Laser interference lithography [3–22] (LIL) is a method to produce periodic structures using two interfering highly-coherent light beams. Typically, light from a source is divided and recombined, forming a periodic intensity pattern that can be recorded by the exposure of a photosensitive substrate. The primary focus of this thesis has been the setting up of a Lloyd’s-Mirror Interferometer. In this chapter, the fundamentals of laser interference lithography will be introduced step by step: The description of the basic theory of LIL, can be found in section 2.1; the working principle of the “Lloyd’s-Mirror Interferometer” and the whole optical setup are introduced in section 2.2; the preparation of the substrates before lithographic exposures and the design of the resist stack for LIL are explained in section 2.3; the aspects of the exposure process are discussed in section 2.4; finally, the structural transfer from the soft resist into a hard substrate by means of reactive ion etching (RIE) and wet chemical etching will be discussed in section 2.5.

2.1 BASIC THEORY: INTERFERENCE OF TWO BEAMS

Figure 1: Thomas Young (1773-1829), first demonstrated the interference of light in 1801 (Figure 1). [23,24] His famous interference experiment gave strong support to the wave theory of
light. This experiment (diagramed above) shows interference fringes created when a coherent light source is shining through double slits. Light sources available in 1800 were essentially flames. He produced coherent light by letting nearly monochromatic light through a pinhole, then using the light from that pinhole to fall on two other pinholes that were very close together.

Nowadays, lasers produce intense beams of monochromatic (single frequency) light. All the waves across the beam are in phase. If we use a laser beam to illuminate the slits, which are narrow to ensure adequate diffraction, the diffracted beams from the two slits overlap causing the superposition of two light waves, which appears on the screen as alternate dark and bright bands, called fringes. The bright fringes are caused by constructive interference and the dark fringes by destructive interference.

For lithographic applications, the most intuitive way to form a set of interference fringes is simply to split a beam into two, and then recombine the two beams. The intensity distribution of a superposition of two plane-waves will give a spatial structure that is non-uniform, known as sinusoidal form (Figure 2). Under the assumption of symmetry of incidence angle, the periodicity ($p$) of the fringe pattern of two interfering beams can be simply described with Equation 2.1, where $\lambda$ is the wavelength of the beams and $\theta$ is the half angle between the two incidence beams.

Figure 2: Interference of two coherent light waves and the intensity profile in a photoresist layer.
Figure 3 shows a simplified configuration of a Mach-Zehnder Interferometer \(^{[25]}\) for lithographic exposures. An UV laser is split in two arms which are recombined using a set of mirrors. Spatial filters in each arm serve to expand the beams for dose uniformity over a large area and to remove the spatial frequency noise. Due to the long propagation distance and the lack of additional optics after the spatial filters, the beams interfering at the substrate can be accurately approximated as spherical. A set of sensors and a compensation system are used to correct the phase errors. The whole setup should be placed on an actively damped optical table in order to filter the vibrations.

![Schematic illustration of a Mach-Zehnder Interferometer](image)

However, accurate positioning and precise alignment are required to produce a single grating structure with Mach-Zehnder Interferometer. When the grating periodicity has
to be changed, a complete and time-consuming re-adjustment of the whole optical setup has to be pursued, which limits the flexibility of Mach-Zehnder Interferometer in many cases.

2.2 EXPERIMENTAL SETUP

2.2.1 LLOYD’S-MIRROR INTERFEROMETER

As introduced above, the versatility of the Mach-Zehnder Interferometer is limited. Furthermore, beyond gratings, there are a number of periodic patterns that can be created through multiple exposures, for example, hexagonal or square arrays. Applications that require a multitude of different periods, such as nanostructures with an anisotropic shape, are difficult to realize using the traditional Mach-Zehnder Interferometer.

Figure 4: Schematic illustration of the principle of Lloyd’s-Mirror system comparing it to the Mach-Zehnder Interferometer [25].

