Soft Nanoimprint Lithography on Curved Surfaces

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Abstract

This thesis addresses the challenges of imprinting on curved surfaces. The imprinting on curved surfaces has gained high relevance due to its increasing demand for application in optics, biomedical implants and sensors. Currently, it is challenging to pattern structures on curved surfaces using conventional photolithography[1] due to the limited depth of focus of the projection system. Herein, rises the use of Nanoimprint Lithography (NIL). NIL allows for uniform molding of structures on highly curved surfaces. It is not limited by optical effects such as scattering, diffraction and interference in a substrate as compared to conventional methods. In this thesis, soft UV-NIL process is developed, optimized and implemented for patterning on non-flat surfaces. It is a mechanical process based on the transfer of structures from a flexible and transparent soft polydimethylsiloxane (PDMS) mold to the substrate in the presence of UV light. Demolding[2] is an important aspect for a successful NIL process. The induced shear stress during the separation of the stamp (mold) from the substrate can lead to structural distortion, specifically on the edges of the curved surface, where the inclination is high.

Soft NIL was applied as it is not dependent on complex machines, strict environmental conditions and optical limitations as compared to conventional lithography. A high precision *Nano-positioning and Nano-measuring Machine* (NPMM) was used to provide controlled positioning of substrate to the stamp. A compact and adjustable soft UV-NIL process was designed, assembled and integrated into the NPM machine. The successful implementation of the fundamental process in the NPMM created a foundation for making a NIL tool to be combined with a rotating device and integrated into the NPMM. The combination enables five degrees of freedom of motion for orthogonal molding and de-molding on edges of curved substrates. The rotating NIL tool addresses the generally overlooked challenge of patterning and characterization on the edges of curved substrate. Regardless of restricted measurement capabilities at high inclinations for high resolution nanostructures, it was possible to perform SEM imaging of the structures on top of the lens substrate as well as at inclination of 45°. It

[1] A fabrication process to selectively pattern a thin film substrate using light to transfer a pattern from a photomask to a light-sensitive photoresist.
[2] It is the separation of the molded pattern from the mold.

has displayed imprinting capabilities on the edge of curved substrate with radius of curvature of approximately 25 mm at a surface normal tilted to 45°. The method enables precise imprinting capabilities at high inclinations, thereby presenting a novel approach of soft NIL on curved surfaces.

Zusammenfassung

Diese Arbeit befasst sich mit den Herausforderungen des Prägens auf gekrümmten Oberflächen. Die Prägung auf gekrümmten Oberflächen hat aufgrund der steigenden Nachfrage nach Anwendungen in der Optik, bei biomedizinischen Implantaten und Sensoren eine hohe Relevanz gewonnen. Gegenwärtig ist es aufgrund der begrenzten Tiefenschärfe des Projektionssystems eine Herausforderung, Strukturen auf gekrümmten Oberflächen mit Hilfe der konventionellen Photolithographie zu strukturieren. Daher wird zunehmend die Nanoimprint-Lithographie (NIL) eingesetzt. NIL ermöglicht die gleichmäßige Abformung von Strukturen auf stark gekrümmten Oberflächen. Sie ist im Vergleich zu herkömmlichen Methoden nicht durch optische Effekte wie Streuung, Beugung und Interferenz in einem Substrat begrenzt. In dieser Arbeit wird ein weicher UV-NIL-Prozess entwickelt, optimiert und für die Strukturierung auf nicht ebenen Oberflächen implementiert. Es handelt sich um einen mechanischen Prozess, der auf der Übertragung von Strukturen von einem flexiblen und transparenten weichen Polydimethylsiloxan (PDMS) Stempel auf das Substrat in Gegenwart von UV-Licht basiert. Die Entformung ist ein wichtiger Aspekt für einen erfolgreichen NIL-Prozess. Die induzierte Scherspannung während der Trennung des Stempels vom Substrat kann zu strukturellen Verzerrungen führen, insbesondere an den Rändern der gekrümmten Oberfläche, wo die Neigung hoch ist.

Das weiche NIL wurde angewandt, da es im Vergleich zur konventionellen Lithographie nicht von komplexen Maschinen, strengen Umgebungsbedingungen und optischen Einschränkungen abhängig ist. Eine hochpräzise Nanopositionierungs- und Nanomessmaschine (NPMM) wurde eingesetzt, um eine kontrollierte Positionierung des Substrats zum Stempel zu ermöglichen. Ein kompakter und einstellbarer weicher UV-NIL-Prozess wurde entworfen, montiert und in die NPM-Maschine integriert. Die erfolgreiche Umsetzung des grundlegenden Prozesses im NPMM schuf die Grundlage für die Herstellung eines NIL-Werkzeugs, das mit einer Drehvorrichtung kombiniert und in das NPMM integriert wurde. Die Kombination ermöglicht fünf Bewegungsfreiheitsgrade für das orthogonale Formen und Entformen an den Kanten gekrümmter Substrate. Das rotierende NIL-Werkzeug spricht die allgemein übersehene Herausforderung der Strukturierung und Charakterisierung an den Kanten gekrümmter Substrate an. Unabhängig von den

eingeschränkten Messmöglichkeiten bei hohen Neigungen für hochauflösende Nanostrukturen war es möglich, die Strukturen sowohl auf dem Linsensubstrat als auch bei einer Neigung von 45° im REM abzubilden. Es hat sich gezeigt, dass es an der Kante eines gekrümmten Substrats mit einem Krümmungsradius von ca. 25 mm bei einer Oberflächennormalen, die um 45° geneigt ist, ein Imprinting durchführen kann. Die Methode ermöglicht präzise Prägefähigkeiten bei hohen Neigungen und stellt damit einen neuartigen Ansatz von weichem NIL auf gekrümmten Oberflächen dar.

Acknowledgements

"Im Bereich der Ideen hängt alles von der Begeisterung ab in der realen Welt beruht alles auf Ausdauer."~ Johann Wolfgang von Goethe

A prominent German writer Johann Wolfgang quoted "*In the realm of ideas everything depends on enthusiasm but in the real world everything depends on perseverance."* About 200 years later from approximately the same geographical location as his abode of writing, this quote could summarize my experience as a PhD student. As many other PhD scholars, I started this journey with a lot of enthusiasm but with passing time it was persistence that helped me walk the journey. The ability to persist came from the support, encouragement and optimism of the people around me from across the desk to across the continent.

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- I would first of all like to thank my colleagues riding on the same boat of PhD for being kind, friendly, supportive and helpful. I cherish the times when we had several

discussions about scientific as well as non-scientific topics. I am also grateful for their valuable scientific suggestions.

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Siegmar Hecht from the Microsystems Technology group for their friendly welcome. I appreciate their valuable suggestions on scientific as well as non-scientific areas.

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Chapter 1

1. Introduction

In the year 1959, Nobel laureate Richard Feynman through his renowned talk *'There's Plenty of Room at the Bottom'* paved way for endless exploration in the field of miniaturisation. He presented the ideas of scaling down information; writing at small scale, reversing the lenses of electron microscope to de-magnify, emitting and focusing ions to a small focused spot. A well-known part of the talk was the notion of writing entire 24 volumes of Encyclopaedia on the head of a pin (Feynman 1960). As a result of the need for continuous shrinking, photolithography which has been the most prominent and conventional lithography technique needs alternatives that would go beyond its resolution limit.

The International Technology Roadmap for Semiconductors (ITRS) in the year 2005 introduced the terms *"More than Moore and More Moore"* denoting diversification and miniaturisation respectively (SEMATECH 2017). The roadmap for semiconductor industry was first mapped by Gordon Moore in 1965 in terms of Moore's law. It stated that the number of transistors per inch square on an integrated circuit would double every two years (Figure 1.1)

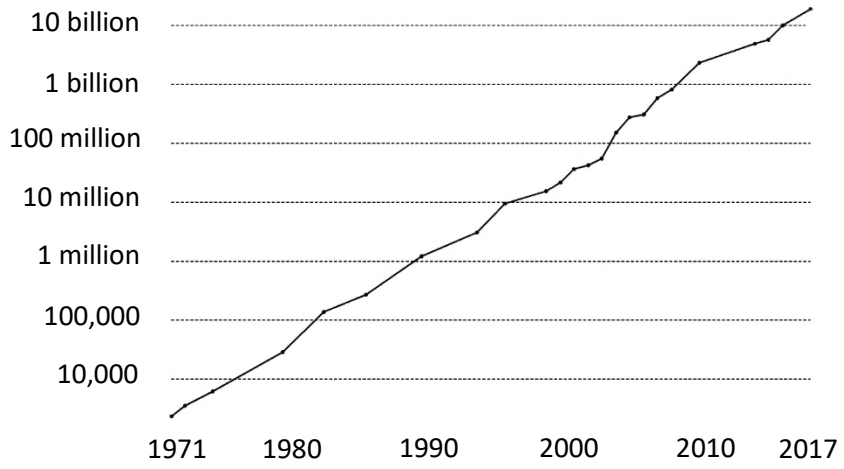

Figure 1.1: Transistors per microprocessor according to Moore's law (Karl Rupp 2018). It depicts the number of transistors that can be fixed in a microprocessor.

Since Moore's law is reaching its limit, the focus is eventually shifting from miniaturisation towards diversification facet. This is leading to placing emphasis on bringing variations in devices and applications and then developing chips accordingly (Waldrop 2016). For several years, photolithography has strongly held its position as the leader in semiconductor manufacturing; as large volume production resolution of the patterns to be transferred is limited by the wavelength of the light used for projection. Different resolution enhancement techniques have been proposed to overcome these limitations (Masato Shibuya 1997).

With each enhancement in resolution, the process becomes more expensive due to modifications in the wavelength or multiple exposures (Mack 2004). Next generation lithography (NGL) techniques overcome the challenges faced by photolithography and pave way for future devices which will not be limited to just semiconductors. The International Roadmap for Devices and Systems (IRDS) which is the successor of ITRS expands beyond semiconductors and expands to Internet of Things (IOT), cloud and mobile computing, systems integration and more. NGL techniques will therefore play key roles in the future development of systems and devices. The prediction of the scaling down of nodes and the mainstream logic devices are given in Figure 1.2.

Production Year	**2019**	**2021**	**2024**	**2027**	**2030**	**2033**
Logic industry Node range labelling (nm)	7	5	3	2.1	1.5	1.0
Logic device	finFET	Lateral Gate All Around (LGAA)	LGAA	LGAA	Vertical Gate All Around (VGAA)	VGAA

Figure 1.2: International roadmap for semiconductor and devices depicting the future of the semiconductor industry in terms of miniaturization.

Nanoimprint lithography (NIL) being one of the major NGL techniques is gaining attention due to its cost effectiveness, simplicity and capability to achieve high resolution (Chou 1996). It is based on the structuring of surface using a mold consisting of patterns. The NIL process

is primarily divided into two categories; UV-based NIL and thermal NIL or Hot embossing. A comparison of the two categories based on their properties is given in Table 1.1. NIL was first reported as thermoplastic molding, and is therefore often referred to as hot embossing. The unique advantage of a thermoplastic material is that the viscosity can be changed to a large extent by simply varying the temperature. The initial stage of the NIL process is the molding of a thin thermoplastic film using a rigid master. During a process cycle, the resist material is made viscous by heating, and shaped by applying pressure. The thermoplastic film is compressed between the stamp and substrate and then the viscous polymer is forced to flow into the cavities of the mold, conforming to the surface patterns of the stamp. When the cavities of the stamps are filled, the polymer is cooled down, while maintaining the pressure. The molten structure is then cooled and hardened. After relieving the pressure, the stamp can be demolded without damage, and reused for the next molding cycle. In a second step, the thickness profile of the polymer film can now be used as a resist for pattern transfer. For this, the residual layer remaining in the thin areas of the resist has to be removed, which is done by homogeneously thinning down the resist in an anisotropic etching process. Therefore, the process windows are opened to the substrate and the polymer can be used as a masking layer for further processing steps (Schift 2008).

Table 1.1: Comparison of Hot embossing and UV-NIL (Schift and Kristensen 2010)

Type of NIL / properties	**NIL (T-NIL)** **hot embossing**	**UV-NIL** **UV-imprint**
Pressure	20–100 bar	0–5 bar
Molding temperature	100–200°C	20 °C (ambient)
Demolding temperature	20–80 °C	20 °C (ambient)
Resist	solid, thermoplastic	liquid, UV-curable
Stamp material	Si, SiO_2 opaque	glass, SiO_2 transparent
Advantage	low-cost large-area equipment and stamps	low viscosity, low pressure
Challenge	process time, thermal expansion due to thermal cycle	step and repeat needed for large areas

1.1. NIL – The Next Generation Lithography

The history of imprint technology as lithography method for pattern replication can be traced back to 1970's but the most significant progress has been made by the research group of S. Chou in the 1990's. Since then, it has become a popular technique with a rapidly growing interest from both research and industrial sides and a variety of new approaches have been proposed along the mainstream scientific advances.

In addition to NIL, other promising NGL techniques are –

- Extreme UV lithography (EUVL)
- e-beam lithography (EBL),
- Focused ion beam lithography (FIB)
- and direct self-assembly (DSA)

Table 1.2 illustrates the characteristics of the different NGL techniques.

Table 1.2: Comparison of the different NGL techniques (Hasan and Luo 2018)

Specifications	NIL	EUVL	Maskless	DSA
Resolution	< 10 nm	< 10 nm	< 5 nm	< 10 nm
Throughput	15 wafers/h per imprint station	> 150 wafers/h	40 wafers/h	~150 wafers/h track process with 5 min anneal time
Cost	Low	Very High	High	Low
Overlay	4.5 nm	< 2 nm	< 20 nm	< 2 nm

EUVL and the mask-less techniques (EBL and FIB) are complex and expensive processes. In comparison to these techniques, NIL enables high resolution patterning at low cost and simplicity. However, since the process is a mechanical contact process, resist filling into the structure cavities and demolding becomes crucial. Misalignment often occurs due to the mechanical shift between the stamp and the substrate during the imprinting process.

Moreover, one of the vital requirements for fabrication of integrated circuits is to achieve overlay of less than 10 nm accuracy (Sreenivasan 2017). Therefore, despite several advantages, such as high resolution, high throughput, cost effectiveness, imprinting on non-flat surfaces, NIL technique is inhibited by the aforementioned challenges for it to be utilised to its full potential.

NIL has variety of applications beyond semiconductors. The applications range across nano-photonics, smartphones, displays, light emitting diodes, solar cells, optical communication, semiconductor ICs, data storage, biotechnology, pharmaceutics, medicine and security features. It further addresses new markets rather than challenging optical lithography or EUV in the IC logic and memory markets. As part of the deal with EV Group, SwissLitho's technology will be used to produce master[3] templates with 3D structures for NIL. EV Group's NIL tools will replicate those structures. Various applications of NIL are shown in Figure 1.3.

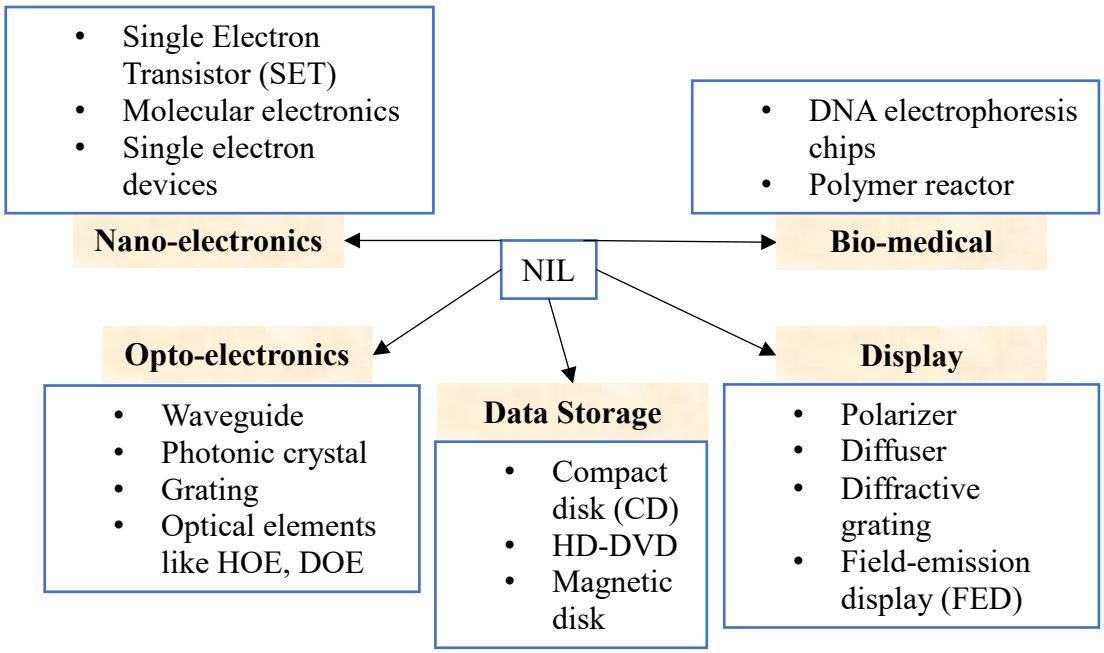

Figure 1.3: Applications of NIL in the fields of Nano-electronics, Opto-electronics, Data storage, Bio-medical and Display

[3] In NIL process, it is the primary source of patterns generated on a substrate using lithographic techniques such as photolithography, E-beam lithography, scanning probe lithography etc. from which pattern replication is carried out.

1.2. Soft UV-NIL process

The Soft UV-NIL process primarily consists of a flexible PDMS stamp, and a UV light source. The PDMS stamp is fabricated from a silicon master containing the structures or patterns. The replication of the stamp from the substrate is an essential part of the process since the stamp forms the basis of the imprinting process in soft UV-NIL. In comparison to thermal nanoimprint lithography (hot embossing), the soft UV-NIL process requires low or negligible pressure to be applied on the stamp to transfer patterns on to the resist. The filling of the resist into the cavities of the structures is promoted by capillary effect. The basic steps of the soft UV-NIL process is shown in Figure 1.4.

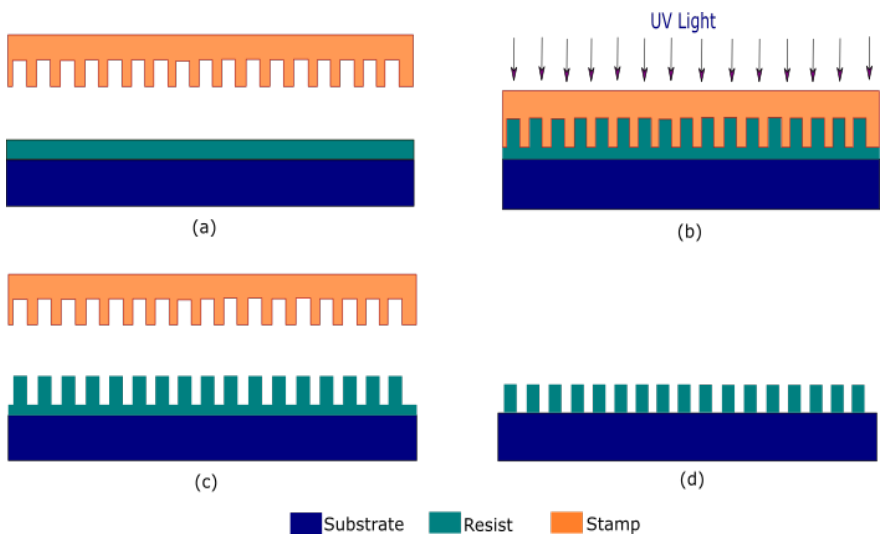

Figure 1.4: Soft UV-NIL Process steps (a) Stamp positioned on top of resist coated substrate, (b) Molding and Curing- stamp brought in contact with the resist coated substrate for filling of resist into cavities and exposed to UV light for hardening of the resist, (c) Demolding- stamp separated from the substrate, (d) Residual layer removal- Patterns transferred onto the resist and residual layer is removed.

Soft UV-NIL process is used in this project which is based on the transfer of structures from a flexible and transparent soft polydimethylsiloxane (PDMS) stamp to the substrate in the presence of UV light. Successful patterning in this technique is largely dependent on the conformity of the stamp to the substrate. The force on the stamp with resist is developed by capillary action. When the stamp comes in contact with the resist, filling of the stamp cavities starts by capillary forces, which pulls the stamp towards the substrate. Therefore, for the

successful filling of the stamp cavities, resist with low viscosities are required for rapid dispensing.

During the contact between the stamp and the resist in presence of UV light, a chemical reaction is inevitable. The contact pressure of UV-NIL leads to stamp deformations, which consists of external and capillary forces:

$$\boldsymbol{p_g(x,y) = p_{external}(x,y) + p_{capillary}(x,y)} \quad (1)$$

In cases where the dissolution of the trapped gas can be a limiting factor, a new pressure term is added with approximate models for pattern-dependent gas entrapment and its dissolution rate. For line structures, the capillary pressure is:

$$\boldsymbol{p_{capillary} = 2\gamma \cos\theta / s} \quad (2)$$

γ, θ, s, stand for surface tension of the resist, stamp-resist contact angle, and feature pitch, respectively. The combination of capillary and external pressures lead to the resist deformation (Yin et al. 2018; Sun et al. 2017).

Soft UV-NIL has been employed to fabricate various micro/nanostructures and devices for nano-electronics, opto-electronics, nano-photonics, optical components, glass, biological applications, etc. It has become a perfect match for some emerging application fields that are in need of large area patterning of sub-micro and nano scale features at a low cost, such as patterned magnetic media, light emitting diodes, optical metamaterials and plasmonic devices for chemical and bio-sensing applications, etc. In particular, this technique has demonstrated great commercial prospects in several market segments, LEDs, laser diodes, solar cells, optical elements, patterned media, flat panel displays, micro-lens, and functional polymer devices (Lan 2013, 2018).

1.3. Nano-positioning and Nano-measuring Machine

The Nano-positioning and Nano-measuring Machine, NMM-1 developed at TU Ilmenau in cooperation with SIOS Meßtechnik GmbH is able to provide a measuring and positioning volume of 25 mm × 25 mm × 5 mm with a resolution of 0.1 nm, an uncertainty of less than 10 nm and positioning repeatability of less than 0.3 nm (Manske et al. 2012) (Manske et al.

