_0/(1 - \nu^2)$. Inserting the value of Poisson’s ratio yields the glassy modulus $E_0$. This result must coincide with the inverse initial glassy creep compliance $1/D_0$, which is derived from the master creep compliance curve. The intrinsic in-plane stress is obtained from the intersection of the graph with the ordinate. This approach is chosen for the parametrization of the short term properties of SU-82002.

minimum random error of 10.3%. The reason are outliers, which are incorporated into the evaluation and distort the result. The sample fabrication is exclusively performed with dry etching techniques (cf. chapter 4.2.1). Since the through-wafer-etch with the ICP setup yields inhomogeneous etching rates and poor imaging performance at greater depth, the results at the edge of the wafer are often of minor quality. Actually, all data with doubtful values stem from membranes at the edge of the wafer. Hence, unforeseen random geometrical error increase the deviation from the measured mean value.

If the outliers are excluded, the glassy plane strain modulus of SU-82002 reduces to the coherent result: $E_0/(1 - \nu^2) = 4.30\,\text{GPa}$ ($\pm 0.19\,\text{GPa}$). The number of the evaluated samples decreases to 16. The upper and lower confidence levels for 95% probability are then 4.61GPa and 3.99GPa, respectively. This interval includes the uncertainties from the systematic modeling errors of absolute stress and pressure induced strain (4% each) as well as the deviation from the unconsidered change of $\sigma_0(t)$ (5%). With the quadratic error propagation, the total systematic uncertainty due to the modeling errors is calculated to be 7.46%. It is added to the measured deviation.

With the measured Poisson’s ratio from the uniaxial tensile test $\nu = 0.295$ ($\pm 0.036$)
Figure 5.3: Improved determination of the glassy plain strain modulus. Since the intrinsic in-plane stress relaxes during the total time of experiment, the glassy plane strain modulus $E_0/(1 - \nu^2)$ is derived from the slope of the graph of the pressure dependent stress $\sigma_{xx,p} = \sigma_{xx} - \sigma_0$ over the pressure dependent transversal strain $\epsilon_{xx,p}$. The intrinsic in-plane stress is determined with resonant vibrometry before every creep test. The stress-strain interrelations are recorded at shortest times possible. The graph intersects the origin.

the mean glassy modulus becomes $E_0 = 3.93\,\text{GPa} \, (\pm 0.41\,\text{GPa})$, and its 95% confidence interval stretches from 3.65GPa to 4.21GPa. Again, the systematic errors are considered and the error of the Poisson’s ratio is incorporated. The results are presented in figure 5.5 with the unvalued outliers in brackets.

The glassy modulus coincides with the tensile test results and the inverse initial glassy creep compliance which is derived from the master creep compliance curves (cf. paragraph 5.2.2), i.e. $1/D_0$ approximates $E_0$. This gives strong indication that the stress-strain measurements contain almost no creep induced strain. However, the results are derived under the assumption of constant intrinsic in-plane stress as explained in section 5.1.1. No resonant vibrometry tests are conducted before the individual measurements. Thus, the values of $E_0$ and $\sigma_0$ contain an unknown systematic error. A decreasing intrinsic in-plane stress during the measurements at different load levels will yield a result of the glassy plain strain modulus which is below the real value and the derived value for $\sigma_0$ is higher than in reality. With the uniaxial tensile test as a reference value and the assumption that the results of the test methods are insignificantly different, the induced unknown systematic error on the glassy modulus is estimated to be $\leq 5\%$. 

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5.1 Short term mechanical properties

Figure 5.4: The mean glassy plane strain modulus of 23 measured SU-8<sub>2002</sub> membranes is determined to be $E_0/(1-\nu^2) = 4.60\text{GPa} (\pm 0.59\text{GPa})$. All membranes are situated on one wafer, hence their fabrication and loading history is exactly the same. The upper and lower confidence levels for 95% probability are 5.06GPa and 4.15GPa, respectively. This interval includes the uncertainty from the systematic modeling error and the deviation from the unconsidered change in the intrinsic in-plane stress $\sigma_0$, accounting to 7.46%. It is determined by quadratic error propagation and added to the standard deviation of the measurement. With a measured Poisson’s ratio of $\nu = 0.295$, the mean glassy modulus is $E_0 = 4.20\text{GPa}$. However, outliers clearly distort the evaluation. This observation is supported by the high deviation, which is above the expected maximum random error of 10.3%. It is noticeable that all data with doubtful value stem from membranes at the edge of the wafer, where the etching process often yields results with minor quality. To avoid this influence, the outliers are excluded in a second analysis, which is presented in figure 5.5.
Figure 5.5: Excluding the outliers (in brackets) from the measurement of the glassy plane strain modulus of SU-8\textsubscript{2002} reduces the evaluated samples to 16 but yields a more coherent result: $E_0/(1-\nu^2) = 4.30\text{GPa} \pm 0.19\text{GPa}$. The upper and lower confidence levels for 95% probability are then 4.61\text{GPa} and 3.99\text{GPa}, respectively. This interval includes the uncertainty from the systematic modeling error, accounting to 7.46%. With the measured Poisson’s ratio from the uniaxial tensile test $\nu = 0.295 \pm 0.036$, the mean glassy modulus becomes $E_0 = 3.93\text{GPa} \pm 0.41\text{GPa}$, and its 95% confidence interval stretches from 3.65\text{GPa} to 4.21\text{GPa}. The insert in the upper right shows the positions of the specimens on the support wafer with the excluded samples in brackets.
5.1 Short term mechanical properties

**Short term bulge test results - glassy modulus of GCM3060**

The measured glassy plane strain modulus of GCM3060 (conductive SU-8) is \( \frac{E_0}{(1 - \nu^2)} = 6.27 \, \text{GPa} \, (\pm 0.80 \, \text{GPa}) \). Nineteen samples are tested and the results are displayed in figure 5.6. Though the relative error is comparable to the above result (cf. paragraph 5.1.1), no clearly assignable outliers are responsible for the deviation from the estimated error, but a generally higher deviation, which is attributed to the observed distinct film thickness variations and film inherent voids (cf. paragraph 4.2.1). With the comparatively high uncertainty in height of \( \pm 21.4\% \), the expected random error for the glassy plane strain modulus lies at 22.5\% and exceeds the measured error. Accounting for the influence of the systematic modeling error, the upper and lower confidence levels for 95\% probability are 6.83GPa and 5.71GPa, respectively. With an assumed Poisson’s ratio of \( \nu = 0.3 \, (\pm 0.045) \), the mean glassy modulus is \( E_0 = 5.71 \, \text{GPa} \, (\pm 0.752 \, \text{GPa}) \). Its 95\% confidence interval stretches from 5.19GPa to 6.22GPa. This is significantly above the value of the unfilled version, as expected by the Hashin-Shtrikman composite model (see paragraph 2.4.3), which estimates an interval from 4.74GPa to 8.40GPa, taking the values of the unfilled SU-8\text{2002}. Considering the observed voids, the modulus of the compact material would presumably be higher, being closer to the mean value of the Hashin-Shtrikman interval.

**Short term bulge test results - glassy modulus of GLM2060**

The glassy plane strain modulus of 32 measured samples made of GLM2060 (SU-8 with dispersed silica nanoparticles) averages at \( \frac{E_0}{(1 - \nu^2)} = 4.91 \, \text{GPa} \, (\pm 0.19 \, \text{GPa}) \). This is slightly higher than the value of the unfilled SU-8\text{2002} (cf. Fig. 5.7). Most notably, the good homogeneity of the specimen after fabrication reduces the deviations greatly, so that a trend can be observed in the measured values: the glassy plane strain modulus decreases with increasing time before measurement. The membranes are all located on one wafer and measured sequentially at constant pressure, hence samples with higher numbers experience a longer loading period before being measured. If the viscoelastic response influences the measurement, the expected creep will increase the measured strain with time. This leads to a decreasing measured modulus with time, as it is observed in figure 5.7. The true plane strain modulus is therefore expected to average at \( \sim 5.25 \, \text{GPa} \).

The upper and lower confidence levels for all measured values with 95\% probability are 5.08GPa and 4.74GPa, respectively. With an assumed Poisson’s ratio of \( \nu = 0.3 \, (\pm 0.045) \), the mean glassy modulus is \( E_0 = 4.47 \, \text{GPa} \, (\pm 0.44 \, \text{GPa}) \), and its 95\% confidence interval stretches from 4.30GPa to 4.63GPa. The mean value is significantly above the value of the unfilled version, as expected by the Hashin-Shtrikman com-
5 Results and Discussion

Figure 5.6: The conductive SU-8 composite GCM3060 has a glassy plane strain modulus of $E_0/(1 - \nu^2) = 6.27\, \text{GPa} \, (\pm 0.80\, \text{GPa})$. The upper and lower confidence levels for 95% probability are 6.83GPa and 5.71GPa, respectively. With an assumed Poisson’s ratio of $\nu = 0.3$, the mean glassy modulus is $E_0 = 5.71\, \text{GPa}$. This is well above the value of the unfilled version, as expected by the Hashin-Shtrikman composite model, which gives an interval from 4.74GPa to 8.40GPa. However, considering the observed voids and the uncertainty in the film thickness, samples of the same material without these defects presumably reacted stiffer.

Short term bulge test results - glassy modulus of polyimide PI2737

The glassy plane strain modulus of polyimide PI2737 is determined to be $E_0/(1 - \nu^2) = 8.79\, \text{GPa} \, (\pm 0.93\, \text{GPa})$. Experimental data of 26 membranes are evaluated, which are all situated on one wafer. The relative error coincides with the expected value of 10.3%. The upper and lower confidence levels for 95% probability are 8.38GPa and 9.16GPa, respectively. These values include the systematic modeling error. With a Poisson’s ratio of $\nu = 0.35$ [146], the mean glassy modulus is $E_0 = 7.71\, \text{GPa} \, (\pm 0.93)$. Its 95% confidence interval stretches from 7.36GPa to 8.30GPa. These values are significantly higher than the values of the filled and unfilled versions of SU-8.
5.1 Short term mechanical properties

Figure 5.7: GLM2060, the SU-8 composite with dispersed silica nanoparticles has a glassy plane strain modulus of $E_0 / (1 - \nu^2) = 4.91$GPa ($\pm 0.19$GPa). The upper and lower confidence levels for 95% probability are 5.08GPa and 4.74GPa, respectively. With an assumed Poisson’s ratio of $\nu = 0.3$, the mean glassy modulus is $E_0 = 4.67$GPa. This is above the value of the unfilled version, as expected by the Hashin-Shtrikman composite model, which gives an interval from 4.43GPa to 5.32GPa. However, the 32 measured membranes, plotted in chronological order of measuring, show a distinct decay in the measurement of $E_0$, indicating beginning creep. Hence, the real glassy plain-strain modulus will rather range around 5.25GPa, which is close to the result of the foremost measured membrane.
Figure 5.8: The measured glassy plane strain modulus of polyimide PI2737 is $E_0/(1 - \nu^2) = 8.79\text{GPa}$ ($\pm 0.93\text{GPa}$). The upper and lower confidence levels for 95% probability are 9.16GPa and 8.38GPa, respectively. Experimental data of 26 membranes are evaluated. With an assumed Poisson’s ratio of $\nu = 0.35$, the glassy modulus is $E_0 = 7.71\text{GPa}$ ($\pm 0.93\text{GPa}$).
5.1 Short term mechanical properties

Tensile test results - glassy modulus of SU-8$_{100}$

The uniaxial tensile test is performed with fifteen bone-shaped SU-8$_{100}$ samples (cf. Fig. 5.9). The unfilled epoxy structures are aged at ambient temperature to obtain a material which is close to its structural equilibrium (cf. section 2.4.4). The strain rate is set to $\dot{\varepsilon} = 10^{-4}$s$^{-1}$. Due to the mounting procedure, the probes have a small slack, which delays the material’s response until the probe is under uniform tensile stress. Hence, all curves are individually shifted on the abscissa, so that the first order polynomial fit in the linear region intersects the origin.

