

Integrated liquid crystalline micro-muscles

Yannick Folwill



Research in Micro-optics

Volume 32

Edited by Prof. Dr. Hans Zappe

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Goerges-Köhler-Allee 102
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Integrated liquid crystalline micro-muscles



**Dissertation zur Erlangung des Doktorgrades
der Technischen Fakultät
der Albert-Ludwigs-Universität Freiburg im Breisgau**

Yannick Folwill

2021

This dissertation was submitted in partial satisfaction of the requirements for the degree of

Doktor-Ingenieur

in

Microsystems Engineering

according to the examination regulations at the University of Freiburg for the Ph.D. in Microsystems Engineering of 2016.

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Submission: November 25, 2020

Disputation: February 5, 2021

Declaration

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I hereby confirm to have written the following thesis on my own,
not having used any other sources or resources than those listed.
Freiburg, March 16, 2021

Yannick Folwill

Contents

Abstract	1
Zusammenfassung	3
1 Introduction	5
1.1 Motivation	5
1.2 State of the art	6
1.3 Approach of this thesis	8
1.4 Core results	11
2 Fundamentals of liquid crystal elastomers	13
2.1 Structure and chemistry	13
2.2 Mechanical and optical properties	14
2.2.1 Thermomechanical effect	14
2.2.2 Birefringence	17
2.3 Comparison of actuation principles	19
2.4 Demonstrations and limitations	20
2.5 Programming radially actuating LCEs	21
2.5.1 Defining the alignment profile	22
2.5.2 Adding constraints	23
3 Fabrication	25
3.1 Previously established processes	25
3.2 Overview	26
3.3 Deposition of liquid crystalline films	27
3.4 Alignment of mesogens	27
3.5 Structuring of actuators	29
3.6 Integration of actuation mechanism	30
3.7 Anchoring and releasing actuators	30
3.8 Main focus of the fabrication	31

4	Deposition	33
4.1	Techniques	33
4.2	Deposition process	34
4.3	Results	35
4.3.1	Solvents	35
4.3.2	Thickness and homogeneity	35
4.3.3	Defects and limitations	37
4.3.4	In situ photoalignment	39
5	Photoalignment	41
5.1	Principle of operation	41
5.2	Design choices	43
5.2.1	Constraints	43
5.2.2	Materials	43
5.2.3	Optical system	44
5.2.4	Previously demonstrated photoalignment systems	45
5.3	Optomechanical Setup	46
5.3.1	Components	46
5.3.2	Assembly	47
5.4	Automation	49
5.5	Environment control	51
5.5.1	Humidity	51
5.5.2	Temperature	52
5.6	Alternative photoalignment materials	52
5.7	Photoalignment system results	53
5.7.1	Optical resolution	53
5.7.2	Vignetting and aberrations	56
5.7.3	Capabilities	57
5.7.4	Highlights	57
6	Characterization	59
6.1	Overview	59
6.1.1	Anisotropy	59
6.1.2	Linear dichroism	60
6.1.3	Birefringence	60
6.1.4	Common measurement techniques	60
6.1.5	Selected measurement techniques	61

6.2	Dichroism imaging	62
6.2.1	Aim of the method	62
6.2.2	Measurement principle	62
6.2.3	Discussion	65
6.3	Retardation measurement	66
6.3.1	Aim of the method	66
6.3.2	Measurement principle	66
6.3.3	Discussion	69
6.4	Stokes parameter alignment measurement	70
6.4.1	Aim of the method	70
6.4.2	Measurement principle	71
6.4.3	Discussion	75
6.5	Characterization results	77
6.5.1	Process optimization	77
6.5.2	Capabilities and limitations	86
7	Structuring	89
7.1	Techniques	89
7.2	Photolithography and dry etching	89
7.3	Maskless lithography	91
7.3.1	Process	92
7.3.2	Results	93
7.4	Discussion	94
8	Actuation	97
8.1	Stimulation of actuation	97
8.1.1	Resistive heating	97
8.1.2	Towards light-actuated LCE actuators	101
8.2	Towards free-moving actuators	102
8.3	Towards radially actuating LCEs	103
9	Summary	105
10	Conclusion	107
A	Appendix	109
A.1	Photoalignment Software	109
A.2	Cleanroom processes	110

Bibliography	111
Author's bibliography	123

Notation

List of symbols

symbol	meaning	unit
a	parameter describing a logarithmic spiral	-
A, B, C, D	intermediate parameters to derive Stokes parameters	-
$A_{\parallel}/A_{\perp}$	absorbance parallel/perpendicular to mesogens	-
α	alignment angle of liquid crystals	$^{\circ}$
b	parameter describing a logarithmic spiral	$1/^{\circ}$
C	contrast, Michelson contrast	-
C	circumference of a circle	m
d	film thickness	m
δ	opening angle of a logarithmic spiral	$^{\circ}$
Δn	birefringence	-
ϵ_x/ϵ_y	axial/transverse strain	-
$\mathcal{F}$	fast Fourier transform	-
θ_s	incremental rotation angle	$^{\circ}$
I	intensity	W/cm^2
λ	wavelength	nm
λ	axial compression	-
M	magnification	-
n	refractive index	-
n_e/n_o	extraordinary/ordinary refractive index	-
ν	Poisson's ratio	-
r, θ	polar coordinates	m, $^{\circ}$
S	order parameter	-
$\hat{\mathbf{S}}$	Stokes vector	-
S_0, S_1, S_2, S_3	Stokes parameters	-
t	exposure time	s
T_g	glass transition temperature	$^{\circ}\text{C}$

symbol	meaning	unit
T_{ni}	nematic-isotropic transition temperature	°C
τ	time constant	s
ϕ	offset angle of a logarithmic spiral	°
ϕ	retardation due to birefringence	°
x, y, z	Cartesian coordinates	-
ω	angular frequency	rad/s

List of abbreviations

abbreviation	meaning
4-ADBB	specific reactive mesogen, see Sec. 2.1
BY	Brilliant Yellow, photoalignment material, azo dye
CH	Chrysophenine, azo dye
CR	Congo Red, azo dye
CMOS	complementary metal-oxide-semiconductor
DC	direct current
DEA	dielectric elastomer actuator
DMD	digital micromirror device
DMF	Dimethylformamide, solvent
DMSO	Dimethyl sulfoxide, solvent
DPO	UV photoinitiator, see Sec. 2.1
DRIE	deep reactive-ion etching
ESF	edge spread function
FFT	fast Fourier transform
FTIR	Fourier-transform infrared (spectroscopy)
FWHM	full width at half maximum
GUI	graphical user interface
HDDA	crosslinker, see Sec. 2.1
HWP	half-wave plate
IPMC	ionic polymer-metal composite
IR	infrared light
LC	liquid crystal
LCD	liquid crystal display
LCE	liquid crystal elastomer
LED	light-emitting diode

abbreviation	meaning
LSF	line spread function
MEMS	microelectromechanical system(s)
MIR	mid-infrared light, 3 μm to 8 μm
MTF	modulus transfer function
NMP	N-Methylpyrrolidone, solvent
PAAD	commercially available photoalignment material
PDMS	Polydimethylsiloxane
PGMEA	Propylene glycol methyl ether acetate, solvent
PMMA	Poly(methyl methacrylate)
POM	polarization microscopy
PVD	physical vapor deposition
QWP	quarter-wave plate
RM257	commercially available reactive mesogen
SD1	commercially available photoalignment material
SLM	spatial light modulator
SMA	shape-memory alloy
SNR	signal-to-noise ratio
SPAMT	Stokes parameter alignment measurement technique
THF	Tetrahydrofuran, solvent
TMU	Tetramethylurea, solvent
USAF	United States airforce resolution target
UV	ultraviolet light, 10 nm to 400 nm
UVA	ultraviolet light, 315 nm to 400 nm
UVB	ultraviolet light, 280 nm to 315 nm
VIS	visible light, 380 nm to 760 nm
XRC	X-ray crystallography

Abstract

Soft matter actuators can be used to mimic complex biological motion, which is interesting to create miniaturized robotic systems. Liquid crystal elastomers (LCEs), in particular, are a versatile actuation material in this class. They show large strain ($>40\%$) and the actuation direction can be freely defined.

This thesis builds a path to harness these properties for use in microelectromechanical systems (MEMS). The motivation is twofold: (1) Macroscopic LCE actuators are limited by relatively large actuation timescales (tens of seconds to minutes). Miniaturization of LCE structures enables faster stimulation of actuation and relaxation. (2) LCE actuators could help realize heretofore impossible complex actuation schemes in MEMS, such as the radial actuation of a human iris. Integrated LCE actuators can enable such applications thanks to their freely definable actuation direction.

This thesis therefore presents the introduction of LCEs into microsystems. Wafer-level fabrication processes to deposit the material, to define and measure the anisotropy, and to structure the actuators were developed.

This work presents the development of a photoalignment system that tackles the major engineering challenge of using LCE actuators, that is controlling the actuation direction. The photoalignment system enables arbitrary alignment of the liquid crystalline material with a spatial resolution of $10\mu\text{m}$ at the wafer level. Two optical measurement techniques are devised, to characterize and optimize the alignment procedure.

Further wafer-level processes are also described that allow for fabrication of LCE structures with a resolution of $10\mu\text{m}$ and which include integrated heating elements to trigger the actuation. Measurement of the phase transition time of the fabricated LCE structures demonstrates sub-second actuation and relaxation times.

The presented work demonstrates processes and recipes to fabricate MEMS compatible LCE actuators. This should form the framework in realization of miniaturized complex actuation systems using soft matter actuators in MEMS.

Keywords: liquid crystal elastomers, liquid crystals, photoalignment, soft matter actuators, micro-actuators, MEMS

Zusammenfassung

Aktoren aus nachgiebigen Materialien können zur Imitation komplexer biologischer Bewegungen verwendet werden, womit miniaturisierte Robotersysteme realisieren lassen. Insbesondere Flüssigkristall-Elastomere (LCEs) sind ein vielseitiger Vertreter dieser Klasse von Aktormaterialien. Sie weisen große Verformungen ($>40\%$) auf, wobei die Orientierung der Bewegung frei festgelegt werden kann.

Um diese Eigenschaften für den Einsatz in mikroelektromechanischen Systemen (MEMS) nutzbar zu machen, wurde in dieser Arbeit ein Prozess entwickelt. Die Motivation dazu ist zweierlei: (1) Die Anwendung von makroskopischen LCE-Aktoren ist durch die relativ großen Reaktionszeiten (mehrere zehn Sekunden bis Minuten) limitiert. Die Miniaturisierung der LCE-Strukturen ermöglicht eine schnellere Stimulation der Aktuierung. (2) Integrierte LCE-Aktoren können dank ihrer frei definierbaren Aktuierungsrichtung dazu beitragen, bisher unmögliche komplexe Betätigungsschemata in MEMS zu realisieren, wie beispielsweise die radiale Aktuierung der menschlichen Iris.

Diese Arbeit stellt daher die Einführung von LCEs in die Mikrosystemtechnik dar. Es wurden Herstellungsprozesse auf Wafer-Ebene zur Abscheidung des Materials, zur Definition und Messung der Anisotropie sowie zur Strukturierung der Aktoren entwickelt. Den Fokus der vorliegenden Arbeit liegt auf der Entwicklung eines Photoalignment-Systems. Dieses nimmt die größte technische Herausforderung der Verwendung von LCE-Aktoren in Angriff, nämlich die Definition der Bewegungsrichtung des Materials. Das Photoalignment-System ermöglicht eine beliebige Ausrichtung des flüssigkristallinen Materials mit einer räumlichen Auflösung von $10\mu\text{m}$ auf Wafer-Ebene. Zur Charakterisierung und Optimierung des Ausrichtungsprozesses wurden außerdem zwei optische Messverfahren entwickelt.

Darüber hinaus werden weitere Prozesse auf Wafer-Ebene beschrieben, welche die Herstellung von LCE-Strukturen mit einer Auflösung von $10\mu\text{m}$ ermöglichen und integrierte Heizelemente zur Auslösung der Aktuierung beinhalten. Die Messungen der Phasenübergangszeit der gefertigten LCE-Strukturen zeigen Aktuierungs- und Relaxationszeiten im Sub-Sekundenbereich.

Die vorliegende Arbeit soll den Rahmen für die Realisierung von miniaturisierten komplexen Aktorsystemen auf Basis von nachgiebigen Materialien in MEMS bilden.

Stichwörter: Flüssigkristall-Elastomere, Photoalignment, Mikroaktoren, MEMS

1 Introduction

In the beginning, there was simplicity.

– Richard Dawkins, *The Selfish Gene*

1.1 Motivation

Biological systems have inspired the development of many inventions that are now ubiquitous in our everyday life. Velcro, the lotus effect and aerodynamic designs are examples of the evolutionary optimization process that have been mimicked by human inventors.

These innovations borrow from either the molecular scale, or the macroscopic architecture of biological organisms. However, an ongoing challenge is the imitation of the movement of plants and animals, which takes place on an intermediate scale in the millimeter to micrometer range. Developing microscopic movement mechanisms that can be integrated flexibly with control hardware is essential for the construction of small-scale robotic systems.

The human iris serves as a good example for a mechanism that is difficult to mimic on a microscopic scale: It consists of two muscle groups, one that opens the iris by pulling radially to allow more light onto the retina. The antagonist muscles, which operate azimuthally, closes the iris on contraction.

Designers of camera systems have long known to imitate this function by a tunable aperture which can be found in any handheld camera. Since a truly radial mechanism is difficult to implement, these tunable apertures consist of multiple overlapping blades that leave an opening in the center. Moving these blades with respect to each other, the diameter of the opening can be increased or decreased. When looking at these tunable apertures in detail, the polygonal shape of the aperture can easily be seen.

Miniaturizing such tunable apertures to smartphone-scale cameras is proving a persistent challenge, such that manufacturers rather include multiple fixed-aperture cameras in one device. In particular, what makes miniaturization of tunable apertures so challenging is the radial deformation, which necessitates an actuator type that can pull or push towards a common center point.

In order to design such complex actuation mechanisms, research turns to mimicking the structure of mammalian muscles by soft matter materials. These so-called artificial muscles encode the actuation mechanism in the material structure itself, similar to the anisotropic structure of mammalian muscles.

Liquid Crystal Elastomers (LCEs) have risen to prominence as a candidate for such artificial muscles. These materials consist of crosslinked, elongated molecules, whose alignment directions define the anisotropy. Modern techniques allow for the definition of the molecules' alignment directions with high spatial resolution, thus enabling the realization of complex actuation profiles, like the mentioned radial actuation. Moreover, by defining specific actuation patterns, out-of-plane movements inspired by origami and kirigami are possible.

Despite the publication of a range of impressive examples, no usable LCE actuator has so far been developed. The main reasons for this are the slow actuation speed, and the difficult integration with other systems. Manual fabrication processes and unreasonable actuation powers prevent the use of the demonstrators which are presented in the following section.

This work aims to overcome these shortcomings and provide a generic template to fabricate LCE structures featuring arbitrary actuation profiles.

1.2 State of the art

The main inspiration of this project is taken from the works by Schuhladen and Petsch, who fabricated LCE-driven optical components, like a tunable iris [1], and a tunable lens [2]. The structures were produced by soft lithography, and resistive heaters were embedded to trigger the actuation. The fabrication process for these applications involved a tedious combination of wafer-level and manual processing. However, the major shortcoming of the tunable iris and lens were the actuation times in the order of tens of seconds.

Even so, the value of their work lies in the demonstration of the capabilities of the LCE material. They achieved strain values in the order of 20 % to 40 %. More importantly, they demonstrated the feasibility of a radial actuation profile, which is defined in the material itself. The two systems, the tunable iris and lens are shown in Fig. 1.1. The tunable iris (Fig. 1.1a) is the first demonstration of truly radial actuation of LCEs, highlighting the potential of the material.

With regard to actuation direction, even more admirable demonstrations have recently been achieved by 3D-printing of LCEs. Ambulo et al. produced thin LCE structures that transformed from a 2D-film to a 3D cone of impressive height on heating, along with a range of other structures that featured fascinating actuation profiles [3]. One of these structures is shown in Fig. 1.1c.

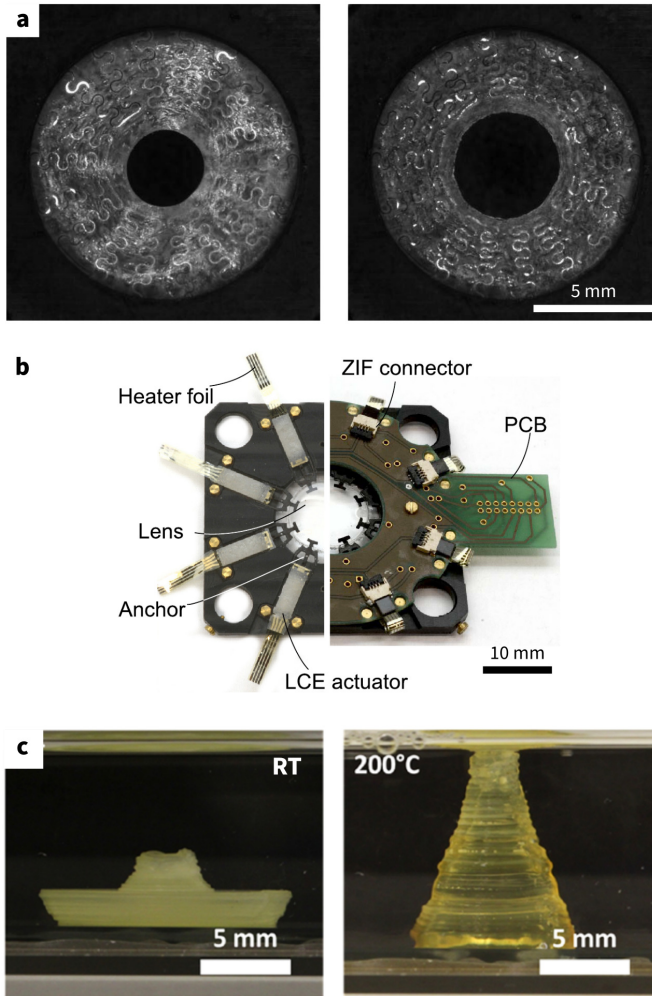


Figure 1.1 – Heat-actuated LCE structures: **a)** The tunable iris with embedded platinum meanders to supply heat to the actuator demonstrated truly radial actuation with LCE for the first time [1]. **b)** Eight linear actuators with integrated platinum heaters were used to apply strain on a polymer lens to tune the focus [2]. **c)** 3D-printing of LCE material highlights the enormous potential of LCEs as actuator material, due to the large strain and flexible actuation patterns [3].

Their fabricated LCE structures did not feature a mechanism to directly heat the material, so they were simply heated on a hot plate. While this again demonstrates the versatility of the material, these structures are not usable directly due to their lack of a control mechanism.

To reduce the actuation time of LCE actuators, miniaturization is the key. The speed is limited by how fast the material can be heated and cooled down. Smaller structures have a lower heat capacity and enable faster heat transmission through the whole material. However, miniaturization also makes it more difficult to fabricate a controllable mechanism to couple heat into the LCE structure. Besides putting the structures on a hot plate or on heated silicone oil, research has therefore resorted to triggering the actuation by light, also termed photoactuation.

Publications are full of LCE films bending on illumination with high-power light. Some of them aim for the imitation of biological systems, like the light-driven artificial flytrap [4] or the self-regulating iris [5], both featured in Fig. 1.2. Even light-driven LCE-grippers have been designed [6, 7]. This variation of examples illustrates the freely definable actuation direction, which is the outstanding property of LCEs. For example the self-regulating iris used petals that would fold inward on illumination (Fig. 1.2a), while the artificial flytrap would bend towards the light.

While these structures are promoted in literature for the prospect of creating “soft robots” and “autonomous systems”, so far all demonstrations relied on a high-power light source, delivering an intensity in the order of 100 mW/cm^2 , which does not seem reasonable for such an application.

Therefore, the future of the field of LCE actuators hinges on the combination of miniaturization, efficient energy coupling for actuation, and integration into usable applications. Microsystems provide a promising platform for this by tackling all these challenges at once.

Two outstanding examples, showing the potential of combining LCEs and microsystems, are the LCE-driven gripper by Sánchez-Ferrer et al. [8] (shown in Fig. 1.3), and the micropillar array by Torras et al. [9]. These structures are actuated by resistive heaters and combine microsystems processes with LCEs. However, both demonstrators involve manual assembly steps. Furthermore, they do not exploit the full potential of LCEs since they only use simple unidirectional alignment. Despite this promising work, not much more has been published towards the integration of LCEs in microsystems.

1.3 Approach of this thesis

The goal of this work is to pave the way for the integration of LCE actuators in microelectromechanical systems (MEMS), to profit from the large strain and the programmability of the material.

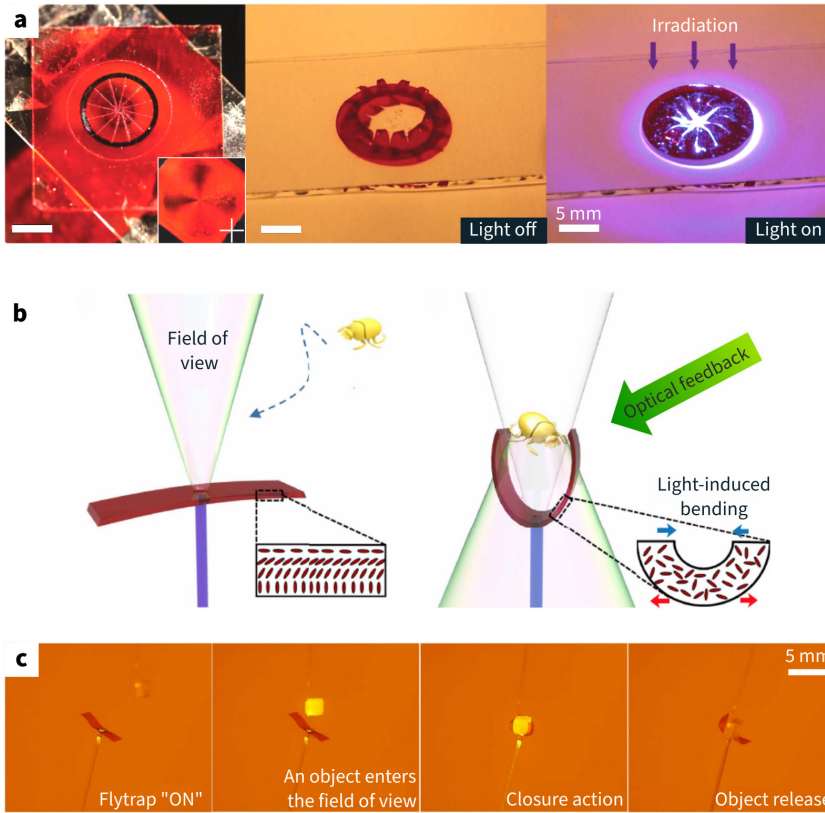


Figure 1.2 – Light-actuated LCE structures: **a)** The petals of this LCE structure fold inward on illumination, forming a light-controlled aperture [5]. **b)** The principle of a light-driven LCE flytrap: Light is coupled out of an optical fiber through the LCE film. On reflection on an object, the LCE actuates and folds inward to capture the object. **c)** Demonstration of the artificial flytrap catching and releasing an object [4].

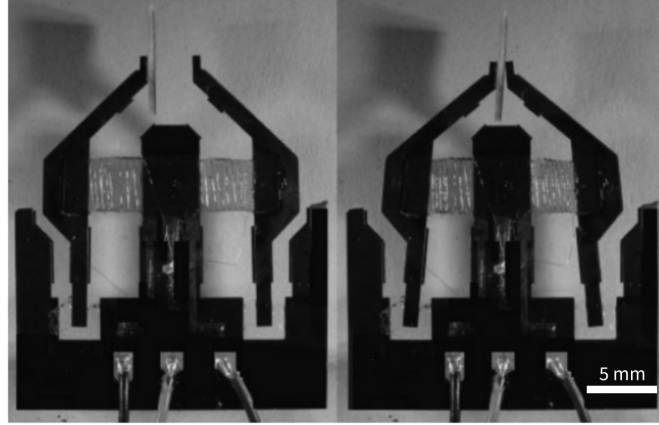


Figure 1.3 – LCE-actuated microgripper: Microsystems-fabricated gripper structure (silicon) with LCE actuator, heated by thin gold wire wrapped around the actuator [8]. The left image shows the ground state, the right image on applying electric current through the gold wires. The gripper joints are held by silicone.

The classic processing steps of fabricating individual LCE actuators in cells and molds are replaced by wafer-level batch processes:

- **Deposition:** Instead of melting the materials to fill molds or cells, the LCE precursor is spin coated and polymerized on the substrate.
- **“Programming”:** The anisotropy, and thus the actuation direction, is defined spatially for the whole wafer.
- **Structuring:** Photolithography and dry etching are used to define the shape of the actuators.
- **Actuation:** Resistive heater structures are fabricated on the same substrate, enabling good coupling of the heat and fast control by applying current.

The vision of this work is the creation of a complete process flow to fabricate a tunable LCE-MEMS iris. At the same time, the process should be a blueprint for integrating LCE actuators in MEMS fabrication.

1.4 Core results

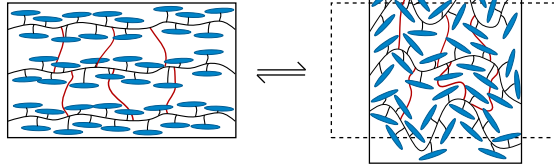
This thesis demonstrates the compatibility of liquid crystal elastomers with MEMS technology. A host of fabrication processes was developed, optimized and evaluated to enable the production of integrated liquid crystalline micro-muscles.

An overview of the developed processes is shown in [Fig. 1.4](#). It summarizes the content of this work:

- As a first step, the liquid crystalline material was coated homogeneously on the wafer. This deposition process is described in [Chapter 4](#).
- The core of LCE actuator fabrication, as well as of this thesis, is the definition of the spatial distribution of alignment of the liquid crystals, which determines the actuation direction. In this work, a process to define the alignment with a spatial resolution of $10\text{ }\mu\text{m}$ on a full 100 mm-wafer level was developed and optimized. The process is detailed in [Chapter 5](#).
- As a side product, a new optical technique to quantify the spatial distribution of alignment and retardation of birefringent materials was developed to characterize the produced LCE films. Another optical technique was devised to quantify the spatial distribution of the alignment of dichroic dyes. These techniques and their findings are reported in [Chapter 6](#).
- Another important topic is the definition of the shape of the LCE actuators. To that end, this work successfully demonstrated two approaches, one based on a maskless lithography, and one based on standard photolithography and dry etching. Both methods and the resulting structures are presented in [Chapter 7](#).
- Finally, the actuators need to be stimulated by heat. Therefore, heater structures need to be fabricated and the actuators need to be partially released from the substrate to move freely. While integration of heaters could be achieved with standard MEMS processes, the partial release is still an ongoing research topic beyond the scope of this thesis. The necessary processes are detailed in [Chapter 8](#).

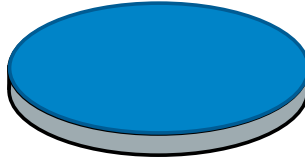
The following [Chapter 2](#) explains the outstanding properties of liquid crystal elastomers as an actuator material. [Chapter 3](#) gives an overview of the developed fabrication process. Each process is then detailed in a further chapter, including a discussion of the achievements and challenges.

fundamentals (Chapter 2)

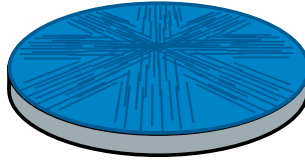


fabrication overview (Chapter 3)

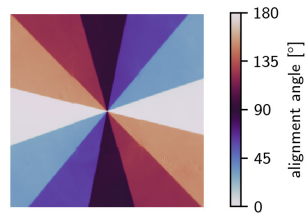
deposition (Chapter 4)



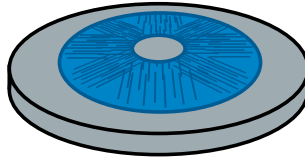
alignment (Chapter 5)



characterization (Chapter 6)



structuring (Chapter 7)



actuation (Chapter 8)

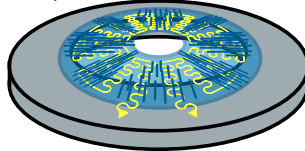


Figure 1.4 – This thesis as a process: After introducing the fundamental characteristics of LCEs and giving an overview of the process, every process step is presented in a separate chapter. The achievements and challenges of each process are discussed within the respective chapter.

2 Fundamentals of liquid crystal elastomers

Fliessende Krystalle! Ist dies nicht ein Widerspruch in sich selbst – wird der Leser der Überschrift fragen –, wie könnte denn ein starres, wohlgeordnetes System von Molekülen, als welches wir uns einen Krystall vorstellen, in ähnliche äussere und innere Bewegungszustände geraten, wie wir sie bei Flüssigkeiten als „Fliesen“ bezeichnen und durch mannigfache Verschiebungen und Drehungen der ohnehin schon des Wärmezustandes halber äusserst lebhaft durcheinander wimmelnden Moleküle zu erklären pflegen?

– Otto v. Lehmann [10]

2.1 Structure and chemistry

Liquid crystals (LCs) have been first described by Reinitzer as early as 1888 [11]. Further investigation and chemical synthesis by Lehmann [10] and Vorländer [12] led to popularization of this fascinating state of matter. In 1975, de Gennes pioneered the field of liquid crystal elastomers by postulating the nonlinear elasticity of loosely crosslinked anisotropic polymers [13]. Finkelmann is credited with first synthesizing such a network and popularizing the term *liquid crystalline elastomer* [14].

