Microfabrication technologies of X-ray optical elements

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Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
Ph.D. thesis

Microfabrication technologies of X-ray optical elements

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Supervisors: Prof. Ole Hansen, Prof. Henri Jansen
Submitted: February 29th, 2020
**Preface**

This thesis is written to fulfil the requirements for the Doctor of Philosophy (Ph.D.) degree at the Technical University of Denmark. The work presented in this thesis has been performed from the 1st of March 2017 to the 29th of February 2020, in collaboration with DTU Nanotech and DTU Danchip/CEN. On January 1st 2019, DTU Danchip/CEN and parts of DTU Nanotech merged and formed DTU Nanolab. All the work performed, and the results submitted for publication before that date, refer to these two departments which no longer exist. All the results submitted after that date, refer to DTU Nanolab.

Some of the work performed was part of a bigger research project, financed by the Innovation Fund Denmark (file number 6150-00032B) while the rest of the project was internally funded. The project was made in collaboration with two other institutes, namely the Danish Meat Research Institute and DTU Physics. The scope of the project was to manufacture X-ray absorbing elements for their respective equipment.

The thesis is structured in six chapters. First I broadly introduces X-ray optical elements, as well as general X-ray phase contrast imaging. X-ray imaging as such was not part of this project and therefore, only little of it is described and discussed in this thesis. The main part consists of the microfabrication of the optical elements, and is structured in three chapters describing the different fabrication techniques. Finally, the conclusion chapter summarises the results.

I believe this thesis will mostly be read by engineers and scientists working in the field of microfabrication, or people who have a good understanding of the common microfabrication technologies. Therefore, I have mostly discussed the fabrication methods and results, rather than the underlying physics behind the different fabrication technologies (e.g. dry etching, photolithography,...). Should the reader be interested in knowing more about these techniques, I suggest the following books, which are, in my opinion, covering these subjects skilfully.


I wish you a pleasant reading.

Copenhagen, February 29th, 2020
Acknowledgment

The work described in this thesis is not the result of one person’s work, but rather the result of a fortunate collaboration between many skilled and committed people. I am grateful to all who have inspired, supported and challenged me during these three years.

I am particularly thankful to my main supervisor, Professor Ole Hansen, whose many ideas are embedded within this thesis. He gave me the opportunity to work in a field that drives me, and he allowed me to freely shape my project, while supporting my effort with guidance. His thorough knowledge on every level of physics and nanotechnology has been essential in the accomplishment of this thesis. He is a supportive, knowledgeable, patient, and inspiring professor, and it has been a great pleasure to work with him.

I also would like to thank my other supervisor Professor Henri Jansen. His outstanding knowledge within every aspect of deep reactive ion etching has contributed towards many of the successful results in this project. His overflowing enthusiasm for dry etching persuaded me that there is, in fact, something truly fascinating in shaping silicon at a nanoscale.

Special thanks are also given to the main external collaborators; Erik Schou Dreier and his colleagues at DTU Physics and Niels Bohr Institute, as well as Lars Bager Christensen and his colleagues at the Danish Meat Research Institute. Their work offered a practical application to my research, in addition to providing me with deeper knowledge of X-ray phase-contrast imaging.

I am grateful to all collaborators at DTU Nanolab who have made this project an enjoyable and successful experience. However, I would like to give special thanks to my colleagues Bingdong Chang, Murat Nulati Yesibolati and Jens H. Hemmingsen at DTU Nanolab for their particular contribution. Bingdong has shown a sincere interest in my project throughout its entirety, in addition to helping me solve many of the unexpected dry etching results. Murat dedicated a lot of his time to experimental support to solve the electroplating dynamic issues, and Jens helped with the laser processing to fabricate a working tungsten device much earlier than I could have hoped for.

I am grateful to Mizushima at IPU and Peter Jacob Schwenck Westerman at DTU Mechanical Engineering for helping me with the gold electroplating setup, in addition to providing valuable knowledge in gold electroplating.

I also would like to thank Anita Stick in the administration of DTU Nanolab. I am one of these people who see administrative tasks as cumbersome hassles that somewhat keep you away from all the exciting laboratory work, yet I understand the unavoidable need for an ordered administrative system. Through her excellent know-how, and understanding of the (unreasonably ?) complex system, Anita has made some administrative tasks a walk in the park, rather than a test of endurance.

I also thank my friends and family for their moral support and understanding.

Finally, I would like to thank the Innovation Fund Denmark, The Otto Mønsted Foundation and the Hartmann Brothers Foundation, for their financial support.
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Abstract

Over the last 15 years, X-ray phase-contrast imaging has shown to overcome the limitations of traditional X-ray absorption imaging. Amongst other benefits of this technique, we find the imaging of weakly absorbing materials. This method was made possible thanks to better detectors as well as improved microfabrications methods. An X-ray phase contrast setup needs one or several optical elements with high absorption contrast. Ideally, the absorbing element is made of alternated absorbing and transparent areas exhibiting high aspect ratio. Despite important research efforts, the microfabrication of these absorbing elements still suffers from limitations. These limitations are partly caused by the high aspect ratio structures required to selectively absorb the photon energy to provide sufficient signal-to-noise ratio. The goal of this thesis was to provide an understanding of the microfabrication limits, and to developed reliably methods to produce these absorbing elements. Silicon is often chosen as an X-ray transparent mould, into which the X-ray absorbing material is placed. Combining silicon with absorbing metal filling, is a common fabrication process that we have investigated. In addition, we proposed a new manufacturing possibility, involving only the absorbing metal eliminating the silicon mould.

First, we proposed a fabrication method to manufacture absorbing linear gold gratings for X-ray Talbot interferometry imaging. The manufacturing process was straight forward, and consisted of an anisotropic dry etching of silicon and gold electroplating. The highest aspect ratio of the manufactured absorbing elements was approximately 12:1. Perhaps the most critical outcome of this study was the understanding of the plating dynamics. Existing literature related to absorbing gratings rarely reports the plating dynamics in deep trenches, and our investigations demonstrated that gold concentration in the electrolyte is a critical factor to consider.

Second, we investigated the use of a short-pulse UV laser to make micron-sized holes in bulk tungsten to fabricate a two-dimensional absorbing mask for X-ray edge illumination imaging. Tungsten is a metal which has similar X-ray absorbing properties to that of gold, yet is significantly cheaper. The intensity of the laser has direct influence on the diameter of the hole. Thus, by adjusting the intensity, micron-sized holes with an aspect ratio as high as 44:1 could be achieved. Arguably, this method is a serial process and does not scale easily without affecting significantly the processing time. On the other hand, it has the non-negligible advantage of involving very few fabrication processes, and only uses the absorbing material, thus removing the need for a silicon mould.

Finally, we proposed a method to fabricate silicon moulds for two-dimensional gratings. The moulds consisted of pillar arrays made using silicon dry etching. This study is slightly different to that of the two previous, as it does yield to a finished absorbing element, but rather proposes a reliable method to fabricate silicon moulds for a wide range of dimensions and shapes. More particularly, this study examines the silicon micro-grass formation. Silicon micro-grass is a common, often unwanted effect, which occurs principally in large open area with a low aspect ratio. This issue is often addressed by modifying the etching parameters to prevent the grass from forming. Unfortunately, the modification of the parameters quickly becomes a time-consuming task, especially when different etching machines are involved. Instead, we investigated the critical dimensions at which the micro-grass forms, and proposed a generic method, based solely on sacrificial geometries to suppress the grass.
Dansk resumé


List of contributions

Peer-reviewed publications

List of the published articles related to the PhD thesis.


Conferences contributions


- Silvestre, Chantal M.; Hemmingsen, Jens H.; Dreier, Erik S.; Kehres, Jan; Hansen, Ole, 44th International Conference on Micro and Nanoengineering, 24-27 September 2018, Copenhagen - Denmark, "High aspect ratio tungsten gratings for X-ray phase-contrast imaging", Poster presentation

- Silvestre, Chantal M.; Henri, Jansen; Hansen, Ole 45th International Conference on Micro and, 23-26 September 2019, Rhodes - Greece, "Deep reactive ion etching of “grass-free” widely spaced periodic 2D structures", Poster presentation
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>AR</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>CEAC</td>
<td>curvature-enhanced accelerator coverage</td>
</tr>
<tr>
<td>CRL</td>
<td>Compound Refractive Index</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DRIE</td>
<td>Deep Reactive Ion Etching</td>
</tr>
<tr>
<td>DMRI</td>
<td>Danish Meat Research Institute</td>
</tr>
<tr>
<td>DM-EI</td>
<td>Double Mask Edge Illumination</td>
</tr>
<tr>
<td>DTU</td>
<td>Danish Technical University</td>
</tr>
<tr>
<td>EI</td>
<td>Edge Illumination</td>
</tr>
<tr>
<td>FZP</td>
<td>Fresnel Zone Plates</td>
</tr>
<tr>
<td>HAR</td>
<td>High Aspect Ratio</td>
</tr>
<tr>
<td>IC</td>
<td>integrated circuit</td>
</tr>
<tr>
<td>LPCVD</td>
<td>low pressure chemical vapour deposition</td>
</tr>
<tr>
<td>OES</td>
<td>optical emission spectroscopy</td>
</tr>
<tr>
<td>PC</td>
<td>Pulse current</td>
</tr>
<tr>
<td>PCI</td>
<td>Phase-contrast Imaging</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma enhanced chemical vapour deposition</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>ToT</td>
<td>Time-of-arrival</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
</tbody>
</table>
# List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>atomic weight</td>
</tr>
<tr>
<td>$A_{th}$</td>
<td>ablation threshold</td>
</tr>
<tr>
<td>$E_B$</td>
<td>binding energy</td>
</tr>
<tr>
<td>$E_{\text{pulse}}$</td>
<td>pulse energy</td>
</tr>
<tr>
<td>$E_0$</td>
<td>peak energy</td>
</tr>
<tr>
<td>$E_{\gamma}$</td>
<td>X-ray energy</td>
</tr>
<tr>
<td>$f$</td>
<td>focal length</td>
</tr>
<tr>
<td>$I_{\text{max}}$</td>
<td>maximum transmitted intensity</td>
</tr>
<tr>
<td>$I_{\text{min}}$</td>
<td>minimum transmitted intensity</td>
</tr>
<tr>
<td>$I_0$</td>
<td>peak intensity</td>
</tr>
<tr>
<td>$J_a$</td>
<td>threshold fluence for single pulse ablation</td>
</tr>
<tr>
<td>$J_0$</td>
<td>peak fluence</td>
</tr>
<tr>
<td>$M$</td>
<td>magnification factor</td>
</tr>
<tr>
<td>$M^2$</td>
<td>beam quality factor</td>
</tr>
<tr>
<td>$n$</td>
<td>refractive index</td>
</tr>
<tr>
<td>$P$</td>
<td>power</td>
</tr>
<tr>
<td>$P_{\text{avg}}$</td>
<td>average power</td>
</tr>
<tr>
<td>$r_a$</td>
<td>ablated radius</td>
</tr>
<tr>
<td>$r_0$</td>
<td>classical electron radius ($2.82 \times 10^{-5}$ Å)</td>
</tr>
<tr>
<td>$V$</td>
<td>volume, or visibility</td>
</tr>
<tr>
<td>$w_0$</td>
<td>beam radius at $1/e^2$ of maximum beam intensity</td>
</tr>
<tr>
<td>$w_l$</td>
<td>laser beam radius before lens</td>
</tr>
<tr>
<td>$Z$</td>
<td>atomic number</td>
</tr>
<tr>
<td>$\beta$</td>
<td>imaginary part of the refractive index, or attenuation coefficient.</td>
</tr>
<tr>
<td>$\delta$</td>
<td>real part of the refractive index, or phase-shifting coefficient.</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
</tr>
<tr>
<td>$\mu$</td>
<td>linear absorption coefficient</td>
</tr>
<tr>
<td>$\nu$</td>
<td>frequency</td>
</tr>
<tr>
<td>$\rho$</td>
<td>material density</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>electron density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>absorption cross-section</td>
</tr>
<tr>
<td>$\tau$</td>
<td>laser pulse duration</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

DTU Nanolab has been very active in the development of microfabrication technologies for a wide range of applications including manufacturing of X-ray optical elements. Microfabrication technology for X-ray optical elements is challenging, but the potential in terms of applications, for a broad range of scientific fields, is rapidly growing. In this chapter, a brief overview of different types of X-ray optical elements is given to introduce the subject. The second part of the chapter covers the motivation behind the work presented in this thesis which is more precisely focused on X-ray optical element for phase-contrast imaging. Finally, the thesis outline is given.

1.1 Introduction to X-ray optical elements

X-rays are electromagnetic waves just like visible light is. However, their energy and wavelength are considerably different. Figure 1.1 illustrates where in the electromagnetic spectrum X-rays are found. X-rays wavelength are in the range of 0.006 nm to 3 nm and thus, the photon energy is several order of magnitude higher (400 eV to 200 keV) than that of visible light which is in the range of 400 nm to 700 nm (1.7 eV to 3 eV). The high energy of X-rays allows them to penetrate all media with a material dependant degree of attenuation, i.e. light elements like carbon, hydrogen or oxygen have less attenuation than heavier elements like calcium, gold or iron.

![Electromagnetic spectrum from visible light to gamma-rays.](image)

These waves were first reported by Wilhelm Röntgen in 1895 [1] and, briefly after, began to extensively be used in medical imaging. X-ray are well known for their utilisation in medical imaging such as radiography or computed tomography, but their range of applications is far wider.
Present utilisation of X-ray includes medical diagnosis, airport security, material characterisation, fundamental research and space exploration. Because the X-rays penetrate most materials with ease, it can be difficult to manufacture optical elements (OE) to guide X-rays. In general, optics capable to manipulate X-rays can be categorised based on how the wavefront interacts with the optical element. We can enumerate 4 main physical interactions: (1) reflection, (2) refraction, (3) diffraction and (4) absorption. Figure 1.2 illustrates these four interactions with typical related optics. Each type of optics will have characteristic features intrinsically linked to the physical light interaction and the manufacturing limitations. There exist a variety of optics for each of the interactions, and research to improve their optical capabilities is an ever-growing subject. Looking closer at the different types of X-ray optical elements, we can cite some examples and critical fabrication requirement.

![Figure 1.2: Schematic examples of X-ray optical elements for (A) reflection, (B) refraction, (C) diffraction, and (D) absorption interactions.](image)

An example of application of reflective optics can be found in some X-ray space telescopes (i.e. Chandra X-ray Observatory, eROSITA, ATHENA,…). In these telescopes, the optical element often consists in an array of several reflective mirrors aligned in a Wolter I configuration as illustrated in Figure 1.2A. Due to the high energy of the photons, the light must arrive at a grazing angle upon the surface of the mirror to ensure total reflection of the light. If the angle of incidence is above the critical angle (usually a few milliradians), the light would propagate into the material instead of being reflected. A critical point in the manufacturing of these reflective mirrors are the reflective coatings which must reflect a broad range of X-ray wavelengths to meet the science objectives of the equipment. Multi-layer thin films with different material density are often chosen to ensure reflection for a broad spectral range [2, 3]. However critical parameters, such as layer thickness, stress and stability over time must be considered in the manufacturing.
process without which the reflective power would be impaired.

A second type of optical elements are refractive optics. These optics utilise the refraction of light occurring between two materials of different refractive index to guide the X-rays. Unlike visible light, the refractive index of X-rays in all materials is marginally below unity. This small value forces the X-rays to refract in the opposite direction than that of visible light, and with only a small refractive angle. Thus, to focus X-ray light in the meter range or below, several concave shape lenses must be aligned to form a compound refractive lens (CRL), as illustrated in Figure 1.2B. Refractive optics can be found in synchrotron beam lines to focus the light to the experimental setup. In such application, the refractive optic consists in a series of cavities manufactured with a high degree of repeatability and precision. Precise radius of curvature, uniformity along the sidewall cavity, and careful choice of the material are important manufacturing parameters to take into account [4, 5].

Diffraction occurs when light hits a periodic structure of similar dimensions to that of the wave front. An example of X-ray optic using diffraction is the Fresnel zone plates (FZP). This optical elements consists in alternate transparent and opaque concentric rings with radially increasing diameters and decreasing widths. As a result of the poor absorption of X-ray light in many materials, the opaque rings are made of high atomic number materials (e.g. some micrometers of gold). A schematic of a FZP is illustrated in Figure 1.2C, and an example of application for this optic is to focus the incoming X-ray light at synchrotron beam lines. Because the spatial resolution is tied to the size of the periodic features, very small structures with high aspect ratio (AR) must be achieved. The AR is defined as the ratio between the height and the width of a structure. As a general rule, the focal point diameter of a FZP is roughly equal to the width of the outermost ring. For example, a focal spot size of 30 nm with a 8keV energy requires a 50 nm wide outermost ring and an gold thickness of 900nm [6]. The manufacturing of FZP usually involves e-beam lithography and electrodeposition [7, 8]. However, for higher energy beams, this microfabrication process has limitation due to the higher thickness requirement, which increases significantly the aspect ratio. Consequently, it becomes difficult to manufacture FZP providing simultaneously sub-micron resolution, and high efficiency [9].

Finally, absorbing X-ray optical elements are utilised to preferentially absorb an incoming radiation as illustrated in Figure 1.2d. X-ray phase-contrast imaging (PCI) is an application which uses absorbing optics. In a nutshell, X-Ray PCI uses the change in angular direction of the light passing through a phase-shifting object. The change in angular direction from the propagation direction is provoked by the real decrement part $\delta$ of the refractive index $n \left( n = 1 - \delta + i\beta \right)$ of the object. For light materials, $\delta$ is several orders of magnitude larger than that of the absorption counterpart $\beta$. Unlike, conventional X-ray absorption imaging which solely relies on $\beta$, X-ray PCI allows to discriminate between media with a similar $\beta$ absorption, but different refractive index. This makes PCI an excellent technique for the non-destructive investigations of samples made of light elements (i.e. soft-matter, biological samples, fabrics cloth,...). Objects can be resolved with a resolution of few tens of micrometers. To take a concrete example of PCI equipment, we can mention the X-ray phase-contrast Talbot Interferometer setup [10]. This equipment requires a set of absorbing gratings to create an interference pattern which acts as the base signal for the measurement of the angular variation. When an object is placed along the prop-
agation direction of the light, it will disturb the interference pattern. The change in the interference pattern is recorded with an appropriate detector and, using computational algorithm, a contrasted image of the object is created. The interference pattern visibility is closely linked to the absorption efficiency of the grating. Because of its large absorption coefficient, gold is often preferred when manufacturing these absorbing gratings. Typically, for a X-ray source of 30 keV the absorbing thickness of gold would be approximately 40 µm to ensure good absorption, and thus high signal to noise ratio [11]. However, the width of the period of these gratings is only few micrometers, thus very high aspect ratio structures are required [12, 13]. This high aspect ratio requirement increases the complexity of the fabrication methods and makes the manufacturing of these gratings difficult for very thick gold layers. It is therefore difficult to achieve good signal to noise ratio for higher energy X-ray sources.

In conclusion, a large variety of optical elements exist to manipulate X-ray light, and improving their performances is subject to ever growing research. Luckily, the continuous development of new fabrication technologies permits to push even further the performances and microfabrication limits of these optics. The field of X-ray optical elements is vast and continues to expand, thus there is room for microfabrication improvement regardless of the type of X-ray optical element. The research presented in this thesis aims at proposing microfabrication methods for X-ray optical elements, and more specifically for absorbing optics for X-ray phase-contrast imaging.

1.2 Project context and general motivation

Until the second half of the years 2000’s, X-ray phase-contrast imaging using absorbing optical elements was restricted to synchrotron radiation due to the rigid requirement on the monochromatic source and the detectors [14, 15]. But, as the technologies related to detectors and optics developed, phase-contrast imaging using polychromatic laboratory sources became conceivable [16, 17, 18]. The possibility to use polychromatic sources allowed to fabricate apparatus with significantly smaller physical dimensions than that of a synchrotron facility. This considerable downsizing made possible to perform phase-contrast imaging with clinical size equipment. Both, the department of physics at the Technical University of Denmark (DTU Physics), and the Danish Meat Research Institute (DMRI) have made the choice to develop such equipment for their respective needs. The work described in this thesis will focus on these two equipments.

