Next-Generation Nanoimprint Lithography: Innovative Approaches Towards Improving Flexibility And Resolution Of Nanofabrication In The Sub-15-nm Region

Stefan Harrer

NEXT-GENERATION NANOIMPRINT LITHOGRAPHY: INNOVATIVE APPROACHES TOWARDS IMPROVING FLEXIBILITY AND RESOLUTION OF NANOFACTORING IN THE SUB-15-NM REGION

Dissertation

submitted to the

Fakultät für Elektrotechnik und Informationstechnik
at
Technische Universität München (TUM)
by

Dipl.-Ing. Univ. Stefan Harrer, BSc.

in partial fulfillment of the requirements for the degree of

Doktor-Ingenieur

Submission date: February 27, 2008
President of examination committee: Prof. Dr. techn. Dr. h.c. Peter Russer (TUM)
Examiner I: Prof. Dr. Paolo Lugli (TUM)
Examiner II: Prof. Dr. Gerhard Abstreiter (TUM)
Advisor I: Prof. Dr. Paolo Lugli (TUM)
Advisor II: Prof. Dr. Karl K. Berggren (MIT)
Nanoimprint lithography (NIL) is a new manufacturing technology which has demonstrated sub-10-nm resolution and high throughput at low cost. NIL is rated as one of the most promising nanolithography techniques in terms of fulfilling future fabrication requirements of the semiconductor industry.

NIL transfers a pattern from a template onto a substrate. Conventional NIL processes are based on the following scheme: one layer of an imprint polymer at a temperature above its glass-transition temperature $T_g$ is deposited on a substrate to be imprinted. A stamp comprising the structure of the final desired pattern is pressed into the polymer layer, deforming it. Before the stamp is removed the imprint polymer layer is cured by cooling it down or exposing it to UV-radiation. The stamp is then removed, and subsequent etching steps allow for transferring the final pattern into the substrate. Variants of this technique exist, including microcontact and nanotransfer printing, step-and-flash nanoimprint lithography, nanoindent lithography, and room-temperature nanoimprint lithography.

A crucial requirement for being able to further extend the success of the NIL technique is to improve flexibility and resolution of conventional NIL schemes as well as to explore unconventional ways to utilize NIL processes for fabrication of novel nanodevices and nanomaterials.

I address these points in my dissertation by introducing an innovative NIL technique that we call Nanotemplate Arbitrary-Imprint Lithography (NAIL). NAIL will allow transfer of arbitrary patterns onto a substrate with higher resolution and flexibility than with any existing writing tool, and will therefore have significant impact on nanotechnology research. NAIL performs multiple imprints with general templates rather than a single imprint with a custom template. This technique represents a fundamental shift in how NIL is performed: it removes the difficult and slow step of custom-
template manufacturing (usually requiring electron-beam lithography) from the process.

We have demonstrated multi-step room-temperature nanoimprint lithography (RTNIL) using polystyrene (PS, average molecular weight 97 kg/mol) as the imprint polymer layer on a silicon substrate for imprinting complex patterns. Single, double, and multiple (up to 10) sequential imprint steps were performed at imprint pressures between 1 to 30 MPa in separate experiments. We also transferred the imprinted patterns from the PS layer into the silicon substrate by means of a reactive-ion etching (RIE) process. To accomplish this demonstration, we designed and custom-built a prototype of a NAIL tool capable of multi-step RTNIL in quasi-arbitrary geometries. The tool controllably and repeatedly translated and pressed a sample into a stationary mold with a demonstrated inter-step alignment accuracy ranging between 80 nm and 380 nm. These experiments revealed that polymer deformation results when NIL is used to further deform a previously structured surface. The molds used in these experiments consisted of 400-nm-period diffraction gratings, as well as of rectangular structures of varying aspect ratios, ranging from 150 nm to 300 nm wide. This work has been carried out in collaboration with MIT during the first half of the PhD project period.

As a first step towards bringing the NAIL technique down into the sub-15-nm region we have developed a single-step RTNIL process using polystyrene (PS, average molecular weights ranging from 13 kg/mol to 97 kg/mol) and the optically active polymer P3HT as imprint polymers provided on a silicon substrate for imprinting rectangular line patterns with varying aspect ratios, ranging from 11 nm to 500 nm wide. To accomplish this demonstration, we designed and built a second prototype NIL-tool that controllably pressed a mold into a stationary imprint sample applying imprint pressures between 280 MPa and 700 MPa. The molds used in these experiments were GaAs/AlGaAs sandwich structures fabricated by molecular beam epitaxy (MBE) that were cleaved and selectively etched afterwards in order to generate 3D grating structures with nanometer resolution on their edges. We fabricated positive and negative molds comprising single-line as well as multi-line patterns with different aspect ratios and linewidths between 9 nm and 300 nm. This work has been carried out in collaboration with the Walter-Schottky-Institute (WSI) of TUM during the second half of the PhD project period.
Using the experimental equipment that we initially designed and built for executing nanoimprint experiments we introduced an innovative direct nanotransfer scheme based on molds fabricated by MBE, and a combination of MBE and cleaved edge overgrowth (CEO) respectively, capable of directly transferring 1D and 2D lateral grating structures with minimum feature sizes in the sub-10-nm region onto silicon substrates. We have demonstrated direct nanoscale transfer printing of PdAu lines from a hard mold onto a hard substrate at room-temperature without employing any flexible buffer layers or organic adhesion promoters or release agent layers. PdAu was evaporated onto the mold surface, and a Ti tie layer was deposited on top of the PdAu layer. By pressing the mold against a Si/SiO$_2$ substrate the Ti/PdAu sandwich structure was directly transferred onto the SiO$_2$ surface. The molds used in these experiments were GaAs/AlGaAs sandwich structures fabricated by molecular-beam epitaxy that we cleaved and selectively etched afterwards in order to generate 3D grating structures with nanometer resolution on their edges. We fabricated positive multi-line molds with different aspect ratios, linewidths between 15 nm and 100 nm, and spacings between lines ranging from 5 nm to 70 nm. We also fabricated negative single-line molds with a positive supporting structure comprising a single 16-nm-wide groove feature. The experiments revealed that direct hard-on-hard transfer of nanoscale structures from a mold onto a substrate can be used to fabricate PdAu gaps with widths of down to 7 nm. This work has also been carried out in collaboration with the Walter-Schottky-Institute (WSI) of TUM during the second half of the PhD project period.

Finally we co-developed an innovative version of NIL in collaboration with micro resist technology GmbH (Berlin, Germany) that combines UV radiation with thermal treatment of imprint polymers (TUV-NIL) thus enabling completely isothermic imprint cycles.

**Keywords**: nanofabrication; nanoimprint lithography; multi-step; quasi-arbitrary patterns; molecular beam epitaxy; room-temperature nanoimprint lithography; thermal nanoimprint lithography; ultraviolet nanoimprint lithography; GaAs/AlGaAs; PdAu; Ti; hard-on-hard; gap; pattern transfer; nanotransfer lithography; cleaved edge overgrowth; isothermic;
Zusammenfassung


das Kosten-und Minnierungssproblem der Nanofabrikation.

Unter Verwendung der Geräte, die wir ursprünglich für Nanoimprint Lithographie Versuche gebaut hatten, entwickelten wir ein neuartiges Nanotransfer Lithographie Verfahren für den sub-10-nm Bereich, das mit Stempeln arbeitet, die mittels Molekularstrahlepition und der sog. Cleaved-Edge-Overgrowth Technik aus GaAs/AlGaAs Komponenten hergestellt werden.

In Zusammenarbeit mit unserem Industriepartner micro resist technology GmbH (Berlin, Deutschland) entwickelten wir zudem einen innovativen Nanoimprintprozess, der thermische und ultraviolette NIL Technologien kombiniert und dadurch komplett isothermische Imprintzyklen ermöglicht.

**Schlüsselbegriffe:** Nanofabrikation; Nanoimprint Lithographie; Multi-Schritt-Verfahren; Quasi-beliebige Muster; Molekularstrahlepition; Raum-Temperatur Nanoimprint Lithographie; Thermische Nanoimprint Lithographie; Ultraviolette Nanoimprint Lithographie; GaAs/AlGaAs; PdAu; Ti; hart-auf-hart; gap; Strukturtransfer; Nanotransfer Lithographie; cleaved edge overgrowth; isothermisch;
Acknowledgments

This thesis was the starting point of, and evolved from a collaboration between the Institute for Nanoelectronics at Technische Universität München, Munich, Germany, and the Quantum Nanostructures and Nanofabrication Group in the Research Laboratory of Electronics at the Massachusetts Institute of Technology, Cambridge, USA. From October 2004 to January 2005 I started my research at TUM under supervision of Prof. Dr. Paolo Lugli. From January 2005 to May 2006 I was invited to work at MIT under supervision of Prof. Dr. Karl K. Berggren, and from June 2006 to January 2008 I finished up my thesis back at TUM.

I am very grateful to my principal doctoral advisor Prof. Dr. Paolo Lugli for his strong interest in establishing and strengthening a collaboration with MIT over the entire duration of my research project. It was first of all his initial openness towards my plans and his ongoing flexibility that enabled me to successfully embed my thesis work in a binational setup. His profound advice regarding scientific guidance as well as operational research project management was, and still is extremely valuable to me. I am deeply thankful for the trust that he always showed in me and my work: I feel especially honored about having been allowed to contribute significantly to building up the nanofabrication laboratory at TUM. Also, working on a quite innovative experimental research project, progress would not have been possible without him continuously believing in the success of the project and, based on his pioneering spirit, providing funding for my position and for building up the equipment enabling all my experimental work.

I am very indebted to my second advisor Prof. Dr. Karl K. Berggren for not only inviting me to join but also for fully integrating me into his group: MIT and Cambridge became a second home to me, not only from a scientific point of view but also from a social perspective. Under his inspiring
supervision my learning curve was incredibly steep - I am deeply grateful for all the time that he put into introducing me to the fields of nanofabrication and nanolithography as well as into teaching me how to write journal papers, how to give a conference talk, and how to compose research grant proposals to just name very few topics. I want to express my great gratitude for his most generous support of my research while I was at MIT as well as his ongoing interest and support of my present efforts towards finding my place and settling down in the research community in the future. I also want to thank him for showing active interest in continuing and strengthening the collaboration with TUM by hosting one of my masters students, Jan Kupec, after I left MIT.

Prof. Dr. Henry I. Smith was not only teaching me valuable lessons in the classroom but also on the tennis courts of Zeisiger Athletics Center - I enjoyed both very much and thank him for the time that he spent with me in the nanoscopic as well as in the macroscopic world.

I conducted most of my research at TUM in close collaboration with the Walter-Schottky-Institute of TUM. This collaboration was initiated and strengthened by Dr. Giuseppe Scarpa who also provided most valuable technical and operational feedback throughout our entire collaboration activities. I feel deeply thankful for all his support and feedback. Experimental progress during my time at TUM happened mostly thanks to the fruitful and most efficient team work of our institute with Dipl. Phys. Sebastian Strobé and his advisors Prof. Dr. Marc Tornow and Prof. Dr. Gerhard Abstreiter. Each single one of the interesting discussions and weekend and late night lab sessions that we had were crucial milestones along our joint research project roadmap. I very much enjoyed working with Sebastian and feel honored that he returned the favor by cutting so much time out of his own schedule to work with me.

My graduate students Jan Kupec and Guillermo Penso-Blanco contributed a lot to the work presented in this thesis. Supervising them was a rewarding and enjoyable task, I wish them all the best for their future at ETH Zurich, and in Madrid respectively.

I am deeply grateful to the president of TUM, Prof. Dr. Wolfgang A. Herrmann, and Dr. Otto Majewski representing and chairing the "Bund der Freunde der TUM" (BdF), and the "Karl-Max-von-Bauernfeind Verein e.V." (KMvB) respectively, for showing strong interest in my research project and
supporting it generously through a "Presidential Science and Engineering Research Fellowship". It was most of all due to this fellowship that I could fully concentrate on my research project without losing precious time and energy. I also want to thank the Karl Chang Innovation Fund at MIT, the Air Force Office of Scientific Research (AFOSR), the cluster of excellence Nanosystems Initiative Munich (NIM), the MRSEC Program of the National Science Foundation under Award DMR02-13282, and the Walter-Schottky-Institute of TUM for their financial support of my thesis work.

I further want to express my gratitude towards Prof. Dr. Caroline A. Ross, Prof. Dr. Minghao Qi, Prof. Dr. Kristine Rosfjord, Prof. Dr. Dirk Grundler, Prof. Dr. Gerhard Franz, Prof. Dr. Stefan Sotier, Prof. Dr. Doris Schmitt-Landsiedel, Prof. Dr. Khaled Karrai, Dr. Christian Jirauschek, Dr. Euclid Moon, Dr. Timothy A. Savas, Dr. Ion Bita, Dr. Ozge A. Halatci, Dr. Vikas Anant, Dr. Dirk Haft, Dr. Francesca Brunetti, Dr. György Csaba, Dr. Paul Berberich, Jerimy Arnold, Christoph M. Erlen, Jim Daley, Jaye Jillson, Marc Mondol, Joel K. W. Yang, Peter Morley, Stan Coutreau, Bryan Cord, Giovanni A. Salvatore, Filip Ilievski, Mike Kubenz, Christine Schuster, Freimut Reuther, Omar Fakhr, Alaa Abdelah, Andreas S. Haese, Jack and Joan for their great hospitality and the pumpkin bread, Wolfgang Bendak, Ade Ziegeltrum, Fritz Sedlmair, Max Bichler, Claudia Paulus, Rosemarie Heilmann, Markus Becherer, and Rainer Emmel.

Finally, I want to thank my parents for laying out the groundwork and seeding the enthusiasm that made me want to be an engineer. Without their ongoing unconditional support I would not have been able to accomplish my goals. I feel deeply thankful and dedicate this thesis to them.

Erding, February 26, 2008
Contents

1 Introduction 1
   1.1 About this thesis 2
   1.2 Goals and project roadmap 5

2 Nanoimprint Lithography 7
   2.1 State-of-the-art nanoimprint lithography: technical overview and potential 7
       2.1.1 Nanoimprint lithography - basic technological approach 7
       2.1.2 Advantages and potential of nanoimprint lithography 8
       2.1.3 Areas of application of nanoimprint lithography 11
   2.2 Mold fabrication techniques 12
   2.3 Nanoimprint polymer materials 14
       2.3.1 Thermoplastic imprint polymers 15
       2.3.2 UV-curable imprint polymers 16
       2.3.3 Novel materials 17
   2.4 Surface forces and mold release 19
   2.5 Mold-substrate alignment and imprint pressure distribution 20
   2.6 State-of-the-art nanoimprint lithography techniques - a survey 21
       2.6.1 AFM-based nanofabrication - nanoindent lithography 21
       2.6.2 Replica molding and reverse nanoimprinting 23
       2.6.3 Soft lithography - nanotransfer printing and microcontact printing 23
       2.6.4 Step-and-repeat UV-nanoimprint lithography 24
       2.6.5 Room-temperature nanoimprint lithography 25

3 Nanotemplate Arbitrary-Imprint Lithography 29
   3.1 Innovative idea and approach 29
3.2 Opportunity ........................................ 31
3.3 Designing a multi-step nanoimprint tool ............... 34
  3.3.1 Design of a NAIL prototype tool: the complete system 35
  3.3.2 Computer controlled stages ....................... 38
  3.3.3 Optical in-situ result verification: CCD-unit ........ 39
  3.3.4 Mold fabrication process and mold holder unit .... 39

3.4 Single-step room-temperature nanoimprint lithography .... 44

3.5 Two-step room-temperature nanoimprint lithography ....... 46

3.6 Establishing NAIL: multi-step room-temperature nanoimprint lithography ................. 47
  3.6.1 Design of NAIL experiment ...................... 48
  3.6.2 Supertemplate fabrication process ............... 50
  3.6.3 Performing the NAIL experiment ................. 52

3.7 Pattern transfer into the silicon substrate ............... 54

3.8 Performance evaluation of the NAIL prototype tool and next steps ......................... 57

4 Sub-15-nm Room-Temperature Nanoimprint Lithography 61
  4.1 Imprint mold fabrication by using molecular beam epitaxy 62
    4.1.1 Negative single-line MBE-molds ............... 64
    4.1.2 Negative multi-line MBE-molds ............... 64
    4.1.3 Positive multi-line MBE-molds ............... 65
    4.1.4 Negative single-line MBE-molds with a positive supporting structure ............... 67

  4.2 Design of nanoimprint tool .......................... 70
    4.2.1 Working principle of the mold holder unit: the mold levelling procedure ............... 71
    4.2.2 Tool calibration .................................. 78

  4.3 Single-step RTNIL using MBE-fabricated molds ............ 78
    4.3.1 Single-step RTNIL process using a single-line negative MBE-mold ............... 80
    4.3.2 Single-step RTNIL process using a positive multi-line MBE-mold ............... 81
    4.3.3 Single-step RTNIL process using a negative single-line MBE-mold with a positive supporting structure ............... 84

  4.4 Process evaluation and next steps ................... 84
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>US National Nanotechnology Initiative</td>
<td>1</td>
</tr>
<tr>
<td>2.1</td>
<td>Working principle of T-NIL and SFIL</td>
<td>9</td>
</tr>
<tr>
<td>3.1</td>
<td>Working principle of NAIL</td>
<td>31</td>
</tr>
<tr>
<td>3.2</td>
<td>NAIL nanotemplates</td>
<td>32</td>
</tr>
<tr>
<td>3.3</td>
<td>NAIL prototype tool: design of the complete system setup</td>
<td>36</td>
</tr>
<tr>
<td>3.4</td>
<td>NAIL prototype tool: realization of the complete system setup</td>
<td>38</td>
</tr>
<tr>
<td>3.5</td>
<td>NAIL prototype tool: the core unit</td>
<td>40</td>
</tr>
<tr>
<td>3.6</td>
<td>NAIL prototype tool: CCD camera and UV-source</td>
<td>41</td>
</tr>
<tr>
<td>3.7</td>
<td>Nontransparent supertemplate</td>
<td>43</td>
</tr>
<tr>
<td>3.8</td>
<td>NAIL prototype tool: simplified version and mold holder unit</td>
<td>44</td>
</tr>
<tr>
<td>3.9</td>
<td>Single-step RTNIL results</td>
<td>46</td>
</tr>
<tr>
<td>3.10</td>
<td>Two-step RTNIL results</td>
<td>47</td>
</tr>
<tr>
<td>3.11</td>
<td>Design of NAIL experiment: the final desired pattern</td>
<td>49</td>
</tr>
<tr>
<td>3.12</td>
<td>Design of NAIL experiment: the multi-step RTNIL cycle</td>
<td>51</td>
</tr>
<tr>
<td>3.13</td>
<td>Transparent supertemplate</td>
<td>53</td>
</tr>
<tr>
<td>3.14</td>
<td>NAIL results</td>
<td>55</td>
</tr>
<tr>
<td>3.15</td>
<td>Theory: pattern transfer of NAIL structures</td>
<td>56</td>
</tr>
<tr>
<td>3.16</td>
<td>Results: pattern transfer of NAIL structures</td>
<td>57</td>
</tr>
<tr>
<td>4.1</td>
<td>MBE-RTNIL, the basic idea: MBE-mold fabrication and imprint scheme</td>
<td>63</td>
</tr>
<tr>
<td>4.2</td>
<td>MBE-RTNIL: single-line negative MBE-mold</td>
<td>65</td>
</tr>
<tr>
<td>4.3</td>
<td>MBE-RTNIL: two types of negative multi-line MBE-molds</td>
<td>66</td>
</tr>
<tr>
<td>4.4</td>
<td>MBE-RTNIL: positive multi-line MBE-mold</td>
<td>68</td>
</tr>
<tr>
<td>4.5</td>
<td>MBE-RTNIL: negative single-line MBE-mold with a positive supporting structure</td>
<td>69</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>MBE-RTNIL prototype tool: design of complete system setup</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>MBE-RTNIL prototype tool: realization of complete system setup</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>MBE-RTNIL prototype tool: schematic design of the mold holder unit</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>MBE-RTNIL prototype tool: realization of the mold holder unit</td>
<td></td>
</tr>
<tr>
<td>4.10</td>
<td>MBE-RTNIL tool: pressure-force-curve used for calibrating the hydraulic control unit</td>
<td></td>
</tr>
<tr>
<td>4.11</td>
<td>MBE-RTNIL: single-step RTNIL result using a single-line negative MBE-mold</td>
<td></td>
</tr>
<tr>
<td>4.12</td>
<td>MBE-RTNIL: single-step RTNIL result using a multi-line positive MBE-mold</td>
<td></td>
</tr>
<tr>
<td>4.13</td>
<td>MBE-RTNIL: single-step RTNIL results using a negative single-line MBE-mold with a positive supporting structure</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Direct nTP: experimental multi-gap results I</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>Direct nTP: experimental multi-gap results II</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>Direct nTP: positive multi-line MBE-molds in different stages of the process</td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>Direct nTP: negative single-line MBE-molds with positive supporting structure in different stages of the process</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>Direct nTP: experimental single-gap results</td>
<td></td>
</tr>
<tr>
<td>5.6</td>
<td>CEO-nTP and CEO-NIL: mold fabrication scheme</td>
<td></td>
</tr>
<tr>
<td>5.7</td>
<td>CEO-nTP: process description</td>
<td></td>
</tr>
<tr>
<td>5.8</td>
<td>CEO-NIL: process description</td>
<td></td>
</tr>
<tr>
<td>A.1</td>
<td>NAIL tool prototype: complete set of machine drawings</td>
<td></td>
</tr>
<tr>
<td>B.1</td>
<td>MBE-RTNIL and MBE-nTP tool prototype: complete set of machine drawings</td>
<td></td>
</tr>
<tr>
<td>C.1</td>
<td>MBE-RTNIL: imprint result using P3HT as imprint polymer</td>
<td></td>
</tr>
<tr>
<td>D.1</td>
<td>Combined thermal and UV-nanoimprint lithography: experimental imprint results</td>
<td></td>
</tr>
<tr>
<td>D.2</td>
<td>Combined thermal and UV-nanoimprint lithography: experimental pattern transfer results</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Nanotechnology is an emerging, highly interdisciplinary research field aiming at the miniaturization of structures, made of a variety of materials down to atomic and molecular scale. By building objects on the nanoscale, new devices and circuits can be developed that may lead to completely new products and applications in computing, energy generation and distribution, life sciences and communications.

The US National Nanotechnology Initiative [1] has allocated 1.2B$ for the 2007 budget. Figure 1.1 shows the growth in this budget in recent years [2]. Meanwhile nanotechnology research investment worldwide is also growing at a breakneck pace. Projects of the same order of magnitude have also been put forward in Europe and Asia.

![Figure 1.1: National Nanotechnology Initiative has 1.2B$ allocated for the 2007 budget [1][2]. The graph shows the historical growth in this budget.](image-url)
1. INTRODUCTION

All methods of fabricating nanodevices are generally referred to as controlled nanomanufacturing (or alternatively as controlled nanofabrication). DARPA more specifically defines controlled nanomanufacturing as

... automated, parallel fabrication of individual nanostructures with control over position, size, shape, and orientation at the nanometer scale, including the ability to fabricate devices with controlled differences in size, shape, and orientation at different positions. This capability should include the ability for in-situ detection of the nanostructure position, size, shape, and orientation, and the ability to repair or re-manufacture structures as needed.

Nanomanufacturing shall not be confused with nanomanipulation that is commonly defined as

... pushing or pulling, cutting, picking and placing, positioning and orienting, assembling, indenting, bending, twisting of nanometer-size objects with a nanometer-size effector with nanometer precision.

Thus, nanomanufacturing includes nanomanipulation as well as chemical and physical reactions that are spatially confined to areas of nanometer dimensions. In this thesis, the above mentioned terms are used strictly according to the respective definition, in literature, however, deviating - and contradictive - definitions may be encountered.

1.1 About this thesis

Nanoimprint Lithography (NIL) emerged in 1995 with the initial publications of S. Y. Chou et al. proposing a system that is capable of performing controlled nanomanufacturing by transferring 25 nm structures [3][6] from a
mold to a substrate. As claimed in these initial publications, NIL was a further development of the compression molding technology used in Compact Disk manufacturing that was used in large scale manufacturing but was not employed in semiconductor fabrication. In this process an imprint mold is fabricated using conventional technologies, such as electron beam lithography and etching techniques. The topography of the mold is then transferred by imprinting into a resist layer that is on the substrate. Subsequent etching steps allow for transferring imprinted patterns from the polymer layer into the substrate. A detailed introduction to state-of-the-art NIL technologies will be given in chapter 2 of this thesis.