2007). The NMM-1 utilises the concept of constant realisation of the *Abbe Comparator Principle* in all three measurement axes for measurement certainty. The remarkable positioning capability of the machine is now being utilised for overcoming challenges in nanofabrication techniques such as direct laser writing. The focus sensor, which belongs to the family of optical sensors was developed within the framework of the Nano-positioning and Nano-measuring machine. Due to the non-rotationally symmetric structure of the hologram laser unit (which is the core of the focus sensor), it can measure surfaces up to approximately 9° in the y-direction, and up to approximately 24° in the x-direction. The focus sensor used in the NMM-1 is based on a hologram laser unit. However, it needs to be calibrated for measurement of structures based on the substrate properties. The calibration is done by determining a focus point on the surface of the substrate.

The machine can be used in two modes, positioning mode and scanning mode:

Scanning Mode: To comply with the *Abbe Comparator Principle*, the machine is operated in sample scanning mode. The basic components of the NMM-1 are given in Figure 1.5. For the operation, it is required that the sensor (2) and the interferometric measuring systems (1) are firmly attached to the metrological frame (5) of the machine. The intersection of the interferometer axes and the (optical or tactile) measuring sensor tip is called Abbe point (3). The sample to be measured is placed on a movable mirror corner (4) and is positioned such that the sensor contacts the surface of the sample at the Abbe point.

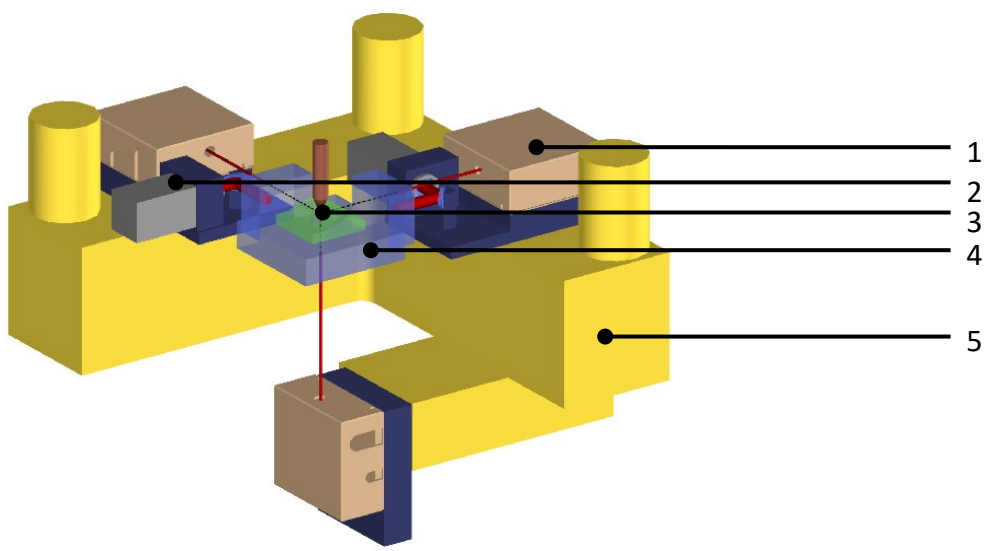

Figure 1.5 : Basic arrangement of the NMM-1: (1) interferometers, (2) sensor, (3) Abbe point, (4) Mirror corner, (5) metrological frame (Felix Gerhard Balzer 2015)

Positioning Mode: The user can control the stage in any direction. Electromagnetic direct drives ensure high-resolution lateral positioning. The axial alignment is based on a moving coil drive. The advantage of these electromagnetic drives is their dynamic behaviour, which is almost linear and enables precise positioning and movement even at high speeds of up to 5 mm/s (Hesse et al. 2012) (Amthor et al. 2008).

1.4. Thesis Background

This inter-disciplinary research is done within the framework of research training group focussing on *'Tip and laser-based 3D nanofabrication in extended macroscopic working areas' (NanoFab)* group. The goal of the research group is to combine advanced nano-fabrication techniques with exceptional positioning and measuring abilities of the NPM machines. In particular, the challenges addressed are the implementation of high-resolution fabrication on non-planar surfaces such as aspheres as well as freeform surfaces. The fabrication challenges are primarily divided into method and object-oriented techniques (Figure 1.6). These are to be realized by possible combination of techniques with different fields of work involving control, metrology and kinematics. Based on these domains, the project is divided into thirteen research themes *(NanoFab 2017)*. Integration of multi-disciplinary fields allows to explore and experiment different approaches for addressing a challenge.

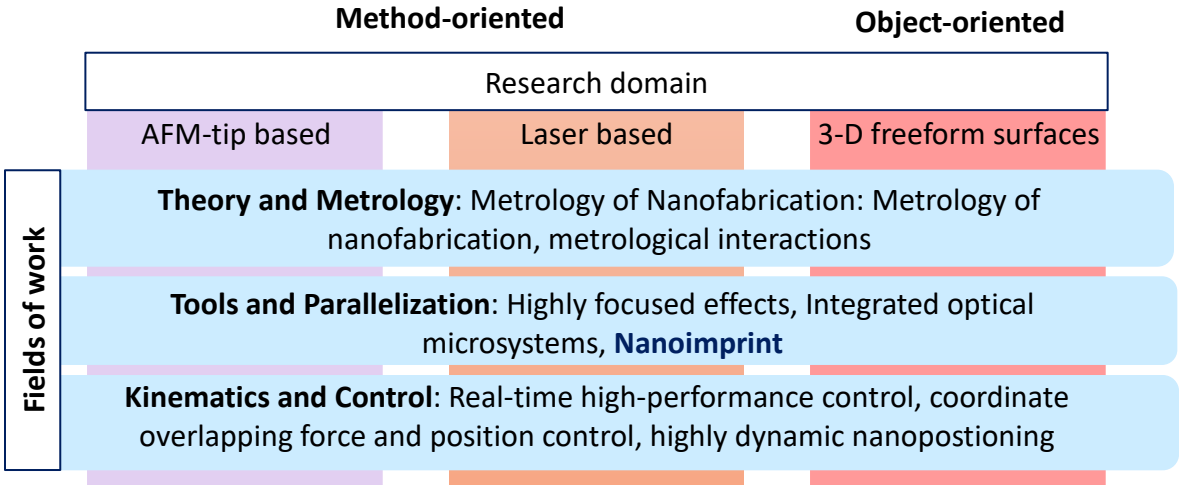

Figure 1.6: Framework of graduate school NanoFab showing the different fields of research and their correlation (NanoFab 2017)

The abundant scope of making modifications in the process and tool enables using it in combination of different existing cutting-edge devices. NIL being a simple, cost efficient and flexible technique makes it feasible to take advantage of the inter-disciplinary nature of the project. This research project explored such combinations in order to fulfil the goal of fabricating on freeform surfaces with an innovative approach. In general, research on freeform or non-flat imprinting surfaces has focused on materials or methods' modifications. This project paved ways for expanding these modifications from materials and process optimization to development of new tools. The implementation of a newly developed, integrated NIL tool for orthogonal imprinting on freeform surfaces is described in chapter 4. Exploration is not just limited to the available devices but also extended to combination of fabrication techniques. The fabrication processes based on laser and probe techniques are limited by throughput. NIL on the other hand, is a replication technique that increases the production volume of such techniques by replicating the patterns faster and easier, numerous times. One such example is that of the "*mix and match*" lithography described in section 3.4. It demonstrated successful replication of a template based on combination of direct laser writing and scanning probe lithography techniques.

1.5. Aim and Structure of Thesis

The aim of this thesis is to establish novel soft NIL processes for imprinting on curved surfaces. To take advantage of the availability of the high precision Nano-positioning machine in the framework of *NanoFab*, a compact and flexible soft UV-NIL process for integration into the NPM machine was designed and developed. After successful implementation of the fundamental process in the NPMM, the focus was to achieve orthogonal molding and de-molding on edges of curved substrates, specifically - Plano-convex[4] and aspherical[5] lenses. Establishment of process steps from mould formation to pattern transfer onto resist formed the foundation for development of a rotating NIL tool which could be used for imprinting on curved surfaces at different inclinations.

[4] These have one surface which is flat while the other one is convex.
[5] These have complex surface profile and are used to eliminate monochromatic aberrations.

Since, imprinting is not performed in a conventional yellow light cleanroom environment, it is challenging to establish an ideal process. These challenges included contamination of PDMS stamp from particles, photosensitivity of resist and impact of atmospheric pressure. Despite the challenges, the technique could be implemented successfully. In addition to material composition and process optimisation, the technique was made finer by modifying parts of the NIL tool. In latter stages of experiments, stamp and substrate holders were designed for easy integration and multi-purpose usage. The primary objective while designing these parts was to make them user-friendly, cost effective and easily replicable. Considering the immense scope of improvisation in NIL, any alteration can lead to productive developments.

In summary, the thesis addresses the challenges of imprinting on non-flat surfaces. The development and optimization of a soft UV-NIL process that could be feasibly incorporated into the NPMM. Based on the optimized process, a new NIL tool was designed and assembled for integration into a rotating device which was then used for imprinting on different inclinations of aspheres and Plano-convex substrates. The rotating tool in combination with the positioning stage of the NPMM aided orthogonal molding and de-molding. This thesis is structured to demonstrate the work flow beginning with an introduction and background to the NIL technology and concluding with the final outcomes and their relevance. A brief summary of the chapters is listed below.

Chapter 1 is preface of the thesis stating the scope of the work and giving brief descriptions of the relevant subjects that form the basis of the thesis. It also provides an insight into the interdisciplinary aspect of the project. Further it reviews the existing techniques of patterning on curved surfaces. It briefly explains the various processes and methods that have been established and implemented through different lithographic techniques. These methods vary not just in the techniques used but also in terms of the geometry of substrates. Finally, the chapter explains the issues that are not addressed by these techniques which form the basis of the thesis work.

Chapter 2 describes the basic materials and processes used for the substrate preparation such as anti-sticking layer coatings and surface modification for replication of PDMS stamps. Since, the PDMS stamp is an integral part of the soft UV-NIL process, its preparation is

crucial for successful patterning. The fabrication techniques for the master template fabrication are mentioned in section 2.1 while the PDMS replication/ stamp formation is described in section 2.2. Lastly, the resist preparation is described in section 2.3. This chapter gives a general process description; specific processes depending on the application are described in the relevant chapters.

Chapter 3 is one of the main experimental chapters which describes the entire work flow including the design, optimization and execution of the NPMM integrated soft UV-NIL process. The experiments utilized the process to its full potential with a goal to achieve high resolution and curved surface imprinting. In section 3.2, the basic design, parameters and process optimization of the soft UV-NIL are explained. Based on the basic process, the development of the integrated process is explained in section 3.3. The application of the integrated process in mix and match lithography is described in section 3.4. Section 3.5-3.7 elaborate on the advantages and challenges of the process which were accomplished in a non-ideal environment. The experiments performed in this chapter laid the fundamentals for the next chapter where the primary focus was imprinting on curved substrates.

Chapter 4 is the primary chapter that focuses on the NIL process for highly curved surface. It describes the development of the rotating NIL tool and its realization in combination with the NPMM. Section 4.2 elaborates the concept of orthogonal molding and demolding on edges of non-flat surface based on multiple degree of freedom movements. Then the process development and optimization is described and analysed in section 4.3. In section 4.4, the results of imprinting at inclination of 45° are analysed by comparing the structure fidelity with the stamp. A further analysis is done by comparing it with conventional soft UV-NIL technique. In the end of the chapter in section 4.5, the conclusions and outlook explain the present limitations and future improvements.

Chapter 5 describes the work conducted at Paul Scherrer Institute, Switzerland during a three-month research stay in the framework of the PhD. The project aimed at performing NIL on a stainless steel cylindrical tube to transfer high contrast speckle patterns onto an area of 1 x 1 cm^2. Section 5.2 describes hot embossing process implemented for pattern transfer onto flexible foil based substrates. The PDMS stamp formation process is explained in section 5.3.

The pattern transfer process onto the metal tube and the results are discussed in section 5.4. Further work on modified micro contact printing is described in section 5.5.

Chapter 6 summarizes the thesis and gives an outlook for future advancements.

Chapter 2

2. Basic Materials and Processes

2.1. Master template for replication

The templates for the replication process are patterned using E-Beam lithography (EULITHA AG) and Field Emission- Scanning Probe Lithography (FE-SPL) techniques. The large patterned area was obtained using the E-Beam technique while the higher resolution of sub-100 nm structures was obtained using the FE-SPL technique. The FE-SPL process developed at TU Ilmenau involves electron emission from a scanning proximal probe tip which is combined with pattern transfer techniques and subsequent cryogenic etching to transfer the pattern onto the silicon surface (Hofmann et al. 2018).

The master template is coated with an Anti-sticking layer (ASL) before it is used for replication. The anti-sticking layer used for this process is a monolayer of perfluorosilane. The silane, FDTS (1H,1H,2H,2H-Perfluorodecyltrichlorosilane), (Sigma 2020) is deposited by vapour deposition. The fluorine atoms of the fluorinated silane assembled on the surface of the silicon substrate after the vapour deposition provides anti-sticking properties. For the silane head to bond to the surface, it is necessary to activate the silicon surface (Schift et al. 2005). This was done by oxygen plasma treatment of the silicon substrate using TEPLA 300 plasma stripper at 50 W for 20 seconds. After the surface activation, it is placed in an oven preheated to 190°C. A few droplets of FDTS are dispensed using a syringe, at a temperature of 190°C in vacuum for 1 hour 30 minutes. The amount of FDTS required depends on the substrate area, a 4” wafer with a patterned area of 30 mm^2 will need approximately 5 µl while an area of 10 mm^2 patterned area requires 2 µl (2 drops) of FDTS.

2.2. PDMS stamp formation

The soft stamp for the process is made from PDMS. The PDMS is poured onto the structures that are present on the master. The PDMS glides into the cavities of the structures filling and heating them. Thus, hardening the structure and promoting demolding from the master.

The PDMS mold was prepared using a silicon template or mask which contained the patterns. From the mask, structures are transferred to the PDMS mold using replica molding. The mask is first treated with an anti-sticking layer of FDTS to reduce surface energy and make the silicon surface hydrophobic to avoid PDMS sticking to the mask. Surface modified silicon has shown significant decrease in surface energy and increase in contact angle (Perumal et al. 2009). The low surface energy enables successful removal of cured PDMS from the silicon master. Then the PDMS mixture is poured on to the mask and heated at 90°C for 30 minutes.

For high resolution nanostructures, the PDMS filling into the master structures was improved in two different methods. The first method was by dilution of the PDMS with solvents such as toluene and heptane. The second method was the use of different mixing ratios of elastomer base and curing agent. Previous results demonstrated by Koo et al. (Koo et al. 2007) showed that the filling of the structures improved drastically with increasing concentration of toluene. A 60% solution by weight of toluene was used. In 3 g of PDMS, 4.5 g of toluene was mixed and stirred for 10 minutes. This formed the carrier layer. The following steps were followed to form the carrier layer:

1. A few drops of the mixture were poured on the Si nanostructure templates, then degassed (in case of presence of any bubbles).
2. The template with the coated PDMS was then baked on a hot plate for 20-30 minutes. at 105°C as shown in the image.
3. After, the stamp was baked, it was peeled off from the template as a thin membrane. The thin membrane was then placed on the aluminium base plate with the structure side facing the plate.
4. Then PDMS is poured on top of the thin membrane uniformly and cured at 80-100°C for 20-30 minutes.

5. After the curing of the PDMS, the stamp is peeled off from the plate and the stamp with the structures is obtained. AFM images of the different PDMS mixtures can be seen in Figure 2.1.

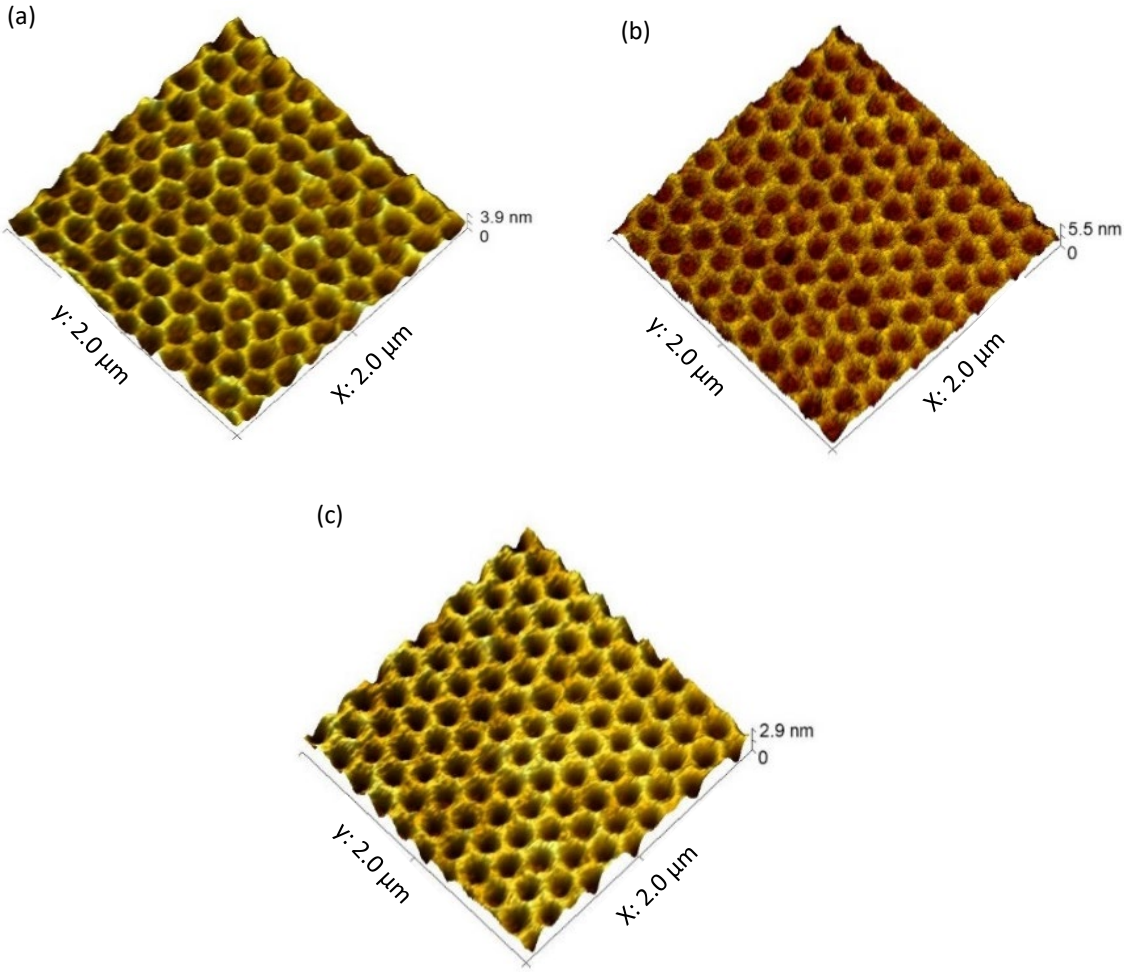

Figure 2.1: AFM images of PDMS stamp for sub 100 nm structures with different PDMS compositions: (a) PDMS diluted with 69 wt% toluene, (b) PDMS: heptane (1:2), (c) UV PDMS. AFM measurements were performed at a scan rate of 1.3 Hz and scan speed of 25 µm/s.

The UV PDMS is a low viscosity and low shrinkage UV curable PDMS containing two mixing parts, part A and part B (Shin Etsu). The final product is obtained by mixing the two parts in equal ratio and degassing it. For the pattern replication of the sub 100 nm structures, a mask aligner was used for UV exposure at an intensity of 2000 mJ/cm^2 for 5 minutes. After

the curing, it was left to sit for 2 hours before peeling off the template. A mixing ratio of 1:2 (base: curing agent) was used for the high resolution nanostructures.

2.3. Resist preparation

Imprint quality and pattern fidelity largely depend on the resist filling into the structure cavities. The filling depends significantly on factors such as resist viscosity, uniformity of coating on non-planar surfaces, imprint pressure applied during the molding process and air bubbles in cavities which could lead to partial filling of the cavities (Michael Wang 2010). The filling of high resolution nanostructures is particularly challenging. This is due to the inability of the thin resist layer to squeeze out trapped air when it comes in contact with the stamp as the contact surface between the stamp and the substrate is not completely flat. When the substrate is non-planar, these effects become greater. To reduce the challenges associated with the resist coating and filling, spray coating is applied instead of conventional spin coating. In spin coating, centrifugal force distributes resist over the substrate, causing a non-uniform resist layer across non-flat surface. While in case of spray coating, the resist is atomized into micrometre droplets and sprayed across the surface (detailed description in section 4.3.1). In case of silicon substrates, (used for imprinting of sub-100 and 200 nm resolution structures) different spin speeds are used to find the optimal resist layer thickness. The resist thickness was measured using an ellipsometer *(SENTECH Instruments GmbH).* The process was optimized for resists, AMONIL MMS 4 and AMONIL MMS 10. The base thickness of the resists at 3000 rpm are 200 nm and 100 nm respectively *(AMO GmbH)*.

In Figure 2.2, the graphs show a comparison between the resist layer thickness for two different samples. At a spin speed of 6000 rpm, the base thickness is significantly reduced. The low surface energy of 39.5 mN/m of the resist promotes easier demolding and multiple imprints with the same stamp before the stamp is contaminated by the resist *(Gorgy Kostovski 2011)*. A reduction of 20-25 % in the resist thickness is seen after the imprint process in the patterned area.