The measured mean glassy modulus $E_0 = 3.73$GPa (±0.32GPa) lies 5% below the mean value of SU-8$_{2002}$, determined with the bulge test. This difference is not significant for the chosen certainty. Upper and lower confidence levels for 95% probability are 3.90GPa and 3.55GPa, respectively. The slight difference can be explained by the variations in source materials and the processing procedures. The difficulty of comparing SU-8 with different thicknesses, solvents and processing procedures is reflected in literature: published values of the initial glassy modulus of SU-8 range from 1.54GPa to 4.02GPa [10–16].

The observed deviation from the mean value is higher than expected in the error analysis of the tensile test setup. Potential reasons are uncertainties in the sample mounting, difficulties in determining the real cross sectional area and fabrication inhomogeneities.

Tensile test results - Poisson’s ratio of SU-8$_{100}$

The lateral contraction ratio, commonly referred to as Poisson’s ratio, is determined for unfilled SU-8$_{100}$ with the uniaxial tensile test. Therefore, the lateral and longitudinal changes in extent are measured and linearly fitted, see figure 5.10. The estimated total error of the longitudinal extension is incorporated. The error in lateral direction is known to be larger, but not quantified. With nine evaluated measurements, the Poisson’s ratio is determined to be 0.295 (±0.036). The 95% confidence interval stretches from 0.267 to 0.323.

Summary

The glassy plain strain moduli $E_0/(1 - \nu^2)$ of SU-8$_{2002}$, SU-8$_{100}$, GLM2060, GCM3060 and PI2737 are determined (cf. Tab. 5.1).

While the bulge test method is used to obtain the relationship between total stress and pressure induced strain, the time-variant intrinsic in-plane stress is quantified before each bulge test at one discrete pressure level (except for the first experiments with SU-8$_{2002}$ for which $\sigma_0$ was erroneously assumed to be constant). Furthermore,
5 Results and Discussion

Figure 5.9: Uniaxial tensile test results for bone shaped SU-8\textsubscript{100} samples. The curves are individually shifted along the abscissa to compensate for the initial slack due to the mounting procedure. The slope is fitted within the linear section, yielding a glassy modulus of $E_0 = 3.73\text{GPa (±0.32GPa)}$ at a strain rate of $\dot{\epsilon} = 10^{-4}\text{s}^{-1}$. The upper and lower confidence levels for 95% probability are 3.91GPa and 3.55GPa, respectively. Six stress-strain graphs out of totally fifteen evaluated samples are shown.

the Poisson’s ratio (0.295) and the glassy modulus are determined for SU-8\textsubscript{100} with the uniaxial tensile test.

While the plain strain moduli of SU-8\textsubscript{2002} (4.30GPa) and SU-8\textsubscript{100} (4.09GPa) are insignificantly different, the filled versions GLM2060 (3.3%vol. solid content) and GCM3060 (10.2%vol. solid content) exhibit - as predicted by the Hashin-Shtrikman model - significantly higher results: 5.25GPa and 6.27GPa, respectively. The polyimide PI2737 shows the highest value of 8.79GPa.

5.1.2 Intrinsic in-plane stress and stress gradient

Thin films often exhibit intrinsic in-plane stress, mostly due to the difference in their coefficient of thermal expansion (CTE) and the CTE of the bulk material they are grown on or applied to. The prestress in common metallic or ceramic MEMS thin films (e.g. made from Al, Ag, Au, Ti; SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4}) does not distinctly change over time and the description with linear elastic models is usually justified. This approach
5.1 Short term mechanical properties

Figure 5.10: Uniaxial strains of a tensile test with SU-8\textsubscript{100} in longitudinal and lateral directions versus the applied load. The initial Poisson’s ratio is determined to be 0.295 (±0.036). Nine samples are evaluated. The strain rate of the tests is $\dot{\epsilon}_{xx} = 10^{-4}$.

Table 5.1: Compilation of the glassy plain strain moduli and the Poisson’s ratio of SU-8\textsubscript{100}. The confidence bounds are given in the text.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_0 / (1 - \nu^2)$</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU-8\textsubscript{100}</td>
<td>4.09GPa</td>
<td>0.295</td>
</tr>
<tr>
<td>SU-8\textsubscript{2002}</td>
<td>4.30GPa</td>
<td></td>
</tr>
<tr>
<td>GLM2060</td>
<td>5.25GPa</td>
<td></td>
</tr>
<tr>
<td>GCM3060</td>
<td>6.27GPa</td>
<td></td>
</tr>
<tr>
<td>PI2737</td>
<td>8.79GPa</td>
<td></td>
</tr>
</tbody>
</table>
was transferred to investigate polymeric materials [13, 16, 56]. Hence, the earliest short term experiments reported in this work with SU-8\textsubscript{2002} are also conducted under the assumption of constant prestress (see also paragraph 5.1.1). Its intrinsic in-plane stress is therefore evaluated with bulge test measurements.

However, if the prestress changed its value during the total time of the experiments due to the material’s viscoelastic behavior, the intrinsic in-plane stress would have to be constantly monitored or at least determined before every individual creep test. Fast and accurate access to the intrinsic in-plane stress is available through vibrometry of dynamically actuated membranes, provided that the associated assumptions (cf. paragraph 2.4.5) are valid.

In order to better understand the characteristics of the intrinsic in-plane stress, the influence of time and temperature on eight unstressed (no external load applied at any time), square SU-8\textsubscript{2002} diaphragms is investigated with the resonant vibrometry method.

Due to our observations [144], constant monitoring of the intrinsic in-plane stress with the vibrometry method is preferable. Hence, this approach is used to quantify $\sigma_0$ before every bulge test measurement for all subsequent experiments with rectangular membranes of filled SU-8 and polyimide.

Furthermore, the out-of-plane stress gradient of a structured SU-8 layer is determined with the passive beam bending test.

**Bulge test: Intrinsic in-plane stress of SU-8\textsubscript{2002}**

The intrinsic in-plane stress of SU-8\textsubscript{2002} is measured with the bulge test, see figure 5.11. It is derived from pressure-deflection curves, whose coordinates are recorded individually at short times where practically no creep is expected. This is accomplished by immediate measurement right after the loading step. By means of Eqs. 2.50 and 2.51, the total stress is plotted as a function of the pressure induced strain (see Fig. 5.2). The intrinsic in-plane stress is obtained from the intersection of the curves with the ordinate. After measuring each membrane on the support wafer at one stress, a relaxation time is conceded. Then, the next measurement procedure is started at the next stress level. The evaluated rectangular membranes are tested for creep in the same experimental procedure (cf. Fig. 5.1).

Constant prestress is assumed throughout all experiments with SU-8\textsubscript{2002}. The measured intrinsic in-plane stress accounts to $\sigma_0 = 21.4\text{MPa} (\pm 9.2\%)$. The same sixteen membranes as in figure 5.5 are measured. The intrinsic in-plane strain is found with Eq. 2.70 to be $\epsilon_0 = 0.0038 (\pm 11.6\%)$.

However, as described in paragraph 5.1.1, the intrinsic in-plane stress is rather a function of time $\sigma_0(t)$ due to the viscoelastic characteristics of the material. Hence, an
5.1 Short term mechanical properties

The intrinsic in-plane stress of SU-8\textsubscript{2002} is determined with the bulge test from short term measurements and accounts to $\sigma_0 = 21.4\text{MPa} \ (\pm 9.2\%)$.

unknown systematic error has to be taken into account. The exact value is not accessible, but it can be stated that the given result of $\sigma_0(\text{SU-8}_{2002})$ lies above the real value at all times. Whereas the given value is close to the real intrinsic in-plane stress at the beginning of the experiments, the error increases with time.

**Vibrometry test: Relaxation of the intrinsic in-plane stress in unstressed SU-8\textsubscript{2002} membranes**

In order to investigate the influence of time and temperature on the intrinsic in-plane stress in SU-8\textsubscript{2002} membranes, the progress of $\sigma_0(t)$ is monitored with the resonant vibrometry method over a period of six months (cf. Figs. 5.16 and 5.17). Therefore, square SU-8\textsubscript{2002} membranes with $2.0\mu\text{m}$ thickness are fabricated. They are not subject to bulge tests, hence no differential pressure is applied. The reason for choosing a square geometry lies in the maximum difference between plate (cf. Eq. 2.35) and membrane response (cf. Eq. 2.43), allowing for facilitated analysis of the diaphragm’s behavior (cf. Fig. 5.14).

A typical spectrum of a $4\times4\text{mm}^2$ diaphragm is shown in figure 5.12. The different resonant frequencies can reliably be related to the different Eigenmodes, as theoretically described in paragraphs 2.3.1 and 2.3.2 and measured with visual represen-
Figure 5.12: Example of a typical square 4x4mm$^2$ membrane’s resonant frequency spectrum measured at $1.4 \cdot 10^{-7}$ bar. The resonant peaks can be precisely assigned to the different Eigen-modes by visualization. The initial tensile in-plane stress of this membrane is approximately 23MPa.
5.1 Short term mechanical properties

<table>
<thead>
<tr>
<th>Eigen mode (measured Eigen frequency)</th>
<th>Theory</th>
<th>Measurement (4x4 mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_{11}$ (17.78 kHz)</td>
<td><img src="image1" alt="Visualization" /></td>
<td><img src="image2" alt="Visualization" /></td>
</tr>
<tr>
<td>$W_{22}$ (36.20 kHz)</td>
<td><img src="image3" alt="Visualization" /></td>
<td><img src="image4" alt="Visualization" /></td>
</tr>
<tr>
<td>$W_{33}$ (58.38 kHz)</td>
<td><img src="image5" alt="Visualization" /></td>
<td><img src="image6" alt="Visualization" /></td>
</tr>
</tbody>
</table>

**Figure 5.13:** Visualization of the resonant modes, obtained from theory and measurements at the resonant frequencies $f_{1,1} = 17.78$Hz, $f_{2,2} = 36.20$Hz and $f_{3,3} = 58.38$Hz on a 4x4mm² diaphragm. The intrinsic tensile in-plane stress of this membrane is approximately 18MPa.

Some results of the three dimensional, time resolved measurements of the Eigenmodes at the resonant frequencies are depicted in figure 5.13.