LCs are elongated molecules, which can flow like a liquid, while at the same time exhibiting crystalline properties, e. g. birefringence or linear dichroism. The molecules, called *mesogens*, can form different states of crystalline order, ranging from positional and directional order (*smectic*) to complete disorder (*isotropic*). An intermediate state, exhibiting only directional order, is termed *nematic*. It can be compared to a stack of raw spaghetti, where all spaghetti lie in parallel, but do not have the regular positional order of a solid crystal. The direction in which the mesogens are aligned on average is called the *director*. This work uses only nematic liquid crystals, i. e. materials that are in the nematic phase at room temperature.

Liquid crystal elastomers are loosely crosslinked networks of LCs, meaning the positions of the mesogens are fixed in the network. While exhibiting similar optical properties as LCs,

the mechanical properties of LCEs are similar to rubber. However, the elasticity is nonlinear and anisotropic [15].

LCEs are usually fabricated from reactive mesogens, i. e. elongated molecules that feature reactive groups to form networks. Depending on the specific mesogens, different types of LCEs can be formed. The two kinds of reactive mesogens used in this work are shown in Fig. 2.1:

- **4-ADBB:** The reactive mesogens (4"-acryloyloxybutyl) 2,5-di(4'-butyloxybenzoyloxy) benzoate (4-ADBB) are elongated molecules with a reactive acrylate group at the side. They are linked by the crosslinker 1,6-hexanediol-diacrylate (HDDA) by means of a radical polymerization, which is initiated by the photoinitiator diphenyl (2,4,6-trimethyl benzoyl)phosphine oxide (DPO). Since the mesogen's reactive group is at the side, a *side-chain* network is formed, in which the mesogens are attached to the polymer backbone.
- **RM257:** The reactive mesogen 1,4-bis-[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene features two reactive acrylate groups which are at the two ends of the elongated molecule. Therefore, no crosslinker is needed to link the molecules. Through a radical polymerization (initiated by DPO), a network can be formed. Since the mesogens are part of the polymer backbone, the structure is called a *main-chain* network.

2.2 Mechanical and optical properties

LCEs combine the mechanical and optical properties of polymers with the anisotropy of solid crystals. The focus of this chapter is limited to the thermomechanical effect, which is harnessed to create versatile actuators, and the birefringence, which is needed for the analysis of the fabricated LCE structures (Chapter 6). Further useful properties are nonlinear elasticity (*soft elasticity*) [15], biocompatibility [16] and transparency of most of the materials for optical applications.

2.2.1 Thermomechanical effect

The outstanding property of LCEs is their ability to change their macroscopic shape on heating. The reason for this is the anisotropic molecular structure which can undergo a phase transition on a change in temperature.

Heating or cooling of LCEs leads to a transition from one phase to another, when crossing certain threshold temperatures. Nematic LCEs change to an isotropic phase when heated

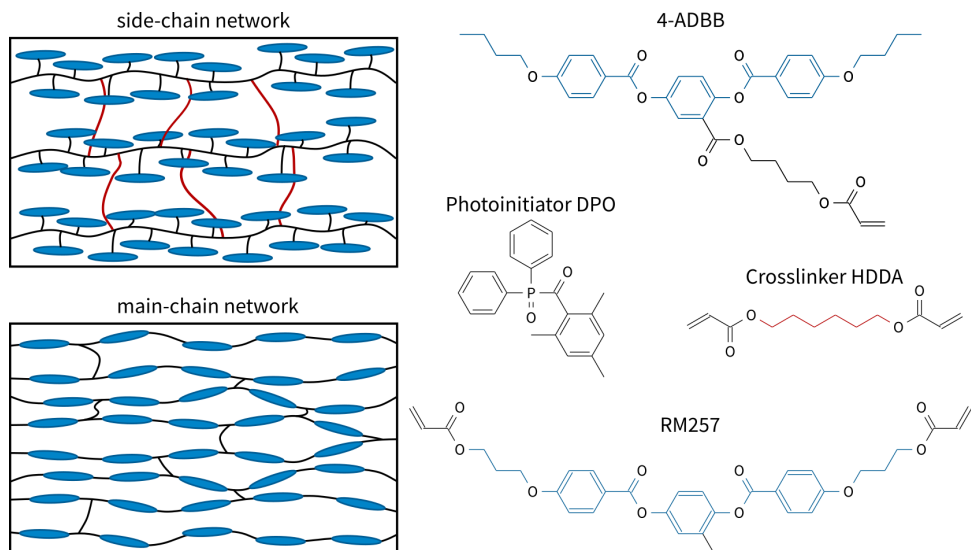


Figure 2.1 – Liquid crystalline network and chemical structures: The mesogen 4-ADBB features one reactive group on the side which can be linked by HDDA to form a side-chain LCE network. RM257 molecules with reactive groups at both ends can be polymerized without crosslinker, resulting in a main-chain network. In both cases, the reaction is driven by a radical polymerization, started by the photoinitiator DPO.

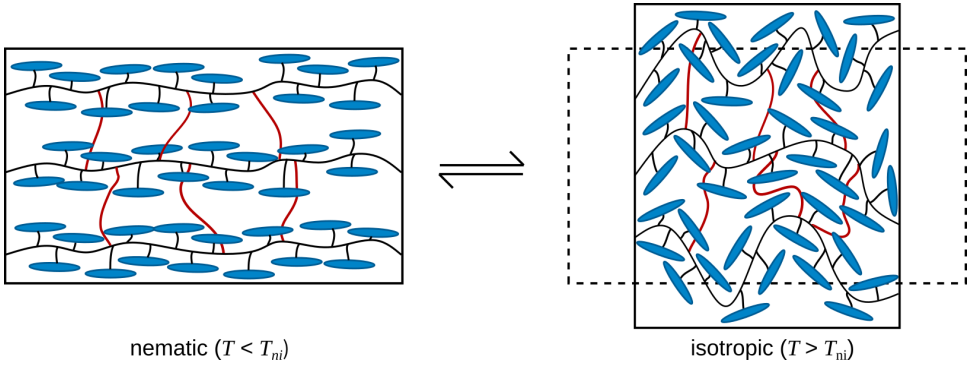


Figure 2.2 – Shape change through phase transition: Heating of a nematic LCE above its transition temperature T_{ni} leads to a deformation of the polymer network, resulting in a macroscopic compression along the axis parallel to the mesogens and an expansion in the orthogonal dimensions. Cooling down reverses the state back to the original shape.

above T_{ni} , the nematic-isotropic transition temperature, which depends on the chemical structure of the network and mesogens. The nematic-isotropic phase transition and the resulting shape change of a liquid crystalline network is schematically shown in Fig. 2.2.

On heating above T_{ni} , the mesogens have enough thermal energy to rotate from their original alignment direction, triggering a deformation of the network. Since the mesogens in a nematic LCE are aligned predominantly in one direction, the deformation yields a compression along this axis, while at the same time expanding in the two orthogonal dimensions.

The crucial difference between LCs and LCEs is that this deformation is reversible in the crosslinked LCEs, which means that the network returns to its original state on cooling down. This thermomechanical effect can thus be exploited as an actuator material [17].

LCEs have triggered extensive research in the fields of artificial muscles and soft matter actuators mainly due to three notable properties:

- **Large strain:** LCEs were shown to reversibly compress to less than 70 % of their original length along the director [18]. While the exact strain depends on the chemistry and mechanical constraints, the record in actuation demonstrated a compression of an LCE fiber to 20 % of the original length [19], with further examples listed in [20].
- **Programmable actuation direction:** The actuation direction, i. e. the direction in which the material contracts, is determined by the alignment direction of the meso-

gens. This is similar to mammalian muscles, where the contraction is defined by the direction of the muscle fibers. Thus, the actuation direction can be *programmed* by defining the nematic director of the LCE. This enables actuation schemes which are hardly feasible with other actuation principles, e. g. radial actuation, where all actuators pull towards a common center point like in the human iris.

Mesogens can be aligned by electric or magnetic fields, polarized light, micro-structured surfaces or shear flow. This host of possibilities allows programming of arbitrary alignment schemes, as demonstrated by the LCE irises from Schuhladen [1] or Zeng [5], as well as a variety of soft robots [21–23].

- **Stimuli-responsiveness:** The phase transition to deform the LCE network is commonly triggered by heat. Since the thermal conductivity of LCEs is low, the actuation speed is mostly limited by how fast the heat can be spread through the network. Therefore, researchers have devised various methods to better couple the heat into the material, e. g. embedded deformable heaters [1], liquid metals [24] or conductive particles [25].

A more versatile method is doping of the LCE actuator with light-absorbing materials which convert the absorbed light into heat, termed *photothermal actuation*. Examples to this end are azo dyes [26, 27], carbon nanotubes [28, 29], carbon particles [30], graphene [31], or gold nanoparticles [32].

Besides heat, the phase transition can be triggered directly by changing the shape of mesogens through isomerization by light (*photochemical actuation*). This is useful for bistable systems in which the phase transition can be switched between nematic and isotropic by different wavelengths [33].

2.2.2 Birefringence

Liquid crystals exhibit uniaxial birefringence due to their inhomogeneous distribution of electric dipoles. The optic axis points in the direction parallel to the alignment direction of the liquid crystals, i. e. the long axis of the mesogens. Liquid crystalline materials therefore show two refractive indices, the extraordinary refractive index n_e for light polarized parallel to the long axis of the mesogens (optic axis), and the ordinary refractive index n_o for light polarized orthogonal to that direction.

As opposed to solid crystals, the optic axis can vary spatially, depending on the alignment direction of the mesogens. Furthermore, the birefringence, i. e. the difference between n_e and n_o , can vary with the degree of order of the mesogens. In the isotropic phase, with no directional order of the mesogens, liquid crystalline materials do not exhibit birefringence.

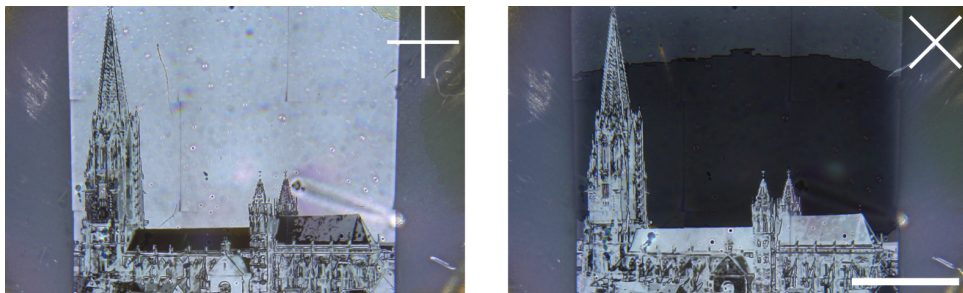


Figure 2.3 – Birefringence of an aligned LCE film: Both images were captured with the sample between crossed polarizers, to visualize the birefringence. The polarizers were rotated by 45° between the left and right image. The dark parts of the images correspond to areas where the mesogens are parallel to one of the polarizers. Brighter parts correspond to increasing angles of the mesogens towards the polarizers. The gray areas on the sides are not aligned and show Schlieren textures when magnified. Scale bar 5 mm.

For LCs, this property is harnessed to create liquid crystal displays (LCDs), spatial light modulators (SLMs) and further optical applications, which depend on modifying the state of polarization of light [34]. For the work with LCEs, birefringence is useful to evaluate the alignment quality, i. e. the degree of order of the liquid crystals as well as the spatial distribution of alignment direction. These quantities are essential feedback mechanisms for the fabrication of LCE actuators.

Qualitatively, thin LCE films can be observed between crossed polarizers. The obtained contrast shows the alignment direction of the liquid crystals. If the alignment of nematic reactive mesogens was not defined before crosslinking, i. e. they do not have a long range order, so-called *Schlieren textures* can be observed. However, if the spatial alignment of the mesogens was defined properly, the aligned domains yield a contrast that depends on the alignment direction. The contrast of an aligned LCE film between crossed polarizers is shown in Fig. 2.3. On rotating the polarizers by 45° , the contrast inverts. The edges are not aligned, but still show weak birefringence due to forming Schlieren patterns, which are anisotropic on a microscopic scale.

To quantify the alignment quality, two techniques were developed and utilized in this work. The first method is a straightforward measurement of the retardation of linearly polarized light (Sec. 6.3). The second technique allows for the measurement of spatial distribution of the alignment and the retardation, independent of alignment direction of the mesogens (Sec. 6.4). Both techniques were used to optimize the fabrication process of miniaturized LCE actuators.

2.3 Comparison of actuation principles

Various actuation mechanisms are well-established in MEMS technology, e. g. electrostatic, piezoelectric, electromagnetic and thermal actuation, each coming with its own up- and downsides. Research has added further candidates to increase the spectrum of possibilities in actuation for microsystems, one of them being liquid crystal elastomers. To put this into context, the following is a comparison of potential actuator materials, which are popularized as *artificial muscles*.

The reason for this term is the notion to find actuators with properties similar to mammalian muscles, strains of up to 40 %, work densities of $>8 \text{ kJ/m}^3$, and frequencies in the order of $>1 \text{ Hz}$ [35]. While the principles mentioned above meet most of these requirements, there are always gaps to be filled by novel mechanisms that exhibit large strain at medium frequencies, with compatibility for microsystems processing. This is a brief overview over some of the more promising candidates under research:

- **Dielectric elastomer actuators (DEA):** This type of actuator consists of two electrodes which use a large electric field to deform an elastomeric material sandwiched between the electrodes. DEAs show great promise as an actuator material, due to large strain (up to 300 %) and fast response time (up to 100 Hz). A major drawback is the high operating voltage which is in the range of $100 \text{ V}/\mu\text{m}$ [35]. While lower voltages are feasible, this reduces the strain significantly [36]. Furthermore, DEAs are difficult to integrate with MEMS and do not offer any more versatility compared to electrostatic actuators.
- **Ionic polymer-metal composites (IPMC):** Similar to DEAs, IPMCs sandwich an ionic polymer between two noble metal electrodes. They utilize low voltage to draw ions to one of the electrodes. This leads to a flow of water following the migration of ions. The material swells at this electrode, causing a bending of the composite. The strain is low compared to DEAs (1 %) and the response time moderate (1 Hz). However, lower voltages are necessary, which allow for better integration in microsystems [36].
- **Shape-memory alloys (SMA):** This type of actuator relies on a transition of crystallinity, usually stimulated by heat. SMAs can exhibit moderate strains (8 %), with large work density (up to 10^5 kJ/m^3) at moderate frequencies ($<5 \text{ Hz}$) [35]. Compatibility with microsystems has been demonstrated with nitinol (NiTi), showing the feasibility of large displacements even on small scales [37]. However, the process is very customized and has severe limitations by the crystallinity of the material. It is therefore difficult to integrate nitinol as a versatile actuator in microsystems.

- **Liquid crystal elastomers (LCE):** The material core to this work has demonstrated strains and work densities comparable to those of mammalian skeletal muscles [35]. Compared to the other actuator materials mentioned in this section, they stand out due to their compatibility with many microsystems processes, e. g. spin coating, lithography, metallization and dry etching [38, 39]. Furthermore, the programmability of actuation direction and stimuli-responsiveness to heat or light (Sec. 2.2.1) makes them an intriguing research subject for MEMS actuators.
- **Piezo-actuators:** In comparison to these soft matter actuators, piezoelectric actuators are orders of magnitude faster (actuation frequencies up to MHz) and stronger (working densities in the order of 1×10^6 kJ/m³). Even more, piezo-actuators have a low power consumption and exhibit long lifetimes, compared to polymeric actuators. These specifications make piezoelectric materials the most attractive actuator for small-scale robotic systems [40, 41]. However, compared to LCE actuators, they show only moderate strain (1 %) and are difficult to integrate in microsystems. Most importantly, piezo-actuators can not be aligned arbitrarily, due to their crystalline nature. Thus, they do not offer the flexibility for arbitrary actuation patterns, which is core to this work.

2.4 Demonstrations and limitations

The potential of utilizing LCEs as actuator material has been demonstrated by a variety of publications. Amongst the most notable demonstrations are a refreshable Braille display [42], a tunable iris [1], a tunable polymer lens [43] and a hybrid LCE-MEMS gripper [8].

While those examples show manifold applications of this soft matter actuator material, all of these suffer from a simple limitation, which is the slow response time in the order of tens of seconds up to minutes, impractical for any application. The limiting process is the heat flow through the LCE network which is necessary to trigger the phase transition. The low thermal conductivity of LCEs restricts the heat from spreading fast.

A variety of solutions to enhance the heat distribution or coupling has been demonstrated, as listed in Sec. 2.2.1. Yet, a further possibility to utilize the actuator is by miniaturization, since reduction in size reduces the heat capacity and therefore the necessary thermal power. This means microscopic LCE systems can be operated with response times useful for MEMS. This work demonstrates phase transition times in the order of 100 ms.

Thus, integration of LCEs shows promise as an actuator material for applications requiring unconventional actuation profiles and/or large strain at frequencies >1 Hz. Therefore, this

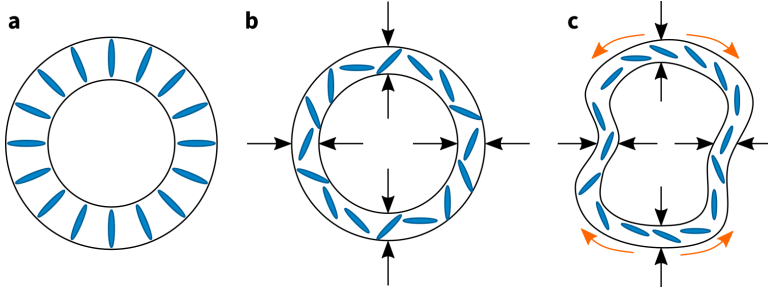


Figure 2.4 – Actuation of a radially aligned LCE ring: **a)** A ring of LCE material, where all the mesogens are pointing towards the center of the ring (radial alignment). **b)** Neglecting transverse strain, actuation (e. g. by heat) leads to axial strain in radial direction, thus shrinking the width of the ring. **c)** The transverse strain, due to volume conservation of LCEs, leads to an increase of the circumference of the ring, generating a mismatch between circumference and radius. This results in a loss of the ring shape, or in out-of-plane deformation in a constrained system.

work aims for the development of wafer-level processes to create enable the fabrication of integrated LCE actuators.

2.5 Programming radially actuating LCEs

One goal of this work is enabling a radially actuating system, in order to fabricate a miniaturized artificial iris mimicking the human iris.

The intuitive approach, followed by Schuhladen et al. in [1], is to align the mesogens in a radial pattern, all pointing towards the center of the iris, as illustrated in Fig. 2.4a. However, this line of thinking does not consider the expansion of the liquid crystalline material perpendicular to the contraction on actuation, thus imagining the deformation to be similar to Fig. 2.4b. In reality, LCEs feature a Poisson's ratio close to $\nu \approx 0.5$, leading to a positive transverse strain in response to the negative strain in axial direction [44]. For the case of radial alignment of the mesogens, this leads to an expansion of the circumference of the ring, which does not match the radius of the ring anymore.

For an unconstrained LCE ring, this would lead to a change of shape, similar to the illustration Fig. 2.4c. In the case of a constrained system, the elongation of the circumference of the ring would force the shape to go out of plane, which is undesirable in a tunable iris.

This issue can be solved by targeting a deformation, where the change in radius matches the change in circumference, thus preserving the ring shape. The following discussion, as

most of this work, is concerned only with the behavior of thin LCE films. This neglects the expansion in the third dimension, which is irrelevant for the actuation in this work, though it can also be used as the driving strain for applications [45].

To design truly radial LCE actuators, two core points have to be considered. (1) The determination of the ratio of radial and azimuthal deformation, and (2) the deformation with regard to mechanical constraints. Both topics are treated in the following sections.

2.5.1 Defining the alignment profile

The strain of an LCE structure depends on the alignment direction. An axial strain of ϵ_x , where x is the direction parallel to the mesogens, translates to a transverse strain of $\epsilon_y = -\nu\epsilon_x$, in a first-order approximation. The Poisson's ratio for LCEs is $\nu \approx 0.5$, similar to rubber [44]. LCEs achieve an axial strain of $\epsilon_x \approx -0.3$ on actuation. This leads to a transverse strain of $\epsilon_y = -\nu\epsilon_x \approx 0.15$. Publications in the field of LCEs sometimes use $\lambda = (1 - \epsilon_x)$ to denote the axial strain and $\epsilon_y = \lambda^{-\nu}$ for the transverse strain, calling ν the "opto-thermal" Poisson's ratio. For simplicity, this section uses the linear convention introduced above.

A unit circle of uniaxially aligned LCEs will thus deform to an ellipse with an axial (small) radius of 0.7, and a transverse (large) radius of 1.15. By choosing an axis with an angle to the alignment direction of the mesogens, the ratio between axial and transverse strain can be selected within the interval $[\epsilon_x/\epsilon_y, \epsilon_y/\epsilon_x]$.

Thus, by aligning the mesogens at a specific angle towards the radial direction, the deformation in radial and azimuthal direction can be matched. The mathematical function that describes a constant angle towards a radial axis is a *logarithmic spiral*, which can be described by

$$r = ae^{b\theta} = e^{-b\phi}e^{b\theta} = e^{b(\theta-\phi)}, \quad (2.1)$$

where $r(\theta)$ represents the spiral in polar coordinates. As illustrated in Fig. 2.5a, a logarithmic spiral can be characterized by its opening angle $\delta = \cot(b)$, and the offset angle ϕ . The plot highlights the constant angle δ against the tangent at any point of the curves, independent of r , θ , or ϕ [46].

Fig. 2.5 further offers different ways to illustrate logarithmic spirals: A variation of ϕ from 0° to 180° features logarithmic spirals with constant opening angle δ , that cover the full coordinate system (Fig. 2.5b). By calculating the angle of the tangent to the x -axis, the alignment angle α of the spirals against a common axis can be obtained and plotted in a cartesian coordinate system. (Fig. 2.5c). This two-dimensional distribution of alignment angles illustrates the spatial alignment distribution of the liquid crystals, which is necessary to achieve radial actuation. Fig. 2.5d shows a cross-section of this heat map along the x -axis

through the center of the logarithmic spiral. It highlights the exponential increase in distance between coordinates of the same angle from the center of the spiral.

In order to create truly radial actuation with LCEs, the alignment pattern thus has to follow a logarithmic spiral. The only parameter to select is the opening angle δ , which determines the ratio of axial and transverse strain. Mostajeran et al. derive

$$\delta = \arcsin \left(\sqrt{\frac{\lambda^{-2\nu} - \lambda^{1-\nu}}{\lambda^{-2\nu} - \lambda^2}} \right) \stackrel{\nu=0.5}{=} \arcsin \left(\sqrt{\frac{\sqrt{\lambda} - 1}{\lambda^3 - 1}} \right) \quad (2.2)$$

as opening angle for an LCE disk to stay flat on actuation [47], where $\lambda = 1 + \epsilon_x$ describes the relative size after contraction. Selecting a Poisson's ratio of $\nu = 0.5$, and a relative size of $\lambda = 0.7$ ($\epsilon_x = -0.3$), results in $\delta \approx 30^\circ$.

Siéfert and Warner worked with anisotropic, inflatable fabric sheets to macroscopically model LCE actuators [48]. They similarly worked out a logarithmic spiral solution depending on the axial strain. However, their model manages to obscure the Poisson's ratio of the material and only yields the same result as Eq. 2.2 under the assumption $\nu = 0$, which seems rather inconceivable. Their calculations result in an opening angle of $\delta(\lambda = 0.7) = 50^\circ$ for the inflatable fabric sheets, which they experimentally verified (see the impressive [supplementary videos](#)). Their experiments demonstrate larger opening angles leading to cone formation, whereas smaller angles result in anti-cones, i. e. saddle shapes.

To address the difference between these two publications, [47] and [48], a discussion of mechanical constraints is necessary.

2.5.2 Adding constraints

The change in radius of an LCE ring depends on how the ring is suspended. If the structure in Fig. 2.4a is attached on its outer edge (which would be the case for a tunable iris), the ring contracts outward on actuation, effectively increasing the radius. On the other hand, if the ring is attached on its inner edge, actuation pulls the ring inward, reducing the radius. Therefore, the desired alignment pattern (i. e. the opening angle of the logarithmic spiral) depends on the mechanical constraints of the ring structure.

The circular disks made of fabric sheets used in [48] are constrained on the inner edge by the material itself, thus the disk's diameter decreases on actuation. Similarly, the calculations in [47] are designed for an unconstrained LCE film which decreases in diameter on actuation. Therefore, neither of these two solutions will lead to a tunable iris with an increasing opening in the center. Correctly modelling this behavior was beyond the constraints of this project and has to be tackled by future research. Still, this work contributed to the tools to experimentally find the opening angle for in-plane radial actuation.

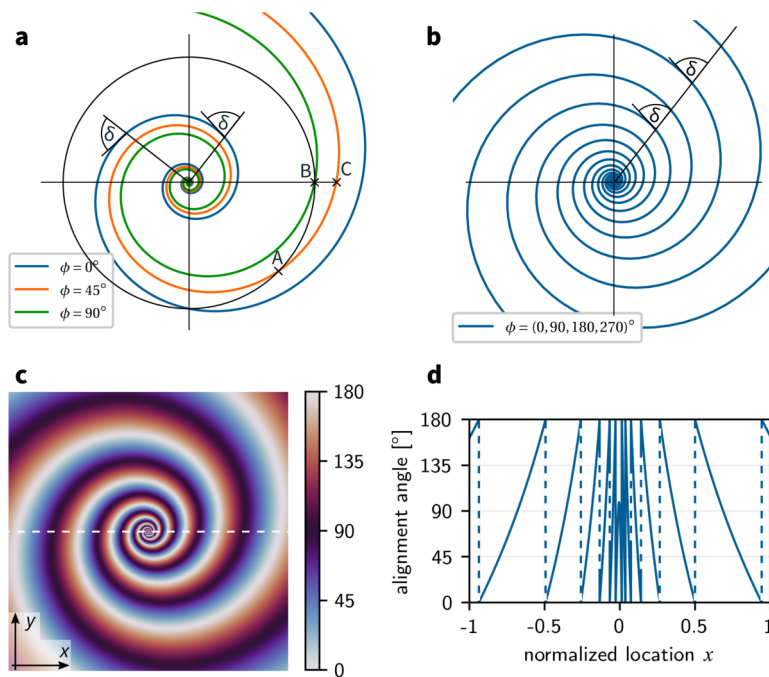


Figure 2.5 – Determination of a spatial logarithmic spiral distribution: **a)** Three logarithmic spirals with the same constant opening angle $\delta = 80^\circ$, and different offset angles ϕ . The points A and B are on a common circle (same r), while A and C are on a curve with constant ϕ . **b)** Logarithmic spirals cover the whole coordinate system, when varying offset angle ϕ from 0° to 360° . The opening angle δ is constant, independent of ϕ or r . **c)** When calculating the angle of such a logarithmic spiral against the x -axis, the spatial distribution of alignment angles α can be visualized by a heat map. Since the mesogens are symmetric with regard to a rotation by 180° , the angle was scaled by modulo 180° . **d)** The cross-section of this heat map, through the center of the spiral highlights the exponential increase in the distance between points having the same alignment angle from the center of the spiral.

3 Fabrication

It is this conformational transition, which can be visualized as a transition from raw spaghetti to cooked spaghetti, that we have exploited in our “muscle”.

– Li et al. [49]

3.1 Previously established processes

This work is a continuation of the PhD projects of Stefan Schuhladen and Sebastian Petsch at the Gisela and Erwin Sick Chair of Micro-optics. They explored the use of LCE actuators to create tunable, miniaturized optics. A tunable iris [1], a tunable elastomer lens [2], and an Alvarez lens [45] have been demonstrated. The tunable iris and lens were combined to design an imaging system mimicking the human eye [43]. These systems were tuned by some variation of an LCE actuator with embedded flexible heaters [17].

None of these applications were fabricated as a batch process on the wafer level. Instead, the LCE actuators were produced individually by a soft lithography step. The liquid crystalline material was cast in a PDMS form and the mesogens were aligned by a strong magnetic field. After polymerization, the molded LCE actuators were manually assembled with the optical components.

This process yielded two major benefits:

- The PDMS molds defining the shape of the LCE structure were fabricated by photolithography. Therefore, arbitrary 2D-shapes of LCE actuators could be produced. Specifically, linear and ring actuators were thus fabricated.
- Microsystems-processed, flexible heaters were integrated into the mold before polymerization of the liquid crystals. This enabled efficient heat coupling into the LCE actuator and simple control through electrical power.

Based on this technology, the above mentioned applications of LCE actuators have been demonstrated. However, the tunable iris and lens both suffered from long actuation times of >20 s. Furthermore, the assembly involved many manual steps and custom-tailored equipment.

One possibility to reduce the response time is further miniaturization (Sec. 2.2.1) by integration into microsystems. This requires a fundamental change of the fabrication procedure since neither manual steps nor magnetic alignment are feasible on the wafer level.

Outside our laboratory, not much research has been dedicated to harnessing the large strain of LCEs for MEMS. The first publication of an integrated LCE actuator demonstrated structuring and actuation of a micro-gripper [8]. However, the process still involved manual assembly steps and required huge magnetic fields.

Ditter et al. demonstrated both alignment and structuring of LCEs on substrate level [39]. However, the structuring relied on the photolithography with a very specific fluorinated resist, which is not easily available. Additionally, they presented only uniaxial alignment, i. e. all mesogens were aligned in the same direction on the substrate. Other publications have demonstrated structuring by lithography [50] and integration of metal heaters [9]. These demonstrations similarly relied on manual assembly steps and only used uniaxial alignment.