The setup developed at DMRI aims at screening food products for the presence of foreign bodies. Current food screening method technologies include conventional X-ray imaging (i.e. absorption based imaging) which is an ideal method for detecting the presence of heavy absorbing foreign bodies (e.g. pieces of metals). However, this technology cannot detect light materials such as paper, wood, fiber cloth or insects, whose presence in food products is potentially dangerous, and can create negative impact on the consumer behaviour. In order to provide better and safer industrially processed food, DMRI developed a phase-contrast imaging equipment for food analysis, which can detect poorly absorptive elements in soft-tissues like meat. Their setup is of the Talbot interferometer type as shortly introduce earlier. A full description of the equipment and its optical requirements will be given in Chapter 2. The overall project involved
several key features which needs to be solved. Among these features, we find (1) the system for conversion of X-rays to visible light and detection (i.e. optical elements and detector), (2) the image reconstruction algorithm, and (3) an overall design suited for industrial food conveyor. The work described in this thesis is part of the conversion of X-rays to visible light feature. The main focus is on the microfabrication of the absorbing optical elements which consist in a set of 3 linear gratings exhibiting relatively high aspect ratio (above 10:1) and good X-ray absorption.

The X-ray phase-contrast imaging setup developed at DTU Physics is part of the 3D Imaging Center (3DIM) at the Technical University of Denmark [19]. The facility offers to industries and academics state-of-the-art equipment and advanced knowledge within imaging. The center is in continuous growth, and new equipment are regularly acquired and developed. Over the last couple of years, DTU Physics has been actively working on a phase-contrast imaging setup of the type Edge illumination [20]. Edge illumination is a type of X-ray phase-contrast imaging apparatus using a conventional laboratory sources but works differently than Talbot interferometry. Briefly, in this technique, the X-ray source is split in a two-dimensional array of single beamlets by means of an absorptive optical element. Each beamlet hits an individual pixel on the detector, thus giving each pixel a reference signal intensity. When a sample is placed on the path of the beamlets, the light refracted by the object will change the beamlets trajectory. That change in the propagation direction will make the beamlets hit different pixels, which will eventually induce a different signal intensity. The recorded change in the intensity of the individual pixels with and without the sample is used to reconstruct a contrasted image of the sample. This technique competes currently with Talbot interferometry in terms of image resolution and potential for clinical and industrial uses. A detailed description of edge illumination setup will be given in Chapter 2. The edge illumination setup at DTU Physics employs a new generation of detector capable to detect photon intensity at a sub-pixel level. The sub-pixel detection gives the potential for higher resolution than that of other edge illumination setups which normally have a resolution limited to the pixel size of the detector (i.e. a few tens of micrometers). A recent experiment, performed at the European Synchrotron Radiation Facility in Grenoble [21] and using the same type of detector, demonstrated the ability to measure a beamlet step of 4.4 μm which is far below the pixel size of the detector (i.e. 55 μm). The use of this advanced sub-pixel detector places the edge illumination setup at the DTU 3D imaging center among the first of its kind. Because of the continuous growth of the center and its versatility, there is an increasing need for in-house knowledge for manufacturing of optical X-ray elements. The ability to manufacture made-to-fit optics will allow more flexibility in the future of the 3D imaging center. In this project, we have focused on the microfabrication of the main optical element of the edge illumination setup.

Despite the fact that the two setups are fundamentally different in the way the phase-shift signal is analysed, the optical elements exhibit similar microfabrication processes. These similarities are caused by the need for the optical components to efficiently and selectively absorb the incoming X-rays to enhance the signal to noise ratio. To efficiently absorb the X-rays, the thickness of the absorbing layer must be several micrometers thick, and the size of the features is often only a few micrometers. Conventional fabrication methods often involve UV-lithography, silicon dry etching and gold electroplating. Alas, issues arise in the manufacturing for structures with aspect ratio above 12:1 often due to the gold electroplating which becomes difficult as the
aspect ratio increases.

### 1.3 Scope of the thesis

This thesis is about the microfabrication of the optical elements for both the DTU Physics setup and the Danish Meat Research Institute setup. While the dimensions of the optical elements in this project are tailored to the dimensions of these setups, the fabrication methods proposed may be used in conjunction with other X-ray phase-contrast imaging equipment.

Beside manufacturing optical elements for these two setups, the project goals were:

- identify current limits in the state-of-the-art manufacturing of gold absorbing gratings.
- develop and propose simple fabrication method to manufacture X-ray absorbing optical elements.
- investigate the use of laser tungsten ablation as an alternative to gold electroplating.

### 1.4 Thesis outline

**Chapter 2** review some general aspects in X-ray imaging and focused primarily on the review of the manufacturing of absorbing optical elements for X-ray phase-contrast imaging. The thesis itself is oriented mostly toward microfabrication techniques, therefore, the X-ray imaging field is only lightly covered, to provide the reader merely a general overview. I review in particular, the current manufacturing methods for absorbing X-ray optical element for phase-contrast imaging. I also present the two main setups for which I manufactured some X-ray absorbing elements.

**Chapter 3** covers the manufacturing of the optical elements for the Talbot interferometer at DMRI. This chapter is particularly oriented toward the absorbing optical elements which are the most difficult to fabricate. In X-ray Talbot Interferometry, the absorbing elements consist of absorbing and transparent alternated lines, making a linear grating. Very often, the manufacturing of these gratings consists in the electroplating of gold a silicon mould with deep trenches exhibiting a high aspect ratio. In this chapter, we used this approach, and prepared a silicon moulds using deep reactive ion etching, that were subsequently electroplated with gold. In state-of-the-art manufacturing of X-ray OE, the aspect ratio of the grating is very often the trouble-maker. Voids in the trenches, and unwanted sidewall plating, are often observed. The chapter describes the results, and encountered difficulties which arose during the gold electroplating of the silicon mould.

**Chapter 4** covers the manufacturing of the absorbing mask for the DTU physics edge illumination setup. Laser ablation of tungsten was the principal fabrication method used in this section. I introduce first a short review of microfabrication using laser ablation and then present the characterization of the laser employed in this project. The manufacturing of the mask and the X-ray tests are described. This chapter covers the result published in the paper in Appendix A.1.
Chapter 5 introduces a method to dry etch widely spaced silicon pillars while avoiding the formation of black silicon. Widely spaced pillars can be used as silicon mould for two dimensional absorbing masks for X-ray edge illumination. The pitch between the holes of these type of masks can be rather large (> 50 µm). The large pitch means that in the silicon scaffold are are widely spaced pillar which leave wide open areas prone to grass formation. This chapter covers the result published in the paper in appendix A.2.
Chapter 2

Background and literature review

In this chapter, I begin by presenting the X-ray absorption imaging and the phase-contrast imaging methods. X-ray experiments were not an inherent part of the project itself, however, the introduction to the different imaging methods gives the reader an overview of the technologies where the optical elements that I developed are used. X-ray phase-contrast imaging is introduced with a level of detail tailored to provide solely a basic understanding of the techniques. Hence, this chapter does not include advanced X-ray phase-contrast physics which can be found in other literature. Finally, I review the current manufacturing of absorbing X-ray optical elements for edge-illumination and Talbot interferometry apparatus.

2.1 X-ray absorbing imaging

X-rays were discovered in the late 19th century by the German physicist Wilhelm Conrad Röntgen. In his paper from February 1896 [1], W. C. Röntgen presented the photograph of the bones in a living human hand with a metal ring on one of the fingers - Hand mit ring (Figure 2.1). This astonishing photograph at that time, revealed details inside a living body which had never been imaged before. In this photograph, the bones and the ring absorbed the X-rays significantly more than that of the surrounding tissue, resulting in a contrasted image. This discovery heralded a substantial change in the field of non-destructive medical imaging in the following century. This contrasted image relies on the interaction of the incoming X-ray light and the matter.

The refractive index

Because X-ray are electromagnetic waves, they interact with matter with scattering and absorption effect just like visible light does. At a macroscopic scale, the interaction of a photon with atoms in the material can be described by the refractive index $n$.

\[ n = 1 - \delta + i \beta \] (2.1)
where $\delta$ is the phase shift decrement of the wave and $\beta$ is the absorption contribution of the refractive index. Both contributions are expressed as [22]:

$$\delta = \frac{\rho e r_o \lambda^2}{2\pi}, \quad \beta = \frac{\mu \lambda}{4\pi}$$ (2.2)

where $\lambda$ is the wavelength (nm), $\mu$ the linear absorption coefficient (cm$^{-1}$), $\rho_e$ the electron density (Å$^{-3}$) and $r_o = 2.82 \times 10^{-5}$ Å is the classical electron radius (i.e. Thomson scattering length).

**Attenuation based imaging**

Current X-ray imaging equipments are, to a large extent, based on the attenuation of the light through an object. This means that they primarily use the contribution $\beta$ of the refractive index. As a general rule, the more X-rays an object absorbs compared to its surrounding, the more contrasted the image. For a homogeneous isotropic material, the intensity transmitted through a medium follows Beer-Lambert’s law:

$$I = I_o e^{-\frac{x}{\mu}}$$ (2.3)

where $I$ and $I_o$ are the attenuated and the initial photon intensity respectively, and $x$ the thickness of a homogeneous object. The linear attenuation coefficient $\mu$, is expressed in terms of a sum of photoelectron absorption cross-sections ($\sigma$) with the chemical elements in the material unit cell volume ($V$) [23].

$$\mu = \frac{1}{V} \sum_{i=1}^{n} \sigma_i$$ (2.4)

From experimental observations, $\mu$ is element dependent, and strongly depends on the X-ray energy. It decreases with the energy with approximately $E^{-3}$ and increases with the atomic number by a factor $Z^4$ such

$$\sigma \propto \frac{\rho Z^4}{AE^5_{\gamma}}$$ (2.5)

where $Z$ is the atomic number, $E_{\gamma}$ the X-ray energy (J), $A$ the atomic mass (kg) and $\rho$ is the material density (kg/m$^3$). Figure 2.2 illustrates the photo-absorption cross-section for a range of elements from $Z = 1$ to $Z = 40$ for three X-ray energies. Absorption edges are visible at $Z = 10$.
(Ne) and Z = 11 (Na) at 1 kev. These edges are created when the energy of the incoming photon \(E_\gamma\) equals the binding energy \(E_B\) of the electron in the outer shell of the atoms \(E_\gamma = E_B\). [24]

Figure 2.2: Photo-absorption cross-section as function of the atomic number Z for 50eV, 1keV and 20keV. Absorption edges (resonance effect) are visible at Z= 10 (Ne) and Z=11 (Na) at 1keV. From [24]

Due to their high energies, X-rays will be transmitted through most materials, but with a variable degree of attenuation proportional to the attenuation coefficient \(\mu\). From equation 2.5 we can see that the atomic number Z influences the attenuation with a power of four. Soft tissues are mostly made of oxygen (Z = 8), hydrogen (Z = 1) and carbon (Z = 6) which absorb X-rays poorly. On the other hand, bones are primarily made of calcium (Z = 20). This difference in absorbing ability is the reason why we see good contrast between bones and soft tissues in X-ray radiography.

Whilst this is an effective and reliable approach to image many objects, it has limitation when imaging objects exhibiting comparable attenuation features. The consequence is reflected in a poorly contrasted image. An alternative approach to enhance the contrast of the image is to exploit the phase change of the light wave through a medium, instead of its attenuation. This technique is called phase-contrast imaging.

2.2 Phase-contrast imaging

Just like for absorption imaging, phase-contrast imaging can be described using the complex refractive index \(n\) of an element. The complex index of refraction was reported in equation 2.1, where \(\delta\) denotes the phase change of the light (refractive decrement), and \(\beta\) denotes the attenuation of the light through a medium. When light travels through a medium of refractive index \(n\), it experiences both effects as illustrated in Figure 2.3a.
For phase-shift imaging, it is the phase change $\delta$ which is the primary effect used. In short, when light enters a medium of different optical density it will slow down. The speed reduction is caused by the interaction between the frequency of the light and the electromagnetic oscillation of the electrons in the medium. The interaction of the two electromagnetic waves results in a slow down of the wavefront and create a phase change. This phase change causes the light to modify its propagation direction and makes the light bent through the material (i.e. refraction). Far from the absorption edge \(^1\) (i.e. atomic resonances), the phase-shift coefficient $\delta$ can be written like in equation 2.2. For the sake of readability, equation 2.2 is repeated here.

\[
\delta = \frac{\rho_e r_0 \lambda^2}{2\pi}
\]

The refraction occurs at the interface between media of different refractive index as illustrated in Figure 2.3b. The bending angle follows Snell-Descartes’ law:

\[
n_1 \cos \theta_1 = n_2 \cos \theta_2
\]  

(2.6)

Where $\theta_1$ and $\theta_2$ are the incident and refracted angles respectively. Unlike visible light, X-ray light will refract toward the surface with a very weak refracted angle, since the refractive index is slightly smaller than unity.

Figure 2.4a illustrates the ratio between the absorption ($\beta$) and the phase shift ($\delta$) of some materials. The kinks at $E=1.83$ keV for silicon and at $7.11$ keV iron are due to the absorption edges of the core electrons. We observe that for materials with low density such as water and polymers, the ratio is several orders of magnitude larger than for elements with higher density such as iron.

\(^1\)Phase-contrast imaging is performed far from the absorption edge.
and silicon. Hence, measuring the phase shift instead of the attenuation can bring higher sensitivity when imaging materials with low X-ray absorption. This imaging method is thus ideal for imaging soft tissues which only have subtle electrons density variation such as malignant and benign cancer cells. Figure 2.4b illustrates how the phase change of a wave front through a phase shifting object influences the intensity on the pixels detectors.

![Figure 2.4: (a) Ratio $\delta/\beta$ as function of energy for iron (Fe), silicon (Si), water ($H_2O$), polymethylmethacrylate (PMMA), polystyrene (PS). Data source from Lawrence Berkeley National Laboratory [26]. (b) Illustration of X-ray through a phase changing object. After refraction, the outgoing wavefront vectors are pointing in different directions and influence the pixel intensities.](image)

In his early work, W. C. Röntgen did not observed any phase-shift. In the publication he reported:

"...I proceeded to investigate whether the X-rays could be deflected by a prism. Investigation with water and carbon bisulphide in mica prism 30° showed no deviation either on the photographic or fluorescent plate."

_W.C.Röntgen, Science, Vol. 3 (Feb. 1896)_

In fact, the refractive angle of X-ray through a material is only a few micro-radians. Hence, early measuring equipment could not reliably measure the refracted angle. It is only in 1965 that U. Bonse and M. Hart highlighted the phase change of X-ray using an single-crystal interferometer system [27, 28]. However, it is 30 years after that Wilkins _et al._ performed the first X-ray phase-contrast image of a single phase object using an analyser-based imaging system [29]. One of the reasons for the slow development of phase-contrast imaging is the requirement for a highly coherent X-ray source. X-ray laboratory sources are generally polychromatic and exhibit large point sources, often millimetre size. These features create a poor coherence of the light and reduce the ability to measure micrometres size phase shift. Sophisticated X-ray optics are required to increase the coherence of these polychromatic sources, but the optic quality showed
slow progress due to manufacturing technology limitations. Moreover, the phase variation induces only a weak intensity difference on the detector. Thus, to detect the variations in intensities, high resolution detectors are required, but generally these detectors have a limited field of view, which reduces the possibilities for industrial or medical use [30]. Strategic optic designs and geometry are commonly investigated to overcome the limitations and new technique are being developed.

### 2.2.1 Early experimental equipments

It is clear that to perform X-ray phase-shift imaging the angular variation of the refracted beam must be measured accurately. Several experimental equipments have been developed in the past to measure the angular variation of the refracted beam using different types of optical design. Both, conventional X-ray sources and highly coherent synchrotron sources have been used.

![Schematic of three phase change measuring techniques. (a) Crystal interferometer. (b) Analyzer-based setup. (c) Propagation-based imaging setup.](image)

Amongst the first X-ray phase-contrast imaging experimental equipments we find the crystal interferometry proposed and developed by U. Bonse and M. Hart [27] in 1965 and illustrated in Figure 2.5a. Here, a monochromatic X-ray beam is split in two by a crystal. While one half of the beam serves as reference, the other half traverses the object and undergoes a phase change. Finally, both beams converge into one another and create an interference pattern caused by the optical path variation between the undisturbed beam and the phase-shifted beam. Although
the principle was demonstrated in the mid-1960’s, imaging merely really arose in the mid-1990’s due to technological restriction. Using crystal interferometry, A. Momose et al. showed high resolution in soft matter such as breast tissues already in 1998 [31] and kidney in 2003 [32]. However, because the sample is placed in one of the beam paths, the size of the sample is often limited to a couple of centimetres [33, 34] which is the size of the crystals. In addition, stability of the system is critical and recurrent issue in X-ray crystal interferometry [34].

Another early technique for phase-contrast imaging is the analyser-based system illustrated in Figure 2.5b. The analyser crystal filters the refracted radiation coming from the sample which fulfils the Bragg diffraction conditions. The angular change in the propagation direction of the beam is interpreted as intensity variations by the detector. The crystal analyser rotates to cover a large band of possible Bragg reflections. This method offers high sensitivity to phase gradients, and creates images which are easy to interpret and require little post-processing [35]. On the other hand, analyser-based system requires monochromatic and collimated beams, hence limiting its application mostly to synchrotron radiation sources [36]. Moreover, a perfect analyser crystal is needed and it must have an accurate angular position controlled, which increases the complexity of the setup.

A much simpler method, also contemporary of the two methods presented, is the propagation-based imaging setup illustrated in Figure 2.5c. This experimental technique requires neither optical elements (OE) nor high stability. These characteristics offer therefore a large advantage over other methods. Here, the refracted beam interferes with the unchanged wavefront creating an interference pattern. To properly detect the interference pattern, high resolution detectors are required. These detectors are generally small and thus practically restricts the field of view. Additionally, this technique offer lower contrast than other imaging methods. In principle, propagation-based imaging requires sources with high spatial coherence. This restriction limits the use of this technique to small or distant sources [35]. On the other hand, the temporal coherence of the light source is not a strict restriction. Therefore, polychromatic laboratory sources can be used, providing that the spatial coherence level is met [37].

These methods are still today subject to research and improvement because all of them have their own asset. However none has yet combined enough advantages to widespread into industrial applications. Source coherency, stability and optics are posing recurrent issues. Over the last couple of decades, two new techniques arose which have been able to show potential for industrial applications. Namely, X-ray Talbot interferometry and edge illumination. As mentioned in Chapter 1, these two techniques, and more precisely their optical systems, have been the subject of this project. Before diving into the manufacturing challenges of their optics, let us look in detail at their mode of operation.

### 2.2.2 X-ray Talbot interferometry

X-ray Talbot interferometry is a grating-based imaging system which has drawn a lot of attention due to its ability to perform simultaneously, conventional absorbing imaging, phase-contrast imaging and dark-field imaging, using a laboratory X-ray source [38]. This method emerged from the other techniques in the early year 2000’s. The first Talbot phase-contrast images ex-
experiment is often attributed to A. Momose et al. [39] in 2003 and was performed at the synchrotron facility SPring-8 in Japan. Successively, T. Weitkamp et al. [15] and C. David et al. [40], implemented this method using synchrotron sources. In 2006, F. Pfeiffer et al. [17] adapted the technique using a laboratory X-ray source with reduced coherence. Since then, continuous improvement of the laboratory Talbot interferometer showed high potential for commercial applications [41]. In August 2017, the research group lead by Prof. Marco Stampanoni at the Paul Scherrer Institut in Switzerland began to commercialise an X-ray Talbot interferometer for contrast imaging through the company GratXray AG (http://www.gratxray.com/). Initially dedicated for medical usage, this equipment can effectively measure small fluctuation in the electron density which is ideal for breast cancer detection.