The measured surface shapes agree very well with the expected results from theory. In order to determine the mechanical behavior (applicable model) of the diaphragms, the measured ratios of various ascending frequencies $f_{mn}$ and $f_{11}$ are compared to the theoretical ratios from membrane and plate theory, which are calculated according to equations 2.35 and 2.43. Figure 5.14 illustrates the correlation between measured data of a diaphragm and the theoretical values. The results match the membrane theory, verifying the assumption of negligible flexural rigidity.

As described in the theory chapter (cf. 2.4.5), the quality factor $Q$ is used to quantify the viscoelastic damping of the system. For the experimental derivation of $Q$, a representative resonance curve at frequency $f_{1,1}$ (cf. figure 5.15) is fitted with the amplitude response of a slightly damped spring-damper-mass system driven by an
5 Results and Discussion

![Figure 5.14: Correlation between measurement data and theoretical values of membrane theory (cf. Eq. 2.43) and plate theory (cf. Eq. 2.35). The SU-8_2002 diaphragms match the membrane theory very well.](image)

**Figure 5.14**: Correlation between measurement data and theoretical values of membrane theory (cf. Eq. 2.43) and plate theory (cf. Eq. 2.35). The SU-8_2002 diaphragms match the membrane theory very well.

The measured amplitude, \(B(f)\) is the amplitude of the external vibration, \(d_0\) is the amplitude of the external vibration, \(f_0\) is the natural frequency of the system and \(f\) is the vibration frequency. Through regression, the quality factor is determined to be \(Q = 791\), indicating a slightly damped system. The result indicates a negligible deviation from an undamped system (cf. Eqn. 2.73):

\[
B(f) = \frac{d_0 \left(\frac{f^2}{f_0^2}\right)}{\sqrt{\left(1 - \frac{f^2}{f_0^2}\right)^2 + \left(\frac{f^2}{f_0^2}\right) \cdot \frac{1}{Q^2}}} \quad (5.1)
\]

where \(B(f)\) is the measured amplitude, \(d_0\) is the amplitude of the external vibration, \(f_0\) is the natural frequency of the system and \(f\) is the vibration frequency. Through regression, the quality factor is determined to be \(Q = 791\), indicating a slightly damped system. The result indicates a negligible deviation from an undamped system (cf. Eqn. 2.73):

\[
f_r = f_0 \cdot (1 - 8 \cdot 10^{-7}) \approx f_0
\]

This leads to the conclusion that a linear-elastic membrane model is applicable. Maximum deflections are measured in the range of 600nm to 900nm. Since the ratio of maximum diaphragm deflection to its lateral dimensions is much smaller than 0.01, non-linearities in vibrations at resonance are not expected.

With the validated assumptions, **long term tests of the intrinsic in-plane stress of**
unstressed $SU-8_{2002}$ membranes are conducted. Figure 5.16 presents the characteristic results of two membranes with different thermal history. The measured resonant frequencies are converted into the initial in-plane stress with equation 2.43.

Two sets of four membranes each (two times 4x4mm$^2$ and two times 5x5mm$^2$) are fabricated on one wafer. They are named type A and type B, respectively. The fabrication of the polymeric films is exactly the same, except for the final release: before the last step, the wafer is diced and the two parts are opened individually in the isotropic dry etching step.

On the basis of two representative membranes out of the two batches, the experimental procedure and the measurement results are explained: The type A membrane is measured right after fabrication for the first time. It shows an intrinsic in-plane stress of $\sigma_0 = 18.6$MPa. Subsequently, this membrane is transferred (time $A_1$) into an oven at 100°C, where it remains until time $A_2$. For the individual measurements (which take about one hour), the membranes are quenched from 100°C to room temperature. These measurements yield a relatively constant value around $\sigma_0(A_1..A_2) = 23.3$MPa. From time $A_2$ to $A_3$, the sample is stored at room temperature (27°C) for over four months. A significant drop of the intrinsic in-plane stress to $\sigma_0(A_3) = 20.8$MPa is observed at the end of this period. The behavior indicates a relaxation process. Reheating to 100°C for three days sets $\sigma_0$ back to the rage of the values mea-
5 Results and Discussion

Figure 5.16: Long term test of the intrinsic in-plane stress of two unloaded SU-8_{2002} membranes. The type A membrane is measured right after fabrication for the first time and then shows an intrinsic in-plane stress of $\sigma_0 = 18.6$MPa. Subsequently, this membrane is transferred (time $A_1$) into an oven at 100°C, where it remains until time $A_2$. During this time, the measurements (which are taken at room temperature) yield a relatively constant value around $\sigma_0 = 23.3$MPa. From time $A_2$ to $A_3$, the sample is stored at room temperature (27°C) for over four months. Thereafter, a significant drop of the intrinsic in-plane stress to $\sigma_0 = 20.8$MPa is observed. This behavior indicates a relaxation process. Reheating to 100°C for three days sets $\sigma_0$ back to 23.7MPa, a value close to the observed values of the type A membrane after thermal treatment. The dotted lines are guide to the eye.

The type B membrane is not measured for the first time six days after fabrication, due to problems with the measurement setup. From time $B_1$ to $B_2$, the sample is stored at room temperature. During these six months, the intrinsic in-plane stress steadily decreases from 18.8MPa to 15.6MPa. Subsequent heating to 100°C for three days increases $\sigma_0$ to 24.1Mpa, which is comparable to the observed values of the type A membrane after thermal treatment.

The dotted lines are guide to the eye.
5.1 Short term mechanical properties

measured in the period $A_1 - A_2$.

The Type B membrane is not measured for the first time six days after fabrication, due to problems with the measurement setup. From time $B_1$ to $B_2$, the sample is stored at room temperature. During these six months, the intrinsic in-plane stress steadily decreases from 18.8MPa to 15.6MPa. The relaxation rate after six months is very low, but equilibrium is not observed. Subsequent heating to 100°C for three days increases $\sigma_0$ to 24.1MPa, which is comparable to the observed values of the type A membrane when stored at 100°C.

The observations strongly suggest that the intrinsic in-plane stress is mainly due to the thermal mismatch between the silicon and the applied polymer. Further, the results show that the intrinsic tensile in-plane stress within the polymer is not constant but shows considerable creep at room temperature. Reproducible rejuvenation in the sense of the intrinsic in-plane stress is feasible by quenching the material stack from structural equilibrium at higher temperature to lower temperature, inducing a thermodynamic disequilibrium. The investigated material SU-8 seems to reach structural equilibrium at 100°C within three days, indicated by the recoverability of the pre-stress values after thermal quenching independently of the previous stress level.

Attributing the observed intrinsic in-plane stress right after quenching to the thermal mismatch between the materials only, the in-plane coefficient of the thermal expansion of SU-8 can be approximated linearly by [198]

$$\alpha_{thermal,SU8} = \frac{\sigma_{0,thermal}}{\Delta T} \cdot \frac{1 - \nu}{E_0} + \alpha_{thermal, Si}$$

to be $\alpha_{thermal, SU8} = 59.4$ppm/K with the coefficient of thermal expansion for silicon $\alpha_{thermal, Si} = 2.6$ppm/K [42, page 20] and a temperature difference of $\Delta T = 100^\circ C - 27^\circ C = 73^\circ C$. The glassy modulus $E_0$ and Poisson’s ratio are taken from table 5.1. The result lays between the published values of 52ppm/K [16] and 87.1ppm/K [12]. Figure 5.17 shows the results of all measurements from square membranes with two different sizes (4x4mm$^2$ and 5x5mm$^2$). The characteristic behavior is observed with all samples.

An unexpectedly large deviation of the intrinsic in-plane stresses is seen for the type A membranes, indicating that the larger variant (5x5mm$^2$) of the specimen shows a higher prestress. However, the deviations are statistically insignificant due to the low number of experimental data. Further, inhomogeneities are observed during the dry etching release to which this phenomenon is attributed to. In order to clarify this issue, further experiments are necessary.
Figure 5.17: The intrinsic in-plane stress of eight unloaded square membranes with different side lengths is measured over a period of six months. All stress patterns of the type A and B membranes correspond to the behavior as described in figure 5.16. The influence of time and temperature is apparent.
Vibrometry test: Validation of the assumptions for rectangular polymer membranes

The validation of the assumptions as presented above for square membranes made of SU-8 is also conducted for the long, rectangular membranes made of GLM2060, GCM3060 and PI2737, which are evaluated for mechanical long term behavior. These membranes are measured with the vibrometry method before each individual creep experiment. Representative results are presented in the following.

Figure 5.18 shows a characteristic spectrum of a tensile-prestressed $1\times7\,\text{mm}^2$ membrane, made of GLM2060. As expected from theory, the resonant frequencies are considerably higher than for the $4\times4\,\text{mm}^2$ square membranes.

By means of visualization and theoretical analysis (see figure 5.19), the different peaks can be clearly assigned to their corresponding Eigenmodes. This procedure allows for a firm classification of the diaphragms regarding their descriptiveness with the plate or membrane model. The results show excellent correlation with the membrane model. An exemplary analysis is depicted in figure 5.20.

The quality factor $Q$ of the first resonant frequency is found to be persistently above 1000, indicating negligible material damping and frequency shift at the observed frequencies. An example is shown in figure 5.21, representing the first resonant fre-
5 Results and Discussion

<table>
<thead>
<tr>
<th>Eigen-mode</th>
<th>Theory</th>
<th>Partial view of the measurement (1x7 mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W_{1,1} ) (86.6 kHz)</td>
<td>![Graph]</td>
<td>![Graph]</td>
</tr>
<tr>
<td>( W_{1,2} ) (88.7 kHz)</td>
<td>![Graph]</td>
<td>![Graph]</td>
</tr>
<tr>
<td>( W_{1,5} ) (102.4 kHz)</td>
<td>![Graph]</td>
<td>![Graph]</td>
</tr>
<tr>
<td>( W_{1,10} ) (141.2 kHz)</td>
<td>![Graph]</td>
<td>![Graph]</td>
</tr>
<tr>
<td>( W_{2,2} ) (174.7 kHz)</td>
<td>![Graph]</td>
<td>![Graph]</td>
</tr>
</tbody>
</table>

Figure 5.19: Visualization of the resonant modes, obtained from theory and measurements at the resonant frequencies \( f_{1,1} = 86.6\,\text{kHz} \), \( f_{1,2} = 88.7\,\text{kHz} \), \( f_{1,5} = 102.4\,\text{kHz} \), \( f_{1,10} = 141.2\,\text{kHz} \) and \( f_{2,2} = 174.7\,\text{kHz} \) on a rectangular diaphragm (\( \sim 1\times7\,\text{mm}^2 \)). The measurements only show a section of the effective membrane surface due to the Laser Doppler Vibrometer’s limited field of view.
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Figure 5.20: Correlation between measured resonant frequency ratios and theoretical values of membrane and plate theory. The rectangular diaphragms match the membrane theory very well.

Hence, the linear elastic model for membranes (cf. paragraph 2.3) is applicable for the evaluation of the intrinsic tensile in-plane stress in the long, rectangular diaphragms, used for creep testing.

Vibrometry test: Intrinsic in-plane stress of rectangular membranes made of GCM3060

The intrinsic in-plane stress of conductive SU-8 (GCM3060) is measured with the resonant vibrometry method before every creep test. As shown in figure 5.22, the intrinsic in-plane stress decreases insignificantly during the complete experiment. However, only few bulge and vibrometry tests are made, since the high deviation in fracture strength destroys many samples during the experiment. Hence, the mechanical history shows low loading magnitudes and time, compared to the other materials in this test. The intrinsic in-plane stress ranges between 22.4MPa and 21.9MPa.
Figure 5.21: Experimental derivation of the Q-factor of a rectangular 1x7mm² membrane: the resonance curve (measured at high vacuum) is fitted with equation 5.1, describing a spring-damper-mass system which is driven by an external vibration. The fitted quality factor is $Q = 1373$.

**Vibrometry test: Intrinsic in-plane stress of rectangular membranes made of GLM2060**

The intrinsic tensile in-plane stress of GLM2060 membranes is measured with the resonant vibrometry method over the complete experimental procedure of 42 days. The results are resumed in figure 5.23. A significant drop in the prestress from 33.8MPa to 30.4MPa is observed. This decrease is faster than the reduction of $\sigma_0$ in the experiments with the unstressed SU-82002 samples (see paragraph 5.1.2). This observation is attributed to the applied mechanical load during the creep tests, which acts in the same direction as the relaxation process.

**Vibrometry test: Intrinsic in-plane stress of rectangular membranes made of the polyimide PI2737**

The intrinsic tensile in-plane stress of long, rectangular polyimide (PI2737) membranes is measured with the resonant vibrometry method over a period of 43 days. In parallel, creep tests are performed with the bulge test. Similar to the investigated prestress in GLM2060 membranes, the intrinsic tensile in-plane stress of the polyimide membranes decreases steadily throughout the testing period from 24.0MPa to 19.8MPa. This characteristic is attributed to the expected relaxation process, which is accelerated by the applied mechanical load during the creep tests.
5.1 Short term mechanical properties

Figure 5.22: Development of the intrinsic tensile in-plane stress in rectangular membranes made of GCM3060 during the complete experimental procedure. The measurements are obtained with the resonant vibrometry method. Due to the large deviation of the fracture strength values, only few experiments are conducted. Hence, no meaningful formation can be observed.
Figure 5.23: Long rectangular membranes made of silica filled SU-8 (GLM2060) are observed with the resonant vibrometry method. The evaluated measurand is the intrinsic tensile in-plane stress. During the experimental procedure of 42 days, these tests run in parallel to the creep tests, which exert an increasing mechanical load. A significant drop in the prestress is observed. The fast decrease is attributed to the relaxation behavior as well as the applied mechanical load during the creep tests, both acting in the same direction.
5.1 Short term mechanical properties

Figure 5.24: The intrinsic tensile in-plane stress of long, rectangular polyimide (PI2737) membranes decreases steadily during the experimental period of 43 days. It is measured with the resonant vibrometry method. In parallel, creep tests are performed with the bulge test, exerting mechanical load to the membranes. This relaxation process is presumed to be accelerated by the applied mechanical load during the creep tests.
Beam bending test: Intrinsic out-of-plane stress gradient of SU-8$_{2025}$

The out-of-plane gradient of the intrinsic in-plane stress in a 30.2 µm thick SU-8$_{2025}$ layer is determined with the passive beam bending test. Therefore, the out-of-plane deflection of freestanding beams is measured optically with the white light interferometer. Figure 5.25 shows a section of one test site with released SU-8 beams of different length. The beams bend downwards, revealing the existence of a residual out-of-plane stress gradient. Assuming a linear relationship, the stress gradient within the thin film can be determined by measuring the curvature of single clamped beams [124]. It is calculated from the cantilever tip deflection $\delta$, by using

$$\frac{\Delta \sigma_0}{\Delta h} = \frac{E_0}{1 - \nu} \frac{2}{l^2} \delta$$

where $\Delta \sigma_0 / \Delta h$ is the linear intrinsic out-of-plane stress gradient in the film, $h$ is the film thickness, $E_0$ is the glassy modulus, $\nu$ is Poisson’s ratio (cf. table 5.1) and $l$ is the length of the cantilever beam.

The stress gradient is determined to be -0.154 MPa/µm ($\pm 0.014$ MPa/µm). With $n = 54$ measurements and a confidence level of $1 - \alpha = 0.95$, the true value of the intrinsic stress gradient lies within a range of $\pm 0.004$ MPa/µm around the measured mean value [125].

Though this result detects a violation of the assumption that the stress is evenly distributed throughout the whole structure, the absolute height-dependent difference in the intrinsic in-plane stress remains below the measured error. Hence, the influence on the load response of the SU-8 layers is assumed to be negligible.

Summary

The time dependent intrinsic in-plane stresses of GLM2060, GCM3060 and PI2737 are monitored during the creep experiments with the resonant vibrometry test method on rectangular membranes. The intrinsic in-plane stress of SU-8$_{2002}$ is determined with the bulge test, analogous to the methodology applicable to linear-elastic materials. This approach results in the lack of time dependent information and thus produces an increased systematic error. Furthermore, the gradient of the intrinsic in-plane stress of SU-8$_{2025}$ is determined with the beam bending method and the influence of time and temperature on $\sigma_0$ is studied with fully crosslinked SU-8$_{2002}$ membranes over a period of six months. The latter specimens are exempt from any static external loads.

For the determination of the intrinsic in-plane stress with resonant high frequency tests, the assumptions of membrane and linear elastic material behavior are verified for all diaphragms. Further, the influence of ambient pressure on the measurements
5.1 Short term mechanical properties

Figure 5.25: The out-of plane gradient of the intrinsic in-plane stress of a structured SU-8\textsubscript{2025} layer is determined with the passive beam bending test. This picture shows a section of one test site of released SU-8 beams with different lengths. The beams bend downwards, revealing a residual in-plane stress gradient. Assuming a linear relationship, the stress gradient within the thin film is determined to be \(-0.154\text{MPa}/\mu\text{m} (\pm 0.014\text{MPa}/\mu\text{m})\). With \(n = 54\) measurements and a confidence level of \(1 - \alpha = 0.95\), the true value of the intrinsic stress gradient lies within a range of \(\pm 0.004\text{MPa}\) around the measured mean value.

is investigated. The maximum pressure below which air-damping is negligible for the tested geometries is determined to be 5Pa (0.05mbar).

A considerable viscoelastic relaxation process is monitored at room temperature reducing the intrinsic in-plane stress of the investigated membranes over time. This general behavior is observed for all membranes (except for GCM3060) - with and without external static loadings. The results are summarized in tables 5.2 and 5.3. The individual results are not comparable quantitatively, since the external static loading history differs for every material.

Tempering the externally unstressed membranes for three days at 100\(^\circ\text{C}\) leads to structural equilibrium. Subsequent quenching to room temperature results in a reproducible rejuvenation of the intrinsic in-plane stress. Thus, the experiments indicate that the intrinsic in-plane stress is mainly due to the thermal mismatch between the support (silicon) and the applied polymer. The coefficient of the thermal expansion of SU-8\textsubscript{2002} can be approximated to be \(\alpha_{\text{thermal, SU-8}} = 59.4\text{ppm/K}\).

The out-of plane gradient of the intrinsic in-plane stress accounts to \(\Delta\sigma_0/\Delta h = -0.154\text{MPa}/\mu\text{m}\) in a SU-8\textsubscript{2025} thin film with a thickness of 30.2\(\mu\text{m}\). An out-of plane gradient of this magnitude is not expected to influence the measurement results of the intrinsic in-plane stress.
5 Results and Discussion

Table 5.2: Compilation of the time-dependent intrinsic in-plane stress experiments on externally stressed membranes with the resonant vibrometry method.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_0(t)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLM2060</td>
<td>33.8MPa .. 30.4MPa</td>
</tr>
<tr>
<td>GCM3060</td>
<td>22.4MPa .. 21.9MPa</td>
</tr>
<tr>
<td>PI2737</td>
<td>24.0MPa .. 19.8MPa</td>
</tr>
</tbody>
</table>

Table 5.3: Compilation of the results of the intrinsic in-plane stress experiments on externally unstressed beams and membranes with the beam bending method and the bulge test, respectively. Note that the prestress data for SU-8_{2002} describe the gradient after fabrication without posterior thermal treatment.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_0(t)$</th>
<th>$\Delta\sigma_0/\Delta h$</th>
<th>$\alpha_{\text{thermal},SU-8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU-8_{2002}</td>
<td>18.8MPa .. 15.6MPa</td>
<td>59.4ppm/k</td>
<td></td>
</tr>
<tr>
<td>SU-8_{2025}</td>
<td>-0.154MPa/µm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.1.3 Fracture strength

The fracture strength values of all investigated materials are measured with the bulge test, which exerts a complex, biaxial state of stress. Since complex states of stress are not directly comparable to results obtained by uniaxial stress tests, the applied stresses are converted to an equivalent stress according to the von Mises criterion (cf. paragraph 2.2.6). Due to the brittle nature of the materials at room temperature, the converted results are evaluated by means of Weibull plots, which are described in the theory chapter 2.5.1. As reference test, the fracture strength of SU-8_{100} is determined with the uniaxially tensile test method.

Fracture strength of SU-8_{2002}

The fracture strengths $\sigma_f$ obtained from eighteen biaxially stressed membranes and for comparison from fifteen uniaxially stressed microtensile test samples are evaluated and shown as Weibull plots in figure 5.26. The strain rate of both testing methods is $\sim \dot{\varepsilon} = 10^{-4}s^{-1}$. Due to the brittle fracture behavior of the material, the results are presented in Weibull plots (cf. subsection 2.5.1). The sample size of both tests equals the fractured specimens (tensile test 15/15, all results from specimens on the same wafer; bulge test 18/18, samples from two wafers with exactly the same processing). The stress of the biaxial test is converted into the equivalent, uniaxial stress $\theta_{eq}$ according to the von Mises criterion (cf. Eq. 2.27). The resulting equivalent fracture stresses correspond well to the outcome of uniaxial testing. The approach of convert-
5.1 Short term mechanical properties

The quantified Weibull modulus from biaxial testing is $b_{biaxial} = 10.37$ (9.27, 11.47) and the measured expected fracture strength $t_{biaxial} = 62.9\text{MPa}$ (62.5MPa, 63.3MPa) with the 95% confidence bounds in brackets. The measured Weibull modulus of the uniaxial tensile test is $b_{uniaxial} = 7.65$ (6.14, 9.16) and the expected fracture strength $t_{uniaxial} = 62.3\text{MPa}$ (61.2MPa, 63.4MPa), with the 95% confidence bounds in brackets. Large values of the Weibull modulus $b$ represent good homogeneity of the material and minor geometrical imperfections, that lead to stress peaks. From the statistical point of view, $b$ is a measure for the strength distribution. The biaxially determined Weibull modulus of $b_{biaxial} = 10.37$ indicates a homogeneous material with few geometrical imperfections. Expectedly, the higher degree of variability in shape and side wall dents due to the fabrication with plastic-foil masks reduces the Weibull modulus of the uniaxial tensile test specimens, compared to the unstructured membranes. In this respect, bulge testing is superior to uniaxial tensile testing since specimen production allows for a better result compared to the ideal design on which the theories are based on.

The measured fracture strengths for the uniaxial and biaxial case agree well, under the assumption of applicability of the von Mises’ stress criterion and are comparable to published values [13].

**Fracture strength of GCM3060**

The fracture strength of GCM3060, a conductive, silver particle filled SU-8 is shown as Weibull plot in figure 5.27. All measurements are taken with the biaxial bulge test. Out of the sample size of totally 32 membranes, 15 burst. As above, the complex state of stress at fracture is converted into the equivalent, uniaxial stress $\theta_{eq}$ according to the von Mises criterion (cf. Eq. 2.27). The result for the Weibull modulus is $b = 2.61$ (2.31, 2.92) and the measured expected fracture strength $t = 65.7\text{MPa}$ (62.7MPa, 68.6MPa) with the 95% confidence bounds in brackets.

The low Weibull modulus directly refers to the inhomogeneous material structure (see figure 4.7), which is revealed by voids and an extremely rough surface ranging from $7\mu m – 13\mu m$ (normally, the surface roughness ranges around 20nm). The measured expected fracture strength lies slightly above the unfilled SU-8, as expected from the results of Nakamura [165].
5 Results and Discussion

Figure 5.26: Weibull plots of the fracture strength of SU-8_{2002}, measured with the bulge test method (burst samples: 18/18) and of SU-8_{100}, measured with the uniaxial microtensile tester (fractured samples 15/15). The stress of the biaxial test is converted into the equivalent, uniaxial stress $\theta_{eq}$ according to the von Mises criterion (cf. Eq. 2.27). The resulting stresses correspond well to the outcome of uniaxial testing. The results for biaxial testing are: measured Weibull modulus $b_{biaxial} = 10.37$ (9.267, 11.47) and measured expected fracture strength $t_{biaxial} = 62.9\text{MPa}$ (62.5MPa, 63.3MPa) with the 95% confidence bounds in brackets. The uniaxial tensile test yields: measured Weibull modulus $b_{uniaxial} = 7.65$ (6.14, 9.16) and measured expected fracture strength $t_{uniaxial} = 62.3\text{MPa}$ (61.2MPa, 63.4MPa), again with the 95% confidence bounds in brackets.
Figure 5.27: Weibull plot of the fracture strength of GCM3060, a conductive, silver particle filled SU-8 formulation, measured with the biaxial bulge test (burst samples: 15/32). The stress at fracture is converted into the equivalent, uniaxial stress $\theta_{eq}$ according to the von Mises criterion (cf. Eq. 2.27). The result for the Weibull modulus is $b = 2.61$ (2.31, 2.92) and the measured expected fracture strength $t = 65.7$MPa (62.7MPa, 68.6MPa) with the 95% confidence bounds in brackets.
5 Results and Discussion

Fracture strength of GLM2060

The strength of \textit{GLM2060} (silica particle filled SU-8) is presented as Weibull plot in figure 5.28. Again, the biaxial bulge test is employed for the measurements. Twenty out of totally 32 membranes were destroyed while testing. The stress at fracture is converted into the equivalent, uniaxial stress $\theta_{eq}$ according to the von Mises criterion (cf. Eq. 2.27). The result for the Weibull modulus is $b = 8.81$ (8.07, 9.56) and the measured expected fracture strength $t = 80.1\text{MPa}$ (79.5\text{MPa}, 80.7\text{MPa}) with the 95\% confidence bounds in brackets.

The Weibull modulus of $b = 8.81$ reflects the homogeneous material with few imperfections. The peak-to-peak surface roughness lies below 25nm, no defects are observable by light and interference microscopy. As expected, the measured expected fracture strength lies considerably above the unfilled SU-8 (cf. Nakamura et al. [165] and paragraph 2.4.3).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_28.png}
\caption{Weibull plot of the fracture strength of GLM2060, measured with the biaxial bulge test (burst samples: 20/32). The stress at fracture is converted into the equivalent, uniaxial stress $\theta_{eq}$ according to the von Mises criterion (cf. Eq. 2.27). The result for the Weibull modulus is $b = 8.81$ (8.07, 9.56) and the measured expected fracture strength $t = 80.1\text{MPa}$ (79.5\text{MPa}, 80.7\text{MPa}) with the 95\% confidence bounds in brackets.}
\end{figure}
5.1 Short term mechanical properties

Fracture strength of the polyimide PI2737

In figure 5.29, the fracture strength of the photostructurable polyimide PI2737 is shown as Weibull plot. The data are obtained with the biaxial bulge test. Twenty membranes out of totally 30 failed. The stress at fracture is converted into the equivalent, uniaxial stress $\sigma_{eq}$ according to the von Mises criterion (cf. Eq. 2.27). The result for the Weibull modulus is $b = 4.10$ (3.53, 4.67) and the measured expected fracture strength is $t = 100.1\text{MPa}$ (97.8MPa, 102.4MPa) with the 95% confidence bounds in brackets. The relatively low Weibull modulus is not expected. No suitable explanation could be found. However, the data stem from one wafer only. In order to investigate this in detail, more specimen would have to be produced and evaluated. The measured expected fracture strength of $t = 100.1\text{MPa}$ ranges above the values of filled and unfilled SU-8.

![Figure 5.29: Weibull plot of the fracture strength of photostructurable polyimide (PI2737), measured with the biaxial bulge test (burst samples: 20/32). The stress at fracture is converted into the equivalent, uniaxial stress $\sigma_{eq}$ according to the von Mises criterion (cf. Eq. 2.27). The result for the Weibull modulus is $b = 4.10$ (3.53, 4.67) and the measured expected fracture strength $t = 100.1\text{MPa}$ (97.8MPa, 102.4MPa) with the 95% confidence bounds in brackets.](image)
Summary

The fracture strengths of SU-8\textsubscript{2002}, GLM2060, GCM3060 and PI2737 are experimentally derived with the bulge test method. As reference, SU-8\textsubscript{100} is tested with an uniaxial tensile test setup. The complex state of stress of the bulge test method is converted by means of the von Mises criterion into an equivalent, uniaxial stress (cf. Eq. 2.27). All results are evaluated with Weibull statistics. The converted fracture strength values from biaxial testing of SU-8\textsubscript{2002} are in good agreement with the uniaxial, direct measurement results of the SU-8\textsubscript{100}, indicating the applicability of the von Mises model. The strengths of both SU-8 formulations are expected to be equal. The polyimide shows the highest fracture strength, however the value is far below the specification of the supplier (∼170MPa), measured with macroscopic samples. Both filled SU-8 formulations have higher fracture strength values than the unfilled versions. The silver filled resin GCM3060 though does not show a significantly higher value and the measurements vary strongly. This is assigned to the observed inhomogeneities of the silver particle dispersion and voids within the thin film layer.

All results, except for the confidence bounds which are found in the individual paragraphs, are summarized in table 5.4.

<table>
<thead>
<tr>
<th>Material</th>
<th>Expected fracture strength [MPa]</th>
<th>Weibull modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU-8\textsubscript{100}</td>
<td>62.3</td>
<td>7.65</td>
</tr>
<tr>
<td>SU-8\textsubscript{2002}</td>
<td>62.9</td>
<td>10.37</td>
</tr>
<tr>
<td>GCM3060</td>
<td>65.7</td>
<td>2.61</td>
</tr>
<tr>
<td>GLM2060</td>
<td>80.1</td>
<td>8.81</td>
</tr>
<tr>
<td>PI2737</td>
<td>100.1</td>
<td>4.10</td>
</tr>
</tbody>
</table>

5.2 Long term mechanical properties

The long term viscoelastic mechanical properties for times \( t > 0 \) are measured with the bulge test method in combination with the resonant frequency method. All hitherto investigated materials are subject to creep compliance studies, where defined constant pressure levels are applied for several hours and the strain response is observed. With the time-stress superposition principle (cf. paragraph 2.4.2), the creep compli-
5.2 Long term mechanical properties

Curves at different stress (pressure) levels of thermorheologically simple, nonlinear viscoelastic materials can be individually shifted in time to construct a master curve with respect to a certain (the lowest) reference stress. The results allow for long term extrapolations (> one year) of the creep compliance. Such master creep compliance curves are obtained from the results for unfilled SU-82002, GLM2060 (SU-8 filled with silica nanoparticles) and the polyimide PI2737. The experiments with GCM3060 (silver filled SU-8) however do not yield interpretable results with the applied methodology.

First, the assumptions of the creep compliance model are verified and discussed. Subsequently, the resulting master creep compliance curves are presented.

5.2.1 Creep compliance

The creep compliance is measured for SU-82002, GLM2060, GCM3060 and the polyimide PI2737. The bulge test is used to determine the time dependent, pressure induced strain and the total stress. The resonant vibrometry method yields the intrinsic in-plane stress (which is convertible into the intrinsic in-plane strain with the glassy modulus and Poisson’s ratio) before every creep test. In the following, the assumptions for the determination of the creep compliance are investigated.

The requirement of infinitely long membranes is validated by the resonant vibrometry measurements (see paragraph 5.1.2) and is further supported by the evaluation of a SU-82002 membrane’s transverse cross section, taken at the relatively low pressure of \( p = 9.6 \text{kPa} \). Its shape coincides with the sector of a circle (see Fig. 5.30) as assumed for membrane behavior [89, page 156].

Before every creep experiment, the height-level in the center of all membranes is measured at zero pressure to verify the complete strain relaxation from the previous creep test. Figure 5.31 shows a characteristic result. The start height fluctuates around the zero position within the limits of the measurement error and the thickness uncertainty. A significant residual strain cannot be observed during the experiment.

Furthermore, the lateral contraction ratio \( \nu \) (Poisson’s ratio) is assumed to be constant. This seems acceptable since measurements on similar materials as used in this work show a relatively slow increase of \( \nu(t) \) within comparable measurement times and strains [145, 146, 164]. The resulting systematic error is therefore assumed to remain \( \leq 5\% \) and is considered in the error analysis of the stated results.

Thus, all pressure and deflection measurements can be converted into stress and strain values by means of equations 2.50 and 2.51, which describe the absolute stress (including intrinsic in-plane stress) and the pressure induced strain in infinitely long rectangular membranes, respectively. Together with the knowledge of the intrinsic in-plane strain, creep compliance curves can be compiled. A characteristic result of
5 Results and Discussion

Figure 5.30: Comparison of a transverse height profile measurement in the center of a long rectangular membrane at a pressure of $p = 9.6\,kPa$ (circles) and the results of the analytical model of a circular section with the same chord as the membrane’s width and the same radius. As can be seen, the correlation is already high at low pressure, giving strong indication that the bending stiffness of the diaphragm is negligible.

Figure 5.31: No significant drift in the zero level at the beginning of the individual creep experiments can be observed during 15 creep compliance measurements. The deviation of the zero levels is in the range of the vertical resolution limit.
various creep compliance curves is shown in figure 5.36.

5.2.2 Master creep compliance curves

Master creep compliance curves are determined for SU-82002, GLM2060 and for PI2737. The construction of a master curve requires creep compliance curves at different stress levels. These compliance curves are shifted on a logarithmic time scale to construct the master creep compliance curve (cf. Fig. 2.12), except for the data recorded at the lowest stress level. These are chosen as reference to which the shifted curves refer to. The derived master creep compliance curve is numerically fitted by Eq. 2.55 to determine the creep parameters at the equivalent stress $\theta_{eq}$ of the reference curve.

Master creep compliance curve of SU-82002

Different pressure levels from 6kPa to 81.2kPa are applied for ten hours each, yielding time dependant deflections $w_0(t)$ of the membrane center. A maximum increase of the center deflection of 2.5µm due to creep can be observed at the highest applied constant pressure of 81.2kPa. The resulting transversal strains $\epsilon_{xx}(t)$ remain below 0.02 and the transversal stresses $\sigma_{xx}$ below 66MPa.

Short term creep compliance curves are established for all membranes by plotting the ratio of strain-to-stress (cf. Eq. 2.71) over time. An example for a single membrane is shown in figure 5.32.

The constructed experimental master creep compliance curves at an averaged equivalent reference stress $\theta_{ref,eq} = 13.2\text{MPa} (\pm 9.3\%)$ can be fitted satisfactorily with Eq. 2.55, yielding an initial creep compliance $D_0$ of 0.251 GPa$^{-1}$ (±13.8%), and a transient component $D_e$ of 0.310 GPa$^{-1}$ (±2.5%). The relaxation time constant $\tau$ is found to be $1.84 \cdot 10^{10}$s (±3.5%) and the exponential parameter $m$ amounts to 0.208 (±5.3%). An example of a master creep compliance curves for the SU-82002 membranes is shown in figure 5.33. Width variations of the membranes lead to an increase in the deviations of the reference stresses at constant pressure. Consequently, the obtained initial compliance $D_0$ shows a greater deviation than the other parameters, whose deviations approach the expected random error. The overall results suggest low creep of fully cured, glassy SU-82002 (< 10% at $t = 10^{10}$s for an equivalent stress of 13.2MPa) with respect to semi-crystalline polymers. Examples for semi-crystalline polymers are isotactic polypropylene (iPP), poly[ethylene terephthalate] (PET), polyamide (PA), isotactic polystyrene (iPS), and poly[ether ether ketone] (PEEK).

The shift factors log $[a(\theta_{eq})]$ are plotted in Fig. 5.34 against the equivalent stress. They can be satisfactorily fitted by Eq. 2.66, yielding a non-linearity parameter $s_0 =
5 Results and Discussion

Figure 5.32: Creep compliance curves of a single, long rectangular membrane made of SU-8_{2002}. The ascending curves refer to increasing pressure (stress) levels. The lowest individual creep compliance curve refers to the reference stress \( \theta_{eq,ref} = 14.7 \text{MPa} \). The legend shows the equivalent stress levels for this specific membrane. Since the data reflect the results of an individual membrane, they differ slightly to the average values.

Figure 5.33: Master creep compliance curve of a single rectangular SU-8_{2002} membrane at the reference stress \( \theta_{eq,ref} = 14.7 \text{MPa} \), constructed by shifting the individual logarithmic time axis by \(- \log[a(\theta_{eq})]\). All measurements, except the reference data at the lowest equivalent stress \( \theta_{eq,ref} \) are shifted on the logarithmic time-scale.
0.45MPa, above which SU-8\textsubscript{2002} behaves in a non-linear viscoelastic way. The measurement results are summarized in table 5.5.

![Logarithm of the shift factors (symbols) of a single SU-8\textsubscript{2002} membrane with respect to $\theta_{eq,ref} = 14.7$MPa as a function of the equivalent stress and their fit (dashed line, cf. Eq. 2.66). The shift factors can be described by the Eyring theory of stress activated plastic flow and yield a non-linearity parameter $s_0 = 0.45$MPa, above which SU-8\textsubscript{2002} behaves in a non-linear viscoelastic way.](image.png)

**Figure 5.34:** Logarithm of the shift factors (symbols) of a single SU-8\textsubscript{2002} membrane with respect to $\theta_{eq,ref} = 14.7$MPa as a function of the equivalent stress and their fit (dashed line, cf. Eq. 2.66). The shift factors can be described by the Eyring theory of stress activated plastic flow and yield a non-linearity parameter $s_0 = 0.45$MPa, above which SU-8\textsubscript{2002} behaves in a non-linear viscoelastic way.

**Remark**
The given values deviate from our published findings in [144] although the data base (measurements) is the same. The reason is a systematic modeling error in the application of equation (1) in the paper. While the equation correctly describes the general model of viscoelastic behavior (cf. Eq. 2.55 in the theory chapter), the ratio

$$\frac{\epsilon(t)}{\sigma_{const}}$$

must transform into

$$\frac{\epsilon_{xx}}{\sigma_{xx}(1 - \nu^2) + \sigma_0(\nu^2 - \nu)}$$

in order to consider the biaxial state of stress in an infinitely long membrane. This conversion was not executed in the data evaluation of the paper. The resulting systematic error for a material with $\nu = 0.295$ and $\sigma_0 = 21.4$MPa decreases from $\sim 30\%$ at zero external load to $\sim 15\%$ at 80MPa ($\geq$ fracture strength) as depicted in figure
5 Results and Discussion

<table>
<thead>
<tr>
<th>Table 5.5: Compilation of the most important, averaged results of SU-82002</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Measurand / Parameter</strong></td>
</tr>
<tr>
<td>Membranes tested</td>
</tr>
<tr>
<td>Initial creep compliance $D_0$</td>
</tr>
<tr>
<td>Transient creep compliance $D_e$</td>
</tr>
<tr>
<td>Time constant $\tau$</td>
</tr>
<tr>
<td>Coupling parameter $m$</td>
</tr>
<tr>
<td>Non-linearity parameter $s_0$</td>
</tr>
<tr>
<td>Equivalent reference stress $\bar{\theta}_{eq,ref}$</td>
</tr>
<tr>
<td>Fracture strength $\sigma_{f,eq}$</td>
</tr>
<tr>
<td>Membrane widths</td>
</tr>
<tr>
<td>Membrane thickness</td>
</tr>
<tr>
<td>Intrinsic in-plane strain $\epsilon_0$</td>
</tr>
<tr>
<td>Intrinsic in-plane stress $\sigma_0$</td>
</tr>
</tbody>
</table>

5.35. This led to underestimated values of the creep compliance and the intrinsic in-plane strain in the publication.

However, the (unjustified) assumption of a constant intrinsic in-plane stress ($\sigma_0$) results in a reduced combined systematic error since $\sigma_0$ decreases with time and the given value of 21.4MPa constitutes an upper boundary.

Master creep compliance curve of GLM2060

Short term creep compliance curves are established for 32 GLM2060 membranes by plotting the ratio of strain-to-stress (cf. Eq. 2.71) over time, see figure 5.36.

Therefore, different pressure levels from 10kPa to 161kPa are applied for six hours each, yielding time dependant deflections $w(t)$ of the membrane center. A maximum increase of the center deflection of 0.94μm due to creep can be observed at the highest applied constant pressure. The resulting transversal strains $\epsilon(t)$ remain below 0.01 and the maximum transversal stress is 69MPa.

The constructed experimental master creep compliance curves at an averaged equivalent reference stress $\theta_{eq,ref} = 21.5$MPa (±7.6%) can be fitted satisfactorily with Eq. 2.55, yielding an initial creep compliance $D_0 = 0.199$GPa$^{-1}$ (±2.7%), and a transient component $D_e = 0.234$GPa$^{-1}$ (±3.44%). The relaxation time constant $\tau$ is found to be $1.86 \cdot 10^{10}$s (±5.0%) and the exponential parameter $m$ amounts to 0.160 (±5.6%). An improved fabrication process and the permanent monitoring of the intrinsic tensile in-plane stress reduce the deviation of the initial compliance $D_0$. The overall results
5.2 Long term mechanical properties

Figure 5.35: Considering the biaxial state of stress in the specimen leads to the given properties in table 5.5. These findings deviate from our statements published in [144] because an uniaxial state of stress was modeled in the paper. The systematic modeling error decreases from approximately 30% at zero pressure induced stress ($\sigma_{xx} = \sigma_0$) to $\sim$ 15% at 80MPa.

Figure 5.36: Creep compliance curves of a single, long rectangular membranes made of GLM2060 (silica filled SU-8). The individual, ascending curves refer to increasing pressure (stress) levels.
are comparable to the unfilled SU-8, except for the lower compliance values, which is due to the filler. Again, comparatively low creep of fully cured, glassy GLM2060 is suggested by the measurement data: $< 10\%$ at $t = 10^{10}$ s although the averaged equivalent stress of 21.5 MPa is higher than the averaged equivalent reference stress of the unfilled SU-8.

The shift factors $\log [a(\theta_{eq})]$ are plotted in Fig. 5.38 against the equivalent stress. They can be satisfactorily fitted by Eq. 2.66, yielding a non-linearity parameter $s_0 = 0.58$ MPa, above which GLM2060 behaves in a non-linear viscoelastic way. According to Ngai [151], the low value of the coupling parameter indicates a low molecular mobility, which is proportional to the crosslinking density of the polymer. This observation is supported by the information on the high functionality of SU-8.

The measurement results of silica particle filled SU-8 (GLM2060 from Gersteltec) are summarized in table 5.6.

**Master creep compliance curve of PI2737**

Short term creep compliance curves of the polyimide PI2737 are established by plotting the ratio of strain-to-stress (cf. Eq. 2.71) over time. An example is shown in figure 5.39.

Ascending pressure levels from 1.5 kPa to 13.1 kPa are applied for five hours each, yielding time dependant deflections $w(t)$ of the membrane center. A maximum increase of the center deflection of 1.3 $\mu$m due to creep can be observed at the highest
5.2 Long term mechanical properties

Figure 5.38: Logarithm of the shift factors (symbols) of GLM2060 with respect to $\theta_{eq,ref} = 22.1 \text{MPa}$ as a function of the equivalent stress and their fit (dashed line, cf. Eq. 2.66). The shift factors can be described by the Eyring theory of stress activated plastic flow and yield a non-linearity parameter $s_0 = 0.58 \text{MPa}$, above which GLM2060 behaves in a non-linear viscoelastic way.

applied constant pressure. The resulting strains $\epsilon(t)$ remain below 0.01 and the maximum stress is 59MPa.

The constructed experimental master creep compliance curves (cf. Fig. 5.40) at an averaged equivalent reference stress $\bar{\theta}_{eq,ref} = 13.8 \text{MPa (±11.1%)}$ can be fitted satisfactorily with Eq. 2.55, yielding an initial creep compliance $D_0$ of $0.110 \text{GPa}^{-1}$ (±6.7%), and a transient component $D_e$ of $0.187 \text{GPa}^{-1}$ (±22%). The relaxation time constant $\tau$ is found to be $1.01 \cdot 10^{10} \text{s (±2.1%)}$ and the exponential parameter $m$ amounts to 0.34 (±11.5%). Though the compliance values are distinctively lower than for SU-8 formulations, the change over time is higher. The larger creep rate indicates higher losses of stored mechanical energy (cf. Eq. 2.80).