Thus far, no usable integration of LCE actuators for microsystems has been demonstrated. Nor is there a process to arbitrarily align and structure LCEs on a wafer level to create MEMS actuators. The following sections discuss the development of a flexible process to fill this gap. Parts of this process were utilized for the first demonstration of an LCE-driven tunable Fabry-Pérot filter [51], which shows the compatibility with other microsystems processes.

3.2 Overview

A variety of processes is necessary to fabricate integrated LCE micro-actuators. While LCE research relies on individually produced LCE stripes, MEMS processing requires processes that can be used on the wafer level, compatible with other MEMS materials. To this end, the following processes were developed in this work:

- **Deposition:** The LCE material needs to be coated as a reasonably thin film over the whole substrate.
- **Alignment:** The actuation direction is determined by the alignment of the LCE mesogens. Therefore, the alignment direction needs to be programmed spatially for the desired actuation direction.
- **Structuring:** To define the shape of the micro-actuators, the LCE film needs to be structured on the wafer level.
- **Actuation:** The deformation of the utilized LCE materials is triggered by heat. Therefore, schemes to efficiently couple heat into the material need to be devised.

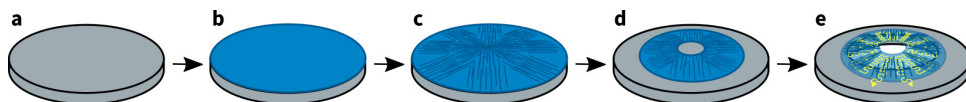


Figure 3.1 – Process steps towards integrated LCE actuators: To create an LCE micro-iris on the wafer level (a), the material needs to be deposited on the substrate (b), and the mesogens need to be aligned to enable the desired actuation, e. g. radial actuation (c). The material can then be structured to form an iris-shaped actuator (d). Furthermore, metal heater structures can be integrated to trigger the actuation. Also, partial release of the structure is necessary for free movement (e).

A simplified process flow to fabricate a micro-iris on the wafer level is illustrated in Fig. 3.1. It already hints at the major challenges, defining the alignment of the mesogens spatially and partially releasing the material from the substrate. The individual process steps and decisions are discussed in detail in the following chapters.

The mainly used liquid crystalline material, RM257, was purchased from Synthon Chemicals Ltd. The side-chain monomer, 4-ADBB, was synthesized according to literature by David Ditter, University of Mainz [18, 39]. Irgacure 784 was purchased from ABCR Ltd. HDDA, DPO and the utilized solvents were obtained from Sigma Aldrich.

3.3 Deposition of liquid crystalline films

The material needs to be homogeneously coated on the substrate, contrary to the traditional method of fabricating LCE actuators in PDMS molds or glass cells. The spin coating process has been demonstrated to work well to that end [39, 52]. The reactive mesogens are dissolved in a solvent, spun onto the substrate, and then polymerized to create the elastomeric film.

Spin coating has been used for optical applications of liquid crystal polymer films, like geometric phase plates [53, 54]. Still, many parameters were tuned in this work to optimize the process for integrated actuators. The reactive mesogens introduced in Sec. 2.1 were tested in a variety of solvents, at different concentrations and spin speeds. The goals were to achieve consistent control over the layer thickness, homogeneous layers, and compatibility with the alignment procedure employed for wafer-level alignment of the mesogens.

3.4 Alignment of mesogens

One of the outstanding properties of LCEs as actuator material is the ability to define the actuation spatially by programming the alignment direction spatially. This is one of the

major challenges of the project, requiring a process to define arbitrary spatial alignment patterns of mesogens on the wafer level, with sufficient resolution.

As an example, fabricating micro-irises would require multiple spatial alignment patterns, which enable radial actuation, on a single substrate. The dimensions for such an iris would be in the order of $10 \times 10 \text{ mm}^2$. The programming of the alignment direction should then feature a spatial resolution in the order of $10 \mu\text{m}$ to enable a reasonably continuous actuation process.

The process of using a radial magnetic field employed by Stefan Schuhladen [1] is hardly scalable to these small dimensions, especially if multiple of these patterns are to be fabricated on one substrate. Likewise, the traditional process of creating small scratches in a soft material by rubbing with a velvet cloth to align the mesogens cannot be used to create arbitrary alignment patterns with the required resolution.

One option to define arbitrary alignments is the creation of micro-grooves that induce alignment of the mesogens parallel to the grooves. Photolithography can be utilized to fabricate such groove patterns for the alignment of LCs [55]. However, the resolution of these patterns needs to be about two orders of magnitude smaller than the desired alignment resolution of $10 \mu\text{m}$. To obtain such sub-micron resolution of alignment grooves, nano-imprint lithography has been demonstrated, with a stamp fabricated by two-photon polymerization. This enabled a line period of 600 nm and a groove depth of 100 nm [56]. A similar process employing nonlinear laser lithography created periodic grooves with a period of 920 nm and depths of 225 nm [57].

These processes demonstrate the definition of the spatial alignment distribution of mesogens with extremely high resolution. However, they rely on the fabrication of structured stamps with specific machines. Whenever a change in the alignment pattern is desired, a new stamp needs to be fabricated. Producing micro-grooves to align LCs is thus a reasonable method for batch processing, though not for prototyping.

A further technique that allows for the desired resolution of alignment is *photoalignment*, i. e. the alignment of the mesogens by light. Specifically, this work utilizes the polarization of light to program the alignment direction. However, since the utilized LCE materials themselves can not be aligned by this technique, the introduction of a so-called *command layer* is necessary. Thus, the general process from Sec. 3.2 has to be expanded to the following steps: (1) A photoalignment layer is deposited by spin coating. (2) The anisotropy of this layer is defined by illumination with spatially defined polarization of light. (3) The LCE material is spin coated on top of the photoalignment layer, the mesogens following the programmed anisotropy.

In literature, this method has been applied to align LCs and LCEs with arbitrary spatial patterns, mostly for optical applications [58] but also for LCE actuators [5]. However, this is the first work scaling photoalignment to a full 100 mm wafer. The process thus enables

prototyping of arbitrary spatial alignment profiles for microsystems applications. The prize for this is the introduction of two more processing steps, the deposition and the alignment of the command layer. Furthermore, the process adds one more layer (with a thickness in the nanometer range) beneath the LCE structures. This can be either an obstacle for further processes or a benefit when using the command layer as a sacrificial layer to release the actuators [59].

3.5 Structuring of actuators

Having an LCE layer with defined alignment, the shape of the actuators needs to be defined. The straightforward process for this is a combination of photolithography and dry etching.

Ditter et al. demonstrated a system of chemical orthogonality [60]: By employing a fluorinated resist, developer, and stripper, chemical interactions with the LCE film were avoided. Dry etching of the LCE was achieved in an oxygen plasma [39]. This chemistry is advantageous over standard photoresists due to the avoidance of swelling of the LCE. However, these fluorinated chemicals are not easily available and still under development.

Rihani et al. showed a more general approach, using a structured silicon nitride mask to fabricate LCE stripes with dry etching [50]. This process demonstrates the feasibility of structuring LCEs by standard cleanroom processes and materials. However, it requires additional process steps by depositing and structuring silicon nitride as a mask.

A simplified process was demonstrated by Akdeniz and Bukusoglu, who directly used the chemistry of the liquid crystalline material to structure the LCE film [61]. Since the LC mesogens are crosslinked by UV light, they can directly be selectively polymerized by illuminating the film through a mask and dissolving the unpolymerized parts. The process is thus simplified since neither a photoresist nor a dry etching step is necessary. McCracken et al. used this process to directly polymerize LCE structures by two-photon direct laser writing [62].

This work employed two approaches to structure the LCE film into the desired actuator shapes:

- **Photolithography and dry etching:** An off-the-shelf photoresist was used as a mask to structure the LCE film in an oxygen plasma. This allows for integration in any standard cleanroom process. The process is detailed in [Sec. 7.2](#).
- **Maskless lithography:** The projection system developed for photoalignment ([Chapter 5](#)) was employed to selectively polymerize the LCE film. The unpolymerized parts could then be dissolved in a solvent. Contrary to the standard photolithography process, no photoresist and dry etching steps are necessary, as demonstrated in [Sec. 7.3](#).

3.6 Integration of actuation mechanism

The processes thus far yield integrated LCE structures with defined alignment and structure. To use these as actuators, a mechanism to stimulate the phase transition of the LCE is necessary. The transition from nematic to isotropic is commonly triggered by applying heat (*thermal actuation*), though specific LCE materials that undergo a phase transition on isomerization by light (*photochemical actuation*) have been demonstrated [63].

The heat needs to be applied and distributed quickly through the whole LCE structure to enable a fast and complete phase transition. Various schemes to couple and spread heat efficiently have been proposed: Liquid metals [24] or conductive particles (graphene [25], carbon nanotubes [64]) in the LCE network enable efficient resistive heating of the actuator.

Furthermore, light-absorbing materials can be doped into the LCE film to convert light into heat (*photothermal actuation*). This enables versatile stimulation of the actuation by controlling the wavelength, intensity, and spatial distribution of the illumination, while also not requiring further structures. For example, azobenzenes [65], carbon nanotubes [66], or gold nanoparticles [32] were demonstrated as suitable candidates for photothermal actuation.

Photothermal actuation has some intriguing features like localized control and wavelength-selectivity. On the other hand, control by resistive heating is better compatible with microsystems. Due to the low thermal mass of the micro-actuators, resistive heating by an embedded metal structure is sufficiently fast to enable sub-second time constants. Therefore, this work targets the integration of flexible platinum heater structures underneath the LCE film, as a scaled-down version of the groundwork by Sebastian Petsch [17].

The metal heaters are fabricated by evaporation, photolithography, and a lift-off process, before depositing the LCE film. They are shaped as meanders to enable deformation of the heater with the contracting LCE actuator.

3.7 Anchoring and releasing actuators

Locally suspending and freeing the LCE actuators are major challenges of the fabrication process. The structures need to be anchored to the substrate in specific places. Where movement is intended, the actuators need to be released from the substrate with sufficient spacing to allow for free deformation.

There is barely any literature dealing with this challenge. Most demonstrations of actuation are either on LCE stripes that are held hanging by a clamp with a weight attached or by simply heating the LCEs in a bath of silicone oil without constraints. Rare demonstrations of LCE actuators as part of a system are manually assembled and glued for anchoring. A

prominent exception is the work of Petsch and Schuhladen [43], which did embed the anchoring structures during the fabrication process of the LCE actuators.

Still, no publication achieved both localized anchoring and release which is scalable to a wafer-level process. Fortunately, microsystems technology offers processes to achieve local release of structures. For example, structuring of a sacrificial layer or etching from the backside can be used to that end.

Dextran and poly(acrylic acid) have been utilized as water-soluble sacrificial layers [67], compatible with LCE fabrication on substrate level [39]. However, the thickness of these sacrificial layers is only in the range of up to a few micrometers, which creates a gap that is too small to fully release the LCE actuators. Dextran and the photoalignment layer (Brilliant Yellow) were used in this work to release full LCE films from the substrate, to investigate free actuation without constraints [68].

A process involving backside etching was contrived in order to create enough space beneath the LCE actuators. The process targeted fabrication of aligned and structured LCE actuators on the front side with the previously discussed processes. Subsequent etching through a mask from the backside is to be utilized to locally release the LCE structures. At the time of writing, this process is still in an experimental stage.

3.8 Main focus of the fabrication

This chapter gave an overview of the utilized fabrication steps, process choices and state of the art of each process with regard to LCE actuators. In the following chapters, these processes and respective achievements within this project will be discussed in detail.

The emphasis, however, is on photoalignment of liquid crystals. Within the boundaries of this project, photoalignment was identified as the key technology to define the actuation direction of LCEs on a wafer level. The programmability of arbitrary alignment patterns is the most significant feature of LCEs. Therefore, the core chapters of this work deal with photoalignment of liquid crystals ([Chapter 5](#)) and subsequent characterization of the alignment ([Chapter 6](#)).

Further emphasis on the actuation of free-standing LCE structures would be appropriate. However, at the time of writing, this is still an ongoing process.

4 Deposition

Using this type of print path, the LCEA transforms into a cone with a maximum height of 6.5 mm when heated above T_{NI} , which corresponds to a 1628 % stroke out-of-plane.

– Kotikian et al. [69]

4.1 Techniques

Fabrication of LCE actuators starts with dispensing the material onto the substrate. However, the alignment of the mesogens cannot be decoupled from the dispensing process. Therefore, any deposition method needs to consider a way to also align the liquid crystals.

The dominating method to create LCE actuators is the fabrication in thin glass cells. The melted liquid crystalline material is pulled into the gap between two parallel glass slides by capillary forces. The alignment of the liquid crystals is induced by thin alignment layers on the two glass slides, often unidirectionally rubbed layers of polyimide or polyvinyl alcohol.

A different approach is soft lithography, where the actuators are shaped by filling a mold, that is often made from PDMS, see e. g. [17]. For this method, alignment can be defined with strong magnetic fields, which severely limits the feasible actuation profiles.

The availability of 3D printers has led to a new process which is often called *4D printing*: The shear forces of the flow of the material align the liquid crystals along the flow direction. Therefore, 3D-printing of LCE material can be used to define the structure of LCE actuators, while simultaneously defining the material's anisotropy by setting the printing direction [3].

Thus, a variety of methods to fabricate freeform LCE actuators exist. However, none of these techniques allows for wafer-level integration in microsystems processing. To fabricate liquid crystalline films on substrates, spin coating has been demonstrated successfully [52]. At the same time, to achieve arbitrary alignment patterns, the only feasible method is photoalignment, as discussed in [Chapter 5](#). This requires the spin coating of a photoalignment layer before depositing the LCE film [70].

While spin coating of LCEs is already well-established for optical applications, this work took it one step further by scaling it to 100 mm substrates. Furthermore, the compatibility of

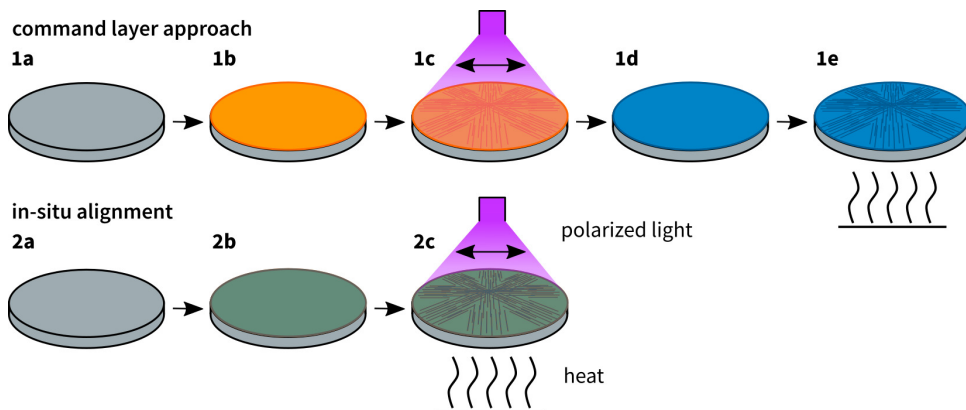


Figure 4.1 – Deposition and alignment of LCEs: In the command layer approach (1a-1e), the command layer (orange) is first spin coated and then photoaligned by linearly polarized light. In another spin coating step, the reactive mesogens (blue) are deposited. Supported by an annealing step, they follow the alignment of the command layer. The in situ alignment process (2a-2c) only requires one spin coating step of a mixture of photoalignment material and reactive mesogens. The photoalignment is then performed on the heated film. In both processes, the liquid crystal film is polymerized by UV light as a last step.

a wide range of solvents with the photoalignment layer was tested and the relation between concentration and thickness was evaluated.

4.2 Deposition process

This work is based on the command-soldier approach for photoalignment [71]. As illustrated in Fig. 4.1(1a-1e), a so-called command layer is spin coated and aligned by linearly polarized light, before spin coating the liquid crystal film. On heating the LCs up to the nematic phase, they follow the alignment of the command layer, like soldiers.

This command layer approach has been widely adopted and yields sufficient alignment quality even for optical applications. However, recent research has demonstrated the feasibility of defining the alignment of liquid crystal mesogens *after* depositing them [72–74]. Inspired by these publications, this work combined spin coating of photoalignment material and liquid crystals in one step. As illustrated in Fig. 4.1(2a-2c), this requires only one spin coating step, but at the cost of heating the film during photoalignment.

At the end of both deposition processes [Fig. 4.1\(1e/2c\)](#), the liquid crystal layers are polymerized by a radical polymerization, initiated by UV light in an inert (oxygen-poor) atmosphere.

4.3 Results

4.3.1 Solvents

Commonly used solvents for liquid crystals are Toluene, Tetrahydrofuran (THF), Chloroform, Propylene glycol methyl ether acetate (PGMEA), Xylene and Dioxane. Further experiments revealed, that also Dimethyl sulfoxide (DMSO), Dimethylformamide (DMF), Dichloromethane, N-Methylpyrrolidone (NMP), Tetramethylurea (TMU), and γ -Butyrolactone are good at dissolving the utilized reactive mesogen RM257, i. e. the liquid crystal material in its non-polymerized state. Of the common cleaning solvents, only Acetone dissolves RM257 well, Isopropanol forms a colloidal solution, and Ethanol and water do not dissolve the reactive mesogens at all.

Most notable, Chloroform, Dichloromethane, Toluene, Xylene and PGMEA do not dissolve Brilliant Yellow, the material that is utilized as photoalignment layer in this work. This yields a large selection of possible solvents to spin coat liquid crystals on top of a Brilliant Yellow photoalignment layer.

Another usable finding are the solvents that are able to dissolve both liquid crystals and Brilliant Yellow: DMF, DMSO, TMU, and NMP. The latter was dropped from further experimentation due to its high toxicity. While these solvents cannot be used to coat liquid crystals on top of the photoalignment layer, they enable mixing Brilliant Yellow and RM257 in one solvent. DMF, DMSO and TMU were thus evaluated to achieve in situ photoalignment, i. e. the deposition of photoalignment layer and liquid crystals in one step ([Sec. 4.3.4](#)).

4.3.2 Thickness and homogeneity

Spin coating is generally considered to be a well-controlled process to deposit homogeneous layers on a wafer. The main parameters influencing the thickness of the coated layers are the rotation speed and the concentration of the material in the solvent, as well as the properties of the solvent [\[75\]](#).

This work found that the choice of solvent has a profound influence not only on the thickness, but also on the quality and homogeneity of the spin coated liquid crystalline layer. Depending on the intended thickness, different solvents seem recommendable.

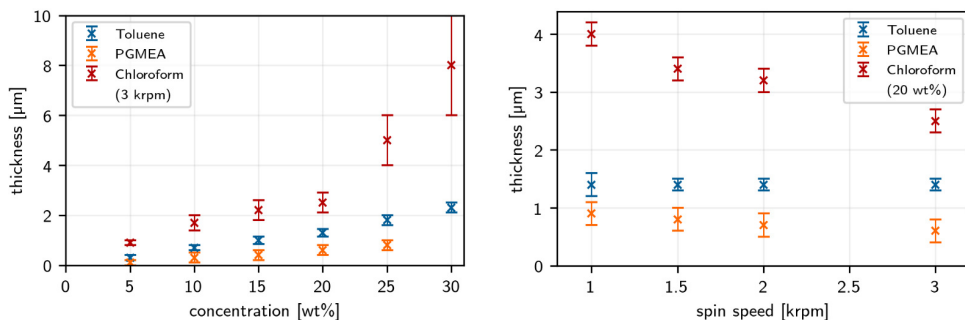


Figure 4.2 – Thickness vs. concentration, spin speed and solvent: The LCE layer thickness (measured by white light interferometry) increases with concentration, and decreases with increasing spin speed. The roughness of the films increases with the concentration and with decreasing spin speed. Chloroform yields thicker layers than Toluene and PGMEA, but also larger roughness.

For thin films up to $2.3\ \mu\text{m}$, Toluene and PGMEA yield very homogeneous layers. Surprisingly, the thickness of layers spin coated with Toluene appears to be independent of the spin speed (within the range of 1000 rpm to 4000 rpm), only influenced by the concentration (Fig. 4.2). This result has been confirmed by multiple experiments. It was found that the spin speed influences the film thickness only at spin speeds lower than 1000 rpm. Thus, the layer thickness is limited by how much RM257 can be dissolved in the solvent. Toluene allows concentrations of up to 30 wt% RM257, PGMEA dissolves up to 25 wt% RM257.

Thicker films can be obtained by using Chloroform as a solvent (Fig. 4.2), with concentrations of up to 30 wt% RM257. However, spin coating at such high concentrations leads to large holes in the film (see Fig. 4.3d). Yet, layers with a thickness up to $8\ \mu\text{m}$ could be spin coated in a single step with Chloroform. However, the layer is highly inhomogeneous, with holes that reach down to substrate level and peaks that reach a layer thickness of $13\ \mu\text{m}$.

Coating multiple layers with Toluene is another possibility to increase the film thickness. This process was shown to yield sufficient quality even for optical applications [70, 76]. However, replication of these studies proved difficult. In the experiments, the second layer would drip off the hydrophobic surface of the first coating. Even the use of a surfactant (2-(N-ethylperfluorooctanesulfonamide) ethyl methacrylate) did not help to improve the adhesion of a second coating. Further experiments revealed the surface to become hydrophobic, due to an annealing step after coating the first layer. Omitting the annealing step, subsequent layers could be coated onto the polymerized layers.

The deposition process could thus be optimized in dependence of the intended layer thickness. For single layer coatings, the process consisted of (1) spin coating the liquid

crystals in a solvent, (2) annealing the substrate which was found to improve the alignment quality, and (3) radical polymerization initiated by UV light in an oxygen-poor environment. For thick films, multilayers were coated by alternating spin coating and polymerization, without any intermediate annealing steps.

4.3.3 Defects and limitations

The experimental results of this work show that spin coating of liquid crystals is a promising road to integrated LCE actuators. However, a variety of pitfalls was found that add some constraints to the process.

Fig. 4.3 shows a comparison of a successfully aligned film with the most common processing errors, all between crossed polarizers: As an example, Fig. 4.3a shows a nicely aligned logarithmic spiral pattern, with minor stitching errors and small defects due to particles.

A common occurrence are so-called Schlieren patterns, shown in Fig. 4.3b. They are visible, when the liquid crystals do not follow a specific alignment direction. The black lines indicate domain interfaces of different alignments, highlighting the microscopic anisotropy that averages out macroscopically. Observing Schlieren patterns with this spin coating process reveals that the photoalignment procedure did not work. Often this was because the humidity was too high, impeding the alignment of the Brilliant Yellow molecules.

More specific errors are shown in Fig. 4.3c/d: If the polymerization of the reactive mesogens did not proceed, the liquid crystals would reorient to form fascinating crystalline structures, which are typical for some smectic phases, like in Fig. 4.3c. The reason for incomplete polymerization was mostly the presence of oxygen during the radical polymerization, where the oxygen molecules would themselves radicalize and stop the chain reaction. Thus, it is important to polymerize the LC films in an inert atmosphere, e. g. in a nitrogen environment.

Finally, one issue that remains puzzling are the defects shown in Fig. 4.3d, the dark spots of various sizes. This sample was created by spin coating with a high concentration (33 wt%) of RM257 in Toluene. The colors are due to large layer thickness which leads to interference effects. The black spots appear presumably because of undissolved reactive mesogen clusters. However, even filtering, stirring or ultrasound-mixing the solution did not reduce the number or size of the defects. It seems that the solution oversaturates in the moment of dispensing, presumably due to evaporation of the solvent.

Therefore, high concentrations of reactive mesogens for spin coating do not lead to usable LCE films. What is considered *high concentration* depends on the solvent: For Toluene and Chloroform 20 wt%, for PGMEA 15 wt% yield reasonably defect-poor layers. Since the densities vary a lot, the volumetric concentrations are quite different.

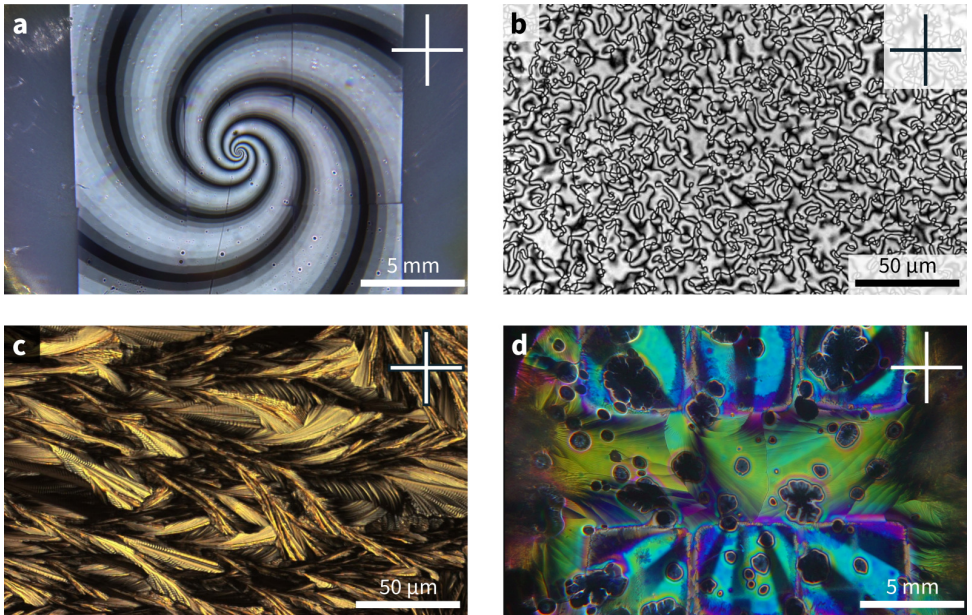


Figure 4.3 – Demonstrations of LC films and defects: All images captured with the sample between crossed polarizers. **a)** A successfully aligned LC film featuring a logarithmic spiral pattern. **b)** Schlieren patterns of an unaligned film. **c)** Self-assembled crystalline phase due to missing polymerization of the LC film. **d)** Thick film created by large concentration of reactive mesogens, leading to many defects. Scale bars are non-uniform, **b)** and **c)** were captured with a 5x objective.

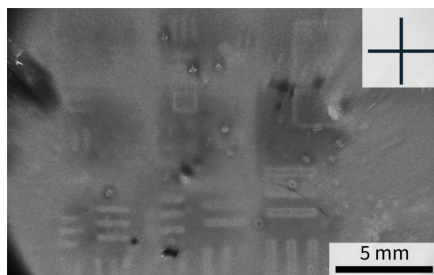


Figure 4.4 – Demonstration of in situ photoalignment: Between crossed polarizers, the photo-aligned USAF target pattern is clearly visible. However, the film shows low contrast at the edges of the stitching from the photoalignment system.

4.3.4 In situ photoalignment

As mentioned above, the solvents DMSO, DMF and TMU could be utilized to dissolve both Brilliant Yellow and RM257. This enabled in situ alignment, i. e. spin coating of photoalignment material and reactive mesogens in one step (Fig. 4.1). Experiments revealed coatings with DMSO to be extremely inhomogeneous. Therefore, a mixture of Brilliant Yellow and RM257 in DMF was utilized for in situ photoalignment.

A solution of 20 wt% RM257 and 3 wt% BY in DMF was prepared. The mixture was spin coated at 3000 rpm onto glass substrates. The substrates were then mounted on a custom-built hot stage inside the photoalignment system. While in a heated state (65 °C), polarized blue light was used to align the BY molecules which in turn triggered the alignment of liquid crystals. After the procedure, the liquid crystal film was polymerized.

The resulting film of such an in situ alignment process is shown in Fig. 4.4 between crossed polarizers. A USAF target was used as a mask for photoalignment in two steps, at 0° and 45°. The target was stitched in 3 × 3 squares. The resulting birefringence Fig. 4.4 shows good alignment of the liquid crystals in the center of each square, while the edges mostly feature unaligned Schlieren textures.

These results show that larger exposure doses are necessary for in situ alignment than for only aligning the command layer, roughly by a factor of ten. Furthermore, the smallest recognizable structures are the lines in the center which have a width of 250 μm. Since these are washed out, the spatial resolution of the in situ alignment is in the order of 500 μm, almost two orders of magnitude larger than the resolution of the imaging system.

Thus, this work demonstrates for the first time in situ photoalignment of arbitrary alignment patterns. In comparison to the classic process utilized throughout the rest of this

work, it requires one less spin coating step, at the price of decreased spatial resolution of the photoalignment. Furthermore, the custom-built hot stage and temperature control system add further complexity to the setup. Hence, in situ photoalignment only saves time for simple spatial alignment patterns, like unidirectional alignment. Working with a separate photoalignment layer enables more elaborate alignment patterns and facilitates troubleshooting.

5 Photoalignment

Photopolymerizable, photoisomerizable, photodimerizable and photoluminescent dichroic chromophores are deliberately designed and used for comprehending the sequential realization of the polyimide-free in situ photoalignment of liquid crystals (LCs).

– Nasrollahi et al. [74]

The work presented in this chapter was carried out in part as the master thesis of Sanket B. Shah, defended 12/2018. Specifically, Sanket contributed significantly to the design decisions, the optomechanical assembly and the environment control.

5.1 Principle of operation

The generation of molecular anisotropy through exposure to light is called *photoalignment*. The anisotropy is usually defined by the polarization of light [77], though alignment by modulation of the light intensity has also been demonstrated [78].