Mach-Zehnder Interferometer and Lloyd’s-Mirror Interferometer, both systems are designed to produce high-contrast interference pattern with a high spatial-frequency over a large exposure area. In fact, as shown in Figure 4, the ideal Lloyd’s-mirror is optically equivalent to half of a Mach-Zehnder Interferometer. Consider the plane of
symmetry for the Mach-Zehnder located halfway between the two sources and which determines the angle of interference. The system on either side of this plane is a mirror image of the other side. Thus, if indeed we would place a mirror in this plane, the resulting set of interference fringes would remain unchanged.\textsuperscript{[25]}

In this work, the Lloyd’s-Mirror Interferometer (Figure 5) was utilized for the lithographic exposures. The Lloyd’s-Mirror Interferometer consists of an aluminum mirror (Linos), which has a roughness \( \leq \lambda/2 \) and a very high reflectivity (> 92\%) for the HeCd laser, placed perpendicular to the sample holder. The aluminium mirror was chosen due to its enhanced UV reflectivity compared to other mirrors and for its essentially constant reflectivity over a broad range of angles. Our interferometer was designed to expose up to 4 inch substrates. To minimize the effects of edge scattering and diffraction, it would be desirable to use a mirror which is larger than the exposed substrate. The mirror currently in use is 10 ×15 cm.

![Figure 5: (a) Schematic illustration of the basic principle of Lloyd’s-Mirror Interferometer; and (b) a photograph of our interferometer.](image)

The laser is expanded and spatially filtered through a pinhole to generate a coherent beam with a ca. 30 cm in diameter at the interferometer. The UV beam illuminates both the mirror and the sample. Part of the light is reflected on the mirror surface and interferes with the portion of the beam that is directly illuminating the sample. This interference will give a line pattern with a periodicity given by Equation 2.1, where \( \lambda \) is the wavelength of the laser beam (here fixed at 325 nm) and \( \theta \) the angle between the incidence light and the sample normal. By changing the incidence angle \( \theta \) with the
rotation stage, the periodicity \((p)\) can easily be adjusted from 170 nm to 1.5 \(\mu m\) in this case.

## 2.2.2 Optical Setup

![Figure 6: Schematic illustration of optical setup of LIL.](image)

A simplified diagram of the optical setup is shown in Figure 6. In this work, we have used a HeCd laser with a wavelength of 325 nm and an output intensity of 60 mW as a light source. HeCd offers a long (30 cm) coherence length at a mid-UV wavelength in a more robust package and at a lower cost than other options, such as argon-ion and excimer lasers. This UV laser is optically filtered with a commercial spatial filter (Newport) consisting of a UV objective lens with a focal distance of 5.77 mm and a pinhole of 5 \(\mu m\) in diameter, which allows high spatial-frequency noise to be removed from the beam to achieve a near-Gaussian beam. The Lloyd’s-Mirror Interferometer itself, consisting of a sample holder, mirror and rotation stage, is placed approximately 2 meters from the spatial filter. To prevent vibrations, which could disturb the interference pattern, the complete setup is built on an actively damped optical table of 1.5\(\times\)2.5 m. The optical components are placed in a closed cabinet to avoid air movements, which could affect the stability of the interference pattern.

As a Gaussian beam expands, it changes in three ways\[25\]. The intensity decreases, the diameter of the beam increases, and the radius of the phase front increases. Lowering the intensity leads to increased exposure times. Because of the Gaussian intensity profile, increasing the beam diameter ensures that the entire interferometer could be illuminated and creates a more uniform intensity distribution over the exposed area.
With this setup highly regular grating patterns can be produced over 2/3 of 4 inch wafer areas. Finally, the increase in radius of the phase front means that the beam more closely approximates a plane-wave over the exposure area, which is a very important assumption for the two-beam interference system. Thus, by maximizing the beam expansion, the exposed grating will have a more linear spatial phase and a more uniform line width, at the expense of a longer exposure time.

### 2.2.3 Calibration of the Experimental Setup

In stark contrast to the Mach-Zehnder Interferometer, the fringe period can be varied by simply rotating the interferometer. However, two conditions must be met to guarantee that to be optically equivalent. One is that the mirror is truly mounted perpendicular to the substrate. The other is that the interferometer axis defined by the intersection of the mirror surface and the substrate surface is the axis of rotation. The Lloyd’s-Mirror Interferometer must be calibrated by exposure experiments and investigations with SEM or AFM. These issues will be discussed further in the following sections.