Unfortunately, the field view of Talbot interferometry is often limited by the size of the OE (i.e. the gratings), but modern fabrication methods allow to reach a size of a few tens of centimetres [42, 16]. This imaging system commonly uses an X-ray source in the energy range of 15-40 keV to image light and thin object [15, 17]. Over the last decade, imaging of dense and thick object have been reported using 60-80 keV energy range [43, 44]. However, the energy is limited by the achievable manufacturing height of the grating structures, and efforts to increase the height are continuously made.

The Talbot effect

Talbot interferometry is based on the self-imaging effect observed and described by Henry Fox Talbot in 1836 [45]. Namely, at the so-called Talbot distance, a self-image of the grating is produced. This peculiar effect is a near-field diffraction which occurs when a spatially coherent wave front travels through a periodic grating upon normal incidence. In 1881, Lord Rayleigh [46] mathematically described the relationship between the distance of the self-repeating image and the grating period. The distance at which the image of the grating is repeated is known as the Talbot length and is expressed in equation (2.7). This equation is true when the wavelength is considered small compared to the period of the grating.

\[ d_T = \frac{2p^2}{\lambda} \]  

Here \( p \) is the pitch of the grating and \( \lambda \) the wavelength.

Figure 2.6a shows a simulation example of a Talbot intensity distribution behind a phase grating with 0.5 duty cycles [47]. The duty cycle of 0.5 means that half of the light undergoes a phase shift, while the other half does not. The amount of phase shift introduced by the grating is given by:

\[ \Delta \phi = \delta \frac{2\pi}{\lambda} h \]  

where \( \delta \) is the real part of the refractive index of the grating material at a given wavelength \( \lambda \), and \( h \) is the height of the structure.

The phase shift grating is made of poorly absorbing material to reduce the attenuation of the light. In general, silicon is preferred due to the ease in manufacturing. In figure 2.6, we can see
that the intensity pattern is repeated at the Talbot distance \( d_T \), but also at half of the Talbot distance \( d = p^2 / \lambda \) with a transverse shift of half the pitch. In fact, in the ideal case (i.e. where the grating does not induce any attenuation of the signal), the intensities at \( d \) and \( d_T \) will continue to repeat at constant \( m \) intervals such as \( d = m p^2 / \lambda \) where \( m \) is a positive integer. When \( \Delta \phi = \pi \), the intensity modulation along the propagation direction will be maximised at the fractional Talbot distances with interval \( d_a = a p^2 / 8 \lambda \) where \( a \) is an odd integer. These modulations are seen in the top part of Figure 2.6b. The intensity profile of the interference pattern can be calculated analytically following Fourier series. This method is widely discussed in related literature [46, 48, 25].

At the bottom of the same figure, we observe a cross-section of the interference pattern intensity fringes at the Talbot distance. It is this interference pattern that acts as the reference signal for X-ray Talbot interferometry imaging. The overall fractal pattern behaviour of the intensity distribution is generally referred to as Talbot carpet [48]. When an object is placed before the grating, the phase change induced by the object, creates a displacement of the Talbot interference pattern. The measurement of the intensity variations by a detector at a given distance \( d \), is the underlying principle of X-ray Talbot interferometry.

![Figure 2.6: Simulation of the intensity distribution of a wavefront passing through a grating with period \( p \), 0.5 duty cycle and phase-shift \( \pi \). Note the revival of the grating image at the Talbot distance \( d_T \) and the half Talbot distance \( d \). (b) Intensity modulation profiles. Top: across the dashed line in (a). The secondary modulations are repeated at regular intervals \( d_a = a p^2 / 8 \lambda \). Bottom: at distance \( d_T \).](image)

In general, the period of a phase shift grating is only a few micrometers (i.e. generally between 2\( \mu \)m and 8\( \mu \)m) in order to meet the overall dimensional requirement of the equipment. As seen on the Talbot carpet image, the reference transverse intensity modulation dimensions are in the same order of magnitude as the grating period. In fact, for a phase shift of \( \pi \), the periodicity of the interference pattern will be 1/2 of the phase grating period [15]. This means that the interference fringes are substantially smaller than conventional pixel size (i.e. a few tens of microm-
eters). Therefore, small transverse changes in the interference fringes are difficult to detect, and current detectors will normally not have enough resolution. A solution is to introduce a second grating immediately in front of the detector. This grating is called an analyser grating and allows using conventional pixel size detectors by applying a measurement technique called phase stepping. Therefore, the main part of an X-ray Talbot interferometer consists of a combination of these two gratings. In case the X-ray Talbot interferometer uses an incoherent laboratory X-ray source, a third grating is placed in front of the source to improve the spatial coherence of the light. Consequently, a conventional laboratory X-ray phase-contrast Talbot interferometer uses three gratings.

**The interferometer**

An illustration of a Talbot interferometer using an incoherent laboratory X-ray source is shown in Figure 2.7a. The setup at DMRI is of this type. In the sketch, a phase-shifting object creates an angular variation $\theta$ in the propagation direction of the light. The grating $G_0$ is called the source grating and it is an efficient absorber placed in front of the source. The grating $G_1$ is the phase grating, introduced above, which creates the Talbot effect. Finally, $G_2$ is the analyser grating which is also an efficient absorber grating. The three gratings have specific functions and dimensions.

![Figure 2.7: Schematic view of a Talbot setup with incoherent X-ray source](image)

Figure 2.7: Schematic view of a Talbot setup with incoherent X-ray source. The source grating $G_0$ transforms the incoherent light into a spatially coherent wave front. The phase grating $G_1$ creates an interference Talbot pattern which repeats periodically in the propagation direction. When a phase-shifting object is placed in the beam path, it causes the light to deviate. This deviation results in the change in the interference pattern in the plane of the analyser grating $G_2$. The disturbed interference pattern caused by the object is measured by the detector placed behind the analyser grating.
The grating $G_2$ is placed just in front of the detector at a finite Talbot distance, and it has the same period as the interference Talbot pattern, which is half of the phase grating. Thus, if $G_1$ has a pitch of $p_1$, $G_2$ will have a pitch of $p_2 = p_1/2$. However, this linear relation merely applies in an ideal case where the wave front is a perfect plane wave coming from a parallel beam. In reality, the source is never placed at infinite distance and the distance between the source and the detector introduces a magnification $M$ due to light divergence. This magnification factor is proportional to the distances between the source and the grating $G_2$ such as $M = (L + D)/L$, where $L$ and $D$ are the distances illustrated in Figure 2.7. In a typical experimental laboratory setup, these distances are several tens of centimetres. The dimensions of period $p_2$ is thus re-expressed as:

$$p_2 = M \frac{p_1}{2} = \frac{L + D}{D} \frac{p_1}{2}$$ (2.9)

This implies that any changes in the dimensions of the setup will require a new set of gratings.

**Phase stepping method**

The perturbation caused by the object on the interference pattern must be detected precisely by the detector. The fundamental idea of the grating $G_2$ is to ensure that the intensity recorded by the individual pixels are different if a small angular variation has occurred. This grating will transform the fringe position into an intensity variation on the detector pixels. For example, in Figure 2.7a, the pixel No. I must have a different intensity than that of pixel No. II because of the interference displacement. To precisely measure the position of the interference pattern, the intensity at each pixel is recorded for different positions of the analyser grating. This method is called stepping method [49]. One technique to perform stepping is to slightly tilt the gratings $G_2$ and $G_1$ with respect to one another, in step of small angles $\alpha$ as illustrated in Figure 2.8a. When tilted, the pitch of the grating will no longer be aligned with the period of the Talbot interference and an optical effect, named Moiré pattern with period $p_M = p_1/\tan \alpha$ appears. By measuring a series of images at different $\alpha$ step, as seen in Figure 2.8b, the position of the interference can be extracted. While this phase stepping is necessary to reconstruct the image, it also has the disadvantage to require motion of the $G_2$ grating. Consequently, the risk of impairing the visibility of the interference pattern rises in case of poor control of the setup stability during motion.

The height of the absorbing grating $G_2$ will depend on the absorption ability of the grating material, as well as the absorption requirement for the equipment. The requirement for the setup are generally set in terms of the visibility $V$. In equation 2.10, $I$ is the maximum intensity transmitted through the non absorptive part of the grating and $I_0$ is the minimum intensity which is still transmitted through the absorbing part of the grating [50].

$$V = \frac{I - I_0}{I + I_0}$$ (2.10)

In general, to ensure a good signal-to-noise ratio (i.e. good contrasted image), $V$ should be as high as possible. It is expected that reasonable contrast can be obtained with 90% of absorption through the absorbing part of the grating. The absorption follows Beer-Lambert’s law as intro-
duced in equation 2.3. Therefore, to have at least 90% the ratio of intensities ratio \( I/I_o \) must be smaller or equal to 0.1. The thickness is given by

\[
x_{p2} = \mu \log \left( \frac{I_0}{I} \right)
\]

(2.11)

The attenuation coefficient \( \mu \) is proportional to the atomic number of the material and the energy of incoming light.

Figure 2.8: (a) The analyzer grating is rotated with a slight degree relative to the phase grating. The horizontal Moiré appears when \( G_1 \) and \( G_2 \) are rotated with an angle \( \alpha \). The period of the Moiré fringes is \( p_M = p_1 / \tan(\alpha) \). (b) Schematic showing the stepping method to extract the phase information. Each pixel's intensity is measured for each step and compared with and without the object.

Figure 2.9 illustrates the results from [39] of a plastic sphere of 1.2 mm with air bubbles obtained with X-ray Talbot interferometry. On the image (a), we can see the Moiré fringes generated by the inclination between \( G_1 \) and \( G_2 \). The phase gradient introduced by the plastic sphere is perceived as a displacement of the Moiré pattern. This result is in good agreement with the simulated image in (b). The image in (c) shows the corrected result of several images recorded using the phase stepping method.

**Incoherent light source**

For the Talbot interference to occur, the light source must exhibit a certain degree of spatial coherence. In brief, the degree of spatial coherence indicates the uniformity of the wavefront phase. For example, a light source is considered spatially coherent when the wave front phases oscillates in a related way, even if different frequency components are present (i.e. poor temporal coherency). While ideal spatial coherency can be obtained at synchrotron facilities, X-ray laboratory sources often fail to provide sufficient quality light. A simple approach to increase the spatial coherence of a laboratory source was proposed in 2006 by F. Pfeiffer et al. [17]. To do so, they used an absorbing grating (\( G_0 \)) placed just in front of the X-ray source. Its function
Figure 2.9: Image showing the image results of Ø1.2 mm plastic sphere. (a) Moiré image of the sphere. (b) simulated image. (c) Computed image using the phase $\phi$ measured with the stepping method. Note the structures inside the sphere. From A. Momose et al. [39]

is to shape the incoming light of a polychromatic laboratory X-ray tube into a array of spatially coherent wave fronts needed to perform the Talbot interference effect. The setup at Teknologiske Institut uses a conventional laboratory source and therefore $G_0$ is required. The period $p_0$ should satisfy the following equation:

$$p_0 = p_2 \frac{L}{D} \quad (2.12)$$

To ensure good selective absorption of the incoming light, $G_0$ is generally made of a heavy X-ray absorbing element, such as gold. Because $G_0$ is an absorbing grating, just like $G_2$, the thickness of its structures is defined by equation 2.11. Absorption above 90% is commonly applied.

**Dimension for the Talbot interferometer at Teknologiske Institut**

Table 2.1 reports the dimensions of the setup at the Teknologiske Institut. The setup uses a source with a spot size of 1 mm. The phase grating $G_1$ is set to give a phase-shift of $\pi$ and the two absorber gratings $G_0$ and $G_2$ must absorb at least 90% of the incoming energy. All gratings have a duty cycle of 0.5. The details on the manufacturing of the gratings will be presented in Chapter 3.

Table 2.1: Overview of the characteristic for the setup at Teknologiske Institute

<table>
<thead>
<tr>
<th>Setup characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
</tr>
<tr>
<td>- X-ray Magnatek MBG90_4</td>
</tr>
<tr>
<td>- Voltage 25 keV</td>
</tr>
<tr>
<td>- Current 4 mA</td>
</tr>
<tr>
<td>- Size 1 mm</td>
</tr>
<tr>
<td>Detector</td>
</tr>
<tr>
<td>- Mitsubishi Chemical DRZ High</td>
</tr>
<tr>
<td>- Type: Gadolinium sulfoxylate (GOS) scintillator</td>
</tr>
<tr>
<td>Gratings</td>
</tr>
<tr>
<td>- $G_0$: absorption $\geq 90%$, $p_0=13 \mu m$, duty cycle 0.5, $2 \times 2 \text{ cm}^2$</td>
</tr>
<tr>
<td>- $G_1$: $\Delta \Phi = \pi$, $p_1=8.2 \mu m$, duty cycle 0.5, $4 \times 4 \text{ cm}^2$</td>
</tr>
<tr>
<td>- $G_2$: absorption $\geq 90%$, $p_2=6 \mu m$, duty cycle 0.5, $4 \times 4 \text{ cm}^2$</td>
</tr>
<tr>
<td>Distances</td>
</tr>
<tr>
<td>- $L$ ($G_0$-$G_1$) 530 mm</td>
</tr>
<tr>
<td>- $D$ ($G_1$-$G_2$) 248 mm</td>
</tr>
</tbody>
</table>

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2.2.3 Edge illumination

Edge illumination (EI) is a non-interferometric phase-contrast imaging technique which uses an absorbing OE, often referred as absorbing mask, to selectively create an array of mutually incoherent beamlets. Early EI setups, which were introduced in the late 90s, used highly coherent synchrotron radiation light source to performed phase-contrast imaging [14]. However, in 2007 A. Olivo et al. [51] demonstrated the first setup using incoherent laboratory X-ray source. Just like in X-ray Tablot interferometry, edge illumination benefits from the ability to use detectors with standard pixels size, and has shown the potential for large field imaging and industrial applications [18, 52]. EI also exhibits some advantages over the Talbot interferometry. Indeed, because no controlled interference pattern is needed, the requirement in the optics alignment is significantly relaxed. In addition, EI allows for larger energy spread (i.e. low temporal coherence) of the source [53, 54]. Finally, even though the stepping-method remains necessary to calculate the image [14, 55], recent advances in the development of EI have shown the possibility to suppress the need for the stepping method [56, 57], hence significantly simplifying the image acquisition.

![Figure 2.10: Schematic view of a single mask edge illumination. The phase variation is calculated directly from the intensity recorded by the detector. The deviation of the beamlet, caused by the sample, induces a spatial shift of the intensity on the pixels detector. The comparison with and without the sample permits to recalculate the image of the object.](image)

Originally, to create an EI X-ray phase-contrasted image, the setup needed two masks: an absorbing pre-sample mask which forms the array of beamlets, and an analyser mask placed in front of the detector. The combination of the two masks gave rise to the name double mask edge illumination (DM-EI). Recent developments in the detector technology have demonstrated the
posibility to remove the analyser grating [56, 20], hence reducing the need to only one grating. This method is sometimes referred to as maskless or single mask edge illumination (SM-EI). This method, which uses a standard pixel size detector, was originally described by F. Kjerci et al. [56] in 2010. In the SM-EI it is the interface between two adjacent pixels that act as the analyser grating. The setup at DTU Physics is one of the kinds and a schematic of its mode of operation is illustrated in Figure 2.10. A polychromatic X-ray laboratory source is placed at a distance $d_{sm}$ from the pre-sample mask. This latter is a two-dimensional array absorption mask. The role of the mask is to split the light in an array of individual beamlets. To ensure good selectivity, the mask is made of a heavy element which absorb X-rays well (e.g. gold or tungsten). Just like for Talbot interferometry, the absorption is often above 90% to guarantee a good signal-to-noise ratio. The thickness of the mask follows equation 2.11. The object is placed at a distance $d_{mo}$ from the mask. The deviated beam caused by the refraction of the light through the object hits the detector at a distance $d_{od}$. SM-EI geometry uses recently developed high resolution detectors, and industrial applications using this technique have not yet emerged. However, because it is the geometry that was part of this project, I will, from now, merely refer to the single mask edge illumination.

**Basic principle**

When passing through an object, the phase of a spatially coherent X-ray wave front deviates from the direction of propagation with a refracted angle $\theta$ proportional to the refractive index (typically a few micro-radians) [58]. The deviation induces a spatial shift $\Delta x = d_{od}\theta$ of the beam when reaching the detector. This value is generally in the sub-micrometer range. The displacement is "sensed" by the interface between the pixel. To illustrate that phenomenon, figure 2.11a shows how the deflection induces a spatial downward shift of the beam from pixel I to pixel II, thereby simultaneously increasing the intensity on one pixel, while reducing it on the other. The alignment of the mask with the detector ensure that every beamlets initially illuminates the intersection of four pixels as shown in Figure 2.11b. The change in the propagation direction of the beam influences the relative intensity profile of the individual pixels across the detector, which is then used to create the image of the object.

The calculation of the individual beamlets displacement on the detector follows the condition [56]:

$$p_m \times \frac{d_{sm} + d_{md}}{d_{md}} = m \times p_d$$  \hspace{1cm} (2.13)

where $p_m$ is the pitch of the mask opening, $m= 2,3,4,...$ and $p_d$ is the detector pitch. As just seen, small displacement of the individual beamlets on the detector causes intensity variations between four neighbouring pixels. Consequently, using a single exposure, allows performing direction differential phase contrast. Figure 2.12 shows resulting images of a moth obtained with a SM-EI technique. The figure compares a standard absorption image (a) an absolute differential phase contrast image (b) and a directional phase image (c). The directional phase contrast shows in which direction the beam was deviated and provides information on the contour in the object.
Sub-pixel detection

The setup at DTU Physic relies on the method described above. However it uses a detector which enables sub-pixel intensity localisation. While the overall principle remains the same, the sub-pixel detection allows increasing the relative resolution of the detector. In a nutshell, the capability to measure sub-pixel intensity relies on the usage of the newly developed CdTe ADVAPIX-Timepix3 detector (https://www.tpxcam.org/). This detector has a $14 \times 14 \text{ mm}^2$ area ($256 \times 256$ pixels with $55 \text{ µm}$ pitch) and is capable of measuring the individual charges deposited in a single pixel. Being able to measure individual photon deposition within a pixel is important to manage the charge-sharing effect between neighbouring pixels. This unwanted effect originates from the ionisation caused by an incoming photon onto the volume of a pixel. In figure 2.13, the initial ionisation spreads out during the charge acquisition of the signal which lasts tens of nanoseconds. Consequently, the signal is no longer collected by a single pixel, but rather a group of adjacent pixels (i.e. a cluster).

When the charges are also collected by the adjacent pixels, the energy resolution is reduced. The total charges measured depend on the photon energy, the depth of the cluster, the bias voltage and the threshold level [59]. Common X-ray detectors suffer from this effect, but the Timepix3 was developed to overcome this concern. The sub-pixel localisation is retrieved by the procedure described in [21]. It consists of segmenting the time-of-arrival (ToT) of the charges. Typically, the pixel in the cluster that received the photon first are the brightest and the pixels
Figure 2.12: X-ray images of a moth (*Lepidoptera*) acquired with a SM-EI system with 50 keV tungsten X-ray source. (a) Absorption image. (b) Absolute differential phase contrast image. (c) Directional differential phase contrast. Adapted from publication in Appendix A.1.