In most cases, the liquid crystal material cannot be photoaligned directly, since it is optimized for its respective application and does not feature the necessary properties for photoalignment. Therefore, a thin film of photoalignable material is used as a so-called *command layer*. This film subsequently induces the alignment of the liquid crystal mesogens, as illustrated in (Fig. 5.1) [79].

There are two major principles of photoalignment by polarized light, both working on the molecular level. The first is based on an anisotropic chemical reaction, the second on linear dichroism, i. e. the dependence of the absorption of light on the polarization exhibited by certain materials [80].

With the first photoalignment principle, the anisotropy is generated through a polarization-sensitive chemical reaction. This process results in crosslinking in only the direction parallel to the polarization. The chemical reaction is usually irreversible and leads to very stable alignment which is not rewritable, i. e. the anisotropy cannot be changed again to a different direction.

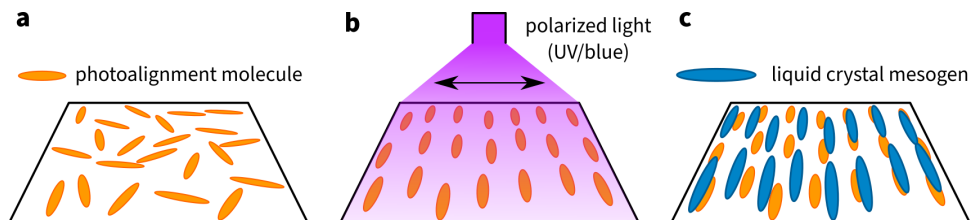


Figure 5.1 – Principle of photoalignment with a command layer: **a)** A thin film of photoalignment material (orange) is dispensed on a substrate. At first, the alignment of the molecules is isotropic. **b)** Exposure to linearly polarized light leads to anisotropic alignment of the molecules. **c)** The mesogens of the subsequently dispensed liquid crystal layer (blue) then follow the alignment of the command layer.

The materials used for this are usually cinnamates which can dimerize anisotropically when exposed to linearly polarized light with a wavelength in the UVB region, i. e. around 300 nm [81].

The second photoalignment principle enables the alignment of molecules by polarization-selective isomerization. Elongated molecules that are parallel to the polarization of incident light undergo a reversible trans-cis isomerization on absorption, kinking the molecule. After returning to the energetically lower trans-state, the molecule has undergone a statistical rotation. If this rotation leaves it perpendicular to the polarization of light, the molecule does not absorb and isomerize again. Molecules which are oriented differently will repeatedly absorb, isomerize and rotate. Hence, after multiple isomerization cycles, the majority of the molecules are aligned perpendicular to the polarization of incident light.

Since the isomerization process is fully reversible, the alignment can be changed again by setting a different polarization of light, enabling rewritability. Azobenzenes are the established material for photoalignment based on trans-cis isomerism, specifically azo dyes featuring two azo groups and an elongated molecular structure. One major advantage of using azo dyes is their absorption wavelength in the visible to UVA range, which is more compatible with optical systems than the UVB for photoaligning cinnamates [82].

By structuring the polarization of light, photoalignment thus allows arbitrary alignment patterns of a command layer. The liquid crystal mesogens follow the alignment of the command layer. This process enables decoupling the alignment of the LC film from the other fabrication steps, allowing for more flexibility with regard to the chemical composition and the processing of the LC film.

5.2 Design choices

5.2.1 Constraints

To align liquid crystal elastomers for MEMS applications, the following requirements need to be fulfilled:

- Arbitrary alignment with a spatial resolution near the smallest feature size (1 μm), angular resolution in the order of 1° ;
- Alignment on the wafer level (diameter 100 mm);
- Compatibility with cleanroom processing, i. e. dust protection and tolerance to heating steps.

For this work, further constraints are flexibility regarding the photoalignment wavelength, and environment control (temperature, humidity) to increase the parameter space for optimization of the system.

5.2.2 Materials

One of the fundamental design choices is the photoalignment material. It defines the wavelength for which the optical setup needs to be optimized.

Some companies offer designated photoalignment materials: Rolic Technologies Ltd. has a product line called *LPP/ROP materials*, which is based on a polarization-selective chemical reaction on exposure to UVB light [83]. Furthermore, BEAM Co. offers their *PAAD* series [84], and DIC Corporation offers the sulfonic azo dye *SD1* [85], both of which are based on reversible trans-cis isomerism on exposure to UVA or blue light.

While some of these materials are frequently used in scientific publications (especially SD1), they are not easily affordable, object to restrictive non-disclosure agreements, and not equally available to all researchers. For these reasons, a lot of public research has focused on using widely available azo dyes that feature trans-cis isomerism at a convenient wavelength with the capability to align liquid crystal mesogens.

The azo dye *Brilliant Yellow* (BY) turned out to be a gem in the field of photoalignment [86]. While commercially available and affordable, it has been shown to yield sufficient alignment quality even for optical applications [54]. At the same time, BY is compatible with many liquid crystalline materials and can be aligned with blue light. Fig. 5.2 displays the molecular structure and the normalized absorption spectrum of BY, measured with a UV-Vis spectrophotometer (Agilent Cary 60).

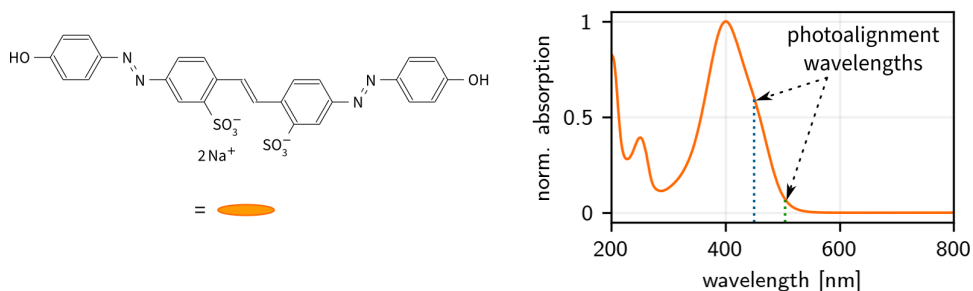


Figure 5.2 – Molecular structure and absorption spectrum of Brilliant Yellow: Brilliant Yellow shows an elongated molecular structure (left) with two azo bonds that show a large absorption peak around 400 nm (right). In this work, photoalignment is demonstrated at 450 nm and 505 nm, indicated by the dotted lines.

A prominent property of BY is that the trans-cis and the cis-trans absorption peak are very close together, with significant overlap, forming a single peak. To effectively rotate the molecules, the photoalignment process needs to continuously trigger both trans-cis and cis-trans isomerization. Thus, the wavelength needs to be selected to fit both absorption bands. Previous research demonstrated alignment in the range of 435 nm to 488 nm, indicating a sizable overlap of the two absorption bands in this region. Therefore, a 450 nm high-power LED was selected as the light source for this work.

Despite its outstanding photoalignment properties, it has been shown that the alignment quality of BY highly depends on the relative humidity at various stages of the process [87, 88]. This dependency adds to the constraints the need to control the humidity during the photoalignment process.

Hence, for this work, Brilliant Yellow was selected as main command layer for its prominent photoalignment properties; its alignment wavelength range, which is convenient for optical systems; its availability, affordability, and compatibility with our integrated process.

As alternatives for BY, similar azo dyes were tested as well, to obtain more flexibility with regard to wavelength and humidity (see Sec. 5.6).

5.2.3 Optical system

For arbitrary photoalignment patterns, it is necessary to flexibly modulate the polarization of light with a high spatial resolution. The smallest feasible structure size of LCEs with photolithography based on foil masks is 10 μm [68]. To be close to this structure size, a

minimum spatial alignment resolution of $10\text{ }\mu\text{m}$ was targeted. Since this should be achieved over a full 100 mm wafer, photoalignment of more than 70 million pixels is required.

While this could be achieved with a laser in combination with a rotating half-wave plate, the timescale of such a single-point exposure would be inconveniently large. Therefore, a projection system is necessary, which can align a certain area in one exposure.

An obvious choice to modulate the polarization arbitrarily with a projection system is a phase-modulating spatial light modulator (SLM), which can set the polarization of all its pixels simultaneously. However, phase-modulating SLMs are based on liquid crystals and do not work well with UV light. Since this work aims at maximum flexibility for photoalignment, it was designed to also work for UV light. Hence, a digital micromirror device (DMD), in combination with a rotating polarizer, was selected as the modulator for the polarization. As a further upside, DMDs are easily available from used projectors.

Even projection systems do not feature enough pixels to photoalign a full wafer at once. Thus, a stitching process was utilized in this work, aligning the wafer in multiple steps.

Hence, the optical system is designed around projecting patterns through a polarizer on a specific area of the wafer. After exposure, the wafer is moved and the next region is exposed. This is detailed further in [Sec. 5.4](#).

5.2.4 Previously demonstrated photoalignment systems

Scientific literature already features some projection systems for photoalignment, which inspired the one in this work. Culbreath et al. demonstrated one of the earliest such systems in 2011 [89]. Their setup utilizes a DMD to project patterns with a resolution of $2.2\text{ }\mu\text{m}$ over an area of $2 \times 2\text{ mm}^2$. Furthermore, they added an autofocus mechanism to their system. Similar DMD-based systems with slightly lower resolution were presented in [90, 91]. These systems show impressive results and high spatial photoalignment resolution. However, none of them is capable of aligning full 100 mm wafers, as demonstrated in this work.

While DMDs enable photoalignment in multiple exposure steps, phase-modulating SLMs can be used to align the whole projection area in a single step, as demonstrated in [92–94].

The afore-mentioned systems were solely utilized to create optical demonstrators. Only few applications for programming actuators have been shown. Wani et al. designed a photoalignment system with a scanning laser that was able to program the alignment with a resolution of $50\text{ }\mu\text{m}$. They fabricated an impressive 4-armed LCE gripper that could be actuated by light [95]. Furthermore, Boothby et al. describe a simplified projection setup (resolution $30\text{ }\mu\text{m}$) to obtain macroscopic LCE stripes with various actuation modes [96].

While the state of the art is admirable, this still leaves a gap in programming liquid crystalline actuators for microsystems, which is tested out in this work. Previous publications have already demonstrated arbitrary high-resolution photoalignment. This work expands

the ideas to program the alignment of LCEs on a wafer level to enable the fabrication of integrated actuators for MEMS.

5.3 Optomechanical Setup

The photoalignment system in this work is designed to program arbitrary alignment patterns of liquid crystals on a 100 mm-wafer level, with a target spatial resolution of $<10\mu\text{m}$. Additionally, it provides an adjustable focus, flexibility with regard to wavelength and the potential to control the atmospheric environment of the processed substrates.

5.3.1 Components

The core piece of the presented photoalignment system is a DMD to modulate the light that is projected on the substrates. The DMD was part of a GEHA compact 283 projector with a resolution of $1024 \times 768\text{px}^2$, a pixel pitch of $13.8\mu\text{m}$ and a diagonal of 18 mm.

The entire optical system was removed from the projector, including the lamp, lenses, color wheel, as well as the cooling fans. To keep the DMD operational, several hacks had to be implemented: Feedback lines from the lamp and the cooling fans were set to the correct voltage; the feedback from the color wheel was replaced by pulse-width modulation of the same frequency and amplitude, generated by an Arduino. Modern projectors that are attractive for higher resolution DMDs have a more elaborate communication protocol between lamp and mainboard, making it more difficult to repurpose them.

With these modifications, the DMD can be controlled like a computer screen, with enough space to assemble a custom illumination and imaging system.

To photoalign Brilliant Yellow, the blue high power LED M450LP1 (Thorlabs Inc.) was selected, which provides an optical output power of up to 2.1 W at 450 nm ($\Delta\lambda_{\text{FWHM}} \approx 18\text{nm}$). The illumination path of the DMD was inspired by the original projector illumination: The LED light is focused into a rectangular tapered light pipe whose output facet is imaged onto the DMD, generating a homogeneously illuminated rectangle.

The pattern on the DMD is imaged through a rotatable polarizer onto the substrate. To achieve a pixel width smaller than the selected target resolution of $10\mu\text{m}$ from the micromirrors (width $13.1\mu\text{m}$) a demagnification of $M = 0.5$ was targeted, leading to a pixel size of $6.5\mu\text{m}$. Only the central square $768 \times 768\text{px}$ of the DMD is being used for the process to limit the field of view to the most homogeneously illuminated area of the DMD, resulting in a projection area of $5 \times 5\text{mm}^2$.

The projection is achieved by assembling an inverted projector objective. An additional benefit of this is the capability to adjust the focus directly on the objective with its inbuilt mechanism.

A non-polarizing beam splitter and a CMOS sensor (UI-1462LE-C, IDS Ltd.) are utilized as a feedback system to correct the focus of the imaging system.

To control the polarization, a polarizer (LPVISE100-A, Thorlabs Inc.) is mounted on a motorized rotation stage (8MPR16-1, Standa Ltd.). Furthermore, stitching requires a motorized xy-stage (8MTF-102LS05, Standa Ltd.) with large travel range (100 mm) and high precision (2.5 μm).

The substrate is placed into a custom-built box with a top glass window to protect it from dust and to allow for control of humidity and temperature during the photoalignment procedure.

5.3.2 Assembly

The photoalignment system is illustrated in full in Fig. 5.3. The repurposed projector is mounted on an optical breadboard with the DMD pointing downward (along the z -axis). The substrate can then be moved in the horizontal xy -plane.

The blue LED is focused into the light pipe. The output facet is mirrored onto the DMD in an angle such that the micromirrors project along the z -axis in the active-on state. In the active-off or powerless state, the light is projected in a different direction so that it does not shine onto the substrate. The distance between the light pipe and the DMD is adjusted such that the exit rectangle of the light pipe is imaged onto the DMD, creating sufficiently homogeneous illumination.

An inverted projector objective, a beam splitter and a polarizer mounted on a motorized rotation stage are stacked along the z -axis, with the feedback sensor and the pilot laser on the two other facets of the beam splitter. The pilot laser is used to reduce the tilt and to center the optical components on the optical axis. The substrate box is mounted on the motorized xy -stage.

To adjust the focus, a sample with a fine target structure is placed in the substrate plane. The lens in front of the feedback sensor is moved until the optimal image of the target structure can be obtained on the sensor. Then, a pattern is projected by the DMD over the target structure. The focus of the projection objective is then tuned with the inbuilt mechanism until both the target structure and projected pattern are in focus on the feedback sensor.

Some iterations of this process are necessary to reduce the defocus due to tilt over the considerable travel range of the xy -stage.

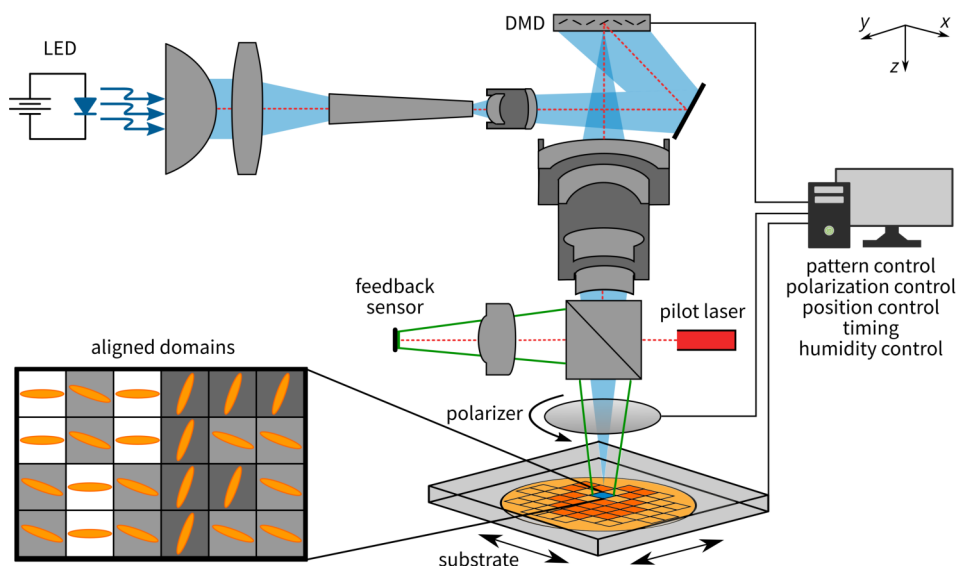


Figure 5.3 – Schematic overview of the photoalignment system: A blue LED is used to illuminate the DMD homogeneously through a tapered light pipe. The pattern on the DMD is projected through an objective, a beam splitter and a rotatable polarizer onto the substrate. A pilot laser is used to align all components along the optical axis. A feedback sensor assists in adjusting the focus of the imaging system. By controlling the pattern on the DMD, the angle of the polarizer and the position of the substrate, the photoalignment molecules on the whole substrate can be oriented in arbitrary directions, with a domain size corresponding to the resolution of the imaging system.

After adjusting all the components, the optomechanical system was left untouched, since the whole process is automated by software, controlling the patterns on the DMD, the angle of the polarizer, the position of the xy-stage, as well as the humidity in the substrate box.

5.4 Automation

The detailed photoalignment procedure consists of the following steps, illustrated in [Fig. 5.4](#):

- A target alignment pattern is created, which can be either a numeric array or an arbitrary digital image. The alignment pattern in [Fig. 5.4](#) illustrates radial alignment, where all the BY molecules point towards the center.
- The alignment pattern is discretized with a freely definable number of bins. This is necessary since the polarizer is always set to a discrete angle, while the DMD projects the respective pattern. Smaller bin size increases the number of exposure steps and therefore the total exposure time (12 steps in the illustration).
- The target pattern is split into small squares according to the absolute size of the projected pattern. In the illustrated case, it is split in nine squares, each of which exposes a square of $5 \times 5 \text{ mm}^2$ on the substrate, yielding a total pattern size of $15 \times 15 \text{ mm}^2$.
- When starting the photoalignment procedure, the software moves to the position of the first square and switches on the LED. The pattern is then split into one mask image for each polarization step (4 masks in the illustration).
- The software then rotates the polarizer to the defined target angle (which is orthogonal to the intended alignment angle) and displays the respective mask on the DMD for the set exposure time. This is repeated for every mask at this position.
- After exposing all masks on one position, the software moves the xy-stage to the next exposure position, to produce the stitched pattern.
- These movements are repeated until the whole pattern is exposed.

The total processing duration for one wafer depends on the number of polarization steps and the exposure time of a single mask. It usually ranges from 15 min for simple patterns like unidirectional alignment up to a few hours for complicated patterns with many steps, e. g. radial alignment.

The software was written in MATLAB to yield a user-friendly GUI, which is shown in the appendix in [Fig. A.1](#). The code can be found on [Github](#). It features the following capabilities:

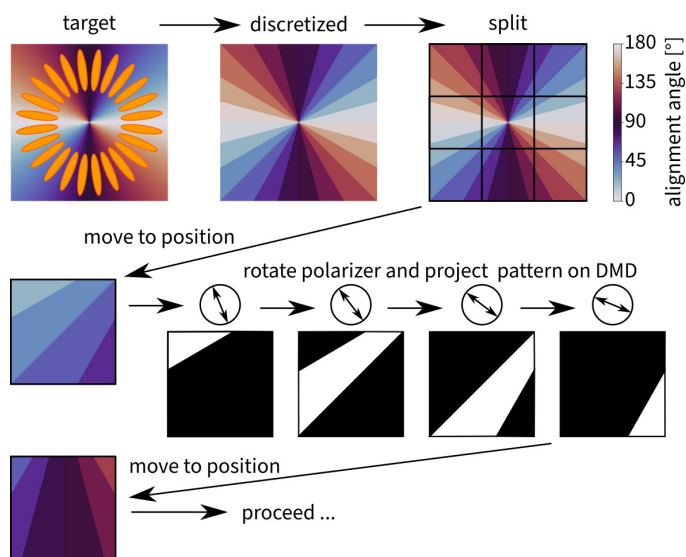


Figure 5.4 – Illustration of the photoalignment procedure: The target radial alignment pattern (all molecules pointing towards the center) is first discretized and then split into multiple squares. The square size represents the projected image size of the DMD on the substrate. The software then moves the substrate to the position of the first square. The image is converted to individual masks for the discrete steps. For each exposure step at this position, the software rotates the polarizer to the defined exposure angle and displays the respective mask on the DMD for the set exposure time. After finish all the exposure steps at this position, the substrate is moved to the next position. This procedure is repeated until the whole pattern is exposed.

- The LED, rotation stage, xy-stage and DMD can be controlled and monitored.
- Arbitrary masks can be imported from image files or MATLAB arrays. This enables users to create alignment patterns, either programmatically or graphically.
- The times and angles can be set for any alignment pattern and every step individually.
- The total pattern size can be adjusted from 100 mm wafer to any substrate shape and size, which is in the travel range of the xy-stage. For evaluation purposes, most of this work was optimized using 25 mm glass substrates since multiple of these can be exposed in one process run.
- The humidity can be monitored and controlled throughout the whole process between 15 %RH and 85 %RH by automatically controlled valves.
- The square size can be corrected to match the actual projected image size, offsets of the rotation or xy-stage can be defined.
- All the data during the exposure is logged and stored for later investigation.

5.5 Environment control

5.5.1 Humidity

Previous research found a significant effect of humidity on the alignment capability of azo dyes [88] and specifically of Brilliant Yellow [87]. According to these findings, BY absorbs water from the environment at high relative humidity and forms a semicrystalline structure [97], which inhibits the photoalignment process.

To achieve photoalignment with BY, the humidity needs to be kept below 45 %RH before and during the photoalignment process. On the other hand, high humidity (80 %RH) *after* the photoalignment exposure was shown to enhance the order of the BY molecules, and to stabilize the alignment [87, 97].

Therefore, the photoalignment process in this work includes measures to control the relative humidity: Spin coating of the command layer takes place in a sealed glovebox with a dehumidifier to keep the humidity below 35 %RH, measured by a Sensirion SHT21 sensor. The substrates are then placed in an enclosed box with a glass window in which they are kept during the photoalignment exposure.

Since the box is not hermetic, the humidity is controlled by automatically adding nitrogen to keep the humidity in the range of 30 %RH to 35 %RH until the exposure is finished. After

that, the samples are humidified by filling the box with humid air, keeping them at 80 %RH for several minutes.

5.5.2 Temperature

The default process utilized in this work uses a separate command layer to align the liquid crystals. This is because the mesogens can only be directly photoaligned if they (1) include a chemical group which can be aligned with polarized light and (2) are in a liquid crystalline phase, i. e. a state where the mesogens are able to move and rotate.

Criterion (1) can be circumvented by doping the liquid crystals with a photoalignable material, e. g. an azo dye like Brilliant Yellow or Methyl Red. However, criterion (2) requires the material to be in a liquid crystalline phase. The reactive mesogens used in this work need to be above 70 °C to satisfy this requirement.

Some groups have demonstrated such in situ photoalignment of liquid crystals [74, 93, 98]. Instead of dispensing the command layer and liquid crystals separately, the process was reduced to a single step. For this, the liquid crystals were either functionalized or doped with a photoalignable chemical. Additionally, the temperature was set such that the materials were in a nematic phase during the photoalignment exposure.

To add the capacity of in situ photoalignment for this work, a heater was set into the substrate holder in the exposure box. With this, the temperature of the substrates can be controlled in a range of room temperature up to 80 °C.

The majority of this work separates command layer and LC film to be able to control the parameters individually. However, temperature control adds the possibility to reduce the process by two steps at the price of flexibility.

5.6 Alternative photoalignment materials

Brilliant Yellow enables adequate alignment of liquid crystals on exposure to polarized blue light, comparable to commercial products. Furthermore, it is compatible with the other utilized materials in this work. However, due to its high sensitivity to humidity it is suboptimal for transferring the process.

The azo dye Chrysophenine (CH), which has a very similar molecular structure to BY, is evaluated as an alternative. Furthermore, Congo Red (CR) is tested to increase the wavelength range of the presented photoalignment system. It was suggested for photoalignment with green light [99]. The structure of both dyes, as well as their UV-Vis absorption spectra (recorded with Agilent Cary 60), are shown in [Fig. 5.5](#).

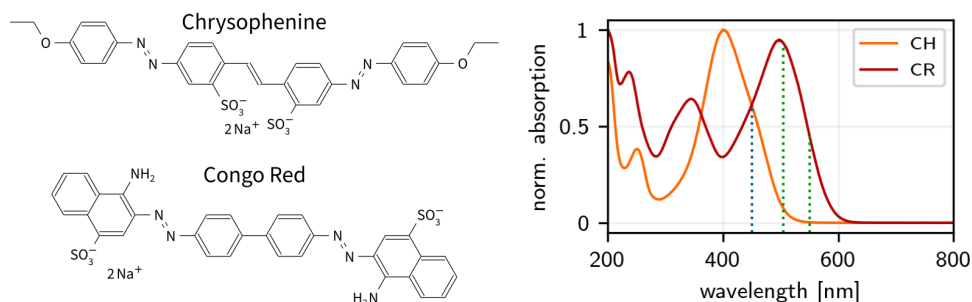


Figure 5.5 – Molecular structures and absorption spectra of CH and CR: Both azo dyes feature an elongated molecular structure and two azo bonds. The maximum absorption of CH is near 400 nm, similar to BY. CR has its maximum absorption near 500 nm, which is suitable for photoalignment by green light. The tested alignment wavelengths 450 nm, 505 nm and 555 nm are indicated by dotted lines.

Both dyes are processed like BY and photoaligned at 450 nm (CH and CR), 505 nm (CR) and 555 nm (CR), to evaluate the alignment capabilities. The LED light sources M450LP1, M505L4, and MINTL5 (the latter with a band-pass filter for 530 nm to 570 nm), Thorlabs Inc., are used for the three wavelengths, respectively.

5.7 Photoalignment system results

This section relates to the characteristics of the photoalignment system. The alignment quality of both the command layer and the liquid crystals are discussed after introducing the characterization methods in [Chapter 6](#).

5.7.1 Optical resolution

The optical performance of the projection system was evaluated by putting an image sensor with a pixel pitch of 2.3 μm (UI-1462LE, IDS Ltd.) in the imaging plane. Using this, the image width is measured to be 4.74 mm, which is slightly smaller than the target size of 5 mm. The magnification is thus $M = 0.45$, the size of a single projected pixel 6.17 μm .

To characterize the optical performance, the Modulation Transfer Function (MTF) was calculated. In theory, this would require the measurement of the imaging properties for an infinitesimal point source. More practical, the MTF can be approximated using the edge

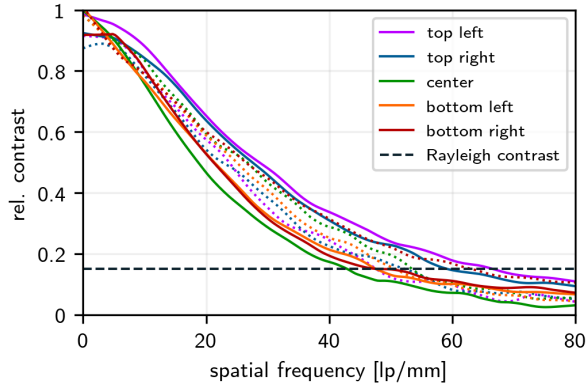


Figure 5.6 – Resolution of the photoalignment system: Calculated MTF curves of the ESF for five image positions in the sagittal and tangential plane (solid and dotted, respectively).

spread function (ESF) of a sharp edge in both horizontal and vertical dimension (termed *sagittal* and *tangential*, respectively) [100].

To measure the ESF, a knife-edge pattern was displayed on the DMD in five spots of the image for both sagittal and tangential direction, resulting in ten intensity distributions in the imaging plane. For each of those, the finite difference (approximating the derivative) was taken to obtain the line spread function (LSF). The Fourier transform of these LSFs yields an approximation of the MTFs in these five positions sagittally and tangentially, shown in Fig. 5.6.

The MTF curves indicate that the resolution in the sagittal plane is inhomogeneous, better at the top than at the bottom of the image plane. The tangential resolution is more homogeneous and shows less dependence on the position on the image. Even for the lowest MTF curve, a resolution of $12.5\ \mu\text{m}$ (40 lp/mm) can be obtained with a contrast larger than the Rayleigh Contrast of 15 %.

To confirm this calculation, a USAF target (shown in Fig. 5.7 (left)) was projected onto the same CMOS sensor. The scaling was selected such that the smallest resolution structure (labeled '6' in the magnified inset) has a width of one pixel. The resulting image (Fig. 5.7 (right)) shows that the projection system can resolve even these small structures, though with reduced contrast. This blurriness is partially due to aliasing by the CMOS sensor since the sensor pixel pitch ($2.3\ \mu\text{m}$) is close to the size of the projected structure ($6.2\ \mu\text{m}$). This image confirms the capability of the photoalignment system to resolve structures with the target resolution of $\approx 10\ \mu\text{m}$.