Pattern generation in conventional NIL technology is parallel, meaning the final desired pattern is generated in its entirety at the same time, similar to conventional optical lithography. This technique requires a custom-mask carrying the final desired pattern to be fabricated, a time-consuming and expensive task. An alternative paradigm of lithography techniques is scanning lithography, such as scanning optical projection lithography and scanning electron-beam lithography (SEBL), generating the final desired pattern in a serial manner. Serial pattern generation is slower than parallel lithography but it does not require the fabrication of a mask/mold carrying the final desired pattern. In the sub-60-nm region masks/molds are usually fabricated by using SEBL, an extremely complex and expensive lithography method. Therefore substituting SEBL by a cheaper and less complex serial NIL method would significantly simplify mask/mold fabrication in the sub-60-nm region, offer all advantages of NIL over EBL, and even push patterning resolution into the sub-10-nm region. This approach can be thought of analogously to the development of the typewriter after the printing press. While a printing press can replicate large-scale molds (entire pages of books) at high rates, in the typewriter, the smallest mold unit was a single letter. But the typewriter was still of great utility in an office environment. The typewriter sacrificed throughput in return for flexibility and low cost. Similarly, by removing the difficult and slow step of custom-template manufacturing from the process, introducing a nano-typewriter would yield a shift in how for instance rapid prototyping processes and research and development applications might be performed in the future. Chapter 3 of this thesis is dedicated to developing such a nanotypewriter, i.e. concepts of multi-step serial NIL aiming at combining core advantages of NIL with the unique
patterning flexibility of serial nanolithography.

Conventional up-to-date step-and-repeat/flash NIL primarily aims at improving throughput rather than increasing patterning flexibility of NIL and still does not allow the imprint of arbitrary patterns. Only nanoindent lithography is capable of fabricating arbitrary patterns in a single lithographic step, without requiring a custom template to be fabricated. But nanoindent lithography is slow and sacrifices resolution and control to achieve its flexibility. One major difficulty that has to be overcome is that heating or UV-curing of the imprinted polymer as used in conventional thermal NIL (T-NIL) and ultraviolet NIL (SFIL), respectively, cannot be applied in multi-step techniques, especially if the areas of sequential imprint steps overlap. Increasing the temperature above the glass transition temperature of the imprint polymer distorts the previously imprinted features, and crosslinking the resist layer changes its properties permanently making subsequent imprint steps impossible. The invention of room-temperature NIL (RTNIL) that does not depend on heating or curing paves the way for the development of such multi-step techniques. The innovative multi-step NIL concept (Nanotemplate Arbitrary-Imprint Lithography, NAIL) introduced in this thesis is based on RTNIL processes, and thus allows for transferring arbitrary patterns onto a substrate with higher flexibility and resolution than with any existing NIL tool. NAIL performs multiple imprints with general templates rather than a single imprint with a custom template to print out a final desired pattern. This technique represents a fundamental shift in how nanoimprint is performed: it removes the difficult and slow step of custom-template/mask manufacturing (usually requiring electron-beam lithography) from the process. Being the first NIL scheme that combines RTNIL techniques with the multi-step NIL approach, NAIL effectively will bring top-down (lithographic) patterning to length scales currently reachable only with bottom-up (chemical- and self-assembly-based) fabrication methods.

Mold design techniques, NAIL process cycles, and the working principle of a custom-built prototype of a NAIL tool are presented in chapter 3. In order to bring the NAIL scheme down into the sub-15-nm region RTNIL processes offering that patterning resolution had to be established. Therefore a single-step RTNIL method using molds fabricated by molecular beam epitaxy (MBE) was developed (MBE-RTNIL). Mold design
1.2. GOALS AND PROJECT ROADMAP

The PhD research project was carried out following a detailed project plan. It included the following core milestones and goals:

1. exploring and extending state-of-the-art high-resolution nanolithography techniques by introducing innovative nanolithography processes for the sub-15-nm region based on basic nanoimprint lithography schemes, i.e. nanoembossing- and nanotransfer-technology,

2. increasing patterning flexibility of state-of-the-art nanoimprint lithography with special focus on potential commercialization of invented techniques, MBE-RTNIL processes, and a custom-built MBE-RTNIL tool that can be extended into a NAIL tool for the sub-15-nm region are presented in chapter 4 and appendix C.

Using experimental equipment and data initially employed for MBE-RTNIL experiments we introduced an innovative direct nanotransfer scheme (MBE-nTP) based on molds fabricated by MBE capable of directly transferring 1D lateral grating structures with minimum feature sizes in the sub-10-nm region onto silicon substrates. Based on MBE-nTP technology we describe CEO-nTP, an extended direct nanotransfer technique that uses molds fabricated through a combination of MBE and cleaved edge overgrowth (CEO), thus enabling nanotransfer of rectangular line patterns with 2D minimum feature sizes in the sub-10-nm region. All details on MBE-nTP and CEO-nTP are laid out in chapter 5.

Two custom-built prototypes of NIL tools were designed, built, and put into operation: Design drawings for the NAIL tool are to be found in appendix A, the design drawings for the MBE-RTNIL/nTP tool are provided in appendix B.

An innovative version of NIL that we co-developed in collaboration with micro resist technology GmbH (Berlin, Germany) combines UV radiation with thermal treatment of imprint polymers [22] (TUV-NIL) enabling completely isothermic imprint cycles [23][24]. The TUV-NIL technique merges advantages of both, T-NIL polymers (2.3.1) and SFIL resists (2.3.2), and is described in appendix D.

1.2 Goals and project roadmap

The PhD research project was carried out following a detailed project plan. It included the following core milestones and goals:
processes in an academic or industrial research and development environment,

3. developing pattern transfer processes based on anisotropic etching techniques for transferring imprinted features into a substrate material,

4. custom-designing, building, assembling and putting into operation tool prototypes for developing and optimizing the introduced nanoimprint lithography processes,

5. developing analytical imaging and metrology methods allowing for characterizing generated nanopatterns, and

6. testing and analyzing materials, such as imprint polymers, stamp and substrate materials, as well as surface chemicals with respect to their suitability for being employed in innovative nanoimprint processes.

An evaluation of the accomplishments of the project with respect to this roadmap will be given in chapter 6. The outcome of the project is also documented in patents, journal and conference papers, as well as in a book chapter. Corresponding bibliography information on these publications is provided in appendix E.
Chapter 2

Nanoimprint Lithography

2.1 State-of-the-art nanoimprint lithography: technical overview and potential

Nanoimprint lithography is a highly innovative technology based on a quite simple principle that has been well known in the macroscopic world for hundreds of years [25][26]. A combination of conceptual simplicity and innovative potential has often been the fingerprint of groundbreaking technologies. NIL fits into that scheme very well, and both aspects, the basic technological idea as well as the evolving economical and research related potential will be discussed in detail in the following sections.

2.1.1 Nanoimprint lithography - basic technological approach

After the initial publication, a wide spectrum of NIL methods were developed. Most methods can be categorized in one of the following two groups or a combination thereof:

1. *Thermal NIL (T-NIL)*[5]: This lithography method is the initial approach. The imprint polymer is heated above its glass transition temperature. In the following imprint step, the stamp is pressed against the substrate at a given pressure for a specific time. The sample is cooled down below the glass transition temperature of the imprint polymer while the stamp is still in contact, then the mold is removed, and the imprinted pattern remains in the polymer layer.
2. NANOIMPRINT LITHOGRAPHY

2. Ultra violet light-based NIL initially introduced as step-and-flash lithography (SFIL): In contrast to the previous approach, in SFIL no heat is applied to the polymer layer. Instead, polymer crosslinking induced by UV radiation is used during the imprint step to prevent deformation of the imprinted pattern after the mold is removed. The most common approach is to apply the UV-light through the mold, which therefore has to be made out of a UV-transparent material such as quartz or fused silica.

Figure 2.1 illustrates both approaches, each consisting of four steps. (1) one layer of an imprint polymer is deposited on the substrate to be imprinted. When performing T-NIL the polymer is heated up at a temperature above its glass transition temperature $T_g$. No heating of the polymer is necessary for SFIL processes. (2) a stamp comprising the structure of the final desired pattern is pressed into the polymer layer, partly deforming, and partly compressing it. (3) before the stamp is removed the imprint polymer layer is cured by cooling it down or exposing it to UV-radiation. (4) the stamp is then removed and subsequent etching steps allow for transferring the final pattern into the substrate. Note that every imprint cycle yields a residual imprint polymer layer at the bottom of imprinted grooves caused by the compression component of the imprint step. Even with mold features being deeper than the thickness of the respective imprint polymer layer and when pressing with maximum imprint force and duration one does not eliminate polymer compression, and hence the formation of a thin residual layer can not be avoided. Reactive-ion-etching (RIE) or oxygen plasma etching processes - optionally in combination with a metal-evaporation step for lift-off purposes - are commonly performed to transfer the imprinted pattern into the substrate using polymer and metal layers as etch masks.

Numerous variants of this technique exist. A detailed overview of state-of-the-art NIL technology including the latest cutting-edge technological approaches and achievements will be given in 2.6.

2.1.2 Advantages and potential of nanoimprint lithography

NIL is an entirely new approach to lithography as the pattern is generated by mechanical forces and not through chemical changes due to radiation exposure. Because of this fundamentally different working principle, NIL is
Figure 2.1: Working principle of T-NIL (left) and SFIL (right) depicting (from top to bottom): alignment of mold and substrate, imprint step, cool down/UV-curing and mold removal.
not limited by diffraction as lithography based on (UV) light, scanning electron beam or X-ray lithography. Instead, resolution in NIL is influenced by mechanical factors involved in the imprint process (such as surface forces, elasticity and viscosity) allowing NIL to push the resolution limit down into the sub-10-nm region. In 2004 a group at the University of Chicago demonstrated the imprint of the shape of a single-walled carbon nanotube. The authors claim to be capable of reproducing objects of molecular dimensions [32]. The same year, Chou et. al. demonstrated the imprint of 5 nm structures. The mold was generated by cleaving a wafer with pre-deposited GaAs/AlGaAs-layers. These layers can be selectively etched to form the mold pattern. Imprint is performed by using the edge of the cleaved wafer [33]. While these experimental results show that imprint of features smaller than 10 nm is possible, the question of the theoretical limit of resolution arises. For thermal NIL the van der Waals bonds (on the order of 1 nm - 3 nm) are considered to be the limiting factor.

Furthermore NIL provides the following process features:

- No exposure of the device to electron-beam or other damaging radiation. This radiation exposure currently makes it difficult to form patterns on certain technologically relevant substrates, for example organic semiconductors and ultra-thin tunneling junctions. These materials are often object of current research, and thus lithography methods that do not harm them are necessary. A NIL system working analogously to e-beam lithography is highly interesting for the scientific community as no high energy radiation is involved in pattern generation.

- No pattern-density-dependent biasing ("proximity") effect. Materials that show large backscattering effects (substrates consisting of atoms with high Z numbers) are difficult to pattern precisely using electron-beam lithography, but can be readily patterned with nanoimprint.

- No shot noise in the replication of devices (although a certain amount of shot noise is unavoidable in the template if it is generated using quanta such as electrons or photons [34]. Nearly identical devices can thus be reproduced quickly and in large quantities.

NIL technology therefore is a major improvement over electron-beam lithography, and any radiation-based lithography techniques.
2.1. STATE-OF-THE-ART NANOIMPRINT LITHOGRAPHY: TECHNICAL OVERVIEW AND POTENTIAL

2.1.3 Areas of application of nanoimprint lithography

Due to the conceptual simplicity of the process and attractiveness from the economical point of view, NIL is today being adopted by the semiconductor industry for large-scale manufacturing and it was included into the International Technology Roadmap for Semiconductors (ITRS) in the year of 2003. It is considered as a feasible technology to achieve the 18 nm node, and the Massachusetts Institute of Technology's "Technology Review" listed NIL amongst the top 10 emerging technologies regarding their future impact on science worldwide.

Leading industrial companies involved in NIL Technology are for example Obducat (Sweden), Süss MicroTec. (Germany), micro resist technology (Germany), Nanonex (USA), NIL Technology (Denmark), Molecular Imprints Inc. (USA), Intel Corp. (USA), IBM (USA), and Hewlett Packard (USA) to name just a few.

NIL technology contributes significantly to research and development on many areas:

- electronics: hybrid plastic electronics, organic electronics and photonics, nanoelectronic devices in Si and in GaAs;
- photonics: organic lasers, conjugated and nonlinear optical polymer nanostructures, high-resolution organic light-emitting diode (OLED) pixels, diffractive optical elements, broadband polarizers;
- magnetic devices: single-domain magnetic structures, high-density patterned magnetic media and high-capacity disks;
- nanoscale control of polymer crystallization;
- biological applications: manipulating DNA in nanofluidic channels, nanoscale protein patterning, and the effect of imprinted nanostructures on cell cultures.

NIL provides the basis for numerous technological solutions in nanofabrication. However, in order to meet the strict requirements of industrial semiconductor manufacturing with special focus on high-throughput fabrication...
and defect control, NIL processes have to be further optimized. As opposed to contactless radiation-based lithography NIL processes incorporate bringing the mold into physical contact with the imprint resist layer causing a mold wearout effect over time. Thus, mold lifetime and imprint quality have to be optimized by systematically collecting and analyzing experimental data on mold and imprint polymer materials as well as by designing NIL tools capable of efficient mold and substrate handling during imprint steps. The following sections provide technical background information on NIL process development, i.e. on mold fabrication techniques, imprint polymer materials science, and crucial considerations regarding mold-substrate handling during imprint cycles.

2.2 Mold fabrication techniques

NIL molds are made of solid materials comprising high rigidity, stability, and endurance also at high temperatures. Such materials include silicon, dielectric components, e.g. silicon nitride, silicon carbide, or silicon dioxide, metals, p.ex. aluminum or nickel, sapphire, diamond films, and polymeric or oligomeric materials with a high Young’s modulus, for example polydimethylsiloxane (PDMS), fluoropolymers (Teflon AF 2400) [65], or ETFE (Dupont) [66]. Fabricating molds using these materials or a combination thereof and considering their material properties such as for example the thermal expansion coefficient and the Young’s modulus when selecting mold materials for specific nanoimprint applications guarantees that nanoscale stamp patterns with minimum feature sizes in the sub-10-nm region are neither deformed nor damaged during the imprint step. For large area imprinting and soft lithography [67] flexible mold materials may substitute rigid components in order to support global physical contact between the surfaces of mold and imprint polymer layer whereas local elastomeric pattern features must yield a higher Young’s modulus than the imprint resist material that is imprinted into. Both, flexible backplane structures and rigid pattern materials can be employed in one single mold in the rigiflex-mold approach [68] enabling imprint of non-flat substrates with conformal contact distribution over the complete mold-substrate interface area. In order to perform SFIL or T-NIL, transparent, or non-transparent molds respectively have to be fabricated. While there is a broad variety of non-transparent components
2.2. MOLD FABRICATION TECHNIQUES

options are somewhat limited for mold materials that are transparent to UV-radiation: quartz or silica templates are suitable substrate materials for rigid SFIL molds while PDMS can be used for fabricating flexible UV-transparent stamps.

Stamp fabrication itself is based on a standard lithographic process: (1) in a first step a resist is spun onto the surface of a substrate material, (2) in a second step conventional lithographic techniques are applied (UV or X-ray optical lithography, electron beam lithography, holographic interference lithography for large-area whole-wafer exposure, immersion lithography) to expose the resist, (3) in a third step the exposed resist is developed, and (4) a metal evaporation-based liftoff process or direct anisotropic reactive ion etching steps allow for transferring either the negative or the positive resist pattern into the underlying substrate.

Step (2) of this fabrication process can be modified by using unconventional lithographic techniques like p.ex. focused ion beam lithography and atomic force microscopy (AFM)-based nanoindent lithography to carve out the pattern topography of the mold, or NIL itself.

Once a master mold has been fabricated, NIL technology itself can subsequently be applied for fabricating up to 20 replicas from the master mold according to the following procedure: (1) the pattern of the master is transferred into PDMS by replica molding (RM), and (2) a liquid precursor is solidified against the PDMS master [69][70]. This technique constitutes a commonly applied mold fabrication technique capable of reproducing features with lateral extensions from $\sim 30 \text{ nm}$ [70][71] down to minimum feature sizes of $\sim 3 \text{ nm}$ in lateral directions [72] and $\sim 1.5 \text{ nm}$ in terms of vertical deflections [73].

Mold fabrication can also be based on completely unconventional techniques such as for example generation of tightly controlled 3D profiles with nanometer scale features [74], and molecular beam epitaxy followed by selective etching steps. Introduced by Chou in 2004 [75][76] the latter concept is a crucial part of a novel NIL technique that is presented in this thesis, and is therefore explained in detail in 4.1.
2.3 Nanoimprint polymer materials

Imprint resist materials are patterned mechanically by transferring the topography of a mold pattern into the resist layer through embossing processes. Therefore an imprint polymer must be capable of being deformed under a specific pressure while at the same time its mechanical properties should include sufficient strength and stability to maintain the imprinted pattern after mold release. Imprintable materials should further provide good mold-substrate detachment characteristics, i.e. no residual resist material should stick to the mold when lifting it from the substrate. For many NIL applications the resist layer is exclusively used as means to an end for transferring the mold pattern into the underlying substrate that carries the imprint polymer layer. In such cases reactive ion etching (RIE) steps are performed for removing residual polymer layer at the bottom of imprinted features. Usually further etching steps follow, and finally residual imprint polymer has to be stripped off the transferred patterns. Imprint polymers employed in such processes have to provide good anisotropic etching properties in addition to all mechanical properties as explained above.

One can specify the described desired mechanical material properties of an imprint polymer by using the three parameters Young’s modulus, shear modulus, and viscosity. A material suitable as imprint polymer will hold the following interdependencies: (i) The Young’s modulus of the polymer is lower than that of the mold material during the imprint step. This might involve having to heat the imprint polymer above or close to its glass transition temperature $T_g$ before imprinting it. (ii) The minimum pressure that has to be applied to deform the polymer during imprint is higher than the shear modulus of the resist [77]. (iii) The viscosity of the polymer is low enough during imprint to enable completion of the resist deformation within a reasonable period of time which I shall refer to as the imprint time $t_{imprint}$ in this thesis [78]. After mold release the viscosity of the polymer should be high enough to preserve the imprinted pattern in the polymer. Based on this general framework detailed mechanical models and simulations of polymer deformation during imprint processes have been performed [31][79][80][81][82][83][84] thus enabling profound NIL process development accompanied by the design of new polymer materials.

[29] and [31] are excellent up-to-date reviews of the latest findings in
2.3 NANOIMPRINT POLYMER MATERIALS

research and development of nanoimprint materials, and also contain an elaborate collection of respective generic publications. The following three sections summarize and highlight important data provided in these reviews and complement this overview by own contributions in terms of experimental results and respective publications.

2.3.1 Thermoplastic imprint polymers

As described in 2.1.1 polymers employed in T-NIL are heated up to generally ca. 60°C - 90°C above their glass transition temperature \( T_g \) before imprinting. This causes the Young’s modulus (approximately constantly \( \sim 3 \) GPa for most polymers slightly below their specific \( T_g \)) as well as the viscosity of the polymer to drop by several orders of magnitude conveying the polymer in a quasi-liquid state [85]. Before mold release the polymer has to be cooled down to below \( T_g \) to bring Young’s modulus and viscosity back to their initial states. It is obvious that \( T_g \) as well as viscosity are crucial parameters for designing T-NIL processes. Therefore designing imprint polymers for T-NIL purposes first of all means designing imprintable polymers with a certain designated glass transition temperature \( T_g \) and a suitable viscosity. The underlying effects can be understood and utilized as follows: once a polymer is heated up to its specific \( T_g \) molecular motion in the material begins to increase rapidly. Hence all external and internal factors that aggravate molecular motion in the polymer simultaneously also raise its \( T_g \) value whereas all factors that catalyze and stimulate molecular motion lower \( T_g \). Examples for factors counteracting molecular motion are intermolecular forces, intrachain steric hindrance such as branching or crosslinking, and bulky and stiff side groups. These factors are generally found in polymers comprising a high molecular weight \( M_w \). Flexible bonds and side groups however are acting in favor of molecular motion [31] and are mostly existent in polymers with low \( M_w \). \( T_g \) and thus the corresponding T-NIL process temperature are indirectly connected to imprint time \( t_{imprint} \) and imprint pressure \( P_{imprint} \) in a tradeoff effect: lowering the process temperature yields increasing \( t_{imprint} \) and \( P_{imprint} \) in order to obtain high-quality imprint results with imprint polymer filling the mold features with maximum efficiency [30]. The viscosity of a polymer can be lowered by solubilizing it in a solvent preferably its monomer [87]. During the imprint step the solvent evaporates out of the heated polymer layer and passes off through a porous stamp, such
as for example a PDMS stamp [58].

T-NIL compatible imprint polymers are usually spin-coated onto the substrate material yielding excellent control over the thicknesses of spun as well as imprinted layers. This is a core advantage of T-NIL polymers enabling RIE-based pattern transfer processes after the imprint step. On the other side T-NIL processes incorporate high imprint pressures, and may have to cope with thermal expansion effects of imprint polymer layer, substrate and mold that can lead to deformation and destruction of mold and imprint features during imprint steps and mold release, especially when performing large-area T-NIL.

Classical thermoplastic imprint polymers are for example poly(methylmethacrylate) (PMMA) [5], and polystyrene (PS), and poly(benzylmethacrylate) (PBMA) [89], and the thermally curable resist mr-I 9000 developed by micro resist technology GmbH. The functionality of mr-I 9000 is based on free radical polymerization of multifunctional aromatic allyl monomers [90] [91].

2.3.2 UV-curable imprint polymers

The generic polymer designed for SFIL purposes is a liquid solution comprising four different components, i.e.

- a monomer containing a large amount of Si and therefore providing high oxygen RIE etch resistance for subsequent pattern transfer steps,
- a photoinitiator sensitive to UV-radiation,
- a difunctional monomer catalyzing crosslinking of molecular chains upon UV-exposure, and
- a monomer with low molecular weight $M_w$ reducing the viscosity of the polymer solution [7](see also previous section 2.3.1).

The low viscosity of the monomer fluid and its low Young’s modulus render SFIL polymers imprintable at or near room-temperature. This eliminates temperature gradients and hence thermal expansion effects during the imprint process yielding favorable mechanic and volumetric properties during and after imprinting [22]. Further on SFIL polymers enable high-throughput large area patterning by repeatedly printing and transferring the
same mold in a step-and-repeat SFIL cycle \[7\][8][9](2.6.4). Since the polymer formulation does not contain any metal components that could compromise proper functioning of semiconductor devices SFIL plays an important role in nanomanufacturing of integrated-circuits. The extremely low viscosity of UV-curable resists however makes them inapplicable to deposition on the substrate by spin-coating. Instead, SFIL polymers are poured onto the substrate before imprinting thus yielding very low control on the initial thickness of the imprint polymer layer. This may cause an inhomogeneous thickness distribution of residual imprint polymer at the bottom of imprinted features potentially complicating subsequent RIE-based pattern transfer steps.

A typical UV-curable imprint resist material is for example the polymer mr-L 6000 designed by micro resist technology GmbH. This negative photoresist is chemically amplified and contains a multifunctional epoxidized novolak resin as well as a photoacid generator. UV flood exposure cross-links the polymer through cationic polymerization of the epoxy resins activated by the acidic components of the formulation \[91\].

### 2.3.3 Novel materials

Current research and development efforts in industrial (p.ex micro resist technology GmbH, Germany; Molecular Imprints Inc., TX, USA; Nanonex, NJ, USA) as well as academic environments focus on constantly developing novel nanoimprint polymers with optimized NIL properties capable of being applied in innovative NIL schemes \[93\][94][95].

An innovative version of NIL that we co-developed in collaboration with micro resist technology GmbH (Berlin, Germany) combines UV radiation with thermal treatment of imprint polymers \[22\] (TUVNIL) enabling completely isothermic imprint cycles \[23\][24]. The TUVNIL technique merges advantages of both, T-NIL polymers (2.3.1) and SFIL resists (2.3.2), and is described in more detail in appendix D.