Figure 2.13: Illustration of the mode of operation of the Timepix3 detector. Image from [59].
Top: schematic of the charge-sharing effect caused by an ionising particle. Bottom: if the collected charge by the pixel is lower than a threshold value, the intensity is not registered.

that read the photon later are less bright. The data readout resolution of the Timepix3 is 1.56 ns which is significantly smaller than the total charge acquisition time of the signal (e.g. tens of ns) [21]. By processing with ToT, M. Khalil *et al.* were able to calculate where the initial ionising particle arrives and adjust for the charge-sharing effect in the computation of the image. As a consequence, the relative resolution of the detector is increased. Sub-pixel detection technique using Timepix3 detector at the laboratory-source setup at DTU Physics is widely described in Erik S. Dreier’s PhD Thesis [60] and the associated publications [20, 61]. Hence, the reader is referred to these documents for further detailed information on the sub-pixel localisation of photons using the Timepix3 detector.
**Dimension and characteristics of the SM-EI at DTU physics**

The setup at DTU physics uses a Hamamatsy Photonics L121661-07 source with a spot size of 5 $\mu$m. The dimensions of the setup and the requirement for the mask are reported in Table 2.2. The mask is designed so that the beamlet hits every fourth pixel corner on the detector. This was chosen to ensure that the beamlets could always be resolved. Thus, because the pixels have 55 $\mu$m side length, the pitch at the detector, after magnification, must be 220 $\mu$m. The overall geometry of the setup was decided somewhat randomly to fit the overall geometry, but the following criteria were considered [60]: (1) Having the sample as close as possible to the mask provides higher sensitivity because the propagation distance $d_{od}$ is longer. (2) Larger ratio of $d_{md}/d_{sm}$ would allow more precise differential phase contrast, but would force $d_{od}$ to be larger. Therefore, reasonable dimension had to be found.

The mask aperture was chosen so that the holes were wide enough to compensate for the natural beam divergence at $d_{sm}$ throughout the mask thickness. To do so, it was assumed that the thickness of the mask would be at least 200 $\mu$m. This thickness is a reasonable assumption for common X-ray absorbing elements (i.e. gold or tungsten) when used with an energy of 50 keV for an absorption of $>$95%. The aperture should, however, not be too large to avoid overlapping of the beamlets on the detector. The detail of the manufacturing process and the thickness will be discussed in Chapter 4.

<table>
<thead>
<tr>
<th>Table 2.2: Characteristic dimensions for the setup and the mask for the setup at DTU Physics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source</strong></td>
</tr>
<tr>
<td>- Hamamatsy Photonics L121661-07</td>
</tr>
<tr>
<td>- Voltage 50 keV</td>
</tr>
<tr>
<td>- Power 3.35 W</td>
</tr>
<tr>
<td>- Size &lt; 5 $\mu$m</td>
</tr>
<tr>
<td><strong>Detector</strong></td>
</tr>
<tr>
<td>- ADVAPIX-Timepix3</td>
</tr>
<tr>
<td>- Crystal CdTe</td>
</tr>
<tr>
<td>- Resolution 256 x 256 pixel</td>
</tr>
<tr>
<td>- Pixel size 55 $\mu$m</td>
</tr>
<tr>
<td><strong>Distance</strong></td>
</tr>
<tr>
<td>- $d_{sm}$: 400 mm</td>
</tr>
<tr>
<td>- $d_{md}$: 480 mm</td>
</tr>
<tr>
<td>- $d_{od}$: 290 mm</td>
</tr>
<tr>
<td><strong>Mask</strong></td>
</tr>
<tr>
<td>- pitch: 100 $\mu$m</td>
</tr>
<tr>
<td>- opening: 12 $\mu$m</td>
</tr>
<tr>
<td>- absorption $\geq$90%</td>
</tr>
</tbody>
</table>

**2.3 Manufacturing of absorbing optical elements**

As seen, the two setups have a different way to construct phase-contrast images, but both require absorbing OE (i.e. mask or grating). When looking a bit closer at the dimensions, the
patterns have in fact some common features and similar aspect ratio (AR). Indeed, the dimensions are somewhat comparable. The mask opening diameter for the SM-EI is 12 µm, and the smallest line width for the absorbing grating G2 for the Talbot interferometry is 3 µm (period of 6 µm with duty cycle of 0.5). The two setups utilise a different energy, namely 25 keV and 50 keV respectively. Thus, the necessary thickness to reach 90% of absorption will be different, but the AR will be rather comparable, providing that the same absorbing material is used.

Several microfabrication methods for EI masks and Talbot interferometer gratings have emerged through the last couple of decades. The increasing need for using higher energy sources has set additional constraints on the optical elements. The thickness of the absorbing layer must increase as the energy increases, while the pitch or aperture remains essentially the same. This constraint induces higher aspect ratio which challenges conventional manufacturing methods.

The most popular way to fabricate X-ray absorbing OE is to pattern the reverse structure into a lightly absorbing material (e.g. silicon or polymer) which acts as a mould. This latter is subsequently transferred to an absorbing material. Normally, the mould is kept as supporting structure because it exhibits poor absorption, and thus, does not affect the visibility too much. Gold is amongst the preferred metals for the absorbing material because it is an ideal absorber for X-rays and can, to some extent, easily be electroplated in the mould. However, other high-absorbing metals or alloys have been proposed using other techniques than electroplating [62, 63, 12, 13, 64, 65]. Table 2.3 shows some key parameters for some good absorber materials. The required thickness to absorb 90% absorption for a typical source of 50 keV is given as an example. In addition, some literature, which uses either the pure element or related alloys are listed in the last column.

Table 2.3: Properties of common X-ray absorbers. The thickness values are calculated for an energy source of 50 keV using values found in ref. [66] for an absorption of 90%. All elements are considered pure. The last column list some related literature where either the pure element or an alloys of the metal are used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number Z</th>
<th>Atomic weight A (g/cm³)</th>
<th>Density ρ (g/cm³)</th>
<th>At 50 keV</th>
<th>Literature examples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Attenuation length (µm)</td>
<td>Thickness at 90% (µm)</td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
<td>196.96</td>
<td>19.30</td>
<td>72.4</td>
<td>167</td>
</tr>
<tr>
<td>W</td>
<td>74</td>
<td>183.84</td>
<td>19.25</td>
<td>89.2</td>
<td>205</td>
</tr>
<tr>
<td>Ir</td>
<td>77</td>
<td>192.22</td>
<td>22.56</td>
<td>68.5</td>
<td>158</td>
</tr>
<tr>
<td>Pt</td>
<td>78</td>
<td>195.08</td>
<td>21.45</td>
<td>69.1</td>
<td>159</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>207.20</td>
<td>11.34</td>
<td>114.0</td>
<td>262</td>
</tr>
<tr>
<td>Bi</td>
<td>83</td>
<td>208.98</td>
<td>9.78</td>
<td>127.6</td>
<td>293</td>
</tr>
</tbody>
</table>

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2.3.1 Polymer mould and gold electroplating

The method

A simple method is to manufacture the reverse pattern in a UV photosensitive polymer on top of a silicon wafer, and proceed to the electroplating of gold. The epoxy-based resist SU-8 is an ideal candidate for that job. It is a UV sensitive resin can be made very thick (i.e. from few micrometres to several tens of micrometres), and is stable in most chemical solutions. In addition, it absorbs X-ray poorly and therefore can be kept on the final device. The polymer mould fabrication method is convenient as it requires only a photolithography step and an electroplating step, hence minimising the fabrication complexity. Additionally, this method offers a great deal of opportunity in terms of which substrate to use, provided that photolithography can be performed on it, and that it sustains the gold electrolyte chemistry. However, one of the drawbacks for using polymer such as SU-8 is the aspect ratio limitation which is still very often limited to AR ≤ 10. This limitation is problematic because to achieve reasonable visibility for X-ray phase-contrast imaging, the grating should absorb at least 90% of the incoming X-ray light. This means that for a gold absorber, the thickness is approximately 35 µm for a source of 25 keV, but increases to 170 µm for an energy source of 50 keV. Since, the dimensions of the structures are in the order of 3 to 8 µm, the AR to achieve can potentially reach 50:1.

Absorbing elements with polymer mould

Linear gold gratings with AR < 10 (lamella height 42 µm), using SU-8 mould, have successfully been demonstrated by C. David et al. [11] using conventional UV photolithography (see in Figure 2.14a) and gold electroplating. However, AR > 10 SU-8 shows resolution limitation [68] and only X-ray photolithography, performed at synchrotron, has shown to work for absorbing OE [50, 69, 70]. The increase in resolution for X-ray lithography is explained by the collimated high-energy X-ray beam which can reach deeper in the polymer, due to less diffraction than that of the UV light, thus leading to a better resolution. Unfortunately, whilst X-ray lithography works better, mechanical instabilities in the polymer occur when the AR is close to 50, forcing the structure to collapse. To prevent collapse of the lamella of the grating, supporting bridges, placed at regular intervals, are needed. An example of supporting bridges is shown in 2.14b. Whilst this addition solves the stability problem, it also creates discontinuities in the X-ray visibility after gold filling of the trenches. J. Mohr et al. [50] showed that by using transverse bars instead of bridges, the discontinuities in the visibility could be decreased. The transverse bars are achieved by additional X-ray photolithography exposures performed on the tilted substrate, and with a lithographic mask consisting of simple columns.

Discussion

The approach made by J. Mohr et al. is admittedly interesting, yet not ideal. Surely, the good visibility requirement seems to be met using transverse bars, but the use of several X-ray photolithography steps raises some concerns. The cause of these concerns are the costly access to synchrotron facilities and the low throughput. Nonetheless, the rather elegant solution of placing transverse bars could potentially be applied to SU-8 mould exposed with standard UV lithography providing that larger AR can be achieved. Indeed, as mentioned earlier, SU-8 shows mi-
Figure 2.14: (a) Typical fabrication process and result cross-section of a gold absorbing grating developed by C. David et al. using SU-8 mould. In this method, the SU-8 was removed after the plating. Image from [11]. (b) Cross-section view of an epoxy-based resist mould with bridges, fabricated by J. Mohr et al. using X-ray lithography. Scale bar: 20 µm. Image from [50].

Microfabrication limitations at high AR when using conventional UV lithography. However, some results report that when using a careful combination of UV exposure, post-exposure bake and development, it is possible to obtain structures with AR close to 50:1 in SU-8 [71], although the instability remains. Consequently, transverse bars combined with optimised UV lithography could potentially be a good candidate for manufacturing these moulds.

2.3.2 Silicon mould

The methods

Using a silicon mould instead of a polymer mould has several advantages. Very high aspect ratio structures in silicon are easier to achieve using plasma dry etching or chemical wet etching. In addition, silicon shows higher mechanical stability than that of SU-8 for the identical AR. The general ideal behind the silicon mould-based manufacturing method is described in Figure 2.15. First a masking material is placed on top of a silicon substrate (I) and subsequently patterned (II). Once patterned, the mask is transferred onto the silicon by means of plasma dry etching or chemical wet etching (III). The phase-shift grating \( G_1 \) in a Talbot interferometer is generally made of only silicon and does not require filling with an absorbing material. Its main requirement is to provide a phase-shift (in our case \( \pi \)) which is defined by the height of the structures. \( G_1 \) is therefore an easier grating to manufacture, and its fabrication method stops after the mask pattern transfer. On the other hand, the gratings \( G_2 \) and \( G_0 \) of the Talbot setup, together with the mask absorber of the EI setup, are absorbing gratings. Consequently, once the mask pattern has been transferred into the silicon an absorbing material must be added (IV). For the sake of providing high contrast during imaging, the filling of the absorbing material must have a good uniformity. The most common way to fill up the absorbing material is electroplating of gold. But other solutions have been proposed and will be discussed in this review section. Two very common ways to pattern high aspect ratio (HAR) silicon structures are wet chemical etching...
and plasma etching also called dry etching. To enable HAR structures, the patterning of the silicon must be anisotropic (i.e. one direction only). Therefore, the wet and the dry etching must have a preferential etching direction.

![Figure 2.15: Illustration of the silicon mould method to manufacture X-ray absorbing optical elements. The masking material is first placed on a silicon substrate (I). The mask is then patterned (II) and transferred (III) to the silicon substrate. For phase shift grating, the manufacturing process stops at (III). But for absorbing OE, the mould is filled up with absorbing material (IV). The mask material depends on the pattern transfer method.](image)

A number of alkaline solutions exist for crystal orientation-dependent silicon etching, but potassium hydroxide (KOH) has come out as one the most often used etchants [72]. The etch rate increases with temperature and typically wet etching is performed at temperature between 80°C to 85°C. When using alkaline etching solutions some crystal planes of the silicon will etch faster than others resulting in the crystal planes orientation-dependent etching. The etch rate of the different planes is controlled by the density of free bonds in the lattice plans [73]. Typically, for a 50 wt% KOH/H₂O at 85°C, the anisotropic etching ratio is 400:200:1 for the (110):(100):(111) planes respectively [74]. Consequently, by carefully choosing the wafer orientation, very high aspect ratio with straight walls can be obtained. The left-hand side of figure 2.16a illustrates how these three crystal planes are etched. On a <100>-oriented silicon wafer, etching essentially stops on (111) planes which forms an angle of 54.7° with the surface. The etch gives a V-shape or truncated V-shape depending on the mask window. However, this shape is not ideal for HAR structures like linear gratings and therefore a <110>-oriented silicon wafer is preferred. The very large etch rate difference between the (110) and (111) planes forms grooves with essentially vertical side-walls. For wet etching, silicon nitride is often preferred for the masking material because it exhibits a very good selectivity toward the KOH. This etching technique is a good solution for batch processes because many devices can be processed in the same solution. However, the patterning of the mask is a critical step. The mask must be aligned perfectly to the crystal orientation. In case of misalignment of the opening with the crystal orientation, the pattern width will be larger than anticipated.

Plasma etching takes place in a reactor chamber where a glow discharge creates reactive radicals and ions from the inlet gas, and the etching process proceeds as either an almost purely chem-
ical etch (isotropic) or an ion-assisted chemical etch which may be anisotropic. The plasma etching can be tailored to create deep vertical structures by changing some process conditions. Two major processes exist for deep reactive etching (DRIE); namely cryogenic etch and cyclic etching (e.g. Bosch etching).

Cryogenic anisotropic etching of silicon was introduced by S. Tachi et al. in 1988 [75] and uses a fluorine-based plasma (often a mixture of SF$_6$/O$_2$). Initially, the etch is isotropic, however for anisotropic etching to occur, the sample is cooled to say between -100 °C and -130°C. The mode of operation behind cryogenic etching is to freeze a layer of SiO$_x$F$_y$ on the sidewall which protects against etching species, while the impinging, energetic ions, by sputter erosion, enable etching at the bottom surface [75]. Surely, cryogenic etching shows good HAR results with very low sidewall roughness [76, 77] and fast etch rate (4 µm/min to 7 µm/min) [78, 79], however, it is rarely used in large scale production. This is partly because it exhibits a few inconveniences beside the need for maintaining a cryogenic temperature. First, the use of standard photoresist masking (e.g. Novolac type resin) is difficult due to temperature stress which induces cracks and delamination and poor selectivity [80]. The epoxy-based SU-8 photoresist has shown to be less vulnerable to cracking due to its exceptional cross-linking density [79], however, removal of cross-linked SU-8 resin is cumbersome, thus reducing its practical applications in many applications. Second, and most likely the most important drawback, is the cryogenic temperature which has a critical dependence on the etch quality. If the right balance between oxygen content and temperature is not struck, the very cold substrate forces the compounds of the plasma to condense onto the surface, creating small micro-masks [80]. Eventually these micro-masks result in the formation of unwanted micro-pillars, also called black silicon or micro-grass. If too much condensation occurs, the etch stops [81]. Consequently, the temperature and the oxygen content have a critical role in the formation of black silicon in cryogenic etch, and the window for well-balanced parameters is small. Therefore, to ensure reproducible results over time, very sensitive control of the gases and the temperature must be performed continuously. Nonetheless, cryogenic etch maintains its attractiveness in many applications where low sidewall roughness is desired.

In the manufacturing of absorbing X-ray OE, the cyclic Bosch process [82] is often preferred. A typical schematic of an anisotropic etching of silicon using a Bosch process is illustrated in Figure 2.16b. This cyclic process creates a periodic wave pattern (i.e. scalloping) on the sidewalls of the structure, as shown in the schematic. The size of the scallops can be minimized by using shorter cycles, but at the cost of a slower etch rate. For absorbing X-ray OE the scallops can be made significantly smaller than that off the size of the structures which are usually a few micrometers in size. Thus, the sidewall roughness, can easily be tolerated. In short, SF$_6$ gas is introduced in the glow discharge for a short period of time and the atomic fluorine radicals etch the silicon isotropically (I). Then, a C$_4$F$_8$ pulse is introduced in the glow discharge and creates a fluorocarbon (FC) passivation film from CF$_2$ radicals on the surface and the sidewalls (II). The following SF$_6$ pulse will etch away the FC at the bottom by ion-assisted etching while the sidewalls remain protected (III). The process is repeated cyclically until the desired depth is reached (IV).
Absorbing element with silicon moulds

A widely applied fabrication methods for absorbing gratings using silicon mould is based on electroplating of gold from a seed layer. The seed layer is needed to initiate the electroplating, and is placed at the bottom of the structure to ensure homogeneous filling from the bottom of the structure. For polymer moulds, the seed layer is placed directly on the substrate prior the polymer patterning. However, for silicon moulds, the seed layer is added after the patterning of the silicon. It usually consists in a directional evaporation of a thin layer of gold [11, 67]. Figure 2.17 illustrates a typical manufacturing method to place the seed layer at the bottom of the linear grating trenches. This method was proposed in 2007 by C. David et al. To ensure that electroplating does not initiate on the sidewalls or on the top of the structure, they used an aluminium shadowing layer to protect the sidewall. The shadowing layer is subsequently removed using chemical lift-off of the aluminium. This way, the gold seed layer is essentially at the bottom of the trench where the gold plating initiates.

This method has the strong advantage of using conventional fabrication techniques such as thermal evaporation, standard UV photolithography and gold plating. S. Rutishauer et al. [83] have used the same approach to create a two-dimensional gold mask for edge illumination setup. Commercially available production of gratings mainly also use gold plating of silicon mould (e.g. Microworks GmbH, Germany). Unfortunately, for linear grating with AR > 12:1 it becomes increasingly more complicated to evaporate the seed layer at the bottom of the trenches or perform the electroplating. A solution is to manufacture the silicon grating with a duty cycle of 0.25 instead of 0.5 and conformally coat by atomic layer deposition (ALD) a seed layer (e.g. Iridium, Platinum). This way, a conformal electroplating of gold can be performed. Using this technique, AR of 24:1 have been reported [84]. Recently, it has also been shown that seedless gold electroplating using low resistivity silicon wafers could lead to linear gratings with AR 25:1 [85]. This method removes the need for a seed layer and uses the silicon as the conductive
So far, gold electroplating has been widely used because it is an ideal material for X-ray absorption (Au, Z = 79, $\rho = 19.3$ g/cm$^3$) and gratings of several square centimetres can be made. However, electroplating is also a time-consuming process because deep structures of several tens of micrometres need to be filled, thus leading to low throughput. In addition, aspect ratio larger than 12:1 are genuinely more difficult to achieve, which is a drawback for high-energy X-ray applications. For these reasons, over the last five years, a few new techniques have emerged. Microcasting of metal alloys rose some interest because it is a much faster process compared to gold electroplating. Shortly, microcasting consists in forming a metal alloy and bring it to a temperature region past the glass transition temperature. In this region, the metal exhibits Newtonian viscous flow [86] and can be microcasted in a silicon mould. In 2014, W. Yashiro et al. showed that AR 2.5:1 could be obtained by casting a Pd-Cu-Ni-P alloy in a silicon mould [87]. Two years later, they fabricated a grating with AR 5:1 using gadolinium-based alloy (Gd, Z = 64, $\rho = 7.9$ g/cm$^3$) which exhibits higher X-ray absorption coefficient than that of palladium (Pd, Z = 46, $\rho = 10.02$ g/cm$^3$) [88]. The same year, Y. Lei et al. proposed a Bismuth-based alloyed (Bi, Z = 83, $\rho = 9.78$ g/cm$^3$) and reached the outstanding AR of 100:1 using a similar method [62]. To ensure good filling of the structure, they pretreated the silicon mould with a Bi$_2$O$_3$ coating which increases the wetability of the viscous metallic glass. The microcasting was also performed in a vacuum chamber to ensure that no air is trapped at the bottom of the trenches. Microcasting method with enhanced wettability is illustrated in 2.18a. The surface modification to increase the wettability is a crucial step for the microcasting of metallic glass in AR 100:1 trenches. Without a suitable wetting layer, the surface tension does not favour the flow of the metal down the trench, leaving large air cavities in the structures (Figure 2.18b right). With enhanced wettabiliy, the filling is significantly improved, yet some cavities seem to remain (Figure 2.18b left). The filling method also creates bismuth blocks at the surface which can eventually affect the phase-contrast imaging quality by reducing locally the visibility. These results demonstrate the potential for very high aspect ratio gratings. Nonetheless, complete filling of the structure and removal of metallic blocks at the surface need to be addressed.
Very high aspect ratio can be obtained with microcasting which makes it a very promising approach. However, it also requires a meticulous control of the temperature to obtain the suitable viscosity. If the viscosity or the wetability of the surface is inappropriate, the flow of the metallic glass will not fill up the structures and lead to cavities in the metal filling. These risks complicate the manufacturing process because temperature control and surface modification are essential to ensure good filling and must be carefully addressed. Besides, these alloys absorb X-ray less than gold for the same aspect ratio. Consequently, a higher silicon mould must be manufactured. On the other hand, microcasting of pure gold would not be easier. Gold has a very high melting point (1064.18 °C) which quickly becomes problematic to handle, and would require expensive quantity of melted material. In 2017, L. Romano et al. [13] adapted the microcasting presented by Y. Lei and W. Yashiro to allow for gold alloy metal filling. They proposed hot embossing of gold-tin foils (Au 80 wt%, Sn 20 wt%) in silicon template. The concentration ratio between the gold and the tin lowers the melting point to 280 °C while still exhibiting a relatively large density ($\rho = 14.7 \text{ g/cm}^3$), thus making this alloy a good material for microcasting.
and X-ray absorption. The hot embossing method is illustrated in Figure 2.19a. A sheet of polydimethylsiloxan (PDMS) is used to even out the pressure. A silicon (Si) flat chip of 500 µm, placed below the PDMS, ensures a flat surface. To avoid sticking, polyimide films are placed in between each layer. The hot plate heats the substrate to the eutectic temperature of 280 °C and a pressure between 1 - 12 MPa (depending on the AR) is applied. The cooling rate has a significant impact on the result. Too short cooling time induces cracks in the crystalline planes of the silicon as seen in the top of Figure 2.19b. The cracks are reduced by reducing the cooling rate. In this case, merely some delaminations are observed (see arrows in the same figure).

![Diagram of hot embossing method](image1)

**Figure 2.19:** (a) Hot embossing method of alloy foil in silicon mould proposed by L. Romano et al.. Image from [13]. (b) Top: SEM cross-section of hot embossed Au-Sn alloy grating with AR 25:1. Fast cooling (< 50min) creates crack along the crystal planes of the silicon wafer. Bottom: Cross section of the same grating with long cooling time (200 min) Images from [64].
Amongst other emerging fabrication methods we find atomic layer deposition (ALD) of iridium (Ir, Z = 77, ρ = 22.56 g/cm³). Iridium has comparable absorbing properties to that of gold, and is therefore an excellent material for X-ray absorbing elements. From a theoretical perspective, ALD is often assumed to coat conformally any surface with complete step coverage in a given time, providing that enough reactant gas and exposing time are supplied. While this assumption is true for low aspect ratio structures and flat surfaces, it does not necessarily reflect the reality for HAR structures. In this case, the gas kinetics affect the deposition rate. Here, the reactant exposure time, needs to be adjusted to account for the diffusion in the structures [89]. Successful linear gratings with AR 30:1 have been proposed and demonstrated by J. Vila-Comamala et al. [12] where the gas kinetics was optimized. The method is divided in 3 steps. First, a layer of aluminium oxide (Al₂O₃) is deposited to promote the nucleation of the iridium. Second, an oxygen plasma enhanced iridium deposition is performed to ensure a uniform nucleation. The last step, is the deposition of the iridium layer. The result of the iridium layer is illustrated in Figure 2.20. For a layer of 500 nm, in trenches with AR of 30:1, the whole process takes approximately 15 days which gives a deposition rate of 1.3 nm/h. This very slow process is justified by the pulse time which must be sufficiently long to allow for the diffusion of the reactant. However, a regular ALD chamber can accommodate several wafers which makes it an good method for batch processes. Nevertheless, ALD is an ideal solution for trenches with width in the order of a few tens to hundreds of nanometres, but for wider gratings, the deposition time can not easily compete with other techniques such as hot embossing, microcasting or electroplating. Moreover, iridium and iridium precursors for ALD are very expensive and would unfortunately lead to high fabrication cost.

Figure 2.20: ALD deposition of 400 nm Ir in AR 30:1 silicon trenches performed by J. Vila-Comamala et al.. Images from [12].
2.3.3 Discussion

Table 2.4 lists the different technique discussed above. Microcasting is a very promising method which yields toward better throughput and potentially higher aspect ratio than gold-plating. Crucial control over the temperature, the chemistry of the metal alloy and the wettability are needed to ensure good filling of the HAR structures. Unfortunately, all of these controls induce tedious process steps which can complicate the fabrication. Moreover, the metallic glass are generally alloys with poorer absorption of X-rays than that of gold, resulting in the need for higher silicon structures. Admittedly, HAR silicon structures are easier to obtain than in polymers, but they are not necessarily trivial to achieve for a whole range of dimensions. Hot embossing, seems to show very promising results with gold alloys which exhibit high X-ray absorption, and AR $\approx 30$ have been successfully achieved using this method. Even higher aspect ratio can be obtained with Pb alloy instead of gold using hot embossing. Unfortunately, the use of Pb raises safety concern in many domains and is often restricted when suitable alternative exists. Nevertheless, the method can potentially fulfil the conditions for good absorption, good uniformity, and large throughput fabrication in aspect ratio.

Table 2.4: Summarising of some of the latest manufacturing techniques for linear high aspect ratio grating.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Year</th>
<th>Filling</th>
<th>Metal</th>
<th>AR</th>
<th>Width (µm)</th>
<th>Height (µm)</th>
<th>Si patterning method</th>
</tr>
</thead>
<tbody>
<tr>
<td>[67]</td>
<td>2004</td>
<td>Electroplating</td>
<td>Au</td>
<td>10</td>
<td>1.0</td>
<td>10</td>
<td>KOH</td>
</tr>
<tr>
<td>[84]</td>
<td>2015</td>
<td>Electroplating</td>
<td>Au</td>
<td>24</td>
<td>0.1</td>
<td>3.3</td>
<td>Cryogenic</td>
</tr>
<tr>
<td>[85]</td>
<td>2019</td>
<td>Electroplating</td>
<td>Au</td>
<td>26</td>
<td>2.7</td>
<td>69</td>
<td>DRIE</td>
</tr>
<tr>
<td>[87]</td>
<td>2014</td>
<td>Microcasting</td>
<td>Pb alloy</td>
<td>2.5</td>
<td>4.0</td>
<td>10</td>
<td>DRIE</td>
</tr>
<tr>
<td>[88]</td>
<td>2016</td>
<td>Microcasting</td>
<td>Gd alloy</td>
<td>5</td>
<td>4.3</td>
<td>23</td>
<td>DRIE</td>
</tr>
<tr>
<td>[62]</td>
<td>2016</td>
<td>Microcasting</td>
<td>Bi alloy</td>
<td>100</td>
<td>1.5</td>
<td>150</td>
<td>DRIE</td>
</tr>
<tr>
<td>[64]</td>
<td>2017</td>
<td>Hot embossing</td>
<td>Au alloy</td>
<td>31</td>
<td>1.3</td>
<td>40</td>
<td>DRIE</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pb alloy</td>
<td>38</td>
<td>0.8</td>
<td>30</td>
<td>DRIE</td>
</tr>
<tr>
<td>[12]</td>
<td>2018</td>
<td>ALD</td>
<td>Ir</td>
<td>70</td>
<td>0.4</td>
<td>30</td>
<td>DRIE</td>
</tr>
</tbody>
</table>

Research still needs to be performed to combine all the essential qualities of an absorbing grating for phase-contrast imaging using emerging techniques. Amongst these qualities we find potential for large area, good uniformity (i.e. no distortion in the grating lines), good absorption and high fabrication throughput. Therefore, gold electroplating with an aspect ratio < 15:1 still remains a very common method.
Chapter 3

Linear gold gratings for Talbot interferometer

In this chapter, I introduce the manufacturing of the 3 gratings for the Talbot interferometer setup at the Danish Meat Research Institut. By the time of the project ended the setup was still under development and therefore the set of gratings had not been tested in X-ray experimental conditions. However, the manufacturing methods described in this chapter includes fabrication difficulties which have been addressed and which can be used, should the gratings be modified. The absorbing gratings proved to be the most complicated to achieve, therefore this chapter focuses mostly on the manufacturing of the absorbing grating with the highest aspect ratio, namely G₂. The fabrication method includes a standard UV-lithography process, a deep reactive ion etching of silicon using a 4-steps Bosch-like cyclic process, and a gold electroplating step.

3.1 Introduction

In Chapter 2 we mentioned that Talbot interferometry is a promising X-ray phase-contrast imaging method with great potential for laboratory applications. This imaging method relies on the Talbot interference created when a spatially coherent light traverses a periodic phase-shifting grating. A schematic of an experimental Talbot interferometer, like the setup we have at the Danish Meat Research Institut, is illustrated in figure 3.1. In a Talbot interferometer, the quality of the X-ray images relies on the optical elements, whose regularities and aspect ratio greatly affect the result. In the manufacturing of these optical elements, the aspect ratio is today one of the main fabrication challenges. A very common method for microfabrication of the absorber gratings involves metal electroplating into HAR silicon structures prepared by photolithography and anisotropic etching of silicon. Gold is often preferred for the absorbing material for these gratings because it is a well-known technology and it is relatively easy to electroplate in aspect ratio < 15:1 [40, 70, 67]. Atomic layer deposition of iridium [12], microcasting of bismuth alloy [62] and hot embossing of gold-based alloys [13, 64] have recently been reported and show promising results for higher aspect ratio. However, these emerging techniques still suffer from high material cost, wetting, alloy availability or sensitive phase transition behaviour. Therefore,
gold electroplating remains the most used method when manufacturing absorbing X-ray optical elements for phase-contrast imaging.

To realise an absorbing gold grating using gold electroplating, it is crucial that the electrodeposition begins at the bottom of the trenches to ensure homogeneous void-free filling. For silicon-based gold gratings, the seed layer is generally placed after the patterning of the silicon template. Typically, the seed layer is evaporated at the bottom of the trenches using directional thermal evaporation. This evaporation step is critical because the wall and top of the silicon template must be free of gold to ensure that the plating begins at the bottom. In this case, a protection layer must be placed at the top of the trenches to act as a shadow mask for gold evaporation. C. David et al. [40] proposed a solution, where the shadow mask is made by using two evaporation steps of aluminium with + and - 45° angle with respect to the grating structured. This step results in aluminium protrusions at the top of the trenches, which protect the top and the sidewalls of the trenches during normal evaporation of the seed layer of gold. Their process flow is shown in Chapter 2 in Figure 2.17. The protrusions are subsequently removed using phosphoric acid. This elegant solution shows good results, and has also successfully been used in the manufacturing of two-dimensional gold masks by S. Rutishauer et al. [83].

In our experiment, we used a similar approach to that of C. David et al. [11]. However, we combined the shadow masking step with a DRIE patterning of the silicon. In our method, the shadow mask is made of accumulated fluorocarbon (FC) at the top of the trenches, which is removed by plasma oxygen after the evaporation of gold. This way, we can remove the need for the additional two aluminium evaporation steps at ± 45°, thus simplifying the fabrication process.


3.2 Experimental methods

In general, the periods of the gratings depend on the dimensions of the setup. Equations 2.9 and 2.12 report their mathematical relations. As a general rule, the shorter the dimensions (L + D), the shorter the period and thus the higher the aspect ratio. Table 3.1 reports the dimensions of the gratings for our setup, using an X-ray energy source of 25 keV.

Table 3.1: Targeted specifications of the three linear gratings and setup dimensions.

<table>
<thead>
<tr>
<th>Grating dimensions</th>
<th>G0</th>
<th>G1</th>
<th>G2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period (µm)</td>
<td>13.0</td>
<td>8.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Duty cycle</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>≥ 28</td>
<td>32</td>
<td>≥ 28</td>
</tr>
<tr>
<td>AR</td>
<td>≥ 4:1</td>
<td>7.8:1</td>
<td>≥ 9:1</td>
</tr>
<tr>
<td>Material</td>
<td>Si/Au</td>
<td>Si/-</td>
<td>Si/Au</td>
</tr>
<tr>
<td>Area (cm²)</td>
<td>2 × 2</td>
<td>4 × 4</td>
<td>4 × 4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Setup dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon energy</td>
</tr>
<tr>
<td>L</td>
</tr>
<tr>
<td>D</td>
</tr>
</tbody>
</table>

The height of the phase-shifting grating (G₁) was set up to provide a phase shift $\Delta \phi = \pi$, and the material was chosen to exhibit poor X-ray absorption to avoid energy loss in the setup. Here, we used silicon for convenience, because it poorly absorbs X-ray photon energy, and can easily be patterned using DRIE. The source X-ray energy is 25 keV and it can therefore be calculated, using equation 2.8, that 32 µm of silicon is needed to provide a phase shift of $\pi$. To achieve a reasonable image contrast, the gratings (G₀) and (G₂) should absorb at least 90%. Using equation 2.11 the minimum gold thickness should be at least 28 µm, leading to aspect ratios of $\geq 4:1$ and $\geq 9:1$ for G₀ and G₂ respectively.

3.2.1 Silicon mould fabrication

The fabrication of the gratings moulds was carried out on 100 mm diameter n-type, 1-20 Ωcm <100> double sided polished silicon wafers, with 100 nm of thermally grown SiO₂. Figure 3.2 illustrates the process flow to fabricate the absorbing gratings. The phase-shifting grating followed the same procedure but the gold evaporation and electroplating steps were omitted.
Figure 3.2: Schematic of process flow for gold absorbing grating. (I) Photolithography on SiO$_2$ layer. (II) SiO$_2$ etch. (III) Deep reactive ion etching using DREAM process. (IV) Gold evaporation for seeding and backside electroplating contact. (V) Lift-off of resist and removal of FC. (VI) Gold electroplating. The phase-shifting grating uses a bar silicon wafer, thus steps II, IV and VI are omitted.

**Silicon oxidation and photolithography**

Prior the photolithography, the wafers were oxidised to lower the risk of spontaneous gold plating on the top of the lines which was sometimes observed during the electrodeposition on the absorbing grating $G_0$ and $G_2$. We performed thermal dry oxidation of 100 nm of SiO$_2$ in a furnace with O$_2$ gas at 1050°C for 1.5 h, followed by an annealing process of 20 minutes in nitrogen gas. Before entering the furnace, the samples were cleaned using a standard RCA procedure named after the company who developed it (i.e. Radio Corporation of America). The RCA cleaning procedure consists in two wet cleaning steps with two intermediate wet oxide etch steps. The cleaning baths were kept at 70 °C. The first step is designed for removal of organic material. It was performed for 10 minutes in a solution of deionised water (DI), ammonium hydroxide (NH$_4$OH, 34% by weight of NH$_3$) and hydrogen peroxide (H$_2$O$_2$), with mixing ratio 5:1:1. The solution has a strong oxidation power and therefore the cleaning step is followed by an immersion in hydrofluoric acid (HF) at room temperature for 30 seconds to remove the thin oxide formed. The second cleaning step is designed for removal of the metallic (ionic) contaminants. It was performed for 10 minutes in a solution of DI water, hydrochloric acid (HCl, 37% by weight) and H$_2$O$_2$ with a mixing ratio of 5:1:1. Finally, the sample underwent a HF clean for 1 minute and a DI water rinse for 5 minute. The thickness of the thermal oxide was chosen to be sufficient to prevent breakdown (only a few nanometres), and thick enough to be visible under electron microscopy. We used a thickness of 100 nm as a reasonable compromise.

The photolithography was made using a positive photoresist (1.5 µm, AZ5214e) and exposed in maskless an i-line aligner (MLA100 from Heidelberg Instruments Mikrotechnik GmbH) with a dose of 70 mJ/cm$^2$. The linear patterns of the three gratings, with the periods and duty cycles,
are reported in Table 3.1. The resist was developed using puddle development for 60 sec with a TMAH-based solution (AZ 726 MIF - 2.38% TMAH in water). We patterned the 100 nm SiO$_2$ in a buffered hydrofluoric acid (bHF) bath for 95 sec.

**Dry etching and seed layer deposition**

The anisotropic etching was performed using a cyclic Bosch-like process, named DREAM (Deposit, Removal, Etch, Asching, Multistep). A comparison between the conventional Bosch process and DREAM is illustrated in Figure 3.3. Unlike, the traditional 2-step Bosch process [82], the DREAM is a 4-step process and is an adaptation of the 3-steps process DREM (Deposit, Removal, Etch, Multistep) proposed by B. Chang *et al.* in 2018 [90].

![Figure 3.3: Comparative schematics of the deep reactive ion etching processes for a 2-step Bosch process and for the 4-steps DREAM process. Note the accumulation of fluorocarbon at the top as the number of cycles increases for the DREAM process.](image)

The DREAM process was proposed by the authors of DREM and is described in detail in [91]. The etching parameters we used are reported in table 3.2. Briefly, the cyclic process begins with an isotropic etch of the silicon (I) in a SF$_6$-based plasma environment. The etching time gradually increased as the trenches becomes deeper. The time ramping ensures that the walls of the structures are not tapered, and that the scallops have a similar size throughout the height. The deposition step (II) protects the mask and the sidewalls by depositing a passivation layer. It takes place in a C$_4$F$_8$-based plasma environment and consists in the deposition of a fluorocarbon (FC) layer from CF$_2$ radicals over the whole surface. Then, the FC layer is removed (III) at the bottom by sputter erosion with argon ions. To ensure directional sputtering, the platen power is activated. The bottom removal time was chosen so that the FC at the bottom was fully removed, but was not too long, to avoid masking material erosion. It cannot be ruled out that a decreasing ramping time for the removal could be used, since gas kinetic is expected to cause thinner FC
layers as the depth increases. However, for the desired depth range of this project (28 to 32 µm), 0.8 s has shown consistent satisfying results. In fact, the selectivity toward the resist, using this time was near infinity for the range of depth tested and we therefore did not investigate further the adjustment of the removal time, nor the deposition time. Finally, the oxygen ashing step (IV) reduces the deposited FC layer to avoid too much accumulation of FC which would eventually close the top part of the trenches. This step does not fully remove the FC, but only reduces it. After several cycles, the accumulation of the FC forms small protrusions at the top of the lines. These protrusions are shown in figure 3.4a and acted as shadow masks for evaporation of the gold seed layer. Without these protrusion, some evaporated gold particulates were visible on the scallops and could trigger unwanted side electroplating.

Table 3.2: Etching parameters for the deep reactive ion etching of the linear gratings.

<table>
<thead>
<tr>
<th>Anisotropic etching parameter for DREAM</th>
<th>Deposition</th>
<th>Bottom removal</th>
<th>Etch</th>
<th>Ashing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (s)</td>
<td>1.5</td>
<td>0.8</td>
<td>from 0.6 to 1.1</td>
<td>1</td>
</tr>
<tr>
<td>C₄F₈ (sccm)</td>
<td>400</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>SF₆ (sccm)</td>
<td>15</td>
<td>15</td>
<td>600</td>
<td>15</td>
</tr>
<tr>
<td>Ar (sccm)</td>
<td>200</td>
<td>250</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>O₂(sccm)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>120</td>
</tr>
<tr>
<td>Coil power (W)</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
</tr>
<tr>
<td>Platen power (W)</td>
<td>1</td>
<td>300</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>28</td>
<td>8</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-19</td>
<td>-19</td>
<td>-19</td>
<td>-19</td>
</tr>
</tbody>
</table>

The microfabrication of the grating G₁ essentially terminated after the dry etch process. We used 113 cycles to reach the desired depth for a phase shift of π. Additionally, we performed an acetone lift-off for 5 minutes in an ultrasonic bath at low power (maximum value × 3/5) to remove the mask pattern, and an oxygen plasma of 60 minutes to remove the remaining of organic compounds. The gratings G₀ and G₂, were processed further to the gold electroplating process step. For G₀ and G₂ we evaporated an electrically conductive seed layer of 10 nm of titanium (adhesion) and 70 nm of gold using an electron beam thermal evaporator system (FerroTech Temescal, FC-2000) with a base pressure of 10⁻⁶ torr. The same process was repeated on the backside of the wafer for the electrical contact for the gold electroplating. The SEM characterisation showed that the protrusions were covered with gold (see figure 3.4b), while the sidewalls below were free of visual gold (3.4c). The gold seed layer was centred at the bottom of the trench as shown by the arrow in figure 3.4d.

Finally, the resist and the fluorocarbons were removed with an acetone lift-off as well as an oxygen plasma ashing. We placed the wafer vertically in an ultrasonic bath with acetone for approximately 5 minutes at very low power (maximum value × 3/5) to avoid breaking the silicon lines. This risk was particularly seen for the grating G₂ which had the highest aspect ratio. Following the acetone lift-off, the fluorocarbon remains as shown in figure 3.5. The FC was slightly
Figure 3.4: Electron microscope images of a silicon mould cross-section for the grating G₂ before electroplating. (a) The lines exhibiting fluorocarbon protrusions on the top. (b) View of the top part of a line after gold evaporation. Zoom images on the FC protrusion showing deposited gold on the FC. (c) Zoom on the sidewall half way through the height showing no gold deposition. (d) Zoom on the bottom of the trench with arrow delimiting the gold seed layer.
hydrophobic, yet did not prevent the electroplating solution to enter the trenches. However, to reduce the risk of delamination, and possible contamination of the electrolyte, we removed it in an oxygen plasma at 1000 W for 60 minutes. After the oxygen plasma ashing FC was not visible in the electron microscope.

Figure 3.5: Electron microscope image of the top of a trench after acetone lift-off. The fluorocarbon remains and needs oxygen plasma during 60 minutes for complete removal.

### 3.2.2 Gold electroplating

Today, a large proportion of the gold deposition solutions is derived from cyanide [92], partly because gold cyanide electroplating is well understood and can work with alkaline, neutral and acid bath which allows for a large field of applications. Moreover the cyanide complex, \( \text{Au(CN)}_2^- \), reduces instability and decomposition of the gold compounds, thus ensuring a long life of the bath [93]. For the plating to occur, the reduction of the electron must take place at the cathode where the sample is mounted. In a cyanide solution, the complex \( \text{Au(CN)}_2^- \) in splits at the polarised substrate, and solid gold is deposited after the electron transfer. The reduction follows the following chemical reaction [84]:

\[
\text{Au(CN)}_2^- + e^- \rightarrow \text{Au} + 2\text{CN}^-
\]

Unfortunately, the cyanide compounds are environmentally hazardous and may cause safety concern in some industrial applications. Therefore, sulphite-based electrolytes are sometimes preferred, but often report less electroplating stability [94, 95, 96, 97], in addition to a shorter shelf-life. For the manufacturing of the absorbing gratings, we primarily used a commercial cyanide-based plating bath (Engtech E-59, pH 6.5). However, some plating investigations, discussed later in this chapter, were performed using a commercial sulphite-based electrolyte (Ellevate Gold D7990, pH 10).

### Method

Prior the plating, the silicon surface was activated with oxygen and nitrogen plasma (400 sccm \( \text{O}_2 / 70 \text{ sccm N}_2 \)) for 10 minutes at 1000 W. Then, the wafer was placed on a electroplating holder.
made of Polytetrafluoroethylene (PTFE) with backside contact. We immersed the holder in DI water and placed it in a desiccator connected to a rough pump for 10 minutes. This step was necessary to remove air bubbles trapped inside the trenches to facilitate the flow of the electrolyte in the trenches. The electrolyte was commercial cyanide-based with initial gold concentration of 15 g/L (0.08 mol/L). The electrodeposition was performed at 50 °C in a beaker, and magnetic steering was applied. The anode was a platinum-coated mesh with a much larger surface area than that of the active area of the gratings. The two electrodes were separated by a distance of ≈ 8 ± 1 cm. The grating G2 exhibits the highest aspect ratio, and it was the most challenging to fill with respect to the electroplating dynamics. The plating parameters were thus, foremost, optimised for G2, and later applied to G0.

**DC plating vs PC plating**

Electroplating can be performed using either direct current (DC) plating or pulse current (PC) plating. In DC mode, a DC current is applied to the electrolytic cell, while in PC mode, the current is applied periodically with a defined duty cycle ratio. For many industrial applications DC plating is ideal. It is a fast and effective way to homogeneously coat a conductive surface. However, when using DC in structures with high aspect ratio, the diffusion of ions within the structure affects the concentration and may cause porous deposition [98]. When plating high aspect ratio trenches, the starting growth behaviour at the bottom of the trenches is crucial. If the plating does not start void-free, it will never yield to a homogeneous filling of the features. On the other hand, if the plating is homogeneous and void-free from the beginning, it will likely continue until complete filling of the trench.

We performed a comparison between DC and PC plating with a cyanide-based electrolyte using a current controlled power supply (Dynatronix DUPR 10-3-6, pulse time ≤ 1 ms) and a ON-time current density of 10 mA/cm². The cross-section image of a partially filled grating made with DC mode is shown in figure 3.6a. Using DC with 10 mA/cm², large voids in the filling are visible. These voids are explained by the depletion gradient in high aspect ratio features, which result in the sidewall creep up of the deposited solid [99]. Several experimental studies have reported that the concentration of additives in gold and copper plating baths affect the deposition dynamic for bottom-up filling when using direct current deposition [100, 101, 102]. To accurately predict the plating dynamic, D. Josell *et al.* [99] proposed the curvature-enhanced accelerator coverage (CEAC) model. The model, which quantitatively predicts the filling behaviour in trenches, presumes that an electrolyte containing additives leads to void-free filling of trenches when; (1) the additives, absorbed on the surface, accelerates the deposition rate at the bottom of the feature, and (2) when the additives remain on the surface during the duration of the deposition [103]. Successful copper, silver and gold plating of trenches have been demonstrated to accurately follow the predicted CEAC model by varying the concentration of additives [104, 100]. Unfortunately, when using a commercially available solution, controlling and modifying the additives can quickly become a complex task because the exact concentration of these additives is not always known, and modifying them is not trivial. As a viable alternative, C. Seah *et al.* [98] proposed to use a two-step deposition to achieve void-free copper filling of via and trench. The first step was to apply a short deposition time with low current density (0.05 A/cm²) to nucleate copper crystallites whole over the surface and to prevent pinch-off at the top of
the trench. The second step involved a longer deposition with a current density three times higher as the first step in order to have a fast deposition. This method requires either a very big sample, or a very low current source for the short deposition at low current density. Thus, this method critically depends on the electroplating setups dimension or available current source. Another viable alternative for void-free bottom-up filling is to use pulse plating. Whilst, pulse plating method can provide void-free filling without the addition of additive, it unfortunately also considerably increases the deposition time. Using C. Seah et al. [98] requires either a very big sample, or a very low current source for the nucleation of the crystallites at low current density. These two requirements can be difficult to achieve depending on the setups dimension or current source.

Based on these observations and reported results, we applied PC mode on an identical silicon grating mould. Our PC procedure was set to an ON/OFF duty cycle ratio of 1:5 with 24 ms cycle length (4 ms ON / 20 ms OFF) and a current density of 10 mA/cm². The result of a partial filling of AR 12:1 trenches, plated with these parameters, and showing void-free gold is illustrated in the figure 3.6b. Void-free filling could also be obtained with ON/OFF duty cycles 1:2 with of 12 ms cycle length (4 ms ON and 8 mA/cm² OFF), thus reducing the overall plating time. Higher current density created dendritic growth, unsuitable for trench filling. The growth of the gold starts on both side of the trench, following a U-shape, and eventually meet at the center, forming an unavoidable seam line.

Based on these observations and reported results, we applied PC mode on an identical silicon grating mould. Our PC procedure was set to an ON/OFF duty cycle ratio of 1:5 with 24 ms cycle length (4 ms ON / 20 ms OFF) and a current density of 10 mA/cm². The result of a partial filling of AR 12:1 trenches, plated with these parameters, and showing void-free gold is illustrated in the figure 3.6b. Void-free filling could also be obtained with ON/OFF duty cycles 1:2 with of 12 ms cycle length (4 ms ON and 8 mA/cm² OFF), thus reducing the overall plating time. Higher current density created dendritic growth, unsuitable for trench filling. The growth of the gold starts on both side of the trench, following a U-shape, and eventually meet at the center, forming an unavoidable seam line.

**Pulse plating with low gold concentration electrolyte**

In a separate analysis, we attempted to fill trenches with AR 9:1 using a sulphite-based electrolyte with a gold concentration of 8.2 g/L (0.04 mol/L). The samples were prepared using the procedure described above. The fluorocarbon was kept on after the resist lift-off. The purpose of this analysis was to observe the plating dynamic when using pulse plating with lower gold concentration.
concentration. The parameters applied in this experiment are the same as the parameters used previously, namely 10 mA/cm\(^2\) with a pulse ratio of 1:5 and a cycle length of 24 ms. Figure 3.7 shows the plating creep of the gold along the sidewalls with increasing plating time. It is clear from the images that the depletion of species inside the trenches forces the gold deposition to follow primarily the sidewalls in a U-Shape which never merges. Longer deposition time yields to large voids, due to the closing up of the trench caused by the accumulated gold at the top (not shown here). This sequence illustrates the dynamic of the pulse plating inside the trench for lower gold concentration. Similar sidewall creep and void, were observed when using a cyanide-based electrolyte with gold concentration of 10 g/L (0.5 mol/L) with the same plating parameters. A comparison of the plating with 10 g/L and 15 g/L is shown in figure 3.8.

Figure 3.7: Filling morphology in partially plated AR 9:1 silicon grating using a sulphite-based gold electrolyte with concentration of 8.2 g/L after effective plating time of (a) 3 minutes (b) 6 minutes (c) 12 minutes. Scale bar 3 µm. All samples were plated using pulse duty cycle of 1:5 with 24 ms cycle length.

Figure 3.8: Filling morphology in partially plated silicon grating with cyanide-based gold solution with: (a) 10 g/l (0.5 mol/L) showing lack of deposition in the middle of the trench and (b) 15 g/l (0.8 mol/L) showing void-free filling. Both samples were plated with a current density of 10 mA/cm\(^2\) and a pulse duty cycle of 1:5 with 24 ms cycle length.
In the attempt to reduce the sidewall deposition creep when using a lower concentration electrolyte, we investigated the possibility to form a passivation layer on the sidewalls. The depletion of gold ions inside the trenches is the reason why sidewall deposition creep occurs, and limiting exchange of electrons with the sidewalls is a potential way to increase the concentration. Consequently, the gold would grow homogeneously from the bottom and upward. We investigate a way to passivate the sidewall which is discussed below. Recently, an approach using sidewall passivation was proposed by M. Kagias et al. [85] who performed seedless plating on low resistivity silicon substrate (0.01-0.1 Ω cm) with SiO₂ sidewall passivation. Thus, supporting our observation showing that sidewall passivation affects the plating dynamics. However, the exact gold concentration of their plating solution is not reported.

We used a combination of Si₃N₄ and SiO₂ for passivating the sidewalls. The schematic of the process flow is illustrated in figure 3.9

![Schematic of the process flow](image)

**Figure 3.9:** Schematic of the process flow for gold deposition with sidewall silicon nitride passivation. (I) Photolithography on SiO₂ layer. (II) Wet chemical etch of SiO₂. (III) Deep reactive ion etching. (IV) Lift-off + O₂ clean. (V) LPCVD SiN. (VI) SiN etch (both sides). (VII) Gold evaporation for seeding and backside electroplating contact. (VIII) Gold electroplating.

The experiment was carried out on 100 mm diameter n-type <100> double sided polished silicon wafers, < 0.025 Ω cm, with 100 nm of thermally grown SiO₂. The first three steps of the fabrication process were identical to that of the fabrication process described earlier and shown in figure 3.2. After the dry etching of the trenches, we performed the lift-off of the resist mask in an acetone bath for 5 minutes at low power (maximum power × 3/5). Then, the samples were placed in an oxygen plasma for 60 minute and further cleaned with a RCA procedure. We homogeneously deposited a layer of 50 nm of silicon nitride (Si₃N₄) across the whole surface of the
structure using low pressure chemical vapour deposition (LPCVD). We used an inductive couple plasma (ICP) dry etching tool (Pro ICP, from SPTS) to remove the Si$_3$N$_4$ at the bottom. The etching parameters are reported in table 3.3 and were tested successfully for trenches up to AR 12:1. During the etching, the silicon wafers were clamped on the chamber chuck using electrostatic clamping, and the chuck was cooled to 0°C. We used an optical emission spectroscopy (OES) system to monitor the end-point of the Si$_3$N$_4$, which corresponded to an increase in the silicon oxide species in the plasma. Approximately 23 seconds of plasma etching was necessary to remove the 50 nm of Si$_3$N$_4$ at the bottom, of which, 3 seconds was an over-etch to ensure full removal across the whole wafer surface.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coil power (W)</td>
<td>1000</td>
</tr>
<tr>
<td>Platen power (W)</td>
<td>200</td>
</tr>
<tr>
<td>Platen temperature</td>
<td>0 °C</td>
</tr>
<tr>
<td>CF$_4$ flow (sccm)</td>
<td>10</td>
</tr>
<tr>
<td>H$_2$ flow (sccm)</td>
<td>28</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>2.5</td>
</tr>
<tr>
<td>Etch time (s)</td>
<td>$\approx 23$</td>
</tr>
</tbody>
</table>

The etch made with these parameters provided a clear removal of the Si$_3$N$_4$ at the bottom, while the SiO$_2$ at the top of the line was only reduced slightly. Figure 3.10 shows the result of the Si$_3$N$_4$ etch. Both, the top and the side of the lines were fully covered with either a layer of Si$_3$N$_4$ or SiO$_2$.

We evaporated an electrically conductive seed layer of 10 nm of titanium (adhesion), and 70 nm of gold using an electron beam thermal evaporator system (FerroTech Temescal, FC-2000) with a base pressure of $10^{-6}$ torr. In general, the gold seed layer was well centred in the trenches as shown in a 5 µm wide silicon trench in figure 3.11a. The evaporation was performed on both sides of the sample to allow for backside contact during electrodeposition. The plating was performed in the sulphite-based solution with a gold concentration of 8.2 g/L with backside contact. Unlike M. Kagias et al., the plating did not start without a seed layer, which can perhaps be explained by the slightly higher resistivity of our substrate (0.025 Ωcm). Nevertheless, when using a seed layer, we could successfully perform bottom-up and seam-free filling, as shown in the partially plated silicon grating in figure 3.11b. Although the top of the lines were generally fully encapsulated in the dielectric layers, we sometimes observed growth at the top of the trenches following the electric field lines. This unwanted growth created protrusions along the top lines, as shown in figure 3.11c. Longer electroplating time caused the protrusions to merge, creating large areas, favouring even further the top gold plating.
We have not fully understood why some silicon lines were more prone to gold protrusions than others. The presence of the gold layer at the top of the lines, consequence of the fabrication step VII, may be the cause. However, potential damage to the silicon oxide top could also be the reasons. The protrusion growth started along the edge of the silicon lines where the electric field lines concentrate. This observation suggests that additional passivation of the corners could potentially reduce this effect. The additional passivation of the corners has not been performed in this experiment. However, as proposed in ref [85], we presume that using a dielectric, deposited by plasma enhanced chemical vapour deposition (PECVD), could potentially offer a local passivation. The PECVD process exhibits poorer conformal trench filling in HAR features than that of LPCVD. Thus, the deposition of the additional dielectric would primarily be at the top part of the line, thus, leaving the seed layer free of passivation at the bottom. Surely, the passivation method using $\text{Si}_3\text{N}_4$ and $\text{SiO}_2$ shows rather promising results for gold electroplating with low concentration electrolytes. However it also involves several fabrication and cleaning steps which quickly increase the overall fabrication cost and complexity.

Figure 3.10: Electron microscope images of the passivation of the silicon lines using $\text{Si}_3\text{N}_4$ and $\text{SiO}_2$ after bottom removal of the $\text{Si}_3\text{N}_4$. (a) Silicon grating with AR 12:1. (b) $\text{SiO}_2$ and $\text{Si}_3\text{N}_4$ passivation at the top and the side of the line. (c) Zoom image on the $\text{Si}_3\text{N}_4$ on the sidewall. (d) Zoom on the bottom of the trench after removal of the $\text{Si}_3\text{N}_4$ by dry etching.
3.3 Microfabrication results

Our experiment demonstrated that using an electroplating solution with gold concentration below 10 g/L could not homogeneously fill AR 12:1 trenches successfully without the use of a passivation layer. Even with sidewall passivation, unwanted top growth remains. The poor filling was observed for both cyanide- and sulphite-based electrolyte in pulse current plating mode for concentration below 10 g/L. Increasing the concentration of the cyanide-based gold solution to 15 g/L, not only showed void-free filling, but removed the need for the sidewall passivation. However it leaves a visible seam at the centre. The seam is not expected to have an impact on the performance of the grating. We used a cyanide-based gold bath with 15 g/L, although we believe that sulphite based solution with similar concentration would work as well. The final dimensions and processing parameters for the manufactured gratings are reported in table 3.4 and figure 3.12 shows some results of the final manufactured devices. The plating of gold for $G_0$ and $G_2$ was done with a current density of 10 mA/cm$^2$. To this date, the Talbot interferometer at the Danish Meat Research Institute is still under development, and the final manufactured gratings have not yet been tested under X-ray condition.
Table 3.4: Overview of the process parameters for the 3 fabricated gratings. All the gratings have a line periodicity with duty cycle of 0.5.

<table>
<thead>
<tr>
<th>General information</th>
<th>DRIE</th>
<th>Plating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycles</td>
<td>Height</td>
</tr>
<tr>
<td><strong>AR</strong></td>
<td><strong>Area</strong></td>
<td><strong>(ms)</strong></td>
</tr>
<tr>
<td>G0</td>
<td>5:1</td>
<td>2 x 2 cm²</td>
</tr>
<tr>
<td>G1</td>
<td>7.8:1</td>
<td>4 x 4 cm²</td>
</tr>
<tr>
<td>G2</td>
<td>11:1</td>
<td>4 x 4 cm²</td>
</tr>
</tbody>
</table>

Figure 3.12: Final gratings. (a) Top view micrograph image of G₀ after gold plating. The brighter areas correspond to the plated gold. (b) SEM cross-section of a G₁ phase-shifting grating. (c) SEM cross-section of a gold plated G₂ absorbing grating.

### 3.4 Discussion

In the current literature related to the microfabrication of absorbing X-ray optical elements, the concentration of the gold electrolyte and the plating parameters are rarely reported. Thus, making a correlation of our plating observations with existing methods, difficult to perform. Regardless, the fabrication of the absorbing grating G₂ is, without any doubt, the most challenging grating to manufacturing in a Talbot interferometer. Indeed, G₂ exhibits the highest aspect ratio of the 3 gratings, and uses X-ray absorbing materials (i.e. gold). We successfully demonstrated a simple method involving standard microfabrication process and gold electroplating. However other methods to simplify the fabrication process and/or increase the aspect ratio has also been proposed over the last twenty years. Methods involving microcasting, atomic layer deposition and other less conventional methods were proposed. Still, electroplating has a non-negligible advantage of being a batch process which can accommodate several wafers at a time, in addition to being well known and relatively cheap compared to ALD deposition, for example. Moreover, it is easy to integrate in an industrial environment. Nevertheless, the limiting factor very often reported is the aspect ratio.

At this point we believe that our method could be applied to higher AR providing that the gold concentration is sufficient. On the other hand, the evaporation of the gold seed layer may become the limiting factor, since it will become increasingly more difficult to evaporate the seed layer at the bottom with the increasing depth. With that in mind, and knowing the plating challenge, we believe that other methods, like for example stacking of lower AR gratings, could yield
to viable microfabrication alternatives of absorbing gratings. Surely, the precise alignment of several low AR gratings needs to be considered, as well as the thickness of the silicon which is meant to be transparent to X-ray. Indeed, if too many gratings are stacked, the absorption of silicon will eventually influence the visibility of the X-ray. Therefore it is necessary to either reduce its thickness using mechanical or chemical polishing after the plating. We have illustrated the proposition in figure 3.13. Essentially, the microfabrication would be the same as described in this chapter, however it involves a final step consisting in the thinning of the substrate to reduce unwanted absorption. Alternatively, using a poorly absorbing substrate (e.g. graphite) could also be considered to reduce the absorption of the photon energy. Using a polymer such as SU-8 for the grating mould would also further reduce the absorption, since polymers absorb X-rays less than silicon. For the alignment, we proposed to use three vertical steel rods to precisely align the stacked wafers. The rods are placed in a through hole made in the substrate using dry etching of silicon with low sidewall roughness. Steel can be polished with surface roughness of 0.4 µm [105] which would be sufficiently low to ensure good alignment.

Figure 3.13: Proposed stacking of low AR grating. (left) Two wafers with low AR are stacked. The thick substrate induces unwanted absorbing of the photon energy in the low absorption part of the grating. (right) Five wafer with low AR are stacked after mechanical or chemical removal of the unsure thickness.
3.5 Conclusion

The microfabrication of absorbing gratings proposed in this chapter was successfully tested up to AR 11:1 trenches, and uses a UV-lithography step, a dry etching step, a metal evaporation step and a gold electroplating step. Our results demonstrated that using concentration electrolyte $\leq 10 \text{ g/L}$ involved complex fabrication processes because of the need for passivation of the silicon sidewalls. Therefore, we used a high concentration gold solution (15 g/L). The fabrication of the silicon grating mould employed for the electroplating, uses accumulated fluorocarbon on top of the dry etched silicon lines, which acts as masking material during the gold seed layer evaporation. The fluorocarbon is then removed using acetone lift-off and oxygen plasma, prior to the gold electroplating. This method uses only standard processes commonly available in micro- and nano-fabrication facilities. We used a commercial cyanide-based gold electrolyte with a concentration of 15 g/L and a pulse plating process, to homogeneously fill the trenches. The fabrication method was applied to the absorbing grating $G_0$ and $G_2$ gratings having a periodicity of 6 µm and 13 µm respectively.
Chapter 4

Two-dimensional tungsten mask for edge illumination

In this chapter I introduce the microfabrication of a two-dimensional hole-array absorbing mask for the edge illumination at DTU Physics. The proposed method involves laser ablation and chemical etching of tungsten. Some sections of this chapter are reprints of the paper in Appendix A.1 entitled:


4.1 Introduction

We have seen in Chapter 2 that gold is often preferred as material for the microfabrication of absorbing optical elements for X-ray phase-contrast imaging. Gold is conventionally electroplated in high aspect ratio structures made of silicon or polymer [11], but other manufacturing processes involving imprinting, hot embossing or atomic layer deposition using other materials have been reported [13, 62, 12].

In this work, we propose to use tungsten (W) as an alternative to gold. The density and atomic number of tungsten (19.25 g/cm$^3$, 74) is comparable to those of gold (19.3 g/cm$^3$, 79) and thus, similar HAR structures are required to get comparable X-ray absorption contrast as shown in Table 4.1, where key parameters for potential absorber materials are listed. For good X-ray absorbers, both the atomic number and the density should be high. Table 1 shows that approximately 205µm W will absorb 90% of the incoming intensity of a 50 keV beam. To achieve a similar absorption only 167µm of gold (Au) is required, however at significantly larger material costs when considering large area gratings. The same applies for iridium (Ir) and platinum (Pt) which are rare and expensive materials. Cheaper materials like tantalum (Ta), bismuth (Bi) and lead (Pb) require larger thicknesses to achieve similar absorption, thus increasing the already difficult-to-achieve high aspect ratio of the grating. Patterning directly on a tungsten substrate
allows for reducing the number of fabrication steps. The fabrication of tungsten gratings for X-ray optical elements using reactive ion etching has previously been reported [106, 107]. However, this technique is, to our knowledge, limited to aspect ratios lower than 10 in tungsten thin films.

Table 4.1: Properties of common X-ray absorber metals. The atomic number Z, the atomic weight A, and the mass density \( \rho \), the attenuation length \( L_{50\text{keV}} \) (1/e attenuation) as well as the required absorber thickness \( x_{90\%} \) for 90% attenuation at 50 keV are listed. Values were calculated using ref. [66]. All elements are assumed pure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number (Z)</th>
<th>Atomic weight (A)</th>
<th>Density ( \rho ) (g/cm(^3))</th>
<th>At 50 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Attenuation length (( \mu )m)</td>
<td>Thickness ( x_{90%} ) (( \mu )m)</td>
</tr>
<tr>
<td>W</td>
<td>74</td>
<td>183,84</td>
<td>19,25</td>
<td>89,2</td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
<td>196,97</td>
<td>19,30</td>
<td>72,4</td>
</tr>
<tr>
<td>Ta</td>
<td>73</td>
<td>180,95</td>
<td>16,65</td>
<td>107,4</td>
</tr>
<tr>
<td>Ir</td>
<td>77</td>
<td>192,22</td>
<td>22,56</td>
<td>68,5</td>
</tr>
<tr>
<td>Pt</td>
<td>78</td>
<td>198,08</td>
<td>21,45</td>
<td>69,1</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>207,20</td>
<td>11,34</td>
<td>34114,0</td>
</tr>
<tr>
<td>Bi</td>
<td>83</td>
<td>208,98</td>
<td>9,78</td>
<td>127,6</td>
</tr>
</tbody>
</table>

To pattern higher aspect ratio holes in tungsten we use a pico-seconds pulsed laser which illuminates the substrate at well-defined spots. By using laser ablation of tungsten we can pattern deeper holes and obtain larger aspect ratios. Ultra-short pulse lasers have already shown the ability to micromachine a wide range of metals and ceramics with a high degree of precision [108, 109, 110]. In our fabrication process, each pulse removes some material until a through-hole of a few micrometres in radius is formed. The through-hole is then widened to the desired diameter by wet chemical etching. Laser ablation of tungsten is a serial fabrication process which prevents high throughput and has a lower pattern resolution, as compared to conventional photolithography methods. However, this presented method has the advantage of requiring only few processes steps, uses a cheaper material and does not use hazardous chemicals such as gold cyanide, which is the preferred electrolyte for Au plating; less harmful electrolytes exist but they suffer from poor shelf life. Additionally, since the tungsten hole grating is a single material structure, it might be easier to curve to the radius of curvature needed to overcome the natural beam divergence of the light source when a larger field of view is desirable.

4.1.1 Working principle of laser ablation

A laser beam is a monochromatic electromagnetic radiation whose intensity profile is often given by a Gaussian function. It is the geometry of the cavity in which the laser beam is generated that will define the shape function of the beam. The shape-function describes the radial intensity profile of the light, and it is commonly referred to as transverse electromagnetic modes (TEM). The fundamental TEM\(_{00}\) corresponds to a Gaussian shape where the intensity profile is symmetric around the axis in the propagation direction. The highest intensity value is at the
centre of the beam and decreases with the radial distance. The quality of the beam is given by the \( M^2 \) factor where 1 corresponds to an exact Gaussian shape.

Conventional laser ablation consists in the irradiation of a material surface, followed by the removal of the said material. Normally, and as opposed to chemical laser processing, no change in the chemical composition of the material occurs [111].

**Two-temperatures model**

Lasers can be classified in two families, namely, the continuous wave (CW) lasers and pulse lasers. Pulse lasers are further divided in "long pulse" and "short pulse". Long pulses are commonly defined as being in the micro- and nano-second range and short pulse in the pico- and femto-second range [112]. However sometimes the short pulse range is more specifically defined with pulses shorter than 1 ps [113]. In long pulse ablation (see Figure 4.1a), the material is heated up until it melts, boils and vaporises. These phase changes create a heat affected zone within the vicinity of the impact and induces micro-cracks in the material. With the increasing intensity, the quantity of vaporised species become more important and the interaction with the next laser pulse induces the ionisation of the species creating a plasma. The plasma interacts with the laser pulse causing non-linear interactions which are difficult to control. Continuous wave lasers (e.g. CO\(_2\) lasers) provide a continuous flow of intensity and consequently also suffer from the non-linear interactions (e.g. absorption, scattering...) caused by the plasma plume. These uncontrolled interactions make manufacturing process suffering from repeatability.

For short pulse lasers (Figure 4.1b), the energy is transferred to the material in a time short enough that no heat is conveyed to the material lattice. The plasma is created at the surface of the material and forms a bubble nucleation zone which eventually forces the plasma to expand. The material removal is caused by the expansion of the plasma [114]. Because the surrounding of the impact area is not heated up during a short pulse ablation, this process is also named "cold" ablation, as opposed to the long pulse which refers to as "hot" ablation. In general, the whole process including the laser impact, nucleation, expansion and removal is shorter than that of the pulse length. Hence, in short pulse laser, non-linear interactions caused by the interaction between the plasma plume and the pulse are more negligible, and process repeatability are easier to achieve.

The resolution of the pattern is in general limited by the heat diffusion in the workpiece. Metal typically have high thermal diffusivity, therefore, for high-precision manufacturing in metal, short pulse lasers are preferred [115].
4.2 Material and methods

The equipment used in this study is a Nd:YVO picosecond pulse laser from Lumentum Operations LCC, mounted in a microSTRUCT vario system (3D Micromac AG, Germany). The system generates pulses with wavelength of 1064 nm and pulse duration of 10 ps. The wavelengths of 532 nm and 355 nm are obtained by a second (SHG) and third-harmonic generator (THG). Table 4.2 report the equipment characteristics.

4.2.1 Laser beam diameter

In our X-ray edge illumination setup, the absorbing mask pattern is a periodic two-dimensional grid of 12 μm diameter holes with a period of 100 μm and an active area of $1.5 \times 1.5$ cm$^2$. The dimensions and details of the setup are reported in table 2.2 in chapter 2.

To assess whether holes of 12 μm could be achieved using our system it was necessary to determine the exact beam diameter after the lens. If the beam diameter is significantly larger than 12 μm, difficulties in achieving smaller holes would arise. On the other hand, if the beam diameter size is significantly smaller than 12 μm, it would require to mill in a circular pattern causing an increase in the processing time. With that in mind, and prior the experiment, we evaluated the beam diameter for the different wavelength available in the system.
Table 4.2: Laser characteristics of the Nd:YVO picosecond laser from Lumentum Operations LCC.

<table>
<thead>
<tr>
<th>Laser general characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Repetition rate ($\nu$)</td>
<td>200 kHz - 8.2 MHz</td>
</tr>
<tr>
<td>Pulse width ($\tau$)</td>
<td>10 ps</td>
</tr>
<tr>
<td>Wavelength ($\lambda$)</td>
<td></td>
</tr>
<tr>
<td>- IR 1064nm</td>
<td></td>
</tr>
<tr>
<td>- SHG: VIS 532 nm</td>
<td></td>
</tr>
<tr>
<td>- THG: UV 355 nm</td>
<td></td>
</tr>
<tr>
<td>Profile</td>
<td>Gaussian, TEM$_{00}$</td>
</tr>
<tr>
<td>Quality factor ($M^2$)</td>
<td>$&lt;1.3$</td>
</tr>
<tr>
<td>Beam diameter ($2w_l$) - before lens</td>
<td></td>
</tr>
<tr>
<td>- 1064nm: 1.1 mm</td>
<td></td>
</tr>
<tr>
<td>- 532 nm: 0.98 mm</td>
<td></td>
</tr>
<tr>
<td>- 355 nm: 0.76 mm</td>
<td></td>
</tr>
<tr>
<td>Lens type</td>
<td>Telecentric F-theta lens</td>
</tr>
<tr>
<td>Focal length ($f$)</td>
<td>103 mm</td>
</tr>
</tbody>
</table>

Mathematically, the radius of the Gaussian beam at $1/e^2$ (= 13.5%) of the intensity at the focal point of the lens is \[ w_0 = \frac{\lambda f}{\pi w_l} \] (4.1)

where $f$ is the focal length and $w_l$ is the radius of the beam prior the lens. Figure 4.2a and b illustrate the beam geometry in the propagation direction.

Figure 4.2: Gaussian geometry of a laser beam. (a) Illustration of the beam divergence at the so-called beam waist. (b) Profile of the Gaussian intensity as function of the beam width.
Applying equation 4.1 we obtain beam radii of $w_0 = 25\, \mu m$, $w_0 = 13\, \mu m$ and $w_0 = 3.5\, \mu m$ for $\lambda = 1064\, nm$, $\lambda = 532\, nm$ and $\lambda = 355\, nm$ respectively.

We further investigated the experimental beam radii using J. M. Liu et al. [117] method to verify if the theoretical values corresponded to the real dimensions. Their method is based on the visible phase transformation of a material under a Gaussian laser beam irradiation. Short pulse lasers usually have a very high repetition rate (e.g. few hundreds kilo-hertz), but a fairly low average output power (e.g. a few watts). It is the short duration of the pulse that makes up for the effective power of the laser. When the beam irradiates the sample at an energy density high enough to induce a visible phase changes, the surface of the material exhibits circular patterns corresponding to an ablated region and an affected region. These regions can be observed under electronic microscopy as shown in Figure 4.3. By recording the increasing phase change diameters as function of the beam energy, it is possible to extract the Gaussian beam profile dimensions.

![Figure 4.3: Example of electron micrograph of a laser impact on tungsten with fitted circumscribed circles for the affected and ablated diameters.](image)

For a given Gaussian beam propagating in free space, the transverse spatial intensity profile is given by

$$I(r, z) = I_0 \left( \frac{w_0}{w(z)} \right)^2 \exp \left( -\frac{2r^2}{w^2(z)} \right)$$  \hspace{1cm} (4.2)

Because the intensity profile varies along the propagation direction, $w$ is function of $z$. The beam will converge and then diverge at the beam waist ($w_0$) where the profile reaches its minimum diameter as illustrated in figure 4.2a. From this point, the beam diverges on both sides of the propagation direction with a divergence angle $\theta = \lambda / \pi w_0$. Thus at the beam-waist, the intensity is

$$I(r) = I_0 \exp \left( -\frac{2r^2}{w_0^2} \right)$$  \hspace{1cm} (4.3)

where the electric field varies as $\exp \left( -\frac{r^2}{w_0^2} \right)$. At $r = w_0$ the intensity thus is $I_0 / e^2 (\approx 13.5\%)$. 

60
The power in the beam is

\[ P = \int_0^\infty I(r)2\pi r \, dr = \frac{\pi}{2} I_0 w_0^2 \]  

(4.4)

The pulse energy is

\[ E_{\text{pulse}} = P \tau \]  

(4.5)

where \( \tau \) is the pulse length, while the average beam power is

\[ P_{\text{avg}} = E_{\text{pulse}} \nu = P \tau \nu \]  

(4.6)

For our equipment, the numerical values for \( \tau \nu \) span from \( \tau \nu = 10 \text{ps} \times 200 \text{kHz} = 2.0 \times 10^{-6} \) to \( \tau \nu = 10 \text{ps} \times 8.2 \text{MHz} = 8.2 \times 10^{-5} \).

Assuming that there is a certain threshold fluence \( J_a \) for single pulse ablation, then the radius \( r_a \) of the ablated spot must fulfil

\[ J_a = \tau I_0 \exp \left( -\frac{2r_a^2}{w_0^2} \right) = J_0 \exp \left( -\frac{2r_a^2}{w_0^2} \right) \Rightarrow \]

\[ r_a^2 = \frac{1}{2} w_0^2 \ln \frac{J_0}{J_a} = \frac{1}{2} w_0^2 (\ln J_0 - \ln J_a) = \]

\[ r_a^2 = \frac{1}{2} \frac{w_0^2}{\log_{10} e} \ln \frac{J_0}{J_a} = \frac{1}{2} \frac{w_0^2}{\log_{10} e} (\ln J_0 - \ln J_a) \]

where \( J_0 \) is the peak fluence. When the beam is scanned such that each spot is only illuminated by one pulse we can replace \( J_0 \) by \( E_{\text{pulse}} \) and \( J_a \) by the power \( E_a \), which is the pulse energy where the single shot illuminated spots are just not ablated. Then we have

\[ r_a^2 = \frac{1}{2} \frac{w_0^2}{\log_{10} e} (\log_{10} E_{\text{pulse}} - \log_{10} E_a) \]  

(4.7)

When each experiment is plotted on a semi-log plot we should expect a straight line with the slope \( S = \frac{1}{2} \frac{w_0^2}{\log_{10} e} \) where the beam radius \( w_0 \) can be extracted. After the beam radius is extracted the fluence for each experiment can be calculated and the data recast as function of fluence to extract the threshold fluence for ablation \( J_a \).

The experiment to evaluate the beam diameter was carried out on a 50 ± 6 µm tungsten foil 99.97% from Plansee AG, Germany. The foil was placed onto the vacuum chuck in ambient air and the surface was irradiated with an increasing power. The repetition rate was set to 200 kHz and the wavelength was 355nm. We ran a series of single pulse across a line and each pulse impact could easily been observed under electron microscopy. We reported two radii that we called "affected" and "ablated" respectively. In their paper, J. M. Liu et al. referred to these radii as outer and inner radii. Since the spots were slightly oval, we use the radius of the circumscribed circle.
Figure 4.4 illustrates how the data of the increasing radii fits to the linearised equation. The extracted slope for the affected and ablated radii were $S = 29.02 \text{ cm}^2$ and $S = 29.07 \text{ cm}^2$ respectively. Using these data, we evaluated the beam spot diameter $(2 \times w_0)$, to be $7.1 \pm 0.3 \mu\text{m}$ for the wavelength $355 \text{ nm}$\(^1\). This value is in very good agreement with the calculated diameters using equation 4.1, and we assumed that the other wavelengths were following the same accuracy level. Figure 4.4b illustrates the increasing radii as function of the energy per unit area obtained using the evaluated beam spot diameter for the wavelength $355 \text{ nm}$. The extrapolation of the fitted line indicates the single-shot threshold fluence. The value is $J_a = 0.40 \pm 0.04 \text{ J/cm}^2$ which is in good agreement with the value $0.44 \pm 0.02 \text{ J/cm}^2$ reported in literature for tungsten [118].

The diameter of the beam for the $\lambda = 355 \text{ nm}$ offers a spot diameter $(2 \times w_0 = 7.1 \pm 0.3 \mu\text{m})$ which allows for better resolution than that of the wavelength $532 \text{ nm}$ $(2 \times w_0 = 26 \mu\text{m})$ and $1064 \text{ nm}$ $(2 \times w_0 = 50 \mu\text{m})$. It is small enough to ensure good resolution and large enough that with sufficient parameters tuning, holes of $12 \mu\text{m}$ can potentially be achieved. We therefore, continue our experiment using mostly the $355 \text{ nm}$ UV wavelength.

### 4.2.2 Through-hole in tungsten

Assuming that the Gaussian profile has a constant diameter independent of the pulse energy, hypothetically, there exists a beam intensity where the diameter at the ablation threshold $(A_{\text{th}})$ matches the desired diameter, providing that the intensity can be increased accordingly. This hypothesis is illustrated in Figure 4.5.

The experiment to evaluate the through-hole diameter was carried out using $200 \mu\text{m}$ thick tungsten foil from the same supplier. The number of pulses needed to drill throughout the thickness of the sample was gradually adjusted with the increasing power. We did not observe any changes in the diameter of the exit holes if the number of pulse were significantly more than what was

---

\(^1\)Corrected diameter which differs from the published paper
Figure 4.5: Illustration showing how the increasing intensity can affect the ablated diameter. a) The diameter at \( A_{th} \) is smaller than that at 13.5% of the maximum intensity. b) Diameter at \( A_{th} \) is equal to that 13.5% of the maximum intensity. In our laser this ablated diameter would be 7.1 ± 0.3 µm. c) Diameter at \( A_{th} \) is larger than that of 13.5% of the maximum intensity which can potentially be the desired 12 µm.

strictly needed to go through the thickness. It was however important to keep the number of pulses as low as possible to reduce the overall processing time. The focal point of the laser on the surface was not adjusted as function of the drilling depth. Finally, the sample was characterized using an electron microscopy (Zeiss, Supra V40) without any prior cleaning of the sample. We evaluated the diameter of the exit holes by fitting circumscribed circles around the visible holes as illustrated in Figure 4.6 (left). We increased the beam intensity and measured the exit hole diameter that we reported as function of the fluence, as shown in 4.6 (right). A total of five holes per intensity were used to evaluate the diameter. Exit holes from 4.5 µm (≈ AR 44:1) to 12 µm (≈ AR 17:1) were achieved by varying the energy density from 12 J/cm\(^2\) to 95 J/cm\(^2\) which was the maximum fluence that the laser could deliver.
Figure 4.6: Gaussian behaviour of the throughout holes in a 200 µm tungsten foil. a) Electron microscope image of the exit holes as seen after laser processing, with increasing fluence. Yellow ring indicates the circumvent diameter of the hole. Scale : 2 µm. b) Average over 5 exit holes diameters for each tested fluence.

4.2.3 2D mask microfabrication

The base materials for the grating were 10 × 10 cm² cold-rolled sheets of tungsten (99.97% from Plansee AG, Germany) with thicknesses of 200 ± 35 µm and 50 ± 6 µm, respectively. The sheets were first diced in 2 × 2 cm² chips. The details of the process parameters used are reported in table 4.3.

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>200 µm</th>
<th>50 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten thickness</td>
<td>200 µm</td>
<td>50 µm</td>
</tr>
<tr>
<td>Wavelength (λ)</td>
<td>355 nm</td>
<td></td>
</tr>
<tr>
<td>Beam diameter (2 w₀)</td>
<td>7.1 ± 0.3 µm*</td>
<td></td>
</tr>
<tr>
<td>Average output power (P_avg)</td>
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<td>0.4 W</td>
</tr>
<tr>
<td>Fluence</td>
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<td>5 J/cm²</td>
</tr>
<tr>
<td>Number of pulse per hole</td>
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<td>1,400</td>
</tr>
<tr>
<td>Effective focal length (f)</td>
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<td></td>
</tr>
<tr>
<td>Repetition rate (ν)</td>
<td>200 kHz</td>
<td></td>
</tr>
<tr>
<td>Total processing time (per grating)</td>
<td>10 h</td>
<td>1.5 h</td>
</tr>
</tbody>
</table>

1Corrected diameter which differs from the published paper.

The tungsten 2 × 2 cm² chips were placed on the vacuum chuck of the tool under ambient atmosphere and pressure, and the focal position of the laser was set at the surface of the work-piece using the embedded camera. During processing, the sample remained stationary while
the beam was guided in the x-y direction using piezo-mounted mirrors as illustrated in figure 4.7. The desired pattern was created using a Visual Basic Script (VBS), and consisted of a matrix of 150 × 150 dots spaced with a pitch of 100 µm and aligned to the centre of the chip.

Although the diameter of the beam was approximately 7 µm, it was possible to obtain through-holes with diameters ranging from 2 µm to 8 µm in 50 µm thick tungsten sheet, and from 4.5 µm to 12 µm in 200 µm tungsten sheets, by adjusting the intensity as illustrated in figure 4.5.

The removal of material takes place when the incident energy density of the beam is larger than the ablation threshold of the material. Thus, reducing the peak intensity to a value near the ablation threshold allows material removal while ensuring opening diameters below the beam width. However, reducing the intensity also affects the ablation rate, and therefore a trade-off between processing time and resolution has to be struck.

Preliminary experiments verified that both the size and shape of the ablated material were affected by the beam power, as well as the repetition rate, thus accurate control of the through-hole diameter by controlling the beam intensity proved difficult. Moreover, the holes were often obstructed by re-deposited material consisting of non-volatile tungsten containing particles. The re-deposition of material during laser ablation also proved difficult to control and impossible to eliminate completely. To overcome these problems, we chose to combine laser ablation of through-holes (with diameters below target) with a wet chemical etching for removal of re-deposited material as well as fine-tuning of the through-hole diameter. This approach was
crucial for achieving well controlled through-hole diameter and obstruction-free through-holes and thus high signal-to-noise ratio (SNR) during X-ray imaging. Wet chemical etching for removal of re-deposits and widening of through-holes was done in an aqueous solution of 1:2 mixture of NH₄OH (29% by weight of NH₃ in water) and (H₂O₂) at 20 °C in an ultrasonic bath. The tungsten etch rate in this solution was measured to 0.5 ± 0.3 µm/min, which allows for decent control of the final through-hole diameter by timed wet etching. An increase in temperature to 40 °C revealed an etch rate of 1.1 ± 0.2 µm/min.

4.3 Results and discussion

4.3.1 Hole grating

Figure 4.8 illustrates a hole filled with redeposited material before and after chemical cleaning/etching at 40 °C. The holes in this sample were made using the parameter in table 4.3 on a 50µm thick tungsten foil. Redeposited material was not visible in all holes, and could also be trapped deep within the through-hole itself. Dark-field optical microscopy images (not shown here) easily revealed whether the holes were clear of redeposited material or not. Note, since the holes are not perfectly circular, the diameter of the circumscribed circle is reported (yellow dashed circles in figure 4.8). The average entrance diameter of the drilled hole in the 50µm thick sample is 2.7 ± 0.4 µm which leads to an aspect ratio of 18.5:1. Taking the exit hole diameter as reference for the aspect ratio gives an AR of 25:1. However, a considerable amount of redeposited material was trapped in most of the holes and thus cleaning was necessary.

![Figure 4.8](image)

Figure 4.8: Example of an exit through-hole made in 50µm thick bulk tungsten. a) Redeposited material inside the hole before cleaning/widening. Ø 2.05µm. b) Same hole after cleaning/widening using 40 °C wet chemical etching. Ø 4.40µm

To further characterise the profile and aspect ratio of the ablated holes, we produced a similar sample using the same fabrication parameters, but now in a 200µm thick tungsten sheet. The sample used for the characterisation was an array of 80 × 50 holes with 100µm pitch and was subsequently diced diagonally through the array of holes in order to increase the probability to have a number of holes diced through the middle. The dicing step was done using an automatic...
A dicing saw (Disco Dicer DAD321) and imaged using scanning electron microscopy (SEM). To allow for a clean image of the cross-section, the sample underwent a short 30 s cleaning in the etch solution at 20 °C in order to remove the redeposited material without influencing the overall shape of the holes too much. In total, 3 holes along the diagonal dicing line were cut in their middle and they allowed for a measurement of the sidewall profile. The results, illustrated in figure 4.9a,b, reveal a conical shape of the hole throughout the thickness, with a slope of $1.3 \pm 0.2\%$. Due to the nature of the cold-rolled tungsten foil fabrication, the top layers of the metal delaminated during the dicing process. To evaluate the aspect ratio we used the diameter of the larger entrance holes prior to dicing. Since the holes are not completely circular, circumscribed circles were fitted to SEM images of the holes on the top of the samples. The average diameter of the entrance holes was $15.7 \pm 0.6 \mu m$ which gives an aspect ratio of 12.7:1. The exit holes show an average diameter of $9.4 \pm 0.3 \mu m$, which is in agreement with the measured slope after dicing.

![Figure 4.9: (a) Cross-section of a through-hole with aspect ratio 12.7:1 (b) Zoom on the conical top part of the hole. The dicing process delaminated the top-most layers of the cold rolled laminated tungsten (c) Photograph of a final 1.5 × 1.5 cm grating (h = 200μm, p = 100μm, Ø = 12.3μm, aspect ratio 9.7:1) with micrograph close view on the active area. (d) Close view of an exit hole with fitted circumscribed circle. Average diameter of the exit holes: 12.3 ± 0.1μm.](image)

Finally, to verify the ability of the tungsten grating to perform X-ray phase-contrast imaging, we tested a $h = 200\mu m$ thick tungsten grating of $1.5 \times 1.5$ (cm$^2$) active area (figure 4.9c), with exit holes of diameter $Ø = 12.3 \pm 0.1 \mu m$ (figure 4.9d), and a chosen pitch of $p = 100\mu m$. Previously obtained X-ray tests performed with $50\mu m$ thick tungsten mask showed high signal to noise ratio and $200\mu m$ was a more suitable alternative, despite the longer processing time. A series of samples were imaged using a single mask phase-contrast imaging setup, as illustrated in figure
4.10 and described in [20] using a tungsten X-ray source operating at 50 keV.

![Figure 4.10: X-ray phase-contrast at DTU Physics imaging setup](image)

**Figure 4.10:** X-ray phase-contrast at DTU Physics imaging setup (a) Schematic of the system using a single two-dimensional periodic array grating. The X-rays are deflected from their original propagation direction which creates an intensity shift on the detector pixels. (b) Actual photograph of the setup during experiment.

The technique uses the single absorption tungsten mask to cut the X-ray beam into multiple beam-lets (micron size X-ray beams). The sample affects the beam-lets through a reduction of their intensity due to absorption, a shift in position due to refraction, and broadening of the beam-lets intensity distribution due to X-ray scattering. By identifying each beamlets photon distribution, it is possible to obtain a traditional absorption image, a phase-contrast image (refraction), and a dark field image (scattering) of the sample in a single acquisition. The beamlets intensity distribution is analysed at the X-ray detector, by using single photon counting techniques, which uses a single-photon counting detector (Timepix3). The method is describe in [20], and available in appendix A.3. Recent experiments have also shown the ability to performed single-shot dark-field imaging using the Timepix3 detector with the tungsten mask in our X-ray phase-contrast setup as described in [61] and available in appendix A.4. An example of an imaged moth is shown in figure 4.11. Here an absolute 2D differential phase-contrast image is compared to a standard absorption image taken with the same X-ray dose, and the improvement in image quality with phase-contrast imaging is striking. Whether this method is comparable to that of gold electroplated gratings, with regards to image quality is subject to further investigations. The small variations in the wall profile, which are seen in the SEM images cross-section, were not observed to affect the final X-ray phase-contrast images. It is estimated that the small contribution to the final beam-let intensity distribution measured on the detector from these variations is insignificant compared to the effect of the X-ray spot size (≈ 5µm), and the non-uniform detector response described in ref. [20]. Nevertheless, this experiment demonstrates that laser ablation of tungsten is a viable technology for the manufacturing of...
HAR microstructures with the aforementioned dimensions.

![Figure 4.11: X-ray image of a moth acquired with a tungsten target X-ray source operating at 50 keV. (a) Absorption image. (b) Directional differential phase contrast (HSV). (c) Absolute differential phase contrast image. Scale bar 1 mm.](image)

### 4.3.2 Linear grating

In a separate investigation on laser ablation, we evaluated the possibility to manufacture a linear grating. Our initial idea was to fabricate two linear gratings which could be placed at 90° to each another, to form a two-dimensional square array with twice the thickness. Because the opening is larger in a line than in a hole, the redeposition is expected to be less. To proceed to this first experiment, we used the infrared wavelength (1064 nm, \(w_0 = 25 \mu m\)) and fluence of 2.6 J/cm\(^2\) which was half of the maximum energy density. The sample was a tungsten sheet of 50 \(\mu m\) thick and we used 20 passes for each line. The pattern consisted in lines made in VBS with a pitch of 115 \(\mu m\) within an active area of 7 \(\times\) 7 mm\(^2\). The dicing order of the lines was random to reduce local heating.

Figure 4.12a shows the photograph of the final grating with line width of \(\approx 50 \mu m\). The cross-section of the linear grating was made using X-ray tomography since mechanical cross-sectioning proved to affect the real shape of the line too much. It is clear from figure 4.12b and c, that the shape of the grating line varies along the length and undulation of the lines are visible. It seems likely that this deformation is caused by the heating of the material. The zones closer to the frame have a larger heat sink to dissipate the heat, while the centre of the line has significantly less surface area at disposal for heat dissipation.
Nevertheless, the grating was tested in the same X-ray imaging setup described in Figure 4.10 using crossed fishing lines. The grid was rotated to acquire first the horizontal and then the vertical phase shift. While these results show some contrast, it is clear that finer grid could yield to better resolution. The infrared wavelength has the larger beam spot size, and is thus not ideal for manufacturing a fine grid. In this case, the UV wavelength should be preferred. Finer lines, down to 3 μm could be obtained using the UV wavelength, unfortunately, heat deformation remained a serious issue. However, it is entirely possible that modifying the parameters such as the laser speed, the intensity and the frequency, can reduce the heat damage and more investigations should be performed to understand better the exact influence of these parameters.
4.4 Conclusion

Our experiment has demonstrated the successful fabrication of two-dimensional $1.5 \times 1.5$ cm$^2$ periodic tungsten gratings using a combination of pico-second pulse laser ablation and chemical etch. Through-holes with a pitch of 100 µm and diameter of 12.3 µm were successfully micro-structured with an aspect ratio of 12.7:1 in 200 µm thick bulk tungsten foils. The diameter of the holes was fine-tuned using a chemical etch solution based on hydrogen peroxide and ammonium hydroxide. We characterized the profile of the periodic pattern using electron microscopy and tested the grating on a phase-contrast imaging system. The characterization of cross-sectioned holes demonstrated a sidewall slope of $1.3 \pm 0.2\%$. The experimental X-ray images obtained showed a large amount of detail that could not be resolved with standard absorption X-ray imaging.

The reported results open the way to a simple method to pattern high aspect ratio holes in bulk tungsten. When using lower energy density we were able to produce through-holes with an exit diameter as small as 4.5 µm in 200 µm thick tungsten, and entrance hole of $\approx 6.5$ µm, thus giving AR 44:1, respectively AR 31:1, depending on which hole diameter is used in the calculation of the AR. We are convinced that, despite the long processing time this method is nonetheless a viable method for creating absorbing gratings for X-ray phase-contrast imaging without the use of any hazardous or expensive wet chemical processes, and for a wide range of dimensions. Furthermore, we consider that the possibility to curve a tungsten grating to a preferred radius of curvature, to correct for the natural divergence of the light, can pave the way for a larger field of view gratings.

While laser patterning of two-dimensional tungsten grating shows promising results, heat transfer in the material remains an issue for linear gratings. Nevertheless, parameters such as power, writing speed and frequency can possibly reduce the deformation caused by the heat, since these parameters have a direct impact on the amount of energy transferred to the material in a given time. Thus, more investigations can potentially lead to use laser ablation for linear grating as well.
Chapter 5

High aspect ratio widely-spaced silicon pillars

This chapter introduces the microfabrication of two-dimensional arrays of widely-spaced pillars using deep reactive ion etching of silicon. Arrays of pillars are traditionally used as mould for gold electroplating to manufacture two-dimensional absorbing masks. In this experiment, the pillars are distributed in a square or hexagonal pattern and have a spacing significantly larger than their width. The spacing between the pillars forms large open zones with low aspect ratio which are prone to grass formation, also call black silicon. We propose a method to suppress the grass in these areas by adding sacrificial geometrical structures, less prone to grass formation. The dimensions presented in this chapter are tailored to the dimensions of the 2D absorbing mask for our edge illumination setup. However, we believe that the proposed principle can apply to a wider range of dimensions. This chapter contains reprints of the published paper in Appendix A2 entitled:

Silvestre, Chantal M.; Nguyen Vy; Jansen, Henri; Hansen, Ole, "Deep reactive ion etching of 'grass-free' widely-spaced periodic 2D arrays, using sacrificial structures", Microelectronic Engineering — 2020, Volume 223, 111228.

5.1 Introduction

Laser ablation of tungsten for the manufacturing of two-dimensional absorbing mask proved to be a simple and viable microfabrication method for X-ray optical elements. However, laser ablation is a serial process, thus limiting the throughput for large scale microfabrication. Traditionally, the fabrication of two-dimensional absorbing mask is similar to that of linear gold grating. That is to say, electroplating of gold in a pre-made reverse pattern mould. In the case of a two-dimensional array, the reverse pattern is an array of pillars, often made of silicon.

Anisotropic etching of silicon using deep reactive ion etching (DRIE) is among the key technolo-
gies for fabrication of microstructures for a wide range of applications [119, 4, 120], including silicon pillars for two-dimensional X-ray absorbing mask [83]. DRIE processes are often based on the cyclic Bosch process [82] shortly introduced in Chapter 3. This process is a two-phase procedure comprising a passivation phase and an etch phase. First, a fluorocarbon (FC) sidewall protection (i.e. passivation phase) is deposited to protect the substrate against etching. Second, the etching phase ideally first removes the protection on horizontal surfaces and then proceeds to etch silicon. The deposition/etching steps are cyclically repeated and this results in a highly anisotropic etching process, alas with significant sidewall scallops. Process control and sidewall morphology can be improved significantly when the Bosch process is modified to a three-phase process: a FC deposition phase, a removal phase that erodes away the FC on horizontal surfaces and a less aggressive etch phase that etches silicon. This three phase procedure, described in [90], is known as DREM (Deposit/Removal/Etch/Multistep).

A critical issue during anisotropic etching of silicon using DRIE is the formation of needle-like structures also known as grass or black silicon. The grass formation is caused by all sorts of micro masking present on the silicon surface. The extrinsic sources of these micro masks are various, such as native oxide or dust on the surface prior to etching [121]. But, micro masking can also occur in the vacuum chamber during the etching process itself. This intrinsic micro masking can either be due to re-deposition of the masking material sputtered by the incoming high energy ions, or from remaining passivation of the surface [122], or from particulates originating from the chamber walls.

The formation of grass is often more pronounced in larger open areas with low aspect ratio than in narrow features with high aspect ratio. This effect is particularly seen when the micro masking originates from the passivation of the surface. Here, the thickness of the passivation layer plays a significant role. In the large spaced areas, where the aspect ratio remains low during the whole etching process, the structures will receive more fluorocarbon species because the cone of incoming fluorocarbon species is wider (Figure 5.1a (1)). As a consequence, residues will build up thicker than in higher aspect ratio. Thus, during the subsequent removal step, parts of the passivating film may remain on the surface (Figure 5.1a (2)) causing micro masking when the removal is insufficient on the bottom surface. This results in the formation of particulates during the etching (Figure 5.1a (3)). The particulates will become taller with the increasing number of cycles and will eventually turn into grass (Figure 5.1a (4)). On the other hand, the deposited fluorocarbon quickly becomes thinner in the narrow spaces as the aspect ratio increases, whereas the removal (which is ideally purely directional), will not decrease as much, thereby ensuring a clean removal of the bottom surface passivation layer after each cycle.

It has been repeatedly demonstrated that parameters such as temperature, ICP power loading and pressure can affect the roughness in large open areas [123],[124],[125]. When the right balance is struck between the parameters, it is possible to obtain a grass-free bottom surface. However, fine-tuning of the etching parameters is often specific to the reactor in which the recipe was optimised. Therefore, a successful recipe is not necessarily working when applied to another reactor, which may have a different geometry or may show what we call a “memory effect” [126] (i.e. contamination of the chamber due to previous usage). More importantly, even minor changes in the mask layout used might have large effect on grass formation. Therefore, in this...
Figure 5.1: Illustration of the grass formation during DRIE process. A: Deposition step, a thicker FC layer deposits in large open area (2) Removal step, intended for removal of FC on horizontal surfaces. (3) Etching step, the remains of the thicker FC layer in larger areas create micro-masking during the etch step (4) Formation of grass due to micro masking in large open area. B: (left) Electron micrograph showing grass formation in large open areas around Ø12 µm pillars. (right) Electron micrograph showing the absence of grass between the same Ø12 µm pillars surrounded by Ø4 µm pillars. