Fabrication of Large-Area 100 nm-Period Gratings using Achromatic Holographic Lithography

by

Anthony Yen
B.S.E.E. Purdue University (1985)
S.M. Massachusetts Institute of Technology (1987)
E.E. Massachusetts Institute of Technology (1988)

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Abstract

Gratings with deep-submicron periods are important for a number of applications including quantum-effect electronics, optoelectronics, diffractive X-ray optics, and atomic interferometry. Holographic lithography (generation of periodic patterns through interference of light) remains the only practical means to obtain such gratings over large areas with uniform period. Lack of lasers with good temporal and spatial coherences in deep-UV makes achromatic holographic lithography the preferred technique for generation of large-area gratings with periods of \( \sim 100 \text{ nm} \) and below. This thesis presents the technique of achromatic holographic lithography for generating gratings with periods of 100 nm and areas of \( \sim 1 \text{ cm}^2 \). Using a free-running ArF excimer laser (193 nm) as the light source, the achromatic holographic configuration was designed and fabricated to give high efficiency and is easily aligned. Hence, despite poor temporal and spatial coherences of the excimer laser, high-contrast gratings can be obtained over an area that is limited only by the size of the configuration. Nevertheless, to obtain high-contrast gratings in the resist, an optimized anti-reflective coating must be used underneath the resist to minimize the reflection from the resist/substrate interface, which produces a standing wave orthogonal to the substrate surface. The formulation of such an anti-reflection coating, specifically to be used with PMMA resist at 193 nm, is described with design principles and experimental results. After the grating is defined in resist, techniques of nanofabrication, i.e., shadow evaporation, reactive-ion etching, gold electroplating, etc. are illustrated in the thesis to transfer the grating pattern into an X-ray absorber, supported by the membrane. These X-ray masks can then be used to replicate, using X-ray lithography, 100 nm-period gratings onto a variety of substrates for the aforementioned applications.

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Chapter 1

Introduction

Over the past few years, gratings with deep-submicron periods have found important applications in a variety of disciplines. Among them are field-effect-controlled quantum-effect electronics [1], distributed-feedback lasers [2], quantum-wire and quantum-box lasers [3, 4], vacuum-UV, X-ray, and matter-wave diffraction and spectroscopy [5, 6], and atomic interferometry [7]. In addition, recent investigations on the Smith-Purcell effect using gratings suggest the possibility of compact free-electron lasers lasing in the X-ray range [8]. In view of these developments, there is an increasing demand for gratings with periods of 100 nm and below.

Coherent holographic lithography (interference of two coherent and expanded laser beams) has been used to generate large-area gratings and grids in photoresists with periods down to 135 nm, using a frequency-doubled Ar-ion laser (257 nm) [9]. In this technique, the grating period $p$, is given by

$$p = \frac{\lambda}{2 \sin \theta}, \quad \text{(1.1)}$$

where $\lambda$ is the laser wavelength and $\theta$ is half the angle between the two beams. Lack of coherent sources with reasonable output power below 257 nm makes the generation, using coherent holographic lithography, of large-area gratings and grids with periods 100 nm and below difficult. ArF excimer lasers ($\lambda = 193$ nm) can,
in principle, be used in this fashion to drive the grating period down to about 100 nm. However, the number of grating lines will be limited by the relatively poor temporal coherence to about $\lambda/(2\Delta\lambda)$ and spatial coherence to about $\tan \theta/(2\Delta\theta)$. For a free-running ArF excimer laser with $\Delta\lambda \sim 0.5$ nm and $\Delta\theta \sim 6$ mrad, the maximum number of grating lines is limited to a few hundred.

Electron-beam lithography and focused-ion-beam lithography are used by other researchers in generating fine-period gratings for aforementioned applications. Indeed, gratings with periods down to 50 and 63 nm have been fabricated using electron-beam lithography and focused-ion-beam implantation and etching [10, 11]. However, there are two shortcomings of these lithographic techniques in generating fine-period gratings. First, gratings thus obtained are not as coherent (i.e., perfectly periodic) as those produced by holographic lithography due to mechanical and thermal drift of the column, chamber, and stage, distortion in the beam deflection system, aberrations of the beam optics, and perhaps many other factors; second, the writing time tends to be long when a large area (or many devices) needs to be covered. For example, to generate a 100 nm-period grating of 1 cm$^2$ area using electron-beam lithography with a beam current of $\sim 10$ pA and a line dose of $\sim 1$ nC/cm [12], the writing time will be $\sim 116$ days! To generate the same grating using focused-ion-beam lithography with a beam current of $\sim 20$ pA and a line dose of $\sim 10$ pC/cm [13], the writing time will be be $\sim 14$ hours. In contrast, if holographic lithography can generate 100 nm-period gratings, it will require at most a few minutes.

This thesis describes the fabrication of large-area ($\sim 1$ cm$^2$) 100 nm-period gratings using the technique of achromatic holographic lithography (AHL). While the area of grating having high contrast is limited by the temporal and spatial coherences of light source in coherent holographic lithography, the same is not true for AHL. As will be discussed in Chapter 2, in AHL source coherences limit only the system depth of focus within which gratings of high contrast can be obtained.
Phase grating efficiencies are also calculated in Chapter 2 as functions of groove profiles.

The AHL configuration is detailed in Chapter 3. A free-running ArF excimer laser ($\lambda = 193$ nm) is used as the light source. Due to the limited system depth of focus, the two fused silica discs containing the phase gratings must be matched in thickness to within 0.5 $\mu$m. A white-light Michelson interferometer was constructed for identifying the thickness mismatch, with resolution well below 0.5 $\mu$m. Alignments for phase grating parallelism and gap uniformity are described. The 200 nm-period phase gratings are fabricated using coherent holographic lithography, shadow evaporation, and RIE. Using the calculated results of Chapter 2, the phase gratings are fabricated to give the AHL configuration high optical efficiency, resulting in relatively short exposure time.

Nevertheless, to obtain high-contrast gratings in the resist, an optimized anti-reflection coating (ARC) must be used underneath the resist to minimize the reflection from the resist/substrate interface. This reflection produces a standing wave orthogonal to the substrate surface which degrades the grating profiles in resist. Chapter 4 presents the formulation of an ARC for use with PMMA resist at 193 nm. It consists of PMMA itself crosslinked by a bis-azide, 4,4'-diazidodiphenyl sulfone (DDS). DDS crosslinks the film after deep UV (260 nm) irradiation and subsequent annealing. This prevents mixing of the ARC and the PMMA resist. The reacted DDS then serves as the absorber for the 193 nm radiation. High-contrast 100 nm-period gratings are obtained in PMMA on top of the ARC.

Chapter 5 illustrates the technique of nanofabrication, i.e., shadow evaporation, reactive-ion etching, gold electroplating, etc. used to transfer the grating pattern in PMMA to an X-ray absorber, supported by the polyimide membrane. Two generations of mask fabrication process are presented. The grating in the polyimide X-ray mask is then replicated, using $C_K$ X-ray lithography, onto an X-ray mask with a SiN$_x$ membrane for durability and freedom of distortion with repeated usage. (As
the technique of reactive-ion etching improves, direct patterning of X-ray absorbers on SiN_x membranes using AHL will become possible.) These SiN_x masks can then be used to replicate, using X-ray lithography, 100 nm-period gratings onto a variety of substrates for aforementioned applications.

Using AHL, 100 nm-period gratings are obtained from a set of phase gratings having periods of 200 nm. Using a bootstrap approach, 50 nm-period gratings can be obtained using a set of gratings with periods of 100 nm. This is proposed as future work in Chapter 6. Undulator radiation (quasi-monochromatic radiation produced by a system of transverse, periodic electromagnetic fields, generally used in a synchrotron) of 14 nm would be used as the radiation source. The grating area obtained could be as large as the area of the 100 nm-period gratings. Since undulators have very good spatial coherence, the system depth of focus is expected to be greater than 50 μm.
Chapter 2

Holographic Lithography

2.1 Coherent Holographic Lithography

As was mentioned in Chapter 1, generation of periodic patterns through interference of light, or holographic lithography, remains the best means for obtaining deep-submicron-period gratings over large areas with uniform periodicity. In coherent holographic lithography, monochromatic light from a laser is first divided by a beam splitter and then recombined using mirrors to form a periodic irradiance distribution, which exposes the resist, as shown in Fig. 2.1.

The irradiance at a given point in space is proportional to the time average of the square of the electric field at that point.\(^1\) The electric fields of two monochromatic light beams arriving at the substrate plane in Fig. 2.1 can be represented by

\[
\begin{align*}
\vec{E}_1 &= A\vec{e}_1 \cos(\Phi_1 - \omega t) \\
\vec{E}_2 &= R A\vec{e}_2 \cos(\Phi_2 - \omega t),
\end{align*}
\]

where \(\Phi = \vec{k} \cdot \vec{r}\) plus the phase at the origin, \(\vec{e}\) is a polarization unit vector, and \(R\) represents the mismatch in magnitudes of the fields. Hence in the plane of the

\(^1\)This is called the electric dipole approximation. It is a good approximation for electron-photon interaction at optical frequencies [14].
Figure 2.1: Idealized setup for coherent holographic lithography.
resist, the irradiance $I$ is proportional to

$$ I \propto <(\vec{E}_1 + \vec{E}_2) \cdot (\vec{E}_1 + \vec{E}_2)> $$

$$ = <\vec{E}_1^2> + <\vec{E}_2^2> + 2 <\vec{E}_1 \cdot \vec{E}_2> $$

$$ = \frac{A^2}{2} + \frac{R^2 A^2}{2} + RA^2(\vec{e}_1 \cdot \vec{e}_2) \cos(\Phi_1 - \Phi_2) $$

$$ = \frac{A^2}{2} \left[1 + R^2 + 2R(\vec{e}_1 \cdot \vec{e}_2) \cos(2kx \sin \theta + k\Delta l)]\right. $$

where $<>$ denotes time averaging and $k \Delta l$ is the phase difference due to the difference in arm lengths $\Delta l$. As we can see, the irradiance has the periodicity $p$ given by Eqn. (1.1). In this calculation, we have neglected contributions to the total field from waves reflected off the substrate. Such reflections cause a standing wave in the $z$ direction and serve to reduce the grating contrast. They are minimized by the use of an anti-reflection coating.

From Eqn. (2.6), we can see that the highest contrast in irradiance is achieved when the two laser beams are balanced ($R = 1$) and the TE polarization ($\vec{e}_1 = \vec{e}_2$) is used. In such cases,

$$ I \propto A^2 \left[1 + \cos(2kx \sin \theta + k\Delta l)\right]. $$

Coherent holographic lithography works well with lasers having good temporal and spatial coherences, usually etalon-tuned for single spectral line and Gaussian beam profile. Spatial filters (pinholes) are used to remove interference effects resulting from dust particles and defects in the beam paths. They also serve to expand the beams so that gratings can be defined over large areas.

In order to prevent drifting of the grating pattern, variation in $\Delta l$ during the exposure must be minimized. This variation can come from, e.g., mechanical movements of the optical components and can be compensated by the use of negative feedback employing a Pockels cell. This scheme is illustrated in Fig. 2.2 [15, 5]. Another approach is the so-called one-arm holographic lithography (Fig. 2.3), where $\Delta l$ itself is minimized and its variation is unlikely. However, due to the cylindrical
symmetry of the beam, the area of uniform dose and periodicity in the one-arm method is limited to one half of that achievable by the two-arm method.