#### 2.2.3.1 Angular Alignment of Mirror

![Figure 7: Misalignment of the mirror from normal by an angle of Δβ.](image)

For mirror angles not equal to 90 degrees, the symmetry will be broken and the image light source will be placed in a different position relative to the substrate than the real
source (Figure 7). This will result in a different incidence angle on the substrate for the reflected portion of the beam while the direct beam remains unchanged. The fringes will not form perpendicularly to the substrate and their periodicity will change. For a mirror angle which is equal to $\beta = 90^\circ + \Delta \beta$, the angle of inclination of the fringes will also be $\Delta \beta$. The periodicity $P_{\Delta \beta}$ of the fringes can be described with Equation 2.2.$^{[25]}$

$$P_{\Delta \beta} = \frac{\lambda}{2 \sin(\theta + \Delta \beta)}$$  \hspace{1cm} \text{Equation 2.2}

The fringe period recorded on the substrate $P_s$, shown in Equation 2.3$^{[25]}$ will be the projection of the new fringe period $P_{\Delta \beta}$ into the substrate plane.

$$P_s = \frac{P_{\Delta \beta}}{\cos(\Delta \beta)}$$  \hspace{1cm} \text{Equation 2.3}

Combining the two equations, we can solve for the grating period on the substrate, shown in Equation 2.4$^{[25]}$.

$$P_s = \frac{\lambda}{2 \sin(\theta + \Delta \beta) \cos(\Delta \beta)}$$  \hspace{1cm} \text{Equation 2.4}

For a tiny deviation $\Delta \beta$ of the mirror from normal, the cosine term can be approximated as unity, leaving $\Delta \beta$ as a calibration error.$^{[25]}$

### 2.2.3.2 Alignment of Rotation Axis

An exaggerated cartoon of the misalignment of rotation axis is show in Figure 8. Under the assumption that the incident light is planar, the direction of the incident wavefronts will be determined by the location of the pinhole or point source. If the axes of the interferometer and the rotation stage are misaligned, there will be a lateral shift of the point source $\Delta P$ as a function of the rotation angle $\alpha$ which creates an error $\alpha'$ in the interference angle $\theta$, where the maximum error will occur when the incidence angle is $90^\circ$ (Equation 2.5$^{[25]}$).
2.2.3.3 CALIBRATION WITH EXPOSED STRUCTURES

If we consider the misalignment of mirror angle and rotation axis, we can summarize the misalignments to a general constant error $p'$ and an angular error $\theta'$ to the period of the structures generated by LIL exposure (Equation 2.6).

$$p = \frac{\lambda}{2 \sin(\theta + \theta')} + p'$$

Equation 2.6
Lines structures were exposed under different incident angles with our interferometer and the periods of the samples were measured with an AFM. The calculated theoretical results comparing with the experimental results are shown in Figure 9a. From the curve it is apparent that all the experimental results are always larger than the corresponding
theoretical results with our interferometer. We can deduce that there must be an initial constant error $p'$ of $\sim 10$ nm, which can be deducted from the results. The angular error $\theta'$ ranging from $2^\circ$ to $4^\circ$ could be calculated from Equation 2.6. The deviations of the measured periods are characterized as error bars in Figure 9b. In case of structures with a period smaller than 500 nm, a deviation of less than 5% could be obtained, which is acceptable for most of the lithography techniques.

2.3  **PRETREATMENT OF THE SUBSTRATE**

2.3.1  **GENERAL INTRODUCTION TO THE SUBSTRATE**

In this work, silicon wafers have been mainly used as substrates for the performance of LIL exposures. The preparation, i.e., the cleaning processes of the wafers will be introduced in section 2.3.2. A SiO$_2$ or Si$_3$N$_4$ layer was usually deposited between silicon wafer and resist stack or on the interface of resist stack for the further structure transfers. The oxide layer on the silicon wafer was thermally oxidized, whereas the SiO$_2$ layer on the interface between resist layers was sputter deposited. As in common lithography techniques, photoresists are employed to record the lithographic pattern. However, the optical reflections on the interfaces could affect the lithographic results in the LIL process. ARC was employed to minimize the negative effects of the unwanted reflections on the interfaces, which will be detailed discussed in section 2.3.4. The typical substrate stack design is schematically illustrated in Figure 10. The polymer layers were realized using spin-coating technique in this work, which will be introduced in section 2.3.3.

![Figure 10: Schematic illustration of the cross-section of typical substrate stack used in this work.](image-url)
2.3.2 Wafer Preparation

As a pre-treatment, silicon wafers were always chemically cleaned in the MPI cleanroom facilities. Standard cleaning procedure, known as RCA-clean, \cite{1,2} which consists of a sequence of different wet clean processes, has been utilized in this work. RCA-1, RCA-2 and HF dip are each effective in removing different types of contaminations. Table 2.1 \cite{1} lists the main processes and information for the RCA-clean commonly in use.

<table>
<thead>
<tr>
<th>Process</th>
<th>Treatment/Chemical composition</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RCA-1 NH(_4)OH:H(_2)O(_2):H(_2)O (1:1:5)</td>
<td>75 °C, 10 min removal of organic dirt</td>
</tr>
<tr>
<td>2</td>
<td>Rinsing DI-water</td>
<td>Room temperature, 5 min</td>
</tr>
<tr>
<td>3</td>
<td>RCA-2 HCl:H(_2)O(_2):H(_2)O (1:1:6)</td>
<td>75 °C, 10 min removal of metal ions</td>
</tr>
<tr>
<td>4</td>
<td>Rinsing DI-water</td>
<td>Room temperature, 5 min</td>
</tr>
<tr>
<td>5</td>
<td>HF dip 1% aqueous HF</td>
<td>Room temperature, 30 sec removal of SiO(_2) layer</td>
</tr>
<tr>
<td>6</td>
<td>Rinsing DI-water</td>
<td>Room temperature, 5 min</td>
</tr>
<tr>
<td>7</td>
<td>Drying Spinning with nitrogen blowing</td>
<td>1(^{st}) step: 1800 U/min, 2min 2(^{nd}) step: 600 U/min, 2min</td>
</tr>
</tbody>
</table>

Standard chemicals come in the following concentrations:

NH\(_4\)OH 29%
2.3.3 Resist Film Deposition: Spin-Coating

The polymer films, such as photoresist and anti-reflection coatings, were deposited on the substrates by using the spin-coating technique. Spin-coating is a very widely used method for resist spinning. It is a reliable process for the deposition of thin films of viscous materials (e.g. polymers or sole gels) with precise control over film thickness on large substrate. A spinner (SÜSS MicroTec) with a typical spin speed up to 6000 rpm was used in this work. The dominant parameters for film thickness control via spin-coating are viscosity, solvent evaporation rate and spin speed. The principle of this technique is schematically illustrated in Figure 11.

![Figure 11: Schematic illustration of spin-coating process.](image)

First, depending on the wafer size and the desired film thickness, a few milliliters of photoresist is dispensed on the substrate surface with clean-room pipettes in static mode or at slow rotation of ca. 300 rpm. Acceleration to the wanted spin speed spreads the liquid resist towards the edges. Half of the solvent can evaporate during the first seconds, but the whole spinning process is usually performed for 1 min. A room temperature spin-coating is always accompanied with a baking step of the resist on a hot
plate in order to achieve a solid resist film. Since the baking is performed before the lithographic exposures, it is called “Pre-bake”. (The spin-curves of the photoresist and Anti-reflection-coating used in this work can be found in Appendix: Spin-curves of PR and ARC)

2.3.4 ANTI-REFLECTION-COATING (ARC)

During interference lithography exposure, in addition to the primary standing wave formed parallel to the substrate, standing waves are also formed perpendicular to the substrate. Because the silicon (or SiO₂) substrate is reflective, the vertical components of the incident light and the light reflected at the interface of substrate and the photoresist layer interfere with each other and form vertical standing waves (Figure 12).

![Figure 12: Reflections on the interfaces.](image)

This standing wave can severely degrade the resist profiles after development if it is not sufficiently suppressed. The period of the vertical standing wave is determined by the following factors: the wavelength of the light, the interference angle and the refractive index \( n \) of the photoresist (Equation 2.7 \[^{[25]}\]).

\[
P_{\text{vertical}} = \frac{\lambda}{2n \cdot \cos(\theta)}
\]

Equation 2.7

The vertical standing wave can “scallopl” the sidewalls of the resist structure to form a narrow waist. This waist can sufficiently weaken the resist structure so that it could break during the wet chemical development or washing process. In a more extreme case, this waist can actually cut through the resist structure and cause the top section to separate. The severity of the vertical standing wave will vary with the contrast of the wave. Obviously, one way to decrease the effect of this standing wave is to minimize
the reflectivity at the interface. Standard procedure is to use an anti-reflection coating (ARC) underneath the resist layer. An interlayer between the resist and the ARC is also sometimes employed to facilitate pattern transfer (will be discussed in section 2.5.2). In general, the ARC works through a combination of absorption and cancellation through interference.\cite{25} Thus, both the thickness and the optical constants of an ARC play a role to suppress the vertical portion of standing wave.

![Schematic illustration of the difference between (a) wet-developable and (b) non-wet-developable ARCs.](image)

Figure 13: Schematic illustration of the difference between (a) wet-developable and (b) non-wet-developable ARCs.

We have used the commercial i-line ARCs of Brewer Science, Inc. in this work. Two kinds of ARCs were chosen for the interference lithographic exposures: wet developable ARC (WiDE-B) and standard ARC (XHRiC). The difference between wet- and non-wet-developable ARCs is schematically illustrated in Figure 13. It is worth pointing out that the process window for the wet-developable ARC WiDE-B is severely dependent on the pre-baking temperature subsequent to the spin-coating deposition.

A simulation program based on “Matlab” written by the MIT Nanostructure Laboratory (Freeware) was employed for calculation of the optimum thickness of each layer of the substrate stack in order to minimize the reflectivity at the interface between resist and substrate. Figure 14 illustrates a typical substrate stack in cross-section view.
The optical constants of each layer and the desired period of the structure are led into the program. The thickness of the ARC layer is the variable for the calculation. The software simulated reflectivity curve relative to the ARC thickness. In this case the software simulated reflectivity curve relative to the ARC thickness is plotted in Figure 15. Usually the reflectivity below 3% is acceptable from experimental aspects. Thus two process windows (ARC thickness at ca. 70 and 185 nm) have been found. In other words, if the ARC thickness is chosen at these values, the vertical standing wave will be most sufficiently suppressed and therefore a high contrast resist profile could be obtained by LIL exposure. In Figure 16, a clear contrast of sufficient and insufficient suppression of the vertical standing wave by using ARC layer has been demonstrated with SEM images.
2.3.5 PHOTORESIST (PR)

As introduced in section 2.1, the periodic fringe pattern produced by interfering of two beams is recorded by the photoresist. Due to its highly non-linear dissolution rate as a function of exposure dose, the sinusoidal intensity pattern becomes a periodic array of individual lines in the developed photoresist.

Commercial i-line (365 nm) positive photoresists: TDMR-AR80 HP and negative photoresist TSMR-iN027 PM (produced by Tokyo OHKA KOGYO Co., Ltd.) were used as a basis in this work. In some cases, in order to improve the resist adhesion to the substrate, an adhesion promoter, hexamethyl disilazane (HMDS, (H₃C)₃-Si-NH-Si-(CH₃)₃) is applied to form a monomolecular layer on the substrate surface, making the substrate hydrophobic, which prevents moisture condensation. For the development of the exposed resist, a standard i-line organic developer (NMD-W, TMAH 2.38%) has been used in this work.
2.4 LIL EXPOSURE

2.4.1 EXPOSURE DOSE: DUTY-CYCLE

\[ DC = \frac{W_{\text{line}}}{P_{\text{grating}}} \]  

Equation 2.8

Figure 17: Schematic illustration of duty cycle.

In order to evaluate exposure the results and the resist contrast, an important index of the LIL technique, the so-called “duty-cycle” (DC) is introduced in this section. The definition of DC, the ratio of the feature size (line width) of the periodic structure generated by LIL in a given period to the period, is described by Equation 2.8 and schematically illustrated in Figure 17. As introduced in Equation 2.1, the periodicity of the structure depends on the wavelength of the laser and the incident angle. Assuming a fixed period, the feature sizes could be controlled by changing the DC value, which depends on the exposed dose.

As schematically illustrated in Figure 18, the spatial variation of the exposure dose generated by LIL could be considered as a sinusoidal distribution. The simplest and most common model for photoresist is the ideal binary response: assuming a negative PR, above a certain threshold value \( D_{\text{clip}} \), the resist is fully exposed and could be maintained in the resist developer, while below that threshold the resist is fully unexposed and could be dissolved during development. In terms of our systematic investigations, three factors have been found, which can affect the DC value of LIL exposures: incident angle, exposure time and postbake temperature. These factors will
be discussed in the following sections.

![Diagram of the binary model for response of the photoresist exposure.](image)

2.4.1.1 **DUTY-CYCLE TO INCIDENT ANGLE: EQUIVALENT DOSE**

The incident dose, defined as the total energy of the exposure, is the product of the incident power per unit area $I_o$ and the exposure time $t$.

$$D_{\text{incident}} = I_o \times t$$  \hspace{1cm} \text{Equation 2.9}

The source power $I_o$ at the initial stage (after pinhole) could be considered as a constant. Thus, the exposure time is the only parameter which can be easily varied. The relationship between exposure time and duty-cycle will be discussed in the next section.

For LIL exposure, one cannot simply assume a constant dose for exposures of different periods, even under identical exposure conditions. There are three parameters which determine the actual dose experienced by the photoresist:

- angle of incidence of the laser beam
- the reflectivity of the top surface of the resist
- the reflectivity of the bottom surface of the resist
As schematically illustrated in Figure 19, the power density on the substrate surface in case of oblique incidence is lower than that of normal incidence because of the exposed area by the laser is larger by oblique exposure. It can be deduced that for smaller structure period longer exposure times are required, because the incident angle for smaller period is larger than that for larger period.

![Figure 19: For fixed laser intensity, the power density on a substrate will be highest at normal incidence. The substrate area illuminated by the laser will be larger at oblique incidence angles.](image)

In addition, the energy reflected off the substrate surface ($R_1$) should be also considered into the reduction of the effective exposure dose, while the reflectivity at the lower surface ($R_2$) will increase the effective intensity. It is apparent that both $R_1$ and $R_2$ depend on the incident angle. These effects are schematically illustrated in Figure 20.

![Figure 20: Schematic illustration of the light reflection on the interface.](image)

Summarized above, the concept of the “equivalent-dose” \cite{25} ($D_{\text{equivalent}}$) is always employed for the description of the effective exposure dose in LIL technique. The incident angle $\theta$, reflections on the top surface and interfaces are all considered in this concept (Equation 2.10 \cite{25}). As introduced in section 2.3.4, the reflections on the
interfaces \( R_2 \), which can damage the structure profile, have been minimized to \(<3\%\) by using an ARC layer, thus it could be ignored in this case. The dominated factors, which affect \( D_{\text{equivalent}} \), are the incident angle and the reflectivity on the PR top surface; thereby affecting the duty-cycle.

\[
D_{\text{equivalent}} = D_{\text{incident}} [(1 - R_1)(1 + R_2) \cos(\theta)]
\]

Equation 2.10

### 2.4.1.2 Duty-Cycle to Exposure Time

![Figure 21: Duty-cycle as a function of exposure time for 800 nm period gratings structure.](image)

The famous Burns-Roscoe reciprocity relation has pointed out: the resist responds equally to high-intensity over short times and low-intensity over long times. It can be deduced that the intensity and exposure time are the most important parameters which can influence the exposure result. For the LIL exposure, it is obvious that there is a linear relationship between equivalent dose and exposure time. To control the DC value, the most direct way is to vary the exposure time at a fixed incident angle. Systematic
investigations have been performed in this work in order to calibrate the resist response: silicon substrates coated with 70 nm thick WiDE-8B ARC and 180 nm thick negative resist TSMR-iN027 have been exposed for various times at 800 nm period. As shown in Figure 21, considering the influences of the misnomer of the SEM measurements, the line width and therefore the duty-cycle increase quasi-linearly by increasing exposure times.

2.4.1.3 Duty-cycle to Postbake Temperature

Besides the incident angle and the exposure time, another parameter which can strongly affect the DC value is the postbake temperature ($T_{PB}$). As schematically illustrated in Figure 22, e.g. for negative resist, if we increase the $T_{PB}$ value, the threshold value of the resist $D_{clip}$ will be decreased. Therefore, the width of the effectively exposed region becomes wider, while the space between two adjacent exposed regions becomes narrower. The DC value increases thereby.

Systematic experiments were performed in this work to investigate the relationship between DC value and $T_{PB}$. A sample was exposed at 800 nm period and broken into 6 pieces for different $T_{PB}$ ranging from 100 to 110 °C. The results are shown in Figure 23: for negative PR, the DC value increases by higher $T_{PB}$. The line width/DC value varied from 207 nm/25.8% to 451 nm/56.3% within this 10 °C interval of $T_{PB}$. 
Figure 22: Schematic illustration of the influence of $T_{PB}$ on the threshold value of the resist and therefore on the duty-cycle of the exposure results.
2.4.2 EXPOSURE ASPECTS: SIMULATION AND EXPOSURE RESULTS

For LIL exposures with our Lloyd’s-Mirror Interferometer, a single exposure forms a grating structure with a certain period. Furthermore, patterns with cubic, hexagonal or another arrangement are made by double exposure with the sample rotated by 90°, 60° or a certain angle between the exposures, respectively. However, circular dot or anti-dot arrays are only available by cubic arrangement, while patterns with another arrangement show elliptical shape with different aspect ratios (long axis: short axis). The shape or the aspect ratio and the arrangement of the structures are determined by the rotation angle between the two exposures. From the other aspect, they are also determined by the exposure dose distribution over the substrate surface. Typical exposure aspects have been simulated with the software “Mathematica” and are shown in Figure 24. Figure 25 shows representative SEM micrographs of LIL exposure results. For double exposure, hole arrays are formed when DC value is <50%, while dot arrays are obtained when DC >50%.
Figure 24: Simulated exposure intensity distribution of (a) single exposure, (b), (c) and (d) double exposure with sample rotation by 30°, 60° and 90°, respectively.

Figure 25: Representative SEM micrographs of LIL exposure results in photoresist layer.
2.5 STRUCTURE TRANSFER

2.5.1 REACTIVE ION ETCHING (RIE)

After LIL patterning of polymers (PR and/or ARC), the large-scale periodic structures are usually transferred into a suitable functional substrate for further applications. Reactive ion etching (RIE) \(^{[1,2,26]}\) is a most common structure transfer technique in semiconductor industry. During the RIE process, reactive gases are used as atmosphere in sputter etching. Cations are produced from the reactive gases, which are accelerated with high energy to the substrate and as well can react chemically with the substrate material. From the reactive gas ions and reactive neutral particles are formed that support the etching process. Choosing adequate etching gases and excitation conditions, RIE combines the specific advantages of plasma etching (high selectivity) and of sputter etching (anisotropic removal). Compared with the wet-chemical etching methods, RIE provides the conveniences of high resolution and anisotropy, which is independent of crystal orientation.

After LIL patterning of polymers (PR and/or ARC), the large-scale periodic structures are usually transferred into a suitable functional substrate for further applications. In this work, a RIE machine of Sentech SI220 with a fluorine-chamber is employed for \(\text{Ar}^+\)-bombardment and the reactive ion etching of silicon, SiO\(_2\), Si\(_3\)N\(_4\) and polymers. The principle and the appearance of the machine are illustrated in Figure 26 schematically. The etching recipes are controlled by computer with user-friendly software. The etchings with chlorine gases are performed with an ICP-RIE machine in the clean-room in our institute. The RIE recipes used in this work are listed in Table 2.2. The etching rate depends on the etching gases, flow rate of the gases, HF power and chamber pressure.
Figure 26: Schematic illustration of the principle of a RIE machine.

Table 2.2 RIE etching recipes

<table>
<thead>
<tr>
<th>Material</th>
<th>Etchant</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR &amp; ARC</td>
<td>O₂</td>
<td>For the removal of residual PR or opening of ARC layer</td>
</tr>
<tr>
<td>SiO₂</td>
<td>CHF₃</td>
<td>Fluorine, polymer mask</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>CHF₃</td>
<td>Fluorine, polymer mask</td>
</tr>
<tr>
<td>silicon</td>
<td>SF₆</td>
<td>Fluorine, SiO₂ mask</td>
</tr>
<tr>
<td></td>
<td>Cl₂</td>
<td>chlorine, polymer mask</td>
</tr>
<tr>
<td>aluminium</td>
<td>BCl₃/CH₄/Cl₂</td>
<td>Chlorine</td>
</tr>
</tbody>
</table>
2.5.2 SiO$_2$ INTERLAYER FOR RIE

Figure 27: Schematic illustration of the use SiO$_2$ interlayer for structure transfer through the non-wet-developable ARC layer. (a) The stack design with SiO$_2$ interlayer; (b) LIL patterning of the PR; (c) RIE of the SiO$_2$ interlayer with CHF$_3$ gas; (d) opening of the ARC layer by RIE with O$_2$ plasma.

For the exposure of smaller structures (period < 300 nm) we have to use standard ARC with non-wet-developable properties. In this case, the structure transfer from PR structures through ARC layer can not be selectively etched with O$_2$-plasma. Usually, the PR layer is etched also faster than the ARC layer, therefore the PR structures generated by LIL can not be transferred into the substrate directly.

In this work, a SiO$_2$ interlayer$^{[25]}$ is deposited between PR and ARC before the LIL exposures. The PR structures were firstly transferred into the SiO$_2$ interlayer by RIE with CHF$_3$ plasma. The patterned SiO$_2$ interlayer was used as a mask to open the ARC
layer with O\textsubscript{2}-plasma and the structures can be transferred into the substrate subsequently. Due to the imperfect anisotropy of the O\textsubscript{2}-plasma etching of the ARC layer, a widening of the ARC structures comparing to the SiO\textsubscript{2} mask occurred. This profile is very suitable for a lift-off process for the fabrication of dot arrays.

### 2.5.3 Anisotropic KOH etching of silicon

Wet anisotropic silicon etching\textsuperscript{[27–31]} is a well-established technology and one of the most important processes in the realization of micromechanical structures in IC industrial productions. In combination with LIL technology, large-area perfectly ordered V-grooves in (100) silicon and U-grooves in (110) silicon are simply available. The LIL patterned polymer or SiO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} layers can serve as a mask for the further wet or dry etchings into the substrate. KOH is the common anisotropic wet etchant for silicon. During KOH etching, the rates of different crystal planes can differ by a factor of 200. Silicon (100) planes could be fast etched in KOH solution, whereas the etching rate of (111) planes are very low. Thus the (111) planes could be considered as etching stop in KOH etchings. With different crystalline orientation of silicon substrates, large variety of shapes could be produced, such as grating and inverse pyramid structures (schematically illustrated in Figure 28). The as-prepared nanostructures have smooth side-walls on an atomic scale, which is unavailable by RIE methods. The applications of the inverse pyramids and grating structures obtained by LIL-tailored anisotropic KOH etching will be introduced in Chapter 4 and 5, respectively.

In this work, typically 40 wt\% KOH solution was used to perform the etching of the above introduced structures. Usually an ultra-sonic assistance was employed during the KOH etching of nanometer-scale structures in order to improve the infiltration of the structures and remove associated gas bubbles which could block the etching process. The main features of the etchant are listed in Table 2.3.
Figure 28: Orientation of structures relative to wafer crystal planes for the anisotropic KOH etching: (a) inverse pyramid structures formed in (100) silicon; (b) grating structure formed in (110) silicon.

Figure 29: SEM micrographs of KOH etched structure in (a) (100) and (b) (110) silicon substrates.

Table 2.3 Main features of the anisotropic KOH etching.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>KOH: H₂O: isopropanol at a weight ratio of 2:2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching rate (@ 80 °C) μ/min</td>
<td>1</td>
</tr>
<tr>
<td>Selectivity (100): (111)</td>
<td>200:1</td>
</tr>
<tr>
<td>Selectivity (100) Si: SiO₂</td>
<td>200:1</td>
</tr>
<tr>
<td>Selectivity (100) Si: Si₃N₄</td>
<td>2000:1</td>
</tr>
</tbody>
</table>