The deviation of the transient creep compliance $D_e$ is high, because the creep induced strains and stresses are relatively low. Thus, the experimental data do not cover the master creep compliance curve as wide as for the tested SU-8 polymers. Expectedly, the uncertainty in the extrapolated region increases.

The shift factors log $[a(\theta_{eq})]$ are plotted in Fig. 5.41 against the equivalent stress. They can be satisfactorily fitted by Eq. 2.66, yielding a non-linearity parameter $s_0 = 0.67 \text{MPa}$,
## Results and Discussion

### Table 5.6: Compilation of the most important, averaged results of GLM2060

<table>
<thead>
<tr>
<th>Measurand / Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membranes tested</td>
<td>32</td>
</tr>
<tr>
<td>Initial creep compliance $D_0$</td>
<td>$0.199\text{GPa}^{-1}$ (±2.7%)</td>
</tr>
<tr>
<td>Transient creep compliance $D_e$</td>
<td>$0.234\text{GPa}^{-1}$ (±3.4%)</td>
</tr>
<tr>
<td>Time constant $\tau$</td>
<td>$1.86 \cdot 10^{10}\text{s}$ (±5.0%)</td>
</tr>
<tr>
<td>Coupling parameter $m$</td>
<td>0.16 (±5.6%)</td>
</tr>
<tr>
<td>Non-linearity parameter $s_0$</td>
<td>0.58\text{MPa}</td>
</tr>
<tr>
<td>Equivalent reference stress $\bar{\theta}_{eq,\text{ref}}$</td>
<td>21.5\text{MPa} (±7.6%)</td>
</tr>
<tr>
<td>Fracture strength $\sigma_{f,eq}$</td>
<td>80.1\text{MPa} (cf. 5.1.3)</td>
</tr>
<tr>
<td>Membrane widths</td>
<td>$908\mu m - 974\mu m$ (±4.35\mu m)</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>5.73\mu m (±0.2%)</td>
</tr>
<tr>
<td>Intrinsic in-plane strain $\epsilon_0$</td>
<td>0.0054..0.0048 (cf. 5.1.2)</td>
</tr>
<tr>
<td>Intrinsic in-plane stress $\sigma_0$</td>
<td>33.8MPa..30.4MPa (cf. 5.1.2)</td>
</tr>
</tbody>
</table>

above which $PI2737$ behaves in a non-linear viscoelastic way.

The measurement results of the polyimide $PI2737$ are summarized in table 5.7.

### Table 5.7: Compilation of the most important, averaged results of the polyimide $PI2737$

<table>
<thead>
<tr>
<th>Measurand / Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membranes tested</td>
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</tr>
<tr>
<td>Initial creep compliance $D_0$</td>
<td>$0.110\text{GPa}^{-1}$ (±6.7%)</td>
</tr>
<tr>
<td>Transient creep compliance $D_e$</td>
<td>$0.187\text{GPa}^{-1}$ (±22%)</td>
</tr>
<tr>
<td>Time constant $\tau$</td>
<td>$1.01 \cdot 10^{10}\text{s}$ (±2.1%)</td>
</tr>
<tr>
<td>Coupling parameter $m$</td>
<td>0.34 (±11.5%)</td>
</tr>
<tr>
<td>Non-linearity parameter $s_0$</td>
<td>0.67\text{MPa}</td>
</tr>
<tr>
<td>Equivalent reference stress $\bar{\theta}_{eq,\text{ref}}$</td>
<td>13.8\text{MPa} (±11.1%)</td>
</tr>
<tr>
<td>Fracture strength $\sigma_{f,eq}$</td>
<td>100.1\text{MPa} (cf. 5.1.3)</td>
</tr>
<tr>
<td>Membrane widths</td>
<td>$910\mu m - 944\mu m$ (±4.35\mu m)</td>
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<tr>
<td>Membrane thickness</td>
<td>865\text{nm} (±0.9%)</td>
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<tr>
<td>Intrinsic in-plane strain $\epsilon_0$</td>
<td>0.0020..0.0019 (cf. 5.1.2)</td>
</tr>
<tr>
<td>Intrinsic in-plane stress $\sigma_0$</td>
<td>23.3\text{MPa}..21.6\text{MPa} (cf. 5.1.2)</td>
</tr>
</tbody>
</table>

### Summary

Creep compliance curves at different stress levels are recorded with the bulge testing and resonant frequency method for $SU-8_{2002}$, $GLM2060$ and $PI2737$. The measure-
5.2 Long term mechanical properties

Figure 5.39: Creep compliance curves of a single, long rectangular membrane made of PI2737. The ascending curves refer to increasing pressure (stress) levels. The lowest individual creep compliance curve refers to the reference stress $\theta_{eq,ref} = 14.3\text{MPa}$. The statement methodology proves to be capable to quantify the desired parameters. According to Eyring’s theory (stress-time superposition), master creep compliance curves can be established for the mentioned polymers by shifting the individual creep compliance curves on a logarithmic time scale. A compilation of all constructed master creep compliance curves is plotted in figure 5.42. The comparison shows the related SU-8 formulations $SU-82002$ and $GLM2060$ on top and in the middle, respectively. The result of the polyimide $PI2737$ is situated below. $PI2737$ shows the highest absolute and relative change in its creep compliance curve $(\Delta(D)_{abs} = 0.077\text{GPa}^{-1}, \Delta(D)_{rel} = 70\%)$ and the lowest initial and transient compliance values $(D_0 = 0.110\text{GPa}^{-1}, D_e = 0.187\text{GPa}^{-1})$. The lowest time constant and the highest coupling parameter value in the test field render the polyimide as the polymer with the highest creep rate. This statement is valid since $SU-82002$ has approximately the same and $GLM2060$ a considerably higher reference stress (which accelerates the creep rate with an increasing value). The initial creep compliances of all three polymers coincide with the results from the short term measurements in paragraph 5.1.1.

The unfilled $SU-82002$ has the highest initial creep compliance $(D_0 = 0.251\text{GPa}^{-1})$. It creeps at a slower rate than the polyimide and the relative and absolute change in creep compliance $(\Delta(D)_{rel} = 19.9\%, \Delta(D)_{abs} = 0.05\text{GPa}^{-1})$ is considerably smaller. The lowest creep rate is observed with $GLM2060$. It shows the lowest absolute as well as relative change of the creep compliance $(\Delta(D)_{abs} = 0.035\text{GPa}^{-1}, \Delta(D)_{rel} = 17.6\%)$, although the underlying reference stress is the highest within the test series.
5 Results and Discussion

![Figure 5.40](image)

**Figure 5.40**: Master creep compliance curve at the reference stress $\theta_{eq, ref} = 14.3\text{MPa}$, constructed by shifting the individual logarithmic time axis by $-\log[a(\theta_{eq})]$ for the measurement data of a single rectangular PI2737 membrane. All measurements, except the reference data at the lowest stress $\theta_{eq, ref}$ are shifted on the logarithmic time-scale.

The obtained results provide important information on the key parameters, as defined in section 3.1. Requiring low creep, GLM2060 performs best with the lowest values for the coupling parameter $m = 0.16$, the lowest relative and absolute change in creep compliance and the highest retardation time $\tau = 1.86 \cdot 10^{10}$.

### 5.2.3 Energy storage

With the gathered information on the fracture strength and the viscoelastic behavior, the materials’ ability to store mechanical energy is evaluated. First, the short term storage capacity is quantified. Then, conclusions are drawn for the long term energy storage capacity of the materials.

#### Short term energy storage

The initial energy density $W_1$ which can be absorbed by the investigated materials at short times is analytically expressed by the first term of equation 2.84:

$$W_1 = \frac{D_0 \sigma^2}{2} \tag{5.2}$$

with the initial creep compliance $D_0$ and the stress $\sigma$. This is valid for both, creep and relaxation testing. The maximum values are obtained right before reaching the individual fracture stress. Hence, the materials become quantitatively comparable.
5.2 Long term mechanical properties

Figure 5.41: Logarithm of the shift factors (symbols) of PI2737 with respect to $\theta_{eq,ref} = 14.3$MPa as a function of the equivalent stress and their fit (dashed line, cf. Eq. 2.66). The shift factors can be described by the Eyring theory of stress activated plastic flow and yield a non-linearity parameter $s_0 = 0.67$MPa, above which the polyimide PI2737 behaves in a non-linear viscoelastic way.

with respect to their short term mechanical energy storage capacity by inserting their fracture stress $\sigma_f$ into equation 5.2. For comparability with other test methods and to account for the complex stress states of the bulge test method, the equivalent uniaxial fracture stress is considered. GLM2060 yields the highest value for the initial energy density $W_{1(GLM2060)} = 0.64$MJ/m$^3$. The polyimide PI2737 and the SU-82002 yield the values $W_{1(PI2737)} = 0.52$MJ/m$^3$ and $W_{1(SU-82002)} = 0.50$MJ/m$^3$, respectively. The conductive SU-8 formulation GCM3060 has the lowest value of $W_{1(GCM3060)} = 0.38$MJ/m$^3$. The values are shown in ascending order in table 5.8 to facilitate the comparison. Further, the results are illustrated graphically as intersections with the ordinate in figure 5.43, which indicate the maximum storage capacities for mechanical energy density at short times.

Through the diminutive volumes of MEMS structures, the total amount of storable energy becomes relatively small in the final size of a device: for an uniaxially loaded volume, which is comparable to the long rectangular membranes of the tests, consisting of GLM2060 with a thickness of 5$\mu$m the total stored energy at time zero is about 50$\mu$J.
Figure 5.42: Compilation of the master creep compliance curves of unfilled SU-82002, GLM2060 (SU-8 filled with silica nanoparticles) and the polyimide PI2737. The long term creep compliances are plotted on a logarithmic time axis. Due to the different glassy compliances, the intersections with the ordinate stretch from 0.110GPa$^{-1}$ to 0.251GPa$^{-1}$. The highest absolute and relative change in the creep compliance shows the polyimide, rising from the initial 0.110GPa$^{-1}$ to the transient value of 0.187GPa$^{-1}$. These values are derived at a similar reference stress (13.8MPa) as for SU-82002 (13.2MPa), which has the highest creep compliance values. It shows a moderate rise in its creep compliance of $\Delta(D_{SU8,2002}(t)) = 0.05$GPa$^{-1}$. The master creep compliance curve of GLM2060 is constructed at a higher reference stress (21.5MPa). However, it exhibits the lowest creep rate and the smallest change of its creep compliance. The graph data are calculated analytically with the experimentally derived properties.

Table 5.8: Compilation of the materials’ short term ability to store mechanical energy per volume.

<table>
<thead>
<tr>
<th>Material</th>
<th>Short term mechanical energy storage capacity [MJ/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCM3060</td>
<td>0.38</td>
</tr>
<tr>
<td>SU-82002</td>
<td>0.50</td>
</tr>
<tr>
<td>PI2737</td>
<td>0.52</td>
</tr>
<tr>
<td>GLM2060</td>
<td>0.64</td>
</tr>
</tbody>
</table>
5.2 Long term mechanical properties

Figure 5.43: The thick curved lines indicate the total, assimilated energy densities of SU-8\textsubscript{2002}, GLM2060 and Pi2737 during a virtual long term creep test with maximum load. The developing of the curves assumes that the probes remain intact irrespective of the additionally assimilated energy due to the creep process (hence no creep induced fracture). In terms of long term energy storage, GLM2060 performs best due to the large time independent fraction of the energy density capacity and the low energy uptake due to creep, indicating low energy losses during relaxation processes. No long term creep data are shown for GCM3060, since the experiments with this inhomogeneous material did not yield interpretable data. The intersections with the ordinate are marked with short dashes and indicate the maxima of the materials’ short term mechanical energy density capacities. These values are derived from their initial creep compliances and fracture strengths. GLM2060 yields the highest value of $W_1(\text{GLM2060}) = 0.64\text{MJ}/m^3$. Pi2737 and SU-8\textsubscript{2002} are almost equal with $W_1(\text{Pi2737}) = 0.52\text{MJ}/m^3$ and $W_1(\text{SU-8\textsubscript{2002}}) = 0.50\text{MJ}/m^3$. GCM3060 has the lowest value $W_1(\text{GCM3060}) = 0.38\text{MJ}/m^3$. For any point in time during a creep test, this is also the maximum energy density that can be recovered instantly upon unloading.
5 Results and Discussion

Long term energy storage

The capability of the materials SU-8\textsubscript{2002}, GLM2060 and PI2737 to store mechanical energy over a long time is qualitatively describable. An analytical solution for the conversion from creep compliance to relaxation modulus is not available for non-linear viscoelastic materials ([18, page 76]) and the differentiation between stored and lost energy can not be made with the empirical model (cf. Eq. 2.55). However, the absolute assimilated energy density (cf. Eq. 2.84) and its intersection with the ordinate at time zero give enough information for the concluding evaluation of the materials. The total assimilated energy densities are plotted as thick curves in figure 5.43. This energy density describes the total energy density that is transferred into a specimen throughout a creep compliance test. It contains an instantly recoverable portion ($W_1$), and a second time dependent part. For highly crosslinked, amorphous polymers, $W_1$ is time independent and remains stored throughout the whole creep test. It is returned almost instantly at unloading (cf. Fig. 2.8). Above all, the value $W_1$ can be seen as the upper boundary for any relaxation test, which describes a real scenario more demonstratively: a maximum load (strain) is suddenly applied to a structure, which shall retain as much of the assimilated mechanical energy as possible over time. Hence, a high initial energy density $W_1$ is desirable and the changes of the energy density must be as small as possible to minimize losses. The latter specification is congruent to a small change in the creep compliance over time.

The time dependent change of the energy density of polyimide is much higher than for the SU-8 materials. This empirical observation is quantitatively described with the shorter time constant $\tau$ and the higher coupling parameter $m$ (cf. paragraph 5.2.2). The filled SU-8 formulation features slightly lower values than the pure SU-8\textsubscript{2002}. These results render GLM2060 as the material with the most favorable properties in the test.

However, care must be taken with the interpretation of the latter section because the master creep compliance curves are derived for reference stresses well below the fracture strength. Due to the non-linear characteristics, the creep rate will rise with an increasing reference stress and creep induced fracture may arises.

Concluding, the most suitable material in this test series to store mechanical energy over a long time is evaluated to be GLM2060, a composite of SU-8 as resin matrix with a 3.3\%\textsubscript{vol} fraction of silica nanoparticles. The polyimide PI2737 and SU-8\textsubscript{2002} perform similar over a time span of three years ($\sim 10^8\text{s}$). Thereafter, the higher creep rate of the polyimide tips the scales in favor of the unfilled SU-8 formulation.

However, the short term energy storage capacity of GLM2060 is still a factor 70 below the figure of merit of single crystal silicon and a factor 10 below aluminum (values from [42, page 29]). And the discrepancy to the silicon will further increase with time.
5.2 Long term mechanical properties

since single crystal silicon is not expected to creep significantly.
6 Conclusion and Outlook

Today, the vast majority of mechanically active microsystems are based on either silicon or metal structures. However, newly emerging product classes of MEMS devices require the employment of materials other than the traditional choices to meet their specifications. It is our group’s vision, to complement the common materials for mechanically active structures in MEMS by well characterized, carefully chosen and possibly tailored polymers.

Conclusion

The present work advances the state-of-the-art with respect to the stated aim by:

- the introduction of a fully MEMS compatible measurement methodology for the determination of viscoelastic materials’ creep compliance curves using the bulge test on microfabricated membranes with tensile prestress.

- presenting new data on the mechanical short-term properties glassy plane strain modulus and fracture strength of the photosensitive resins GLM2060, GCM3060 and PI2737.

- validating the von-Mises model for the description of fracture strength under complex loading conditions for SU-8.

- investigating the time and temperature dependence of the intrinsic in-plane stress in fully cured SU-82002 membranes.

- showing the non-linear viscoelastic characteristics and the applicability of the time-stress superposition principle for SU-82002, GLM2060 and PI2737.

- providing extrapolated master creep compliance curves of SU-82002, GLM2060 and PI2737.

- extracting GLM2060 from the tested resins as the most promising photosensitive formulation for mechanically active MEMS applications.
Four negative photoresist formulations are selected for investigations by means of the specified key parameters: the highly cross-linked epoxy resin SU-8$_{2002}$, the polyimide PI2737, GLM2060 a composite version of SU-8 filled with silica nanoparticles and the conductive SU-8 composite GCM3060 which is filled with silver microclusters.

The first three polymers are thoroughly characterized. According to the time-stress superposition principle, master creep compliance curves, spanning a time frame of $t > 10^{10}$s can be constructed from isothermal series of short term creep compliance measurements on long rectangular membranes. The shift factors can be described by the Eyring theory of stress activated plastic flow for all experiments. This is a strong indication for the applicability of the suggested time-stress superposition principle. The long-term tests suggest low creep of fully cured glassy SU-8 without fillers and with silica nanoparticles ($< 10\%$ at $t = 10^{10}$s) at room temperature and under a constant equivalent stress of 13.2MPa and 21.5MPa, respectively. The polyimide PI2737 shows a distinctively higher creep rate. However, the creep rate of all evaluated resins are low compared to semicrystalline polymers.

The conductive SU-8 composite GCM3060 can be characterized by short-term measurements only, due to its inhomogeneous structure.

The polyimide performs well in the the fracture strength test. With an equivalent fracture stress of 100.1MPa, PI2737 withstands a 25% higher load than GLM2060 and an over 50% higher equivalent stress than SU-8$_{2002}$ and GCM3060. Further, it reacts stiffer to surge load: the glassy modulus ranges at 7.71GPa, whereas the initial glassy moduli of SU-8$_{2002}$, GLM2060 and GCM3060 are 3.93GPa, 4.78GPa and 5.71GPa, respectively. The initial moduli of the SU-8 formulations with fillers lie within the prediction-boundaries of the Hashin-Shtrikman composite model.

The highest initial mechanical energy storage capacity per volume of 0.64MJ/m$^3$ and the lowest creep of the tested polymers yield the silica filled SU-8 GLM2060 as the investigated material which meets the requirements for a potential application in mechanically active MEMS devices best.

The intrinsic in-plane stress in fully cured SU-8$_{2002}$ membranes is found to decrease with time, even at room temperature. Its time dependent relaxation behavior is monitored over a period of six months. The intrinsic in-plane stress is furthermore strongly influenceable by thermal treatment. A rejuvenation in the sense of setting the intrinsic in-plane stress back to a defined level is demonstrated. This observations is associated with the thermal mismatch of the material stack. The argument is supported by the calculated coefficient of thermal expansion for the SU-8 formulation, being similar to published values. Additional mechanical load is found to accelerate the relaxation process.
A fully automated bulge test setup for high throughput measurements of the mechanical properties of thin films is built and characterized. Additionally, an existing vibrometry test stand is modified to comply with the measurement demands. The established models are verified and hence capable to describe short-term properties and the non-linear viscoelastic creep behavior of the polymers with the chosen specimen geometry and loading conditions.

A fabrication process is established for fully clamped, free standing thin films of arbitrary organic material and for free standing cantilevers of photosensitive resist on wafer level.

**Outlook**

Though the project’s goals are reached successfully, further improvement and evolution is within reach. One enhanceable shortcoming is the relatively low measurement speed of the white light interferometer. This is acceptable for the tested polymers and similar materials with relatively low creep rates. However, organic films with shorter retardation times demand a faster non-interacting test system, ideally measuring with real-time speed. Holographic systems seem to be a promising alternative. Furthermore, a closed loop pressure control with a higher sensitivity than the actual system would allow for the application of the readily implemented stress control, which keeps the equivalent stress in the membranes constant throughout the creep test by tracking the pressure iteratively, depending on the measured deflection.

An interesting advancement would be the measurement of the vertical deflection with the path decoder of the vibrometer. If the membrane was loaded with a constant pressure and a superimposed high frequency chirp signal from an ultrasonic piezoactuator and if the vibrometer software offered the analyzation of time and frequency domain in parallel, this approach would allow for a fully time resolved differentiation of the intrinsic in-plane stress and the pressure induced stress, the simultaneous quantification of the pressure induced strain and of the glassy modulus.

In order to further improve the accuracy of the proposed methodology, efforts should be spent on improving the determination of the lateral dimensions.

Continuing the investigations in thermally induced intrinsic tensile in-plane stress may lead to an hitherto unpublished, elegant way of conducting relaxation tests with suspended polymeric membranes. Further, from the investigation’s findings it seems feasible to reduce the prestress in MEMS devices significantly by establishing well-balanced temperature ramps after the hard bake and possibly by applying appropriate solvents, which temporarily increase the intermolecular mobility.

For future material investigations and potential product applications, polymeric composites seem to be the most promising candidates in mechanical MEMS structures.
List of publications

Reviewed Journal Publications


Refereed Non-Journal Publications


Bibliography


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Bibliography


Bibliography


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Bibliography


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Lastly, and most importantly, I wish to thank my family. To them I dedicate this thesis.
Curriculum vitae

Personal Details
Bernd Michael Schöberle

Date of birth 16.07.1976
Nationality German
Marital status Married

Education and Qualifications

2003 – 2008 ETH Zürich, Switzerland
Dissertation at the Chair of Micro- and Nanosystems

1997 – 2002 Albert Ludwigs Universität Freiburg, Germany
Imperial College London, Great Britain
Diplom Ingenieur der Mikrosystemtechnik

1987 – 1996 Albert Schweitzer Gymnasium Gundelfingen, Germany
Allgemeine Hochschulreife (Abitur)

Languages
German Native language
English Fluent
French Working knowledge

Work Experience

Roche Diagnostics AG (CH)
11.2007 – ongoing
Department Project Leader, Advanced Systems Group

ETH Zurich (CH)
03.2003 - 07.2007
Assistant to Prof. Hierold, Group of Micro and Nanosystems

Aclara BioSciences (US)
01.2001 - 04.2003
Internship in the MicroFab department

Temic Automotive (SG)
08.2000 - 11.2000
Internship as Management Trainee

Infineon, München (DE)
03.2000 - 05.2000
Internship in the MEMS department

Fraunhofer Gesellschaft, IPM Freiburg (DE)
03.1998 - 02.2000
Research Associate with Dr. Lambrecht, Process Monitoring