Since there are no commercially available lasers with good temporal and spatial coherences below 257 nm (frequency-doubled Ar), the smallest grating period obtainable with coherent holographic lithography in air is \( \sim 135 \) nm [9]. A "quick-fix" technique to reduce the grating period other than reducing the laser wavelength is to place a prism on top of the resist-coated substrate, with a index matching fluid such as xylene to fill the air gap between them (see Fig. 2.4) [16, 17]. Using this method, the minimum period obtainable is (taking the prism and xylene index of refraction to be 1.5) \( \sim 90 \) nm, using a frequency-doubled Ar-ion laser (257 nm) [18]. However, it is difficult to achieve uniform exposures using this technique in practice. The prism must be reflection-free on all surfaces or there will be multiple reflections within the prism and in the xylene-filled gap. These reflections result in standing
Figure 2.3: One-arm holographic lithography.

wave patterns in the resist from random interferences [19].

Another method involves reducing the wavelength of the light from the laser using materials suitable for second or third harmonic generation [20]. The difficulty with this method, except for the commercially available frequency-doubled Ar-ion laser (257 nm), is in the elaborate setup and amount of adjustment needed to arrive at conditions necessary for reasonable conversion efficiency.

Excimer lasers with wavelengths below 257 nm are commercially available. However, these lasers are not as coherent as the continuous wave lasers. Can coherent holographic lithography be done with light sources with limited temporal and spatial coherences? The answer is yes, but the area of the grating will be small. We shall first give a brief account of the physics of excimer lasers and then apply them to coherent holographic lithography.
Figure 2.4: Holographic lithography with a prism and index matching fluid.

2.2 Coherent Holographic Lithography with Excimer Lasers

Excimers are molecules that are bound in their excited electronic states but are unstable in their ground states (see Fig. 2.5). Examples of excimers are argon fluoride (ArF), krypton fluoride (KrF), xenon chloride (XeCl), and xenon fluoride (XeF). Since excimers are thermally unstable in their ground states, they are ideal as active media for lasers. With fast molecular dissociation time (10^{-12} - 10^{-13} sec.), population inversion is automatically achieved when the medium is pumped. Pumping is accomplished by high voltage ionization discharge or high energy, high intensity electron beams [21, 22].

Due to multiple molecular vibration energy levels associated with the excited state, the bandwidth $\Delta \lambda$ for lasing transition in a free-running (vs. spectral-narrowed) excimer laser is on the order of 1 nm. For ArF, $\lambda = 193$ nm, $\Delta \lambda \approx 0.5$ nm, this gives a temporal coherence length of $l_c = c/\Delta \nu = \lambda^2/\Delta \lambda \approx 75 \mu$m. Furthermore, short pulse duration ($\sim 15$ ns for ArF) means that its beam size and divergence
Figure 2.5: Ground and excited states of an excimer.

are determined by the electrode geometry. (Since it takes several nanoseconds for light to make a round trip between the laser cavity mirrors, the mirrors can only exert a slight influence on the coherence of the output beam.) Most excimer lasers have highly non-Gaussian, nearly rectangular beams with large cross-sections, commonly 2-3 cm in the long dimension (usually horizontal) and about 1 cm in the short dimension (usually vertical). The corresponding beam divergences are about 6 mrad in the long dimension and 2 mrad in the short dimension [23]. Source characteristics of an excimer laser is summarized in Fig. 2.6.

To improve temporal and spatial coherences, injection-locked oscillator-amplifier excimer lasers were developed over the years [24]. Such lasers have bandwidths of < 5 pm ($l_c = 10$ mm at $\lambda = 193$ nm) and output a single spatial mode. The divergence of the beam is < 0.2 mrad, which is nearly diffraction limited. However, the cost of such a laser is in excess of $100,000 [25].

Excimer lasers were first used to generate gratings by Hawryluk et al. using a technique called spatial-frequency doubling [26]. With an ArF excimer laser and a parent grating of 198 nm period, gratings of 99 nm periods were exposed in resist
using the near-field diffraction pattern of the parent grating. (A major drawback of this technique is its inability to block out the zero-order diffracted beam. As a result, there is always a component of the fundamental spatial frequency present in the exposed patterns.) Grating generation by coherent holographic lithography using an excimer laser has been carried out by Ahlhorn et al. [27]. Using an injection-locked KrF excimer laser ($\lambda = 248$ nm), gratings with periods down to 140 nm were obtained in resist.

Let us now calculate grating sizes achievable by coherent holographic lithography, using a source (infinite in extent) with spectral width $\Delta \lambda$ and angular width $\Delta \theta$. The irradiance at the substrate surface of such a source is proportional to

$$I(x) \propto \int_{\lambda_0-\Delta \lambda/2}^{\lambda_0+\Delta \lambda/2} \int_{\theta_0-\Delta \theta/2}^{\theta_0+\Delta \theta/2} [1 + \cos \Delta \Phi(x, \lambda, \theta)] d\lambda d\theta,$$

where $\Delta \Phi$ is the phase difference of the two arms. Referring to Fig. 2.7, for position $x$ on the substrate, the phase of the left arm is

$$k\overline{AP} = k(l + x \sin \theta_0 + x \cos \theta_0 \tan \alpha) \cos \alpha,$$

Figure 2.6: Temporal and spatial characteristics of an excimer laser.
Figure 2.7: Diagram for calculating optical paths in coherent holographic lithography.

and that for the right arm is

\[ k\overline{BP} = k(l - x \sin \theta_0 - x \cos \theta_0 \tan \alpha) \cos \alpha, \]  

(2.10)

where \( k = 2\pi/\lambda \) and \( \alpha = \theta - \theta_0 \). Hence

\[ \Delta \Phi = k(\overline{AP} - \overline{BP}) = 2kx(\sin \theta_0 + \alpha \cos \theta_0), \]  

(2.11)

where we used \( \cos \alpha \approx 1 \) and \( \tan \alpha \approx \alpha \) for small \( \alpha \). Instead of evaluating the integral, let us evaluate the variation in \( \Delta \Phi \) as a result of variations in \( k \) and \( \alpha \).

\[ d\Delta \Phi(x, k, \alpha) = \left| \frac{\partial \Delta \Phi}{\partial k} \right| dk + \left| \frac{\partial \Delta \Phi}{\partial \alpha} \right| d\alpha. \]  

(2.12)

\[ \quad = 2x(\sin \theta_0 dk + k_0 \cos \theta_0 d\alpha) \]  

(2.13)

We demand that the maximum variation of \( \Delta \Phi \) be \( \pi/2 \), beyond which the grating lines wash out. Denoting \( x_{\text{max}} = N/2 \cdot p \), where \( N \) is the number of grating lines,
we have

\[ \frac{\pi}{2} = Np \left( \sin \theta_0 \frac{\pi \Delta \lambda}{\lambda_0^2} + \frac{2\pi}{\lambda_0} \cos \theta_0 \frac{\Delta \theta}{2} \right) . \]  

(2.14)

From this we obtain the maximum number of grating lines \( N \) to be

\[ N = \frac{1}{(\Delta \lambda/\lambda_0) + (\Delta \theta/\tan \theta_0)} , \]

(2.15)

where we used Eqn. (1.1) for \( p \).

If we were to generate 100 nm-period gratings using coherent holographic lithography with a free-running ArF excimer laser having \( \Delta \lambda \approx 0.5 \) nm and \( \Delta \theta \approx 6 \) mrad, the maximum number of grating lines achievable is \( \sim 200 \). If we use an injection-locked ArF excimer laser with \( \Delta \lambda \approx 5 \) pm, this number is \( \sim 40,000 \), which translates to a grating size of 4 mm. Hence we believe that coherent holographic lithography is not suitable for generating large-area high contrast gratings in the 100-nm period range.

### 2.3 Achromatic Holographic Lithography

To generate 100 nm-period gratings holographically, despite the poor coherence of the ArF excimer lasers, achromatic schemes should be used [29, 15]. Figure 2.8 shows such a scheme. It consists of two identical gratings of period 200 nm. They are usually phase gratings and are fabricated using coherent holographic lithography and dry processing. The first 200 nm grating splits the normally incident light into zero- and first-order beams. After blocking the zero-order beam, the second 200 nm grating recombines the first-order beams by second-order diffraction. The resulting standing interference pattern is periodic with a period of 100 nm, one half that of the 200 nm grating, and independent of the wavelength of the incident light.

The AHL configuration is based on the idea of the grating interferometer, originally proposed by Weinberg and Wood [30]. Similar setups have been used in

\[ \text{\footnote{This and the next section closely follow author's paper "An achromatic holographic configuration for 100 nm-period lithography" [28].}} \]
Figure 2.8: A schematic for Achromatic holographic lithography
recording white-light holograms [31, 32] and more recently, in recording large-area gratings with periods well above 1 µm [33, 34, 35].

Chang et al. [36] have analyzed in detail grating interferometers in which the Fresnel diffraction formula was used to calculate the propagation of fields. However, the Fresnel formula is only a first-order approximation, and is inadequate for our case because λ/p is as high as 0.965. Cheng [37] and Swanson [38] have carried out the analysis of the grating interferometer to higher orders. The two methods are equivalent. Swanson's method allows one to obtain ΔΦ in a simple closed form without using Taylor's expansion. In the following calculation we employ his method. Referring to Fig. 2.9,

\[ \beta = \sin^{-1} \frac{1}{n} (\lambda/p + \sin \theta) \]  

(2.16)
\[ \gamma = \sin^{-1} \frac{1}{n} (\lambda/p - \sin \theta). \]  

The transmittance of phase gratings \( G_1 \) and \( G_2 \) can be expressed as

\[ T_1(x) = \sum_m A_m \exp \left( i \frac{2 \pi m}{p} x \right) \]  

and

\[ T_2(x) = \sum_m B_m \exp \left( i \frac{2 \pi m}{p} x \right). \]

The fields in the plane of substrate can be easily written down as

\[ E_1 = A_1 \exp \left( i \frac{2 \pi}{p} x \right) \exp \left( i \frac{2 \pi n}{\lambda} d \cos \gamma \right) \exp \left( i \frac{2 \pi}{\lambda} g \cos \gamma' \right) \times B_{-2} \exp \left( -i \frac{2 \pi}{p} x \right) \exp \left( i \frac{2 \pi n}{\lambda} (d - \delta) \cos \beta \right) \exp \left( i \frac{2 \pi}{\lambda} (g + \delta') \cos \beta' \right). \]  

and

\[ E_2 = A_{-1} \exp \left( -i \frac{2 \pi}{p} x \right) \exp \left( i \frac{2 \pi n}{\lambda} d \cos \beta \right) \exp \left( i \frac{2 \pi}{\lambda} g \cos \beta' \right) \times B_2 \exp \left( i \frac{2 \pi}{p} x \right) \exp \left( i \frac{2 \pi n}{\lambda} (d - \delta) \cos \gamma \right) \exp \left( i \frac{2 \pi}{\lambda} (g + \delta') \cos \gamma' \right). \]

Since \( \theta \) is small, \( \sin \theta = \theta \), \( A_1 = A_{-1} \), and \( B_2 = B_{-2} \). Hence

\[ \Delta \Phi = -\frac{4 \pi}{p} x - \frac{2 \pi n}{\lambda} \delta (\cos \beta - \cos \gamma) + \frac{2 \pi}{\lambda} \delta' (\cos \beta' - \cos \gamma') \]
\[ = -\frac{4 \pi}{p} x - \frac{2 \pi}{\lambda} \delta \left( \sqrt{n^2 - (\lambda/p + \theta)^2} - \sqrt{n^2 - (\lambda/p - \theta)^2} \right) \]
\[ + \frac{2 \pi}{\lambda} \delta' \left( \sqrt{1 - (\lambda/p + \theta)^2} - \sqrt{1 - (\lambda/p - \theta)^2} \right). \]