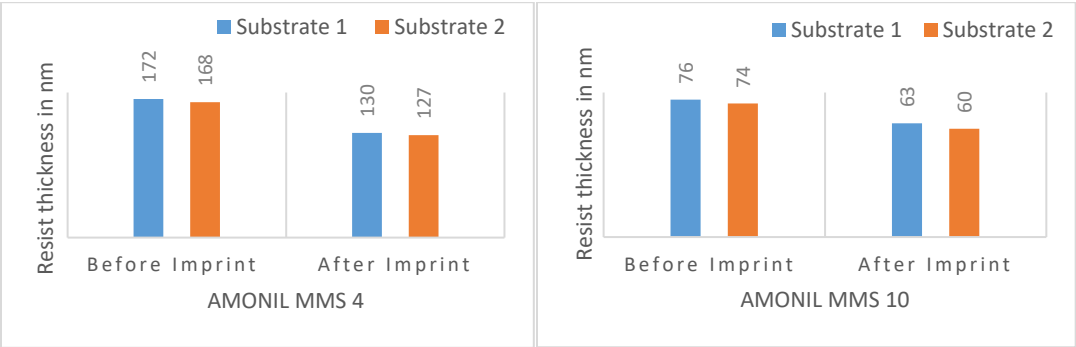

Figure 2.2: Resist layer thickness for AMONIL MMS 4 and AMONIL MMS 10 before imprinting and after imprinting on silicon substrate, spin coated at a speed of 6000 rpm

Chapter 3

3. Integration of the soft UV NIL process into the NPMM

3.1. Introduction

An essential advantage presented by the NPM machine is the use of the high precision motion for the implementation of the step and repeat process. The multi-coordinate control of the machine allows precise movements in multiple directions enabling stamping next to each other with precise alignment (Kühnel et al. 2018). The step and repeat feature of NIL provides higher throughput for low throughput technique like scanning probe lithography which has serial nature of patterning (Lawson and Robinson 2016). The NPM machine is able to provide a measuring and positioning volume of 25 mm x 25 mm x 5 mm, with a resolution of 0.1 nm. An uncertainty of less than 10 nm provides opportunity to implement the step and repeat NIL process by integrating a compact NIL tool (Manske et al. 2015). The flexibility and simplicity of the soft UV-NIL process makes it feasible to integrate into the machine.

In this chapter, the process development of a soft UV- NIL process integrated into the NPM machine is discussed. The positioning accuracy of the NPMM provides the possibility to achieve high accuracy alignment of the stamp to the substrate. To implement the process, a UV-LED based soft UV-NIL setup is designed, assembled and integrated into the NPMM. The positioning stage of the NPMM is used as the base for substrate and the movement of the positioning stage in the z direction enables the nanoimprinting process by bringing the stamp in contact with the substrate. The positioning accuracy enables successful molding and demolding of structures in the nanometre range with high fidelity. The precise movement of the stage in the x and y directions makes it possible to use it for *step and repeat* process with high accuracy to replicate small area patterns to larger area.

3.2. Compact soft UV-NIL setup

Limited working volume of the NPM machine and the requirement for a dismountable setup were taken into account while considering the development of the tool. The soft UV-NIL tool components consist of a ring UV LED light source (LED RL 4-UV 400, 400 nm wavelength), a substrate holder and a stamp holder. For the initial optimization of the process parameters, the components were integrated into a guiding rail with an additional piezo stage onto which the substrate holder was mounted (Figure 3.1). This enabled the movement of the substrates in the z-direction (upward) to come in contact with the soft stamp.

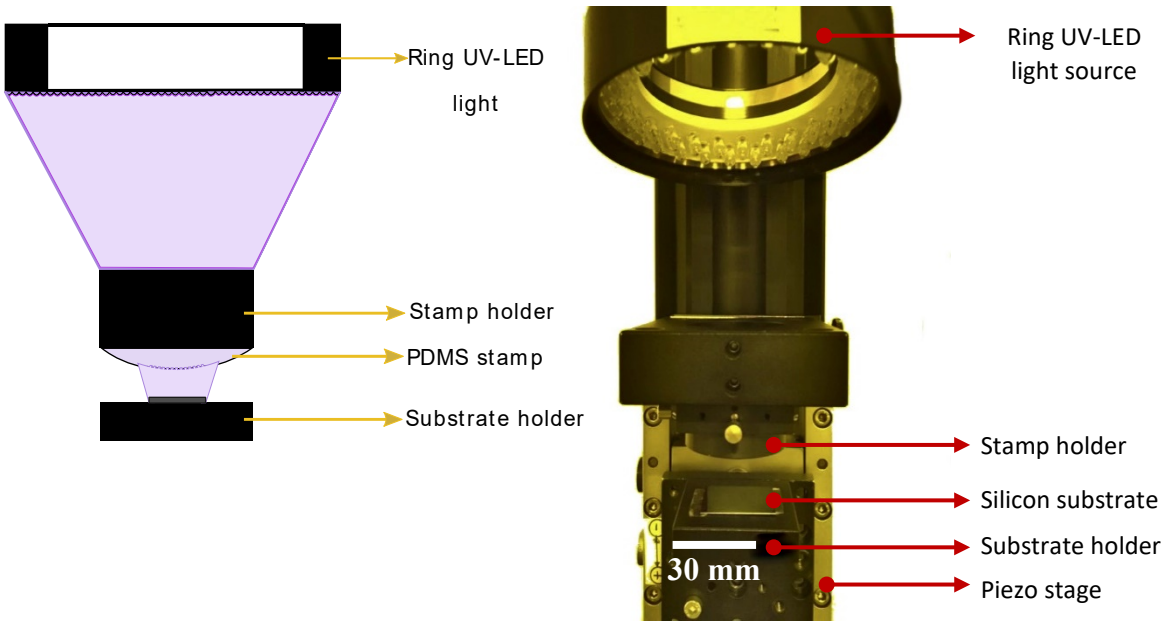

Figure 3.1: Schematic and image of the developed test setup for soft UV-NIL including a stamp holder, a substrate holder fixed to a piezo stage and a ring UV-LED light mounted on a guiding rail.

The vertical velocity of the stage was set to 5 mm/s initially for both molding and demolding. After the components were set up, the process parameters were optimized. The position of the UV light was adjusted so as to get the optimal intensity and to have exposure for maximum area. The maximum intensity was measured at a distance of 8 to 10 cm from the light source; the substrate was placed at this position. Furthermore, to observe the positioning

and stamp conformity during the molding and demolding process, a CMOS camera was mounted on the top in the final setup.

Initial results after the imprinting and subsequent etching showed good fidelity of the structures. A standard lens mount of approximately 30 mm diameter was used as the stamp holder to fix the PDMS stamp. Due to the flexibility of the PDMS stamp, it could be fixed with the retaining ring present in the inner edge of the holder. The substrates used in the process were of smaller dimensions than the stamp to promote imprinting on the entire surface of the substrate. A silicon wafer of 2 x 2 cm^2 was used as substrate. The procedure was as follows:

1. The wafer was first cleaned with acetone and isopropanol and then coated with adhesion promoter using the general process mentioned in Chapter 3.
2. Then, it was spin coated with NIL resist mr-NIL210-500 nm *(micro resist technology GmbH)* at a spin speed of 3000 rpm for 60 seconds
3. Finally, it was soft baked at 115°C for 30 seconds. A contact time of 5 minutes was set for the capillary filling of the structure cavities.

At the maximum intensity of 11 mW/cm^2 of the ring UV light, an exposure time of 15 minutes was required to completely cure an exposed area of 7 cm^2. The total time for the replication process including the filling and curing was 20 minutes. The imprinted structures on the resist were nanopillars of diameter 450 nm and pitch 1000 nm. The etching was done using a cryogenic etching process in a *PlasmaPro 100 Cobra (Oxford Instruments)* etching machine. The etching parameters used for the imprinted structures were a temperature of -110°C, pressure of 8 mTorr, ICP source power of 1000 W, bias power of 50 W and gas flow ratio of 50:10 sccm for SF_6:O_2 was used respectively (Table 3.1).

Table 3.1: Cryogenic etching parameters for residual layer removal

Duration (s)	*Temperature (°C)*	*SF_6 : O_2 (sccm)*	*Pressure (mTorr)*	*RF /ICP (W)*
30	-110	50:10	8	50/1000

After the etching process, resist stripping was done in the TEPLA 300 plasma stripper with a plasma power of 400 W and a duration of 3 minutes. The SEM images of the imprinted nanopillar structures after the etching and descumming shows good fidelity and uniformity (Figure 3.2).

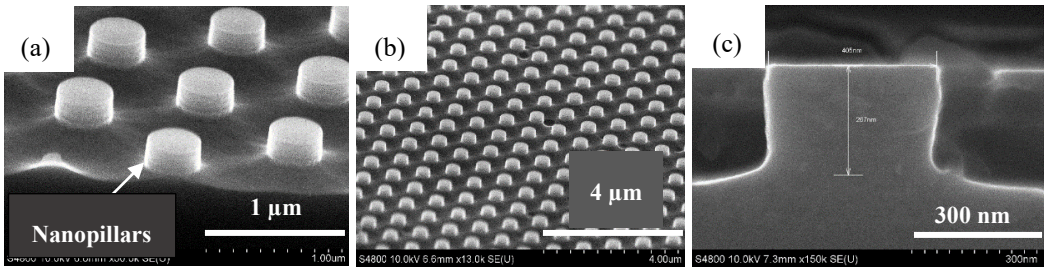

Figure 3.2: (a-b) SEM images of imprinted nanopillar structures on silicon substrate and (c) cross-section image of the nanopillar, after cryogenic etching and descumming process.

3.3. Process development and positioning using NPMM

After the implementation of the NIL process using the experimental setup, the process was optimized and the setup re-designed for incorporation into the NPMM. The redesigning was done using the basic components of the experimental setup - UV light source, stamp holder and substrate holder. The piezo stage was replaced by the positioning stage of the NPMM with additional coordinate movements and high precision. Since, the parts for the experimental setup were already designed according to the dimensions of the positioning stage, these parts could be reused in the model for the basic imprinting process. The basic parts and design of the integrated UV-NIL setup is given in Figure 3.3.

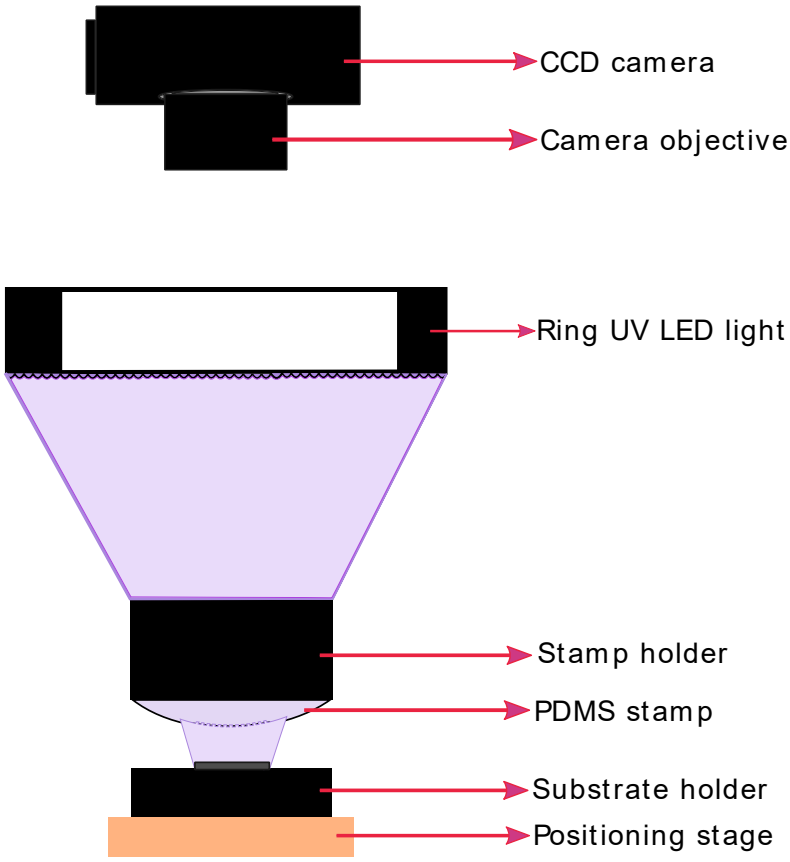

Figure 3.3: Schematic design of NPMM integrated UV-NIL setup. The setup includes the basic components of the experimental setup - UV light source, stamp holder and substrate holder.

One of the essential criteria for imprinting using the soft UV-NIL process is the uniform contact of the stamp to the substrate. Since the process was being developed for imprinting both on flat and non-flat surface (Plano-convex lens in particular), the fundamentals of wafer bowing technique was applied (Wei et al. 2008). The technique allows imprint force to be applied uniformly and systematically from centre to edge and prevent any air from being trapped between the mold and substrate (Michael Wang 2010). In integrated UV-NIL setup no external gas pressure is applied onto the stamp, the force is exerted from the movement of the positioning stage. It was therefore essential to have substantial length of the stamp that allows the bowing of the stamp when fixed to the stamp holder to conform completely to the substrate. The addition of the mounted camera into the setup was beneficial for observing the contact process between the stamp and the substrate (Figure 3.4).

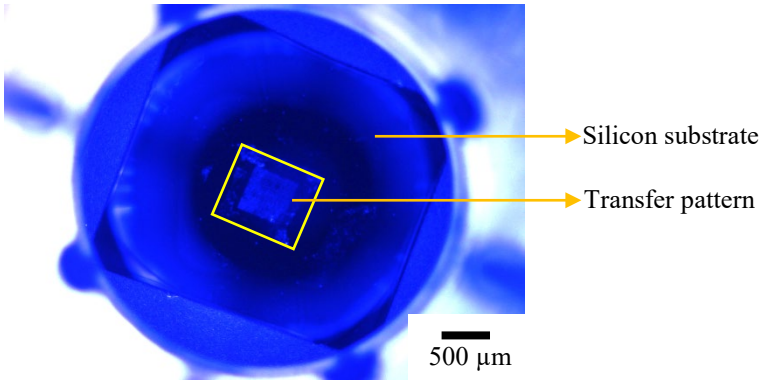

Figure 3.4: Top view of the stamp in contact with substrate (highlighted region in the centre shows the pattern which is transferred from the stamp to the substrate)

The process development involved both planar and non-planar substrates. Initially, the non-planar substrates were limited to low curvature fused silica Plano-convex lens (QIOPTIQ) with diameter 22 mm and multiple focal lengths of 40, 50, 75 and 100. The experimental setup was designed for it to be easy to assemble and disassemble. It was first incorporated into a support structure, and was then integrated into the NPMM as shown in Figure 3.5.

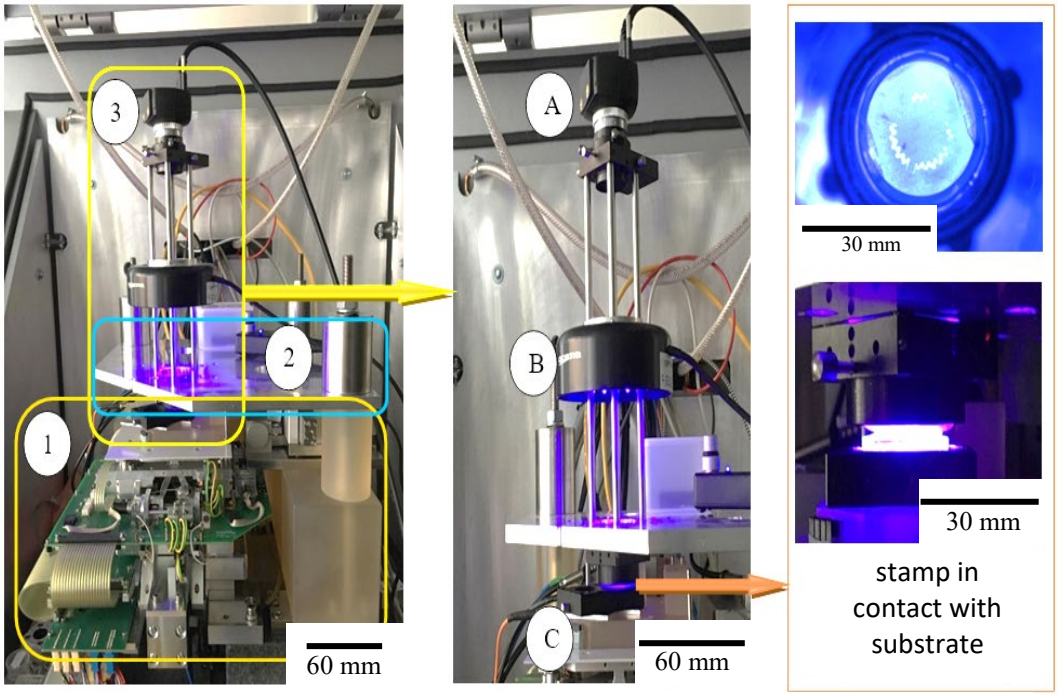

Figure 3.5: Integrated UV-NIL setup in the NPMM (1- NPMM, 2- Support structure, 3- UV-NIL setup, A- Mounted Camera, B- Ring UV-LED light source, C- Positioning stage), top view (obtained from the mounted camera) and side view of stamp in contact with the substrate

After the integration of the developed setup into the NPMM using a support structure, the substrate was fixed to the positioning stage. The experiment was then conducted with the integrated NIL system in the NPMM. The duration for the entire process, including the molding, curing and demolding was approximately 20 minutes. The capillary filling time for the resist in the cavities of the stamp was 5 minutes. Then, the UV light was exposed onto the structures for 15 minutes. The moving range of the stage in the z-direction is limited to 7 mm. Therefore, the substrate height had to be adjusted accordingly, to enable complete contact with the stamp. This was done either by re-arranging the number of spacers between the plate and the NPMM or by elevating the substrate. Figure 3.6 shows the process overview.

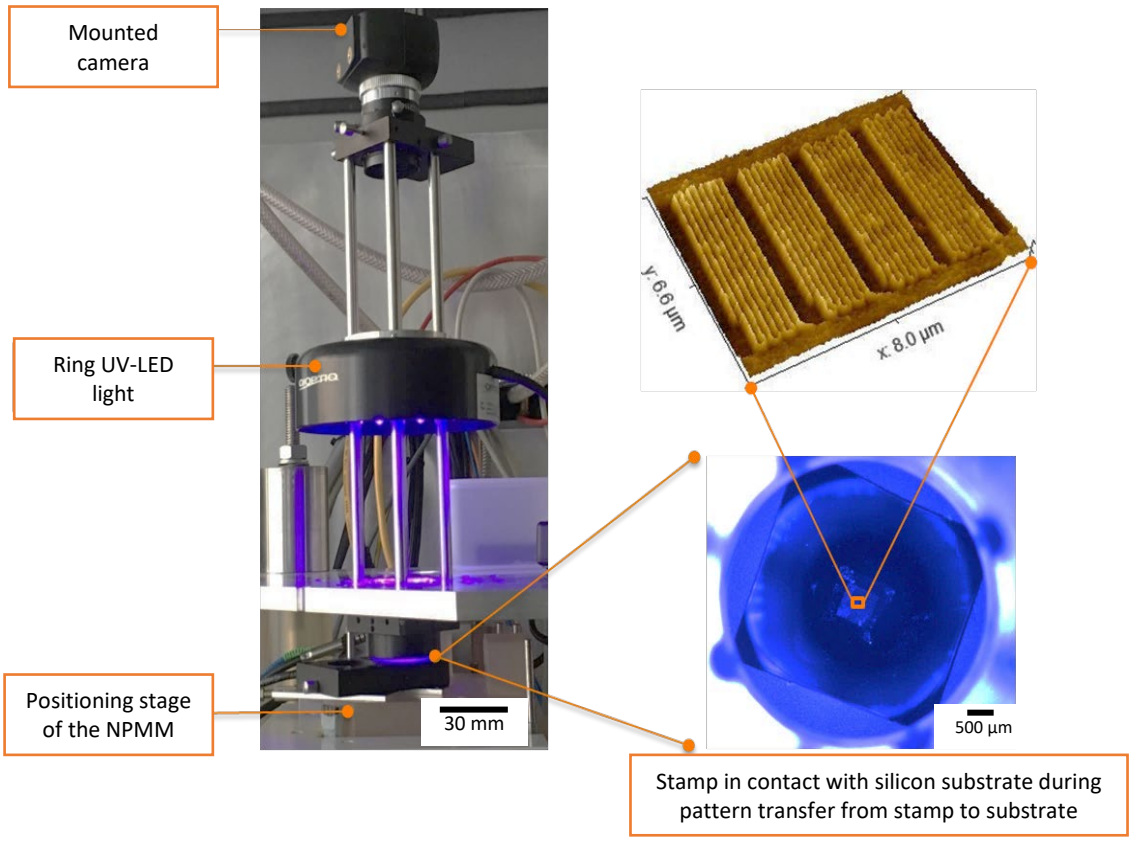

Figure 3.6: Process stages for the integrated soft UV-NIL depicting the contact of stamp to substrate and the resulting structure due to pattern transfer from the stamp onto the resist coated substrate.

3.3.1. Substrate preparation: Plano-convex lens and silicon

The Plano-convex lens was first cleaned by dipping in methanol, followed by acetone and isopropanol cleaning. Then, it was dried with a nitrogen gun and heated for 1 min at 115°C to remove moisture. After the pre-coating with adhesion promoter, the coating process is a two-step process. In the first step, it is coated with mr-NIL 210 resist 500 nm at a spin speed of 5000 rpm for 1 min and then soft baked at 115°C for 1 minute. In the second step, the spin speed is reduced to 3000 rpm while the rest of the parameters are identical to the first step. The silicon substrate preparation for resist coating to imprint microstructures in the range of 1.2 µm to tens of microns are similar to the parameters mentioned in *section 3.2*. However, high-resolution nanostructures with a linewidth of 200 nm required low viscosity resist to fill into the narrow structure cavities. After the pre-cleaning of the substrate with acetone and isopropanol, AMONIL MMS 4 *(AMO GmbH)* was spin coated on a silicon wafer at a spin speed of 5000 rpm for 1 min and then soft baked at 115°C for 30 seconds.

3.3.2. Imprint Results

Initial imprint results showed good structure fidelity for the microstructures as well as high resolution nanostructures.

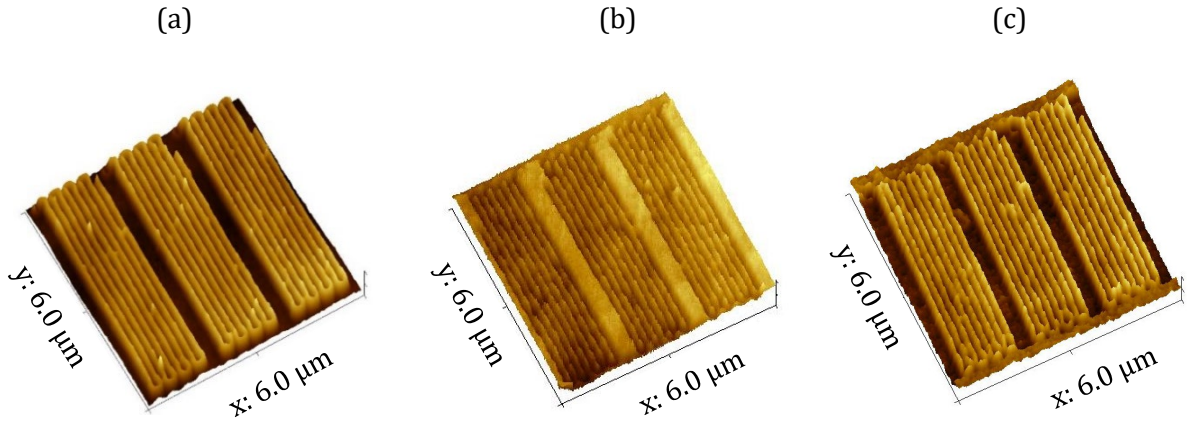

Figure 3.7: AFM images of Soft UV-NIL process flow: (a) Master template (b) Replicated PDMS stamp (c) Imprint. The AFM measurements are done in AC mode with a scan rate of 1 Hz and scan speed of 25 µm/s.

In Figure 3.7, AFM images of the replication process from the master to the stamp and subsequent pattern transfer into the resist can be seen. Furthermore, the pattern fidelity was measured for the imprinted pattern and compared to the master pattern. In Figure 3.8, the profile of the structure in both cases can be seen. It is observed that the pattern is not completely replicated with the central region appearing to be unfilled. The complete filling for high resolution structures could be obtained by modifying the stamp to increase the force in the area where the structures were concentrated. In the next section, the development and implementation of such stamp for high resolution patterning is described.

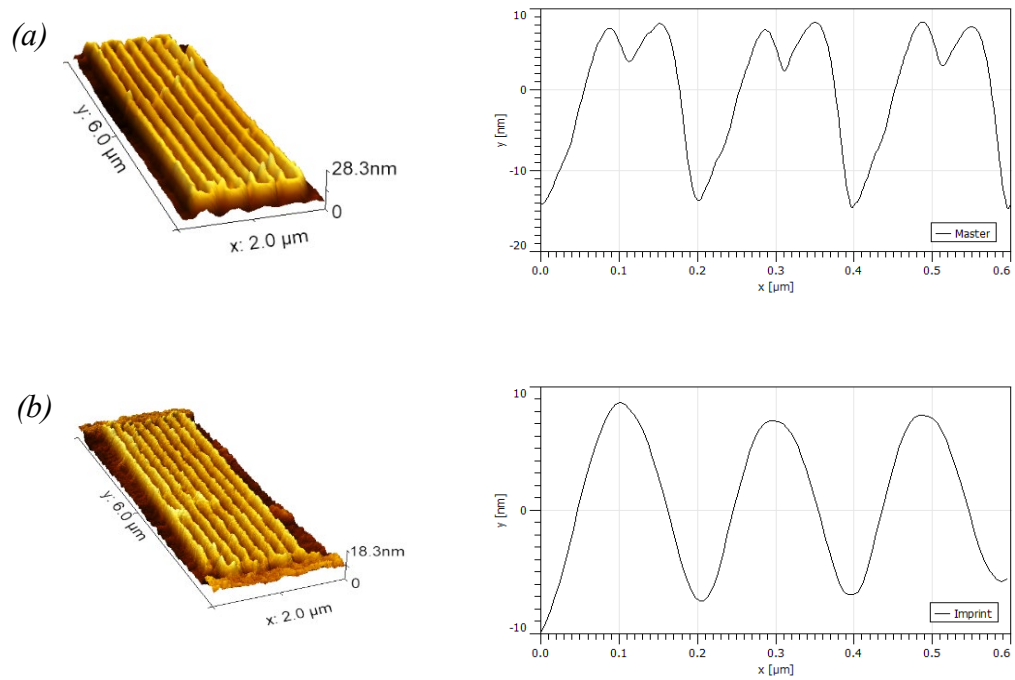

Figure 3.8: AFM images and structure fidelity of nanostructures (a) master structures patterned on silicon using Field Emission Scanning Probe Lithography, (b) imprinted pattern on resist layer. The AFM measurements were performed at a scan speed of 25 µm/s and scan rate of 1.2 Hz.

3.4. Mix and Match Lithography pattern replication

The combination of two lithography techniques, FE-SPL and Direct Laser Writing (DLW) created a mix and match pattern by stitching nanometre features into micrometre electrode layout on 1.5 mm x 1.5 mm area *(Hofmann et al. 2020)*. The process is however limited by

*This section of work has been done in collaboration with Martin Hofmann and Laura Weidenfeller

throughput when it comes to implementation for high volume production in semiconductor industry. Therefore, the NIL process can be used to enable replication on larger areas.

In this section, the replication process of the master structures containing combination of high resolution sub-100 nm structures and micrometre structures and the imprinting process are described. The resulting structure on resist and the transfer into silicon by etching are discussed further. To enable filling of PDMS into the small structural cavities and the resist into the stamp cavities, it was necessary to modify the stamp. The stamp was modified into a holder which could be used for the PDMS molding process as well as the imprinting process. The aim was to exert pressure on a concentrated point. Since the patterned area was limited to a small region of 1.5 x 1.5 mm^2, the flexibility of the soft stamp was not required. Therefore, the soft stamp was moulded to act like a semi-hard stamp. To attain this, a mould with diameter of 30 mm was designed with a window of 10 x 10 mm^2 area in the centre to create a thick layer of PDMS in the region. The stamp formation process is shown in Figure 3.9.

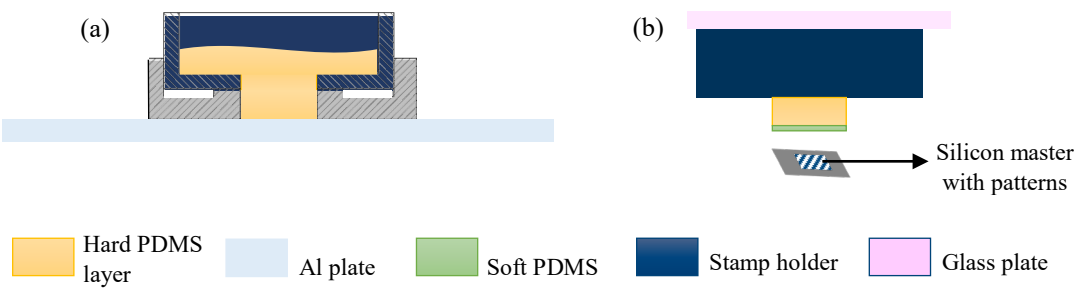

Figure 3.9: Stamp optimization for better conformity of stamp to substrate. (a) Cross-section depiction of PDMS filling in the stamp holder placed on aluminium plate for subsequent heating and hardening, (b) Side view depiction of stamp holder with protruding PDMS stamp and a thin soft PDMS layer onto which the patterns are transferred from silicon master.

The master template is first coated with an anti-sticking layer of FDTS (1H,1H,2H,2H Perfluorodecyltrichlorosilane). The FDTS is deposited in vapour phase within 1 hour 30 minutes at a temperature of 200°C. After the deposition of the ASL coating, a PDMS mixture is prepared at a mixing ratio of 2:1 (elastomer base: curing agent) by weight for the pattern layer. The mixture is then poured onto the ASL coated master template and then cured for 20 minutes at 90°C. At the beginning of the curing process for the pattern

layer, the base PDMS layer prepared with a mixing ratio of 10:1 (elastomer base: curing agent) by weight and cured at 90°C for 30 minutes is placed on top of the pattern layer.

For NIL, integrated soft UV-NIL process was used. A silicon wafer used as the substrate was cleaned and coated with AMONIL MMS 10 (AMO GmbH) resist by spin-coating at 6000 rpm for 1 min. After a pre-bake step at 115°C for 30 seconds, the layer thickness resulted in 75 nm. For imprinting, the stamp and the AMONIL coated substrate was brought in contact. By this, the capillary effect promoted the resist to fill the stamp cavities, which is then cured by exposure to UV light (400 nm wavelength) at 148 mW/cm^2 for 1 minute allowing a pattern transfer. Images of the NIL stamp and a first imprint were done by means of a laser microscope Figure 3.10.

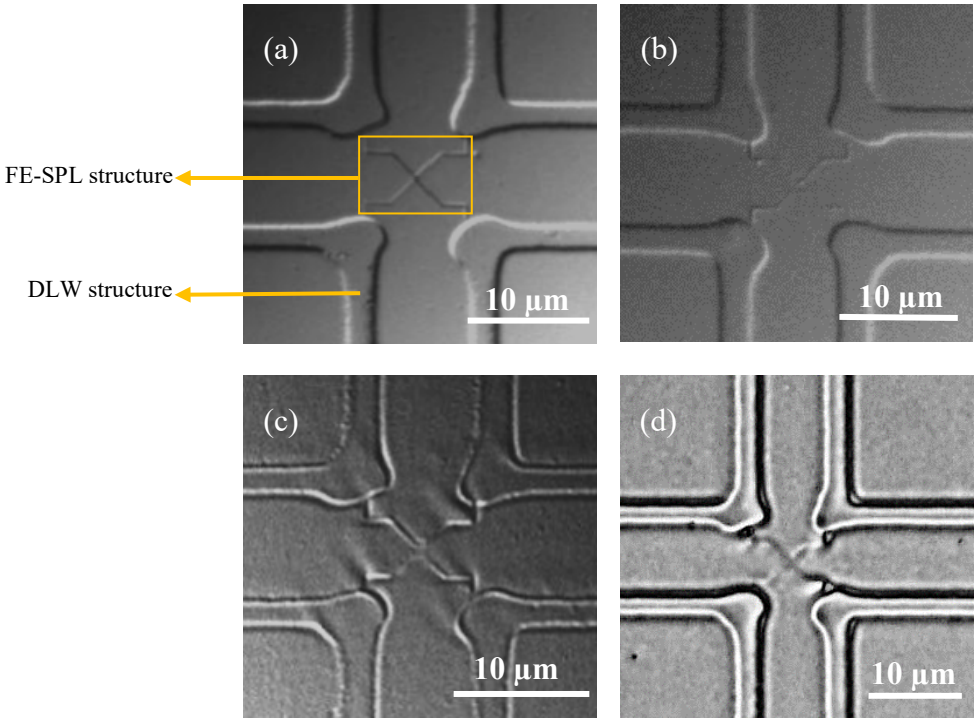

Figure 3.10: Process steps for mix and match lithography template replication using soft UV-NIL. SEM images of (a) Master template on silicon (b) Replicated PDMS stamp (c) NIL Imprint on resist (d) cryogenically etched pattern into silicon

The residual resist layer was removed using Reactive Ion Etching (RIE) process. It is a directional etching process which uses ion bombardment to remove material (Shuhao Si 2018). The process uses a chemically reactive plasma in a vacuum chamber to aggressively etch in a vertical direction (downwards).

However, ions are not always sufficient to achieve deep etching, especially when very reactive species are produced in the plasma and react spontaneously with the material to be etched, which leads to more or less isotropic profiles. This is the reason why additional gases are commonly used to create a passivation layer on the vertical sidewalls in order to prevent their erosion by spontaneous chemical reactions. Cryogenic etching of silicon was first introduced by Tachi et al in 1988. In cryogenic-DRIE, the wafer is chilled to −110 °C (163 K). The low temperature slows down the chemical reaction that produces isotropic etching. However, ions continue to bombard upward-facing surfaces and etch them away. This process produces trenches with highly vertical sidewalls (Dussart et al. 2014). The basic process steps involved in an etching process is shown in Figure 3.11.

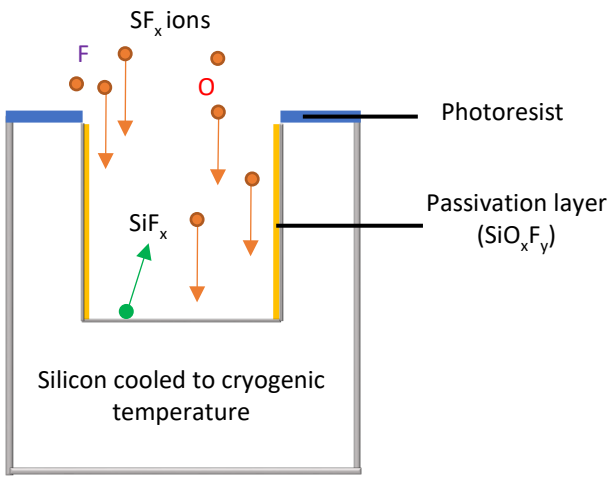

Figure 3.11: Schematic design of basic principle of Cryogenic etching process with addition of Oxygen (O) for formation of passivation layer (SiO_xF_y). During the process, SF_x, Flourine (F) and Oxygen ions are generated in the plasma source and diffused towards the substrate. The formation of SiF_x molecules take place when the Flourine radicals react with silicon. The indices x and y represent stoichiometric values. (Dussart et al. 2014)

The parameters used for the etching are given in Table 3.2. The AMONIL resist contains silicon dioxide (SiO_2) nanoparticles which act as mask layer. Removal of the resist layer leads to the structuring of the silicon surface. Thereafter, using the RIE process, the silicon surface is etched to transfer the pattern onto the silicon. A cryogenic process using a combination of SF_6 and O_2 gases was used. A low temperature of -120°C was used.

Table 3.2: Etching parameters for AMONIL residual layer removal

CHF_3: CF_4 (sccm)	*Pressure (mTorr)*	*ICP/ RF (W)*	*Temperature (°C)*	*Etch Time (sec)*
15:15	*4*	*0/75*	*20*	*120*

After the etching process, the silicon was cleaned with *Piranha* solution for the removal of any residue or dirt on the sample. The silicon wafer was dipped in the solution for 20 minutes at 90°C and stirred. Then, the sample is rinsed in DI water and dried with Nitrogen gun.

The etched pattern did not show good fidelity. There is a possibility for error during the template fabrication due to non-uniform etching of the micro and nanostructures which could lead to different structure depths. This in turn leads to partial or no filling of cavities in certain segments. Thereby, resulting in no pattern transfer after the final etching step. It is further required to conduct more experiments and analyse the pattern transfer process beginning with the template fabrication step itself.

3.5. Pattern stitching

An important aspect of the step and repeat process (Figure 3.12) is the stitching of the patterns. The accurate alignment of the Nano-positioning machine makes it a promising approach that could be carried out to achieve high throughput fabrication. The stitching process requires some pre-conditions that need to be considered. These conditions include the controlled curing of the resist so as to prevent any adjacent regions to be cured. Additionally, since the soft UV-NIL is a contact process, the resist squeezes out to the edges of the stamp resulting in a thick layer of resist. It, in turn, leads to non-uniformity of structures at the edges where the stitching is crucial. Moreover, due to the flexibility of the PDMS stamp, the uncontrolled spreading of the stamp at the edges makes it challenging to align at high precision. In some initial experiments conducted, these issues were observed.

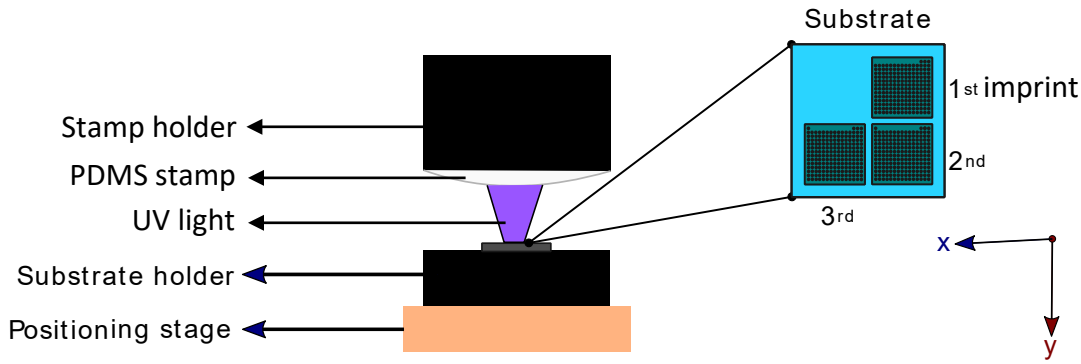

Figure 3.12: Step and repeat process for multiple imprints. The protruding small stamp area containing the patterns allowed to imprint multiple times on one substrate. After the 1st imprint, the positioning stage was moved over the entire distance of the 1st imprint and the subsequent 2nd imprint was done and similarly, the 3rd imprint.

For the stitching process to be carried out, it was necessary to measure the dimensions of the stamp accurately. In the first instance stitching was attempted in one direction. Only the width of the stamp was measured. Since, the size of the stamp is considerably large, the measurement was done using stitching method in a Laser Scanning Microscope (Figure 3.13). The width was measured by stitching the entire surface of the PDMS stamp.

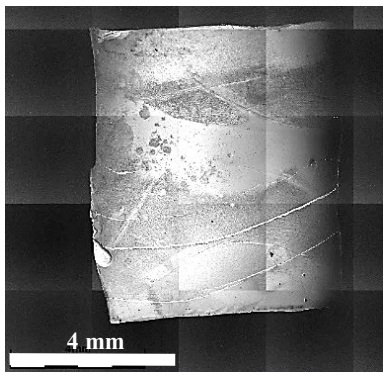

Figure 3.13: LSM image of stitched PDMS stamp using the stitching feature to quilt multiple images of the PDMS together to form the overall image of the entire stamp.

3.6. Challenges

The flexibility of the soft UV-NIL process made it feasible to integrate a setup that could be easily assembled and disassembled. However, there were several challenges pertaining to the execution of the process. Since the NIL process was not carried out in a cleanroom

environment, the environmental conditions such as the presence of dust particles, extended time gap between the soft bake and the imprint process may have impacted the process adversely. It was noticed that a longer delay than 10 minutes between the baking and imprint process prevented the filling of the resist into the structural cavities. In case of the step and repeat process, due to longer process times and the implementation of the process in ambient oxygen containing conditions (Si and Hoffmann 2017), it was challenging to have multiple number of steps before the resist could not flow into the cavities anymore. In a time span of 20 minutes between the soft bake and the last imprint, two steps of imprinting were carried out; while one step was partially successful before the process was ineffective.

3.7. Conclusions and Outlook

The soft UV Nanoimprint Lithography process was integrated into the Nano-positioning and Nano-measuring machine (NPMM). The aim of the integration is to utilize the high accuracy and positioning ability of the NPMM to precisely control the positioning of a flexible soft stamp to the substrate. The imprinting of micro- and nanostructures was carried out on flat substrates as well as on Plano-convex lens substrates using an integrated soft UV-NIL setup. The accurate positioning of the Plano-convex lens promoted conformity to the stamp; however, in certain cases it was not conformal and therefore needs to be optimized further. The imprinted structures had a resolution varying from 100 nm to a few tens of micrometre and the fidelity of the imprinted structures was observed to be good.

One of the major advantages of integrating the soft UV-NIL into the NPMM is the implementation of step and repeat NIL process with high accuracy. The primary setup used for conventional imprinting required modifications to implement the method. Essential factors that were required for its successful implementation were - controlled contact between the stamp and the substrate and rapid and focused exposure of UV light on the resist to prevent curing of the adjacent regions. The *step and repeat* process was implemented in the setup by optimizing the process parameters- specifically, the UV intensity and the stamp conformity to the substrate. However, due to environmental conditions mentioned in *section 3.6*, the initial experiments conducted with the process showed limited pattern replication. In the best conditions, the steps could be repeated three times before the resist did not fill into

the structure cavities of the PDMS stamp. Furthermore, to stitch multiple imprints with high resolution nanostructures, the process needs optimization in terms of restricting the squeezing of the resist to the edges of the structures. The accumulation of the resist on the edges leads to non-uniformity of resist thickness and leads to failure in cavity filling of high resolution structures. Additionally, it was not feasible to control the flexibility of the PDMS stamp at the edges, which in turn led to overlapping of the structures in certain areas while non-contact in other areas. It therefore needs further analysis and optimization to successfully implement the technique.

The successful integration and implementation of the integrated soft UV-NIL process demonstrate good imprinting capabilities for structures down to 50 nm linewidth. The processes can be implemented for both planar and non-planar substrates on 20x20 mm^2 area and 25 mm diameter. It demonstrated good results in non-ambient conditions specifically for high resolution structures. Furthermore, it establishes the foundation for possible implementation of methods such as *step and repeat* NIL and overlay alignment for future applications.

Chapter 4

4. Soft UV-NIL on highly curved surface using NPMM integrated rotating device

4.1. Introduction

One of the major factors responsible for a successful NIL process is the demolding (Zheng Cui 2008; Sreenivasan 2017). It is the step that is crucial during the solid phase or the post UV curing phase of the NIL process. The problem arises due to induced shear stress developed from the separation of the stamp and the resist coated substrate. This stress can lead to structure distortion and pattern collapse in case of high aspect ratio structures. Moreover, in case of high resolution structures of sub-100nm, the high internal stress generated in the small cavities of the structures can weaken the rigidity of the polymer and lead to deformation. The internal stress is therefore an inevitable part of the demolding process. So far, different methods have been implemented to reduce the stress by reducing the surface adhesion such as coating the stamp with anti-sticking layer, using alternative stamp materials with low surface energy which makes the stamp surface hydrophobic (Zheng Cui 2008).

The methods proposed are mostly focused on changing the material properties to reduce the friction caused between the stamp and the substrate. However, changes in the mechanical aspect of the demolding process for the reduction of friction remains less explored. The effect of the shearing will be enhanced in case of substrates with high curvature due to the required additional force exerted at the edges for having a conformal contact across the curvature. In different approaches that have been implemented before such as gasbag chamber, modification of the stamp to conform to the shape of the substrate, the demolding process at the edges of the substrate had not been given the importance that would be needed to analyse the fidelity of the structures in case of such substrates (Chang et al. 2005; Chen et al. 2008;

*This work is done in collaboration with Ralf Schienbein.

Farshchian et al. 2011). In these processes, the emphasis had been on the process itself and not primarily on the fidelity of the structures formed. Also, the influence of the shear force caused due to the highly non-planar demolding process is not discussed. An overview of the fabrication process of concave gratings using pre-shaping film, as developed by Chen et al. is shown in Figure 4.1.

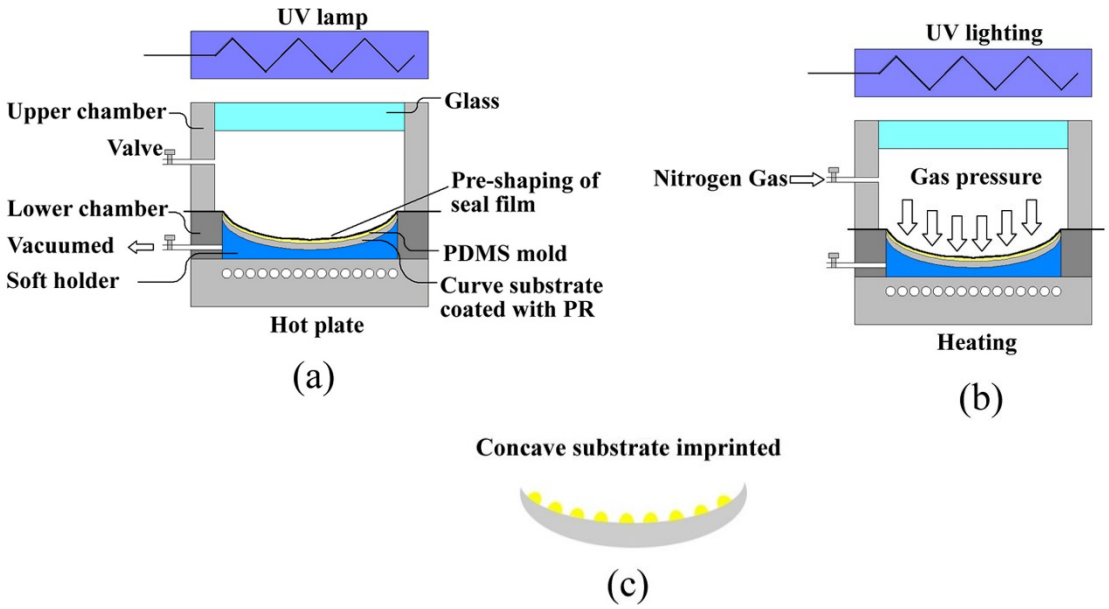

Figure 4.1: Fabrication of concave gratings using pre-shaping film as demonstrated by Chen et al. (Chen et al. 2008)

In this chapter, a combination of a novel rotating NIL tool and the nano-positioning stage of the NMM-1 (Figure 4.2) is used to achieve a high precision orthogonal molding and demolding process of soft UV-Nanoimprint lithography (NIL). The process is carried out on the edges of highly curved substrates to demonstrate structure uniformity at the edges of large Plano-convex surfaces. The imprinting of both high resolution nanostructures of sub-200 nm lateral dimension and microstructures in tens of microns was demonstrated.

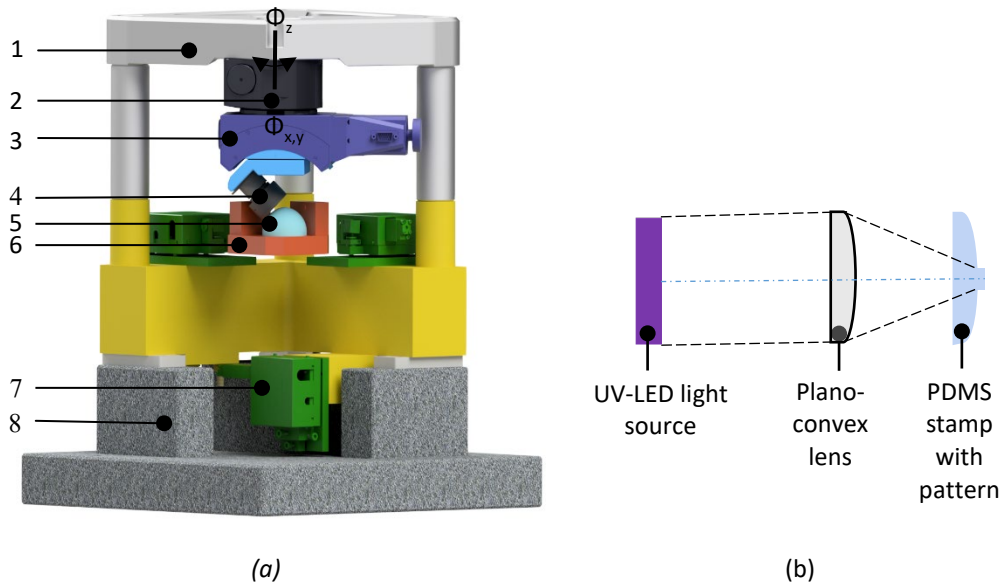

Figure 4.2: (a) Basic model of the Nano-positioning and Nano-measuring machine with additional rotating nanoimprint tool: (1) Metrological frame of the NMM-1; (2) Rotation stage ($ø_z$); (3) Goniometer stage ($ø_{x,y}$) ; (4) Nanoimprint Lithography (NIL) tool; (5) substrate; (6) Mirror corner of the linear stage (moved in x,y,z); (7) Three interferometers of the NMM-1; (8) Metrological frame of the NMM-1, (b) Detailed schematic of developed NIL tool

The positioning of the substrate is based on three independent linear movements in a Cartesian coordinate system of the NMM-1. This, in combination with the fixed nanoimprint tool, limits the addressable substrate geometries. An enhancement is introduced by the implementation of ultra-precise rotational movements of the tool while keeping the precision in the nanometer range. The integrated kinematic is based on the serial combination of a L-611 Precision Rotation Stage *(PI Instruments GmbH and Co. KG 2018a)* and a WT-90 Motorized Precision Goniometer *(PI Instruments GmbH and Co. KG 2018b)*.

4.2. Basic Concept of additional rotations in NPMM

The NPMM is based on three independent linear movements with a repeatability in the nanometre range. The laser interferometric measurement by the actualization of the Abbe comparator principle in the three measuring axes enables nanometre uncertainty and sub-nanometre resolution (Mastylo et al. 2005). The development of multiaxial machine

structures by implementation of rotational movements combined with the high precision of the NPMM enables high precision freeform measuring and manufacturing. A common center of rotation in the tool centre point (TCP) is considered. The TCP is in compliance to the Abbe Point of the NPMM which results in a minimization of first order positioning errors. A combination of a rotary stage and goniometer is used to implement the additional rotations into the NPMM. The additional tool rotations of 360° around ø and 90° around ø of the NMM-1 enable the addressing of a hemisphere orthogonally to its surface. Since the TCP corresponds to the intersection of the three interferometers of the NMM-1, the Abbe comparator principle is adhered to for all axes. This avoids first order positioning errors, linear correction movements for the tool rotation and enables orthogonal nanoimprinting on nearly free-formed surfaces (Figure 4.3).

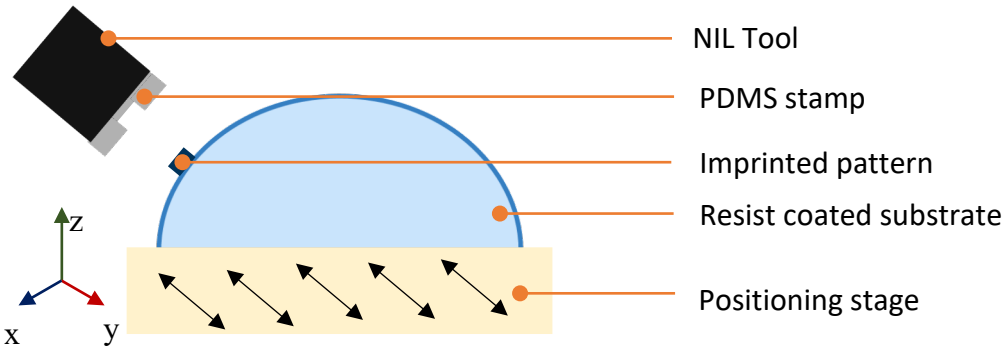

Figure 4.3: Orthogonal molding and demolding on curved substrate enabled by diagonal movement of the positioning stage. The arrows represent the diagonal motion of the positioning stage. During molding, the stage moves towards the NIL tool and during demolding, it moves away from the NIL tool.

Due to the strong curvature of the macroscopic substrates, their entire surface cannot be structured uniformly with a single stamping process. Instead, the entire procedure must be divided into individual imprint processes and the individual surfaces must be stitched together. For nanometer-accuracy stitching over the entire surface of the strongly curved substrate, ultra-precise positioning of the stamp relative to the substrate is necessary. For this purpose, the highest possible reproducibility of the positioning in conjunction with a corresponding in situ measurement of the position deviations is indispensable. This is

achieved for the three linear axes of the NMM-1 by position detection of the mirror corner via laser interferometers and autocollimators. The maximum measured position repeatability of the TCP over the entire rotation is ± 100 nm for the x- and y-direction and ± 150 nm in the z-direction. A higher positioning accuracy requires the in situ position determination of the rotating tool. Further steps include the final assembly of such a developed system, the integration of the nanoimprinting tool and development of the stitching process.

4.2.1. Multiple Degree of Freedom motions

The 5 DOF combination of rotational bearings (rotary stage) and segmental rotational bearings (goniometer) provides an optimal solution for miscellaneous challenges. One such challenge is a combination of two rotational axes whose rotation axes crossing under 90° is not possible due to working space limitations. An additional crossing angle would lead to non-independent behaviour of the two axes. The combination of segmentally rotational bearing mounted on the rotational bearing fulfils all requirements without any restrictions in the measurement volume. Therefore, a goniometer stage is mounted on a rotary stage (Fern et al. 2018).

The goniometer which now forms an integral part of the entire rotating mechanism enables rotation in a precise angular position. Additionally, the goniometer stage provides ±45° rotation in x and y direction by using a curved, profiled rail guide and a precision worm gear driven by a servo motor. In combination with the rotary stage which is active at 360° in the z-axis, the goniometer stage enables ultra-high resolution for small ranges of motion in micro- and nano-positioning. Thus, the combined motions i.e., 3 translational motions of the NPMM and 2 rotational motions of the goniometer and rotation stage enables 5 degrees of freedom (DOF) motions.

The rotation tool is optimized to be able to address a hemisphere orthogonally. For this purpose, several possible kinematic variants are determined and analysed by using parameter based evaluation system. A high degree of fulfilment is shown by these variants for the rotation of the tool. However, due to the unknown structure of the substrate sample, linear corrections need to be made for addressing the entire surface of the substrate. If the sample

fits to the dimensions derived from the given Cartesian volume, any hemisphere within the characteristic volume can be measured.

4.2.2. Design of rotating NIL tool

The integrated rotating nanoimprint tool is developed based on the basic components of soft UV-NIL. It consists of a UV LED light source *(Lumitronix LED Technik GmbH)* with a wavelength of 365 nm and an intensity of 148 mW/cm^2. A fused silica Plano-convex lens is used to focus the light on an area of approximately 20 mm^2. The focused light is transmitted through the patterned area of 25 mm^2 on the PDMS stamp. The stamp of diameter 20 mm is fixed to the edge of the NIL tool with the help of a retaining ring. The capillary filling time for the process is 1 minute with a UV exposure time of 1 minute. The exposure time can however be varied based on the intensity of the light. The resist is shaped by a moderate pressure, and by exposing light through the transparent stamp the resist is cross-linked and hardened. The process patterning on non-flat substrates or over topography therefore requires a planarization strategy and often small stamps (Schift and Kristensen 2010).

The imprint tool was used at angles of rotation of 45°, 60° and 90° and for substrates with different geometries such as Plano-convex lenses with medium to high curvatures and inclined glass mirror (Figure 4.4). The multiple angles of rotation in combination with the precise positioning of the mirror corner enabled the NIL process on such surfaces. The entire process is broken down into different steps for optimization.

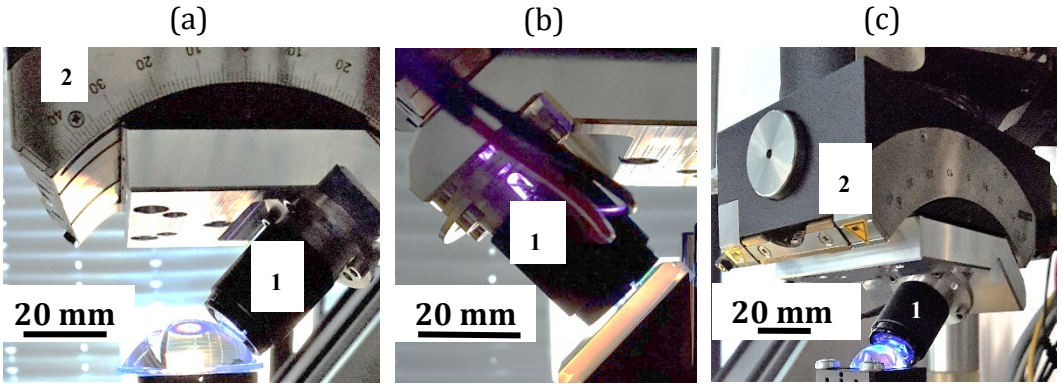

Figure 4.4: Rotating nanoimprint tool **(1)** (fixed to the goniometer stage **(2)**) in contact with substrates during the molding and curing phase, at different angles of rotation: (a) 45°, (b) 60°, (c) 45°

The initial step consists of finding the position coordinates for each substrate in accordance with the position of the rotating NIL tool. Since the height and diameter or width of each substrate is different, the x, y and z position of the mirror corner is set in a way such that the multiple imprint steps can be carried out. After the optimization of positions according to the rotating tool, the second step is to coordinate the movement of the mirror corner to enable the molding and demolding process. Finally, the diagonal motion of the mirror corner facilitated the orthogonal molding and demolding.

The 5 DOF rotations further enable the NIL tool to be rotated around the z-axis. Since, the imprinted area is comparatively smaller than the working range of the NPM machine, rotation of the NIL tool in combination with a slight movement of the mirror corner is used to imprint multiple times on the top region of the substrate at high precision. Further, the process can be developed to stitch the multiple imprints, however there are some challenges that will have to be addressed. These tasks can be categorized based on the two main components of the process: the mechanical challenges posed by the current limitations of the devices and the complications arising with the fabrication process. The limitations of the device have been discussed in the previous section.

As deduced from the initial experiments described in section 3.3, the major challenges come from the molding process wherein the flexibility of the PDMS stamp makes it difficult to stitch. The stamp on coming in contact with the resist coated substrate results in the resist to flow to the edges of the structures due to sandwiching. This leads to accumulation of thicker layers of resist at the edges thereby causing stitching errors (Schift and Kristensen 2010). Furthermore, due to the uncontrolled stretching of the PDMS stamp upon contact with the substrate, it was not possible to stitch without causing overlapping of structures at some points. Finally, the UV curing could lead to over exposure and cause the resist in the adjacent areas to be cured.

4.3. Process Development

4.3.1. Spray coating for Plano-convex lens

Spray coating technique in comparison to spin coating requires the optimization of various parameters such as relative velocity of the nozzle to the substrate, distance between nozzle and substrate, gas flow rate, angle and aperture of the spray nozzle *(Pham et al. 2005)*. The initial step involves the transfer of resist into a syringe tube which stores it and gradually small amounts of resist releases for the coating process. The resist is then atomized by an ultrasonic nozzle and subsequently sprayed on to the substrate (Titus Rinke and Christian Koch 2017). The substrate at this point is rotating at a set speed on the chuck. The resulting effect of the spray process of the moving nozzle and rotating substrate is a layer of droplets throughout the surface of the substrate (Pham et al. 2006). The basic design of EVG 101 spray coater can be seen in Figure 4.5. Due to the process being highly dependent and sensitive to the parameters, it is reproducible only in case of substrates with similar geometries and material; thereby making it a time consuming and complicated process. However, it enables resist deposition on complex structures and non-planar and freeform surfaces. Furthermore, the extensive control of the process makes it effective for unknown geometries.

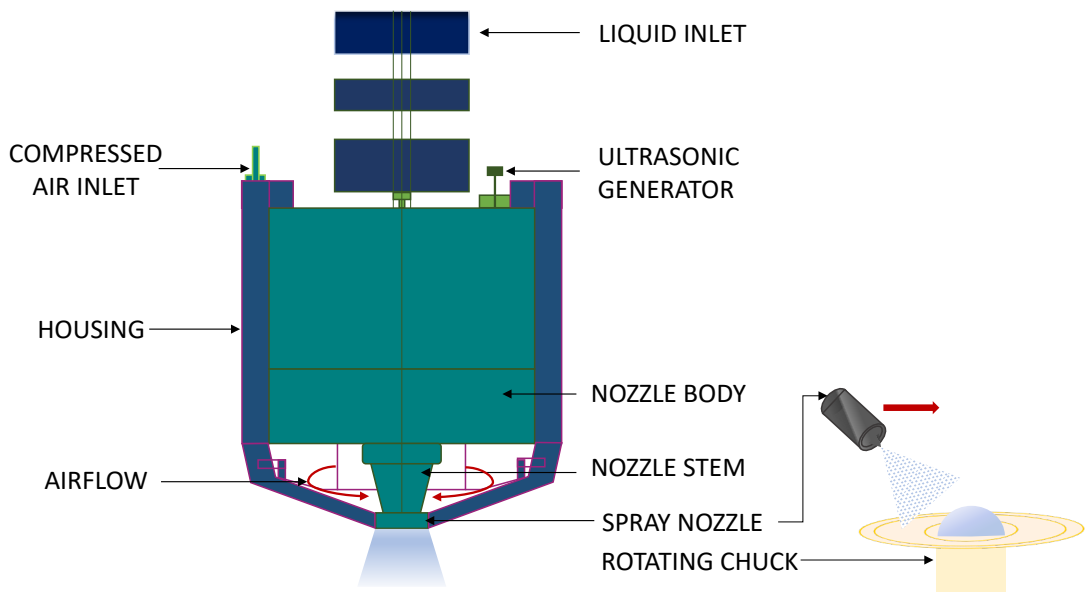

Figure 4.5: Basic design of spray coater EVG 101 [EVG 101 Spray coater]

The spray coating is carried out using EVG 101 spray coater *(EV Group)*. In case of non-planar surfaces such as the Plano-convex lens, a multiple layer coating is required to achieve better homogeneity and coverage. Before starting the spray coating process, the lens is cleaned using Acetone and Isopropanol and placed on hotplate for 10 minutes at 115°C to remove any moisture from the surface of the lens. It is then coated with adhesion promoter, TI Prime *(Microchemicals GmbH)* using spin coating at 4000 rpm and again baked for 2 minutes at 115°C on the hotplate.

Prior to the spray coating process, the ultrasonic nozzle used in the spray coating process is cleaned using acetone. Then the resist, AMONIL MMS4 (AMO GmbH) is filled in the syringe pump of the spray coater. The minimum amount of resist required for the spray coating process to function is 20 ml. Although a large amount of resist is wasted due to overspraying and to fulfil the minimum requirement of the syringe pump for the process initiation, it requires a relatively low amount of resist per area of substrate for deposition.

*The process in this sub-section has been developed by Patrick Feßer

After filling the syringe with the resist, the parameters of the spray coater are adjusted. From additional tests done on varying geometries, it is observed that the individual parameters of the spray coater need to be optimized according to the geometries (length, width, height and diameter). Two layers of spray coating are done, during which the dispense rate and nozzle flow is changed for each layer (Table 4.1). However, the HF power and the spin speed are kept constant at 0.7 W and 50 rpm respectively. For the first layer, a dispense rate of 6 µl/s and nozzle flow rate of 180 dl/min is used. After the coating of the first layer, a soft bake is done for 15 seconds at 100°C. The second layer of coating is done at a dispense rate of 11 µl/s and a nozzle flow rate of 150 dl/min. Thereafter, the lens is again soft baked on the hotplate at 100°C for 45 seconds.

Table 4.1: Parameters for spray coating process of the Plano-convex lens

	Dispense Rate (µl/s)	*Nozzle flow (dl/min)*	*HF Power (W)*	*Spin Speed (rpm)*
Layer 1	*6*	*180*	*0.7*	*50*
Layer 2	*11*	*150*		

Further to the above mentioned parameters, an important parameter influencing the homogeneity of resist coating on non-flat surfaces is the velocity profile of the nozzle. The nozzle speed defines the lateral speed of the spray nozzle across the substrate holder. It is divided into several indices which define the nozzle speed in different segments of the substrate. Out of a total of 15 indices, 7 of the indices are used based on the geometry of the lens substrate used for experiments. The nozzle speed profile is given in Figure 4.6.

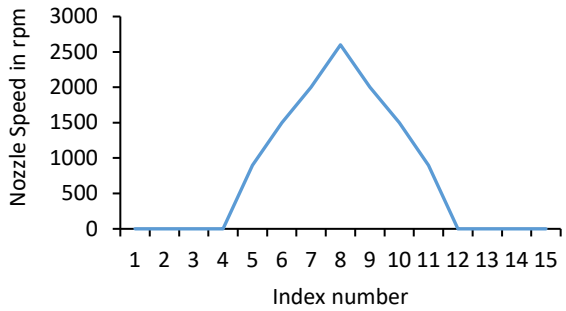

Figure 4.6: Nozzle speed variation across the lens surface. The nozzle speed defines the lateral speed of the spray nozzle across the substrate holder. It is divided into several indices which define the nozzle speed in different segments of the substrate. Out of a total of 15 indices, 7 of the indices are used based on the geometry of the lens substrate used for experiments.

The spray coating parameters are optimized to have a good coverage and uniformity throughout the surface of the lens substrate. In some cases, it was observed that the coverage of the resist was not uniform across the entire surface leaving voids. These voids were however removed by adding an additional layer of resist coating as well as modifying the parameters for the spray coating. The flow rate was changed to increase the speed of the droplets and reducing the droplet size that led to filling of the small voids on the surface of the substrate.

4.3.2. NIL process optimization

The developed process is carried out with a resist filling time of 1 minute for the filling of resist into the cavities of the microstructures during molding. Then a subsequent step for resist curing by exposure to UV light for 1 minute is carried out, after which the demolding is done. The imprinting can be implemented multiple times on a single substrate at different angles of rotation. The number of imprints that can be carried out before the process does not work due to the resist becoming dry - for capillary filling is 5 imprints by step and repeat process on an area of 20 mm^2 each time. The imprinting process involved the synchronization of the movement of the rotating tool as well as the mirror corner so as to successfully implement the diagonal molding and demolding process. The controlling of both the tools

was done manually at this stage to coordinate. A complete process flow of the orthogonal imprint process is given in Figure 4.7.

The resist uniformity across the surface of the lens is considerably good. The measured average resist thickness after two layers of spray coating is 1.5 µm at the top of the lens. The values are measured at four different points where the maximum thickness is 1.565 µm and

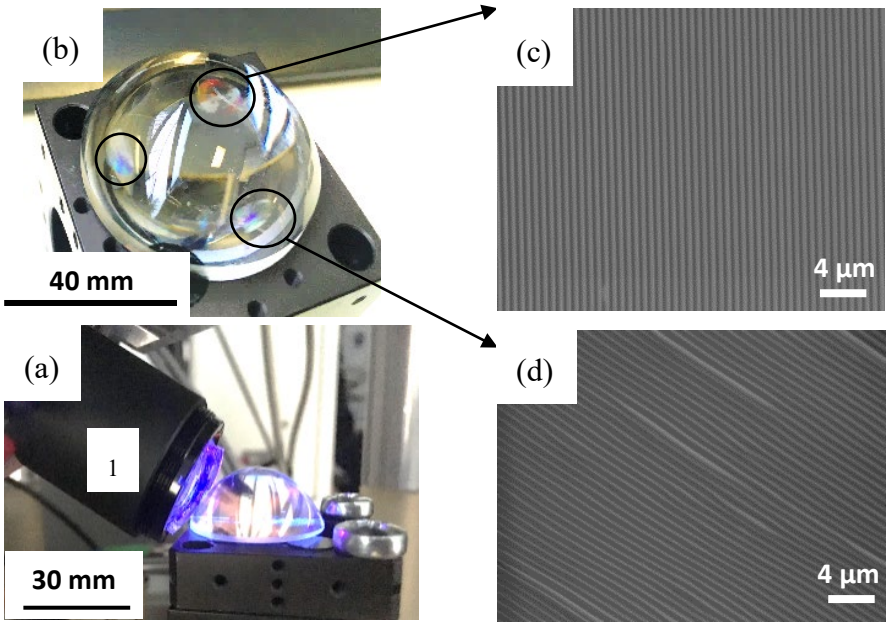

Figure 4.7: Soft UV-NIL process overview using the rotating NIL tool. (a) Rotating NIL tool **(1)** in contact with the substrate, (b) Imprinted substrate, (c) SEM image of imprinted pattern on top of substrate, and (d) imprinted pattern on the edge of substrate

the minimum thickness is 1.452 µm as measured with a laser scanning microscope. Furthermore, the coverage of the resist is improved with a second layer of coating. It can be seen in Figure 4.8, the resist layer had voids after a single layer of coating. However, a second layer of coating fills the voids mostly and improves the coverage of the resist. To achieve a better coverage, the nozzle flow is first increased to cover the edges of the substrate as it increases the amount of resist that is deposited on the substrate. However, the faster the resist flow, the quicker it becomes more viscous and therefore in case of two layers of coating, the flow rate for the first layer is lower than the flow rate for the second layer. The second layer can then be deposited at a faster flow rate while the first layer still has liquid consistency. In case of the process being carried out vice versa, the high viscosity of the first layer compared

to the second layer will lead to the dissolution of the initial layer droplets by the second layer of coating.

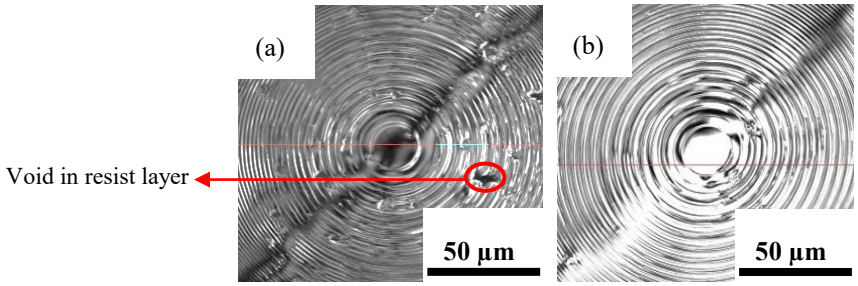

Figure 4.8: Imprint pattern on the Plano-convex lens (a) with voids after a single layer of resist coating, (b) without voids after multiple layers of resist coating

4.4. Imprinting and characterization on edges

The imprinting process was done for micro- structures as well as nanostructures. Initially, nanostructures were imprinted, but due to the high curvature of the lenses, it is difficult to characterize them at the edges. The imaging of the edges using an SEM is improved by coating the lens with carbon to reduce the charging effect. However, it was still difficult to characterize the patterns and observe the resist filling at the edges due to the excess resist thickness and thinner carbon layer coating. Therefore, a pre-existing PDMS stamp with microstructures was used for the process. These microstructures could be characterized using other means such as LSM, profilometry and white light interferometry. These methods provided measurement of the structure profile (Figure 4.9), however, the accuracy in the nanometer range is challenging. The uncertainty of measurement is in the range of +/-15 nm.

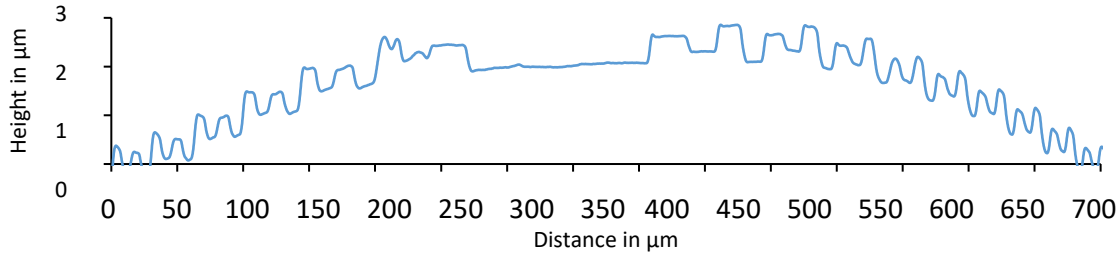

Figure 4.9: Imprinted structure profile as measured using the laser scanning microscope. The x-axis represents the lateral distance of structure scanning on the lens surface and the y-axis represents the measured structure height across the distance.

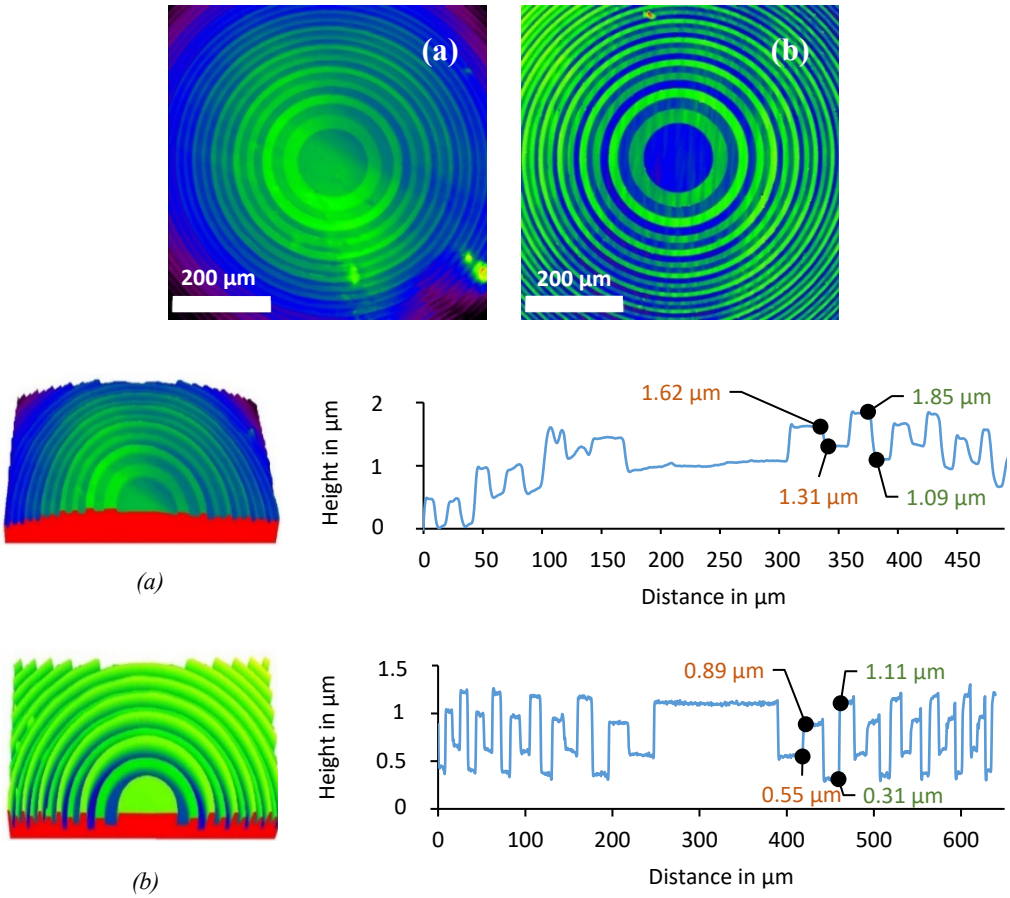

Figure 4.10: 3-D Laser scanning microscope images and corresponding structure profile of (a) Imprinted pattern on resist, (b) Master pattern on PDMS stamp.

The measured imprinted structures at an angle of 45° on the edge of the lens are found to be uniform and of good fidelity when compared to the structure profile of the stamp as seen in Figure 4.10. The imprinted structures are further scanned using a profilometer to get a better profile of the structures. The measured difference in the structure heights between the stamp and the imprint at two different steps of the structure profile are measured to be 0.03 µm and 0.04 µm. These differences are calculated for two different levels of the microstructure as marked in the graphs. Table 4.2 summarises the structure height differences between the stamp and the imprint at two different steps.

Table 4.2: Structure height comparison between the stamp and the imprint at two different steps

Height (µm)	***Step 1***	***Step 2***
Stamp	*0.34*	*0.80*
Imprint	*0.31*	*0.76*
Height difference (µm)	*0.03*	*0.04*

Further the process is compared to the conventional soft UV-NIL process. In the conventional process, the stamp is aligned on top of the substrate and is brought in contact. In case of flat and slightly curved substrates, it is convenient to have a conformal contact due to the flexibility of the PDMS stamp. However, for highly curved substrates, an ambient process is needed to achieve conformity throughout the surface of the substrate. Since, the molding and demolding process is crucial to achieve a good fidelity, the pressure needs to be uniform and sufficient at the edges. The conventional process is carried out using NIL machine, GD-N-03 manufactured by GD Nano (Guang Duo Micronano, China). A pressure of 0.5 kPa for imprinting on Plano-convex lens had been used and shown promising results. However, the curvature of the lens used in the process is significantly smaller.

The same process is carried out for the highly curved Plano-convex lens using the same parameters. However, it is not possible to imprint on large diameter and large curvature lens due to the limitation of the device to accommodate the sample. So, a lens with smaller diameter but with high curvature is used. The patterns were imprinted on the top region of the substrate. The resulting structures obtained are mostly of good fidelity with some anomalies. The irregularities can be deduced from shearing caused during the demolding process or due to non-uniformity of the resist layer. Further, to analyse the filling of the resist into the cavities of the structures, the depth of the structures was measured using a Dektak profilometer and Laser Scanning Microscope. The imprinted pattern and the structure profile can be seen in Figure 4.11.

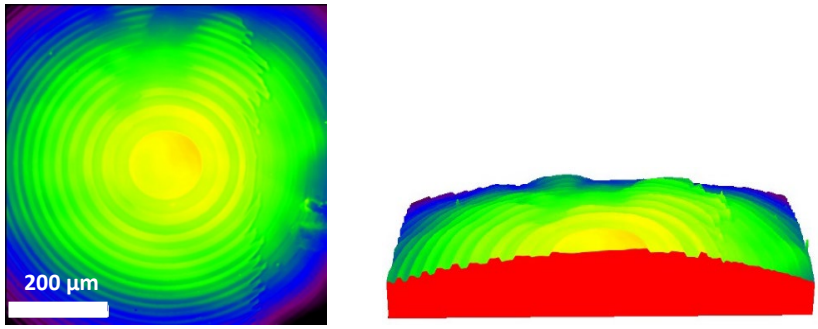

Figure 4.11: 3-D Laser scanning microscope image of imprinted pattern using conventional soft UV-NIL.

The profile of the structures imprinted using the orthogonal NIL process and the conventional process are compared in Table 4.3. The structure heights of the stamp and the imprint are compared to determine the effect of the process variations. From the differences in the structure heights it can be concluded that the filling of the structures at the edges of highly curved lens is comparatively better. Although the position of the imprinting is significantly different in both the cases, a better structure fidelity in the case of orthogonal imprinting is seen.

Table 4.3: Comparison of structure heights of imprint pattern using the rotational NIL and conventional NIL at two different step heights

	Step 1		***Step 2***	
	Conventional NIL step height (µm)	*Rotational NIL step height (µm)*	*Conventional NIL step height (µm)*	*Rotational NIL step height (µm)*
Stamp	*0.82*	*0.78*	*0.60*	*0.35*
Imprint	*0.76*	*0.76*	*0.51*	*0.31*
Height Difference	*0.06*	*0.02*	*0.09*	*0.04*

Since, the difference in the filling is in the nanometre scale, it may not be a crucial aspect for microstructures, but with the scaling down of the structures, the filling becomes critical even in the nanometre range. Though in case of high resolution nanostructures of sub-200 nm range the filling gains extreme importance. The low viscosity of the resist promotes better filling; although inadequate conformity can hinder the filling. Thus, the imprinting of the 100 nm structures provided a better insight into the process. In Figure 4.12, the SEM images of the master template structures and the imprinted patterns on the top and the edges of the Plano-convex lens is seen. The replicated pattern on the top is of good fidelity. On the edges, the patterns could be characterized only at lower magnification due to the limitations of imaging caused by charging effect.

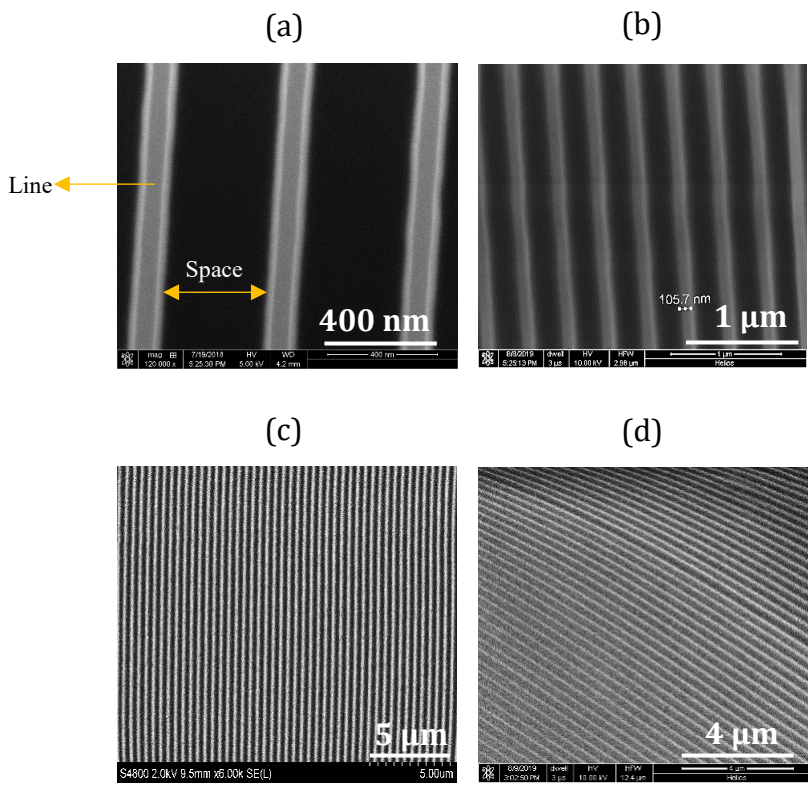

Figure 4.12: SEM images of high resolution nanostructures (lines and spaces pattern): (a) Master pattern, (b-c) Imprinted pattern on the top of the Plano-convex lens, (d) edge of the plano-convex lens.

4.5. Conclusions

The newly developed rotating NIL tool in combination with the NPM machine allowed orthogonal imprinting on the edges of highly curved substrates and also provided possibilities to imprint on freeform surfaces with high accuracy and precision. The integration of the two tools lead to the combination of advantages of both and provide a unique method to implement the soft UV-NIL process. The soft stamp could be used as a hard stamp, thereby discarding its disadvantage of bending of structures at high curvatures. The previously established methods for NIL process on curved surfaces focused mostly on the PDMS stamp formation or the modification of the process conditions itself. However, these processes either focused on small sized substrates mostly in the micrometre or millimeter range or neglected the characterization of the structures at the edges due to the challenges posed by the complexities of the processes (Chen et al. 2008; Chang et al. 2005). With the development of the rotating NIL tool, these facets are explored.

It was possible to imprint on edges of large Plano-lens with a diameter of 48.7 mm and corresponding height of 18.6 mm at angles of 45°, 60° and 90° from the center of rotation of the rotating tool. Additionally, the placement of the substrate on the mirror corner of the NPM machine enabled highly precise diagonal motion of the substrate which in turn allowed orthogonal molding and demolding at the different angles. The high resolution and accuracy of the positioning stage ensures a smooth demolding process without shear effects which addresses one of the major issues in the NIL process. The imprinted high resolution nanostructures with good fidelity at the edges of the high curvature substrates depict a desirable outcome considering the intricacy of high resolution soft UV-NIL process even on flat substrates.

Thus, the tool based on fundamental concepts of the soft UV-NIL process in combination with a high precision positioning machine and a multiple degrees of freedom rotating tool combines the best features of each and enables successful orthogonal imprinting process. The further optimization of the process can lead to the enabling of stitching for covering entire surfaces of the substrate.

Chapter 5

5. Hot embossing and soft NIL on non-flat surfaces

5.1. Introduction

In hot embossing, the pattern is embossed into a polymer substrate by softening it by heating it above its glass transition temperature. When the polymer is heated above the glass transition temperature, it starts flowing into the cavities of the structures on the master stamp under high pressure. It is then cooled down to harden the structures and demould. The need for high pressure for the process makes it challenging to implement on hard non-flat surfaces.

The aim of the work done in this chapter in collaboration with the Paul Scherrer Institute (PSI) was to imprint speckle pattern structures on a cylindrical stainless steel metallic tube with a diameter of 11 mm to observe deformations caused in the tube when subjected to mechanical stress. The goal of the work was to develop a suitable process to pattern structures on cylindrical metal tubes and further analyse the structure homogeneity.

Engineering structures are generally subjected to thermal and mechanical loadings resulting in fatigue. It is therefore necessary to analyse the effect of different loadings for determining the longevity and reliability of such structures (Chen et al. 2019). Digital Image Correlation (DIC) technique enables the determination of material deformation when subjected to any type of loading. The displacement caused by the loading effect is measured by correlating a specific section of the first image of the material to consecutive images of the same section. This helps in establishing the displacement of one or more points of the selected section of the first image in comparison to the consecutive images. The efficient use of the technique is done by using a speckle pattern image. A speckle pattern can be created in different ways such as spraying which creates random speckle patterns; secondly, numerically created speckle patterns which have defined sizes of the patterns. However, no two patterns are identical (D. Lecomptea et al. 2006).

In material testing, the bending and twisting of the metal tube causes fractures on the surface of the tube. These fractures can be identified with the digital image correlation technique by having speckle patterns on the surface of the tube. Such numerically created speckle patterns in the range of sub 20 microns are difficult to achieve on a metal tube with high curvature. It is not feasible to realize the patterns using conventional lithography techniques. In this case, the extremely high surface roughness makes it additionally challenging to transfer and further identify the structures for the imaging process. Moreover, the transparency of the resist made it challenging to do the imaging. To implement the patterning on to the metal tube, both hot embossing and soft NIL were considered.

5.2. Hot Embossing on flexible substrates

In the hot embossing process, the base plate is heated to a temperature above the glass transition temperature of the substrates, such as Polycarbonate (PC)/ Polyetherimide (PEI)/ Polyether ether ketone (PEEK foil), then a pressure of about 10 kN is applied on the foil/ substrate for the molding process to take place. The temperature at which the process is carried out depends on the glass transition temperature of the substrate. The force applied on the substrate was generally 10 kN. However, for thin foil of 12 µm thickness (PEI foil), higher force of 20 kN was applied. Figure 5.1 shows the hot embossing machine used for the implementation of the process. The high pressure enables good fidelity for the embossing of the structures in the substrate or the flexible foil. However, it was not possible to imprint on the cylindrical metal tube using the embossing tool, considering the high pressure that would be applied onto the metal cylinder with discrete shape. Therefore, soft nanoimprint lithography was then experimented with.

*This Hot embossing process was developed solely by the Polymer Nanotechnology group at PSI.

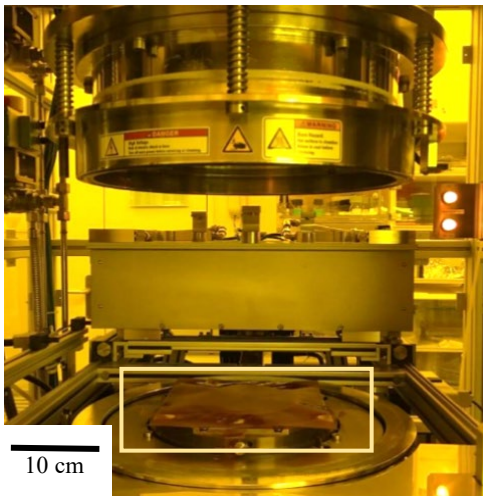

Figure 5.1: Jenoptik Hot Embossing machine (HEX 03) at PSI (highlighted: Base plate for placement of stamp and substrate in the embossing machine)

5.3. Soft Nanoimprint Lithography

The soft nanoimprint lithography was based on UV PDMS stamp. The flexibility and adhesion of the PDMS stamp to the metal promoted imprinting on the tube, therefore it was the preferred solution for imprinting on the metal tube. Also, the extremely low pressure made it viable to imprint using this process since it was suitable for the resist to fill into the cavities of the structures through capillary filling. Unlike, in hot embossing where much higher pressure and temperature is required, the moderate parameters needed in the soft nanoimprint process made it an effective and successful process.

5.3.1. Foil based and liquid based molds

The foil based substrates are replicated from the master using the hot embossing process. Ormostamp *(micro resist technology GmbH)* and UV PDMS *(Shin Etsu)* based molds are replicated using different process steps. The process steps for both the molds follow some common steps such as coating of the master with an anti-sticking layer. The coating of the ASL is enhanced by activating the silicon master using oxygen plasma treatment. The Ormostamp copy is prepared by pouring the Ormostamp on to the master and then on top of

it, a thin fused silica glass wafer of 200 µm thickness is placed to apply pressure and increase the filling of the Ormostamp into the cavities of the structures. After the Ormostamp had spread across and covered the entire surface of the master, it was then cured in the UV light for 5 minutes at 30 mW/cm^2. Finally, it is placed in the oven for 30 minutes at 120°C. The different foil material stamps (Polycarbonate, PEI, PEEK) are prepared using the hot embossing process as described in section 5.2.

Once the mold is created with Ormostamp, it can be used as master for subsequent molding. Therefore, the same procedure for the preparation of the Ormostamp master is followed as the one for the silicon master. The UV PDMS mold is prepared by mixing equal parts of solvent A and B. Then it is mixed and degassed in the oven at room temperature and vacuum. After it had been degassed, it is poured onto the Ormostamp master and is cured under the UV light for 5 minutes at 30 mW/cm^2. Finally, it is placed on the hot plate for 3 minutes at 50°C and again exposed to UV light for 3 minutes. Thereafter, the PDMS is peeled off from the substrate, a layer of PDMS with structures is thus obtained as shown in Figure 5.2.

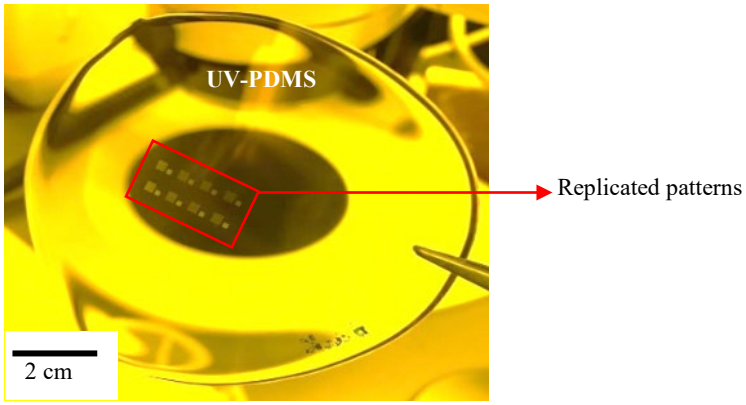

Figure 5.2: Replicated speckle patterns from hard Ormostamp master into UV-PDMS.

5.4. Pattern replication onto metal tube

A thermal UV NIL resist was used for the process. The resist, mr-NIL 6000.3 is a photochemically curing resist used for thermal nanoimprint lithography. The resist was dispensed on to the metal tube using the droplet dispensing method. Before dispensing the resist, adhesion promoter mr-APS1 was coated on the substrate. It was dispensed on to the

tube and baked at 100°C. Then, the resist was dispensed onto the primer coated substrate and prebaked at 120°C for 2 minutes. The flexible PDMS stamp was then bonded on to the metal tube *(as depicted in Figure 5.3)* for the filling of the cavities of the structures to take place using capillary filling for approximately 5 minutes. Thereafter, it was placed in the oven, where the annealing of the resist was done at temperature of 80-100°C for 3 minutes. After the annealing, the resist was then exposed to UV light for 5 minutes at 30 mW/cm^2.

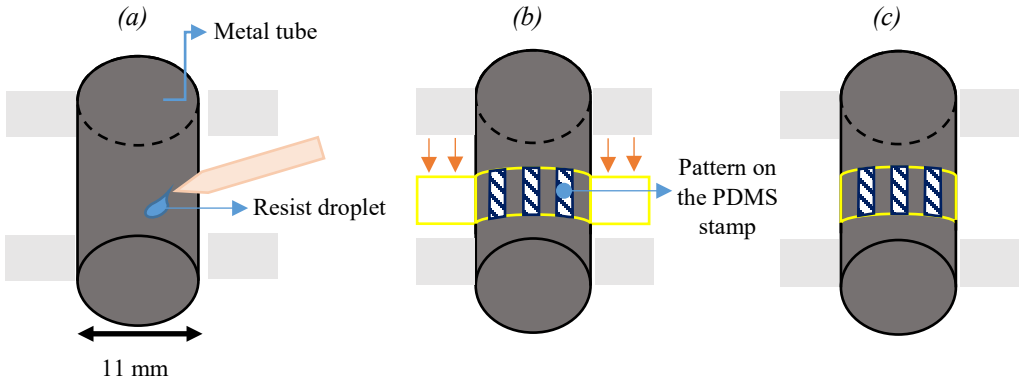

Figure 5.3: NIL process steps for pattern transfer on tube surface: (a) Resist droplet dispensed using pipette on top of adhesion promoter, (b) PDMS stamp pressed onto tube and fixed on edges with adhesive tape, (c) PDMS stamp fixed around the tube

The second resist used for the process was UV-NIL resist which cures only with the exposure to UV light and does not require additional curing by heating. The mr- NIL 210 resist which had a base thickness of 200 nm (at 3000 rpm) is a low viscosity resist that helps in easier filling of structure cavities. But, in case of non- flat substrates such as that of a cylindrical tube, the low viscosity causes the resist to slide off the surface regardless of the additional layer of adhesion promoter on the surface. However, the experiment was conducted with the resist. In this case, adhesion promoter was not applied to the substrate. The resist was first dispensed on to the metal tube and baked at 120°C for 1 minute 30 seconds. Then the PDMS stamp was pressed onto the resist and allowed for the capillary filling to take place for 5 minutes. It was then exposed to UV light for 5 minutes at 30 mW/cm^2. Then, the PDMS stamp was removed from the metal tube, resulting in the structures imprinted on the metal tube.

5.4.1. Results & Characterization

The structures were successfully imprinted on the required area of 5x5 mm^2 or even on larger area in some cases. Some of the structures were further coated with a 20 nm thick layer of chromium using sputtering process for further characterization. It enhanced the imaging for microscopic images (Figure 5.4).

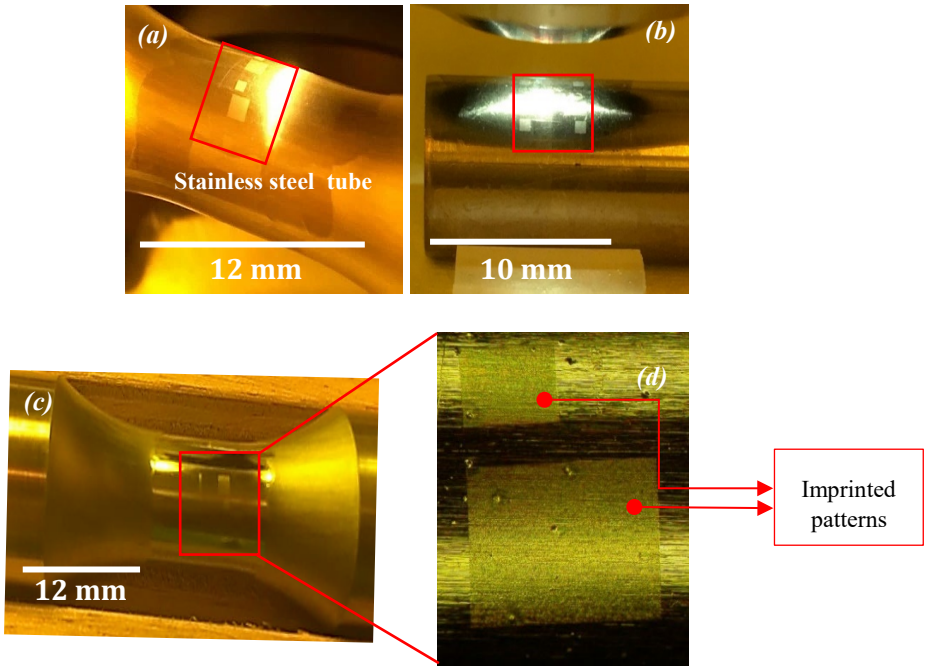

Figure 5.4: (a), (b) Imprinted speckle pattern (highlighted in red) on stainless steel tubes with different diameters, (c) Chromium coated tube (a), (d) Microscopic image of imprinted fields

The imprinted structures were further characterized using LSM to analyse its fidelity across the curved surface. The structure height measured at four different steps were 282 nm, 295 nm, 283 nm, 283 nm across 200 µm. The structures were found to be considerably homogeneous as deduced from Figure 5.5.

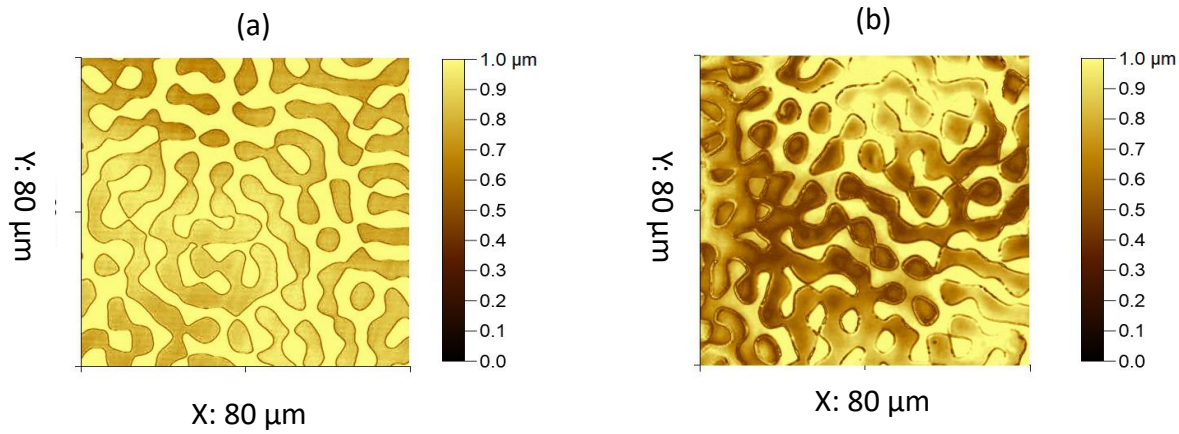

Figure 5.5: Profile of imprinted speckle pattern for (a) stamp and (b) stainless steel tube as obtained from LSM measurements.

5.4.2. Surface roughness of the metal tubes

The surface roughness of the metal tubes was found to be very high (approximately 280 nm, Figure 5.6); therefore, it was extremely challenging to achieve a uniform layer of resist on top of the surface. Also, the characterization of the structures, even after the coating of a chromium layer was challenging. However, initial characterization results showed that the structures were imprinted uniformly at some regions while some other regions showed non-uniformity or could not be characterized. Therefore, it further needs to be analysed if a thicker layer of resist would be suitable or additional metal layer should be coated. It greatly depends on the requirements and suitability for the testing of the metal deformation when subjected to mechanical stress.

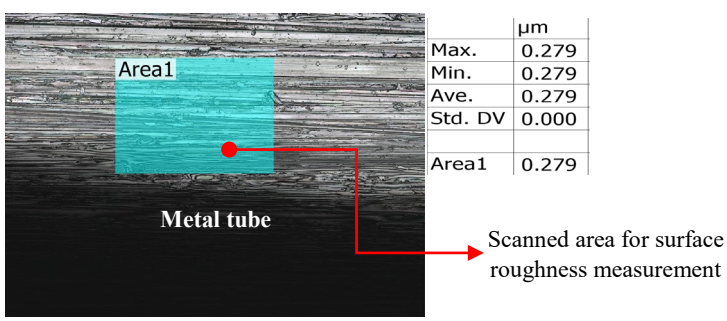

Figure 5.6: Surface roughness of metal tube measured using LSM. The measured roughness was approximately 280 µm.

5.5. Modified micro contact printing based imprinting

To observe the deformation caused due to mechanical stress, a stark contrast between the patterns was required, typically of black and white colour. The development of such a pattern was carried out by mixing dye in the NIL resist. After conducting tests by mixing several different dyes, a non-fluorescent blue-black coloured dye namely Sudan Black B is mixed in different ratios with the mr-NIL 6000.3 resist. The Sudan Black B dye commonly known by the name Solvent Black 3 is a diazo dye used to stain lipids and some lipoproteins (World of Chemicals). Its solubility in alcohol makes it suitable to be mixed with resist. It was mixed in the following ratios; 20 mg in 1 ml resist, 10 mg in 1 ml resist and 100 mg in 1 ml resist.

The imprinting process was then carried out using similar steps as the process mentioned in section 6.4 with reduced curing time. The dye stained resist was firstly dispensed on to the metal tube using droplet dispensing method. Then, the resist was prebaked at 100°C for 1 min. The flexible PDMS stamp is then bonded on to the metal tube and let the filling of the cavities of the structures take place using capillary filling for 5 minutes. It was then placed in the oven, where the annealing of the resist was done at temperature of 100°C for 1.5 minutes. After the annealing, the resist was finally exposed to UV light for 5 minutes at 30 mW/cm^2. The microscopic images of the structures imprinted on the metal tube using the dye stained resist can be seen in Figure 5.7.

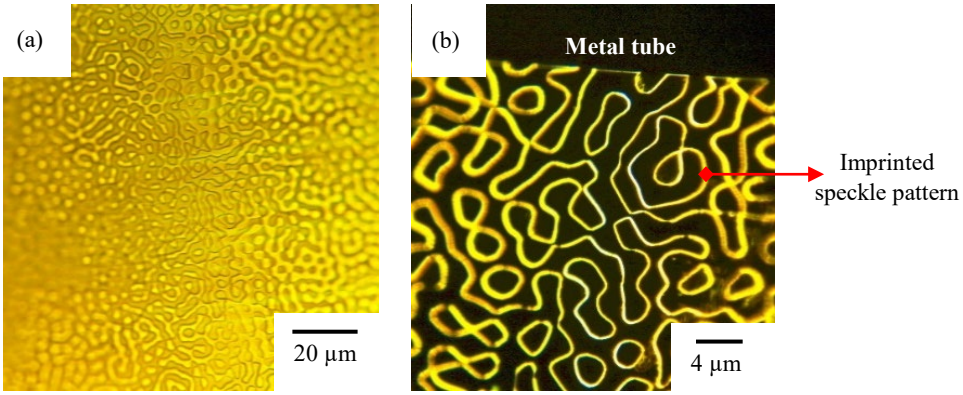

Figure 5.7: Microscopic images of patterned structure on metal tube using blue-black dye stained resist. (a) shows bright field image of the pattern and (b) shows dark field image of the pattern.

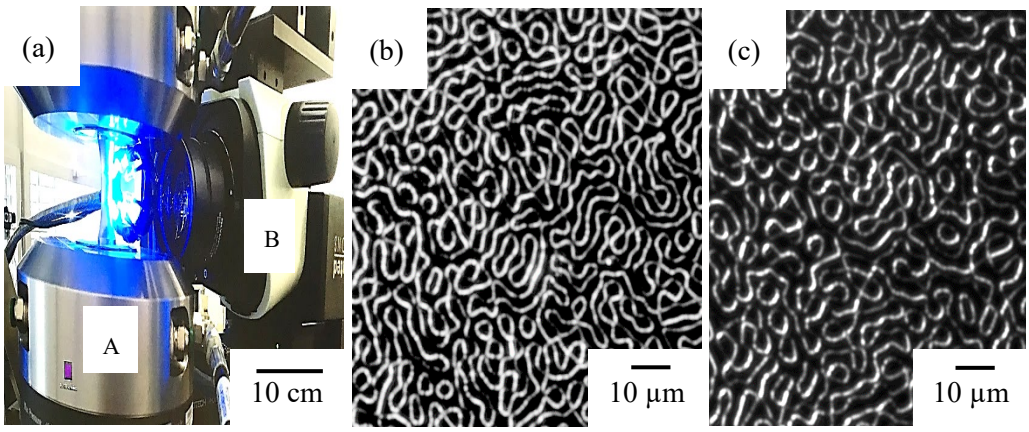

Figure 5.8: (a) Torsional test system **(A)** with metal tube mounted on it, (b-c) Camera **(B)** images of the speckle patterns imprinted on metal tube as obtained from the two different cameras of the torsional test equipment setup

The uneven ratio of the black and white colours in the pattern imaging was still not suitable for the torsional equipment setup (Figure 5.8). Therefore, a white colour was required to be added to the patterns. This enhanced the percentage of area comprising white background. The process was based on Microcontact printing. It is a pattern transferring technique in which an ink solution is transferred from an elastomeric mold such as PDMS onto a substrate by bringing the inked stamp in contact with the substrate (Fernandes et al. 2013). The pattern transfer was carried out by using a corrector liquid as white ink. A drop of diluted Tipp Ex corrector liquid *(TIPP-EX ECOLUTIONS CORRECTION FLUID)* was dispensed on the PDMS stamp containing the speckle pattern structures. Then a stroke of wipe was applied to remove the excess liquid. Since it is a water based corrector, it was left to dry for 2 minutes. Simultaneously, the dye stained resist was dispensed on the substrate and heated for 1 minute at 100°C. Then the stamp was brought in contact with the resist coated substrate and thereafter placed on the hotplate at 100°C for 1.5 minutes. Finally, it was exposed to UV light for 5 minutes at 30 mW/cm^2. The patterned structures were henceforth obtained. In the microscopic images in Figure 5.9, it can be seen that the speckle patterns are in black and white contrast. However, the patterns are not completely filled with the white colour and is patchy.

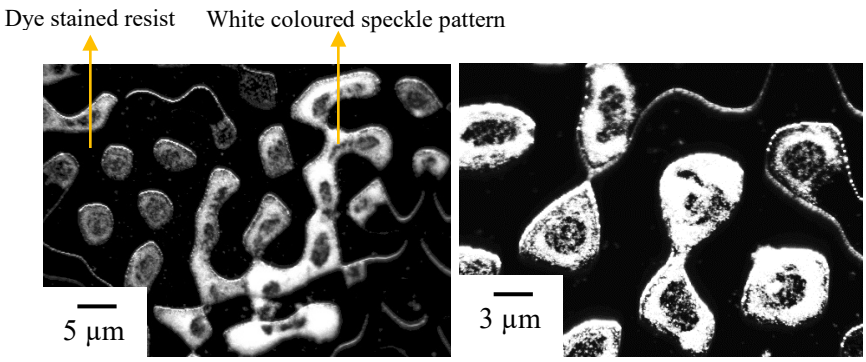

Figure 5.9: Microscopic images of speckle pattern imprinted on silicon wafer using µ-contact printing process. The speckle patterns were obtained using white liquid corrector on blue-black dye stained resist.

5.6. Conclusions and Outlook

In this chapter, the aim of the work was to pattern speckle patterns on an area of 1x1 cm^2 on a stainless steel cylindrical tube. Several experiments were conducted with different flexible stamp materials based on foil and PDMS. The patterns were transferred from silicon master onto the foils using hot embossing. The adhesion of the foil to the metal tube was extremely poor resulting in no pattern transfer. Following the unsuccessful pattern transfer with foil based stamps, PDMS was used. The faster processing time and low shrinkage of UV-PDMS made it the preferred choice for mold. The selection of the resist material was equally important as that of the mold. The adhesion of the resist to the highly curved tube was a challenge. In order to overcome this challenge, adhesion promoter was used. The imprinting process was conducted by binding the stamp around the tube without any application of external pressure. The resulting patterns were characterized using optical and confocal laser microscope. The patterns showed good fidelity but the required contrast was not achieved. A micro contact printing inspired process was developed to achieve high contrast speckle patterns. A dark (brown-black) background was attained by dissolving dye in resist and white foreground was achieved using diluted corrector. The microscope images of the first results were promising. Although, it requires further investigations and optimization.

Chapter 6

6.Summary and Outlook

The predicted shift of the semiconductor industry towards diversification and the approaching limits in miniaturization has given rise to the need for exploring new applications. These applications are based on 3-D structuring, flexible electronics, optoelectronic devices, and energy harvesting devices. A common idea behind all the mentioned applications is going beyond the conventional silicon based semiconductor manufacturing. Soft NIL provides an interface between the two facets of Moore's law. It enables high resolution patterning on flexible and other non-flat substrates. The applications however are not solely limited to semiconductor manufacturing but extends to several other fields. Through this thesis work, both sides of the technology have been investigated by extending the implementation of the patterning technique into high precision devices.