We analyzed the new epoxy-based imprint polymer mr-NIL 6000 developed for combined thermal and ultraviolet NIL (TUVNIL) by micro resist technology GmbH. Performing TUV-NIL on this polymer, resulted in imprinted features showing good thermal stability and excellent release properties. We fabricated structures comprising different shapes (e.g. lines, squares and circles) achieving feature sizes of down to 50 nm, with a height of 140 nm and with a residual layer thickness of about 30 nm. Furthermore, dry etching
(i.e. fluorine based RIE) experiments on silicon oxide substrates have been performed in order to test the suitability of the imprint polymers for different process steps and their etch resistance. The etch resistance of the tested imprint polymer was good and allowed for pattern transfer of the imprinted features from the imprint polymer layer into underlying layers.

Recently Guo et al. have investigated three newly developed NIL polymers [31]:

- thermoplastic siloxane copolymers including
  - poly(dimethyl siloxane)-block-polystyrene (PDMS-b-PS),
  - poly(dimethyl siloxane)-graft-poly(methacrylate)-co-poly(isobornyl-acrylate), and
  - poly(dimethyl siloxane)-graft-poly(methylmethacrylate) (PDMS-g-PMMA).
  These polymers show reportedly excellent mold-release properties with simultaneously yielding high-resolution features with high aspect ratios [96].

- a thermally curable PDMS-based liquid polymer that can be thermally crosslinked in an extremely short period of time, i.e. \( \sim 10 \text{ s} \) [97].

- a UV-curable liquid resist based on cationic polymerization of silicone epoxies minimizing defect areas, exhibiting very good dry etching resistance and low shrinkage after curing [66].

Optically and electrically active novel materials have been patterned by NIL leading to applications in photonics, biotechnology, and on the area of nanofluidic channels. 2D photonic-crystals in nonlinear optical polymers [47] and laser devices in conjugated polymers and oligomers could be fabricated by NIL whereas optical properties of the patterned layers were completely preserved [13,16]. Organic solar cells comprising a conjugated-polymer-based electron donor layer [98] and PEDOT-based organic thin-film transistors [40] were also manufactured by using NIL processes. Lab-on-a-chip environments were fabricated by patterning the cyclic olefin copolymer "Topas" by T-NIL [99], and the low-\( k \) dielectric fluoropolymer "CYTOP" can be structured by NIL and used for protein absorption prevention in biotechnological applications [100]. Biodegradable polymers such as for example poly-(L-lactic acid) (PLA) are capable of being imprinted by conventional
2.4. SURFACE FORCES AND MOLD RELEASE

T-NIL and can be applied for fabricating nanochannels and nanoscale hole arrays, DNA and protein analysis chips, and supporting structures in tissue engineering [31][77]. Hydrogen silsequioxane (HSQ) is commonly used as resist for EBL processes but can also be structured by T-NIL near room-temperature [101][102][103] yielding nanoscale fluidic channels that can be functionalized for analyzing biomolecules like DNAs [60][61] and proteins.

As more and more new applications of NIL arise in numerous research areas, development of imprintable materials will remain an highly active area of interdisciplinary research connecting the fields of materials science, chemistry, solid state physics, biotechnology, and nanotechnology.

2.4 Surface forces and mold release

As illustrated in Fig. 2.1 the contact surface between the mold and the imprint polymer is higher than the interface area between the imprint polymer and the substrate. As a consequence, mold release is a non-trivial issue. This circumstance is considered to be a significant limitation of the NIL technology as it limits the aspect ratio of the reproducible patterns [30].

To reduce the effects of adhesion, several approaches have evolved:

- Adhesion promoters can be used to create a stronger bond between the substrate and the imprint resist. This approach, however, involves an additional substance to be coated on the substrate which in turn could complicate subsequent pattern transfer etching processes.

- Adhesion forces between the mold and the imprint polymer can be reduced. This is achieved by coating the mold with adhesion inhibitors. For quartz and silicon molds, it is possible to replace the hydroxyl groups terminating the surface with fluorinated carbon chains, literally creating a Teflon anti-sticking layer [30]. The basic approach is to create a self-assembled monolayer of a fluorosilane anti-sticking component on the surface of the mold. Examples for such release agents are tridecafluoro 1,1,2,2 tetrahydrooctyl trichlorosilane or 1,1,2,2 perfluorodecyl-trichlorosilane. They can be applied to the mold surface by either a solution-phase or a vapor-phase reaction [104][105]. Anti-sticking characteristics of fluorinated trichlorosilane layers can be optimized by additional deposition of monochlorosilanes [106]. Once coated with
such an anti-sticking layer a Si mold can be used hundreds of times before anti-adhesion properties degrade and the release layer has to be renewed [31].

- An internal release agent can be incorporated in the imprint polymer composition.
- If applicable materials with an intrinsically low surface energy should be used for mold fabrication.

### 2.5 Mold-substrate alignment and imprint pressure distribution

A crucial issue in nanoimprint lithography is alignment between mold and imprint polymer layer. The direction of motion of the mold during an imprint step should be in normal direction to the surface plane of the imprint polymer layer whereas the imprint pressure should be distributed homogeniously over the complete mold-polymer interface. If these requirements are not met the mold is driven into the sample at an angle yielding shear forces between the edges of the mold and the polymer layer. Imprint shear forces bear the following severe problems:

- Formation of a residual polymer layer with varying thickness at the bottom of imprinted grooves. Homogenous pattern transfer of imprinted patterns into the substrate is no longer possible because the etching time necessary to remove all residual layer in an anisotropic etching process is not homogenously distributed over the entire imprinted pattern.

- Mold features are generally extremely robust when loaded in a direction normal to their imprint surface plane but rather fragile when pressed in a direction that is parallel to their imprint surface plane. The higher the shear forces the larger the parallel component of the imprint force and the more likely mold features will be damaged or destroyed.

- Small shear forces may not damage the mold. However, in that case the parallel component of the imprint force will either yield uneven polymer deformation or substrate displacement, or a combination thereof.
2.6 STATE-OF-THE-ART NANOIMPRINT LITHOGRAPHY
TECHNIQUES - A SURVEY

Substrate displacement is highly undesirable for multi-step imprint processes, where mold- and substrate positioning accuracy between subsequent imprint steps is the key to successfully imprinting a final desired pattern.

Designing a NIL tool means first of all incorporating mechanisms that guarantee homogenous imprint pressure distribution, and minimize or ideally eliminate shear forces between mold and substrate during the imprint step.

2.6 State-of-the-art nanoimprint lithography techniques - a survey

A variety of different technological approaches has evolved from the basic NIL concept. Selected NIL techniques are described in the following sections. Besides nanoindent lithography and reverse NIL, nanotransfer and microcontact printing both emerging from the field of soft lithography, step-and-repeat SFIL, as well as room-temperature NIL have been chosen because these NIL technologies are closely bound to the innovative NIL schemes described in this thesis later on.

2.6.1 AFM-based nanofabrication - nanoindent lithography

Atomic force microscopy (AFM) tips have an interesting and unique potential as nanomanufacturing tools. They presently serve as one of the most broadly useful tools that can reach across the interface from macro to micro/nano. The scientific community has 20 years of experience in building macroscopic instruments for manipulation of AFM tips, adding functionality to those tips, and extracting signals and information from surfaces and interfaces through interactions with those tips. Functionalized AFM cantilevers and tips can manipulate environments at the sub-micrometer scale on the surface of a substrate, creating high temperatures, high electric and magnetic fields, high fluxes of many types, as well as rapid temporal and spatial variations of all of the above and more. The submicron region near a functionalized tip is a unique, localized, controllable manufacturing environment, wherein new methods for controlled nanofabrication are possible.

In 1999 Mirkin et. al. introduced the dip-pen lithography technique that seizes the conventional ink-jet printer concept by using an AFM-tip
as a "pen", a hard Au substrate as "paper" and molecules with a chemical affinity for the substrate as "ink". The ink is transferred from the AFM tip to the substrate by capillary transport of molecules through a water meniscus thus enabling direct writing of patterns consisting of a small collection of molecules comprising nanometer dimensions [107].

The simplest method of imprinting by using a functionalized AFM tip operated in tapping mode is by moving the entire AFM-cantilever towards the surface of the substrate and force it into contact with the imprint polymer. The bending of the cantilever induced by the actuation creates a force indenting the surface. This technique is called nanoindent lithography and was first introduced by Wendel et. al. in 1994 [108][109]. Once the tip has indented the polymer surface the cantilever can either be moved in lateral direction with the tip remaining in lowered position (dynamic plowing lithography) or the tip can be released from the polymer layer after each indentation and before moving the cantilever to a different position in order to perform the next nanoindentation step (force displacement nanoindentation) [110].

Perhaps the most notable and successful application of nanoindent lithography is the IBM Millipede program [111][112][113]. The goal of this effort at IBM is a topographic data storage technology that uses large arrays of AFM cantilevers to form indentations by heating and to detect those indentations by a thermal method. The present demonstrations include parallel fabrication, detection, and modification of indentations with spacing of 18 nm between tracks and 9 nm within a track, and depth of 1 nm. This work includes many of the features of controlled nanomanufacturing, and is a strong motivation to consider AFM tips as tools for nanomanufacturing in a much broader sense.

The IBM Millipede motivated other research institutions to focus on similar concepts of nanoindent lithography employing different approaches. Microcantilever arrays for nanomanipulation of surfaces are in the middle of focus of the Micro and Nanotechnology Laboratory at the University of Illinois. In several high-impact publications different approaches were demonstrated and evaluated, including passive cantilever arrays [114], thermally actuated arrays [115][116] and arrays with electrostatic actuation [117].
2.6. STATE-OF-THE-ART NANOIMPRINT LITHOGRAPHY
TECHNIQUES - A SURVEY

2.6.2 Replica molding and reverse nanoimprinting

Reverse nanoimprinting is a two step process [118]: (1) the 3D topography of a master mold is filled by means of a polymer film that is spin-coated onto the patterned surface of the mold and subsequently cured, thus forming a complete negative replica of the master mold pattern. (2) establishing physical contact between the replica film and a substrate yields transfer of the replica film onto the substrate if the mold has a lower surface energy than the substrate material. Instead of spinning the imprint polymer onto the substrate before imprint, the polymer is first patterned on the mold and then transferred onto the substrate. Therefore reverse NIL is capable of transferring patterns onto substrates that are prepatterned and/or non-flat, i.e. not suitable for spin-coating thus not allowing application of conventional lithography techniques. Reverse NIL can also be used for fabricating multi-layer 3D polymer structures by performing multiple sequential reverse NIL steps generating a stack of patterned polymer films arrayed on top of each other [118][119]. Such 3D multi-layer structures can for example serve as microfluidic channels in biomedical applications.

Replica molding employs the negative replica obtained from the first step of reverse NIL as mold in a classical NIL process [67]. Performing a positive transfer process of the imprinted pattern into a substrate reproduces another version of the master mold consisting of the substrate material.

2.6.3 Soft lithography - nanotransfer printing and microcontact printing

Nanoscale transfer printing (nTP) and microcontact printing (µCP) evolved from soft nanoimprint lithography (NIL) [67] introducing a modified NIL approach. Instead of pressing a mold into a polymer layer according to classical NIL technology in nTP as well as in µCP a stamp coated with one single transfer material or a combination of multiple transfer materials is pressed against a substrate that has been coated with a self-assembled monolayer (SAM) acting as covalent "glue" and release layer. During separation of stamp and substrate transfer material adheres to the SAM activated surface, and is thus transferred from mold to substrate [120][121][122][123][124][125][126]. While nTP is a purely additive patterning technique, µCP employs the transferred material as an etch mask thus relying on subsequent etching
steps after the transfer process is completed.

A variety of nTP techniques and applications exists. Ensuring large-area optimum physical contact between mold and substrate under ambient conditions and without having to apply pressure, the most common approach employs either a flexible stamp pressed against a rigid substrate or a hard stamp against a flexible substrate. High modulus poly(dimethylsiloxane) (h-PDMS), non-modified PDMS [120] [123] [127], and acryloxy perfluoropolyether (a-PFPE) [128] are widely adopted as flexible components, while GaAs [120] [129] [130] and Si/SiO$_2$ [126] [131] as well as plastic substrates such as poly(ethylene terephthalate) (PET) [120] are examples for rigid mold or substrate materials. Ojima et. al. used the nTP approach applying a hard-on-hard mold-substrate combination for printing gold electrodes having micrometer dimensions [131].

Commonly used transfer materials are for example gold [125] [131], and copper [130]. A broad spectrum of SAM formulations exists: thiol-terminated SAMs are suitable to catalyze transfer of gold [125]. 1,8-octanediithiol is employed as adhesion promoter in copper nTP processes [123] [130]. 3-mercaptopropyltrimethoxysilane (MPTMS) can be used as SAM for transferring gold from a PDMS stamp onto a SiO$_2$ surface that has been activated with hydroxyl groups [120].

nTP processes are part of a wide field of applications and serve as nanofabrication technique for manufacturing electrodes [122] [131], microfluidic channels [123], plastic [120] [122], molecular [132] [133], and organic [126] electronic devices as well as subwavelength photonic elements [120].

2.6.4 Step-and-repeat UV-nanoimprint lithography

Step-and-flash NIL (SFIL) was introduced by Colburn et. al. in 1999 [7]. Initially SFIL was used to create one final desired pattern per SFIL process cycle according to the technique and using the materials described in sections 2.1 2.4 and 2.3.2. It was obvious that by using SFIL multiple, sequential imprint cycles could be carried out in a step-and-repeat SFIL scheme capable of patterning entire wafers. Starting with manually loaded and unloaded 200-nm diameter wafers and up to 20 sequential SFIL steps in 2000 [9] [134] multi-step SFIL tools were further developed and became commercially available soon after [8]. Core challenges that had to be overcome were locally dispensing the UV-curable resist before every SFIL step,
securing homogenous physical contact between mold and substrate during the complete step-and-repeat SFIL cycle, as well as interstep alignment of mask and substrate if printing out multi-layer structures consisting of several layers subsequently imprinted vertically on top of each other. Special x-y-z-stages allowing for adjusting tilt- and rotation errors as well as an automated fluid delivery system allowing for pouring single droplets of UV-resist with a volume less than 5 nl precisely at the designated position under the mold were developed. It could be shown that molds applied in step-and-repeat SFIL processes are self cleaning whereas the anti-sticking surface layers on their surfaces are preserved well over thousands of imprint steps.

Today commercialized versions of SFIL tools capable of performing step-and-repeat SFIL are available from several industrial vendors. For example Molecular Imprints Inc. (USA), EV Group (Austria), Nanonex (USA), Obducat (Sweden), and Suss Microtec (Germany) include state-of-the-art multi-step SFIL systems in their product portfolio. These tools offer a process resolution of down to 20 nm and allow for fully automated patterning of 300 mm wafers with a mold-to-wafer overlay accuracy of ~250 nm. Multi-step SFIL aims at repeating the same final desired pattern over and over again thus enabling high throughput nanofabrication achieved by sequential processing of entire wafers. However, step-and-repeat SFIL still relies on fabricating one custom-designed mold per final desired pattern and does not allow the imprint of arbitrary patterns through multi-step imprinting. We have developed a multi-step NIL technique based on room-temperature NIL instead of SFIL that overcomes that limitation and performs multiple imprints with general templates rather than a single imprint with a custom template to print out a complex final desired pattern. Before we introduce this innovative technology in detail in chapter we will describe the concept and background of room-temperature NIL technology in the following section.

2.6.5 Room-temperature nanoimprint lithography

Room-temperature lithography (RTNIL) technology is the most basic implementation of the classical nanoimprint idea. Similar to conventional T-NIL
an imprint polymer is provided on a substrate. Instead of heating up the polymer to a temperature above its glass-transition temperature before imprinting it, a mold is pressed into the polymer layer at room-temperature. Hence, patterning of the polymer by embossing completely relies on its plastic flow under compressive stress along with free-volume contraction, and plastic deformation. Imprinting a polymer in a RTNIL process undergoes mainly two phases: (1) free volume in the polymer material is compacted, and (2) once the applied imprint stress exceeds the yield stress of the imprint polymer it is further compressed by plastic deformation [10]. Hard substrate materials such as p.ex. silicon/silicon oxide or silicon carbide have a Young’s modulus in the order of $\sim 150 \text{ GPa}$ and comprise a yield stress of $\sim 1 \text{ GPa}$. Young’s modulus and yield stress of most polymer materials are in the range of $\sim 3 \text{ GPa}$, and $\sim 0.05 \text{ GPa}$ respectively. Hence, in order to achieve optimum deformation in RTNIL processes that employ silicon molds imprint pressures between 100 MPa and 800 MPa have to be applied. These imprint pressures are significantly larger than imprint pressures applied in classical T-NIL processes. Therefore highly robust and rigid tool setups are required for performing RTNIL experiments.

RTNIL has two core advantages with respect to classical T-NIL:

- RTNIL can be used to pattern electrically, optically or magnetically active polymer materials that may change or even lose their distinct functionality upon heating in T-NIL processes or exposure to radiation in conventional optical, e-beam, or UV-curing lithography. RTNIL was for example used in conjugated polymer-based photonics [13], and to fabricate oligomer-based organic distributed feedback lasers [11] as well as near-infrared imprinted distributed feedback lasers [12].

- RTNIL allows for patterning the same area or closely neighboring areas of an imprint polymer layer through sequential step-and-repeat NIL cycles. By contrast, heating or UV-curing of the imprinted polymer as used in conventional T-NIL, and step-and-repeat SFIL respectively, does not allow multi-step patterning of areas that are identical, overlap, or are in the immediate vicinity of each other. Increasing the temperature above the glass transition temperature of the imprint polymer distorts the previously imprinted features, and crosslinking the resist layer changes its properties permanently making subsequent imprint
steps impossible. RTNIL overcomes that limitation and therefore offers higher patterning flexibility than any other NIL technique. Up to now this potential of RTNIL has been extremely underemployed. A core part of the work presented in this thesis seizes that potential for introducing a novel multi-step RTNIL scheme capable of imprinting complex near-arbitrary patterns by using a set of simple nanotemplate molds [14]-[16].

We have custom-built a RTNIL prototype tool and produced imprinted patterns with minimum feature sizes of down to 11 nm by performing single-step RTNIL experiments using polystyrene as imprint polymer in combination with molds that we fabricated through a combination of molecular beam epitaxy and selective wet etching techniques [18][19]. This is the highest resolution that has been reported for RTNIL processes to date. We have also patterned the optical active polymer P3HT by RTNIL resulting in minimum imprinted feature sizes significantly smaller than 50 nm [appendix C].
Chapter 3

Nanotemplate Arbitary-Imprint Lithography

3.1 Innovative idea and approach

A variety of different forms of NIL have been demonstrated in the past, but all of these existing techniques focus on pattern replication using one, or at most two, imprint steps. To make arbitrary and complex patterns, these techniques require the pre-fabrication of a custom template using some other form of lithography (typically electron-beam lithography). Our motivation in pursuing multi-step RTNIL is to create a new pattern-generation method, able to create complex and arbitrary patterns without requiring a custom template for each new pattern. In the innovative approach presented in this thesis, the spatial extent of each of the starting templates is only a fraction of the extent of the desired final pattern; i.e. each template is much smaller than the final pattern. Performing multiple aligned sequential imprints at room temperature with such structures would allow one to create complex near-arbitrary structures in a sample using simple nanotemplate structures. We therefore call this technique Nanotemplate Arbitrary-Imprint Lithography (NAIL). RTNIL is the only viable approach to this challenge, because it permits the mold to be removed while the polymer pattern is incomplete, thus no curing of the film is necessary. Finally the imprinted patterns must be transferred from the imprint polymer layer into the underlaying substrate. Therefore an imprint polymer has to be used that is not only capable of being imprinted by room-temperature nanoimprint lithography but also of
selectively being etched with respect to its carrier substrate.

The NAIL technique is illustrated schematically in fig. 3.1. One or more starting nanotemplates are supplied with a positive pattern, e.g., an "I"-shaped die. The extent of each of the starting nanotemplates is only a fraction of the extent of the desired final pattern; i.e. each nanotemplate is smaller than the final pattern and does not provide the final pattern alone. An imprint layer such as a polymer is provided on top of a substrate. Once the nanotemplate is pushed down as indicated by the arrow, the nanotemplate pattern is pressed into the imprint layer causing the layer to deform. After lifting the nanotemplate, the trench will remain, generating an "I"-shaped pattern in the imprint layer. The nanotemplate can then be translated and re-aligned with the substrate to perform a second imprint step.

In case connected features have to be created by two subsequent imprint steps, the second imprint step must overlap with the trench from the first NAIL step. This overlap is necessary because otherwise with each imprint step polymer material would be forced into the trench left empty from the last step (the "ends" of the feature), and not to the sides of the feature. Both trenches then combine to form a single trench with uniform depth. The imprint procedure can be continued to yield, e.g., a long trench or separated features in the imprint polymer layer.

Applying the NAIL procedure using an "I"-shaped die allows parallel but non-crossing lines to be formed on a substrate as shown in fig. 3.1a. One can generate more complicated patterns by using the same "I"-shaped die for subsequent imprint steps but rotate it laterally between these imprint steps as illustrated in fig. 3.1b. A further increase of information transfer onto the imprint layer can be achieved by for example using "+", "L"-, or "T"-shaped dice, and their rotation- and mirror-images. Further possible nanotemplate shapes are given in fig. 3.2.

Since fabricating a custom template is one of the most expensive and time-consuming steps in conventional nanoimprint lithography, and since our approach requires only simple nanotemplates, it will be significantly cheaper than any conventional nanoimprint lithography technique. It has to be pointed out that NAIL also allows for patterning a custom template for massively parallel lithography. One can use NAIL to fabricate custom templates for step-and-repeat fabrication processes where the use of custom
templates speeds up the process of printing out large-area patterns, i.e. conventional step-and-repeat NIL. NAIL can therefore be used as a low-cost and time-saving technique to build arbitrary high-resolution molds for other fabrication processes.

3.2 Opportunity

There are two new key opportunities enabled by NAIL: (1) the creation of a capability to make new kinds of nanodevices, and (2) the creation of a low-cost nanolithography tool that will fill a need in the market.

1. New technologically relevant materials, for example organic semiconductors and ultra-thin tunneling junctions are playing a crucial role for fabricating optical and/or electronic next-generation nano-devices. Hence techniques for patterning these new materials without modifying
Figure 3.2: The above nanotemplate shapes are only a small fraction of all possible and useful shapes that NAIL imprint templates can have. The general rule for which feature shapes are useful for NAIL is as follows: The final desired pattern to be imprinted by one whole NAIL cycle is broken down into "smaller units" as far as possible, i.e., the "smaller units" should be part of the final desired pattern multiple times. All these smaller units are then suitable to be used as imprint nanotemplates for NAIL. The extent of each nanotemplate shape is thus much less than the extent of the final design produced by one NAIL cycle, and each nanotemplate shape is only a portion of the final design. The goal of NAIL is not to use complex pattern forms but nanotemplate forms that are as uncomplicated as possible.

their optical or physical characteristics are of great importance. NAIL technology is capable of patterning surfaces without changing their material properties whatsoever. Besides this high degree of softness, NAIL technology will be capable of patterning surfaces with a higher resolution (sub-10-nm) and arbitrariness than any existing patterning technique can achieve.

2. The recent increase in national research emphasis on nanotechnology has highlighted the need for improved patterning capabilities at the nanometer length-scale. Currently no practical solution exists for the researcher who wishes to get complex sub-10-nm-length-scale designs from conception to a substrate: even cutting-edge state-of-the-art optical projection lithographic techniques like p.ex. immersion lithography [137] and deep-UV lithography [138] cannot print features below \( \sim 20 \) nm, while electron-beam lithography and ion-beam lithography becomes exceedingly difficult at length scales less than \( \sim 20 \) nm [29] [139]. Furthermore, with new-tool costs currently between 5M\$ and 50M\$ and rising fast, even these approaches are becoming uneconomical for the research community as well as for the industry. What is needed
3.2. OPPORTUNITY

is a broadly-available, flexible, low-cost technology that can be easily integrated in a laboratory and used for nanotechnology patterning [8].

Now I will summarize how the NAIL approach addresses each of these opportunities:

1. By enabling device patterning by nanoimprint using only a single step, without requiring the fabrication of a customized template for each device, NAIL would effectively bring top-down (lithographic) patterning to the length scales currently reachable only with bottom-up (chemical- and self-assembly-based) fabrication methods. NAIL would be of particularly high utility to researchers, for whom it would enable more rapid development of nanotechnology. Only nanoindent lithography is capable of fabricating arbitrary patterns in a single lithographic step, without requiring a custom template to be fabricated. But nanoindent lithography is slow and sacrifices resolution and control to achieve its flexibility. Our invention avoids such compromises. A tool performing the NAIL method would be a major improvement over both electron-beam lithography and nanoimprint technology. It would improve on electron-beam lithography by eliminating the proximity effect and by demonstrating near-1-nm feature dimensions [32]. It would improve on nanoimprint lithography by enabling the imprinting of arbitrary features without first requiring the fabrication of a custom template. It would also share the existing advantages of nanoimprint-technology over electron-beam lithography, first of all the lack of exposure of the device to electron-beam or other damaging radiation.