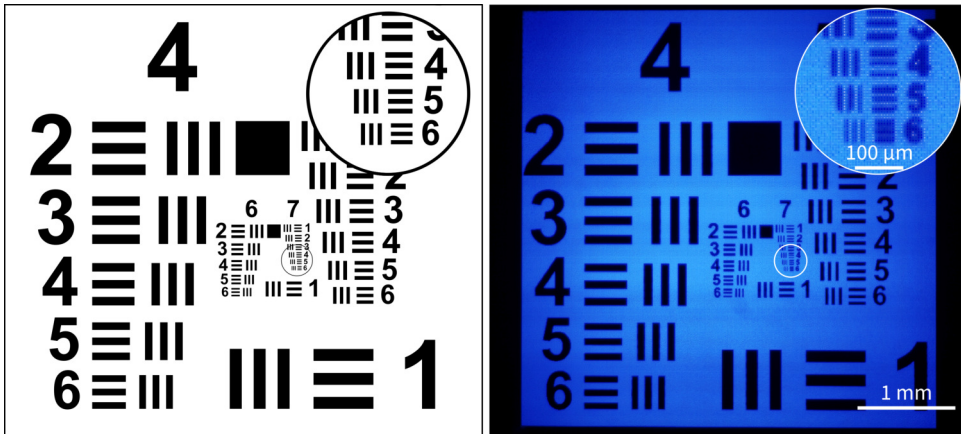


Figure 5.7 – Demonstration of the resolution: A USAF resolution test target (left) was projected by the photoalignment system onto a CMOS sensor. The smallest projected pattern width (magnified inset, '6') is the same size as a single pixel on the projector DMD. The resulting image (right) shows that the single-pixel projection can be barely resolved in the image plane. The blur (magnified inset) is partially due to aliasing because of the sensor pixel size and partially due to the limits of the projection system. Furthermore, the image also displays the uneven brightness distribution.

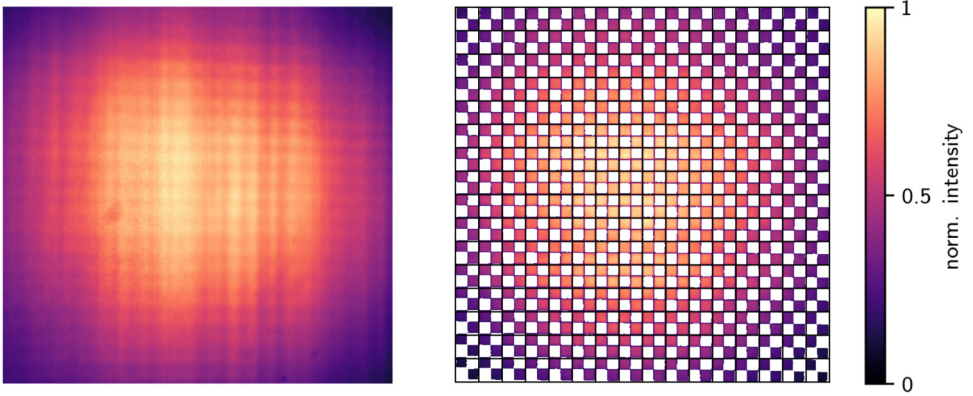


Figure 5.8 – Vignetting and distortions: The heat map (left) shows the normalized intensity distribution of the projected image, captured with the unsaturated CMOS sensor. The vignetting leads to a drop of the intensity to 50 % in a radius of roughly half the image width around the center, resulting in much lower intensity in the corners. The checkerboard pattern (right) with an overlaid regular black grid highlights some aberrations of the system. The white squares are masked by the DMD, while the colored ones encode the relative intensity. While not showing any barrel or pincushion distortion, the bottom right corner deviates strongly from the regular grid, showing some tilt.

5.7.2 Vignetting and aberrations

As can be seen in [Fig. 5.7](#), the intensity of the projected image is inhomogeneous, with the center being much brighter than the edges. To investigate the so-called vignetting, a blank square was projected by the DMD onto the CMOS sensor. The measured normalized intensity distribution is displayed in [Fig. 5.8](#).

The system shows strong vignetting, with the intensity dropping to 50 % in a radius of roughly half of the image width around the center, i. e. the intensity in the corners is significantly lower than in the center. Since photoalignment is a statistical process depending on the exposure power, lower intensity needs to be compensated by setting a larger exposure time for similar alignment contrast.

To evaluate the system's aberrations, a checkerboard pattern with a period of 48 px was projected onto the CMOS sensor. The resulting image is shown as a heat map in [Fig. 5.8](#), overlaid by an artificial regular grid. The white pixels are where no light was projected, to emphasize the contrast. The regular grid matches the checkerboard very well over most of the image, but a strong deviation can be seen in the lower right corner, indicating a tilt.

No visible barrel or pincushion distortion occurs and further investigation also shows coma to be negligible. The system suffers from astigmatism which is expressed by the difference between sagittal and tangential MTF in Fig. 5.6. However, strong vignetting is the major limitation of the system.

The vignetting could be compensated by using a smaller section in the center of the DMD to project patterns, to reduce inhomogeneity. This would require more steps to stitch large areas. Due to the high intensity, the exposure time per step could be decreased though, resulting in a just slightly increased exposure time. Practical tests of the systems have shown the performance to be sufficient for the intended photoalignment application, so the image size did not have to be set smaller.

5.7.3 Capabilities

The aim of this photoalignment system is the definition of arbitrary alignment patterns of liquid crystals on substrates. As discussed above, the optical properties meet the requirements in terms of resolution and optical performance. The control system offers enough versatility to produce and scale any alignment pattern.

As a proof of concept, the seal of the University of Freiburg was selected and photoaligned on a 100 mm wafer. Just two alignment directions (0° and 45°) were selected to obtain good contrast on imaging the sample between crossed polarizers. The achieved alignment of a thin LC film is demonstrated in Fig. 5.9. The crossed polarizers were rotated by 45° between the two photos, inverting the contrast due to the birefringence.

The resulting image clearly shows good alignment contrast in the two intended alignment directions. The defects in the center and on the edge of the wafer are mainly due to the spin coating process of the liquid crystals. However, the grid that is visible in the photo indicates imprecision on stitching the pattern.

Yet, this was the first demonstration of photoalignment on a full 100 mm wafer, featuring a spatial resolution in the order of $10\text{ }\mu\text{m}$.

5.7.4 Highlights

Similar photoalignment systems have been proposed and demonstrated before [89–91, 96]. However, the specific aim of this work was to create a platform for aligning LCEs on the wafer level.

This led to a system with several unique features:

- Spatial alignment resolution of $10\text{ }\mu\text{m}$ over an area of $100 \times 100\text{ mm}^2$;
- Selection of arbitrary alignment patterns;



Figure 5.9 – Photoaligned wafer between crossed polarizers: The seal of the University of Freiburg was photoaligned in two steps (0° and 45°). The dark patches show liquid crystals which are parallel to one of the polarizers (no effective birefringence). On rotation of the polarizers (right), the contrast inverts, indicating that the previously white patches are now parallel to one of the polarizers. Hence, the liquid crystals display the intended alignment pattern for the whole wafer, with major defects in the center and at the edges.

- Compatible with a wide range of wavelengths;
- High degree of automation;
- Control of humidity and potentially temperature.

This work makes use of this versatile system, to first analyze and optimize the photoalignment process, and second to structure micron-scale LCE actuators. For the optimization, measurement techniques had to be developed, to characterize the alignment of both BY and LCs. The particular challenges and respective techniques are presented in the following chapter. The use case of structuring actuators is discussed in [Chapter 7](#).

6 Characterization

Thus, we come to the conclusion, that the process of the photo-induction of the optical anisotropy in PVCi films is complicated.

– Kozenkov et al. [101]

6.1 Overview

6.1.1 Anisotropy

To evaluate the performance of the photoalignment process, the alignment quality needs to be measured on two different levels: How good is the alignment of the command layer (BY), and how well do the liquid crystal mesogens follow this alignment?

Both questions boil down to the issue of quantifying the anisotropy of the two layers, which is determined by the distribution of the alignment of the respective molecules. If the alignment is isotropic, i. e. the alignment is truly random, no mechanical or optical anisotropy arises. However, if a significant share of molecules is pointing in one direction, anisotropic properties can be obtained e. g. linear dichroism or birefringence.

These anisotropic properties are commonly exhibited by solid crystals. Yet, they also account for the popularity of liquid crystals. While the anisotropy is fixed in solids, it can be continuously tuned in liquid crystalline materials by manipulating the order of the mesogens. For example, LCDs rely on modifying the alignment direction of mesogens by using electric fields, resulting in a change in birefringence.

This work limits itself to discussing alignment in two dimensions. The utilized materials exhibit strong preference for planar alignment, where the long axis of the molecules lies in a plane parallel to the substrate. This is because the molecules have hydrophilic side groups which tend to align parallel to the equally hydrophilic substrate. The same property leads to strong surface tension, so that the molecules at the interface to air tend to align parallel to the interface. Therefore, the molecules in the whole thin film can be assumed to be planarly aligned. Hence, the following discussion is simplified by the assumption of alignment in just two dimensions, parallel to the substrate.

Both anisotropic optical properties, linear dichroism and birefringence, arise from the asymmetry in the elongated molecules themselves.

6.1.2 Linear dichroism

Linear dichroism describes the property of the absorption depending on the polarization of incident light. In terms of the Lambert-Beer law, it means that the extinction coefficient is not a scalar. Linear dichroism is caused by an anisotropic alignment of absorbing chemical groups.

In this work, linear dichroism is displayed prominently by the azo groups of BY, which absorb strongly, if the polarization of light is parallel to the N-N double bond (π bond). Other chemical groups can also lead to linear dichroism, if anisotropically aligned. However, in most cases the dichroism will be in the mid-infrared region, which is more troublesome to image optically.

The linear dichroism on molecular level results in macroscopic dichroism in dependence of the order of molecules. If all molecules point in the same direction, the strongest possible dichroism will be obtained. Isotropically aligned molecules will exhibit no dependence of the absorption on the polarization of light. Depending on the degree of order of the molecules, a state between these two extremes will be obtained.

6.1.3 Birefringence

Birefringence describes the property of the effective refractive index depending on the polarization of light. Birefringence arises by an anisotropic distribution of dipole moments. Asymmetric crystals and other ordered materials can feature birefringence.

Similar to linear dichroism, no birefringence will arise if the molecules are isotropically aligned. The minor variations due to each molecule would cancel out on average. However, if all the molecules point in one direction, the effects will add up to macroscopic birefringence. This can be observed on PMMA which features birefringence due to the polymer chains being oriented anisotropically.

The liquid crystalline material in this work (RM257) exhibits strong birefringence (0.17 at 589 nm [102]) in the nematic phase. The birefringence can thus be used as an indicator to quantify alignment order.

6.1.4 Common measurement techniques

Before diving into the methods selected for this work, this section gives a quick reference to the current state of measurement techniques for LCs in literature.

The *order parameter* S is a commonly used quantity in the field of LCs to express the alignment quality of the mesogens. It is theoretically defined as the average of the alignment angles between the mesogens' major axes and the local alignment direction. A theoretical value of $S = 1$ resembles perfect alignment, while isotropic alignment is defined as $S = 0$.

In practice, the order parameter is often approximated by optically determining the linear dichroism:

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}, \quad (6.1)$$

where $A_{\parallel}$ and $A_{\perp}$ represent the absorbance parallel and perpendicular to the absorption axis of a specific chemical group of the mesogen, measured at the maximum absorption wavelength of the respective group [103, 104].

The order parameter is often determined by measuring polarized FTIR spectra. This method makes use of the anisotropy in the distribution of C=C groups (in-plane stretch, 2.99 μm) [18] or C $\equiv$ N groups (4.49 μm) [105]. The trans-cis isomerism of azobenzenes can also be used to determine the order parameter, which has the advantage of being in the visible wavelength region [97, 106]. FTIR is only used as a single point measurement, whereas the linear dichroism in the visible region is convenient also for imaging. The measurement technique to evaluate the command layer (Sec. 6.2) is a refinement of this idea.

The de facto standard to characterize liquid crystal films is polarization microscopy (POM): The LC sample is observed under a microscope between crossed polarizers, as shown in Fig. 5.9. This technique is usually sufficient to confirm whether the mesogens are aligned as intended. However, the rotation of a polarized light beam by LCs is a function of birefringence *and* thickness of the film. Hence, getting quantitative information about the order of LCs with POM requires a more elaborate setup [107] which is rarely used. The method presented in Sec. 6.4, while not much simpler, yields quantitative spatial information for both the alignment direction and the retardation of the film.

Another frequently used method to analyze LC alignment is X-ray crystallography (XRC), specifically wide-angle and small-angle X-ray scattering. XRC can be utilized to determine the direction of alignment as well as the degree of order of the molecules directly by analyzing the diffraction patterns of X-rays [97]. This method is highly agnostic to the type of molecule used and is a superior method to measure LC alignment. However, it is a single point measurement and thus not useful to image non-uniaxial LC alignment patterns.

6.1.5 Selected measurement techniques

In this work, the alignment quality of both photoalignment and liquid crystal layer was to be measured. As a major constraint, it needed to be quantified spatially, not just as a single point measurement. Therefore, the following techniques were developed and applied:

- **Dichroism imaging:** A technique to quantify the linear dichroism was designed to obtain the spatial distribution of alignment direction and quality of the thin Brilliant Yellow command layer (Sec. 6.2).
- **Birefringence imaging:** An optical measurement technique to quantify the spatial distribution of the birefringence of the LC film was developed and set up (Sec. 6.3).
- **Stokes parameter alignment measurement:** A technique to measure the spatial distribution of the alignment direction of the LC layer was devised, set up and evaluated. It can additionally be used to measure the birefringence which could be compared to the results of the birefringence imaging (Sec. 6.4).

6.2 Dichroism imaging

Parts of this section were published in Liquid Crystals (Taylor & Francis) [108].

6.2.1 Aim of the method

The layer thickness used for photoalignment is in the order of 10 nm. Since this just resembles a stack roughly in the order of 100 molecules, a measurement technique to quantify the alignment quality needs a high signal-to-noise ratio. Fortunately, Brilliant Yellow shows strong linear dichroism in the blue wavelength region, due to its two parallel azo bonds, which are also parallel to the long axis of the molecule. This leads to much larger absorption for light that is polarized parallel to, than light that is polarized orthogonal to the BY molecules.

Therefore, the alignment direction and the quality of alignment can be determined by measuring the absorbance as a function of light polarization. This work aims at obtaining the spatial distribution of both alignment direction and quality. Hence, the measurement of linear dichroism was performed with an imaging system.

6.2.2 Measurement principle

Measurement setup and principle are illustrated in Fig. 6.1. A blue LED (LED430L, Thorlabs Inc., $\lambda = 430\text{ nm}$) at large distance is used to homogeneously illuminate the sample through a polarizer mounted in a motorized rotation stage. The sample with photoaligned BY layer is projected by a 4f imaging system onto a CMOS sensor with a field of view of roughly $14 \times 14\text{ mm}^2$ (Fig. 6.1a).

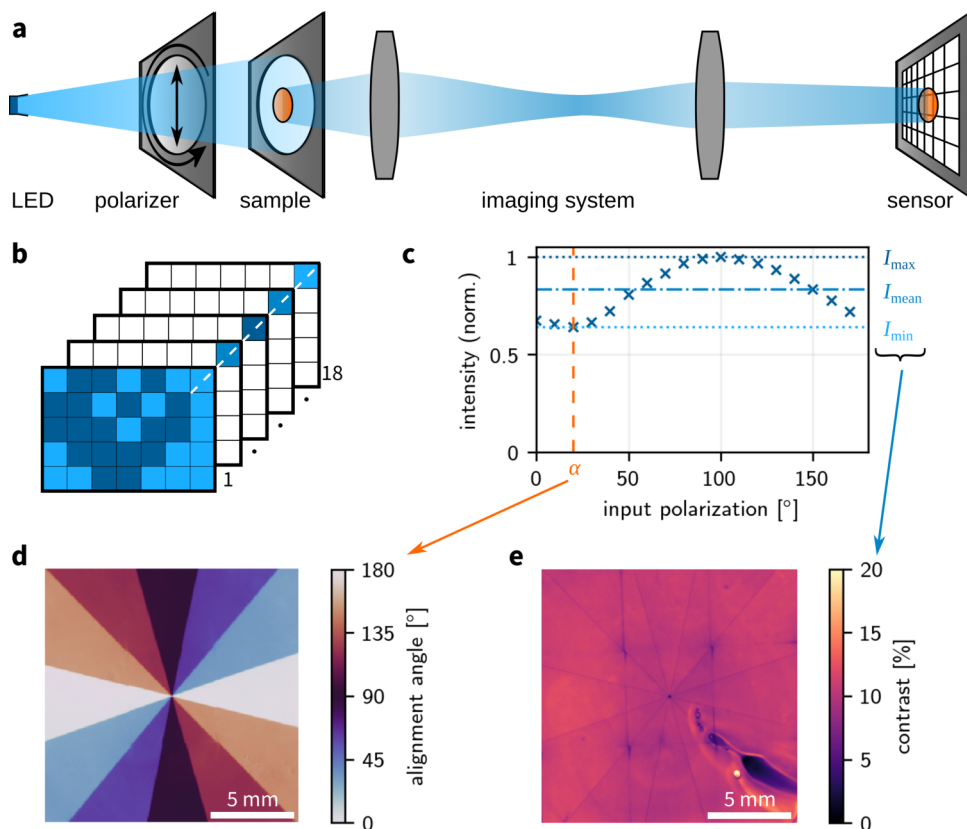


Figure 6.1 – Setup and principle for imaging linear dichroism: **a)** The sample is illuminated through a polarizer in a motorized rotation stage. A 4f imaging system is used to project the sample onto a CMOS sensor. **b)** While the polarizer is rotated, a snapshot is captured at every increment of 10°, up to 180°. **c)** The captured intensity for every pixel should yield a sinusoidal curve. The phase depends on the alignment direction, whereas the amplitude is determined by the alignment quality and layer thickness. **d)** Displaying the phase of the minimum for every pixel shows the alignment direction of the BY molecules. The measurement reveals the sample shown here to be aligned radially in six discrete steps. **e)** The Michelson contrast (same sample) is used to illustrate the alignment quality of BY. The image highlights the lower contrast at the edges and corners of the stitched pattern, where the photoalignment intensity is lower. Despite the low contrast near the bottom right (**e**), the alignment measurement (**d**) shows the correct alignment in this area.

The polarizer is rotated in discrete steps (e. g. 10°) up to 180° . The intensity on the sensor is captured at every step, resulting in a stack of (e. g. 18) intensity maps (Fig. 6.1b). The stack of each pixel encodes the local polarization-dependency of the absorbance, as shown in Fig. 6.1c for a real measurement. When the BY molecules are aligned in one direction, the recorded curve will resemble a sinusoidal curve, where the minimum intensity occurs when the polarization is parallel to the molecules. Hence, the polarization angle at the minimum represents the alignment angle α of the BY molecules.

The difference between the minimum and maximum intensity describes the quality of alignment. However, the absolute intensity values also depend on the thickness of the BY layer, intensity of illumination, and integration time of the sensor. Therefore, the Michelson contrast C is used to describe the alignment quality:

$$C = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} = \frac{I_{\max} - I_{\min}}{2I_{\text{mean}}}, \quad (6.2)$$

where $I_{\max}$, $I_{\min}$ and I_{mean} describe the maximum, minimum and mean intensity, respectively, that was recorded on the sensor (Fig. 6.1c).

The Michelson contrast is preferred over the order parameter described in Sec. 6.1.4 since it does not require measurement of the absolute absorbances or layer thicknesses. While not giving absolute alignment values, Eq. 6.2 yields a quantity that can be used to compare relative alignment qualities, as long as the layer thickness is constant.

While simple enough, the direct approach to obtaining α and C from the measurement data is prone to noise, especially for low alignment quality and thin layers, which result in a low signal-to-noise ratio. Thus, a mathematically more elegant approach was applied. Since the expected curve resembles a sinusoid, a discrete Fourier analysis can be used to remove the noise. Hence, a fast Fourier transform was applied to the measured intensity: $\mathcal{F} = \text{FFT}(I)$.

The DC part ($\mathcal{F}(\omega_0 = 0)$) stands for the mean value of the curve. The FFT of the first frequency $\mathcal{F}(\omega_1 = 1/180^\circ)$ represents a sinusoid with exactly one period within the range of the input polarization angle (see Fig. 6.1c). Since this is the expected curve for a dichroic sample, all higher frequency components are due to noise and can be neglected in this approach.

The phase component of $\mathcal{F}(\omega_1)$ entails the information at which input polarization angle the minimum of the curve occurs. Therefore, the alignment angle α can be directly obtained from the phase component of $\mathcal{F}(\omega_1)$. The contrast C can be determined by taking the ratio of the absolute values of $\mathcal{F}(\omega_1)$ (amplitude of sinusoid) and $\mathcal{F}(\omega_0)$ (mean value), hence

$$\alpha = \text{Arg}(\mathcal{F}(\omega_1)) \quad \text{and} \quad C = \frac{\text{abs}(\mathcal{F}(\omega_1))}{\text{abs}(\mathcal{F}(\omega_0))}. \quad (6.3)$$

This method is easy to implement and computationally inexpensive enough to scale for all the pixels of a CMOS sensor. A user-friendly MATLAB program to quantify the dichroic contrast and alignment direction was published on [Github](#).

[Fig. 6.1d](#) and [Fig. 6.1e](#) show a photoaligned sample, analyzed with this technique, featuring a resolution of $360 \times 360 \text{ px}^2$. Higher resolutions could be obtained, but did not appear to give more useful results.

The measurement of the alignment angle ([Fig. 6.1d](#)) reveals a radially aligned sample, with six discrete steps. The contrast measurement of the same sample [Fig. 6.1e](#) shows a mostly homogeneous alignment contrast for the whole sample, with two notable flaws. An obvious defect occurred in the lower right of the image, probably due to a particle in the spin coating process. The low contrast here is because of a lower thickness of the layer, as could be observed by eye. The other flaw is a lower contrast in the corners and on the edges of the photoaligned squares, revealing an imperfect stitching process and vignetting during the photoalignment process, as discussed in [Sec. 5.7](#).

6.2.3 Discussion

The appeal of this method lies in the combination of precision and scale. Due to the Fourier analysis, the spatial distribution of alignment and contrast of dichroic dyes can be quickly measured, even for very thin layers.

However, not all azo dyes exhibit linear dichroism. Brilliant Yellow showed good dichroic contrast at 430 nm, 450 nm and could even be measured with an LED at 505 nm. Chrysophenine, which features a similar structure showed a similar behavior, though the dichroic contrast is lower. On the other hand, Congo Red did not exhibit dichroism at any visible wavelength, despite its capability to be photoaligned by polarized light.

This measurement of dichroism also does not help to quantify the alignment of the liquid crystalline materials used in this work. That is because the LCs only exhibit dichroism in the infrared region, which is not compatible with the presented optical system. To overcome this limit, researchers have doped specific dichroic dyes, that exhibit dichroism in the visible range, into the liquid crystalline material. These dyes follow the alignment of the LCs. Hence, measurement of the dichroism can be used to analyze the alignment of the LCs [\[109\]](#).

6.3 Retardation measurement

6.3.1 Aim of the method

The dichroism measurement could only be used to evaluate the quality of the photoalignment layer. To quantify the alignment of the liquid crystal film, the retardation was measured.

Two techniques were employed: The first, introduced in this section, is a straightforward technique to measure only the retardation. However, it is only suitable for unidirectional alignment, since it relies on the LCs being at a specific angle to the optical components. Therefore, the second technique, *Stokes parameter alignment measurement technique (SPAMT)*, was developed (Sec. 6.4), to enable the measurement of arbitrary alignment patterns.

The facile retardation measurement was employed in this work to compare the alignment quality of LC film versus the alignment quality of the photoalignment layer. Furthermore, its results were used to confirm the retardation measurements obtained via SPAMT.

6.3.2 Measurement principle

To evaluate the alignment quality of the LC film, the retardation was measured, i. e. the phase shift of linearly polarized light, that occurs due to the birefringence of the LC layer. The retardation ϕ in a birefringent material is given by

$$\phi = \frac{2\pi}{\lambda} \Delta n d, \quad (6.4)$$

depending on the wavelength λ , the thickness of the LC layer d and the birefringence Δn . The birefringence Δn is the difference in refractive index experienced by the two orthogonal components of linearly polarized light.

As discussed above, this work only considers the alignment of LCs in a plane parallel to the substrate. Therefore, the birefringence can be modeled similar to a uniaxial crystal with its optic axis in the plane of the LC film. It is determined by the refractive index in the direction of the liquid crystals' major axes n_e and the refractive index of the perpendicular axis n_o . However, the equation $\Delta n = n_e - n_o$ is only valid if the LCs are aligned at 45° to the polarization direction. In this case, the two orthogonal components of the linearly polarized light experience n_e and n_o , respectively.

Crucially, n_e and n_o depend on the order of the LCs. No difference between the two refractive indices will be observed if the mesogens are aligned isotropically, i. e. $\Delta n = 0$. On the other hand, if all the LCs are aligned in one direction, the material exhibits its maximum

birefringence $\Delta n = \Delta n_{\max}$. Hence, the birefringence Δn indicates the order of the liquid crystals. The birefringence can be obtained from the retardation Eq. 6.4. Therefore, a technique to measure the retardation was devised in this work.

Similar to the dichroism measurement (Sec. 6.2), a major requirement was the computation of the spatial distribution of the retardation, as opposed to a single-point measurement. The setup is shown in Fig. 6.2a. A red LED ($\lambda = 633 \text{ nm}$) at long distance is used to illuminate the LC film homogeneously through a fixed polarizer. The sample is then imaged by the same 4f imaging system as in Sec. 6.2. Another polarizer (termed *analyzer*), is placed in front of the CMOS sensor, with the same polarization direction as the first polarizer.

With this setup, the intensity on the sensor I is a periodic function of the retardation ϕ , with its maxima $I_{\max}$ at $\phi = n2\pi$ and minima at $\phi = (2n + 1)\pi$, $n \in \mathbb{N}_0$. It can be expressed as

$$I = I_{\max} \left(\cos \frac{\phi}{2} \right)^2. \quad (6.5)$$

Since this function is periodic, the relation between intensity and retardation is only unambiguous if the retardation is in a range between 0 and $180^\circ (= \pi)$. This means for definite measurements, the layer thickness should be smaller than $d_{\max} = 1.8 \mu\text{m}$, assuming a wavelength of $\lambda = 633 \text{ nm}$ and a maximum birefringence of the used material of $\Delta n_{\max} = 0.18$ (Eq. 6.4).

The maximum intensity $I_{\max}$ was measured with a blank substrate to include the reflection losses of the actual sample. Next, an LC film sample with uniaxial alignment was inserted, with the LC alignment direction at 45° to the polarization direction of the polarizers, to create the maximum retardation. With the measurement of the intensity I , the retardation could be determined by

$$\phi = 2 \arccos(\sqrt{I/I_{\max}}). \quad (6.6)$$

The birefringence is then directly proportional to the retardation

$$\Delta n = \frac{\lambda}{\pi d} \arccos(\sqrt{I/I_{\max}}), \quad (6.7)$$

only depending on the layer thickness d , which was kept constant during the experiments. Hence, the order of the liquid crystals could be expressed through the birefringence simply by measuring the intensity between parallel polarizers.

An example of the spatial distribution of retardation obtained by this method is shown in Fig. 6.2b. From this heat map, two things can be observed: First, the sample shows a lot of defects. This is due to particles in the LC film, which were not dissolved. This was fixed later by either using thinner concentrations or filtering the LC solutions before spin coating. Second, the heat map reveals the stitched squares of the photoalignment process,

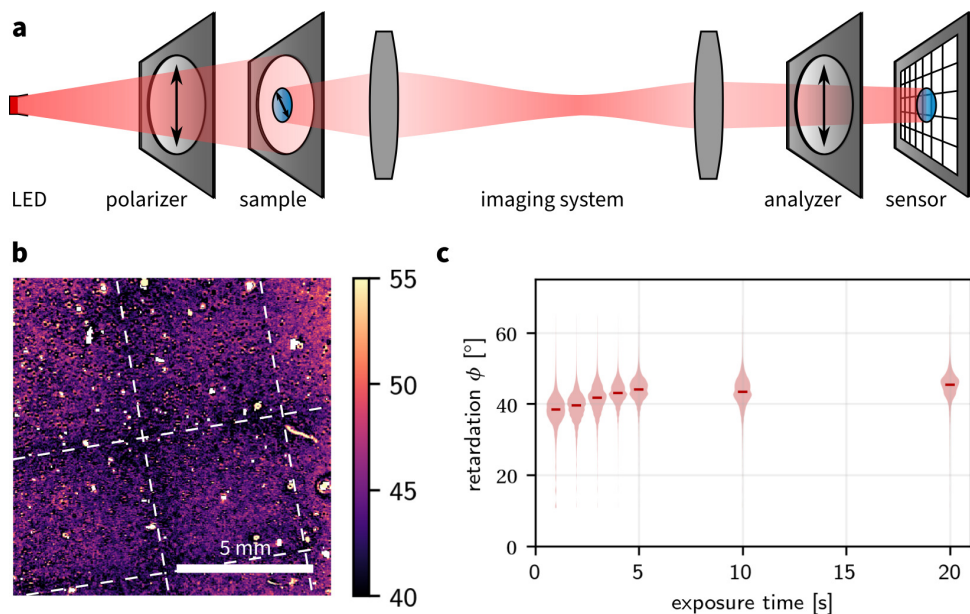


Figure 6.2 – Setup and principle for optical retardation imaging: **a)** A red LED illuminates the LC film through a polarizer. The sample is then imaged by a 4f-system onto a CMOS sensor. The second fixed polarizer, in front of the sensor, is parallel to the first polarizer, to obtain the modulation by the birefringence of the film. For this method, it is essential to have uniaxial alignment of the LCs at 45° to the direction of the polarizers. **b)** Heat map that shows the calculated spatial distribution of retardation for a sample LC film. Artifacts due to particles in the LC film can be observed. Furthermore, the stitched squares of the photoalignment exposure are visible in this image (indicated by the dashed white lines), highlighting the differences in alignment quality. **c)** Violin plots showing the distribution of the retardation for seven samples that were photoaligned with exposure times in the range of 1 s to 20 s (with marked median value). A slight improvement in retardation and hence in birefringence with exposure time can be seen, saturating somewhere around 10 s. However, the distributions also show the high variation of the retardation due to inhomogeneity of the film, both in thickness and birefringence.

where the edges of the squares have lower retardation than the center (indicated by the dashed lines). This indicates higher birefringence due to higher LC order in the center of the exposed squares. From this, it can be inferred, that the exposure dose on the edges of the photoalignment projection is not enough to saturate the alignment (see also the discussion on vignetting in [Sec. 5.7](#)).