This result shows that the configuration is truly achromatic with fringe period equal to \( p/2 \) if the thicknesses of the plates and gaps are precisely matched, i.e., when \( \delta = \delta' = 0 \). When these thicknesses are not matched, the optical path difference varies with variations in \( \lambda \) and \( \theta \). Assuming the nominal wavelength of the source to be \( \lambda_0 \) and nominal angle of incidence (very small) to be \( \theta_0 \), the change in \( \Delta \Phi \) to the first order is

\[ 2\pi \delta \left( \frac{2 \lambda_0 \theta_0}{(n^2 p^2 - \lambda_0^2)^{3/2}} d\lambda + \frac{2}{\sqrt{n^2 p^2 - \lambda_0^2}} d\theta \right) - 2\pi \delta' \left( \frac{2 \lambda_0 \theta_0}{(p^2 - \lambda_0^2)^{3/2}} d\lambda + \frac{2}{\sqrt{p^2 - \lambda_0^2}} d\theta \right). \]  

(2.23)
If \( \theta_0 \) is less than 1°, then terms associated with \( d\lambda \) are much smaller than those associated with \( d\theta \) and hence can be neglected. Therefore, to record high-contrast fringes, we demand that

\[
-\frac{\pi}{2} \leq 4\pi d\theta \left( \frac{\delta}{\sqrt{n^2p^2 - \lambda_0^2}} - \frac{\delta'}{\sqrt{p^2 - \lambda_0^2}} \right) \leq \frac{\pi}{2}.
\]  

(2.24)

Since \( \delta \) is usually fixed once the plates are polished and \(-\Delta\theta/2 \leq d\theta \leq \Delta\theta/2\), the range of the gap variation is

\[
-\frac{\sqrt{p^2 - \lambda_0^2}}{4\Delta\theta} + \delta \sqrt{\frac{p^2 - \lambda_0^2}{n^2p^2 - \lambda_0^2}} \leq \delta' \leq \frac{\sqrt{p^2 - \lambda_0^2}}{4\Delta\theta} + \delta \sqrt{\frac{p^2 - \lambda_0^2}{n^2p^2 - \lambda_0^2}}.
\]  

(2.25)

Hence the depth of focus can be expressed as

\[
\sqrt{\frac{p^2 - \lambda_0^2}{2\Delta\theta}}.
\]  

(2.26)

For \( p = 200 \) nm, \( \lambda_0 = 193 \) nm, and \( \Delta\theta = 6 \) mrad, the depth of focus is about 4 \( \mu \)m. Precision spacers are used to control the gap variations to within this number.

In addition to unequal gaps, imperfection in alignment also results from grating lines in \( G_1 \) and \( G_2 \) not being prefectly parallel. In practice, this error is usually about 1 mrad. A calculation following Chang's [36] first-order analysis shows that the phase variation resulting from a 1 mrad azimuthal error between \( G_1 \) and \( G_2 \) is less than \( 10^{-5} \) rad.

In practice the laser beam is also divergent in the direction parallel to the phase grating lines. However it can be shown that the depth of focus is not affected by this divergence.

### 2.4 Phase Grating Efficiencies

Phase gratings are used instead of amplitude gratings (e.g., metal lines on optical flats) for the AHL configuration mainly due to the high damage threshold of the former in high power laser beams. Fused silica was chosen as the material for phase
gratings due to its high transparency at 193 nm. Fabrication of phase gratings with periods of 200 nm will be discussed in Chapter 3.

Since the AHL configuration uses first- and second-order diffracted beams, the efficiencies of the phase gratings determine the final intensity arriving at the resist surface, which in turn determines the exposure time. Hence it is of interest to find the relationship between the grating efficiencies and the grating profiles.

Gaylord and Moharam have reviewed electromagnetic calculations of diffraction gratings [39]. The most common methods used in analyzing grating diffraction are the coupled-wave approach and the modal approach. In the absence of approximations they are completely equivalent formulations [40]. Using the modal approach, Knop [41] first numerically solved for diffraction efficiencies of phase gratings with rectangular grooves. Anderson [15] improved upon Knop’s method using a two-step calculation. First, approximate eigenvalues are found by solving a matrix equation. These answers then serve as trial roots in an algebraic equation for eigenvalues. Solving the equation by iteration gives highly accurate eigenvalues and hence accurate results regarding efficiencies of various diffracted orders. Since the calculation allows for complex indices of refraction, \( n + ik \), it can be used for both amplitude and phase gratings. An input file consists of the grating period, width and depth of the grooves, refractive index of the material, wavelength, polarization, and angle of the incident light. His approach is summarized below. Additional details of the method can be found in Ref. [15].

Referring to Fig. 2.10, the wave equation for, e.g., TE polarization in region II is

\[
\frac{\partial^2 E_{II}}{\partial x^2} + \frac{\partial^2 E_{II}}{\partial z^2} + k_0^2 \epsilon(x)E_{II} = 0,
\]

where \( k_0 = 2\pi/\lambda \) and \( \epsilon(x) \) is the dielectric constant. Since \( \epsilon(x) \) is periodic in the \( x \) direction only, \( E_{II}(x, z) \) can be separated into \( E_{II}(x, z) = A(x)B(z) \). Substituting this expression into equation 2.27, \( B(z) \) is solved to be

\[
B(z) = B \exp(ikz),
\]
Figure 2.10: Diagram of a phase grating showing various parameters needed in diffraction efficiency calculations.
and the master equation for $A(x)$ is then
\[ \frac{d^2 A(x)}{dx^2} + [k_0^2 \epsilon(x) - \kappa^2] A(x) = 0. \quad (2.29) \]

Since $\epsilon(x)$ is periodic, this equation has the same form as the Schrödinger Equation for a periodic potential [42]. Hence $A(x)$ has the form
\[ A(x) = U(x) \exp(i\phi x), \quad (2.30) \]

where $U(x)$ is periodic with the grating period $\Lambda$ and phase factor $\phi$ is equal to $k_0 \sin \theta$. ($\theta$ is the angle of incidence.) This is because in the case $\epsilon = 1$, $E_{II}$ must be phase matched to the incident field. Since $U(x) = U(x + p)$, it may be written as
\[ U(x) = \sum_{m=-\infty}^{\infty} a_m \exp \left( i \frac{2\pi m}{p} x \right). \quad (2.31) \]

Now since $\epsilon(x)$ is known (described by $p$, $n$, $b$, $d$), it can be expressed as a Fourier series with known coefficients. Substituting all this into the master equation for $A(x)$ results in a matrix equation
\[ M \cdot a = \kappa^2 a, \quad (2.32) \]

from which we obtain a set of $a_m$’s for each $\kappa^2$.

However, the master equation (2.29) can also be solved for sub-regions within Region II where $\epsilon(x) = 1$ and $\epsilon(x) = n^2$, respectively. Continuity requirements at the sub-region boundary and also the requirement that $A(x)$ be in Bloch form gives an algebraic equation for $\kappa^2$. The trick here is to use the matrix method to obtain the approximate values for $\kappa^2$ and then use these values as starting points to find grating eigenvalues to high accuracy from the algebraic equation for $\kappa^2$.

The complete solution for region II is the superposition of all “modes”. That is,
\[ E_{II} = \sum_{m,q} a_{mq} \exp \left[ i \left( \frac{2\pi m}{p} + \phi \right) x \right] [b_q \exp(i\kappa_q x) + c_q \exp(-i\kappa_q x)]. \quad (2.33) \]

Fields in regions I and III can be expressed as
\[ E_I = \exp(i\vec{k}_0 \cdot \vec{r}) + \sum_{m=-\infty}^{\infty} R_m \exp(i\vec{k}_1 m \cdot \vec{r}) \quad (2.34) \]
and

\[ E_{III} = \sum_{m=-\infty}^{\infty} T_m \exp[ik_0 \cdot (\vec{r} - \hat{z} d)], \]

where \( \exp(i\vec{k}_0 \cdot \vec{r}) \) is the incident field and \( R_m \) and \( T_m \) are amplitudes of the \( m \)th-order diffracted fields in reflection and transmission, respectively.

Diffraction efficiency for \( m \)th order transmitted wave is defined as

\[ \frac{\langle \hat{S}_{3m} \cdot \hat{z} \rangle}{\langle \hat{S}_{\text{inc.}} \cdot \hat{z} \rangle} \]

which is equal to \( |T_m|^2 n \cos \theta_m / \cos \theta \). To solve for \( T_m \) and \( \theta_m \), we use boundary conditions, which require that \( E \) and \( B_z \) be continuous at the boundary between regions I and II, and between regions II and III. These conditions provide enough equations to obtain the diffraction efficiency.

Figures 2.11 – 2.14 show contour plots of efficiencies for the beam splitter and recombiner gratings as functions of the fractional line width \( b \) and groove depth \( d \). The index of refraction of fused silica at 193 nm is 1.561. The incident angle for the beam-splitter grating is 0°, and for the recombiner grating is 74.8°. The imaginary part of the refractive index \( k \) is neglected compared to \( n \) since it is \( < 10^{-6} \) at 193 nm.

In fabricating the phase gratings, we chose equal line-to-space ratio for both beam-splitter and recombining gratings. Choosing equal line-to-space ratio in the latter eliminates the TM wave (the laser is unpolarized). This is desirable since a TM polarization yields low fringe contrast. Groove depth was chosen to be \( \sim 150 \) nm to obtain sufficient grating efficiency while not putting excessive strain on the fabrication technology.

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Figure 2.11: 1st-order diffraction efficiency of a 200 nm-period phase grating for TE polarized light at 193 nm, as a function of the fractional line width $b$ (ordinate scale) and groove depth $d$. Normal incidence. Each contour represents a 10% increase in efficiency. Matrix size: $10 \times 10$.
Figure 2.12: 1st-order diffraction efficiency of a 200 nm-period phase grating for TM polarized light at 193 nm, as a function of the fractional line width $b$ and groove depth $d$. Normal incidence. Matrix size: $10 \times 10$. 
Figure 2.13: 2nd-order diffraction efficiency of a 200 nm-period phase grating for TE polarized light at 193 nm, as a function of the fractional line width $b$ and groove depth $d$. Angle of incidence: 74.8°. Matrix size: 10 × 10.
Figure 2.14: 2nd-order diffraction efficiency of a 200 nm-period phase grating for TM polarized light at 193 nm, as a function of the fractional line width $b$ and groove depth $d$. Angle of incidence: 74.8°. Matrix size: 10 × 10.
Chapter 3

Achromatic Holographic Configuration

3.1 The Light Source

The light source used for all the experiments was a TE-861 excimer laser made by Lumonics, Inc. [43] in 1979, and is on loan to us from Prof. Marc Kastner of MIT. It is a free-running excimer laser switched by a thyatron. Much has been learned about this laser since the start of the thesis work such that it is now relatively easy to repair and maintain.

The laser is equipped with two parallel power supplies for high pulse repetition rates. However it was our experience that operating the laser with dual power supplies did not increase the output power of the laser by a significant amount compared to running it with a single power supply. As a result, we now operate the laser with one power supply and keep the other one as a spare part.
3.1.1 Optics

The laser had been configured for operation with CO₂ gas before being brought to our laboratory. The optics was then replaced to convert it for operation with ArF, lasing at 193 nm. The optics used in the laser, namely the front window (output coupler) and the rear reflector, are 2 inches in diameter and made of either CaF₂ or MgF₂ (Although fused silica is also highly transparent at 193 nm, it is slowly etched in a fluorine-containing environment). The front window is an uncoated flat substrate and the rear reflector is a plano-convex lens with a 10 meter radius of curvature, with the plano surface facing the laser cavity. The convex surface is coated with a reflective material so that the lens serves as a concave reflector of light. In this scheme, the coating never comes into contact with the corrosive gas.

Either Al or multilayer dielectrics can be used as the reflective coating. The problem with the Al coating is that the laser beam will slowly ablate it away. When small holes appear in the center of the reflector, it is time to strip the coating and evaporate a fresh layer. If etching is done beyond the room temperature, one must wait for the optic (CaF₂ or MgF₂) to cool down naturally before rinsing it with deionized water, or it will crack due to thermal shock. The usual thickness of evaporated Al is 200 nm, plus 60 nm of MgF₂ as a protective coating.

Although it is more expensive, we have had better experience with the multilayer dielectric coating(coated by Acton Research Corp [44]). First, under the same conditions, 20% more output power is obtained with the dielectric coating (reflectivity is 96% at 193 nm). Second, the damage threshold is high enough that we don't need to worry about recoating the mirror.

The front window must be cleaned periodically due to “fogging up” caused by laser-induced deposition of impurities insider the laser cavity. The deposition may be removed by polishing the window using a slurry of tin oxide and deionized water. If this method fails, the optic must be sent to an optical shop to be ground and polished.
We also experienced radiation-induced formation of color centers in one CaF$_2$ window piece. When this happens, the area where the laser beam penetrates turns blue permanently, with loss of laser output power. This is an indication of the presence of defects and imperfections in the material and the piece should be returned to the manufacturer.

3.1.2 Gases

Gases used for ArF operation are a mixture of 0.4% F$_2$, 20% Ar, and the balance He. Although one can mix gases inside the laser cavity by purchasing individual gases and using a feed manifold, we have bought premixed gas cylinders from Spectra Gases Inc. There are two reasons for doing this. First, pure F$_2$ is very toxic to have around. Second, leaks are more likely to develop in a system with a lot of gas tubing present. A gas "scrubber" was installed to trap fluorine when lasing gases are pumped out; it is inserted between the laser cavity and the mechanical pump. It consists of copper wool, soda lime (NaOH + Ca(OH)$_2$), glass fiber, and molecular sieve. The combination of copper wool, soda lime, and glass fiber reduces the concentration of F$_2$ by a factor of 500 [45] while molecular sieve, soda lime, and glass fiber are used to prevent back streaming of pump oil to the laser cavity during pump down. The contents of the scrubber should be replaced every few months, and are available as kits from Lumonics.

3.1.3 Repair/Passivation

Due to its vintage, the laser broke down on several occasions. One recurring problem was the fracture of the coupler between the shafts of the circulating/cooling fan inside the laser cavity and its motor, which is outside the cavity. When this happened, the fan stopped running, and the laser could only be pulsed at very low repetition rates. This is due to the fact that fresh gas cannot get in between the
electrodes to replace the reacted gas fast enough without the fan running. After the problem was identified, the repair was quite simple. Finally, a switch was installed so that the fan could be turned off when the laser idled in between exposures. The coupler has not broken down since then.

A major failure was due to the fracture of the cooling water coil inside the laser cavity. We had to be very cautious when opening the cavity because hydrofluoric acid was formed when fluorine mixed with water. Repair in this case consisted of replacing the cooling coil and cleaning and glass beading all the parts inside the cavity.

Since the cavity is exposed to air during repair, it must be passivated before one can obtain appreciable amount of output power. The first step is to remove the moisture adhering to the inside of the cavity. This is done by running the laser filled with He (to 31 psi) without cooling water for 15 minutes. Then pump out the gas and repeat the same operation two to three times. The fiberglass vessel (cavity) should be warm. The next step is to fluorinate the surface of everything inside the cavity. This can be done by running the laser filled with ArF (to 31 psi) as in normal operation and with a voltage of 30 kV. The output of the laser should diminish quickly, as F₂ is consumed by materials inside the cavity. Pump out the gas when the power meter reading goes to zero. Repeat the same operation till the half power point occurs after $5 \times 10^4$ shots. The laser is then considered passivated. This step may take a few days.

### 3.1.4 Specifications

The ArF excimer laser outputs a rectangular beam of $\sim 2.5$ cm in the horizontal direction and $\sim 0.5$ cm in the vertical direction. For exposure uniformity, only the middle 1 cm of the beam is used, and the beam is scanned vertically using a pair of beam-steering optics.

The temporal coherence of the excimer laser was measured using Newton’s ring
Figure 3.1: Measuring the temporal coherence of the ArF excimer laser using a Newton's ring method.

interferometry, see Fig. 3.1. By directing the laser beam downward towards a plano-convex fused silica lens with the convex side resting on a resist-coated (in this case PMMA) wafer, Newton's rings were recorded in the resist. Since the dimensions of the lens could be measured with a micrometer, the temporal coherence of the laser could be obtained by measuring, using the scales in a microscope, the distance from the center of the rings to where the rings disappear. Using this method, the temporal coherence of the laser was found to be $\sim 70$ $\mu$m. This is an important number. Since we do not want interference effects from multiple reflections in the gaps, spacers for the gaps must be thicker than 70 $\mu$m. In our case, the spacer thickness is about $\sim 100$ $\mu$m.

The spatial coherence of the excimer laser is related to the beam divergence, which is $\sim 6$ mrad in the horizontal direction and $\sim 2$ mrad in the vertical direction. Horizontal beam divergence determines the depth of focus of our AHL configuration, as discussed in Chapter 2. This divergence can be made smaller if one uses a pair of beam expanding optics, at the expense of the intensity of the light.
The average intensity (since the beam is scanned) of the incident 193 nm radiation is kept at \( \sim 0.3 \) W/cm\(^2\). Higher intensity is available from the laser. However, the output power is kept low to avoid radiation damage of the fused silica discs.

### 3.2 Achromatic Holographic Configuration

The AHL configuration consists of two 12.7 mm-thick fused silica discs into which 76.2 mm-diameter 200 nm-period phase gratings were etched, and a 76.2 mm-diameter pinchuck fabricated in silicon. The whole assembly is mounted on a 1 inch-thick Al block, which rests on a vibration-damped optical table. The mount for the second phase grating is fixed, while those for the first grating and the pinchuck can press them against the second grating and are adjustable with micrometers. A thin strip (\( \sim 12 \) \( \mu m \)) of Al foil is used to block the zero-order beam. (No sign of laser ablation of the foil was observed.) Figure 3.2 is a photograph of the AHL configuration before the substrate is mounted and the configuration aligned and pressed together. A sketch of the configuration showing its main components and the optical paths is given in Fig. 3.3.

The depth of focus of the AHL configuration employing a free-running ArF excimer laser was shown in Chapter 2 to be \( \sim 4 \) \( \mu m \). To ensure that the substrate surface is within this range, the thicknesses of the two phase gratings are matched to within 0.5 \( \mu m \) and all faces of the phase gratings are flat to within 0.16 \( \mu m \). (Fabrication of these gratings are detailed in the next section.) Strips of \( \sim 100 \) \( \mu m \)-thick plastic tape are used as spacers. Good mechanical stability is achieved through large contact areas. With the plastic tape, variation in gap thickness can be kept to within \( \sim 1 \) \( \mu m \) throughout a \( \sim 76 \) mm-diameter area. The silicon pinchuck which mounts the resist-coated substrate has a surface polished down to 0.16 \( \mu m \) in flatness. Since silicon substrates in their relaxed states are often bowed, the pinchuck is essential in keeping the substrate surface within the depth of focus. (The largest
Figure 3.2: Achromatic holographic configuration for generating 100 nm-period gratings.
Figure 3.3: A sketch of the AHL configuration showing its main components and the optical paths.

part of the depth of focus budget is still taken by the non-flatness of the substrate.) Figure 3.4 shows a 3 inch diameter silicon wafer before and after conforming to the pinchuck, which was provided by IBM Corporation.

In aligning the AHL assembly, a He-Cd laser ($\lambda = 325$ nm) is used to obtain parallelism of the two phase grating orientations. To find the grating orientation, diffracted beams other than the zero-order beam must be used. For back diffraction, we have

$$\sin \theta_0 + \sin \theta = m\lambda/p,$$

(3.1)

where $\theta_0$ is the incident angle, $\theta$ is the angle of $m$th-order back diffracted beam, $\lambda$ is the laser wavelength, and $p$ is the grating period. With $\lambda = 325$ nm and $p = 200$ nm, we can only have the zero-order and one of the first-order back diffracted beams. The two gratings are aligned as we turn the orientation of the first grating by adjusting the micrometer such that first-order back-diffracted beams from both
Figure 3.4: A 3" Si wafer (a) before and (b) after conforming to the pinchuck.

gratings coincide with the incident beam, as depicted in Fig. 3.5.

From Eq. (3.1), we find that this condition occurs at $\theta_0 = 54.3^\circ$. Using this method, orientations of the two phase gratings can be made parallel to within 1 mrad.

This alignment can also be accomplished using the ArF excimer laser itself, if the phase gratings have good efficiencies. The ArF beam is passed through a 2 mm hole and through the first phase grating outside the zero-order stop. Figure 3.6 shows the two back diffracted beams which, when the grating orientations are parallel, interfere to give fringes at the screen.

Figure 3.7 shows an interferometer used to establish gap parallelism. The beam from a He-Ne laser is expanded 75 times to form a $\sim$ 76 mm-diameter collimated beam. The input lens for the beam expander has an aperture of 3.2 mm and a focal length of -4 mm. The collimating lens has an aperture of 76.2 mm and a focal length of 300 mm. Fine adjustments with micrometers are carried out to
Figure 3.5: Alignment of the 200 nm-period phase gratings using a He-Cd laser.

Figure 3.6: Alignment of the phase gratings using the ArF laser itself. Only diffracted beams used for the alignment are shown.
Figure 3.7: Establishing gap uniformity using a simple interferometer employing a He-Ne laser and beam-expanding optics.
maximize the parallelism between the two phase gratings and between the second phase grating and the chucked substrate. Gap parallelism of < 1 µm can be easily achieved.

3.3 Phase Grating Fabrication

Phase gratings are used instead of amplitude gratings (metal lines on optical flats) in our AHL configuration mainly due to their high damage threshold in intense laser beams. Fused silica (Dynasil 1000 [46]) was chosen as the material for phase gratings due to its high transparency at 193 nm (> 80% for a thickness of 1/2 inch). The substrates are discs 12.7 mm thick and 76.2 mm in diameter. They were ordered from an optical shop with the following specifications: thicknesses of the two discs must match to within 0.5 µm and all faces must be flat to within 0.16 µm. While it is easy to meet the specification for surface flatness, meeting the specification for thickness matching requires skillful optical shop techniques. A white-light Michelson interferometer was built to inspect the blank discs from the optical shop. Figure 3.8 is a schematic of our white-light Michelson interferometer employing a halogen lamp. Before inserting the test pieces, the two arms of the interferometer are adjusted by moving the mirrors (mounted on micrometer-controlled stages) to give color fringes on the screen. This happens when the optical path length difference of the two arms is within the temporal coherence length of the halogen lamp, which is only a few micrometers. Once this is done, the fused silica discs are inserted into the optical paths. Mismatch in their thicknesses will result in a shift of the color fringes. By moving one of the mirrors by an amount δ, we can get back the fringe pattern that existed before the discs are inserted. Hence the thickness mismatch of the discs δ' is equal to

\[ \delta' = \frac{\delta}{n - 1} \]  

(3.2)
Figure 3.8: A white-light Michelson interferometer for measuring the thickness difference of the two phase grating blanks.
where $n$ is the refractive index of fused silica. Sets of discs with mismatch greater than the specification were rejected and reworked.

Once the specifications had been met, phase gratings with periods of 200 nm were fabricated in these discs by coherent holographic lithography using an etalon-tuned Ar-ion laser ($\lambda = 351$ nm), shadow evaporation of an etch mask, and reactive-ion etching (RIE), see Fig. 5. It is necessary that the two discs be exposed in a single holography session in order that they have exactly the same periodicity. Spatial filters (pinholes) are used in coherent holographic lithography to remove interference effects from dust particles and defects existing in the beam paths. This necessarily results in the expanded beams being spherical. Variation in periodicity introduced by this is, however, very small compared to the periodicity itself. In our system, the pinhole-to-sample distance is $\sim 1$ m. For this distance, the maximum variation in period $\Delta p$ within the central 80 mm-diameter area is calculated to be $< 0.2$ nm.

In order to obtain high-contrast 200 nm-period gratings in photoresist, we must suppress reflections from the substrate. At 351 nm, the refractive indices for the positive photoresist [48] and fused silica are $1.73 + i0.07$ and 1.48, respectively. The calculated TE reflectivity at the resist/fused silica interface (using Eqn. 4.2) is only 1.3% for the incident angle required to generate 200 nm-period gratings. However, fused silica is transparent at 351 nm and the reflectivity from the back surface (fused silica/air interface) is 18%. Furthermore, since we do not know the exact thickness of the disc to within the wavelength of the light, we cannot predict the total reflectivity from the front and the back surface of the disc, which can vary between 10% and 27% due to destructive or constructive interference (see Appendix A for this type of calculations). To suppress the reflection at the fused silica/air interface, the back surface was painted with an anti-reflective coating (ARC) [47], with refractive index equal to $1.66 + i0.14$ at 351 nm. As a result, the back surface reflectivity was reduced to 1.1% (using Eqn. 4.2, assuming that ARC was thick enough to be totally opaque) and the total reflectivity could now vary only between $< 0.1$% and 4.8%.
Anti-reflective coatings are usually spin-coated on the front surface of the substrate and oven baked before the photoresist is coated. In order to maintain good linewidth control during subsequent oxygen RIE, only 180 nm of ARC was coated. Calculations using the method described in Appendix A showed that 180 nm of ARC on the front surface alone could result in the total reflectivity in the resist to vary between 0.8% and 3.8%. In our case, 180 nm of ARC was spin-coated on the front surface in addition to painting ARC on the back surface. As a result, the total reflectivity was < 0.7% and high-contrast grating lines were obtained in the resist, as shown in Fig. 3.9. Another advantage of the painted ARC on the back surface was that it served as a protective coating against scratching during the fabrication process.

After 200 nm-period gratings were defined in resist using coherent holographic lithography, the samples were shadow-evaporated [49] with 5 nm of nickel to serve as an etch mask for RIE in O₂ and CHF₃ plasma. The angle of evaporation determines the final groove width of the phase grating. Oxygen RIE formed grating lines down to the base of the ARC layer. The pattern was then transferred into fused silica by RIE in CHF₃. For both beam-splitter and recombining gratings, the groove depth achieved is ~ 200 nm and line-to-space ratio is about 1:1. This was realized without putting excessive strain on the fabrication technology. It yields an ~ 4% overall grating efficiency for the AHL configuration (without considering attenuations in fused silica and reflection losses at the surfaces) while eliminating the TM polarized wave, as shown in Chapter 2 using electromagnetic calculations. Grating lines in resist and ARC on top of fused silica were removed by an RCA clean [50].

The above fabrication process was first carried out on quartz microscope slides, which allowed inspection under the scanning electron microscope to fine tune various parameters for desired width and depth of the grooves.

An account of the efficiency of the AHL configuration is in order here. The combined efficiency of the two phase gratings is ~ 4%, as mentioned in the last
Figure 3.9: Fabrication process of the 200 nm-period phase grating by coherent holographic lithography, shadow evaporation, and reactive-ion etching.
section. The transmittance through each fused silica disc is $\sim 75\%$ (the light paths are longer than the thickness of the disc). In addition, there is also reflection from the back surface of each disc, and only $58\%$ of the light is transmitted. Putting all this together, the total efficiency of the AHL configuration is $\sim 0.75\%$. 
Chapter 4

Formulation of Anti-Reflection Coating

4.1 Introduction

Despite its relatively low sensitivity and poor plasma-etch resistance, poly(methyl methacrylate) (PMMA) continues to be used as a resist for ArF excimer laser lithography (193 nm) due to its high transparency and high inherent resolution [51]. In fact, Sasago et al. [52] studied several commercially available deep-UV resists and found that only PMMA was useful for 193 nm lithography. Aluminum oxides have been demonstrated as imaging materials for ArF lithography [53]. Although features as small as 0.1 μm has been achieved, the amount of single-pulse energy required for the photochemical etching process exceeds that available at the surface of the resist in AHL. Polysilanes have also been demonstrated as self-developed resists at 193 nm [54]. Again, these are not suitable candidates for AHL since a large amount of single-pulse energy is needed for exposures. Hence, PMMA was used as the resist for AHL in this thesis. Recent reports on silylation process at 193 nm [55] is worth investigating in the future.

Due to the high transparency of PMMA at 193 nm, an anti-reflection coating
(ARC) is needed to attenuate the standing wave orthogonal to the substrate surface. Polyimide [56] was first used as the ARC since it is highly absorbing at 193 nm. In fact, all polymers that contain a high concentration of aromatic groups are highly absorbing at this wavelength. Although polyimide was effective in eliminating the reflection from the substrate, the orthogonal standing wave was still present in PMMA due to reflection at the PMMA/polyimide interface caused by the mismatch in the complex index of refraction, as discussed below. Figure 4.1 shows 100 nm-period gratings in PMMA, exposed at three different doses on top of polyimide. The non-vertical resist profiles and their changing character with increasing dose are clear indications of the presence of an orthogonal standing wave [58]. To solve this problem, an ARC was designed with a complex index of refraction that closely matches that of PMMA at 193 nm.  

4.2 The Complex Indices of Refraction at 193 nm

In order to design an ARC, one must know the complex indices of refraction of PMMA, the ARC, and the substrate at 193 nm. The complex index of refraction is given by the expression

\[ N = n + ik, \]  

(4.1)

where \( n \) accounts for the change in wavelength of light in a material, and \( k \) accounts for attenuation. Complex indices of refraction of many substances, including Si, SiO\(_2\), and many metals, have been measured from x-ray to infrared wavelengths using a variety of techniques such as reflectivity, transmissivity, and ellipsometry. In general, the complex index of refraction of a material at various optical wavelengths can be determined accurately using spectroscopic ellipsometry because such

\footnote{The rest of this chapter closely follows author's paper "An Anti-Reflection Coating for Use with PMMA at 193 nm" [57].}
Figure 4.1: Scanning electron micrograph showing 100 nm-period gratings in PMMA on top of 140 nm of polyimide. Exposure dose increases from (a) to (c); development times are equal.
measurements are insensitive to variations of source irradiance and non-specular scattering from the sample surface. However, spectroscopic ellipsometry cannot be readily used at 193 nm because the polarizer material – calcite – is opaque for wavelengths below 230 nm. It is also difficult to find broad band sources with significant output below 200 nm [59]. To obtain complex indices of refraction in the vacuum UV region, reflectivity methods are used almost exclusively [60].

In this work, the real part, \( n \), of the complex refractive index of PMMA was measured from 1 \( \mu \)m \( (n = 1.47) \) down to 250 nm \( (n = 1.57) \) using spectroscopic ellipsometry [61]. The data was then extrapolated from 250 nm to 193 nm using the Cauchy model [62]. This yields an \( n = 1.68 \) at 193 nm. This extrapolation is reasonable since PMMA has only a weak absorption band between 193 and 250 nm. The imaginary part, \( k \), of the complex refractive index was obtained by measuring the transmission through a thin film at 193 nm. It’s value increases to approximately 0.02 as PMMA is exposed, in agreement with results of Choi et al. [63]. Since the absorption of PMMA is so low compared to the ARC and the substrate, we will assume it to be transparent, i.e., \( k = 0 \).

Extrapolation of ellipsometry data from 250 to 193 nm cannot be used for polymers containing aromatic groups because of the strong absorption in that region. Therefore reflectivity and transmissivity measurements were carried out to find \( n \) and \( k \), using the ArF excimer laser itself as the light source.

To find \( n \) and \( k \) for polyimide, a 1 \( \mu \)m-thick film was deposited onto a quartz substrate by spin-coating and processed using the standard 1 hour bake at 180 °C. No transmission through the substrate was observed at 193 nm. Hence, the film fully absorbed the incident light and we did not need to account for the substrate in our calculations. Reflection coefficients for the TE and TM polarizations are given by [62]:

\[
\begin{align*}
\tau_{01}^* &= \frac{N_0 \cos \phi_0 - N_1 \cos \phi_1}{N_0 \cos \phi_0 + N_1 \cos \phi_1} \quad (4.2)
\end{align*}
\]
\[ r_{01}^p = \frac{N_1 \cos \phi_0 - N_0 \cos \phi_1}{N_1 \cos \phi_0 + N_0 \cos \phi_1}, \] (4.3)

where the subscripts 0 and 1 refer to air and the polyimide film, respectively, \( N_0 = n_0 = 1 \), \( \phi_0 \) is the angle of incidence (measured from the normal), \( N_1 = n_1 + ik_1 \), and \( N_1 \sin \phi_1 = N_0 \sin \phi_0 \). Since the laser is unpolarized, the reflectivity is given by

\[ R = \frac{|r_{01}^p|^2 + |r_{01}^s|^2}{2}. \] (4.4)

Reflectivity was taken at two angles of incidence. This gave two equations for \( n_1 \) and \( k_1 \). These equations were solved numerically to yield \( n_1 \) and \( k_1 \) for polyimide. Several pairs of data were taken to give \( n_1 = 1.33 \pm 0.1 \) and \( k_1 = 0.52 \pm 0.02 \). The value for \( k_1 \) was verified by transmissivity measurements on thin (< 60 nm) films of polyimide.

If the polymer film is not opaque at 193 nm, the effect of the substrate must be taken into account. Reflection coefficients are then given by

\[ r^s = \frac{r_{01}^s + r_{12}^s \exp(2i\delta_1)}{1 + r_{01}^s r_{12}^s \exp(2i\delta_1)}, \] (4.5)

\[ r^p = \frac{r_{01}^p + r_{12}^p \exp(2i\delta_1)}{1 + r_{01}^p r_{12}^p \exp(2i\delta_1)}, \] (4.6)

where \( r_{12} \), the reflectivity at the film – substrate interface, has the same form as \( r_{01} \), \( \delta_1 = (2\pi/\lambda)N_1 d_1 \cos \phi_1 \), and \( d_1 \) is the thickness of the film. The reflectivity will then be given by

\[ R = \frac{|r^s|^2 + |r^p|^2}{2}. \] (4.7)

The main source of error in \( n \) and \( k \) comes from the limited accuracy in our reflectivity measurements. At the low powers required to prevent film ablation, the calorimeter we used was subject to background fluctuations from the environment.

Having found indices of refraction of PMMA and polyimide, the reflectivity at the PMMA – polyimide interface was calculated using the same equations given above, except the subscript 0 now refers to PMMA instead of air. A Si substrate was assumed. Figure 4.2 (solid curve) shows that the TE (the polarization employed...
to achieve high contrast) reflectivity from the interface for incident angle = 74.8° (100 nm-period grating, 50 nm linewidth) is about 10 %. The modulation of the orthogonal standing wave is proportional to the square root of the reflectivity, and hence is about 0.32. This high reflectivity caused the poor resist profiles shown in Fig. 4.1. Note that the mismatch results in greater reflectivities for smaller grating periods, i.e., larger angles of incidence. For example, the reflectivity would be only about 4 % at a grating period of 1 μm (incident angle = 5.5°), as shown in Fig. 4.2 (dashed curve). Figure 4.2 also shows that the substrate effect disappears when the polyimide thickness exceeds ~100 nm.

The optimal ARC is one that minimizes the reflection at the resist - ARC interface, but whose effectiveness is not critically dependent upon the angle of incidence, the ARC thickness, or the nature of the substrate. Based upon numerical simulations using Eqn. (4.2) and (4.5), and \( R = |r|^2 \), as shown in Fig. 4.3, we conclude that the combination of \( k_1 \sim 0.25 \) and \( n_1 \sim 1.5-1.9 \) is near optimal. Another requirement of the ARC is that it be insoluble in the solvents used for PMMA spin-coating and developing so that mixing of the two materials during PMMA coating and development is prevented.

### 4.3 Experimental Results

To meet these requirements, an ARC was formulated consisting of PMMA itself and a \( \text{bis-azide} \), \( 4,4'-\text{diazidodiphenyl sulfone} \), or DDS [64], using cyclopentanone as the solvent. The molecular structure and the UV absorption spectrum of DDS is shown in Fig. 4.4 (after Ref. [65]). The purpose of the DDS is twofold: it serves as an absorber for the 193 nm radiation and also as a film crosslinker to prevent mixing of the resist and the ARC. Crosslinking of PMMA by this particular \( \text{bis-azide} \) was reported by Han and Corelli in making PMMA a negative deep-UV resist [65]. The mechanism for crosslinking is the formation of secondary amines upon photo-
Figure 4.2: TE reflectivity at the PMMA-polyimide interface versus polyimide thickness for incident angles appropriate for holographically generating 100 nm and 1000 nm-period gratings. The wavelength of the incident radiation is 193 nm, and a Si substrate is assumed. Indices of refraction are as follows: PMMA, $N = 1.68 + i0$; polyimide, $N = 1.33 + i0.52$; Si, $N = 0.88 + i2.77$. 
Figure 4.3: Simulated TE reflectivity at the PMMA-ARC interface for a number of indices, $n_1$ and $k_1$, for the incident angle appropriate for holographically generating 100 nm-period gratings. The wavelength of the incident radiation is 193 nm, and a Si substrate is assumed. Indices of refraction are as follows: PMMA, $N = 1.68 + i0$; Si, $N = 0.88 + 2.77$. 
Figure 4.4: Molecular structure and UV absorption spectrum of 4,4'-diazidodiphenyl sulfone (DDS) in ethanol solution.

irradiation [66]. However, this is the first time where DDS serves a dual function. The extinction coefficient of the ARC can be tailored by the amount of DDS mixed into PMMA.

In order for the formulated ARC to provide enough absorption at 193 nm, 7 parts of DDS were mixed with 10 parts of PMMA by weight, using cyclopentanone as a solvent. The bis-azide did not completely dissolve in the solvent and the residue was removed by filtration through a 0.2 μm pore filter. The solution was refiltered when it was applied to the substrate from a syringe. Prebaking the samples at 90 °C before the crosslinking exposure was unnecessary.

The crosslinking exposure was performed using a Hg-Xe arc lamp filtered to give 260 nm radiation. The incident irradiance was measured with a photovoltaic intensity meter sensitive to 220 nm – 290 nm light [67]. After the crosslinking exposure, samples were annealed in a convection oven for 30 minutes at 160 °C. After annealing, no dissolution of the film was observed in chlorobenzene (a solvent for PMMA) if the incident dose at 260 nm exceeded 20 mJ/cm². No crystallization was observed.

Since PMMA is sensitive to radiation below 260 nm, substrates coated only with
PMMA were irradiated with the same lamp to test the effectiveness of the 260 nm filter. (This was important since we wanted only crosslinking to occur in the ARC film and not chain scissioning to compete with it.) Noticeable chain scission began when the incident dose exceeded 2 J/cm$^2$, indicating that some radiation below 260 nm passed through the filter. However, this dose far exceeded that needed for crosslinking.

The components of the complex index of refraction determined using the reflectivity method described above were: $n = 1.52 \pm 0.1$ and $k = 0.25 \pm 0.02$. The value for $k$ agrees with that obtained from transmission measurements. The reflectivity at the PMMA/ARC interface was calculated to be about 2% for the incident angle corresponding to a grating with 100 nm period – a five fold reduction over the PMMA/polyimide combination, as shown in Fig. 4.5. The substrate effect is absent when the ARC thickness exceeds 150 nm. Also shown in Fig. 4.5 are reflectivity curves for 500 nm and 1000 nm-period gratings. Note that in general an ARC thickness of over 150 nm is sufficient to ensure low reflectivity regardless of the spatial frequency of the irradiance distribution.

Figure 4.6 shows a 100 nm-period grating in PMMA on top of the formulated, crosslinked ARC after an achromatic holographic exposure and resist development. The orthogonal standing wave has been significantly reduced, and is not visible in the micrograph. To produce a relief structure that extends all the way to the substrate, oblique shadowing and oxygen reactive-ion etching are used, as will be discussed in the next chapter. For this it is important that PMMA and the ARC have similar etching rates. The etching rate of the crosslinked and annealed film in an oxygen plasma was found to be 70% of the rate of pure PMMA under the same conditions. This reduction in etching rate may be due to the effective quenching of the excited electronic states in the polymer after crosslinking and annealing, as explained by Tsuda et al. [68].
Figure 4.5: TE reflectivity at the PMMA-ARC(PMMA crosslinked by DDS) interface versus ARC thickness for incident angles appropriate for holographically generating 100 nm, 500 nm, and 1000 nm-period gratings. The wavelength of the incident radiation is 193 nm, and a Si substrate is assumed. Indices of refraction are as follows: PMMA, $N = 1.68 + i0$; ARC, $N = 1.52 + i0.25$; Si, $N = 0.88 + i2.77$. 
Figure 4.6: A 100 nm-period grating in PMMA produced by AHL on top of 140 nm of DDS-crosslinked PMMA serving as an ARC.
Chapter 5

X-ray Mask Fabrication

5.1 First-Generation X-Ray Masks

X-ray masks of 100 nm-period gratings had been fabricated before the successful formulation of the PMMA-bisazide ARC, using either gold or tungsten as the X-ray absorber. A silicon wafer was first coated with 1 μm of polyimide [56] as the mask membrane material. The polyimide was cured at 400°C for one hour. At this point, either 15 nm of gold plating base was deposited using electron-beam evaporation, or 65 nm of low-stress tungsten (5 × 10^{-7} dynes/cm^2) was sputter-deposited [69]. The resist/ARC system was a bilayer of 150 nm of dyed PMMA on top of 130 nm of soft-baked (at 180°C) polyimide. In order to reduce the orthogonal standing wave, PMMA was dyed with Coumarin 6 [70] to be more absorbing to the 193 nm radiation. The resist profile after the AHL exposure and development was similar to that of Fig. 4.1 (b).

Figure 5.1 shows the steps used to transfer the grating pattern into gold or tungsten absorber lines. The sample was first shadow-evaporated (electron-beam evaporation) with 8 nm of aluminum as an etch mask and reactive-ion etched (RIE) in oxygen plasma. The parameters used were: power, 0.15 W/cm^2 (400 V bias voltage); pressure, 10 mtorr; flow rate, 15 sccm. An intermittent etching scheme with
plasma on for only 10 seconds was used to prevent the softening of grating lines in resist due to plasma heating. However, it was very difficult to reach the bottom of the ARC layer with a one-step shadow/RIE process. Differences in RIE rates between PMMA and polyimide (the etch rate of PMMA is almost twice that of polyimide) resulted in PMMA lines being “pinched off” before etching reaches the bottom of the polyimide layer. This problem was alleviated by employing a two-step process: after a surface corrugation was established in the polyimide layer, the PMMA lines were dissolved using acetone, and the sample was again shadow-evaporated with 8 nm of magnesium fluoride and etched in an oxygen plasma. Electroplating of gold was performed in BDT-510 plating solution [71] at 33°C and a current of 8 mA. The RIE of tungsten was carried out using a mixture of CHF\textsubscript{3}/CCl\textsubscript{2}/O\textsubscript{2} with flow rates 20.4/15.0/13.6 sccm, etch power of 77 mW/cm\textsuperscript{2} (100 V bias voltage), and a total pressure of 8 mtorr. Thickness of plated gold was 80 nm and that of etched W was 65 nm. These absorber thicknesses provide 10 dB contrast at the carbon K X-ray line ($\lambda = 4.5$ nm).

The mask fabrication was completed by etching away the silicon substrate in a mixture of hydrofluoric and nitrid acid, leaving the X-ray absorber pattern supported by the 1 $\mu$m-thick membrane. Figure 5.2 shows grating lines in PMMA as a result of an X-ray exposure of the mask made with tungsten absorber.

Above mask fabrication techniques resulted in only limited success. The main reason for this limited success was not the complicated fabrication process, but the difficulty in maintaining a uniform resist profile throughout the area of exposure in the presence of the orthogonal standing wave, i.e., it was difficult to get the entire area of exposure to be that of Fig. 4.1 (b), and not (a) or (c). Although Coumarin 6 was used to make PMMA more absorbing at 193 nm in an attempt to reduce the orthogonal standing wave, crystallization of the film after baking would result if the concentration of Coumarin 6 in PMMA exceeded 12% of the PMMA weight. Reliable mask fabrication techniques had to await the successful formulation of the
Figure 5.1: Fabrication of first-generation $C_K$ X-ray masks using Au or W as X-ray absorbers.
Figure 5.2: A 100 nm-period grating defined in PMMA by contact printing using $C_K$ X rays. The absorber is 65 nm of tungsten.
ARC that is DDS-crosslinked PMMA.

5.2 Second-Generation X-Ray Masks

The successful formulation of the ARC that is DDS-crosslinked PMMA has two major implications: first, the resist profile after AHL exposure and development is uniform and extends down to the PMMA/ARC interface due to the suppression of the orthogonal standing wave; second, since the ARC contains about 60% of PMMA, the difference in RIE rates for PMMA and ARC is small so that only a single RIE step is needed for the etch to reach the bottom of the ARC. As a result, the process for X-ray mask fabrication is now more reliable. Key steps of the fabrication process are described below. The fabrication run sheet is given in Appendix B.

As was with the first-generation X-ray masks, the silicon wafer is coated with polyimide and cured, and a gold plating base is deposited. At this point, 140 nm of PMMA-bisazide ARC is spin-coated, crosslinked by a deep-UV exposure at 260 nm with a dose of 200 mJ/cm², and baked at 160°C for 30 min. Then 120 nm of PMMA is spin-coated on top of the ARC and baked at 180°C for 1 hr. The output power of the laser is kept at 0.3 W during the exposure and the beam is scanned in the verticle direction for exposure uniformity. The average incident energy is ~ 25 J/cm². Since the total efficiency of the AHL configuration is ~ 0.75%, the dose in PMMA is ~ 200 mJ/cm². Resist development is carried out in a mixture of methyl isobutyl ketone and isopropyl alcohol (3:2) for 10 sec. at 21°C. A 100 nm-period grating should now be present in PMMA and developed down to the PMMA/ARC interface (see Fig. 4.6).

Next, the sample is shadow-evaporated with 7 nm of silicon dioxide to serve as the etch mask, and etched by RIE in oxygen plasma down to the plating base. Electroplating of gold is then performed immediately after the RIE. Figure 5.3 shows the process of grating pattern transfer and Fig. 5.4 shows a 100 nm-period grating in
Figure 5.3: Fabrication process of second-generation C\textsubscript{K} X-ray masks.

100nm-thick gold after the removal of the plating mold by a dip in hydrofluoric acid (to remove SiO\textsubscript{2}) and oxygen plasma ashing (to remove resist and ARC). Again, the mask is formed by etching away the silicon substrate, leaving the gold X-ray absorber supported by the polyimide membrane.