2. Fundamentally nanoimprint as it is currently implemented does not solve the start-to-finish problem of transferring a device design onto a substrate because it still relies on electron-beam lithography to fabricate the template. We have developed a custom-built nanoimprint tool using multiple imprints with general templates rather than a single imprint with a custom template. Since fabricating a custom template is one of the most expensive steps in conventional nanoimprint lithography a NAIL compatible tool will be significantly cheaper than any conventional nanoimprint lithography tool.
3.3 Designing a multi-step nanoimprint tool

A multi-step RTNIL tool capable of imprinting arbitrary patterns has to meet certain criteria to have the potential for success as a scientific instrument:

1. Small minimum feature size: An useful system has to allow the imprint of arbitrary patterns in the sub-150 nm region to have comparable performance to scanning optical lithography tools. In order to compete with electron beam lithography, sub-15-nm features have to be reliably imprintable.

2. Heterogeneity: It has to be possible to create structures of heterogeneous dimensions and orientation. In NAIL maximum heterogeneity is achieved by the dimensions of fabricable structures only being limited by the minimum feature size and shape of the used specific nanotemplate set.

3. Sufficient imprint speed: The imprint of a specific final desired pattern has to be possible at acceptable speed. The writing speed of e-beam lithography for this specific final desired pattern is an acceptable reference.

4. High lateral accuracy and reproducibility: The accuracy of the imprint tool has to be sufficiently high to match the systems minimum feature size. Deviations from the nominal position shall not extend half of the minimum feature size at any point of the imprinted pattern.

5. Minimum damage to fabricated features in subsequent fabricated steps: Because of the serial imprint process, imprinting in close proximity of previously imprinted features shall not distort the previously written features. Pattern pre-distortion to compensate proximity effects has to be employed similar to the "mouse bite"-design in optical mask design.

6. In-situ result verification: The ability to image during imprint steps has to be possible with a NAIL device. This feature creates a unique advantage as the verification of the imprint during the imprint step cannot be achieved with conventional methods.
7. Use of various resists/polymers: A NAIL tool has to offer the possibility to pattern different resists as the tool should be used for various substrates and processes, each involving a different set of resists.

In the following sections I will describe how each of these challenges is addressed in the tool design. An evaluation of the tool performance regarding the above criteria is provided at the end of this chapter in section 3.8.

3.3.1 Design of a NAIL prototype tool: the complete system

A specific apparatus for the control and motion of nanotemplates in carrying out a NAIL process was designed. Figure 3.3 provides a schematic view of the mechanical system. Detailed technical machine drawings can be found in appendix A. Under selected and controllable conditions, this system can enable accuracy in alignment between multiple sequential NAIL imprint steps to about 400 nm and as low as 80 nm.

The NAIL processing system includes a sample holder consisting of a vacuum wafer chuck mounted to linear $x$, $y$, $z$-translation stages, two linear tilt stages and a rotation stage. The stage is driven by computer-controlled stepper motors. A heater is included if heating of the substrate is desired. A conventional vacuum pump is employed to mechanically rigidly support the substrate on the optionally-heated sample holder-chuck arrangement.

The translation stage is a 6-axis stage having a $z$-stage mounted to a bottom sliding plate to move all components on top of the $z$-stage up and down in the $z$-direction, whereas the $x$, $y$, and $z$-directions are defined in fig. 3.3. An $x$-stage is provided to move all components on top of the $x$-stage in $x$-direction, and a $y$-stage is provided to move all stage components that sit on top of it back and forth in $y$-direction. The $x$-stage, $y$-stage, and $z$-stage are moved by computer-controlled motor actuators, such as DC stepper drives. To optimize process resolution, the stepper drives have to be operated with micrometer resolution. Additionally, the $x$-stage and the $y$-stage are fine-tuned by piezoelectric motion controllers that are capable of sub-10-nm resolution. A rotation stage is included for enabling rotation of the imprint layer between steps of a NAIL process around the $z$-axis. Two tilt-stages enable the substrate holder unit to be tilted around the $z$-axis, and the $y$-axis respectively. The rotation stage is exclusively controlled by piezoelectric motion controllers.
Figure 3.3: Design study of our NAIL prototype tool: the system setup mainly consists of three core units: mold holder unit and tool frame, 6-axes wafer stage and wafer chuck, and optical microscope and CCD camera as in-situ feedback loop.

As explained above, a heater can be included for heating the wafer chuck if the selected imprint layer material requires such. If the imprint layer need not be heated, then the heating system need not be included or can be inactivated. The mold holder is a rigid frame that is adapted to support a planar supertemplate to be employed for a NAIL process. A supertemplate consists of a set of nanotemplates or a mold rigidly mounted onto the surface of a substrate such as a transparent planar fused silica plate. The nanotemplate or mold can be glued or otherwise affixed to the fused silica plate.

The NAIL system is disposed on an optical table to minimize vibrations. Because only relative movement between a supertemplate and an imprint polymer layer is necessary, the system maintains fixed the position of the planar supertemplate, and the substrate providing an imprint polymer layer to be processed is moved by the x-, y-, z-stages as well as the rotation and tilt stages. The template features are oriented with the imprint polymer layer to
face each other. Supertemplates used for multi-step RTNIL processes have to be transparent for enabling substrate-mold alignment, and optical in-situ imprint result verification based on the following techniques:

A light source is included to shine through the supertemplate onto the imprint polymer surface, thus enabling observation of optical Newton fringes between the bottom surface of the supertemplate and the top surface of a substrate to be processed. The fringes are used to determine the variation in spacing between the two surfaces. With this information, the surfaces can be aligned to be parallel. To this end, the tilt stages can be used to adjust the tilt of the chuck. As pointed out previously it is of crucial importance that a supertemplate surface and an imprint polymer layer surface are nearly perfectly levelled in order to avoid shear forces during an imprint step, which can reduce alignment accuracy and even destroy a template.

During a NAIL process, the light source is removed so that an optical microscope with a long-working-distance objective can be employed to image imprinted geometric trenches in an imprint polymer layer by focussing through the supertemplate. The microscope is connected to a charged coupled device (CCD) camera and a screen. This configuration enables a feedback loop that enforces a significant degree of alignment. During a NAIL process data from the motion controllers and piezoelectric controllers can be continuously analyzed and processed by a computer that can be programmed to signal movement of the stages according to a prespecified sequence of NAIL imprint steps to be carried out for a given NAIL process.

In order to decrease misalignment, a number of nanotemplate geometries provided on a planar supertemplate are designated as alignment marks that are imprinted into an imprint polymer layer during each imprint step of the NAIL process. After carrying out a complete NAIL cycle and removing the imprinted sample from the system, the position of the imprinted alignment marks can be measured by an SEM and/or AFM. By comparing the actual positions of the impressed marks with their designated calculated positions as laid out by the computer program controlling the stages, constant x- and y-misalignment resulting from non-linearities in the voltage-motion characteristics of the motor actuators and/or piezo actuators can be determined. With this information, when a new NAIL process is to be carried out with a new supertemplate, the piezo/motor actuators can be calibrated to correct any misalignment.
Since particle contamination of substrate and/or supertemplate has to be minimized to guarantee high-quality imprint results the tool is installed in a cleanroom environment.

Figure 3.4 provides a photograph of the complete tool as realized according to the design description above. I will show and explain selected details of the tool in the following sections. The machine drawings for all tool components and the complete tool design can be found in appendix A and [16].

3.3.2 Computer controlled stages

The tool consists of a sample chuck mounted to a linear $x$-, $y$-, $z$-translation stage, two tilt-stages, and one rotation stage. The $x$-, $y$-, $z$-translation stage as well as the tilt-stages were driven by computer-controlled stepper motors ($x$-, $y$-stages: PI Physik Instrumente, Auburn, MA, USA - $z$ stage: Newport Corp., Irvine, CA, USA) each with a minimum linear incremental step size of 50 nm. Movement of the $x$-, $y$-translation stages was additionally
fine-tuned in the sub-10-nm region by two piezo actuators (PI Physik Instrumente). Such a piezo actuator was also used to control the rotation stage. Repeatability, i.e. the capability to drive the stage exactly to a certain designated position multiple times during a multi-step imprint cycle is determined by the positioning accuracy of the used stepper motors which is ≤ 100 nm. Piezo actuators can be used for optional in-situ misalignment corrections after moving the stepper motors to a programmed designated position. The maximum area that can be imprinted on our tool is given by the maximum scan range of the \(x\)-, \(y\)-stages which is a square comprising a sidelength of \(\sim 20\) mm. Figure 3.5 shows how the stages are implemented in the tool setup. The tool was designed to optionally also enable conventional SFIL. Therefore a plexiglas shield is used to block UV-radiation.

### 3.3.3 Optical in-situ result verification: CCD-unit

During multi-step imprint procedures we used an optical microscope with a long-working-distance objective (Carl Zeiss, Germany) to image imprinted structures including alignment marks in the polymer surface by focusing through transparent supertemplates. The microscope was connected to a charged coupled device (CCD) camera and a display. This setup allowed us to ensure that misalignment between imprints was less than 380 nm. In our best results, the alignment accuracy between ten sequential imprint steps was 80 nm. Figure 3.6 shows how the CCD-unit is integrated into the tool setup, and fig. 3.8 provides details on how the long-working-distance objective is positioned with respect to a transparent supertemplate during multi-step imprint cycles.

### 3.3.4 Mold fabrication process and mold holder unit

**Single-step RTNIL and two-step RTNIL molds**

First aiming at establishing a single-step and two-step RTNIL process we fabricated two types of molds:

1. silicon molds with a 400-nm-period grating structure etched to a depth of 40 nm into the silicon (fig. 3.7b), and
2. silicon molds with a 400-nm-period grating structure etched to a depth of 125 nm into the silicon (fig. 3.7c).
Figure 3.5: (top) NAIL system setup also capable of UV-curing NIL: (1) mask holder unit with removable UV-light guide top, (2) slide carrying the wafer stage, (3) six-axes wafer stage, (4) movable microscope for alignment, (5) liquid UV-light guide, and (6) plexiglas shield blocking UV-radiation. (bottom) Detailed picture of the 6-axes wafer stage: (3a) wafer chuck, (3b) piezo motion controller, (3c) motor actuators, and (6a) removable front plate enabling optimum stage handling. The stage has no heated wafer chuck since we are focusing on RTNIL. The z-stage as well as the $x$, $y$-stages are computer controlled.
Figure 3.6: NAIL system setup also capable of UV-curing NIL: view of the complete system including (7) a CCD-camera connected to a screen, and (8) the UV-radiation source.

Both types of molds were fabricated using a combination of interference lithography and reactive ion etching (RIE). A tri-layer resist process [140] was used to minimize surface reflections. The tri-layer resist consisted of 200 nm Sumitomo PFI-88 positive photoresist/40 nm evaporated SiO$_2$/400 nm AZ Clariant BARLi-0.25 anti-reflective coating (ARC). After exposure and wet development, three RIE steps were used to transfer the resist pattern into the silicon substrate: first CF$_4$-RIE was used to transfer the pattern into the silica interlayer, next O$_2$-RIE was used to etch the ARC and finally CF$_4$-RIE was used to etch the silicon substrate. Remaining organic residues were removed by a 15-minute immersion in H$_2$O:H$_2$O$_2$:NH$_4$OH solution in ratio 5:1:1 at 80°C. To avoid adhesion of the imprinted polymer to the mold, the surface was fluorinated by vapor deposition of tridecafluoro 1,1,2,2 tetrahydrooctyl trichlorosilane [105] (CF$_3$-(CF$_2$)$_5$-CH$_2$-CH$_2$-SiCl$_3$ from Gelest, Inc.).

Before imprint each silicon mold was glued onto a fused silica plate which then was in turn mounted in a Newport kinematic optical mount that was
affixed to a rigid frame. While a silica plate is transparent for visible light, a silicon mold is not. Hence mold and fused silica plate form a non-transparent supertemplate. Gluing a silicon mold onto a fused silica plate was done according to the following procedure: (1) a glue layer was manually applied to the backside of the silicon mold, (2) the silicon mold was then put upside down on a sample substrate placed on the stage so that the glue layer was facing towards the optical mount, (3) a fused silica plate was mounted in the optical mount, (4) the z-stage was driven upwards so that the glue layer was pressed against the fused silica plate, (5) after the glue was hardened in that position we moved the z-stage downwards separating mold and sample substrate. This procedure enables optimum alignment accuracy between mold and imprint substrate since the glue can still be deformed when the mold is pressed against the fused silica plate in step (4). The glue layer therefore acts as self-adjusting layer leveling out the surface planes of mold, fused silica plate, and stage. Figure 3.7a schematically shows the described supertemplate fabrication scheme. Figure 3.7b and fig. 3.7c show SEM images of the two types of silicon molds that we fabricated and used for single-step RTNIL and two-step RTNIL processes.

Multi-step RTNIL molds

As pointed out previously for alignment and template protection purposes supertemplates capable of being used for carrying out multi-step RTNIL processes need to be completely transparent. Therefore etching mold patterns into silicon and gluing these silicon molds onto a fused silica plate as done for one-step and two-step RTNIL experiments is not applicable for multi-step RTNIL cycles. Instead we etched the nanotemplate patterns directly into the surface of fused silica plates yielding completely transparent supertemplates. Such a supertemplate was then directly mounted in the optical mount of the NAIL tool. Pattern design schemes and experimental fabrication details of specific transparent supertemplates will be given in section 3.6.2.

Simplified NAIL tool and mold holder unit

Figure 3.8a shows a simplified version of the NAIL prototype tool without rotation-, and tilt-stages. Fig. 3.8b and Fig. 3.8c provide more details of the mold holder unit. The core component of the mold holder unit is a New-
Figure 3.7: SuperTemplates consisting of a silicon mold glued onto a transparent fused silica plate were used for one-step RTNIL and two-step RTNIL experiments. (a) Mold features were first etched into a silicon wafer which we then cleaved and glued onto the surface of a transparent fused silica plate. Silicon mold and fused silica plate form a superTemplate. While the silicon mold is non-transparent for visible light, the surrounding surface area of the fused silica plate is, and thus can be used for optical leveling of superTemplate and imprint polymer layer. (b) SEM image of a silicon mold with a 400-nm-period grating structure etched to a depth of 40 nm into the silicon, and (c) SEM image of a silicon mold with a 400-nm-period grating structure etched to a depth of 125 nm into the silicon.

A superTemplate was rigidly mounted in this kinematic mount before imprint. Especially when performing multi-step RTNIL processes using transparent superTemplates it was crucial in our setup to ensure that the surfaces of superTemplate and substrate were nearly perfectly levelled in order to avoid shear forces during imprint which otherwise reduced alignment accuracy and could even lead to significant superTemplate and substrate damage. We approached this issue by using a narrow-band green light source to shine through the superTemplate onto the substrate in order to observe optical fringes between the bottom surface of the superTemplate and the top surface of the substrate. The fringes were used to determine the variation in spacing between the two surfaces. Once the number of fringes approaches one, superTemplate and substrate are in parallel to within 150 nm error across the superTemplate-substrate interface. These surfaces were aligned to be parallel by adjusting the tilt of the mold using the set screws of the kinematic optical mount to reduce the number of optical fringes before bringing
Figure 3.8: (a) photograph of a simplified version of the designed NAIL prototype tool without tilt- and rotation-stages. We used exclusively the setscrews of the mold holder unit to manually level out the supertemplate with respect to the surface of the substrate. The design of the proof-of-concept NAIL experiment described in section 3.6 that we carried out on this tool required only linear movement of the stage between subsequent imprint steps, the rotation stage could be removed. The picture shows (1) rails, (2) slide, (3) z-stage, (4) x-stage, (5) y-stage, (6) y-stage stepper motor, (7) x-stage piezo actuator, (8) mold holder unit, and (9) the optical microscope with a long-working-distance objective. (b) detailed picture of the mold holder unit (8) consisting of (10) screw clamps for pre-adjusting the kinematic optical mount assembly, (11) set screws for leveling out the kinematic optical mount, and (12) the long-working distance objective in multi-step imprint position. (c) Close-up photograph of the kinematic optical mount showing a transparent planar supertemplate (13) held in the rigid steal frame (14) of the optical mount.

the two surfaces into hard contact.

3.4 Single-step room-temperature nanoimprint lithography

As a first step towards performing multi-step RTNIL cycles we investigated patterns formed in a single imprint step. One single-step RTNIL experiment consisted of the following elements: (1) spinning an imprint polymer onto a
3.4. SINGLE-STEP ROOM-TEMPERATURE NANOIMPRINT LITHOGRAPHY

silicon wafer and baking it, (2) pressing a mold against the imprint polymer layer and imprinting it, and (3) releasing the mold from the imprint polymer layer and imaging the imprinted patterns. The main purpose of these experiments was to determine and optimize the RTNIL parameters, including imprint pressure and maximum imprint depth, when polystyrene (PS) with an average molecular weight of 97 kg/mol was used as the imprint polymer (purchased from H.W. Sands Corp.).

The maximum imprint depth depended on the depth of the mold features, the imprint pressure, the imprint duration, i.e. the period of time that the mold was in physical contact with the imprint polymer layer, as well as on the overall surface area of the imprinted pattern. In order to analyze this dependency and to determine the maximum imprint depths for different depths of corresponding mold features, each single-step RTNIL experiment was performed twice using nominally identical imprint polymer layers. First a silicon mold with a 400-nm-period grating structure etched to a depth of 40 nm into the silicon was used to imprint the first imprint polymer layer. Then a mold with a 400-nm-period grating structure etched to a depth of 125 nm into silicon was used to imprint the second imprint polymer layer.

The imprint polymer layer that we imprinted into consisted of polystyrene that was first dissolved in toluene to a concentration of 5% by weight. We then spin-coated the PS/Toluene solution onto a silicon wafer at 2500 rpm and baked it at 120°C for 2 minutes resulting in a 330-nm-thick PS layer.

We used the simplified tool as shown in fig. 3.8 to perform one imprint step at room-temperature under atmospheric conditions by applying an imprint pressure of ~30 MPa. This imprint pressure was achieved by driving the z-stage into the mold surface and tightening the set-screws on the optical mount. We used a strain gauge sensor mounted between stage and optical mount to measure the force with which the stage was pressed against the optical mount during an imprint step. We then calculated the imprint pressure using the known imprint area. Both types of molds were released from the imprint polymer layer after 10 s as this imprint duration proved to be the minimum period of time after which the maximum imprint depth could be achieved for both cases: the maximum imprint depth was 100 nm for the 125-nm-deep mold, and 30 nm for the 40-nm-deep mold. The imprint results presented in fig. 3.9 show good sidewall and surface characteristics.
Figure 3.9: (a) Scanning electron micrograph (SEM) image of the imprinted grating structure in PS after single-step RTNIL showing 100-nm-deep grooves. The grooves of the corresponding mold were 125 nm deep. (b) SEM image of structures imprinted into PS using a 40-nm-deep grating. The imprinted grooves are 30 nm deep. Insets show a magnified view of the same grating structures. The scale bars in the insets represent 200 nm.

3.5 Two-step room-temperature nanoimprint lithography

As a second step towards enabling multi-step RTNIL cycles we used the same molds to perform two-step RTNIL cycles. We conducted two subsequent imprint steps onto the same area of the same imprint polymer layer with the same mold. We rotated the mold by 90° between the two imprint steps. Analogously to the described single-step RTNIL experiments, we conducted each two-step RTNIL experiment twice using nominally identical imprint polymer layers for each experiment as well as two types of molds comprising different feature depths. Figure 3.10 shows the results that we obtained from using the same molds, materials, and imprint parameters as were used in the one-step RTNIL results shown in fig. 3.9. During the first imprint step the grating lines on the mold pointed in horizontal direction. The two-step RTNIL results for the mold with deeper grooves show that features that were imprinted during the first imprint step were symmetrically deformed during the second imprint step: imprint polymer was partly pressed into grooves that were imprinted during the first imprint step, forming the eye-shaped structures shown in fig. 3.10a. This deformation could be significantly reduced by using a mold with less deep features as shown in fig. 3.10b. When a 40-nm-deep template was used instead of a 125-nm-deep template, the structure of the imprinted features after the second imprint
3.6 Establishing NAIL: multi-step room-temperature nanoimprint lithography

Since a NAIL tool is first of all to be seen as a nano-typewriter a proof-of-concept experiment for the NAIL technique should primarily demonstrate the nano-typewriting capabilities of our NAIL prototype.

**Figure 3.10:** (a) SEM image showing the result of two-step RTNIL with 100-nm-deep gratings. In the second imprint, the gratings were along the vertical direction. Inset shows polymer deformation/spread caused by the second imprint creating the curved edges. (b) SEM image showing the result of two-step RTNIL with 30-nm-deep grooves. With the shallower grating structure the polymer deformation caused by the second imprint was less obvious. The scale bars in the insets represent a length of 200 nm. (c)-(e) SEM images showing three phases of the evolution of the polymer deformation during the second imprint step: (c) initial state of imprinted line features after completing the first RTNIL imprint step. (d) the same line features after being deformed by an incomplete second imprint step with the grating lines of the mold being perpendicular with respect to the line features imprinted in the first imprint step, and (e) the same line features further deformed after continuing the second imprint step. Stressing out of polymer material at the edges of imprinted lines into imprinted grooves forming the eye-shaped structures as shown in (a) and (b) can be observed.

step became more rectangular. Figures 3.10c-e illustrate the evolution of the polymer deformation leading to the eye-shaped deformation.
Macroscopically speaking, each text to be printed out on a typewriter requires a set of letters, most likely the complete alphabet, to be employed in the printhead of the typewriter. In order to print out a line of words, and eventually a complete page each letter has to be typed at a special designated position on the paper. In order to fill a whole page paper and printhead have to be displaced with respect to each other in both lateral directions of the paper plane. In order to fill only a single line this displacement can be reduced to one lateral direction. Additionally, cutting down the line to a single word significantly narrows down the variety of different letters that one needs to type this word. Aiming at using a very basic set of simple nanotemplates and first analyzing and optimizing alignment accuracy of supertemplate and substrate in one single lateral direction, the nanoscopic NAIL experiment we designed can be compared to the macroscopic task of printing out one single word.

Besides having to fabricate an appropriate set of nanotemplates and to optimize all parameters of conventional single-step NIL, designing a NAIL process creates an additional challenge: continuously monitoring and adjusting alignment of mold and substrate during the multi-step RTNIL cycle is of crucial importance for successfully imprinting a complex pattern in a controlled manner. As laid out in the above paragraph the designed NAIL experiment requires relative movement of supertemplate and substrate in between subsequent imprint steps in only one lateral direction in order to print out the final desired pattern. However misalignment in both lateral directions is possible and has to be continuously monitored and readjusted if necessary. The design of a specific supertemplate that comprises an appropriate set of nanotemplates capable of imprinting a specific complex final desired pattern in a way that meets the above process simplification criteria, the design of such a pattern, and the process flow design of the complete corresponding NAIL experiment will be given in the following section.

3.6.1 Design of NAIL experiment

In this section, we will describe a multi-step RTNIL process for imprinting a complex pattern (in this case, the MIT logo, see fig. 3.14a and fig. 3.11a) by sequentially imprinting a set of custom-designed nanotemplates. We fabricated a completely transparent supertemplate consisting of a variety of rectangular shaped nanotemplates, arrayed across the surface of a
3.6. ESTABLISHING NAIL: MULTI-STEP ROOM-TEMPERATURE NANOIMPRINT LITHOGRAPHY

Figure 3.11: NAIL is a technology that prints out a complex pattern using nanotemplates comprising simple shapes. We chose the MIT-logo as the complex final desired pattern to be printed out in the designed proof-of-concept NAIL experiment by using a set of 7 rectangularly shaped nanotemplates. (a) graphical representation of the official MIT logo (left). The logo consists of 7 rectangles constituting the set of nanotemplates required to print out the logo in subsequent imprint steps (right). (b) design of the multi-step RTNIL process flow: numbers and color code indicate the order in which parts of the final pattern will be imprinted. We merged 4 of the 7 nanotemplates to form two pairs of nanotemplates highlighted in brown color, and violet color respectively. Hence, 5 subsequent imprint steps are necessary to print out the complete final desired pattern.

fused silica template in a pattern designed specifically for imprinting the logo, such that a total of five imprint steps were required (fig. 3.12). The detailed supertemplate fabrication process is described in section 3.6.2. The order in which the imprints were made to create the final result is shown in Fig. 3.11b. Structures on the mold consisted of the six rectangles and one square that make up the pattern and several alignment control marks; with the elements of each imprint step vertically displaced from the other by a distance of 2.5 μm.

To form one complete pattern, we needed to translate the sample along the y-axis by a step-size $D$ of 2.5 μm in between the five imprint steps. Figure 3.12a schematically shows the process flow: At a time $t_0$ the first
imprint is made by pressing the super-template into the polymer layer in $z$-direction. The super-template is released and translated by the step-size $D$ along the $y$-axis before imprinted again at $t_1$. The MIT logo evolves step by step in $x$-direction. Hence movement of the super-template along the $y$-axis is transformed into a nanotyping NAIL scheme carried out in $x$-direction, similar to macroscopic typewriter performance. This scheme is continued until one complete logo is imprinted at $t_4$. One can of course continue the NAIL scheme after the fifth imprint step, yielding one more completed MIT logo per additional imprint step.

Note that two pairs of parallel alignment marks are generated for each pair of subsequent imprint steps A and B during the NAIL cycle: one pair points in $y$-direction, the other pair is aligned in $x$-direction, and each pair consists of one feature generated in step A and one feature generated in step B. Using such pairs of alignment marks linear $x$-, $y$-misalignment between two steps A and B can be measured and readjusted for all imprint steps according to the following mechanism: After completion of the NAIL cycle and removing the imprinted sample from the system misalignment in $y$-direction for each imprint step with respect to the previous and following imprint steps can be determined by measuring the actual spacing between the alignment marks of the pairs that are aligned in $x$-direction and comparing this measurement with the set-value calculated from the mold design and its defined step-size $D$. Analogously, misalignment in $x$-direction can be determined by measuring the spacing between imprinted alignment marks of the pairs aligned in $y$-direction. Alignment marks are shown on the right side of the blue dash-dotted line in fig. 3.12. This misalignment detection mechanism can be used to calibrate the NAIL process for tool-dependent linear misalignment effects. Significant non-linear misalignment effects can be detected by in-situ result verification of multi-step imprint results focusing the optical microscope through the transparent super-template during a NAIL cycle.

3.6.2 Supertemplate fabrication process

The transparent super-template was fabricated using 30 keV electron-beam lithography to define the rectangular nanotemplate structures in 950 kg/mol polymethyl-methacrylate (PMMA) spun to a thickness of 150 nm onto a 3.81-cm-diameter fused silica parallel window from CVI Laser (PW1-1525-
Figure 3.12: (a) Flow chart of the 5-step NAIL cycle showing schematic top view snap-shots of the imprinted pattern after each imprint step. For each snap-shot the part of the imprinted pattern that is generated in the respective imprint step in z-direction is highlighted in black while the part of the pattern that has been imprinted in all previous imprint steps is highlighted in white. (caption contd. on next page)
UV). A thin layer of conductive film (Mitsubishi Aquasave) was spin-coated onto PMMA to prevent charging during electron-beam lithography. The sample was developed in 3:1 isopropyl alcohol:methyl iso-butyl ketone for 60s. Then 40 nm of chrome was deposited onto the sample using electron-beam evaporation and patterned by using liftoff. With chrome as the etch mask, the nanotemplate structures were etched into the substrate to a depth of 270 nm by CF$_4$-RIE. Figure 3.13a schematically illustrates the overall design of a transparent supertemplate. Figures 3.13b-d show SEM images of master nanotemplate structures on a transparent supertemplate that we fabricated for printing the MIT logo in three different sizes following the experimental scheme described in section 3.6.1.

### 3.6.3 Performing the NAIL experiment

The transparent supertemplate was loaded into the mold holder unit in such a way that the $y$-direction of the mold design (fig. 3.12) and the direction of motion of the $y$-stage were aligned. This alignment was done visually by using a microscope with a long working distance objective. A slight misalignment of the $y$-axes of mold and $y$-stage would cause a constant $x$-misalignment of imprinted features during NAIL cycles, and can not be detected and eliminated by exclusively using an optical microscope. However, since being a linear misalignment effect, this misalignment could be analyzed and minimized by using the previously described tool calibration process based on post-imprint analysis of imprinted misalignment marks (section 3.6.1). Calibration was done by performing the following procedure: (1) a silicon wafer spin-coated with 330 nm of PS was used as imprint sample, and was loaded onto our tool, held in place by concentric vacuum rings on the chuck. The surfaces of supertemplate and substrate were levelled using the

"caption of fig. 3.12 contd.: The supertemplate is moved in positive $y$-direction between imprint steps. By carrying out this NAIL cycle the MIT-logo evolves on the left side of the blue dash-dotted line in positive $x$-direction as indicated by the arrows. The imprint procedure also generates additional alignment features evolving on the right side of the blue dash-dotted line. (b) schematic snapshot of the final imprinted pattern after the 5th imprint step (compare red-dashed rectangle in (a, top)): The MIT-logo has been imprinted exactly following the experimental design of the NAIL proof-of-concept experiment as laid out in fig. 3.11. Alignment marks and redundant features are blanked out. (c) design of the transparent supertemplate comprising the complete set of nanotemplates necessary to carry out the experiment. Nanotemplate features are highlighted in black (compare red-dashed rectangle in (a, bottom)) and are directly etched into the surface of a planar fused silica plate. They therefore have a fixed position with respect to each other."
3.6. ESTABLISHING NAIL: MULTI-STEP ROOM-TEMPERATURE NANOIMPRINT LITHOGRAPHY

Figure 3.13: Supertemplates capable of performing NAIL processes have to be completely transparent for visible light in order to enable alignment and levelling procedures. Therefore the nanotemplate structures are directly etched into the surface of a transparent fused silica plate which then constitutes a NAIL supertemplate. (a) schematic drawing of a NAIL compatible supertemplate, and fabricated nanotemplate structures in three different sizes. (b) features comprise a linewidth of 150 nm, (c) 200 nm, and (d) 300 nm.

Previously described optical levelling procedure (section 3.3.4), (2) y-stage and z-stage were programmed to carry out a NAIL cycle that consisted of 10 subsequent imprint steps carried out by the z-stage while the x-stage was locked, with each imprint step followed by a translation step carried out by the y-stage while the mold was released from the substrate and the z-stage was locked. Imprints were performed by driving the z-stage to a stop into the mold. As the total area that was imprinted into PS was small ($\sim (3.5 \text{ mm})^2$), the force applied by driving the z-stage into the mold was sufficient to imprint the rectangular structures without having to manually tighten the set screws on the optical mount as described in section 3.4 and 3.5. Translation steps were done by moving the y-stage by the step-size $D = 2.5 \mu m$. (3) after finishing the calibration NAIL cycle the imprinted sample was re-
moved from the system, and (4) imprinted alignment marks were imaged under an SEM and AFM. (5) an average value for the \( x \)-misalignment was determined. Constant \( y \)-misalignment was also detected by measuring the displacement between the respective imprinted horizontal alignment marks, especially after putting new \( y \)-stepper motors into operation: programmed set-step-size \( D \) and the actually carried out step-size showed a constant mismatch and had to be recalibrated. (6) using the averaged constant values for \( x \)-misalignment and \( y \)-misalignment the NAIL program code was finally adjusted for both misalignment effects. The calibrated tool could now be loaded with a new imprint sample and NAIL cycles yielding minimum misalignment could be performed.

Using a calibrated tool NAIL cycles consisting of a total of ten subsequent imprint steps were performed that resulted in six completed MIT logos. Figures 3.14b-d show the imprinted result of MIT logos of different sizes. Several neighboring patterns generated in different imprint steps are distorted. In contrast, isolated features (which were not in the proximity of subsequently imprinted features) did not show evidence of distortion. In our best results, the alignment accuracy in \( y \)-direction between ten sequential imprint steps was 80 nm. More typically, alignment to \( \pm 400 \) nm was readily achievable. Misalignment in \( x \)-direction could be limited to 50 nm or less.

### 3.7 Pattern transfer into the silicon substrate

The multi-step room-temperature nanoimprint lithography procedure was completed by transferring the imprinted patterns from the PS layer into the silicon substrate. At the start of this step the wafer had a 5-nm-thick residual PdAu layer, used to alleviate charging during SEM imaging. First we performed a combined CF\(_4\)- and O\(_2\)-RIE for 4 min to etch down the PS layer everywhere until all residual PS was removed from the bottom areas of the imprinted grooves (figures 3.15a/b). In order to prevent the imprint polymer from heating up and losing its imprinted shape during the RIE process, we split this etching step into two subsequent 2-min-long etching steps that also removed the \( \sim 5 \) nm thick PdAu coating. The multi-step room-temperature process is a volume preserving patterning process, thus causing imprint polymer material to be pushed away from mold features and forming raised deformations at the edges of imprinted features with an
3.7. PATTERN TRANSFER INTO THE SILICON SUBSTRATE

Figure 3.14: Results of a 5-step RTNIL imprint cycle for different mold dimensions: (a) graphical representation of desired final pattern to be printed out. The numbers indicate the order in which parts of the final pattern were imprinted. After the 5th imprint step the pattern was complete. We performed several 5-step RT-NIL cycles using molds with different feature sizes: The linewidth of the imprinted pattern in (b) is 300 nm, the linewidth in (c) is 200 nm, and in (d) is 150 nm. The observed vertical and horizontal misalignment was between 80 nm and 380 nm.

average height of 40 nm. These deformations must not be transferred into the silicon. Therefore we stopped the CF$_4$-RIE before the remaining PS layer in the non-imprinted region had cleared after three subsequent 2-min-long steps (figures 3.15b/c). The etch rate of the CF$_4$/O$_2$-RIE for PS was $\sim$ 40 nm/min and the etch rate of CF$_4$ for silicon was $\sim$ 25 nm/min. We could etch the transfer pattern $\sim$ 100 nm into the silicon layer. Finally the deformed residual PS patterns were stripped off in an O$_2$ plasma asher for 5 min (figures 3.15c/d).

Figures 3.16a-c show experimental results for the described pattern transfer process for the exact same structures as shown in figures 3.14b-d. All PS material had been stripped off, so the images show silicon surfaces. Figure 3.16 shows that local surface roughness of the PS layer and deformations at the edges of imprinted PS features were eliminated throughout the RIE steps.
**Figure 3.15:** Pattern transfer process: in a first step (a) the imprinted and coated sample is treated with a combined CF$_4$- and O$_2$-RIE removing the coating layer as well as residual PS from the bottom of imprinted grooves. Note that the polymer material has deformations close to the edges of imprinted grooves where polymer was pushed to the side during imprint (figures 3.14b-d). In a second step (b) CF$_4$-RIE was used to etch the imprinted pattern into the silicon substrate. In a third step (c) these residual deformed PS structures were stripped off by means of an O$_2$ plasma asher completing the transfer of the imprinted pattern from the PS layer into the silicon substrate (d).
3.8 Performance evaluation of the NAIL prototype tool and next steps

Guidelines for designing a multi-step RTNIL tool were given in section 3.3. I will now evaluate the performance of the implemented NAIL prototype tool based on this framework and discuss next steps towards further developing the invented NAIL technique.

1. Small minimum feature size: The demonstrated minimum feature size accomplished by the NAIL technique was 150 nm. This is the upper resolution limit for getting in direct competition with conventional scanning optical lithography. The resolution of NAIL has to be further improved to be able to compete against electron beam lithography.

Figure 3.16: SEM and AFM images of etched patterns shown in figures 3.14-(a)-(d): SEM images of (a) a 300-nm-linewidth pattern after being transferred into the silicon substrate, (b) a transferred 200-nm-linewidth pattern, and (c) a 150-nm-linewidth pattern. (d)-(f) are AFM images of the exact same features as shown in (a)-(c). PS was completely removed by means of an O₂ plasma ash. Throughout the pattern-transfer-etching process, features were partly merging because the corresponding imprinted PS features were deformed during the multi-step room-temperature nanoimprint process and therefore not perfectly separated from each other before the pattern transfer. SEM images were taken at a slight angle revealing the sidewalls of transferred trenches.
2. Heterogenity: rectangular structures of heterogenous dimensions and orientation have been generated in the demonstrated NAIL process. A set of very simple nanotemplates was used to imprint a complex final desired pattern.

3. Sufficient imprint speed: The complete final desired pattern was generated in $\sim 1 \text{ min}$. The imprinted area is $\sim (3.5 \text{ mm})^2$. Once a set of nanotemplates is available NAIL already at this stage is a significantly faster patterning technique than electron-beam lithography. Since NAIL does not require the fabrication of a custom-mask for every new final desired pattern that can be composed of an existing nanotemplate set it is also much faster and cheaper than optical lithography. However, once NAIL is brought down into the sub-15-nm region the comparison with EBL will have to be reevaluated since with decreasing NAIL step-size alignment and stitching errors become more and more dominant.

4. High lateral accuracy and reproducibility: In our best results y-misalignment was $\sim 80 \text{ nm}$, and $x$-misalignment was $\leq 50 \text{ nm}$ in 10-step imprint cycles. Hence, even for the minimum feature size (150 nm) of imprinted NAIL patterns the deviations from the nominal position are in the order of half of the minimum feature size at any point of the imprinted pattern. When decreasing the minimum feature size down to the sub-15-nm region meeting this requirement will afford new approaches to nanotemplate movement and positioning [16].

5. Minimum damage to fabricated features in subsequent fabricated steps: We observed distortion of neighboring patterns generated in different imprint steps. In contrast, isolated features (which were not in the proximity of subsequently imprinted features) did not show evidence of distortion. The distortion effect has to be further analyzed. Theoretical simulations of material deformation in RTNIL processes combined with NAIL experiments using different imprint polymers will be first steps in that direction.

6. In-situ result verification: An optical microscope with a long-working distance objective and a CCD camera proved to be a reliable in-situ instrumentation for monitoring imprint results with a resolution of down
3.8. PERFORMANCE EVALUATION OF THE NAIL PROTOTYPE TOOL AND NEXT STEPS

to 150 nm. Alignment as well as pattern quality could be controlled during the NAIL cycle. Because of limitations of optical microscopy this mechanism will not work for NAIL processes in the sub-100-nm region. An AFM-based advanced prototype [16] could provide in-situ pattern verification capabilities in the sub-10-nm region.

7. Use of various resists/polymer: Polystyrene proved to be a polymer very well suited for being employed in RTNIL processes. We performed experiments with polystyrene samples comprising molecular weights from 13 kg/mol - 97 kg/mol as well as with the optically active polymer P3HT. Collecting empirical data on deformation and distortion characteristics of these polymers will be an important prerequisite for understanding and minimizing the pattern distortion effect that we observed in the demonstrated NAIL experiment.

The NAIL prototype tool that we built operates in good agreement with all design requirements that we complied with in the first place. Before this technique can be used as it is ultimately intended, as a method for the generation of complex patterns using only a simple set of generic template structures and a maximum resolution in the sub-10-nm region, at least four key issues must be addressed: (i) the invented NAIL technology is based on room-temperature nanoimprint lithography - therefore developed RTNIL processes have to be demonstrated in the sub-15-nm region; (ii) mold and substrate alignment after arbitrary translations must be demonstrated (in the current work, translations were made monotonically along the y-axis in sequential imprints); (iii) the distortion effect must be understood and controlled (we believe the observed distortion could be reduced by working with a thinner resist layer); and (iv) the ability to perform overlapping imprints and thus to create extended features (such as wires) must be demonstrated. Additionally, the pattern-transfer process has to be improved to allow control of the depth of the features etched into the silicon substrate independent of the thickness of the imprint polymer layer. One could perhaps address that issue by including a SiO₂ layer between the silicon substrate and the imprint polymer layer that acts as a hard etch mask for CF₄-RIE. Nonetheless, the work provides a key demonstration that NAIL is a useful pattern-generation tool. By building a custom tool, and by using low density polystyrene (97 kg/mol) and small-area molds, we were able to create a
complex non-regular pattern out of a set of aligned sequential imprints using a set of simple nanotemplates. Using this setup, we also performed one- and two-step RTNIL using a mold with a 400-nm-pitch grating. We further developed a pattern-transfer procedure that allowed transfer of the imprinted patterns from the PS layer into the silicon substrate. Next steps will focus on improving the alignment capabilities, understanding and correcting the observed image distortion of imprinted patterns as well as of etched transfer patterns, and creating increasingly complex, high-resolution, and useful structures.

The essential challenge in addressing all these tasks is bringing the NAIL scheme down into a region where it can efficiently challenge e-beam lithography, i.e. the sub-15-nm region. As pointed out above the only NAIL-enabling lithography technique is RTNIL. Hence demonstrating RTNIL in the sub-15-nm region is a crucial requirement for any further development of NAIL. The following chapter shows how we accomplished sub-15-nm RTNIL by introducing another innovative RTNIL scheme.
Chapter 4

Sub-15-nm Room-Temperature Nanoimprint Lithography

A crucial requirement for being able to further extend the success of the NAIL technique is to improve its resolution, and explore unconventional ways to utilize NAIL processes for fabrication of novel nanodevices and nanomaterials [141]. I address these points in this chapter by introducing a room-temperature NIL (RTNIL) technique pushing the patterning resolution in the sub-15-nm region.

The RTNIL technique that we present uses molds that are fabricated by molecular beam epitaxy (MBE). MBE growth processes allow for precisely controlling the thicknesses of grown crystalline layers with atomic resolution. This resolution directly determines the minimum size of the mold features to be imprinted. It has been shown that MBE-molds can be used to perform SFIL in the sub-10-nm region [76] [142] [143] [144]. Following the invention of the nano-typewriter which uses multi-step RTNIL to print out complex patterns, an investigation of polymer flow and polymer deformation during RTNIL processes in the sub-15-nm region is needed [141] [151]. In order to conduct that investigation we have designed and built a new NIL-tool that is capable of performing single-step RTNIL using MBE-molds that we fabricated.

In section 4.1 we present MBE-mold fabrication schemes, technical details of our custom-built NIL-tool are provided in section 4.2 and results on polymer flow and polymer deformation when performing single-step RTNIL on this tool are shown in section 4.3. Finally, in section 4.4 I conclude with
a discussion and summary of key results and future plans.

4.1 Imprint mold fabrication by using molecular beam epitaxy

Molecular beam epitaxy is a well-known technique to realize semiconductor heterostructures [145][146]. Such structures can be used to fabricate NIL molds [147][148][149] as well as extremely precise templates for nanos-structure fabrication [147][148][149]. The simplest mold fabrication scheme consists of three process steps: (1) in a first MBE-step a crystalline layer of a material B is grown on top of a substrate material A, (2) in a second MBE-step a second layer of a material A is grown on top of the grown layer of material B. Materials A and B have to be chosen in such a way that they can be selectively etched with respect to each other. (3) in a third step the MBE-grown sandwich structure is cleaved perpendicular to the growth direction and the grown layers are selectively wet-etched. As a result of the wet-etching procedure the cleaved edges now comprise a 3D topographical surface structure forming either a positive line feature (if material A was etched faster with respect to material B) or a negative groove structure (if material B was etched faster with respect to material A). The described scheme can be extended to fabricate 3D grating features by growing more than two layers of optionally also more than two different materials on top of the substrate and selectively etching the grown sandwich structures afterwards. The thicknesses of MBE-grown layers can be controlled with monolayer precision, i.e. with sub-nanometer resolution. Hence the linewidths of the 3D grating features on the edges of the cleaved and etched MBE-grown samples can be designed with the same precision. These 3D grating features can now directly be transferred into an imprint polymer layer by pressing the respective edge of the MBE-sample into the polymer. In this thesis I refer to these ultra-high resolution MBE-fabricated NIL-molds as MBE-molds. Figure 4.1 schematically shows the general fabrication scheme of MBE-molds as described above.

We fabricated several types of MBE-molds: (i) negative single-line MBE-molds, (ii) negative multi-line MBE-molds, (iii) positive multi-line MBE-molds, and (iv) negative single-line MBE-molds with a supporting positive structure. For all types of MBE-molds an epi-ready (001) GaAs wafer
Figure 4.1: Nanoimprint lithography scheme using MBE-molds: first a MBE-mold is fabricated by (a) MBE-growth of a material B onto a substrate material A, and cleaving the grown sandwich structure afterwards. (b) material B is selectively etched with respect to material A or vice versa yielding negative or positive line features on the cleaved edge. The generated structure can be used as a mold to imprint into a polymer layer provided on a substrate material following a classical RTNIL process consisting of (c) imprint, and (d) mold release.
was used as the starting material. The overall dimensions of all MBE-molds that we applied in RTNIL imprint processes were in the range of $\sim 400 \mu m \times 3 \text{mm} \times \sim 6 \text{mm}$, whereas the active mold area, i.e. the surface on one edge carrying the grating patterns, covered an overall area of $\sim 3 \mu m \times \sim 3 \text{mm}$. All MBE-growth processes were performed at the Walter-Schottky-Institute (WSI) of TUM.

4.1.1 Negativ single-line MBE-molds

Negative single-line MBE-molds comprise a single groove-shaped feature on their edge. They are fabricated according to the following four-step scheme: (1) in a first MBE-step a 300-nm-thick $\text{Al}_0\text{.8Ga}_0\text{.2As}$ layer is grown on top of the GaAs substrate, whereas the thickness of the grown layer defines the width of the groove-shaped mold feature generated in step (3); (2) a 4.5-µm-thick GaAs layer is grown on top of the $\text{Al}_0\text{.8Ga}_0\text{.2As}$; (3) samples with orthogonal and parallel facets are generated by cleaving the wafer along its $\{110\}$ planes; and (4) the $\text{Al}_0\text{.8Ga}_0\text{.2As}$ layer is selectively removed by wet etching the cleaved sample in a 5% hydrofluoric acid (HF) solution for 60 s yielding a $\sim 400$-nm-deep and $\sim 300$-nm-wide trench on the edge of the sample. It has been shown that HF is very well suited to selectively etch AlGaAs with respect to GaAs [150]. Figure 4.2 shows a SEM top-view image and an AFM cross-section image of a negative single-line MBE-mold that we fabricated.

4.1.2 Negative multi-line MBE-molds

Negative multi-line MBE-molds have multiple lines and grooves with various linewidths ranging from 9 nm to 100 nm on their edges. The fabrication process is analogous to the one described for generating negative single-line MBE-molds: instead of performing the process steps (1) and (2) only once, both steps are alternately repeated multiple times with growth parameters generating various designated thicknesses of grown layers. Figure 4.3 shows two SEM top-view images and a corresponding AFM cross-section image of two types of negative multi-line MBE-molds that we fabricated according to the scheme described above. The number as well as the thicknesses of grown layers varies. The MBE-mold shown in fig. 4.3a consists of 6 grown layers, the wet etching-step was performed using a 5% HF solution for 5 s.
4.1. IMPRINT MOLD FABRICATION BY USING MOLECULAR BEAM
EPITAXY

Figure 4.2: Single-line negative MBE-mold: SEM top-view image and AFM cross-
section image of the 3D surface profile of a negative MBE-mold after selective
etching. The white area on the far right side of the image is the surface area of the
grown GaAs layer. The negative pattern can be used as MBE-mold to imprint a
positive line into an imprint polymer layer.

The MBE-mold presented in fig. 4.3b comprises 20 grown layers and was
selectively etched in 50% HF vapour for 1 s. A 10-nm-wide groove and a 5-
nm-wide groove that should appear between the 20-nm-wide groove and the
dge of the mold at the very right side of the image are not visible because the
etching time was not long enough to form these ultra-thin features. This is
a major challenge when etching multi-line structures: aspect ratios for wider
features may get too large when etching long enough to generate smaller
features.

4.1.3 Positive multi-line MBE-molds

Positive multi-line MBE-molds comprise positive multi-line features on their
edges. For such molds, the mold pattern to be pressed into the imprint
polymer consists of lines whose surface areas are elevated with respect to the
overall surface area of the edge also being on the same level as the grooves of
the mold pattern. As opposed to negative single-line and multi-line MBE-
molds the imprint pressure is exclusively applied to the patterned part of the
Figure 4.3: Two types of negative multi-line MBE-molds: (a) SEM top-view image and AFM cross-section image of the 3D surface profile of a negative MBE-mold. Three layers of AlGaAs with thicknesses of 100 nm, 60 nm and 30 nm and three layers of GaAs were alternately grown on top of a GaAs substrate before all AlGaAs layers were selectively etched with respect to GaAs layers. The AFM cross-section image shows that etch rates decrease for thinner layers. AFM tip convolution effects limit the resolution of AFM cross-section images of etch profiles. Further experimental work will include assessing relative etch rates of different aspect ratio grooves, and examining the morphology of the floors of such grooves by means of cross-sectional TEM. (b) SEM top-view image of the 3D surface profile of a 5-line/2-groove negative MBE-mold. Lines are colored brightly while grooves are represented by dark lines. A line feature generated from a 5-nm-thick grown AlGaAs layer can clearly be observed between the 21-nm-wide line feature and the 32-nm-wide groove feature, and its linewidth was measured as 9 nm.

edge when using positive MBE-molds. This allows for significantly decreasing the imprint force, and releasing stress from the supporting substrate portion of the MBE-mold with both effects in turn minimizing deformation and bending of mold and substrate during the imprint step.

The fabrication principle of positive multi-line MBE-molds follows exactly the process flow for negative multi-line MBE-molds except for the fact that all GaAs layers including the substrate area of the mold are etched selectively with respect to AlGaAs layers. Figure 4.4 shows SEM side-view as well as SEM top-view images of a positive multi-line MBE-mold that we fabricated according to the following 22-step scheme: (1)-(20) using an epitaxially grown (001) GaAs wafer as the starting material 10 layers of Al$_{0.8}$Ga$_{0.2}$As and 10 layers of GaAs with various thicknesses were alternately grown on top of each other in 20 subsequent MBE-steps, (21) in a twenty-first step samples with orthogonal and parallel facets are generated by cleaving the wafer along its 110 planes, and (22) in a twenty-second step GaAs layers are
selectively removed by wet etching the cleaved sample in a 50-s-immersion in citric acid solution (CAS):H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O in ratio 1:2:9 yielding \(~300\)-nm-deep trenches with various widths on the edge of the sample. Neither one of the grown 5-nm-wide mold features yielded a topographic 3D surface structure. Even though a line may have the same width as a groove, in reality the linewidth appears to be larger than the width of the corresponding groove when comparing both features under an SEM due to secondary electron interference effects.

4.1.4 Negativ e single-line MBE-molds with a positive supporting structure

Negative single-line MBE-molds with a positive supporting structure provide a 16-nm-wide negative single-line feature defined by two 1-\(\mu\)m-thick AlGaAs layers that are positive with respect to the GaAs substrate layer. This type of mold combines advantages of positive and negative MBE-molds. Essentially all imprint force is acting on a very small area of the mold cross-section, i.e. the microscopic positive supporting AlGaAs layers. This means that the imprint pressure is concentrated exclusively on the portion of the mold cross-section that comprises mold features to be imprinted. The supporting GaAs substrate is therefore not exposed to stress and deformation during the imprint step which is the core advantage of using positive MBE-molds. On the other side, the supporting macroscopic AlGaAs layers and the nanoscopic GaAs mold feature form a local negative single-line MBE-mold with respect to the overall MBE-mold structure. Thus negative single-line molds are extremely stable as opposed to positive MBE-molds whose stand-alone structures tend to break off and bend during the imprint step. Figure 4.5a illustrates the building scheme of a negative single-line MBE-mold with a positive supporting structure.

The fabrication principle of negative single-line MBE-molds with a positive supporting structure is that of a positive multi-line MBE-mold as described in section 4.1.3 above, whereas the first and third grown layers are made of AlGaAs and the second grown layer contains GaAs. The thicknesses of AlGaAs layers have to be macroscopic with respect to the thickness of the GaAs layer which is typically in the sub-30-nm region. Since the etch rate decreases with decreasing layer thickness, the etch rate for the microscopic AlGaAs layers is higher than the etch rate for the nanoscopic GaAs lay-
Figure 4.4: Positive multi-line MBE-mold: (a) SEM top-view image of the 3D surface profile of the edge of the mold and (b) SEM side-view image of the same area. 10 layers of AlGaAs and 10 layers of GaAs with thicknesses from 100 nm to 5 nm were alternately MBE-grown on top of a GaAs substrate before GaAs layers were selectively etched with respect to AlGaAs layers. Positive line features are colored brightly while grooves are represented by dark lines. A measured 19-nm-wide line is the smallest feature that could be created out of a grown 10-nm-thick layer by the selective etching process.
4.1. IMPRINT MOLD FABRICATION BY USING MOLECULAR BEAM EPITAXY

![Diagram of AlGaAs and GaAs layers](image)

(a)

![SEM images of negative single-line MBE-mold with a positive supporting structure](image)

(b)

Figure 4.5: Negative single-line MBE-mold with a positive supporting structure: (a) schematic cross-section drawing of the mold: it combines the core advantage of a negative MBE-mold, i.e. no delicate stand-alone mold features, with advantages of a positive mold, i.e. no exposure of the supporting substrate layer to imprint pressure preventing the mold to bend during imprint. (b) SEM side-view and top-view images of a negative single-line MBE-mold with a positive 2-µm-thick supporting structure that we fabricated. The inset provides a SEM top view image of the negative line feature defined by two supporting AlGaAs layers.

ers allowing for fully developing the nanoscopic groove. Figure 4.5 shows a negative single-line MBE-mold with a positive supporting structure that we fabricated. The width of the negative mold feature was measured as 16 nm by means of a SEM. Due to noise related imaging limits of our SEM this measured linewidth differs from the actual thickness of the corresponding grown GaAs layer which was 10 nm. Since the MBE-growth process can be controlled with sub-nanometer precision we expect the actual width of the line feature to be significantly smaller than 16 nm, i.e. close to its MBE-grown thickness of 10 nm. The supporting positive AlGaAs layers are 1-µm-thick. Due to noise-related imaging limits of our SEM its measured linewidth differs from the thickness of the corresponding grown GaAs layer.
However, measuring AlGaAs/GaAs structures in the sub-30-nm region generally yields more precise results than measuring imprint polymer layers because AlGaAs/GaAs compounds show very good contrast performance during SEM imaging unlike even metal coated polymer surfaces.

4.2 Design of nanoimprint tool

We have designed and built a nanoimprint lithography tool that is capable of performing single-step RTNIL using MBE-molds fabricated according to the schemes presented above. The schematic diagram of the RTNIL tool is shown in fig. 4.6. Detailed technical drawings can be found in appendix B.

The tool consists of a vacuum sample chuck mounted upside down on top of three metal poles that are in turn mounted on a metal baseplate. Sample chuck and baseplate are arranged parallel with respect to each other. Mounted imprint samples are held in a position so that the imprint polymer layer on top of the substrate faces downwards towards the baseplate. A hydraulic cylinder (Merkle Hydraulikzylinder) is mounted on the baseplate between baseplate and sample chuck and acts in a direction that is normal to the surface planes of baseplate and sample chuck. The free end of the hydraulic cylinder that faces the sample chuck carries a mold holder unit which in turn holds the MBE-mold. During a RTNIL step, the hydraulic cylinder moves towards the sample chuck, automatically levels out the mold, and presses it into the polymer layer on the imprint substrate. The hydraulic cylinder is manually controlled by a hydraulic system (Hoerbiger Hydraulik GmbH) that consists of a hydraulic pump, a high-precision manometer, and a valve system allowing for in-situ setting and monitoring oil pressure and oil flow, i.e. imprint pressure and speed of motion of cylinder and mold. Once the desired imprint pressure is reached the valve system locks cylinder and mold for the desired imprint time and releases the mold afterwards. The hydraulic cylinder is capable of applying imprint forces between 0.5 kN and 25 kN with a force resolution of $\sim 0.05$ kN. Once the optimum imprint pressure and duration for a specific mold/imprint polymer combination and the imprint cross-section area of the mold are known, the NIL-tool can be manually programmed to conduct an optimized RTNIL step. Figure 4.7 shows a picture of the complete system setup that we built.
4.2. DESIGN OF NANOIMPRINT TOOL

4.2.1 Working principle of the mold holder unit: the mold levelling procedure

As pointed out previously, a core requirement for successfully performing NIL without having to cope with shear forces during the imprint step is to guarantee optimum mold-substrate alignment. If a slightly unlevelled mold approaches a substrate, depending on the specific mold-substrate misalignment, a certain portion of the active area at the edge of the mold establishes physical contact with the imprint polymer layer before any other portion of the active area touches the substrate. From this point on further approach of the mold causes shear forces between mold and imprint polymer.
Figure 4.7: Realization of the complete MBE-RTNIL prototype tool setup: (a) photograph of the complete system, (b) closeup view of the mold holder unit, and (c) closeup of the core unit as also schematically shown in Fig. 4.6. The following tool components are visible: (1) the core unit consisting of the baseplate, (1a) high-precision manometer and valve, (1b) hydraulic cylinder, (1c) metal poles carrying the wafer chuck (1d), mold holder unit (1e), (1f) white background screen for visual mold leveling, (2) hydraulic system with (2a) oil tubes connecting pump and hydraulic cylinder, (3) vacuum pump and (3a) vacuum tubes, (4) controller for optional piezo-z-stage, (5) manual VCR up/down switches for hydraulic cylinder, (6) nitrogen gun, (7) optical table, (8) light source with flexible light guides (8a) for visual mold leveling and post-imprint result verification of the samples on the workspace (9). The complete setup is operated under a laminar flow box atmosphere (10).
layer accompanied by a self-levelling momentum trying to parallelly align the mold-substrate interface. While shear forces generally have to be avoided, the self-levelling momentum is an effect that can be used in favor of the imprint process. Especially when imprinting extremely robust planar large-area non-transparent molds self-levelling momenta are used to compensate for non-applicable optical levelling procedures. A short summary of main prerequisites justifying and supporting the self-levelling technique is given below:

- The mold should be non-transparent thus eliminating conventional optical levelling procedures;
- Mold features should be extremely robust to be able to withstand residual shear forces going hand in hand with the self-levelling momentum;
- Mold features should be homogenously distributed over the active surface of the mold, and the active surface should be point-symmetric yielding a homogenous momentum distribution with respect to the mold features;
- The active surface should be large with respect to the overall dimensions of the mold to minimize shear forces and maximize the self-levelling momentum.

As opposed to NIL technologies applying conventional planar large-area molds, we are using non-transparent MBE-fabricated molds with the pattern to be imprinted only covering a very small portion of one edge of the mold. The active mold surface, i.e. the surface area of the mold that interfaces the imprint polymer layer is very small in relation to the overall dimension of the mold (comp. section 4.1) and also not point-symmetric. Additionally, an MBE-mold has to be mounted with its main surface area plane being aligned in imprint direction, normal to the active mold surface. Hence, based on the criteria listed above using MBE-molds requires self-levelling while simultaneously the geometric shape of MBE-molds supports that technique only in a very limited way.

The mold-holder unit we designed takes advantage of the MBE-mold characteristics that promote self-levelling and eliminates all factors not supporting that technique. Figure 4.8 shows a schematic drawing of the mold-holder unit in its assembled state with a mounted MBE-mold, fig. 4.8b is
an explosion drawing of the same unit. Detailed machine drawings can be found in appendix [3]. Figure 4.9 shows a picture of the mold holder unit with an MBE-mold in imprint position below the sample chuck, with no imprint sample mounted in the system.

**Mounting the MBE-mold**

The mold holder unit is mounted rigidly on the hydraulic cylinder as shown in fig. 4.8a by sliding the adapter (7) into the bottom inset hole of the mold holder unit and tightening the adapter lock screws. The mold holder unit itself consists of two main parts: a cover plate (1) and a L-plate (2), whereas the cover plate fits exactly into the rectangular knee-shaped leftout part of the L-plate. The cover plate is rigidly screwed against the vertical part of the L-plate in the $y$-$z$-plane using the cover plate locks pointing in negative $x$-direction. Two spacers at the interface between cover plate and L-plate create a $\sim 500$-$\mu$m-wide slid between the two plates that is open in both $y$-directions and in positive $z$-direction while the horizontal part of the L-plate in the $x$-$y$-plane closes it at the bottom in negative $z$-direction.

The slid is filled with several components: a spring or optionally a squeezable foam stripe (6) sits at the bottom and carries a T-plate (5) comprising a thickness that almost completely fills the slid but still allows the T-plate to initially move freely in the $y$-$z$-plane. The MBE-mold is manually slid onto the T-plate through the open top of the slid so that the edge of the mold carrying the grating features to be imprinted faces upwards in positive $z$-direction. Molds should have a length in $z$-direction of at least $\sim 6$ mm so that the active surface of the mounted mold is slightly elevated with respect to the joint top $x$-$y$-plane of L-plate and cover plate. The cover plate has two insets facing towards the slid in negative $x$-direction. One inset holds a mold-lock clamp, the other inset holds a T-plate lock clamp. In the initial state after mounting the mold neither one of the clamps reaches into the slid. Both clamps can be separately activated and moved into the slid in negative $x$-direction by using the mold-lock clamp screws, and the T-plate lock clamp screws respectively. The mold-lock clamp is adjusted at a $z$-position that allows it to press exclusively against the mounted mold when activated, analogously the T-plate clamp is positioned in such a way that it presses exclusively against the T-plate after activation.
4.2. DESIGN OF NANOIMPRINT TOOL

Figure 4.8: Designing a self-levelling mold holder unit for holding and imprinting MBE-molds: (a) schematic drawing of the unit in an assembled state, and (b) explosion drawing of the same unit, no MBE-mold showing. The self-levelling mechanism is explained in detail in the main text.
Figure 4.9: Picture of the mold-holder unit of the custom-built RTNIL tool for imprinting MBE-molds. A MBE-mold is mounted in the system. The screws are used for leveling out the mold before the actual imprint step and for locking the mold and holding it in position during the imprint process. The picture also shows previously described components of the NIL-tool. No imprint sample is mounted, the inner vacuum grooves of the sample chuck are visible.

Self-levelling the mold and imprint step

After mounting the mold in the mold holder unit and the substrate on the wafer chuck the MBE-RTNIL process can be started. First the MBE-mold has to be levelled with respect to the surface plane of the imprint polymer layer. Because of the geometry of the active mold surface a self-levelling momentum is only generated around the $x$-axis while there is practically none acting around the $y$-axis. Hence the MBE-mold needs to be optimally levelled out in the $x$-$z$-plane before the imprint step is started. This is achieved by tightening the mold-lock clamp screws and pressing the mold against the $y$-$z$-plane of the L-plate facing towards the slid. The mold-lock clamp screws are then untightened a notch so that the MBE-mold his still held in the $y$-$z$-plane but again has minimum play to move around.
freely in the $y$-$z$-plane. Direction of movement of the hydraulic cylinder, the adapter connecting the cylinder with the mold holder unit as well as the poles carrying the wafer chuck have been adjusted and aligned in $z$-direction with ultra-high precision during assembly of the tool. After this step the MBE-mold shows optimum levelling in the $x$-$z$-plane.

In a second step the hydraulic cylinder is moved upwards in positive $z$-direction until the active mold surface establishes physical contact with the imprint polymer layer. Continued upwards motion of the hydraulic cylinder yields a self-levelling momentum around the $x$-axis. This momentum slightly rotates the mold in the $y$-$z$-plane whereas this rotation is enabled by the mold pressing against the movable T-plate which in turn can compress the spring, or squeeze the foam stripe respectively. The length of the mold in $y$-direction has to be at least $\sim 3 \text{ mm}$ to guarantee a sufficiently high self-levelling momentum. A conventional light source comprising a flexible light guide pointing at the mold-substrate interface from the backside in positive $x$-direction allows for highly-precise visual control of the quality of alignment: as soon as there is no light shining through the interface anymore the mold has completely levelled itself out in the $y$-$z$-plane. Once this point is reached the hydraulic cylinder is stopped and the mold-lock clamps are tightened completely holding the levelled mold in place.

During an imprint step extremely high imprint forces pointing in negative $z$-direction are acting on the mold. Pressing it against the L-plate exclusively by means of the mold-lock clamp does not prevent the mold from sliding into the slid in $z$-direction. Additionally, the T-plate must now be locked tightly in order to block the slid beneath the levelled mold. In order to not expose the mold features to random shear forces in $x$-direction caused by vibration of the system setup during the tightening step the mold holder unit is lowered again in negative $z$-direction until the active mold surface detaches from the substrate. Because of the tightened mold-lock clamp screws the mold stays in the levelled position. The T-plate lock clamp screws are now tightened and the system is now ready for imprinting. The hydraulic cylinder is moved upwards in positive $z$-direction until the mold touches the imprint polymer layer and eventually imprints into it. The levelled mold can be used multiple times for imprinting several substrates without having to perform the levelling procedure before every new imprint step.
4.2.2 Tool calibration

In order to achieve highest-quality imprint results accompanied by a long life time cycle of used MBE-molds the imprint pressure, i.e. the pressure at the interface of active mold surface and imprint polymer layer, has to be monitored, preset, and controllably kept at the specific value required for individual mold geometries and/or various imprint polymer materials. The overall active surface area of each MBE-mold can easily and precisely be determined from the MBE-growth scheme that was applied to fabricate a specific MBE-mold and the macroscopic mold geometry that can be measured after the mold has been cleaved to its final shape. For each moment at which the force is known with which the hydraulic cylinder presses the mold against the substrate during an imprint step the corresponding imprint pressure can directly be calculated.

We have calibrated the tool according to the following scheme: (1) we substituted the mold holder unit by a high-precision load cell (Instron GmbH, Germany), (2) activated the hydraulic pump unit, (3) monitored the force measured by the load cell as well as the hydraulic pressure measured by the high-precision manometer as shown in fig. 4.6 and (4) based on that data determined the cylinder force vs. hydraulic pressure-curve for our tool. Figure 4.10 shows the obtained data. It can be seen that the tool has a constant hydraulic threshold pressure of $\sim 4$ bar that is necessary to move the hydraulic cylinder without load, i.e. before it presses the load cell against the blank wafer chuck. After load cell and wafer chuck are in contact the load cell is compressed by an increasing hydraulic pressure in the bottom cylinder chamber and the shown curve evolves. After resubstitution of load cell against mold holder unit this curve enables us to constantly monitor and control the imprint pressure for a specific MBE-mold during an imprint step by reading out and transforming data from the high-precision manometer.

4.3 Single-step RTNIL using MBE-fabricated molds

One single-step RTNIL experiment consisted of the following elements: (1) spinning an imprint polymer onto a silicon wafer and baking it, (2) pressing a MBE-mold against the imprint polymer layer and imprinting it, (3) releasing the mold from the imprint polymer layer, and (4) imaging the imprinted patterns by means of an AFM and/or SEM. The main purpose of these
4.3. SINGLE-STEP RTNIL USING MBE-FABRICATED MOLDS

Figure 4.10: Measured pressure-force curve used for calibrating the hydraulic control unit under load conditions: a pressure of \( \sim 4 \) bar is necessary to move the cylinder without load. Increasing the hydraulic oil pressure yields an increasing cylinder force with which the cylinder presses against the wafer chuck. When performing optimized MBE-RTNIL processes the tool cylinder was operated in the region indicated by the red dashed rectangle.

Experiments was to determine and optimize the RTNIL parameters, including imprint pressure and imprint time.

It has to be pointed out that achieving maximum imprint depth is not necessarily accompanied by imprint polymer filling the mold features at an optimized level. Besides material characteristics of the imprint polymer, the imprint time significantly determines the flow performance of the imprint polymer during the imprint step. We used different types of polystyrene with varying molecular weights between 13 kg/mol, and 97 kg/mol respectively as imprint polymers. Imprint depths decreased significantly when using PS with higher molecular weight, i.e. features imprinted into 13 kg/mol PS were in good approximation twice as deep as patterns imprinted into 97 kg/mol PS when imprinting both polymers under identical imprint conditions using the same MBE-molds. No anti-sticking layer was necessary to promote mold release after imprint. When used as imprint polymer in combination with GaAs/AlGaAs molds polystyrene can be imprinted at room-temperature.
4. SUB-15-NM ROOM-TEMPERATURE NANOIMPRINT LITHOGRAPHY

without having to apply any additional anti-sticking surface chemistry.

We also determined the minimum imprint pressure \( P_{\text{min}} \) (the imprint pressure at which the mold starts to imprint the polymer layer), the optimum imprint pressure \( P_{\text{opt}} \) (the imprint pressure at which the mold features are transferred into the polymer layer with maximum imprint depth without damaging imprint sample and/or mold), and the breakthrough imprint pressure \( P_{\text{break}} \) (the imprint pressure at which the mold starts to crack) as \( P_{\text{min}} \sim 280 \text{ MPa}, \ P_{\text{opt}} \sim 350 \text{ MPa}, \) and \( P_{\text{break}} \sim 700 \text{ MPa} \) valid for all four types of fabricated MBE-molds and for all molecular weights of PS. Imprint pressures were achieved by driving the hydraulic cylinder and hence the mold into the surface of the imprint sample and locking the valves once the desired imprint pressure was applied. All imprint experiments described in the following sections were performed at \( P_{\text{opt}} \), whereas \( P_{\text{opt}} \) was individually determined for each used mold based on its specific imprint-cross-section area and by adjusting the cylinder force accordingly using the data presented in section 4.2.2. The mold was released from the imprint polymer layer after 10 s as this imprint duration proved to be the minimum period of time after which the maximum imprint depth could be achieved at \( P_{\text{opt}} \) for all four types of MBE-molds [14].

4.3.1 Single-step RTNIL process using a single-line negative MBE-mold

The imprint polymer layer consisted of polystyrene (PS) with an average molecular weight of 13 kg/mol (purchased from Alfa Aesar) that was first dissolved in toluene to a concentration of 10\% by weight. We cleaned a silicon wafer in an oxygen plasma asher for 2 min, spin-coated the PS/Toluene solution onto it at 1500 rpm, and baked it at 140°C for 2 minutes resulting in a 600-nm-thick PS layer. The imprint sample was then cleaved into rectangles with an average length of \( \sim 2 \text{ cm} \) and an average width of \( \sim 0.5 \text{ cm} \). We used one of these rectangular imprint samples per single-step RTNIL experiment. The imprint sample was mounted onto a flat metal plate before imprinting it. We then adjusted the metal plate/imprint sample unit on the wafer chuck in such a way that the direction of the longer edge of the rectangular imprint sample was aligned with the lines on the edge of the MBE-mold sitting in the mold holder unit below it. This mounting procedure counteracts the bending of the imprint sample during the actual imprint.
4.3. SINGLE-STEP RTNIL USING MBE-FABRICATED MOLDS

step.

We used the tool described in section 4.2 and the negative single-line MBE-mold shown in fig. 4.2 to perform separate single-step RTNIL experiments at room-temperature under atmospheric conditions at $P_{opt}$. The imprint cross-section area of the negative single-line MBE-mold was $\sim 1.8 \text{ mm}^2$. Figure 4.11 shows our best imprint result of this experiment imaged by means of an optical microscope as well as by using an AFM. The width of the imprinted positive line feature is $\sim 500 \text{ nm}$ and does not match the width of the negative line feature of the used MBE-mold which is $\sim 300 \text{ nm}$. A possible explanation for this mismatch of linewidths is the high imprint pressure acting on the complete cross-section area of the MBE-mold causing either mold or imprint sample or both components to bend and hence to broaden the negative line-feature during the imprint step. We can avoid this effect by using positive MBE-molds instead of negative MBE-molds as described in the following section.

4.3.2 Single-step RTNIL process using a positive multi-line MBE-mold

The imprint polymer layer that we imprinted into consisted of polystyrene (PS) with an average molecular weight of 65 kg/mol (purchased from Alfa Aesar) that was first dissolved in toluene to a concentration of 10% by weight. We cleaved a square-shaped piece having a sidelength of $\sim 1 \text{ cm}$ out of a 500-$\mu\text{m}$-thick silicon wafer and cleaned it in an oxygen plasma asher for 2 min. We then spin-coated the PS/toluene solution onto it at 1500 rpm, and baked it at 140$^\circ$C for 2 minutes resulting in a 700-nm-thick PS layer. As part of a different research project we also employed the optically active polymer P3HT as imprint polymer for this experiment. In order to maintain thematical consistency respective experimental results are provided in appendix C. All results that we report of in this section were exclusively obtained by using PS as imprint polymer.

Imprint sample and positive MBE-mold were then mounted in our custom-built MBE-NIL tool as described in section 4.2 with introducing two adjustments: (i) a hardened steel plate with an ultra-flat surface was mounted between imprint sample and wafer chuck to support homogenous distribution of the force applied by the wafer chuck counteracting the imprint force during the imprint step, and (ii) the mold-holder unit was operated in such
4. SUB-15-NM ROOM-TEMPERATURE NANOIMPRINT LITHOGRAPHY

Figure 4.11: Optical microscope top-view and AFM cross-section image of a single-step RTNIL result using the single-line MBE-mold shown in fig. 4.2 and 13 kg/mol-polystyrene as imprint polymer. Both images show two positive polymer lines separated by a distance of $\sim 4.5 \, \mu m$. This distance matches the spacing of etched negative line and the edge of the mold of the used single-line MBE-mold. The left line is the imprinted negative line feature of the MBE-mold, the right line is formed by polymer that was pushed to the side of the edge of the mold during the imprint step. The width of the mold feature is $300 \, \text{nm}$, the width of the imprinted line is $\sim 500 \, \text{nm}$ and its height is $\sim 100 \, \text{nm}$. This mismatch of linewidths results from the high imprint pressure causing the mold to bend and hence broaden the negative line-feature during the imprint step.

a way that the cylinder force was partly absorbed in the mold holder unit before transferred to the MBE-mold. This buffer function becomes necessary when using positive MBE-molds since stand-alone positive mold features are highly sensitive to even slightest variations of the imprint pressure.

We used the tool described in section 4.2 and the positive multi-line MBE-mold shown in fig. 4.4 to perform separate single-step RTNIL experiments at room-temperature under atmospheric conditions at $P_{opt}$ following the same imprint procedure as previously described in section 4.3.1 except for not rigidly fixing the mold after levelling it out. The imprint cross-section area of the used positive multi-line MBE-mold was $\sim 2100 \, \mu m^2$, the imprint
4.3. SINGLE-STEP RTNIL USING MBE-FABRICATED MOLDS

Figure 4.12: SEM top-view image of a single-step RTNIL result using the multi-line positive MBE-mold shown in fig. 4.4 and 65 kg/mol-polystyrene as imprint polymer. The complete positive multi-line mold pattern could be transferred into the imprint polymer layer yielding lines and grooves with good surface and sidewall characteristics. Both insets show imprinted lines, and grooves respectively.

duration was 10 s.

We could imprint the complete positive multi-line MBE-mold pattern provided on the mold. Figure 4.12 shows that all imprinted lines and grooves show good surface characteristics on large parts of the imprinted area. A 3-nm-thick titanium layer used to alleviate charging during SEM imaging was evaporated onto the imprinted polymer layer. Imaging imprinted polymer structures in the sub-30-nm region turned out to be increasingly challenging due to interference effects and decreased contrast. As stated previously when measuring dimensions of imprinted features using a SEM system lines appear to be wider, and grooves thinner than they are in reality.
4.3.3 Single-step RTNIL process using a negative single-line MBE-mold with a positive supporting structure

The imprint polymer layer that we imprinted into consisted of polystyrene (PS) with an average molecular weight of 97 kg/mol (purchased from Alfa Aesar). We generated two polymer solutions by dissolving PS in toluene to a concentration of 10% by weight, and 2% by weight respectively. We cleaved a square-shaped piece having a sidelength of \( \sim 1 \) cm out of a 500-\( \mu \)m-thick silicon wafer and cleaned it in an oxygen plasma asher for 2 min. We then spin-coated the 10%-PS/toluene solution onto it at 9000 rpm, and baked it at 140°C for 2 minutes resulting in a 300-nm-thick PS layer (type I imprint sample). Spin-coating the 2%-PS/toluene solution onto such a silicon sample at 9000 rpm and baking it at 140°C for 2 minutes yielded a 60-nm-thick PS layer (type II imprint sample).

We mounted a type II imprint sample and the negative single-line MBE-mold with a positive supporting structure shown in fig. 4.5b in our custom-built MBE-tool and performed the exact same imprint procedure as described in section 4.3.2. Figure 4.13a shows a SEM image of the imprint result for this experiment. The imprinted positive line feature is clearly visible but shows poor sidewall characteristics. Performing the same imprint procedure onto type I imprint samples yielded improved sidewall and surface characteristics of imprinted lines as shown in fig. 4.13b. Measuring the width of imprinted polymer lines in the sub-30-nm region, even though coated with titanium to prevent charging effects, was accompanied by an increasing error margin of our SEM system caused by its resolution limit combined with a significantly decreased contrast level. Although the measured linewidth is 20 nm we expect the real linewidth to be significantly smaller, i.e. in the 10-nm-region. Since the imprinted line feature is only \( \sim 10 \) nm high, further measurements by means of an AFM using high-aspect ratio tips will reveal sidewall and surface characteristics of the imprinted feature in more detail. Additional measurements on high-precision imaging tools have to be made to determine the actual feature size of imprinted lines.

4.4 Process evaluation and next steps

MBE-RTNIL experiments showed that polystyrene can be used as a RTNIL imprint polymer for imprinting in the sub-15-nm region. Further ultrasonic-
4.4. PROCESS EVALUATION AND NEXT STEPS

Figure 4.13: SEM top-view images of two single-step RTNIL results using the negative single-line MBE-mold with a positive supporting structure shown in Fig. 4.5. (a) imprinting into a 60-nm-thick PS layer yields poor sidewall characteristic of the imprinted line-feature while (b) imprinting into a 300-nm-thick PS layer leads to improved sidewall and surface quality of imprinted lines. The negative mold feature comprises a measured width of 16 nm while the measured width of the imprinted feature is 20 nm. A 3-nm-thick titanium layer was evaporated onto each sample before SEM imaging to prevent charging effects.

bath enhanced selective etching of MBE-grown GaAs/AlGaAs sandwich structures will be performed to also create 3D mold features in the sub-5-nm region. Imprint polymer flow characteristics and the stability of MBE-molds and imprint samples under RTNIL conditions have to be further analyzed and optimized in order to bring the MBE-RTNIL scheme down to the sub-5-nm region. We will also investigate other RTNIL imprint polymers with respect to their flow characteristics and their capability to fill mold features during the imprint step for various imprint times and imprint temperatures.

Experimental results presented in this chapter constitute the highest-resolution room-temperature NIL reported in scientific literature to date. This is an important step towards bringing the invented NAIL technology down into the sub-15-nm region. However, results presented in this chapter were obtained exclusively from single-step RTNIL cycles. In order to demonstrate NAIL in the sub-15-nm region repeatable multi-step RTNIL experi-
ments yielding complex patterns with feature sizes below 15 nm have to be produced. Future work will approach that task by equipping our RTNIL prototype tool with an ultra-high precision computer controlled closed-loop $x$-$y$-$z$-piezo-stage (attocube systems, Germany) enabling multi-step MBE-RTNIL, thus establishing a first limited implementation of NAIL technology in the sub-15-nm region.
Chapter 5

Sub-10-nm Direct Nanotransfer Printing

5.1 Nanotransfer printing using MBE-molds

Melosh et. al. have applied molds fabricated by molecular beam epitaxy (MBE) in superlattice nanowire transfer processes (SNAP) creating metal nanowires in the sub-10-nm region [148]. But SNAP technology sacrifices the stamp in each transfer step as opposed to conventional nanotransfer printing (nTP), and relies on additional etching steps for transferring material from the mold onto the substrate. A detailed introduction to the field of nanotransfer printing (nTP) was given in section 2.6.3 of this thesis.

We have developed a direct room-temperature nTP process that uses hard MBE-molds to transfer a patterned PdAu/Ti layer from a mold onto the silicon oxide surface of a rigid silicon substrate without employing any flexible buffer layer or organic adhesion promoter or release agent in between mold and substrate. Our approach merges the ultra-high-resolution provided by the SNAP technology with the conceptual simplicity of nTP processes into a new nTP scheme for the sub-10-nm region that does not incorporate any SAM layers or release agents and preserves the stamp during the transfer process.

We used our custom-built prototype tool capable of leveling out MBE-molds (comp. section 4.2) for developing and optimizing the innovative direct nTP scheme. Mold fabrication processes for positive multi-line MBE-molds and negative MBE-molds with a positive supporting structure as well as the
5.1.1 Direct nanotransfer printing (nTP) - the experimental process

One nTP experiment consisted of the following elements: (1) activating the SiO$_2$ substrate surface in a 10-min-immersion in H$_2$O:H$_2$O$_2$:HCl solution in ratio 6:1:1 at 75°C and blowing it dry with nitrogen [120], (2) shadow-mask evaporating (base pressure $\sim 8 \times 10^{-7}$ mbar) a 8-nm-thick PdAu (20/80) layer (growth rate 0.1 nm/s), and then a 3-nm-thick titanium layer (growth rate 0.05 nm/s) onto the patterned edge of the MBE-mold at an angle of $\sim 85^\circ$ with respect to the surface plane of the mold pattern (as indicated by the large arrow in fig. 5.3b), (3) activating the surface of the oxidized Ti layer on the mold by UV flood-exposing it for 1 h [151], (4) mounting MBE-mold and substrate in the nTP-prototype tool, (5) pressing the MBE-mold against the substrate for 30 s applying a contact pressure of $\sim 300$ MPa and thereby transferring the PdAu/Ti layer onto the activated SiO$_2$ surface, (6) releasing the mold from the substrate, and (7) imaging the transferred patterns as well as the used mold by means of an SEM.

5.1.2 Direct nTP using positive multi-line MBE-molds

Figure 5.1 and fig. 5.2 show results of nTP processes obtained by using positive multi-line MBE-molds displayed in fig. 5.3. MBE-molds were designed in such a way that neighboring lines were spaced from each other by gaps with various measured widths including a 14-nm-wide, a 19-nm-wide, a 29-nm-wide, and a 65-nm-wide gap (fig. 5.3b).

Performing nTP experiments using these molds and following the process scheme introduced above yielded gaps between transferred lines having widths of down to 7 nm, whereas a 14-nm-wide gap on the mold led to a 7-nm-wide gap in the transfer pattern, the 19-nm-wide gap corresponds with a 10-nm-wide transfer gap, and the 29-nm-wide and 65-nm-wide gaps on the mold let to 24-nm-wide, and 50-nm-wide transferred gaps (fig. 5.2c and fig. 5.2d). This narrowing of initial gap sizes results from the angle at which transfer layers are evaporated onto the mold features causing asymmetric edge overgrowth of gap sidewalls. During mold release transfer material
5.1. NANOTRANSFER PRINTING USING MBE-MOLDS

Figure 5.1: SEM top-view images of PdAu lines transferred onto a SiO$_2$ surface by direct nTP. Lines were transferred on a total length of $\sim 2$ mm, i.e. the complete length of the patterned edge of the MBE-mold. (a) while thinner lines (top) show poor surface quality and deformed and rough edges, broader transferred lines (bottom) have good surface characteristics and comprise sharp edges. (b) close-up view of 5 parallel gaps separating lines 1-6 counted from the bottom. The first three gaps are clearly visible and separation of transferred lines is obvious. Gap 5 and 6 can be located in the corridors indicated by the dashed lines but no clear separation of transferred lines can be detected any more. This is due to SEM related imaging limits caused by secondary electron interference effects that significantly impact our imaging and hence measuring capabilities in the sub-15-nm region. (c) transferred lines 1 and 2 are separated by a 11-nm-wide gap.

that had been shadow-mask evaporated onto sidewalls and partly the bottom of groove features sticks to the transfer material evaporated onto the top surface of mold features, and all transfer material detaches from the mold. Material components originating from sidewalls and bottom areas of mold features get deposited in the transferred gap thus narrowing it with respect to its initial size measured in top-view on the mold before evaporation. Figures 5.3-a-c provide SEM-images illustrating the described effect by showing an MBE-mold in different stages of the nTP process with special
Figure 5.2: SEM top-view images of PdAu lines transferred onto a SiO$_2$ surface by direct nTP. SEM images of the used MBE-mold before and after the nTP process are shown in fig. 5.3, and fig. 5.3 respectively. The length of the patterned edge of the MBE-mold was $\sim 4$ mm and could be transferred with an overall pattern transfer efficiency of $\sim 80\%$: (a) lines located at the outer edge of the mold pattern (bottom) are transferred with higher efficiency than lines located at the inner edge of the mold pattern (top) due to slightly uneven pressure distribution over the mold-substrate interface during the transfer step. Additionally, since no flexible layer is employed between mold and substrate in nTP processes, local contaminations on the interface area compromise physical contact between mold and substrate thus inhibiting line transfer around the contaminated areas yielding missing line features in the transfer pattern. (b) close-up of a part of the transfer pattern that is incomplete due to the described contamination effect, (c) a 50-nm-wide gap, a 24-nm-wide gap, and (d) a 10-nm-wide gap and a 7-nm-wide gap, all separating two transferred lines from each other. All gaps are several micrometers long and show excellent side-wall characteristics. Note that due to noise-related interference effects the given measurements of widths of negative groove features include an absolute inaccuracy of $\sim \pm 5$ nm.
Figure 5.3: SEM side-view and top-view images of two positive multi-line MBE-molds evolving from the same design batch in different stages of the nTP process. (b) and (c) show pictures of the same mold that was applied in the nTP process yielding the transfer results shown in fig. 5.2 (a) picture of a first MBE-mold after finishing the mold fabrication scheme. No transfer material has been evaporated onto the mold surface yet. The inset provides a close-up view of the inner gap section of the mold showing measured 14-nm-wide, 19-nm-wide, 29-nm-wide gaps as well as a 65-nm-wide gap $g$ and a 100-nm-wide line $L$. (caption contd. on next page)
focus on the impact of shadow-mask evaporation. The gap narrowing effect scales with the initial widths of gaps on the mold pattern before evaporation, hence becoming less influential with decreasing initial gap sizes. Another effect contributing to gap restriction is deformation and lateral stretching of transfer layers during transfer step and mold release.

We want to point out that provided measurements of widths of negative groove features on molds and as part of transfer patterns include an absolute inaccuracy of around ±5 nm due to noise-related interference effects in our SEM system.

5.1.3 Direct nTP using negative single-line MBE-molds with a positive supporting structure

We have also used negative single-line MBE-molds with a positive supporting structure to carry out nTP experiments according to the scheme described above. Figure 5.4 shows SEM-images of such molds before and after nTP processing. Each mold comprised a single groove feature having a SEM-measured width of 16 nm and two supporting structures having a width of ~800 nm on its ~3-mm-long patterned edge. Figure 5.5 shows corresponding transfer results. A ~13-nm-wide gap was generated on the SiO$_2$ substrate surface in each nTP experiment.

As observed previously, measured widths of transferred gaps are narrower than the corresponding groove feature in the mold pattern before evaporation. However, the ratio of transferred gap size to initial gap size on the mold approaches 1 for decreasing gap sizes in the sub-20-nm region since the impact of shadow mask evaporation on sidewall deposition becomes negligible for ultra-narrow gaps. Shadow-mask evaporation of transfer material during mold preparation is a powerful tool of improving resolution of the
Figure 5.4: SEM top-view images of single-line MBE-molds with a $\sim 800$-nm-wide positive supporting structure evolving from the same design batch (a) before performing a nTP experiment and already carrying transfer material layers, as well as (b) after completion of the nTP step. The width of the negative line-feature remained effectively constant during the nTP experiment. Based on transfer results shown in fig. 5.5 slight gap restriction caused by shadow-mask evaporation of the transfer layers can be detected. The inset of (b) shows few remains of residual transfer layer material sticking to the edges of the negative groove feature.
developed direct nTP process yielding transferred gap sizes of down to 7 nm resulting from significantly larger initial gap sizes of the mold pattern before evaporation.

We have developed a mold-preserving direct nTP process that uses hard MBE-molds to transfer a patterned PdAu layer from a MBE-mold onto a SiO$_2$ surface at room temperature and without employing any flexible buffer layer or organic adhesion promoter or release agent in between mold and substrate. Using the developed direct nTP process we created PdAu gaps comprising widths significantly smaller than 15 nm. Experiments revealed that the resolution of the process can be improved by inducing gap narrowing through shadow-mask evaporation of transfer material onto the mold pattern.

High contact pressure in a "hard-on-hard" mold/substrate arrangement during nTP cycles yields a high mold wear. Additionally, since no flexible interface layer exists even slightest particle contamination of the mold/substrate interface causes mold features either to bend, break or not be in physical contact with each other. Therefore our best direct nTP results show a pattern transfer efficiency of $\sim 80\%$, i.e. approximately 80% of the coated total mold pattern area is transferred onto the substrate in each nTP experiment (fig. 5.1a, fig. 5.2a), and $\sim 80\%$ of all mold structures are well preserved during the process (fig. 5.3b, fig. 5.3c, fig. 5.4b).

The introduced direct nTP scheme is capable of generating grating struc-
5.2 ULTRA-HIGH RESOLUTION DIRECT NTP AND NIL USING CEO-MOLDS

There are possibilities with sub-10-nm resolution. Pitch and linewidth variations are the two 1D degrees of freedom regarding the design of these grating structures. However, applications can be thought of that require fabrication of 2D nano-electronic or nano-optoelectronic circuits comprising molecular dimensions and components: sensors, (photo)detectors, measuring setups enabling physical characterization of molecules, and data storage units. In the following section I will discuss how the demonstrated 1D direct nTP process could be expanded into a nTP technique that will be capable of repeatably printing 2D rectangular structures with feature sizes in the sub-10-nm region forming orthogonal pattern geometries having molecular dimensions.

5.2 Ultra-high resolution direct nTP and NIL using CEO-molds

The extended nTP technique that we introduce is based on an innovative mold fabrication process expanding the already demonstrated fabrication scheme for MBE-molds by incorporating cleaved edge overgrowth-technology (CEO) [20]. CEO can be used to create 2D and lower dimensional quantum wire structures by in situ cleaving a MBE treated sample and further growing of additional layers on the cleaved edge [152][153][154][155]. However, up to date these techniques were exclusively used to generate a 2D charge doping landscape around the cleaved edges but no topographical 2D landscape. Our innovative extension of these techniques is to selectively etch the layers grown by CEO in order to generate a three-dimensional surface profile that we then use as CEO-molds to perform the demonstrated direct nTP process yielding transferred orthogonal patterns with sub-10-nm resolution. We refer to this ultra-high resolution nanotransfer printing scheme as cleaved-edge-overgrowth nanotransfer printing (CEO-nTP).

Our invented CEO-mold fabrication technique provides 3D rectangular mold patterns with molecular resolution in both 2D lateral directions because the dimensions in both lateral directions are determined through the subsequent MBE growth steps as part of the CEO mold fabrication procedure. Hence the innovative scheme that we introduce extends current state-of-the-art high-resolution mold-fabrication techniques [18][76][142] from fabricating 3D rectangular mold patterns with longitudinal 1D molecular resolution to fabricating 3D rectangular mold patterns with lateral 2D molecular reso-
lution. The complexity of the lateral 2D mold geometry of CEO-molds is exclusively determined by the CEO growth scheme since the selective etch characteristics of the CEO grown layer sequence is determined by the layer materials and thicknesses.

CEO-molds could also be applied in various nanoimprint techniques (CEO-NIL), such as for example conventional thermal NIL, RTNIL, or SFIL. Figure 5.6 illustrates the fabrication scheme of a CEO-mold. Figure 5.7 and Fig. 5.8 demonstrate the principles of CEO-nTP, and CEO-NIL respectively.

CEO-nTP and CEO-NIL will be the first lithography techniques capable of generating 2D orthogonal pattern geometries in the sub-10-nm region in a repeatable and predefined way. Experiments are currently being prepared to demonstrate CEO-nTP and CEO-NIL. If for example employed in NAIL processes CEO-molds will offer more degrees of freedom regarding the design of pattern geometry in controlled nanomanufacturing than any other existing lithography technique.
5.2. ULTRA-HIGH RESOLUTION DIRECT NTP AND NIL USING CEO-MOLDS

Figure 5.6: CEO-mold fabrication scheme: (a) in a first MBE step a sequence of layers of AlGaAs and GaAs comprising thicknesses of down to a few nanometers is grown on a GaAs substrate, (b) in a first cleaving step the sample is cleaved whereas the cleaving plane is perpendicular to the MBE growth plane, (c) in a second MBE step a sequence of layers of AlGaAs and GaAs comprising thicknesses of down to a few nanometers is grown on the cleaving plane, (d) in a second cleaving step the sample is cleaved in a plane that is perpendicular to both MBE growth planes as defined in steps (a) and (c), and a topographical 3D landscape with 2D lateral molecular resolution is created by selectively etching AlGaAs with respect to GaAs or vice versa. These 2D lateral directions are spanning a plane that is perpendicular to both cleaving planes. The spacing between lines and grooves as well as the number of lines and grooves are dependent on the character of the layer sequences grown in steps (a) and (c).
Figure 5.7: Ultra-high resolution nano-transfer printing using CEO-molds: (a)-(c) the CEO-molds are prepared and the nanotransfer printing procedure is carried out according to the demonstrated direct nTP scheme. The invented CEO-nTP procedure allows for achieving 2D molecular resolution and simultaneously a significantly higher flexibility of the printed patterns. (d) these patterns could for example be used to build the first molecular three terminal device, such as for example the first molecule-based transistor, a task that has been pursued with great vigour by leading research groups in the field. While the spacing between contact pads reaches molecular dimensions the overall dimensions of the pattern components can be much bigger allowing for contacting these components by classical optical or e-beam lithography.
5.2. ULTRA-HIGH RESOLUTION DIRECT NTP AND NIL USING CEO-MOLDS

Figure 5.8: Ultra-high resolution nanoimprint using CEO-molds: (a), (b) the nanoimprint lithography process is based on conventional NIL processes. If one uses a transparent substrate material as carrier for the imprint polymer layer UV- and/or, infrared-curing NIL can be performed by applying backside exposure of the sample. The imprinted pattern can be transferred into the underlying substrate layer in two different ways that yield a positive, or negative pattern structure respectively. (c) if a negative final desired pattern is needed in the substrate a lift-off process is performed: After a thin-film etch mask (e.g. metal) has been evaporated onto substrate and imprinted polymer areas the positive components of the imprint polymer are removed while the non-imprinted areas are preserved. After removal of all polymer material the imprinted pattern can be etched into the substrate layer. Residual etch mask material is stripped off. (c) if one aims at a positive final desired pattern in the substrate layer a RIE-based pattern transfer process as described in section 3.7 of this thesis is carried out.
Chapter 6

Conclusion and Outlook

Based on the project roadmap as laid out in section 1.2 of this thesis the core accomplishments of the presented work can now be summarized. It has to be emphasized that all three demonstrated nanoimprint techniques (NAIL, MBE-RTNIL, and direct MBE-nTP/CEO-NIL) are innovative process schemes that were introduced to the nanofabrication community for the first time. Our respective generic publications and patent references are listed in appendix E and are also included in the following summarizing overview:

1. We demonstrated for the first time sub-15-nm room-temperature nanoimprint lithography (RTNIL) and sub-10-nm direct nanotransfer lithography (nTP) using GaAs/AlGaAs stamps fabricated by molecular-beam-epitaxy (MBE) and selective etching. Polystyrene was employed as RTNIL polymer, and PdAu/Ti served as nTP transfer materials. Silicon/siliconoxide was chosen as substrate material for both developed nanolithography techniques. An extended technological approach enabling ultra-high-resolution RTNIL and nTP by using stamps fabricated by a combination of MBE and cleaved-edge overgrowth (CEO) was theoretically introduced.  

2. An innovative multi-step room-temperature nanoimprint lithography technology that we call Nanotemplate Arbitrary-Imprint Lithography (NAIL) has been developed. NAIL is capable of creating complex and near-arbitrary patterns without requiring a custom template for each new pattern. NAIL performs multiple imprints with general templates
rather than a single imprint with a custom template to print out a final desired pattern. This technique represents a fundamental shift in how nanoimprint is performed: it removes the difficult, slow, and cost-intensive step of custom-mask manufacturing from the process. Rapid prototyping applications in academic as well as industrial research and development environments could significantly profit from NAIL technology. [14][15][16][17]

3. We developed a pattern transfer process based on RIE and oxygen plasma etching steps for transferring complex patterns generated in NAIL experiments into silicon/siliconoxide substrates. The complete nanofabrication process cycle from geometric pattern design via establishing a lithographic process for structuring a resist layer to post-processing generated patterns finally transferring them into a substrate material could be demonstrated. [14][15][17]

4. A tool prototype capable of performing multi-step RTNIL (NAIL) cycles was designed, built, assembled and put into operation. Allowing to develop and optimize an advanced proof-of-concept experiment for the invented NAIL technology this tool prototype showed that NAIL technology bares the potential to become an attractive competitor of current state-of-the-art radiation based parallel nanolithography techniques such as p.ex. electron beam lithography, and focused-ion-beam lithography. [14][15][17]

5. A second tool prototype enabling high-precision mounting, leveling, and positioning of MBE-stamps in RTNIL and direct nTP processes was designed, built, assembled and started up. A special hydraulic cylinder and hydraulic control unit was custom-built in cooperation with several industry partners to enable ultra-fine motion of delicate MBE-molds. Design and performance of the prototype tool opened a new field for applications of hydraulic machine design. [20][21][appendix E]

6. Imaging schemes based on a combination of dark-field optical microscopy, atomic force microscopy using high-resolution tips, as well as scanning electron beam microscopy were established enabling analyses of imprinted and transferred patterns. Since the innovative nano-
lithography processes that we introduced yield feature sizes in the sub-10-nm region imaging becomes increasingly demanding, and requires complex sample preparation incorporating special cleaving procedures and sputtering techniques as well as professional microscope operation.

7. We tested and analyzed a large spectrum of imprint polymers (p.ex. polystyrene (PS) with different molecular weights, PMMA, HSQ, P3HT, PDMS, mr-NIL 6000), transfer materials (Au, PdAu, Pt), substrate materials (for example fused silica quartz plates, silicon/siliconoxide, PDMS), mold components (p.ex. silicon, fused silica quartz disks, GaAs/AlGaAs), and surface chemicals and self-assembled monolayers (various silane formulas, titanium) and extracted data for developing and optimizing innovative nanotransfer and nanoimprint lithography processes. [14][15][17][18][19][22][44][156]

Further work will concentrate on designing, building and putting into operation an advanced NAIL prototype for the sub-15-nm region offering improved mold-substrate alignment and positioning capabilities, thus minimizing imprint polymer deformation and distortion. We will also demonstrate ultra-high resolution CEO-NIL and CEO-nTP using experimental data obtained from MBE-NIL, and MBE-nTP respectively. Transferred PdAu/Ti structures that we generated by direct MBT-nTP will be used as platform for electronic measurements, eventually enabling electronic characterization of a variety of not only elemental, but also artificially synthesized, custom-designed molecules that we are currently developing in close cooperation with several industrial and academic collaboration partners.

Our work proved that although numerous impressive and creative technological achievements have emerged in the recent past, the field of nanoimprint lithography still remains an highly active area of research that offers great potential for developing and improving methods of ultra-high-resolution controlled nanomanufacturing in the future.
Appendix A

Design Drawings for NAIL-Tool

The machine drawings provided on the following pages have been used to machine the prototype tool for introducing the invented NAIL technology (chapter 3). All drawings were generated manually. The complete tool design is protected by [16].

Figure A.1: Photograph of the complete assembled core unit of the NAIL prototype system as described in the attached set of machine drawings.
Nanoimprintlithography System

(Machine Drawings)

folder contains one assembly drawing plus
detailed machine drawings for the UV-shield as
well as for the mask-holder unit

<table>
<thead>
<tr>
<th>label</th>
<th>description</th>
<th>material</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>UV-shield/left side</td>
<td>plexiglas</td>
</tr>
<tr>
<td>s2</td>
<td>UV-shield/right side</td>
<td>plexiglas</td>
</tr>
<tr>
<td>s3</td>
<td>UV-shield/front side</td>
<td>plexiglas</td>
</tr>
<tr>
<td>s3a</td>
<td>UV-shield/front side window</td>
<td>plexiglas</td>
</tr>
<tr>
<td>s4</td>
<td>UV-shield/back side</td>
<td>plexiglas</td>
</tr>
<tr>
<td>s4a</td>
<td>slide lock/articulation</td>
<td>stainless steel</td>
</tr>
<tr>
<td>s4b</td>
<td>slide lock/articulation</td>
<td>stainless steel</td>
</tr>
<tr>
<td>s4c</td>
<td>slide lock/lever</td>
<td>stainless steel/rubber</td>
</tr>
<tr>
<td>s4d</td>
<td>slide lock/lever</td>
<td>stainless steel/rubber</td>
</tr>
<tr>
<td>s5 &amp; wgm</td>
<td>UV-shield/fixed top cover &amp;</td>
<td>plexiglas</td>
</tr>
<tr>
<td>s6</td>
<td>UV-shield/removable top cover</td>
<td>plexiglas</td>
</tr>
<tr>
<td>s7a</td>
<td>mount for s2 on optical bench</td>
<td>any metal</td>
</tr>
<tr>
<td>s7b</td>
<td>mount for s2 on optical bench</td>
<td>any metal</td>
</tr>
<tr>
<td>s7c</td>
<td>mount for s1 on optical bench</td>
<td>any metal</td>
</tr>
<tr>
<td>s7d</td>
<td>mount for s1 on optical bench</td>
<td>any metal</td>
</tr>
<tr>
<td>p1</td>
<td>pole for mask-holder</td>
<td>stainless steel</td>
</tr>
<tr>
<td>p2</td>
<td>pole for mask-holder</td>
<td>stainless steel</td>
</tr>
<tr>
<td>p3</td>
<td>pole for mask-holder</td>
<td>stainless steel</td>
</tr>
<tr>
<td>m1</td>
<td>Mask-holder</td>
<td>stainless steel</td>
</tr>
<tr>
<td>microscope extension plate</td>
<td>y-extension plate for microscope stage</td>
<td>stainless steel</td>
</tr>
<tr>
<td>wafer vacuum plate</td>
<td>wafer vacuum plate</td>
<td>aluminium</td>
</tr>
</tbody>
</table>

Stefan Harrer
same measurements at piece s1

s1 & s2 replaced by m1 & m2 (→ drawing below)

---

all measurements in [mm] (not indicated = [mch])
s3a
- piece s3a fills exactly the red colored space in the machine drawing of piece s3.
- get measurements from __________
- for better survey ________ exploded drawing

s4
- piece s4 is exactly the same as piece s3 EXCEPT:
  red colored space in the machine drawing of piece s3 is not cut out (no window s3a)
- get measurements from machine drawing of __________
- for better survey ________ exploded drawing
A. DESIGN DRAWINGS FOR NAIL-TOOL

All measurements in [mm]
A. DESIGN DRAWINGS FOR NAIL-TOOL

- 2002
- top view
- side view of level 1
- side view of level 2
- I need that cut-out plate @ wave guide mount wgn

if not indicated differently:
all measurements in mm
any metal will do

basically any metal angle will do - given measurements are bench marks ±5 mm, except h (see machine drawing for piece s1)

(all measurements in mm)
p2 & p3 are exactly the same as p1

level 1

level 2

top view and bottom view respectively are exactly the same (level 1 = level 2)

tolerance: ±0.01 mm

all measurements in [mm]
Appendix B

Design Drawings for MBE-RTNIL/nTP Tool

The machine drawings (generated in MS O PPT 07) provided on the following pages have been used to machine the sub-15-nm MBE-RTNIL prototype-tool (chapter 4). Drawings 11/12 describe adapter plates allowing for including a high-precision x-y-z-stage upgrading the MBE-RTNIL tool to a simplified NAIL-tool. The complete tool design is protected by [20].

Figure B.1: Photograph of the complete assembled core unit of the MBE-RTNIL/nTP prototype system as described in the attached set of machine drawings.
Bauplan für ein hydraulikgesteuertes single-step Nanoimprintlithographie Gerät für den sub-10-nm Bereich

(Stefan Harrer, Sebastian Strobel, Kontaktinfo auf S.16)

Dezember 2006

- 16 Blattincl. Titelblatt, Bausatz beschreibt 14 Einzelteile, Hydraulikzylinder nicht enthalten -
3. **Stempelklemmplatte** | alle Maße in [mm] | Stahl | Toleranz [mm]
---|---|---|---
1 x

![Diagram of Stempelklemmplatte]

4. **Klemmplatte für bewegliche Platte** | alle Maße in [mm] | Stahl | Toleranz [mm]
---|---|---|---
1 x

![Diagram of Klemmplatte für bewegliche Platte]
### Bewegliche Platte

<table>
<thead>
<tr>
<th>1 x</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Maße in mm</th>
<th>Stahl</th>
<th>Toleranz</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>15</td>
<td>125</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

Draufsicht | Seitenansicht

SB = Schlitzbreite = \( 0.5 + 0.01 \) nicht maßstabsgetreu

### Schaumstoffstreifen

<table>
<thead>
<tr>
<th>1 x</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Maße in mm</th>
<th>Schaumstoff</th>
<th>Toleranz</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Draufsicht | Seitenansicht

SB = Schlitzbreite = \( 0.5 + 0.01 \) nicht maßstabsgetreu
Kontakt:

?Stefan Harrer
Lehrstuhl für Nanoelektronik (TUM)
phone: +49-(0)89-289-25320
mobile: +49-(0)171-490-7673
fax: +49-(0)89-289-25337
email: sharrer@tum.de

?Sebastian Strobel
Walter-Schottky-Institut (TUM)
phone: +49-(0)89-289-12775
fax: +49-(0)89-320-6620
email: mail@sstrobel.de
Appendix C

MBE-RTNIL using P3HT as Imprint Polymer

The $p$-type semiconducting polymer poly(3-hexylthiophene) (P3HT) is one of the most efficient optically active materials primarily employed in fabrication processes of organic solar cells [157][158], and organic thin film transistors [159]. Developing a RTNIL process enabling direct patterning of a P3HT layer yielding a 3D surface topography with feature sizes in the sub-50-nm region could enable high-throughput, and large-area fabrication of organic solar cells.

We investigated the potential of the developed MBE-RTNIL process (chapter 4) for being able to provide that patterning capability. The imprint polymer layer consisted of P3HT (purchased from Rieke) that was first dissolved in toluene to a concentration of 2% by weight. We cleaned a silicon wafer in an oxygen plasma ashing for 2min, spin-coated the P3HT/Toluene solution onto it at 1 krpm, and baked it at 140°C for 15 minutes resulting in a 100-nm-thick P3HT layer. Using a positive multi-line MBE-mold as shown in fig. 4.4 we then carried out the exact same single-step MBE-RTNIL process as described in section 4.3.2 of this thesis. Experimental results are shown in fig. 4.1.

Sidewall and surface characteristics of imprinted P3HT patterns have to be improved in order to establish a RTNIL process that is capable of reproducing high-quality sub-50-nm features. However, we could demonstrate that P3HT can be imprinted in the sub-50-nm region at room-temperature by performing the developed MBE-RTNIL scheme.
Figure C.1: SEM top-view images of a multi-line pattern imprinted into a P3HT layer at room-temperature using a positive multi-line MBE-mold as shown in fig. 4.4 and carrying out the exact same MBE-RTNIL process as described for PS as imprint polymer (section 4.3.2). The SEM images show three imprinted grooves whereas the 21-nm-wide groove was generated by the 19-nm-wide line on the mold, the 39-nm-wide groove corresponds with the 36-nm-wide line on the mold, and the 51-nm-wide groove results from imprinting the 55-nm-wide line on the mold. As opposed to results obtained for PS (Fig. 4.12) imprinted P3HT patterns show poor sidewall and surface characteristics and are less deep. Performing MBE-RTNIL using the same MBE-mold and imprint parameters yielded wider imprinted grooves for P3HT than for PS.
Appendix D

Combined Thermal and UV-NIL

The introduction of deep UV lithography with improved quartz lenses and high-output light sources brought major improvements to conventional lithography techniques [138]. Milestones of the development of UV Lithography (UVL) were the invention of UV-zone-plate array lithography (UV-ZPAL) [162] and immersion ZPAL [163]. Recently reported results show that UV-nanoimprint lithography (SFIL) in general has reached a level that allows the fabrication of electronic devices (such as amorphous silicon thin-film transistors (TFT) [161]) and structures reaching the 20-nm-scale [28]. In order to further extend the success of the SFIL technique, its resolution, overlay, and throughput need to be improved [141]. This can be done by developing new imprint polymers, looking in particular at critical parameters such as sensitivity to UV light, thermal stability, surface tension, shrinkage, Young modulus, viscosity, and etch resistance. A novel version of NIL that we introduced combines UV radiation with thermal treatment of imprint polymers [22]. Combined thermal NIL and SFIL (TUV-NIL) uses the effect that a polymer patterned by thermal NIL can be cured by exposing it to UV radiation while keeping it at its imprint temperature $T_{\text{imprint}}$ before stamp release. This enables a complete isothermic imprint cycle at $T_{\text{imprint}}$ [23] [24]. Further more, TUV-NIL imprint polymers can be designed in such a way that their imprint temperature $T_{\text{imprint}}$ matches a desired constant process temperature. As opposed to conventional SFIL using polymers that are in a liquid state before they are cured, TUVNIL polymers form a solid
film after spin-coating the polymer solutions and a post-apply bake and are therefore not only easier to handle when distributed over the substrate, but also show a significantly lower tendency to adhere contaminating particles before the imprint step.

Hence TUV-NIL technology has three major advantages when compared to conventional thermal NIL, and conventional SFIL respectively: (i) as opposed to conventional SFIL processes which employ imprint liquids that are poured onto a substrate TUV-NIL is based on an imprint polymer that can be spun onto a substrate and therefore allows for precisely controlling the thicknesses of polymer layers before and after imprinting them, (ii) all TUV-NIL process steps are performed at the same temperature $T_{imprint}$, i.e. no cooling of the imprinted polymer is necessary in order to cure it before mold release. TUV-NIL cycles are therefore significantly shorter than conventional thermal NIL processes. (iii) thermal expansion effects of mold features with respect to the substrate material during the imprint cycle are completely eliminated since no temperature gradient exists during the isothermal TUV-NIL process.

D.1 Description of TUV-NIL tool

We used a commercially available state-of-the-art NIL tool (Obducat 2.5" equipment, Obducat, Sweden) for carrying out the TUV-NIL processes. The mold is manually positioned upside down onto the imprint polymer layer on the silicon/silicon oxide substrate so that the features on the mold face the surface of the imprint polymer layer. This mold/substrate sandwich structure is put onto the bottom plate of a gas-tight and optionally heatable / coolable chamber which can also optionally be flooded with UV-light through its top plate. The mold/substrate-unit is covered with a UV-transparent PDMS foil separating the chamber into two sections: the upper section between top plate and foil, and the bottom section between foil and bottom plate (containing also the mold/substrate-unit). The imprint step is performed by pumping air into the upper section pressing foil and mold down against the substrate and hence the mold features into the imprint polymer layer. The imprint pressure is directly determined by the amount of air that is pressed into the upper section. Imprint duration, imprint temperature, imprint pressure as well as UV-exposure process steps are computer-controlled,
D.2. DEVELOPMENT OF TUV-NIL PROCESS

We used two types of commercially available quartz molds, both types being transparent to UV-light and comprising the following positive features on their surfaces: a type I mold (Obducat, Sweden) provided (i) 150-nm-deep and 300-nm-wide lines, (ii) 150-nm-deep and 100-nm-wide lines, and (iii) 150-nm-deep squares having a side length of 200 nm, while a type II mold (NIL Technology, Denmark) carried (iv) 190-nm-high circular pillars with a diameter of 50 nm.

All stamps were cleaned by a 15-minute-immersion in H$_2$O:H$_2$O$_2$:NH$_4$OH solution in ratio 5:1:1 at 80°C removing organic residues before imprinting. To avoid adhesion of the imprinted polymer to the molds, their surfaces were first fluorinated by vapor deposition of tridecafluoro 1,1,2,2-tetrahydrooctyl thichlorosilane [105] (CF$_3$-(CF$_2$)$_5$-CH$_2$-CH$_2$-SiCl$_3$ from Gelest, Inc.) and then post-baked at 100°C for 1 h. We spun the epoxy-based imprint polymer mr-NIL 6000 onto a silicon substrate covered with a 200-nm-thick silicon oxide layer at 3000 rpm for 30 s and post-apply baked it for 3 min at 100°C yielding a 200-nm-thick imprint polymer layer. The TUV-NIL cycle began by heating the polymer up to an imprint temperature $T_{imprint}$ of 100°C and then imprinting it at 50 bar for 240 s. The glass transition temperature $T_g$ of uncured mr-NIL 6000 is 40°C. Then the imprinted polymer was cured by flood-exposing it to UV-light for 30 s while holding the imprint temperature constant. Before mold release the imprinted and cured imprint polymer was annealed at $T_{imprint}$ for 300 s supporting stress release in the deformed polymer material. Figure D.1 shows imprinted polymer surfaces structured by the described TUV-NIL process for all four different kinds of mold features (i)-(iv).

When using a type I mold we observed a constant imprint depth of 150 nm and a constant thickness of the residual polymer layer at the bottom of imprinted structures of 50 nm. The imprint depth for imprinted type II mold features was 180 nm, the corresponding thickness of the residual layer was 20 nm. These measurements indicate that the imprint polymer completely filled the patterns of the mold during the imprint process. All imprint results
Figure D.1: Imprint results for a standard combined thermal and UV-nanoimprint lithography process into a mr-NIL 6000 imprint polymer layer using transparent quartz molds: SEM top-views of (a) 300-nm-wide lines, (b) 100-nm-wide lines, and (c) squares comprising a side length of 200 nm all fabricated using type I molds (Osbudcat, Sweden), and (d) AFM 3-D topographic top view of 50-nm-diameter holes imprinted by means of type II molds (NILT Technology, Denmark). All imprint results show good surface characteristics as well as constant imprint depth and thickness of residual polymer layer at the bottom of imprinted grooves.

show very low surface roughness.

D.3 Pattern transfer into underlying layers

The TUV-NIL procedure was completed by transferring the imprinted patterns from the imprint polymer layer into the silicon oxide layer on top of the silicon substrate. In a first step we performed an O$_2$ reactive ion etch (RIE) introducing an oxygen flux of 10 sccm under a pressure of approximately 10$^{-5}$ bar and applying a power of 80 W for 1 min (type I mold patterns) and for 40 s (type II mold patterns) to etch down the mr-NIL 6000 layer everywhere until all residual polymer was removed from the bottom areas of imprinted grooves. The etch rate of the O$_2$-RIE for mr-NIL 6000 was $\sim 50$ nm/min. In a second step we transferred the imprinted patterns into the silicon oxide layer by means of a combined C$_4$F$_8$ (30 sccm)/SF$_6$ (20 sccm) RIE process applying a power of 15 W for 5 min. The etch rate of the combined C$_4$F$_8$/SF$_6$-RIE process for silicon oxide was $\sim 0.5$ nm/min. We could
etch the transfer pattern $\sim 25\,\text{nm}$ into the silicon oxide layer. Finally the residual polymer material was stripped off in an $O_2$ plasma asher for 10 min. Figure D.2a and fig. D.2b show experimental results for this pattern transfer process for the same structures as shown in fig. D.1a and fig. D.1c. All residual polymer material had been removed, so the images show clean silicon oxide surfaces.

We demonstrated combined thermal and UV-nanolithography (TUV-NIL) using UV-transparent quartz molds for imprinting into the epoxy-based nanoimprint polymer mr-NIL 6000 spun on silicon oxide. Our best imprint results showed feature sizes of down to 50 nm whereas this limit was determined by the minimum feature size of commercially available mold structures. All imprint results showed good surface characteristics. Current work focuses on (i) transferring imprinted features with dimensions between 50 nm and 100 nm into the silicon oxide layer yielding transfer patterns with good surface and sidewall characteristics as well as (ii) further pushing the minimum feature size of imprinted patterns into the sub-50-nm region. Further work will incorporate decreasing the total TUV-NIL process time, thus enabling TUV-NIL to become applicable for high-throughput purposes.

**Figure D.2:** SEM images of etched patterns shown in Fig. D.1a and D.1c: SEM images of (a) a 300-nm-linewidth pattern, and (b) a 200-nm-sidelength square pattern after being transferred into the underlying silicon oxide layer. Residual mr-NIL 6000 imprint polymer was completely removed by means of an $O_2$ plasma asher.
D. COMBINED THERMAL AND UV-NIL
Nomenclature

Latin Letters

- $T_g$: glass transition temperature
- $M_w$: molecular weight
- $Z$: atomic number
- $t_{imprint}$: imprinting time
- $T_{imprint}$: imprinting temperature
- $P_{imprint}$: imprinting pressure
- $P_{min}$: minimum imprinting pressure
- $P_{opt}$: optimum imprinting pressure
- $P_{break}$: mold-breaking imprinting pressure
- $D$: step size
- $t_n$: distinct points of time in nan imprint sequences
- $g$: gap size
- $L$: linewidth
- $s$: linewidth covered by transfer material
- $sg$: linewidth not covered by transfer material
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIL</td>
<td>Nanoimprint Lithography</td>
</tr>
<tr>
<td>nTP</td>
<td>Nanotransfer Lithography</td>
</tr>
<tr>
<td>SNAP</td>
<td>Superlattice Nanowire Pattern Transfer</td>
</tr>
<tr>
<td>µCP</td>
<td>Micro Contact Printing</td>
</tr>
<tr>
<td>ZPAL</td>
<td>Zone Plate Array Lithography</td>
</tr>
<tr>
<td>T−NIL</td>
<td>Thermal Nanoimprint Lithography</td>
</tr>
<tr>
<td>SFIL</td>
<td>Step-and-Flash Imprint Lithography</td>
</tr>
<tr>
<td>(S)EBL</td>
<td>(Scanning) Electron Beam Lithography</td>
</tr>
<tr>
<td>NAIL</td>
<td>Nanotemplate Arbitrary-Imprint Lithography</td>
</tr>
<tr>
<td>RTNIL</td>
<td>Room-Temperature Nanoimprint Lithography</td>
</tr>
<tr>
<td>TUV−NIL</td>
<td>Combined Thermal and Ultraviolet-Curing Nanoimprint Lithography</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>MBE−RTNIL</td>
<td>Room-Temperature Nanoimprint Lithography using Molds fabricated by MBE</td>
</tr>
<tr>
<td>MBE−nTP</td>
<td>Nanotransfer Lithography using Molds fabricated by MBE</td>
</tr>
<tr>
<td>CEO</td>
<td>Cleaved Edge Overgrowth</td>
</tr>
<tr>
<td>Term</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------------------------------</td>
</tr>
<tr>
<td>CEO − NIL</td>
<td>Nanoimprint Lithography using Molds fabricated by a combination of MBE and CEO</td>
</tr>
<tr>
<td>CEO − nTP</td>
<td>Nanotransfer Lithography using Molds fabricated by a combination of MBE and CEO</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Lithography</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Lithography</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive Ion Etching</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
</tr>
<tr>
<td>HSQ</td>
<td>Hydrogen silsequioxane</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric Acid</td>
</tr>
<tr>
<td>CAS</td>
<td>Citric Acid Solution</td>
</tr>
<tr>
<td>SAM</td>
<td>Self Assembled Monolayer</td>
</tr>
<tr>
<td>ARC</td>
<td>Anti Reflection Coating</td>
</tr>
</tbody>
</table>
Appendix E

List of Publications

The following publications directly evolved from this thesis:

Conference proceedings papers


Peer reviewed journal papers


Patents


Book chapter


---

This paper was awarded the 2006 IEEE Student Best Paper Award in Nanotechnology [http://www.ececs.uc.edu/~mealhay/Nano2006/index2006.html]
Press coverage and miscellaneous


Bibliography


barella, and L. Favaretto. Oligomer-based organic distributed feedback
lasers by room-temperature nanoimprint lithography. Applied Physics

[12] P. Del Carro, A. Camposeo, R. Stabile, E. Mele, L. Persano, R. Cing-
golani, and D. Pisignano. Near-infrared imprinted distributed feedback

Multilevel, room-temperature nanoimprint lithography for conjugated

and C.A. Ross. Pattern Generation by Using Multi-Step Room-
Temperature Nanoimprint Lithography. Nanotechnology, IEEE Trans-

Pattern generation by using multi-step room-temperature nanoimprint

MIT 11746.

Pattern Generation by Using Multi-Step, Room-Temperature, Nano-
imprint Lithography. Progress Report 2006, Research Laboratory of

P. Lugli. Room-Temperature Nanoimprint Lithography Using Molds
Fabricated by Molecular-Beam-Epitaxy. Nanotechnology, IEEE Trans-
actions on, 2, 2008.

and G. Abstreiter. Advances in nanoimprint lithography, invited paper. In

P. Lugli, and G. Abstreiter. Ultrahigh Resolution Nanoimprint Lithog-
raphy and Ultrahigh Resolution Nanotransfer Printing in the sub-
10-nm Region by Using Molds Fabricated through a Combination of
Molecular Beam Epitaxy and Cleaved Edge Overgrowth, 2007. PCT


[76] M.D. Austin, W. Zhang, H. Ge, D. Wasserman, SA Lyon, and S.Y. Chou. 6 nm half-pitch lines and 0.04 μm² static random access memory patterns by nanoimprint lithography. *Nanotechnology*, 16(8):1058–1061, 2005.