It is difficult to compare differences between samples through heat maps. Therefore, histograms (in the form of violin plots) were used to compare the difference in retardation on tuning various process parameters. [Fig. 6.2c](#) illustrates such a comparison of samples. Each violin shows the measured distribution of retardation (as a vertical histogram) of one sample that was photoaligned with a certain exposure time, up to 20 s. The median value is highlighted for each distribution. Longer exposure times during photoalignment clearly increase the retardation and hence the birefringence, up to a saturation value that is reached between 5 s and 10 s.

Both the heat map and the violin plots show that the measured retardation has a large standard deviation. This is due to the defects and variation of the birefringence, as can be observed in the heat map [Fig. 6.2b](#). Additionally, white-light interferometry shows that the thickness of the LC films is also not completely homogeneous, contributing to the variation of retardation over each sample. As discussed in [Sec. 4.3](#), the number of defects and the surface roughness depend on the utilized solvent and concentration during spin coating the liquid crystalline layer.

6.3.3 Discussion

The proposed retardation measurement technique is an elegant tool to evaluate the spatial distribution of retardation of LC films. While most other methods to measure retardation are only single-point measurements, this technique can image the spatial distribution of retardation, thereby allowing simple intra- and inter-sample comparison. In contrast to polarization microscopy, which most publications just discuss qualitatively, the retardation can be quantified by the proposed technique, enabling a more precise discussion of LC alignment.

However, the proposed technique is mostly limited to thin LC films, with a retardation $<180^\circ$. Films featuring larger retardation require additional knowledge of thickness and birefringence to yield absolute results. Furthermore, this method can only be used to measure uniaxially aligned LC films, though modifications of the method for arbitrary alignments are possible.

As a particular advantage for this work, the setup to measure dichroism just needed minor modifications in order to measure the retardation, namely a different light source, two fixed polarizers and a different data processing algorithm. The retardation measurement

technique was used both to optimize the photoalignment process and as a sanity check for the Stokes parameter alignment measurement technique, introduced in the next section.

6.4 Stokes parameter alignment measurement

The work presented in this section was first presented at the SPIE Photonics Europe 2020 [110], and further extended and published in OSA Applied Optics [111].

6.4.1 Aim of the method

The two previously introduced measurement techniques yield the spatial distribution of alignment and contrast of the command layer, as well as the spatial distribution of retardation of the LC film. This still leaves one major unknown, namely the spatial distribution of alignment of the LC film.

Spatial variation of the alignment direction of the LC mesogens is a prerequisite, for both optical and soft actuator applications of LCEs. Therefore, it is important to verify the obtained spatial distribution of alignment in order to control the actuation mode. In this work, the alignment is programmed through photoalignment (Chapter 5), enabling arbitrary alignment patterns.

In many publications, the alignment is verified by observation of the LC film between crossed polarizers (POM), exploiting the material's birefringence. Areas where the LCs are parallel to one of the polarizers, show no effective birefringence, hence no transmission is visible. However, areas in which the LCs are at a different angle to the polarizers exhibit some birefringence and therefore rotate the polarization of light, enabling transmission in dependence of the angle and the layer thickness. For thin films (maximum retardation 90°), POM is a useful tool to evaluate alignment quality.

However, the resulting polarization microscopy images are not unambiguous. The intensity information is just modulo 90° , i. e. orthogonal alignment directions yield the same contrast. As an example, POM cannot distinguish between radial (all LCs pointing to the center) and azimuthal (all LCs aligned tangentially to the center) alignment patterns. Both alignment patterns are illustrated in Fig. 6.4, besides POM images of samples with the respective alignment. Even though the difference between the two alignment patterns is fundamental for any application, it cannot be distinguished with POM. This can be overcome by adding a quarter-wave plate (QWP) between the two crossed polarizers, resulting in a contrast between orthogonal alignment directions. However, the resulting intensity map cannot be directly correlated with the alignment direction since it is a function of

layer thickness and material birefringence. Hence, adding a QWP does not directly help in measuring the alignment direction.

Another downside of POM is the limitation to films with retardation of less than 90° . Thicker films can well be imaged and yield a contrast, however the measured intensity is a periodic function of the birefringence. Therefore, higher transmitted intensity does not necessarily indicate a larger angle to the polarizer.

Other techniques to measure the alignment unambiguously also suffer from trade-offs that were not satisfactory for this work: X-ray diffraction only works as a single-point measurement and does not produce a spatial distribution [112]. Measurement of dichroism (discussed in Sec. 6.2) requires a specific dichroic group in the LC film. Selection of one of the chemical groups of the LC mesogens ($C=C$, $C\equiv N$) would demand for an MIR imaging system, which is inconvenient and costly to build. Another option for imaging dichroism would be the addition of a dichroic dye into the LC network, where the dye molecules align with the LC mesogens [113]. This is a convenient option to characterize the alignment of the LC films. However, the dye molecules clearly change the mechanical and optical properties of the network.

Lin et al. have proposed a promising approach to measure the alignment of LCs by means of birefringence [114], which inspired the technique presented here. Similar to POM, their approach could only quantify alignment angles in a range of 0° to 90° , since they used linearly polarized input light on their system. Additionally, they just developed it as a single-point measurement, while this work demands for an imaging system.

Therefore, this work expands the cited approach by using circularly polarized input light and measuring the influence of the birefringence on the polarization. Furthermore, it is set up as an imaging technique, to obtain the spatial distribution of alignment with the full range of 0° to 180° . As an additional benefit, the measurement technique yields the spatial distribution of retardation, in a range of 0° to 180° . Since the method is based on measuring of the Stokes parameters, it is called *Stokes parameter alignment measurement technique* (SPAMT) in the further paragraphs.

6.4.2 Measurement principle

The Stokes parameters form a vector of four components that can be used to represent the polarization of light, $\mathbf{S} = (S_0, S_1, S_2, S_3)$. The component S_0 represents the total intensity, S_1 and S_2 stand for the linearly, and S_3 the circularly polarized components of intensity.

Stokes vectors are convenient to express the influence of optical components on the state of polarization, by means of Mueller calculus. The change of polarization state of a light

beam on transmission through a wave plate can be expressed by

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos^2 2\alpha + \cos \phi \sin^2 2\alpha & (1 - \cos \phi) \sin 2\alpha \cos 2\alpha & -\sin \phi \sin 2\alpha \\ 0 & (1 - \cos \phi) \sin 2\alpha \cos 2\alpha & \sin^2 2\alpha + \cos \phi \cos^2 2\alpha & \sin \phi \cos 2\alpha \\ 0 & \sin \phi \sin 2\alpha & -\sin \phi \cos 2\alpha & \cos \phi \end{pmatrix} \begin{pmatrix} \hat{S}_0 \\ \hat{S}_1 \\ \hat{S}_2 \\ \hat{S}_3 \end{pmatrix}. \quad (6.8)$$

Here, the input polarization state $\hat{\mathbf{S}}$ is changed to the output state $\mathbf{S}$ by a wave plate with retardation ϕ and major axis angle α [115].

Liquid crystal films can be modeled as wave plates, where the retardation is determined by the birefringence and thickness (Eq. 6.4) and the major axis angle represents the alignment direction of the mesogens.

Therefore, if input and output polarization ($\hat{\mathbf{S}}$, $\mathbf{S}$) are known, the above Eq. 6.8 can be solved numerically for α to determine the alignment direction of the LCs. While feasible for a single point, this method is computationally too expensive for a whole image.

Previous work has simplified Eq. 6.8 by using linearly polarized input light [114]. Since this is not sufficient to obtain the alignment angle in the full range of 0° to 180° , this work used circularly polarized light as input, represented by $\hat{\mathbf{S}} = (\hat{S}_0, 0, 0, \hat{S}_3)$. This can be used to simplify Eq. 6.8 to

$$\begin{aligned} S_0 &= \hat{S}_0 & S_1 &= -\sin \phi \sin 2\alpha \cdot \hat{S}_3 \\ S_2 &= \sin \phi \cos 2\alpha \cdot \hat{S}_3 & S_3 &= \cos \phi \cdot \hat{S}_3, \end{aligned} \quad (6.9)$$

which can be solved to yield the retardation ϕ , as well as two expressions for the alignment angle α :

$$\phi = \arccos \frac{S_3}{\hat{S}_3} \quad \alpha_1 = 0.5 \arccos \frac{S_2}{\sqrt{\hat{S}_3^2 - S_3^2}} \quad \alpha_2 = 0.5 \arcsin \frac{-S_1}{\sqrt{\hat{S}_3^2 - S_3^2}}. \quad (6.10)$$

Both arcus functions are periodic in the range of 0° to 180° . Therefore, the retardation ϕ can be quantified absolutely up to 180° .

The inverse trigonometric functions to calculate the alignment angle are multiplied by 0.5. Therefore, the output values for α_1 and α_2 are in the range of 0° to 90° and -45° to 45° , respectively, beyond which they repeat periodically. Since these intervals overlap partially, the knowledge of both values can be combined to an alignment angle α that is in the range of 0° to 180° :

$$\alpha = \begin{cases} \alpha_1 & \text{if } \alpha_2 > 0^\circ \\ -\alpha_1 & \text{if } \alpha_2 < 0^\circ. \end{cases} \quad (6.11)$$

Hence, by measuring the Stokes parameters after transmission of circularly polarized light through an LC film, the alignment angle and the retardation can be calculated.

To obtain the Stokes parameters in an automatable fashion, a method with one rotating QWP in front of a fixed polarizer was implemented [116, 117]. A QWP is rotated in N steps of θ_s from 0° to 360° in front of a fixed linear polarizer. The intensity $I(\theta)$ is measured at every step. From these measurements, the intermediate parameters $A - D$ can be calculated as

$$\begin{aligned} A &= \frac{2}{N} \sum_{n=1}^N I(n\theta_s) & B &= \frac{4}{N} \sum_{n=1}^N I(n\theta_s) \sin 2n\theta_s \\ C &= \frac{4}{N} \sum_{n=1}^N I(n\theta_s) \cos 4n\theta_s & D &= \frac{4}{N} \sum_{n=1}^N I(n\theta_s) \sin 4n\theta_s. \end{aligned} \quad (6.12)$$

The parameters $A - D$ can then be combined to yield the Stokes parameters through

$$\begin{aligned} S_0 &= A - C & S_1 &= 2C \\ S_2 &= 2D & S_3 &= B. \end{aligned} \quad (6.13)$$

This method to calculate $S_0 - S_3$ was reproduced from literature [117]. However, this work expanded this idea by implementing it in an imaging system, to quantify the spatial distribution of polarization.

The full measurement system is illustrated in Fig. 6.3a. A red LED with band-pass filter (LED630L and FL632.8-1, Thorlabs Inc.) is used as light source. A linear polarizer and a fixed QWP are used to illuminate the sample with circularly polarized light. The same 4f imaging system as for the dichroic and retardation measurement is employed to project the sample on a CMOS sensor. A second QWP, mounted on a motorized rotation stage, and a fixed polarizer are used to obtain the Stokes parameters.

Fig. 6.3b summarizes the measurement flow. The second QWP is rotated in discrete steps and an intensity image is captured at every step. For each pixel, this results in a sinusoidal curve, similar to Fig. 6.3c. From this curve, the parameters $A - D$ and then $S_0 - S_3$ are calculated for every pixel (Eq. 6.12, Eq. 6.13). The alignment angle α and retardation ϕ are then computed following Eq. 6.10 and Eq. 6.11.

As a result, the spatial distribution of LC alignment and retardation are obtained, shown by an example measurement in Fig. 6.3d and Fig. 6.3e, respectively. The example shows a radial alignment, with the LC major axes aligned towards the center, divided in six discrete steps. The retardation of the same samples appears mostly homogeneous, as it should be for LC films with constant thickness and birefringence. However, the discrete alignment steps can be seen weakly in the retardation measurement, which reveals some inaccuracy in the measurement. The retardation should be independent of the alignment direction. The measurement in Fig. 6.3e reveals either the imperfect circular input polarization or inaccuracy in the measurement due to the nonlinear response of the CMOS sensor.

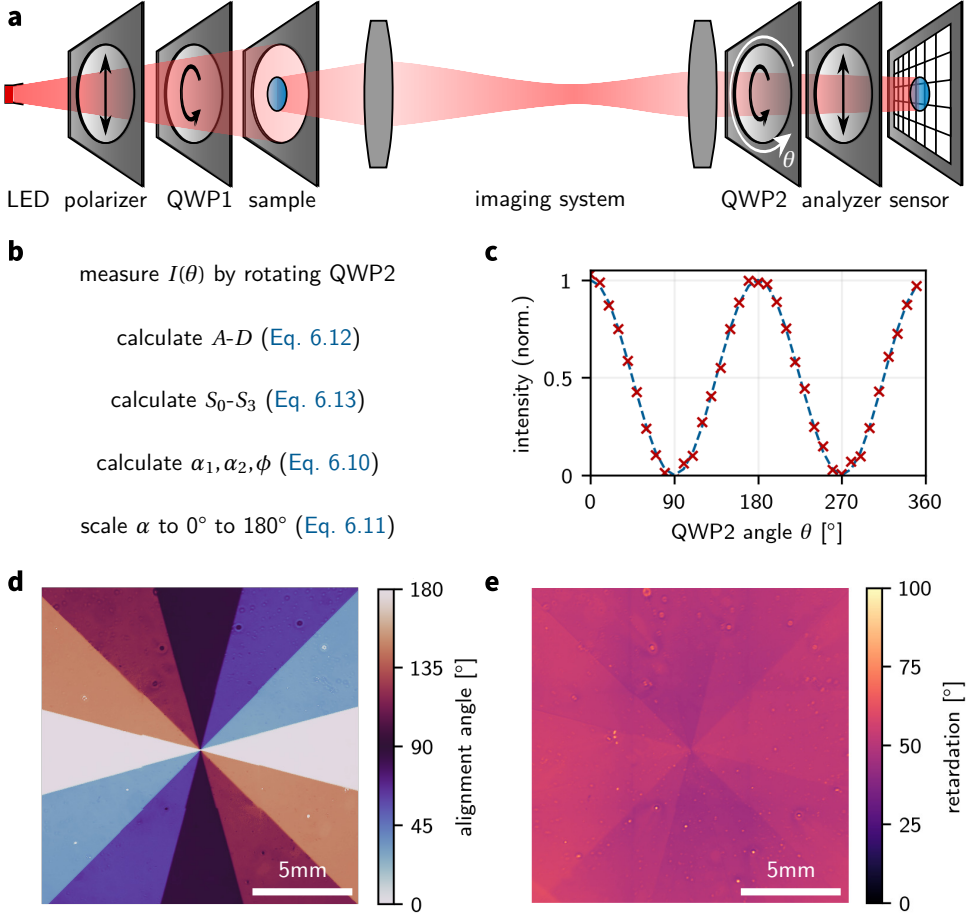


Figure 6.3 – Setup and principle of SPAMT: **a)** Schematic of the measurement setup. A red LED with a polarizer and QWP create circularly polarized light to illuminate the LC film. The sample is imaged by a 4f system onto a CMOS sensor. A second QWP on a motorized rotation stage and a fixed polarizer enable the measurement of the Stokes parameters. **b)** Overview of the steps to go from measurements of the intensity to the alignment direction and retardation of LCs. **c)** Example modulation of the intensity of a single pixel by rotation of QWP in discrete steps. **d/e)** Sample images obtained by SPAMT for a sample with radial alignment in six discrete steps, alignment angle α and retardation ϕ , respectively.

6.4.3 Discussion

Alignment direction

The alignment direction of LCs is crucial for any application. This work aims at paving the way for integration of LCE actuators in microsystems. Therefore, this work required a method to measure the spatial distribution of LCs with a spatial resolution in the order of $10\text{ }\mu\text{m}$, close to the minimum alignment pixel size from the photoalignment process.

A clear goal was to surpass the capabilities of polarization microscopy, by distinguishing orthogonal alignment states. As an example, the method developed here should enable distinction between radial (all molecules pointing to the center) and azimuthal (all molecules tangential to the center) alignment. Both alignment patterns are illustrated in Fig. 6.4. To highlight the advantages of SPAMT over POM, one sample with radial and another with azimuthal alignment is shown between crossed polarizers (Fig. 6.4b/e). While these orthogonal alignment patterns cannot be distinguished with this technique, the measurement results of SPAMT (Fig. 6.4c/f) reveal a clear difference.

Further demonstrations of the capabilities can be found in the publications of the system [110]. More detailed investigation revealed the following specifications: The system is capable of measuring the spatial distribution of alignment over an area of $14 \times 14\text{ mm}^2$, with a spatial resolution $<100\text{ }\mu\text{m}$. A further benefit is the high tolerance to defects on the sample. Compare the particles on the samples Fig. 6.4b-c/e-f.

Retardation

As a bonus, SPAMT also yields the spatial distribution of retardation, with the same spatial resolution as the alignment, $<100\text{ }\mu\text{m}$. Compared to the retardation measurement described above (Sec. 6.3), SPAMT can be used to quantify the retardation for arbitrary alignment patterns, not just for uniaxial alignment.

In principle, the retardation of the LC film is independent of the alignment direction. However, as the example in Fig. 6.3e already shows, this is not completely correct for the demonstrated system. One reason for this is presumably the impure circular polarization of the input light, which still has a residual share of linearly polarization.

Accuracy

To investigate the accuracy of the system, the mathematical derivation has to be considered, specifically Eq. 6.10. The derivatives of both the arcsine and arccosine are nonlinear functions. Therefore, the accuracy of both alignment and retardation measurement depends on the retardation of the birefringent film. If the value of $|S_3|$ approaches the value of $\hat{S}_3$, the

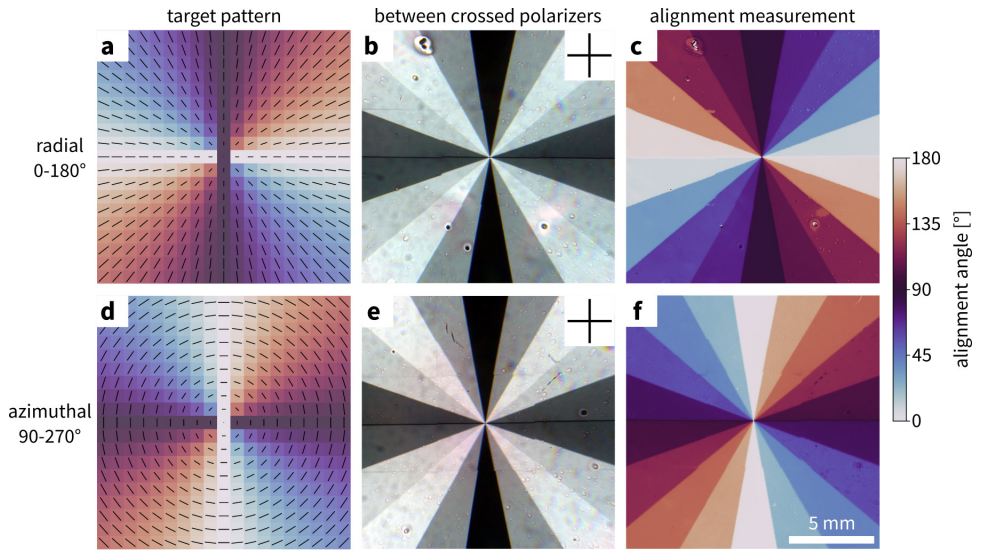


Figure 6.4 – Comparison of radial and azimuthal alignment: **a/d)** Schematic of radial and azimuthal alignment, where the alignment direction of every pixel is indicated by the angle of the line segments. **b/e)** Samples with radial and azimuthal alignment (in nine discrete steps) between crossed polarizers, respectively. The alignment is not distinguishable with this technique. **c/f)** Results of the SPAMT measurement for the same samples as in **b)** and **e)**, respectively. The alignment can be clearly distinguished.

calculated retardation ϕ tends towards infinity. Similarly, the alignment angles (α_1 and α_2) approach an undefined value, with S_1 and S_2 getting close to zero. This case happens, when the retardation is close to being a multiple of 180° .

This was tested by characterizing both a quarter-wave plate (QWP) and a half-wave plate (HWP) with the SPAMT setup, with the optic axes varying from 0° to 180° .

The results showed that the QWP could be quantified at a retardation of $89.8^\circ \pm 0.3^\circ$ and the alignment angle gave reasonable values with an accuracy of 15° . Contrary, the HWP was measured with a retardation of $164.3^\circ \pm 4.0^\circ$, which shows an offset from the expected 180° that is almost independent of the alignment direction of the HWP. Thus, the measurement of the retardation is not very accurate, though precise, for retardation values near the half-wave condition. The alignment angles measured for the HWP showed no reasonable results.

This demonstrates a blind spot of this method, when the retardation of the LC film is close to an integer multiple of 180° . On the other hand, the test with the QWP displays an impressive accuracy of the retardation measurement independent of the alignment angle, when the retardation is close to 90° . SPAMT is thus a powerful method for quantifying spatial information of a birefringent film, although it requires a contextual estimate of the expected retardation to yield reliable results.

6.5 Characterization results

The main objective of all characterization methods introduced in this section was to obtain quantitative feedback in order to optimize the photoalignment process. In the following paragraphs, the primary results of this analysis are summarized and illustrated.

6.5.1 Process optimization

Solvents

The commonly used solvent for azo dye-based photoalignment layers (e. g. Brilliant Yellow, SD1) is DMF. On the plus side, DMF is available to most research groups and has been shown to work well even for optical applications of photoalignment. However, DMF is considered harmful to humans. Furthermore, DMF is a strong solvent for a wide range of materials, which might lead to incompatibility with other processes.

Therefore, the solubility and the photoalignment quality of BY were investigated for a variety of different solvents. Since the solubility as well as the homogeneity of the photoalignment layer can be observed directly, no quantitative analysis is given.

The following core results were established:

- DMSO and TMU were found to yield alignment quality similar to DMF.
- Ethylene glycol and Methanol dissolve BY well, but are problematic to spin coat due to their high surface tension. While BY in Methanol gives acceptable homogeneity when spin coating at high speed (5000 rpm), the photoalignment quality was never as uniform as with the other solvents.
- NMP dissolves BY well and can be used for photoalignment. However, due to NMP's high toxicity it was dropped from further experimentation after one successful demonstration.
- Toluene, Chloroform, THF, Dioxane, Acetone, Isopropanol, PGMEA and Xylene did not dissolve BY. This is important, because these solvents are often used in either LC fabrication (especially Toluene), microsystems processes (e. g. PGMEA) or cleaning steps (Acetone, Isopropanol).

Thus, DMF, TMU and DMSO were established for fabrication of photoalignment layers with BY. Since TMU is considered less harmful than DMF, it was used for all further experiments described in this section.

Additionally, Toluene, PGMEA and Chloroform were successfully utilized to coat LC films on top of the photoalignment layer. Due to its simple handling, Toluene was used to dissolve the liquid crystalline material RM257 for the experiments in this section.

As a further result, DMF, TMU and DMSO show the capability to dissolve both BY and RM257. Therefore, the photoalignment and the LC material can be mixed in one solution, to reduce the film fabrication to a single spin coating step. This approach, *in situ* alignment, was examined in [Sec. 4.3.4](#).

Photoalignment layer thickness

One parameter that varies between publications is the thickness of the photoalignment layer. This is, because groups choose different concentrations (usually 0.5 wt% to 2 wt%) of photoalignment material and different spin speeds (1000 rpm to 4000 rpm). A major question is whether and how this influences the alignment quality of the film.

To evaluate the influence of the photoalignment layer thickness on the alignment strength, samples were coated with different concentrations of BY in TMU, 0.5 wt%, 1 wt%, 3 wt% and 5 wt%, all at 3000 rpm. After photoalignment exposure, the dichroic contrast of the BY layer ([Sec. 6.2](#)) and the retardation of a subsequently coated LC film ([Sec. 6.3](#)) were measured.

The dichroic contrast depends on the thickness of the BY layer. This is not because of a change in alignment quality, but because the absorption follows the nonlinear Lambert-Beer

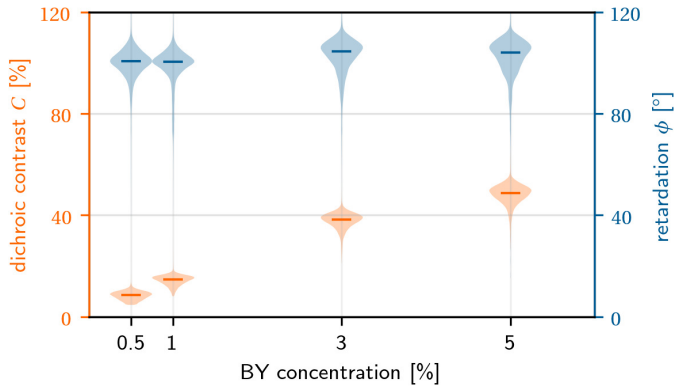


Figure 6.5 – Dichroic contrast and retardation vs. BY concentration: The dichroic contrast of BY (orange) increases with increased concentration, due to the layer becoming thicker. However, the retardation of the subsequent LC layer (blue) is independent of the BY concentration.

law, with two distinct absorption coefficients for the direction parallel and orthogonal to the alignment direction of the dipoles. The dichroic ratio is thus a nonlinear function of the layer thickness.

The alignment quality of LC films for different BY concentrations was evaluated by measuring the retardation. The results of both the dichroism imaging and the retardation measurement are shown in Fig. 6.5.

These results show that the alignment strength of BY is independent of the command layer thickness for the selected range of BY concentration and thin LC films with a thickness around $1\ \mu\text{m}$.

Thus, the concentration of BY can be selected suitable for the desired application. For optical applications, low absorption and hence thin BY layers are desirable. On the other hand, thicker BY layers are convenient for metrology and quality assessment, due to the larger dichroic contrast.

Exposure dose

Two essential parameters for photoalignment are the exposure time and light intensity which combine to the exposure dose. Intuitively, the photoalignment quality increases with larger exposure dose, though in dependence of the light intensity.

To test this in detail, samples were prepared with BY layers, exposed with both varying exposure times and intensities (tuned by the current of the LED). The dichroic contrast and

the retardation of a subsequent LC layer were measured. The measurement data of the dichroic contrast is shown in Fig. 6.6.

The results show that the dichroic contrast follows an exponential decay curve, fitted in Fig. 6.6a with

$$C(t) = C_{\max} (1 - e^{-t/\tau}), \quad (6.14)$$

where $C_{\max}$ stands for the maximum contrast, t for the exposure time and τ for the time constant of the saturation function.

In the shown data, the dichroic contrast saturates at the same value $C_{\max} \approx 48\%$ for intensities larger than 6 mW/cm^2 . The time constant τ depends on the intensity, at 45 mW/cm^2 , $\tau \approx 2.3 \text{ s}$. For lower intensities, the dichroic contrast does not reach the same saturation value even at longer exposure times.

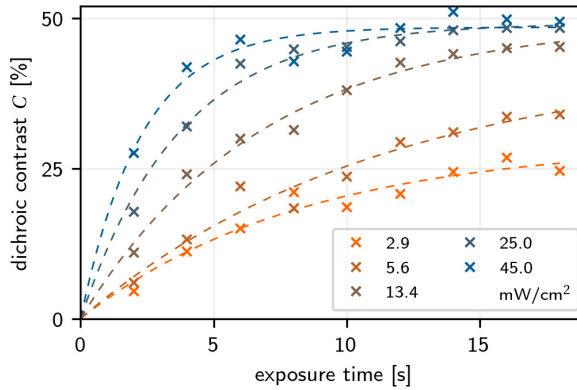
To fit the dependency of dichroic contrast on the exposure dose, the same equation as Eq. 6.14 was used, only with the time replaced by the energy dose. The decay constant is then also an energy dose with a unit of energy per area. The measured values (for intensities $>6 \text{ mW/cm}^2$) follow an exponential decay curve (Fig. 6.6b) with an energy dose constant of 74 mJ/cm^2 , i. e. on exposure with a dose of 74 mJ/cm^2 , the dichroic contrast reaches a value of $(1 - e^{-1}) \approx 64\%$ of its maximum value $C_{\max}$. To reach a contrast of 95% , an energy dose of 222 mJ/cm^2 is necessary, requiring an exposure time of 5 s at the highest intensity (45 mW/cm^2) of the presented photoalignment system.

The values utilized in literature range from 72 mJ/cm^2 to 15000 mJ/cm^2 [54, 118], which is a range of three orders of magnitude. The findings in this work indicate that many publications use excessive intensity or exposure times. Commercial azo dyes show a similar order of exposure dose: sulfonic azo dye SD1 requires an exposure dose of 50 mJ/cm^2 [119]; PAAD was used at 420 mJ/cm^2 [120].

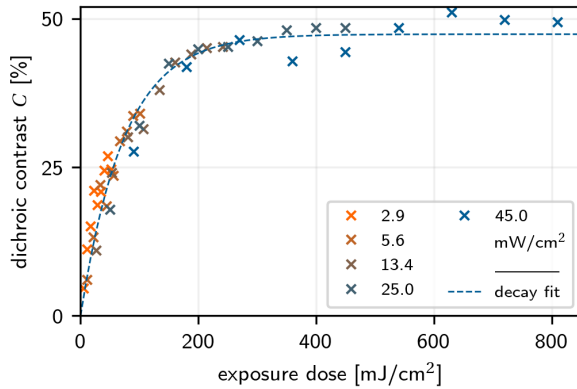
Interestingly, the exposure time can be kept very short on high intensity. For example, an exposure time of 10 ms was demonstrated to be enough to align PAAD at an intensity of 42 W/cm^2 [120]. This confirms that the alignment quality is only a linear function of exposure dose, for a wide range of intensities [82].

So far, the discussion was limited to the dichroic contrast of the photoalignment layer. More important is the alignment quality of the subsequent LC film, which is quantified by the retardation (Sec. 6.3). Therefore, the retardation of LC films on the above samples was measured, after the exposure of 18 s of the respective intensities. The resulting values are shown in Fig. 6.7.

The data shows a jump to saturation already at 100 mJ/cm^2 , even though the dichroic contrast is not saturated at this value (see Fig. 6.6a, at 5.6 mW/cm^2 after 18 s). Thus, the alignment of BY does not need to be optimal in order to achieve the best alignment quality of the liquid crystals, at least for thin films (in this case about 500 nm). This matches other



(a) Dichroic contrast vs. exposure time of a BY film for different exposure intensities. The dashed lines follow an exponential decay fit for each intensity value.



(b) Dichroic contrast vs. exposure dose, like (a) but multiplied with the respective intensity and exponential decay fit.

Figure 6.6 – Dichroic contrast vs. exposure time, intensity and dose: The dichroic contrast follows a saturation curve with the saturation time depending on the intensity of light. For low intensities ($<6 \text{ mW/cm}^2$), the dichroic contrast does not seem to saturate on a reasonable timescale. On multiplication with the intensity, for intensities $>6 \text{ mW/cm}^2$, the measured values follow an exponential saturation curve with a maximum contrast of 48 % and an energy dose constant of 74 mJ/cm^2 .

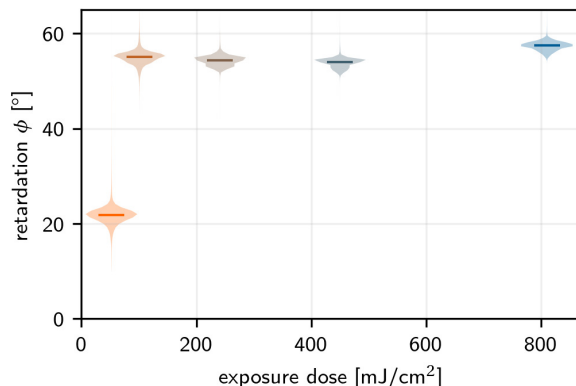


Figure 6.7 – Retardation vs. exposure dose: The retardation of a thin LC film on the above BY samples exposed to different intensities was measured after the exposure time of 18 s. Since the thickness of the LC films is the same for all samples, this data shows a saturation of the birefringence, and thus the alignment quality at a dose of 100 mJ/cm².

experiments which show good alignment quality even when exposing with an exposure dose of 90 mJ/cm².

In summary, these results show that an exposure dose of 220 mJ/cm² is sufficient to saturate the alignment quality of Brilliant Yellow. To saturate the alignment of a subsequent thin LC layer, an even lower dose of 100 mJ/cm² is found to be sufficient.

Annealing steps

In photolithography, annealing steps are essential to evaporate solvents and support the chemical processes of the resist. Similarly, annealing steps are utilized in literature to remove solvents from the photoalignment layer (annealing before exposure), and to increase the order of the liquid crystals (annealing after spin coating of LC film).

To test the first step, BY was spin coated and the samples were left on a hot plate at 100 °C for times in a range of 0 min to 20 min. No difference in dichroic contrast was observed between the samples after photoalignment.

In a second experiment, samples were put at a hot plate after spin coating the LC film (RM257 in Toluene), before polymerization. Temperatures of 80 °C and 100 °C were selected to have the RM257 monomers in the nematic state. The measured retardation showed increases of 10 % and 6 % after 30 min for the two temperatures, respectively. On inspection

under the microscope, the LC films annealed at 100 °C showed small air bubbles, which could be due to the solvent evaporating too fast at this temperature.

A further effect of the annealing step was found after polymerization of the reactive mesogens. If the annealing step was left out, the polymerized film would tear everywhere, when put into a solvent that swells the network (e. g. Toluene, PGMEA). If annealed prior to polymerization, the films would stay stable and not tear when exposed to one of these solvents.

A likely explanation is that the film creates internal stress, when the LC material is polymerized in a swollen state (with solvent still inside the network). On re-swelling, the stress is released by tearing of the films.

Thus, this work finds no use in heating the photoalignment films after spin coating. However, annealing the LC film (80 °C for 10 min to 30 min) prior to polymerization is beneficial for both alignment quality and the stability of the LC network for liquid crystal polymers.

Humidity

BY and SD1, the dominant azo dyes used for photoalignment, are both hygroscopic. This obstructs the alignment, because moisture in the material impedes the rotation of the molecules [119]. Previous research specifically found BY to not be photoalignable when the humidity was too high before or during the exposure to polarized light, a property that was confirmed by the experience in this work. Furthermore, the alignment contrast and the stability were found to increase on exposure to high humidity after the photoalignment process [87, 88].

To validate and investigate this in detail, BY was spin coated and exposed in a controlled environment. During spin coating, the humidity was kept at 20 %RH to 28 %RH inside a glovebox. Then, samples were exposed inside a closed box while at the same time controlling the humidity in a range of 30 %RH to 60 %RH. The dichroic contrast was measured, before and after subjecting the samples to a subsequent humidification step at (80 %RH) for 15 min. The measurement results are shown in Fig. 6.8.

In a wide range of low humidity, the contrast is unaffected by moisture. However, the contrast drops drastically if the humidity before exposure is higher than 50 %RH. This matches well with previous findings, which recommend keeping the humidity lower than 45 %RH [87].

Additionally, the contrast almost doubles due to the humidification step. Again, this is consistent with other findings that recommend a humidification at 80 %RH for 20 min [87]. Further detailed experiments in this work revealed, that the dichroic contrast saturates already after 5 min at 70 %RH. On the other hand, humidification at 50 %RH or 60 %RH was not found to be sufficient to reach the saturation dichroic contrast even after 2 h.

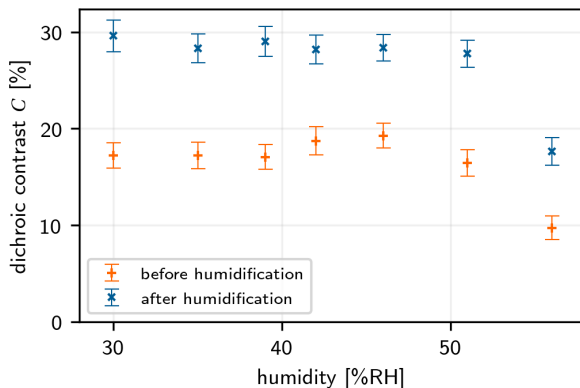


Figure 6.8 – Dichroic contrast as function of humidity: The dichroic contrast of photoaligned LCE films prepared at varying humidity, measured before (orange) and after (blue) a humidification step following the photoalignment exposure. At high humidity during exposure, the films align only with low contrast. Humidification after exposure improves the dichroic contrast for all samples.

In summary, low humidity (<45 %RH) is essential before and during the photoalignment exposure of BY. High humidity (5 min at >70 %RH) after the exposure increases the dichroic contrast of photoalignment layer.

Stability

Since high humidity obstructs the rotation of molecules, humidification should lead to higher stability of the photoalignment layer. This was tested by subjecting photoaligned BY films to different humidity values for 10 min after the alignment process. To see whether the already aligned films were rewritable, the samples were then photoaligned a second time.

Samples exposed to a humidity of <40 %RH were found to completely follow the new alignment. At 45 %RH to 50 %RH, the samples could be realigned but preserved parts of the original alignment pattern. At 55 %RH, the films did not realign. However, previously unaligned areas were aligned by the new pattern. Films subjected to >60 %RH for 10 min could not be realigned at all.

In another experiment, half of the samples were humidified after the photoalignment process (80 %RH, 20 min), while the other half were kept in laboratory humidity. The samples were then stored in different environments for two weeks, in a dark box, in yellow laboratory light, or in office light (with glass-filtered sunshine). The dichroic contrast was measured before and after humidification, as well as after two weeks in the respective environment. The

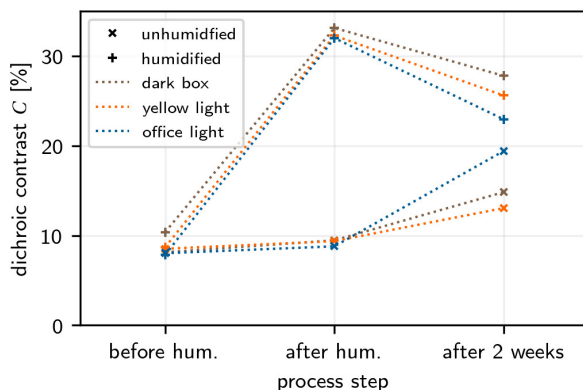


Figure 6.9 – Stability of photoaligned BY films: Dichroic contrast of photoaligned samples exposed to various environmental light conditions for two weeks. The contrast was measured before and after a humidification step of half of the samples, as well as after two weeks in different light conditions.

humidity in office and lab was comparable at 40 %RH to 45 %RH. The measured contrasts are shown in Fig. 6.9.

The measured data confirms again, that the dichroic contrast increases for the humidified samples. After two weeks, the contrast of the humidified samples decreases. As expected, the contrast reduces more for samples that are subjected to more light, while the samples in the dark box suffered the lowest loss in contrast.

On the other hand, the contrast change of the unhumidified samples is quite puzzling. All of them increased in contrast, especially the one subjected to sunlight inside the office. A reasonable explanation is that all unhumidified samples added moisture from the environment, forming semicrystalline structures with water molecules similar to the humidified samples. The samples left in office light had the largest increase in dichroic contrast. This could be due to the higher energy input helping to form the semicrystalline structures.

In summary, humidity of >60 %RH was found to prevent realignment and increase the stability. On the other hand, all the films showed stability to environmental light conditions, even to glass-filtered sunshine and white office light. The implication is that the alignment of BY, once successful, can be considered stable against all common environmental light conditions, enabling storage of aligned BY films even for weeks.

6.5.2 Capabilities and limitations

Overall, [Sec. 6.5.1](#) has demonstrated the value of having different techniques to assess the alignment quality of photoalignment and LC layer.

Dichroism imaging

Measuring the spatial distribution of linear dichroism enables optimization of the photoalignment process, where many parameters need to be tuned in order to achieve a consistent, stable process. Specifically, it enables quality control at an intermediate process, which is crucial to find out which processing step did not work correctly.

Most researchers in the field of liquid crystals are in the habit of assessing the optical order parameter [104]. This yields a quantity which is valuable to compare results between research groups and processes. However, the method is based on measuring absolute absorption values, which is impractical when intending to find the spatial distribution of the order parameter.

The dichroic contrast utilized in this work is much easier to determine, almost free of noise, and computationally efficient due to elegant math. For constant layer thickness, it can be used for quality control and process optimization without any disadvantage compared to the order parameter. Therefore, this work encourages the use of dichroic contrast and the presented imaging technique for evaluation of the alignment quality of dichroic dyes with spatially varying features.

Retardation measurement

The proposed retardation measurement is a straight-forward approach familiar to most researchers in the field of optics. However, this work demonstrated how to utilize it specifically to measure the spatial distribution of retardation which is useful to evaluate the alignment quality of liquid crystalline materials over an area. Combined with the dichroism imaging technique, this enables quality control throughout the whole process.

However, the retardation measurement in the presented form is limited to evaluating unidirectionally aligned LC films.

SPAMT

While different techniques to examine the alignment direction of LCs are established, they are usually either single-point measurements (e.g. XRD) or do not yield unambiguous results (e.g. POM). The proposed technique was developed in this work specifically to overcome the ambiguity. SPAMT enables measuring the spatial distribution of the alignment

direction of arbitrary alignment patterns of birefringent materials. As a side result, the spatial distribution of retardation of the birefringent film can be obtained, independent of the alignment direction.

This yields a powerful technique to complement the dichroism imaging method, so that the alignment can be evaluated and quantified at every process step. It can be used to verify the results of the retardation measurement, though it is not limited to unidirectionally aligned films. A major limitation of SPAMT is its unreliability when the retardation of the film is close to 180° . More details of this can be found in [111].

Comparison of SPAMT and retardation measurement revealed a higher precision and less sensitivity to defects of the former system. However, SPAMT requires more components, data processing and measurement time. Therefore, SPAMT is mostly recommended for measuring the spatial distribution of alignment or evaluating the homogeneity of the retardation on one sample. The retardation measurement is a much simpler method to compare the retardation between different samples.

7 Structuring

The ability of prepatterned liquid crystalline medium to streamline the chaotic movements of swimming bacteria into polar jets that can carry cargo along a predesigned trajectory opens the door for potential applications in cell sorting, microscale delivery and soft microrobotics.

– Turiv et al. [121]

7.1 Techniques

Within this work, two different processes were used to structure LCEs on a wafer level.

The first technique, photolithography and dry etch, is an established microsystems process to structure polymers. The technique has been successfully used to structure LCE films by means of special fluorinated resists [39, 60] or masks of silicon nitride [50]. This work goes one step further by using standard photoresists to the same end and applying the structuring technique to 100 mm wafers.

A quicker way to structure LCEs is by spatially selective polymerization [61, 62]. This work exploits the photoalignment system to directly create the target LCE structures on the substrate, without the use of any additional photosensitive material.

These two techniques are described, evaluated and compared in the following sections.

7.2 Photolithography and dry etching

The lithography process consists of structuring a photosensitive material (*resist*) on top of the target material. Using an etching step, the pattern is then transferred to the target material. This process, adapted to structure LCEs, is shown in Fig. 7.1: The aligned LCE film is covered by a positive photoresist. The photoresist is spatially exposed to UV light and developed in a solvent. The pattern of the photoresist is then transferred to the LCE film by dry etching. Finally, the photoresist is stripped in another solvent.

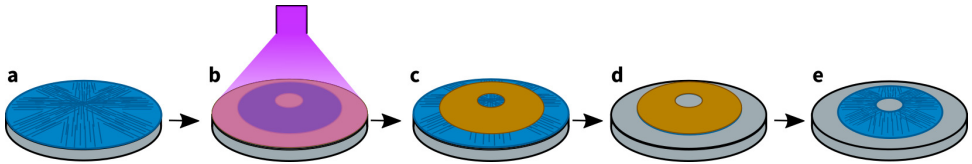


Figure 7.1 – Photolithography and dry etch: **a)** Before structuring, the photoaligned LCE film covers the whole wafer. **b)** To structure the film, it is coated by a photoresist, which is patterned by masked illumination with UV light. **c)** The positive resist is structured by dissolving the exposed parts in a developer. **d)** The structure of the resist is transferred to the LCE film by dry etching. **e)** Finally, the resist is stripped with a solvent, revealing the desired LCE structure.

While previous publications used special fluorinated resist [39] or silicon nitride [50], this work employs a standard positive resist, AZ 9260 (thickness $7\text{ }\mu\text{m}$), as a mask. The dry etching was performed in oxygen plasma. The etch rate of the LCE film was found to be about $1.5\text{ }\mu\text{m/h}$, which is similar to the etch rate of the photoresist. Therefore, the resist needs to be thicker than the LCE film in order to mask it. The detailed process can be found in the appendix (Sec. A.2).

As an example, LCE pillars with varying diameter were created by the above process. The resulting structures between crossed polarizers (Fig. 7.2) feature pillars with a diameter as small as $20\text{ }\mu\text{m}$, and a height of $3\text{ }\mu\text{m}$. The resolution limit of the utilized foil mask for photolithography is about $10\text{ }\mu\text{m}$. The limitation of resolution in this process is therefore in the foil mask step, not in the process itself. Thus, LCE structures with resolution of better than $10\text{ }\mu\text{m}$ appear feasible by this process. Another example structure is shown in Fig. 8.1.

A major challenge of this process is the interaction between the solvents of the photoresist and the photoalignment film. Spin coating the AZ 9260 resist (solvent PGMEA), and developing with AZ400K developer (buffered KOH), worked well with both Brilliant Yellow and RM257. However, on stripping the resist in DMSO, the photoalignment film got dissolved, releasing the LCE structures from the wafer.

There is a variety of solutions to this, three of which have been tried out within this work:

- **Different photoalignment material:** Instead of Brilliant Yellow or similar azobenzenes, photoalignment materials that rely on a chemical reaction (e. g. cinnamates) appear stable against stripping in DMSO. The material ROP108 by Rolic, was found to work well to that end [39, 51]. However, it requires linearly polarized UVB light (280 nm to 330 nm) for photoalignment, which is not compatible with the projection system developed in this work. ROP108 was thus only used for uniaxial alignment successfully, mainly for the tunable Fabry-Pérot filter in [51].

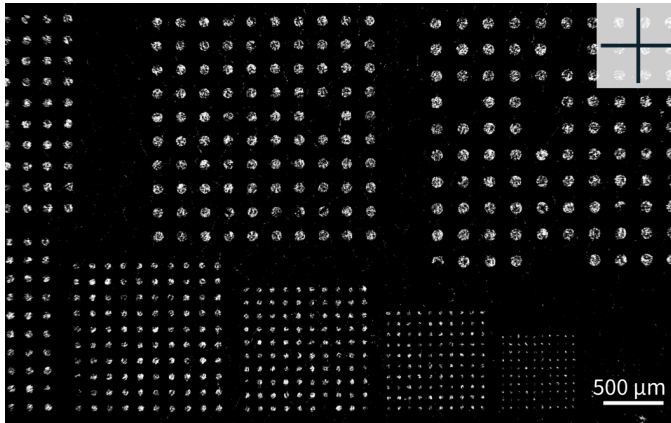


Figure 7.2 – LCE structures on wafer: Between crossed polarizers, the LCE pillars of varying diameter are clearly visible due to their birefringence. The smallest visible structures have a diameter of $30\text{ }\mu\text{m}$, the largest structures $100\text{ }\mu\text{m}$.

- **Use the bug as feature:** Since BY dissolves well in DMSO, and even in water, it can be used as a sacrificial layer. This idea was used to release LCE films from the substrate to demonstrate different actuation profiles of free-floating films on silicone oil [68].

To use this method for fabrication of integrated actuators, one more step needs to be added. The idea is to transfer the LCE structures from the first wafer, with BY photoalignment and sacrificial layer, to a second wafer. The LCE structures can be bonded to the second wafer by oxygen plasma. The first wafer can be released by dissolving the BY layer. This idea has not been implemented within this work, though.

- **Maskless lithography:** Since the LCE film relies on polymerization triggered by light, it can be directly patterned by spatially structured light, similar to the photoresist. This process is described in the following section.

7.3 Maskless lithography

The radical polymerization of the LCE materials in this work is initiated by light. This offers the possibility of structuring the LCE film directly by spatially patterning the polymerizing light.

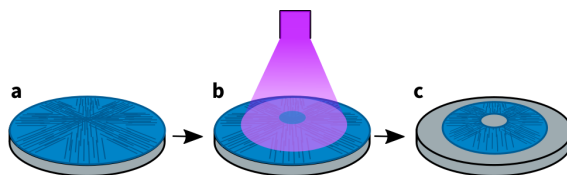


Figure 7.3 – Maskless lithography: **a)** Before structuring, the photoaligned LCE film covers the whole wafer. **b)** The aligned, unpolymerized LC film is illuminated by spatially structured light. **c)** On immersion in a solvent, the LCs in the unilluminated areas get washed off, while the illuminated regions form polymerized LCEs that stick to the substrate.

One option would be the use of a photomask, similar to photolithography. Higher versatility can be achieved by using the projection system which was developed for photoalignment ([Chapter 5](#)). Since the illumination can be spatially defined with high resolution ($10\text{ }\mu\text{m}$ for blue light), the LCE film can be structured by setting a projection pattern on the software side. This so-called maskless lithography enables definition of LCE structures without printed mask, enabling quicker test cycles and more flexibility.

7.3.1 Process

The process is illustrated in [Fig. 7.3](#). The aligned, unpolymerized LC-film is illuminated by spatially patterned light. The illuminated areas are polymerized, forming crosslinked LCEs. On immersion in a solvent, the unpolymerized parts are washed off, while the polymerized parts stay attached to the substrate. Compared to the lithography step ([Fig. 7.1](#)), no additional photoresist and no dry etching steps are necessary.

Two crucial points need to be considered for this process: (1) The radical polymerization needs to happen in an inert atmosphere, i. e. with no oxygen present which would inhibit the chain reaction. The photoalignment system was already designed with the substrate inside a closed box. This box was thus flooded with nitrogen during the illumination, to obtain an inert atmosphere. (2) The exposure dose is the most critical parameter in photolithography. Overexposure leads to the polymerization of adjacent areas, reducing the resolution of the structures, or even leading to polymerization of the whole film. On the other hand, too little exposure dose leads to insufficient polymerization, resulting in the washing off of the entire LC film in the solvent.

7.3.2 Results

The photoinitiator used throughout this work (DPO, Fig. 2.1) can be radicalized by UV light at 365 nm. However, the projection system for photoalignment and specifically the DMD are optimized for visible light. Measurements thus revealed that of the 1.4 W optical power (M365LP1, Thorlabs Inc.) put into the system, only 50 μW reached the substrate. Still, it was found that 10 s of exposure was enough to polymerize the intended regions with DPO, resembling an exposure dose of 2 mJ/cm^2 .

Since the photoalignment system was optimized for blue light, DPO was replaced by a visible light photoinitiator, Irgacure 784, for further experiments. Glass substrates were first coated with Brilliant Yellow and photoaligned. Then, they were coated by a mixture of Irgacure 784 and RM257 (mass ratio 1/100), 25 wt% in Toluene. Instead of polymerizing the whole film, the samples were put into the photoalignment system again for spatially selective polymerization. The current of the blue LED was reduced to yield only 100 μW of optical power in the image plane. It was found that the optimal exposure time for spatially selective polymerization was 5 s, yielding an exposure dose of 2 mJ/cm^2 , similar to the dose found for the UV-photoinitiator DPO.

Two successful demonstrations of photoalignment *and* maskless lithography, using the same projection system, are shown in Fig. 7.4 between crossed polarizers. They were fabricated by photoaligning BY, spin coating of RM257 (20 wt%) and Irgacure 784 (1 wt%) in Toluene, and exposure to structured light in the photoalignment system. After this exposure, the unpolymerized RM257 was washed off by dipping the samples in Toluene for 2 min.

Fig. 7.4a shows an iris-like structure (circular shape with hole in the center), aligned as a logarithmic spiral. This is the target alignment and structure assumed to lead to an integrated micro-iris with radial actuation (see Sec. 2.5). The second sample, in Fig. 7.4b/c was also structured to form an aperture with a hole in the center. However, it was photoaligned with a USAF resolution target in two steps (0° , 45°), which is revealed by rotating the two crossed polarizers.

These images highlight at the same time the capabilities, as well as the limitations of the photoalignment system. While the alignment and structuring produced the intended alignment and structure, there are (1) clear stitching errors and (2) an offset between the two processes.

(1) The stitching error of the photoalignment process only causes a minor defect line. However, the low intensity near the edges and corners of the exposure lead to unpolymerized lines on structuring. The liquid crystalline material is thus washed away at the intersections of the stitching pattern. (2) The samples have to be mounted twice in the photoalignment system. If the sample is not mounted in exactly the same position on the second exposure as in the first, an offset between photoalignment pattern and shape occurs. This can be seen

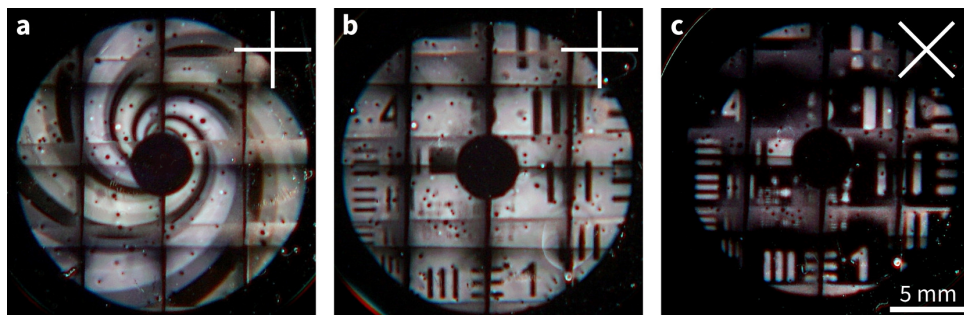


Figure 7.4 – Photoaligned and structured LCE film: Two LCE films, structured by maskless lithography to form a circular micro-iris with a hole in the center. **a)** The film was photoaligned to yield a logarithmic spiral alignment. **b-c)** The film was aligned with a USAF resolution target at 0° and 45°, which is revealed by rotation of the crossed polarizers. The samples show errors from stitching, both from photoalignment and maskless lithography. Furthermore, a lot of defects are visible on both structures.

from the mismatch of the stitching lines in Fig. 7.4.

A further observation regards the high number of defects in these images. As discussed above, those are particles or holes from the spin coating of the LCE solution with high concentration. Further optimization is needed to reduce the number of these defects, not only for maskless lithography, but also for photolithography.

7.4 Discussion

This chapter presented two approaches for structuring LCE films on the wafer level. By using the technique of photolithography and dry etching, it is possible to structure LCEs with standardized AZ 9260 without any need of specialized fluorinated resists. Furthermore, one can even eliminate the need for all these processes with maskless photolithography.

By employing the same optomechanical system for photoalignment and structuring, maskless lithography requires fewer materials and process steps than photolithography with a photoresist. However, the maskless lithography does not yield a resolution as good as the photolithography with dry etching. Experimental results showed the smallest structure size, obtained by maskless lithography, to be about 50 μm . The self-built projection system offers a resolution of <10 μm . Even though this is not as good as the resolution of a commercial photolithography system, it does not seem to be the limiting factor. Multiple reflections,

rough surfaces, and potentially the extension of the chemical chain reaction does not allow for spatial transitions between polymerized and non-polymerized regions that are sharper than $50\text{ }\mu\text{m}$.

Further obstacles of the maskless lithography process in this work are the strong offset (1 mm) between photoalignment pattern and LCE structure, and the spatial inhomogeneity of the light intensity leading to unpolymerized lines along the stitching edges. Both of these are technical difficulties, that can be overcome by an improved optomechanical setup of the system.

This work thus shows maskless lithography by means of a projection system to be advantageous for higher throughput and faster prototyping. However, for high-resolution LCE structuring, photolithography and dry etching are indispensable, though two-photon polymerization has been demonstrated to achieve submicron resolution of LCE structures by direct laser writing [62].

In the end, both processes to structure LCEs highlight the compatibility of the material with microsystems processing. Thus, aligned structures of LCEs can be defined on a wafer level. However, in order to use the resulting structures as actuators, they still need a stimulus to trigger the phase transition, as well as some leeway and constraints to enable movement. Both topics are discussed in the following chapter.

8 Actuation

The use of LCEs in the laboratory to detect traces of chemical vapors seems as promising as their use as temperature indicators.

– Junren Wang [122]

In order to use LCE structures as actuators for MEMS, two more requirements need to be met: (1) A path to reversibly trigger the phase transition has to be implemented. (2) In order to enable a specified movement, the actuator structure has to be partially released from the substrate. There is a variety of approaches to both of these requirements which are discussed in this chapter.

Within this work, only the feasibility of embedding heaters to trigger the actuation has been demonstrated. Except for this achievement, this chapter serves as an outlook regarding future research paths towards integration of LCEs as actuators for MEMS.

8.1 Stimulation of actuation

The nematic-isotropic phase transition of LCEs can be triggered by various stimuli, the most practicable of which are heat and light. Naturally, heat can also be applied by means of light. However, the focus for this work was on heating the LCE structure directly through Joule heating. Future work will put more emphasis on harvesting light to that end.

8.1.1 Resistive heating

Previous projects have developed flexible platinum heater structures, which were embedded in LCE actuators. By applying an electric current, the LCE structure was heated, triggering the phase transition and thus contraction of the actuator [1, 17, 43, 45]. The downsides of these demonstrators were the high power consumption (several watt) and large actuation times (tens of seconds). These drawbacks can be solved by miniaturization of the LCE structures, thus decreasing the required thermal power as well as the actuation time.

To evaluate the possible actuation times, integrated LCE structures were fabricated on top of platinum heaters on a Pyrex wafer with the LCE fabrication steps from [Sec. 7.2](#). The process consisted of the following steps:

- Deposition and structuring of a negative resist (ma-N 1420);
- Deposition of WTi (adhesion layer) and Pt layer as resistive heater;
- Lift-off of the negative resist to structure the metal layer;
- Deposition of LCE film by spin coating, and subsequent polymerization;
- Deposition and structuring of a positive resist (AZ 9260);
- Dry etching of the LCE film in oxygen plasma;
- Stripping of the positive resist.

The detailed process can be found in [Sec. A.2](#). As a proof of concept, in this fabrication run, the alignment of the LCEs was done by a magnetic field (0.4 T) perpendicular to the wafer surface, instead of the photoalignment procedure. However, the magnetic force seemed not strong enough to induce this vertical alignment in thin films.

The hereby achieved LCE structures thus do not show a preferential alignment. Even so, the material forms a nematic phase at room temperature, leading to birefringence. By applying an electric current through the platinum heaters, the LCEs can be heated beyond the phase transition temperature. This triggers the change to the isotropic phase which does not show any birefringence. Hence, the reaction time to the resistive heating can still be evaluated by looking at the LCE structure between crossed polarizers.

Results

[Fig. 8.1a/b](#) shows a square-shaped LCE structure on top of a platinum heater, with and without crossed polarizers, respectively. By Joule heating, the LCE undergoes a phase transition from nematic (showing birefringence) to isotropic (no birefringence). As can be seen in the image series [Fig. 8.1c-d](#), the transition is highly sensitive to the temperature. Since the temperature in the center of the structure is highest, the phase transition progresses there at lower current than on the edge of the structure.

The phase transition of this specific structure (size $2 \times 2 \text{ mm}^2$, thickness $3 \mu\text{m}$) starts at an electrical power of 230 mW, with a driving voltage of 12 V. On applying an electrical power of 400 mW (17 V), the phase transition is complete.

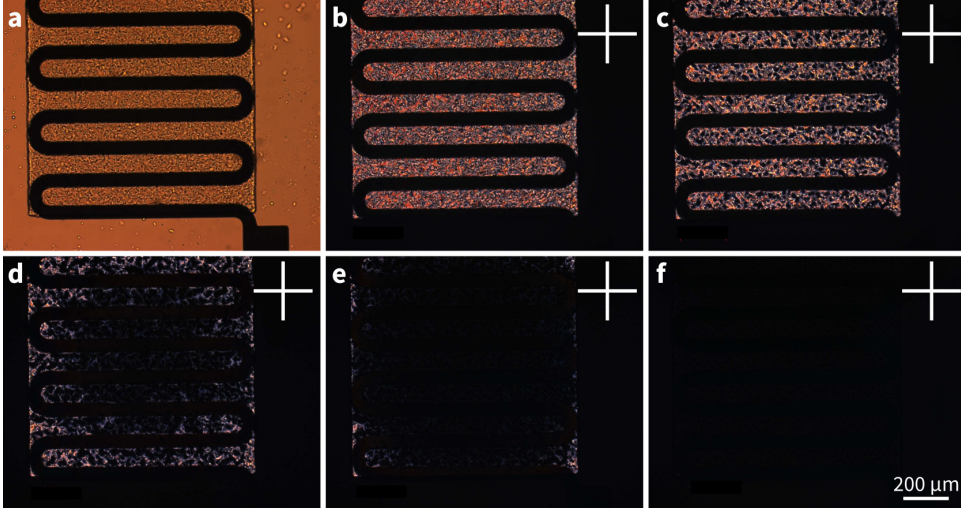


Figure 8.1 – LCE phase transition stimulated by heat: **a)** A square-shaped LCE structure ($2 \times 2 \text{ mm}^2$, thickness $3 \mu\text{m}$) on top of a meandering platinum heater. **b)** Adding crossed polarizers reveals the birefringence of the nematic phase. **c-f)** On applying heat by electric current, the LCE transitions to the isotropic phase which is not birefringent. This image series at increasing currents reveals the inhomogeneity, where the LCE in the center transitions at lower current, due to the higher temperature. **f)** The transition is only complete for the whole structure in the last image (400 mW).

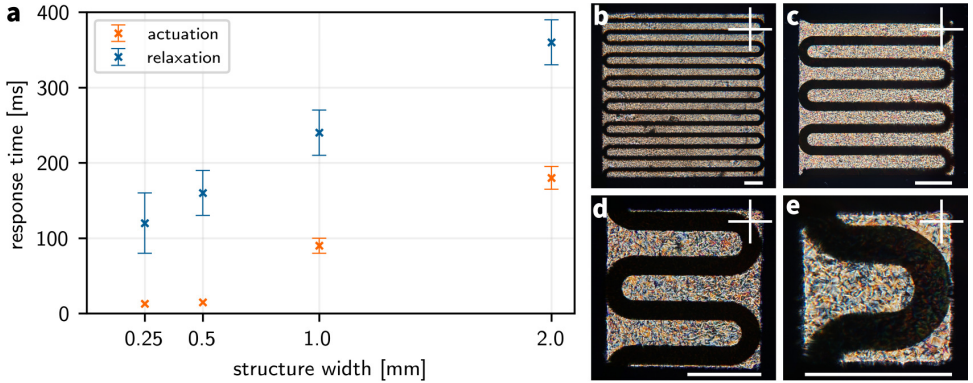


Figure 8.2 – Actuation times of LCE structures: **a)** Actuation and relaxation times of the phase transition for different structure sizes, shown at different magnifications in **b-e)**. The nematic-isotropic phase transition (actuation) is one order of magnitude faster than the back-transition (relaxation). Furthermore, the phase transition time strongly depends on the LCE structure size. Scale bars of **b-e)** 250 μm.

By measuring the time between the rising edge of the electric current and the decrease in optical transmission, the delay between applying heat and the phase transition can be quantified. To that end, a function generator was used to periodically trigger the phase transition of LCE structures with different sizes (width of 0.25 mm, 0.5 mm, 1 mm and 2 mm, thickness 3 μm). A visible light photodiode was used to measure the transmission of the LCE film between crossed polarizers. By this method, the actuation and relaxation time of the phase transition could be quantified.

Fig. 8.2a shows the phase transition times in dependency of the structure width. The LCE structures, fabricated on top of meandering platinum heaters, are shown at different magnifications in Fig. 8.2b-e. The shown values were obtained by measuring the time difference between 10 % and 90 % of the change in optical transmission. On heating the LCE structures, the transmission decreases quickly due to the phase transition from nematic to isotropic. The relaxation to the nematic state occurs when switching off the electric current, thereby letting the LCE structure cool down.

The results in Fig. 8.2 reveal the actuation speed to be highly dependent on the structure size. Phase transition times as low as 13 ms can be obtained at an LCE structure size of 250 μm. However, the relaxation time is one order of magnitude larger. Even for the smallest structure size, the transition from the isotropic to the nematic phase takes >100 ms.

Besides the actuation time, the power consumption of the platinum heater is a further

consideration. The tested structures with the widths of 0.25 mm, 0.5 mm, 1 mm and 2 mm showed an electrical power consumption of 180 mW, 250 mW, 320 mW and 400 mW, respectively. The necessary voltage ranges from 3 V to 20 V at currents of <40 mA.

Discussion

These results demonstrate that miniaturization of LCE actuators enables practical actuation times for applications, compared to many demonstrations that needed tens of seconds up to minutes to actuate [1, 45]. Furthermore, miniaturized LCE structures can actuate under reasonable voltages compared to other soft matter actuators. The response time measurements show the promise of decreasing the size of the LCE structures. Furthermore, the results reveal the bottleneck to be the relaxation of the material, which is due to the slow cooling down process.

Thus, the actuation time can be reduced by enhancing the heat coupling out of the LCE structure. Instead of glass substrates, the LCE actuators can be fabricated on a substrate with better thermal conductivity. Additionally, the thermal conductivity of the liquid crystalline material can be improved. By making the LCE structure conductive, the heat coupling into and out of the actuator can be increased.

Instead of the platinum heater structure underneath the actuator, the LCE can be either made conductive or coated by a conductive layer. Options to make LCE films conductive include doping with carbon nanoparticles [25], carbon nanotubes [66, 123], and liquid metal microparticles [24]. As an alternative, the surface of the LCE structure can be coated by a conductive layer of silver nanowires [124].

Each of these solutions influences the mechanical response of the actuator, as does the platinum heater structure proposed in this work. However, the silver nanowires show a lot of promise due to their high flexibility, compared to the rigid platinum heaters. Since they can also be spin coated, flexible silver nanowires seem compatible with the other processes in this work and could be investigated as resistive heater material in a future project.

8.1.2 Towards light-actuated LCE actuators

Illumination with ultraviolet, visible or infrared light provides another approach to trigger the phase transition of LCEs [125, 126]. More specifically, there are two types of *photoactuation*: (1) stimulation by introducing heat through light (*photothermal actuation*) and (2) stimulation of the phase transition by directly isomerizing the mesogens in the LCE network (*photochemical actuation*) [127].

While photochemical actuation requires a specialized chemistry (often containing azo groups), it shows promise for bistable switches: The isomerization from a nematic state

to an isotropic state can be triggered by a wavelength different from the one to trigger the reverse isomerization [128].

For continuously tunable actuators, photothermal actuation offers more flexibility with regard to fabrication, wavelength, and actuation mechanism. Photothermal actuation of LCEs has been demonstrated by doping the network with azobenzenes (stimulation by UV/visible light) [5, 129, 130], gold nanoparticles (IR) [131], carbon (IR) [30], carbon nanotubes (IR) [66], and nanoparticles (IR) [132]. This selection of materials highlights the number of potential paths towards light-actuated LCEs.

A lot of the current LCE research is focused on exploiting these materials to create untethered systems [35] that can either be controlled remotely by light [133] and even work autonomously [5, 6].

With regard to MEMS, resistive heating seems preferable due to the easier implementation of heater structures compared to light sources. On the other hand, integrated fabrication methods can complement the realization of miniaturized light-driven robotic systems. Both approaches, electrothermal actuation and photoactuation, are thus of interest for future applications of soft matter actuators.

8.2 Towards free-moving actuators

While this work has demonstrated the feasibility of LCE actuators on the wafer level, the definition of mechanical constraints is still lacking. With the process described in [Sec. 8.1](#), the LCE structures are fully attached to the substrate and thus unable to move freely. For applications of LCE actuators, the structures need to be suspended, i. e. partially attached and partially released from the substrate.

Here, I want to suggest and discuss four methods to achieve suspended LCE structures, which are illustrated in [Fig. 8.3](#):

- **Structured sacrificial layer:** A sacrificial layer can be deposited and structured before defining the LCE actuator. By dissolving the sacrificial layer, the LCE structure is partially suspended from the substrate ([Fig. 8.3a](#)). Examples for sacrificial layers that work well with LCEs include dextran, poly(vinyl alcohol), poly(acrylic alcohol) and poly(2-ethyl-2-oxazoline) [39, 134].

The main limitation of this method is the thickness of the achieved cavity underneath the LCE structure. The sacrificial layer can only be as thick as the LCE film to obtain reasonable coverage by spin coating. Therefore, the cavity thickness after dissolving the sacrificial layer will only be in the order of a few microns. Since the LCE structure becomes soft on actuation, it might thus get attached to the substrate due to the small

gap and not actuate reversibly. For small actuator structures, this may be feasible, but for larger muscles in the millimeter range the gap to the substrate needs to be larger.

- **Selective substrate etching:** A small gap to the substrate can also be achieved by selectively etching the substrate, e. g. xenon fluoride can be employed to etch silicon selectively to polymers. By masking the substrate correctly, a cavity can be etched underneath the LCE structure (Fig. 8.3b). Similar to the structured sacrificial layer, this method can only be used to achieve small gaps underneath the LCE film, in the order of 10 μm . Again, this may be sufficient for small LCE actuators.
- **Backside etching:** Larger space beneath the LCE structure can be achieved by etching the substrate from the backside, either by wet etching in KOH or by dry etching with DRIE (Fig. 8.3c). Dry etching offers more flexibility in terms of orientation of the cavity geometry, since wet etching is constrained by the crystalline structure of the substrate.
- **Wafer transfer:** The difficulty in etching from the backside is stopping the process before the LCE film is attacked. A solution to this could be the transfer of the LCE structure to an already etched wafer (Fig. 8.3d). By employing a sacrificial layer underneath the LCE film, it can be released from the processing wafer and bonded to a structured wafer by means of plasma activation or an additional adhesive.

This work aimed to create relatively large LCE structures (length and width in the millimeter range) on a wafer level. Therefore, ongoing experiments are focused on backside etching to create free-standing actuators.

Since research work is never truly complete, future work and further projects have to demonstrate whether these methods can successfully be applied to that end.

8.3 Towards radially actuating LCEs

As discussed in Sec. 2.5, a tunable LCE iris requires a logarithmic spiral alignment pattern. Therefore, the photoalignment system in this work was used to create logarithmic spiral alignment, see Fig. 4.3a. The opening angle of the spiral can be selected to optimize the actuation in-plane. However, since the project did not reach the mature stage of creating freely moving actuators (see Chapter 8), no empirical actuation data could be obtained within this work.

With regard to radial actuation, one puzzling data point remains: The tunable LCE iris by Schuhladen et al., which was radially aligned and appears to create radial movement (Fig. 1.1a). Potentially, the symmetric arrangement of embedded heater structures forced the

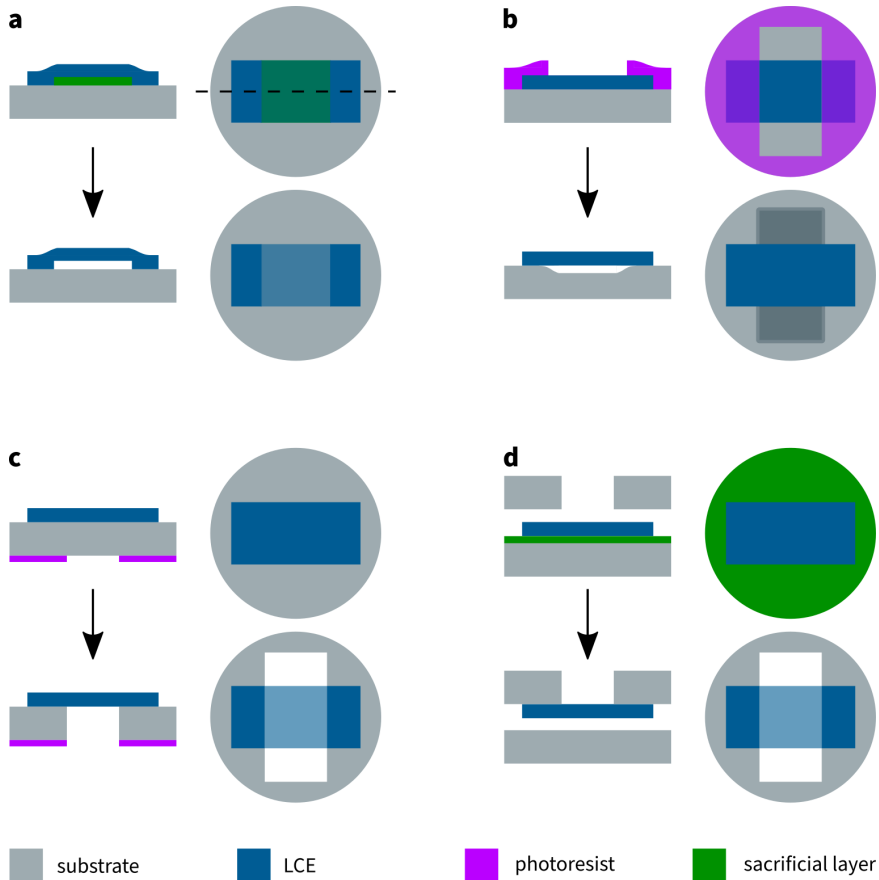


Figure 8.3 – Partial release methods for LCE structures: **a)** Removal of a structured sacrificial layer underneath the LCE. **b)** Selective etching of the substrate through a photomask. **c)** Anisotropic backside etch. **d)** Transfer of the LCE film to a structured wafer by means of a sacrificial layer.

LCE actuator to stay in-plane and allowed for this kind of movement. All other considerations point to logarithmic spiral alignment as the solution to in-plane radial actuation with LCEs, and in general, for anisotropic actuators that have a Poisson's ratio $\nu \neq 0$ [47, 48].

9 Summary

Stimuli-responsive soft matters can be ideal candidates for applying in smart windows, flexible electronics, security printings, microactuators, and medical diagnostics. [126]

Within this work, a chain of processes to fabricate liquid crystal elastomer actuators on the wafer level has been developed, evaluated, and optimized. The fabrication steps involve deposition of thin LCE films, arbitrary definition of the alignment direction of the liquid crystals, and structuring of the material.

The focus was placed on defining the alignment of the LCEs in a flexible manner. To that end, an optomechanical apparatus for photoalignment was designed and implemented. The system can be used to define arbitrary alignment patterns of LCs on 100 mm substrates with a spatial resolution of 10 μm . Emphasis was placed on maximum flexibility, to allow for light exposure at different wavelengths, control of humidity, and automation.

To optimize the photoalignment process, two optical methods to evaluate the resulting films were developed. The first technique allows to quantify the alignment of dichroic molecules with a signal-to-noise ratio that is sufficient for dichroic layers as thin as a few nanometers. The second technique enables the measurement of the spatial distribution of retardation and alignment direction of liquid crystals. The accuracy of this method relies on the retardation of the LC film. In general, it can be applied to measure the distribution of birefringence in anisotropic materials as long as the retardation is not close to integer multiples of 180°.

Having optimized the photoalignment process, two fabrication processes to structure LCEs on a wafer level were developed. With standard photolithography and dry etching, structure sizes with a resolution of 10 μm were fabricated. As an alternative, the photoalignment system was used to structure the LCE films by maskless lithography, realizing feature sizes of 100 μm , without the need for a photoresist or dry etching.

Furthermore, resistive heaters were implemented within the process flow to trigger the phase transition of the LCE actuators. This enabled the characterization of the actuation speed for different structure sizes. The fastest LCE structure with a width of 250 μm enabled transition times of 13 ms (nematic-isotropic) and 160 ms (isotropic-nematic).

Despite the successful development of these processes, further fabrication and optimization is necessary to exploit the full potential of LCE actuators for microsystems. Most notably, the actuators need to be partially released from the substrate to enable free movement.

10 Conclusion

Nous concluons que si des systèmes (vulcanisés) [...] s'avèrent chimiquement réalisables, ils montreront peut-être une élasticité non linéaire, et un « point critique mécanique » assez remarquables.

– Pierre-Gilles de Gennes [13]

This project aimed at investigating the feasibility of liquid crystal elastomers as a generic actuator material for microsystems. The advantage of this particular soft matter actuator over other materials and mechanisms is the free programmability of actuation direction in the material itself, which shows promise at imitating complex biological systems, like the mammalian iris.

The experimental results in this work demonstrate the following points:

- Liquid crystal elastomers are compatible with a wide range of microsystems processes and can be integrated in wafer-level fabrication of MEMS. While some challenges remain to be solved, deposition, alignment, structuring and embedding of a heating mechanism are feasible as batch processes.
- Photoalignment enables the definition of arbitrary alignment patterns on a wafer level, allowing for unprecedented actuation schemes. The experimental methods and results of this work pave the way for target-specific designs of photoalignment systems.
- Miniaturization to thin films reduces the response time of LCE actuators to the sub-second region. The heat coupling is clearly the limiting factor, especially for the back-actuation. Thus, smaller heat capacity and higher heat conductivity enable optimization for even faster response times.

Further work is necessary to combine these processes in order to obtain viable applications, like miniaturized tunable apertures, micro-grippers, and other systems requiring large strain or complex actuation schemes. Due to the versatility of the material with regard to actuation direction and stimulation, it will be of continuing interest for mimicking biological systems. I hope this work will support the development and fabrication of such replicas.

A Appendix

A.1 Photoalignment Software

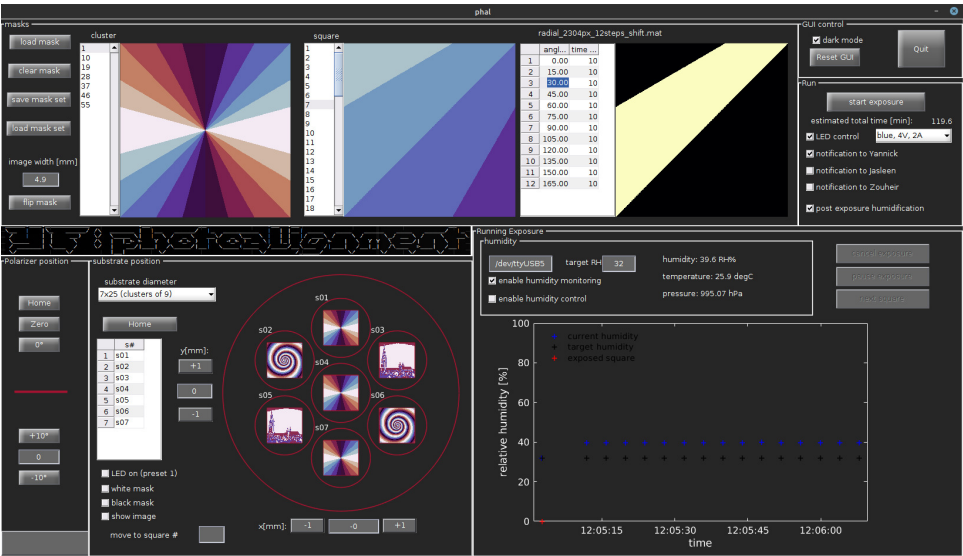


Figure A.1 – Example image of the MATLAB GUI for photoalignment: Arbitrary alignment patterns can be imported and configured for photoalignment. Additionally, LED, rotation stage, xy-stage, DMD and humidity can be controlled and monitored. The code is available at <https://github.com/yannfol/photoalignment>.

A.2 Cleanroom processes

- start with Pyrex wafer, thickness 500 μm
- HDMS-priming
- spin coating of ma-N 1420, 4000 rpm, 30 s, static
- soft bake, 100 $^{\circ}\text{C}$, 120 s
- UV exposure with foil mask, 60 s, 9 mW
- develop in ma-D 533/S, 1.5 min, rinse, spin dry
- PVD: DC-sputtering of adhesion layer WTi, 15 nm (100 W, 2.5 min, Leybold UNIVEX 500)
- PVD: DC-sputtering of Pt: 100 nm (400 W, 2×50 s, wait interval 20 min, Leybold UNIVEX 500)
- lift-off Pt in DMSO over night, then with DMSO and ultrasound
- annealing step, 2 h, 250 $^{\circ}\text{C}$
- plasma activation, 3 min, 100 W
- spin coating of LCE in Dioxane (10 wt%), 30 s, 1000 rpm
- polymerization of LCE under UV lamp in nitrogen atmosphere
- spin coating of AZ 9260 (Microchemicals Ltd.), 4000 rpm, 30 s, static, target thickness 7 μm
- level out for 3 min
- soft bake, 100 $^{\circ}\text{C}$, 8 min
- rehydration, 1 h, 60 %RH
- multi-exposure with foil mask: 9×4 s, 9 mW, wait interval 30 s
- develop with AZ400k/water, 1/3, 3 min
- dry etch in oxygen plasma, 100 W, 2.5 h
- resist stripping in DMSO over night, then with DMSO and ultrasound

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Journal articles

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Conference contributions

1. Y. Folwill and H. Zappe, “[Measuring the spatial distribution of liquid crystal alignment and retardation using stokes polarimetry](#)”, in *Optics and Photonics for Advanced Dimensional Metrology*, vol. 11352, Online Only: SPIE, 2020, pp. 191–196.
2. Y. Folwill, S. B. Shah, and H. Zappe, “[MEMS-processed artificial muscles with freely-programmable actuation direction](#)”, in *2019 20th International Conference on Solid-State Sensors, Actuators and Microsystems Eurosensors XXXIII (TRANSDUCERS EUROSENSORS XXXIII)*, Berlin, Germany: IEEE, 2019, pp. 92–95.
3. Z. Wang, Y. Folwill, P.-H. Cu-Nguyen, and H. Zappe, “[Tunable bandpass filter for mid-infrared wavelengths using liquid crystal elastomer actuators](#)”, in *Proc. SPIE 10545, MOEMS and Miniaturized Systems XVII*, 2018, p. 12.

Oral presentations

1. Y. Folwill: "Wafer-Level Fabrication of Miniaturized LCE Actuators for Microsystems", at International Liquid Crystal Elastomer Conference (ILCEC), Eindhoven, The Netherlands, September 17, 2019.

Software

1. The code which was developed for the automated photoalignment system (Sec. 5.4) can be found at <https://github.com/yannfol/photoalignment>.
2. The code which was developed for quantifying the dichroism (Sec. 6.2) can be found at <https://github.com/yannfol/dichroimag>.

A spectrum of gratitude

This work was supported by the [Deutsche Forschungsgemeinschaft](#) (DFG, German Research Foundation) under Grant 316245751 (“MuscleMEMS”).

Q: *How many existentialists does it take to screw in a light bulb?*

A: *Two. One to screw it in and one to observe how the light bulb itself symbolizes a single incandescent beacon of subjective reality in a netherworld of endless absurdity reaching out toward a maudlin cosmos of nothingness.*

Q: *How many people did it take to create this PhD thesis?*

A: *Uncountable. It took at least...*

- One [Sergio Vilches](#), work wife, mentor and student. I don't find the words to describe how formative and valuable the time with you has been and will be to me.
- One [Jasleen Lall](#), arguably work wife, bookworm, fellow traveler on the roads of science, engineering, mind games and applied philosophy. I am looking forward to further discussions of any subject that happens to appear in our minds.
- One [Sanket Shah](#), work wife and/or master student, whose endless energy and creativity not only pushed this project forward significantly, but also inspired deep, valuable and lasting discussions. It was a pleasure working with you and sharing the road with you on this part of our lives.
- One [Kaustubh Banerjee](#), mentor and accomplice, to nourish my open source enthusiasm and teach me the value of simplicity. I am glad to again and again slide down a spiral of topics with you, even if the whole day passes by.
- One [Gerardo González-Cerdas](#), whose quick-wittedness never ceases to amaze me. It's always a pleasure to enjoy your energy and good mood, or to suffer from your well-versed sarcasm.
- One [Ziyu Wang](#), whose creative mind showed me to spot beauty in the overlooked parts of my life. Thank you for helping me to get started in the lab and guiding me on our shared journeys.

- One [Yanis Taege](#), who brought a lot of fresh energy and enthusiasm to our lab and keeps on improving it. It's a pleasure to work with a kindred soul, optimizing the world and caring about scientific clarity. Thank you for the very many productive discussions.
- One [David Iliaë](#), pundit of puns, whose enthusiastic "pura vida" has enriched many a day in our lab. It is enjoyable sharing stories, meals and ideas with you. And thanks for all the puns...
- Innumerable colleagues, [Simon Kretschmer](#), [Daniel Kopp](#), [Pouya Rajaeipour](#), [Yannick Minet](#), [Sophie Jenne](#), [Alex Dorn](#), [Phuong Ha Cu Nguyen](#), [Pengpeng Zhao](#), [Vahideh Karbasi](#), [Pei Li](#), [Guoliang Wang](#), who not only left my optical table untouched, but also always took the time to help me with my frequent questions. Thank you for your ceaseless support, and for saving me from many moody days.
- Three student assistants, [Timo Villinger](#), [Akash Gupta](#) and [Zouheir Zeitouny](#), who not only supported my project, but also taught me valuable lessons about personality and different cultures.
- One Mensa, which is the place where ideas are created, modified and spread between colleagues. And thanks for all the Milchreis.
- Two chemists: [David Ditter](#), University of Mainz, who helped me get started with my project and would answer patiently all of my chemistry-related questions. [Paula Straub](#), who supported Jasleen and me with her chemistry fervor. It is always a pleasure to learn chemistry from you.
- One [Stefan Schuhladen](#), who captured me for the project and laid the foundational work that enabled this thesis.
- One [Dr. Çağlar Ataman](#), first for hiring me of the street, second for finding the time to answer many optics questions, but most of all for fruitful discussions about the secrets of the universe and the meaning of life.
- One [Nadja Katthagen](#), to support us in the battle with the GUBO. Thank you for helping me fill out all the necessary forms and your patience when fixing my administrative issues.
- Two Technicians, [Bernd Aatz](#) and [Torsten Rehwald](#), who helped to keep the lab running and safe. Thank you for supporting me in the production of various parts of my setup.

- One [Prof. Hans Zappe](#), to supervise this mob of sciengineers, and to teach micro-optics to the people. Thank you for placing the trust in me to tackle this PhD project, for your continuous, kind support, and for living a good example how to teach classes and treat colleagues. Thank you for creating such a constructive environment, which gives ideas and people space to mature.
- One [Ingo Breunig](#), to drag me into the light (or potentially the dark lab), with his ceaseless enthusiasm for the mathematical elegance of optics. It was a pleasure participating in your lecture and solving your exercises. Thank you for supervising first my master's project and now also my PhD thesis.
- One [Simon Herr](#), who not only taught me best practices how to preserve both eyes when working in a laser lab, but also pushed my master's project with incessant motivation and patience.
- A whole team of sportive and spirited personalities. Thank you, dear [Disconnection-](#)players, for all the running and disk-throwing, and the enjoyable time we socialized and competed in tournaments.
- Helluvalot of software developers, who created and maintained the tools that are indispensable to conduct scientific research, see [Fig. A.1](#). A big "Thank you!", to all the developers, who contribute to this essential software. Specifically, my eyes want to thank the developers of the dark mode in almost any software.
- My parents [Volker](#) and [Brigitte](#), and my siblings [Jens](#) and [Friederike](#), who persistently encourage me on my path, believing that it will lead somewhere sane. Thank you for accepting the changes in my mindset and behavior, which have been shaped by the last few years. And thank you for being open-minded, healthy and my family.
- My grandparents, specifically Gunhild, because she wanted to be mentioned here.
- One [Maren](#). Having written a whole PhD thesis, I still lack the words to describe how grateful I am for your encouragement, your patience, and understanding. For the lack of a suitable word, I will call the time with you marenificent. Thank you for following the changes in my life, and for being part of that change.