A novel rotating nanoimprint tool was designed and manufactured for promoting orthogonal molding and demolding NIL process. The integration of this tool into the NPM machine enabled precise separation of the substrate during the demolding process. It addresses a major challenge of shear effects induced during demolding of stamp from substrate. The impact of shear stress can cause patterns to deform and even collapse in case of high aspect ratio structures. The intensity of the challenge increases at edges of high curvature substrates. In addition to shear effects, the conformity of the stamp to the substrate becomes difficult. Different techniques have been applied previously such as gasbag chamber, modification of stamp as a negative replica of the substrate (mentioned in Chapter 4). Although such techniques were successfully implemented, the characterization of structures on the edges of the large area substrates have been ignored. Some researchers displayed good structure fidelity on high slopes, although the imprint area was considerably small. The rotating NIL tool on the other hand addresses the generally overlooked challenging task of patterning and characterization on the edges of curved substrate. It has displayed imprinting capabilities on the edge of spherical substrate with radius of curvature of approximately 25 mm at a surface

normal tilted to 45°. The methodology was designed to analyse high resolution nanostructures at first, but due to restricted measurement capabilities, the characterization was extremely challenging. Due to charging effects and limitations in sample chamber of SEM and AFM devices, the characterization was severely affected and limited.

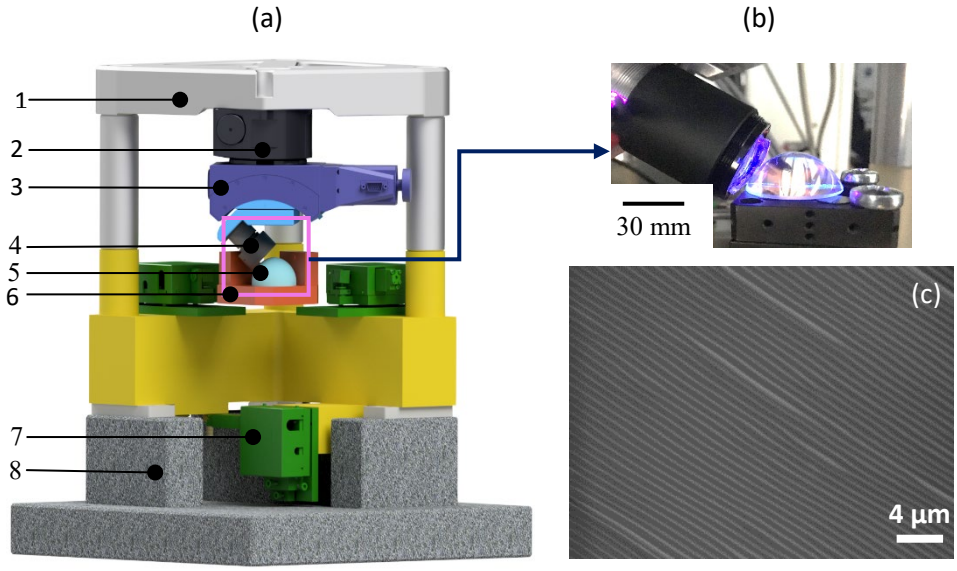

Figure 6.1: Orthogonal imprinting process on edges of curved surface using a newly developed rotating NIL tool: (a) Basic model of the Nano-positioning and Nano-measuring machine with additional rotating nanoimprint tool (highlighted in the centre), (1) Metrological frame of the NMM-1; (2) Rotation stage ($ø_z$); (3) Goniometer stage ($ø_{x,y}$) ; (4) Nanoimprint Lithography (NIL) tool; (5) substrate; (6) Mirror corner of the linear stage (moved in x,y,z); (7) Three interferometers of the NMM-1; (8) Metrological frame of the NMM-1, (b) soft UV-NIL process at the edge of Plano-convex lens using the rotating NIL tool, (c) SEM image of the imprinted nanostructures at an inclination of 45°

Figure 6.1 shows the process overview of orthogonal imprinting on edges of curved surface using the rotating NIL tool. Despite the challenges in characterization, it was possible to perform SEM imaging of the structures on top of the lens substrate as well as at inclination of 45°. As part of future work, use of different materials for improved imaging can be considered.

The integration of the soft UV-NIL process into the NPM machine created a wide range of possibilities for advancements in positioning and alignment. The scope of this thesis is limited to basic implementation of the process and positioning of the stamp to the substrate.

In comparison to maskless lithographic techniques, this contact based process presents a challenging task of molding and demolding in sub-nanometer resolution of the machine. A set of experiments were conducted with varying conditions and parameters. These experiments resulted in successful imprinting of sub-200 nm patterns on silicon substrates and on low curvature Plano-convex lenses (focal lengths of 50, 75 and 100). A subsequent improvisation in the mold design and increase in intensity of UV light source accelerated the process. The new mold was designed to reduce the area, thereby increasing the pressure which enabled successful imprinting of high resolution nanostructures. As first experiments for the step and repeat process with stitching, critical issues were observed. The primary challenges were the irregularities of the mold shape and squeezing of resist caused by sandwiching of the mold and substrate. As a positive outlook, these issues can be undertaken by further improvements in the mold design and assessing the force exerted during the molding process in order to control the flow of resist to outer edges of the pattern. The resolution of these issues would pave ways for more advancements. One such development will be overlay, which is crucial in several applications for semiconductor manufacturing. The accurate positioning capabilities of the NPMM can provide excellent overlay conditions, considering that the above mentioned challenges in the process are resolved.

With a view of the future transition of semiconductor technology to engage in diversification for development of systems and devices, distinctive approaches were realized. The interdisciplinary structure of the project combined with the flexibility of the soft NIL technique contributed to the fulfilment of these approaches. The challenge of pattern transfer to non-flat surfaces has been accomplished in different methods. The outcomes of the thesis would provide foundation for new concepts.

Glossary

- **Adhesion Promoter:** It is applied to the substrate to improve the adhesion of the resist to the substrate. Generally, adhesion promoters are based on silanes and act as the bonding agent between organic and inorganic materials.
- **ASL:** In NIL, ASL is used to reduce the surface energy of the master template or mold in order to avoid adhesions, material transfer or contaminations when in contact with another material.
- **Demolding:** It is the separation of the molded pattern from the mold by delamination in case of thin thermoplastic polymer films or parallel separation in case of rigid molds.
- **Etching:** In semiconductor technology, etching is used to selectively remove layers from a surface, primarily for pattern transferring. The process can be carried out in two different methods: wet etching and dry etching. Liquid etchants are used for wet etching while gas etchants are used for dry etching.
- **Master template:** In NIL process, it is the primary source of patterns generated on a substrate using lithographic techniques such as photolithography, E-beam lithography, scanning probe lithography etc. from which pattern replication is carried out.
- **Molding:** In case of NIL, it is the shaping of resist or thermoplastic polymers to transfer patterns by applying mechanical pressure using a rigid or flexible **mold or stamp**. Polymers can replicate high fidelity structures which make them suitable for use in the nanofabrication process.
- **PDMS:** It is a liquid silicone polymer which is optically transparent, soft and elastomeric at higher molecular weights. The fluidic properties of PDMS allows it to flow smoothly into cavities. Its high gas permeability enables diffusion of gases like oxygen and carbon dioxide.
- **Piranha solution:** It is a solution of concentrated sulphuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2), usually in a ratio of 3:1 to 7:1. It is used to remove organic residues such as resist from the surface of substrates. The reaction of hydrogen

peroxide with concentrated sulphuric acid produces oxidizing peroxymonosulphuric acid (H_2SO_5), also called Caro's acid.

- **Plano-convex lens:** In optics, these lenses are used as magnifiers, collimators and condensers. As the name suggests, these have one surface which is flat while the other one is convex. The two surfaces work together to focus parallel light rays to a positive focal point, thereby forming real images.
- **Resist:** Resists used in NIL are polymers defined by their chemical composition and physical properties. In the case of molding these are often long-chain molecules, with a molecular weight. It has been known for a long time, that polymers can replicate topographies with high fidelity. Thin-film rheology plays a central role of the understanding of the nanoimprint process, since the resist is patterned by mechanical deformation.
- **UV-PDMS**: It is a UV curable liquid silicone polymer. In contrast to the conventional PDMS, the UV-PDMS is photo-sensitive thereby the cross-linking occurs by UV-exposure. This enables full curing at room temperature.
- **Wafer:** It is a thin slice of semiconductor material such used as a platform for fabrication of integrated circuits and semiconductor devices. Crystalline silicon is a widely used material for the manufacturing of wafers.

Acronyms

AFM	Atomic Force Microscopy
ASL	Anti-Sticking Layer
CMOS	Complementary Metal Oxide Semiconductor
CD	Compact Disk
DI	Deionized
DLW	Direct Laser Writing
DOE	Diffractive Optical Element
DOF	Degrees of Freedom
DVD	Digital Versatile Disk
EUVL	Extreme Ultraviolet lithography
FDTS	Perflourodecyltrichlorosilane
FED	Field Emission Display
FE-SPL	Field Emission – Scanning Probe Lithography
FET	Field Effect Transistor
HD-DVD	High Definition DVD
HOE	Holographic Optical Element
ICP	Inductively Coupled Plasma
IOT	Internet of Things
IRDS	International Roadmap for Devices and Systems
ITRS	International Technology Roadmap for Semiconductors
LED	Light Emitting Diode
LGAA	Lateral Gate All Around
NGL	Next Generation Lithography
NIL	Nanoimprint Lithography
NMM	Nano-measuring machine
NPM	Nano-positioning machine

NPMM	Nano-positioning and Nano-measuring machine
PDMS	Polydimethylsiloxane
RF	Radio Frequency
RIE	Reactive Ion Etching
SEM	Scanning Electron Microscopy
SET	Single Electron Transistor
TCP	Tool Center Point
TU	Technische Universität
UV	Ultraviolet
VGAA	Vertical Gate All Around
ZMN	Zentrum für Mikro-und Nanotechnologien

Publications and Conferences

Journal Papers

Hofmann, M., Weidenfeller, L., **Supreeti, S**., Mechold, S., Holz, M., Reuter, C., Sinzinger, S., Manske, E. and Rangelow, I.W., 2020. Mix-and-match lithography and cryogenic etching for NIL template fabrication. Microelectronic Engineering, p.111234.

Supreeti, S., Schienbein, R., Fesser, P., Fern, F., Hoffmann, M., Sinzinger, S., Nanoimprint lithography on edges of curved substrate using a rotating nanoimprint tool. (submitted)

Weidenfeller, L., Hofmann, M., **Supreeti, S**., Mechold, S., Holz, M., Reuter, C., Manske, E. and Rangelow, I.W., Cryogenic etching for pattern transfer into silicon of Mix-and-Match structured resist layers. (submitted)

Conference Proceedings

Supreeti, S., Kirchner, J., Hofmann, M., Mastylo, R., Rangelow, I.W., Manske, E., Hoffmann, M. and Sinzinger, S., 2019, March. Integrated soft UV-nanoimprint lithography in a nano-positioning and nanomeasuring machine for accurate positioning of stamp to substrate. In *Novel Patterning Technologies for Semiconductors, MEMS/NEMS, and MOEMS 2019* (Vol. 10958, p. 1095819). International Society for Optics and Photonics.

Weidenfeller, L., Hofmann, M., Kirchner, J., **Supreeti, S**., Rangelow, I.W., Sinzinger, S. and Manske, E., 2019, June. Micro-and nanofabrication technologies using the nanopositioning and nanomeasuring machines. In *Optical Measurement Systems for Industrial Inspection XI* (Vol. 11056, p. 1105637). International Society for Optics and Photonics.

Ortlepp, I., Kühnel, M., Hofmann, M., Weidenfeller, L., Kirchner, J., **Supreeti, S**., Mastylo, R., Holz, M., Michels, T., Füßl, R. and Rangelow, I.W., 2020, March. Tip-and laser-based nanofabrication up to 100 mm with sub-nanometre precision. In *Novel Patterning Technologies for Semiconductors, MEMS/NEMS and MOEMS 2020* (Vol. 11324, p. 113240A). International Society for Optics and Photonics.

Conference Participations/ Contributions

Supreeti, S., Kirchner, J., Hofmann, M., Mastylo, R., Rangelow, I.W., Manske, E., Hoffmann, M. and Sinzinger, S., "Integrated soft UV-nanoimprint lithography in a nanopositioning and nanomeasuring machine for accurate positioning of stamp to substrate," in SPIE Advanced Lithography 2019, San Jose, USA (24-27th February 2019).

Supreeti, S., Hofmann, M., Mastylo, R., Manske, E., Rangelow, Ivo.W., Hoffmann, M., Sinzinger, S., "Integration of a UV-Nanoimprint Lithography tool into a Nanopositioning and Nanomeasuring machine", in 32nd International Microprocesses and Nanotechnology Conference 2019, Hiroshima, Japan (28th-31st October 2019).

Hofmann, M., Weidenfeller, L., **Supreeti, S**., Mechold, S., Holz, M., Reuter, C., Sinzinger, S., Manske, E. and Rangelow, I.W., "Mix-and-match lithography and cryogenic etching for NIL template fabrication", in 45th International Conference on Micro and Nanoengineering, Rhodes, Greece (23rd-26th September 2019).

Weidenfeller, L., Hofmann, M., Kirchner, J., **Supreeti, S**., Rangelow, I.W., Sinzinger, S. and Manske, E., "Micro-and nanofabrication technologies using the nanopositioning and nanomeasuring machines", in SPIE Optical Metrology 2019, Munich, Germany (24th-27th June 2019).

Kühnel, M., Ortlepp, I., Hofmann, M., Weidenfeller, L., Kirchner, J., **Supreeti, S.**, Mastylo, R., Füßl, R., Rangelow,I., Fröhlich, T., Manske, E., "Nanopositioning and Nanomeasuring Machines (NPMM) and their application for nanofabrication in extended working volumes", in 14th International Symposium on Measurement Technology and Intelligent Instruments, Niigata, Japan (1st-4th September 2019).

Ortlepp I., Kühnel M., Hofmann, M., Weidenfeller, L., Kirchner, J., **Supreeti, S.**, Mastylo, R., Holz, M., Michels T., R., Füßl, R., Rangelow,I., Fröhlich, T., Donstov, D., Schäffel C., Manske, E., "Tip- and Laser based nanofabrication up to 100 mm with sub-nanometer precision" in SPIE Advanced Lithography 2020, San Jose, USA (24th-27th February 2020).

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Hofmann, Martin; Weidenfeller, Laura; Supreeti, Shraddha; Mechold, Stephan; Holz, Mathias; Reuter, Christoph et al. (2020): Mix-and-match lithography and cryogenic etching for NIL template fabrication. In *Microelectronic Engineering*. Available online at https://doi.org/10.1016/j.mee.2020.111234.

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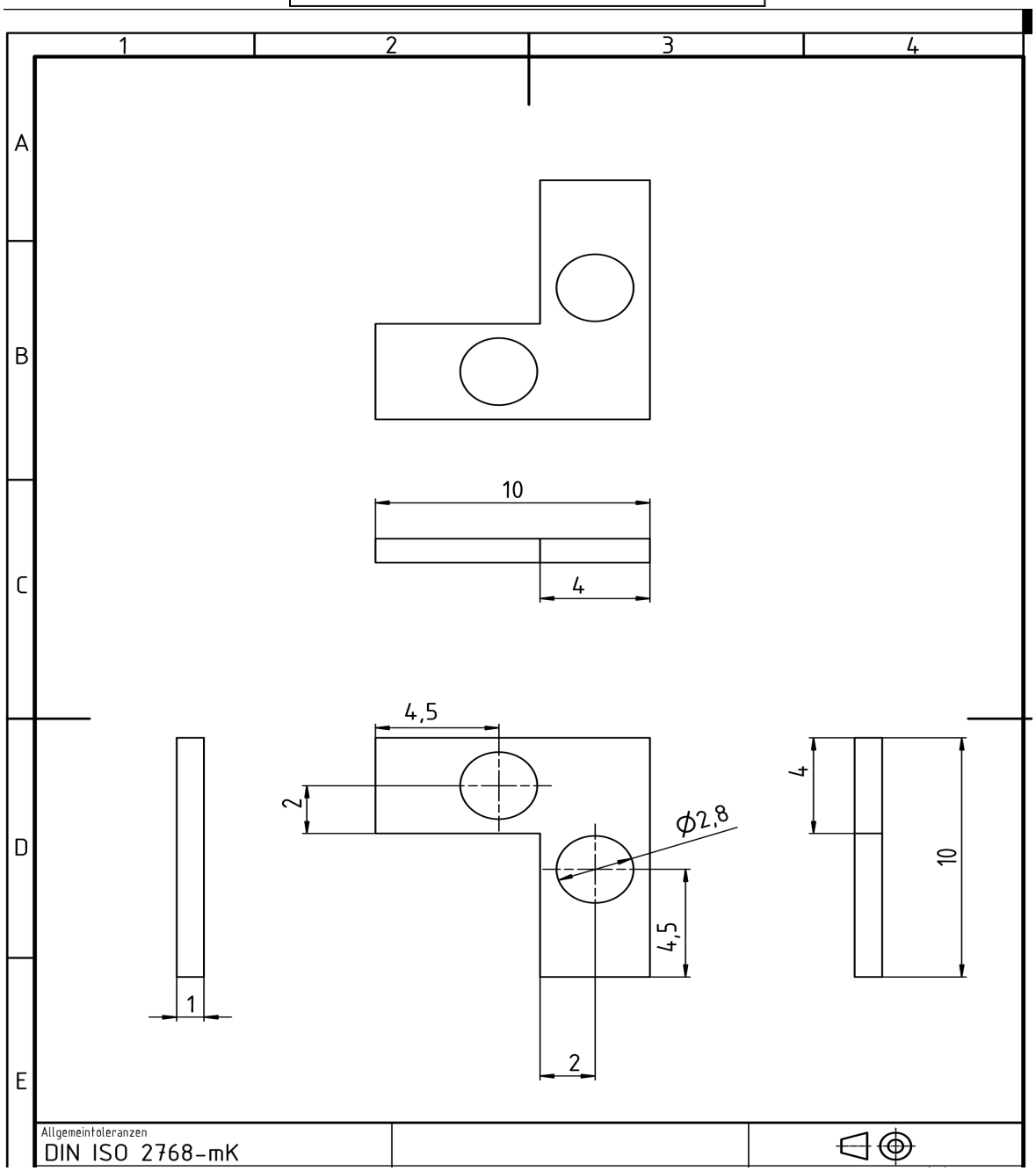
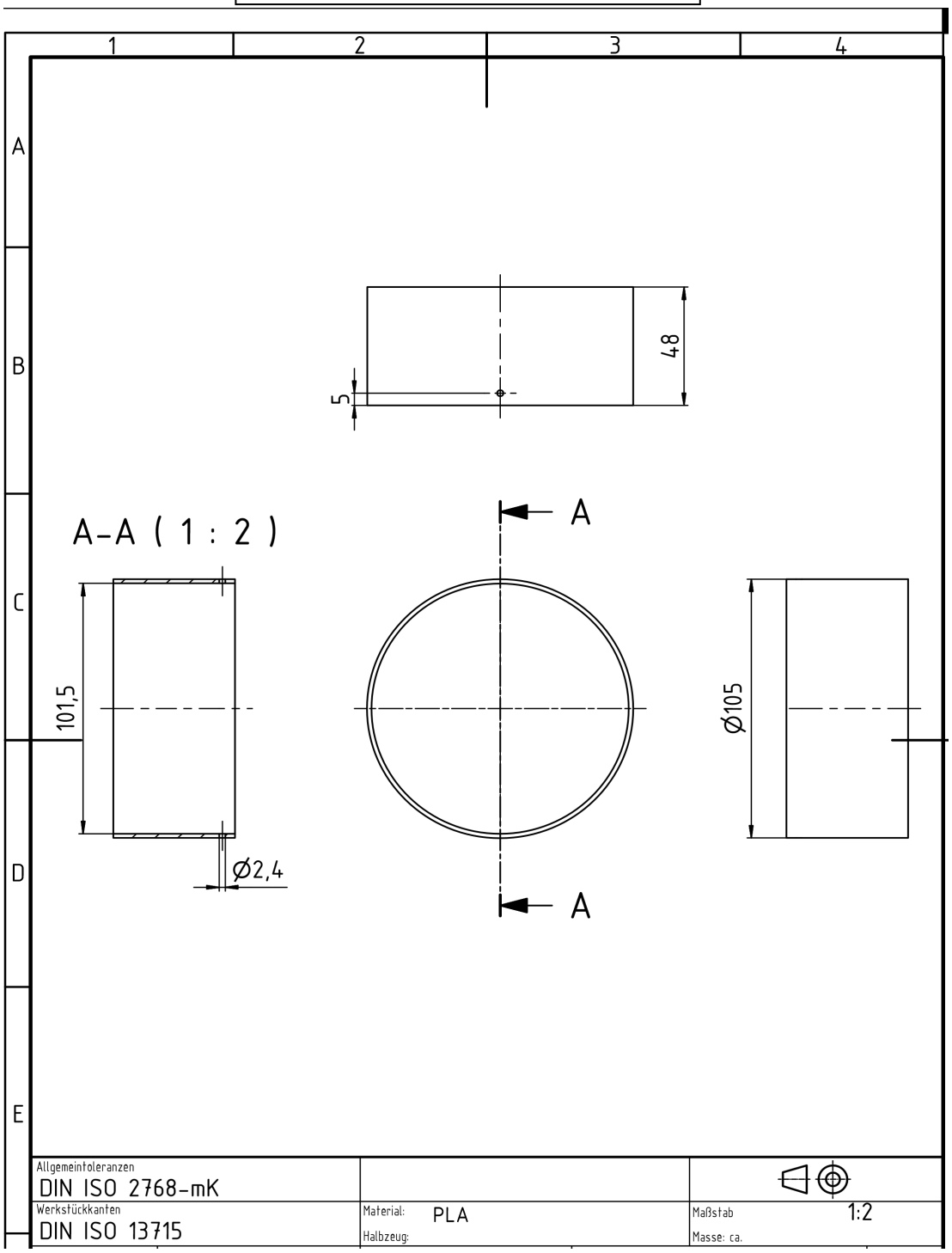
Appendix

CAD design for substrate holder to fix the substrate to base



CAD design for casing of ring UV-LED light



CAD design for UV-LED holder mounted in integrated soft UV-NIL