In fabricating the first-generation X-ray masks, both gold and tungsten absorbers were used. However, RIE of tungsten is not possible with the new fabrication process. Experiments showed that the PMMA/ARC lines were “pinched off” due to side-wall etching and fell over before completing the tungsten etch. (This did not happen to polyimide in the old fabrication process because it has a much slower etch rate under the same etching conditions.) This isotropy in RIE (i.e., side-wall etching) may be suppressed if the substrate can be cooled down to below 0°C during the RIE. Side-wall etching is mainly due to the spontaneous (not aided by ions, which strike only in the verticle direction) etching by neutral atomic species present in the plasma (e.g., oxygen atoms in O\textsubscript{2} RIE). At low temperatures, etching rarely occurs without the assistance of energetic ions. Hence the side-wall etching is greatly reduced. There may also exist a passivation layer consisting of the condensation of
Figure 5.4: A 100 nm-period grating in 100 nm-thick Au. The plating mold has been removed.
Figure 5.5: Top view of a 100 nm-period grating in gold on a SiN$_x$ membrane.

several reaction products to inhibit side-wall etching [72].

The grating pattern in the polyimide X-ray mask is then replicated, by contact exposure using $C_K$ X-rays and electroplating of gold, onto an X-ray mask blank with a SiN$_x$ membrane [73] for durability and freedom of distortion with repeated usage. (As the technique of RIE improves, direct patterning of 100 nm-period X-ray absorbers on SiN$_x$ membranes using AHL will become possible.) Figure 5.5 shows a top view of a 100 nm-period grating in plated gold on a SiN$_x$ membrane, after the removal of the plating mold (PMMA) by oxygen plasma ashing. The process of transferring the grating pattern from a polyimide mask to a SiN$_x$ mask is detailed in Appendix C. These SiN$_x$ masks can then be used to replicate, using X-ray lithography, 100nm-period gratings onto a variety of substrates.
Chapter 6

Summary and Future Work

This thesis describes the fabrication of large-area 100 nm-period gratings using the technique of achromatic holographic lithography (AHL). It was demonstrated for the first time that such gratings could be reliably produced by optical means with high contrast; this was also the first time that 100 nm-period gratings with such large areas were produced by any means. The experimental results obtained in this thesis tell us that high contrast gratings can be obtained despite the poor coherence properties of the light source. Hence it should be possible, using AHL and bootstrap operations, to generate large-area gratings of 50 nm periods and below, where highly coherent sources are not yet available.

Thickness matching for the two fused silica discs containing 200 nm-period phase gratings was crucial due to the relatively small depth of focus (~ 4 μm) of the AHL configuration. The white-light Michelson interferometer played an important role in identifying the thickness mismatch to well below 0.5 μm. Using theoretical modelling, the phase gratings were fabricated to give the AHL configuration high optical efficiency, which resulted in relatively short exposure time (a few minutes). Nevertheless, recording high-contrast gratings in PMMA would not be possible without formulating an optimized anti-reflection coating (ARC) for PMMA at 193 nm. Finally, transferring the grating pattern into the absorber of an X-ray mask makes
the recording of the 100 nm-period grating onto a variety of substrates possible, by X-ray lithography.

For future work I propose to extend AHL to the fabrication of large-area (≈ 1 cm$^2$), 50 nm-period gratings.$^1$ Figure 6.1 shows a schematic of the proposed AHL configuration for producing 50 nm-period gratings. Transmission gratings $G_1$, $G_2$, and $G_3$ are 100 nm in period. They can be fabricated by deep-UV AHL or electron-beam lithography [75]. Soft x-rays of 14 nm wavelength would be used as the radiation source. As depicted, $G_1$ serves as a beam-splitter grating. The zero-order beam is stopped and the first-order beams are rediffracted by transmission gratings $G_2$ and $G_3$. Recombination onto a resist-coated substrate occurs by second-order diffraction, as indicated.

Earlier, a technique, called spatial-period division [76] was used with soft x-rays to double the spatial frequency of a grating using its near-field diffraction pattern [76, 77]. This technique has, however, a major drawback. Since it is not possible to fully block out the zero-order diffracted beam, there is always a component of the fundamental spatial frequency present in the exposed patterns. With an AHL configuration the zero order is readily stopped.

In order for the AHL configuration to be reasonably compact, enabling alignment and gap control to be achieved easily, the angle of the first-order diffraction by the beam-splitter grating should be greater than 5°. This implies that soft x-rays with wavelengths above 10 nm should be used. The undulator radiation at 14 nm is proposed because it has the lowest attenuation through silicon (7.6 dB/μm [78], see Fig. 6.2), which would be used as the membrane material for transmission gratings $G_1$, $G_2$, and $G_3$. Techniques for fabricating silicon membranes are well known. For rigidity, the silicon substrates supporting these membranes would be anodically bonded to Pyrex rings of equal thickness using techniques recently established in

$^1$What follows may also be found in author's paper "Achromatic holographic lithography for 50 nm-period gratings" [74].
Figure 6.1: AHL configuration for generating 50 nm-period gratings. Note that transmission gratings $G_2$ and $G_3$ are on the same substrate, which also serves as the stop for the zero-order beam from $G_1$. Spacers to fix the distance $d$ are not shown.
Figure 6.2: Attenuation in silicon and gold for x-ray wavelengths from 0.1 to 50 nm.

the MIT Submicron Structures Laboratory [73]. To obtain grating areas of ~ 1 cm², geometry dictates that the separation d in Fig. 6.1 be ~ 7 cm. Since the beam size from an undulator is usually much smaller than 1 cm², the AHL configuration will have to be scanned through the beam, or the beam expanded, for example with a Schwarzschild objective.

Fabrication of $G_1$, $G_2$, and $G_3$ would consist of the following steps: a 100 nm-period grating would first be recorded in PMMA resist on top of ARC using AHL and the ArF excimer laser; dry processing would then transfer the grating pattern down to the ARC/membrane interface; finally a gold lift-off would form the x-ray absorber gratings. The thickness of gold needed to provide 10 dB of contrast at 14 nm is ~ 40 nm [78]. Electron-beam lithography could also be used to create the 100 nm-period parent gratings, $G_1$, $G_2$, and $G_3$. However this technique has difficulty creating gratings that are coherent over large areas, and suffers from inordinately
long exposure times at such fine periods.

The diffraction efficiencies of 100 nm-period gold transmission gratings was calculated with the same method used for phase grating efficiencies, discussed in Chapter 2, assuming the width and height of the gold absorbers to be 50 nm and 40 nm, respectively. The complex index of refraction of gold is taken from Ref. [78] to be $0.897 + i6.02 \times 10^{-2}$ at 14.0 nm. For TE radiation, the efficiency of $G_1$ is 13.2%, and that of $G_2$ and $G_3$ is 0.27%. For TM radiation, the efficiency of $G_1$ is 13.0%, and that of $G_2$ and $G_3$ is 0.26%. Hence, the overall diffraction efficiency of the proposed AHL configuration is $3.5 \times 10^{-4}$. If the silicon membranes are 0.5 μm thick, the transmission for each membrane is 42%, and the overall efficiency of the AHL configuration is $6 \times 10^{-5}$.

Alignment of the $G_1$ grating to $G_2$ and $G_3$ can be done using the partial polarization property of transmission gratings, in a technique that employs a photoelastic modulator, as described by Anderson et al. [79].

For radiation normally incident, the depth-of-focus of a grating-type interferometer is limited by the spatial coherence of the source to be (see Chapter 2)

$$\frac{\sqrt{p^2 - \lambda^2}}{2\Delta\theta},$$

where $p$ is the period of $G_1$, $G_2$, and $G_3$, $\lambda$ is the x-ray wavelength, and $\Delta\theta$ is the range of angles of incidence. Since undulators have very good spatial coherence, $\Delta\theta$ should be much less than 1 mrad. As a result, the depth of focus is expected to be much greater than 50 μm. It should be quite easy to locate the final substrate within this range.

PMMA is proposed as the resist for exposure at 14 nm. In spite of its high absorbance at this wavelength, it has been shown that full development of PMMA can be obtained in thicknesses as great as 200 nm [80]. Its sensitivity at 13 nm is $\sim 55$ mJ/cm$^2$ [81]. Hence, the exposure time will be $\sim 7$ minutes if the average irradiance reaching the substrate is $\sim 1$ mW/cm$^2$.  

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Appendix A

Iterative Calculation of TE Reflectivity in the Resist for an $n$-Layer System

In minimizing the standing wave in the resist that is perpendicular to the substrate, one needs to minimize the intensity of the reflected light in the resist. In holographic lithography, only TE polarized light is used in order to obtain high contrast. For an $n$-layer system, e.g., a five-layer system consisting of resist, ARC, Au plating base, SiN$_x$ membrane, and air, what is the TE reflectivity in the resist given the complex index of refraction $N$ and thickness $d$ for each layer, the frequency $\omega$, and the incident angle $\theta$ of the light?

In the $l$th layer ($l = 1$ for resist), the electric field can be expressed as

$$E_{ly} = [A_l \exp(ik_{lz}z) + B_l \exp(-ik_{lz}z)] \exp(ik_x x), \quad (A.1)$$

and the tangential component of the magnetic field is

$$H_{lz} = -\frac{k_{lz}}{\omega/c} [A_l \exp(i k_{lz}z) - B_l \exp(-i k_{lz}z)] \exp(i k_x x), \quad (A.2)$$

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where
\[ k_{x}^2 + k_{z}^2 = \left( \frac{\omega}{c} \right)^2 N_l^2 \]  
(A.3)

from the dispersion relation. Phase matching conditions demand that \( k_x \) be the same for all layers. Hence

\[ k_x = \frac{\omega}{c} \sin \theta. \]  
(A.4)

Since \( E_{ly} \) and \( H_{lz} \) are continuous at the boundary between the \( l \)th layer and the \((l + 1)\)th layer, one can solve for \( A_l/B_l \) in terms of \( A_{l+1}/B_{l+1} \). However \( A_n/B_n = 0 \) because \( A_n = 0 \) (no reflection in the last layer), \( A_{n-1}/B_{n-1} \) can be solved. Working backwards toward the first (resist) layer, one can obtain the reflectivity in the resist

\[ R = \left( \frac{A_1}{B_1} \right)^2 \]  
(A.5)

This calculation was implemented using a Fortran program, as listed below.

* Program to calculate reflectivity in the resist vs. ARC
* thickness for an N-layer system with various incident
* angles (grating periods).

real D1(1000), Y(1000,6), FAM(6), MAXX, MAXY, MINX, MINY,
. N(0:10), N2(0:10), D(10), L, Q(6), W(10)

integer K, NUMFAM, NUMLAY, M

complex j, E(0:10), KZ(0:10), P(0:10), R(0:10), C(10), A, B

character*(4) RESNAM, LAYER(10)

j = (0., 1.)
PI = acos(-1.)
NUMPT = 200
D(1) = 0.
MINX = 0.
MAXX = 350.
MINY = 0.

* Input information needed to perform the calculation.

write(6,*) 'What is the wavelength of the light?'
read(5,*) L
write(6,*) 'What is the refractive index of the resist?'
read(5,*) N(0)
write(6,*) 'What is the extinction coefficient of the resist?'
read(5,*) N2(0)
write(6,*) 'What is the name of the resist?'
read(5,*) RESNAM
write(6,*) 'What are N1 and K1 of ARC?'
write(6,*) 'N1 = ?'
read(5,*) N(1)
write(6,*) 'K1 = ?'
read(5,*) N2(1)
write(6,*) 'How many grating periods do you want to plot?'
read(5,*) NUMFAM
do 3 K=1,NUMFAM
write(6,*) 'What is the grating period?'
read(5,*) FAM(K)
3 continue

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write(6,*) 'How many layers do you wish to include in the'
write(6,*) 'calculation (inc. sub. or in case of membrane, air)?'
read(5,*) NUMLAY
write(6,*) 'Start entering data for layers below ARC.'
do 2 M=2, NUMLAY-1
write(6,*) 'What is N for this layer?'
read(5,*) N(M)
write(6,*) 'What is K for this layer?'
read(5,*) N2(M)
write(6,*) 'What is the name of this layer (up to 4 char.)?'
read(5,*) LAYER(M)
write(6,*) 'and its thickness?'
read(5,*) D(M)
W(M) = D(M)
D(M) = D(M) + D(M-1)
2 continue

* Calculation starts here.

do 5 K=1,NUMFAM
Q(K)=asin(L/(2*FAM(K)))

do 7 M=0,NUMLAY-1
E(M) = (N(M)**2 - N2(M)**2) + j*(2*N(M)*N2(M))
KZ(M) = (2*PI/L)*((E(M) - sin(Q(K))**2)**0.5)
7 continue

do 30 M=0,NUMLAY-2
\[ P(M) = \frac{KZ(M+1)}{KZ(M)} \]
\[ R(M) = \frac{(1 - P(M))/(1 + P(M))}{1} \]

30 continue

\[ C(NUMLAY-1) = 0. \]

do 10 I=1,NUMPT+1
\[ D1(I) = \text{real}(I-1)*(MAXX-MINX)/\text{real}(NUMPT) + MINX \]

do 40 M=NUMLAY-2,2,-1
\[ A = (1 - 1/(R(M)**2))*\exp(j*2*(KZ(M+1) + KZ(M)))*D1(I) + D(M)) \]
\[ B = (1/R(M))*\exp(j*2*KZ(M+1)*D1(I)+D(M)) + C(M+1) \]
\[ C(M) = \exp(j*2*KZ(M)*(D1(I)+D(M)))/R(M) + A/B \]
40 continue

\[ A = (1 - 1/(R(1)**2))*\exp(j*2*(KZ(2) + KZ(1))*D1(I)) \]
\[ B = (1/R(1))*\exp(j*2*KZ(2)*D1(I)) + C(2) \]
\[ C(1) = \exp(j*2*KZ(1)*D1(I))/R(1) + A/B \]
\[ C(0) = 1/R(0) + (1 - 1/(R(0)**2))/(1/R(0) + C(1)) \]
\[ Y(I,K) = C(0)*\text{conjg}(C(0)) \]
if (I.eq.1.and.K.eq.1) then
\[ MAXY = Y(I,K) \]
endif
\[ MAXY = \text{max}(MAXY,Y(I,K)) \]
10 continue

5 continue
* Output into a graph file.

write(11,170) RESNAM
170 format(’title TE Reflectivity at ’,A,’/ARC Interface’) 
write(11,190) RESNAM, N(0), N2(0)
write(11,180) L, N(1), N2(1)
180 format(’title wavelength = ’,f4.0,’ ARC index = ’,f4.2,’ + i’,f4.2 
.)
190 format(’title ’,A,’ index = ’,f4.2,’ + i’,f4.2)

do 100 M=2,NUMLAY-1
write(11,195) LAYER(M), N(M), N2(M), W(M)
195 format(’title ’,A,’ index = ’,f4.2,’ + i’,f4.2,
. ’, thickness = ’,f5.0,’ nm’)
100 continue

write(11,*) ’linear xmin=’,MINX,’ xmax=’,MAXX,’ ymin=’,MINY,
. ’ ymax=’,MAXY
write(11,*) ’xlabel ARC thickness (nm)’
write(11,*) ’ylabel Reflectivity’
write(11,*) ’key x=’,MAXX*.6,’ y=’,MAXY*.9,’ right upper’
200 format(a8)

do 115 K=1,NUMFAM
write(11,*) ’read comfile=true xexp=x yexp=y’
write(11,200) ’.col x y’
do 120 I=1,NUMPT+1
   write(11,*) D1(I),Y(I,K)
120 continue

write(11,210) '.end'
write(11,217) FAM(K)
217 format('legend grating period =',f5.0,' nm')
210 format(a4)
   if (K.eq.1) then
      write(11,*) 'plot curve color=foreground linestyle=solid'
   else
      write(11,*) 'plot curve color=foreground linestyle=next'
   endif
115 continue

write(11,*) 'end'

stop

end
Appendix B

Fabrication Run Sheet of Masks for $C_K$ X Rays with 100 nm-Period Gratings

1. Spin-coat Du Pont PI-2610D polyimide onto a clean silicon substrate @ 5000 rpm for 60 sec. Bake the polyimide @ 130 °C for 30 min. with the wafer in the horizontal position and then @ 400 °C for 1 hr. Final thickness of the polyimide is $\sim 1 \mu$m. Inspect these mask blanks with the aid of a fiber light and reject ones with defects in the central 1 inch-diameter region.

2. Evaporate 50 Å of NiCr for adhesion and 150 Å of Au as the plating base.

3. Prepare the resist/ARC layer for the achromatic holographic exposure as follows, immediately after Au evaporation: spin-coat 1400 Å of PMMA:DDS 4:3 as the ARC from a syringe with a 0.2 μm pore filter; crosslink the ARC by deep-UV exposure at 260 nm with a dose of 200 mJ/cm²; bake the wafer @ 160 °C for 30 min.

4. Spin-coat 1200 Å of PMMA 950K and bake the wafer @ 180 °C for 1 hr.
5. Expose PMMA using achromatic holographic lithography for an incident dose of \(~ 25 \text{ J/cm}^2\) (0.3 W laser output power) and develop it in a 3:2 MIBK:IPA solution for 10 sec. @ 21.5 °C. A 100nm-period grating should now be present in PMMA and developed down to the PMMA/ARC interface.

6. Shadow evaporate, double-sided, @ 55° from the verticle direction, 70 Å of SiO₂ at a slow rate. Cover the wafer other than the grating and the monitor area with a mask.

7. Reactive-ion etch for 50 sec. in oxygen plasma with \(~ 0.15 \text{ W/cm}^2\) (400 V bias) @ 10 mtorr and 15 sccm. To make certain that the sample remains cold during the RIE, apply vacuum grease to the back of the substrate. Etching is done intermittently (10 sec. etching, 1 min. rest). Lightly drop a TEM grid as etch mask just outside the monitor area. It will be used to check the thickness of the plated Au.

8. Plate Au immediately after O₂ RIE at 33°C and 4 mA. Plate a monitor sample with the same geometry first to obtain the plating rate. Plate ~ 1000 Å of Au.

9. Remove the plating mold by dipping the sample in buffered oxide etch for 20 sec., followed by DI rinse and a plasma ashing in He/O₂ for 5 min. using standard conditions.

10. Spin-coat \(~ 2000 \text{ Å}\) of PI-2610D polyimide (e.g., PI:NMP 5:6 by weight @ 3000 rpm, 60 sec. Check thickness with a monitor beforehand. Bake @ 130 °C for 30 min. and @ 250 °C for 30 min.

11. Plasma ash for 6 sec in He/O₂ gas using standard conditions.

12. Immediately spin-coat \(~ 800 \text{ Å}\) of PI-2610D polyimide (e.g., PI:NMP 5:15 by weight @ 3500 rpm, 60 sec). Check thickness with a monitor beforehand.
Bake for 30 min. @ 180 °C. It is crucial to keep the oven temperature as close to this value as possible. Process a monitor first.

13. Spin-coat ~ 5000 Å of positive photoresist (e.g., Shipley 1805 @ 3000rpm, 30 sec.) Bake @ 90 °C for 25 min.

14. Using the UV flood exposure tool (Tamarack), record a 100 μm period grating in resist perpendicular to the 100 nm-period grating lines using contact exposure with a flex-mask and a dose of 32 mJ/cm². Develop with fresh, flowing 1:5 Microposit 351:DI H₂O for 20 sec. (The developer also etches the soft-baked polyimide layer.) Rinse with flowing DI H₂O for 20 sec. Dry with N₂ jet. Inspect with optical microscope.

15. Remove the remaining resist with acetone and rinse with methanol. Dry with N₂ jet. Inspect with optical microscope. Verify that the 100 μm period polyimide grating remains and there is no photoresist residue.

16. Bake the wafer @ 250 °C for 30 min.

17. Glue the wafer to a cleaned PVC pipe with black wax. If the wax is too thick use 1,1,1-trichloroethane as a thinner. Use the wax sparingly since some of the wax might be forced into the pipe. Face mask area into the pipe. Cover the edge and the sides of the wafer with black wax to prevent HF from peeling the membrane. Allow the wax to dry thoroughly (a few hours).

18. Etch away the Si substrate in 96% HF/4% HNO₃ acid mixture. Pour 450 ml of HF into a teflon beaker and add 18 ml of HNO₃. See if it is the right amount, you might have to pour some out. Cover pipe with a lid while etching. Rinse thoroughly with flowing DI H₂O. Dry with N₂ jet. Inspect membrane with a fiber light.
19. Stick a cleaned x-ray mask ring (made of polyimide) to a glass slide with two small rectangles of double-sided tape. Apply a uniform thin bead of 24 hour epoxy (Tracon BA-2115) to the other side of the ring. Lower the prepared ring onto the membrane with the slide assembly and wait 24 hours for the epoxy to cure.

20. Clean a 45 degree mask holder and a wafer plate with methanol.

21. Slice away the ring from the pipe with an Exacto knife and carefully trim the polyimide remnants. Don’t get them on the membrane. Carefully pry the mask from the tape squares with tweezers. Mount the mask in the special 45 degree mask holder.

22. Evaporate 300 Å of “clean” aluminum (using Cr or Ti gettering).

23. Using a wood stick with steal needle apply a small bead of 24-hour silver epoxy (Tracon BA-2902) to the membrane-ring edge to establish electric contact to the membrane. Leave enough epoxy on the ring to form a contact area for the mask clip. Glue a handle (made of brass) to the mask ring with the same epoxy.

24. Cure the epoxy by letting it dry for 24 hours.
Appendix C

Fabrication Run Sheet of SiN$_x$
X-ray Masks with 100 nm-Period Gratings

1. Clean a standard 31 mm SiN$_x$ X-ray mask blank (piranha etch followed by an RCA clean).

2. Evaporate 50 Å of NiCr for adhesion, 200 Å of gold as the plating base, and 2000 Å of gold for mesa step coverage.

3. Immediately spin-coat ~ 2500 Å of PMMA 950K (4% @ 5 kRPM) and bake the sample @ 180 °C for 2 hrs.

4. Replicate the grating pattern from the polyimide mask using contact exposure with C$_K$ X rays. Parameters used are: power, 6 kV and 50 mA; source-to-sample distance, 13.1 cm; exposure time, 31 hrs. The ring of the polyimide mask must rest on the mesa of the SiN$_x$ mask. Also, to prevent the SiN$_x$ membrane from bursting during pump down, a trough is machined in the copper chuck for the air underneath the membrane to escape.
5. Carefully remove the polyimide mask from the SiNₓ membrane with the help of IPA.

6. Develop the PMMA by immersing the SiNₓ mask into a mixture of 40:60 MIBK:IPA @ ~ 21.5 °C for 50 sec. Rinse in IPA.

7. Before the IPA dries, immerse the mask into a petri dish filled with DI water.

8. Carefully immerse the petri dish into the plating solution (BDT-510). Keep the grating area wet throughout this process or the grating lines in PMMA will be pulled together by surface tension.

9. Electroplate gold @ 33 °C with a current of 8 mA. Stop the spin bar and circulation pump during plating. Plate ~ 2000 Å of gold. To find the rate of plating, plate first on a 3” wafer with identical processing steps as those of the SiNₓ mask and look at the cross section of the plated grating in the SEM.

10. Remove the plating mold (PMMA) by an oxygen plasma ash (~ 5 min.).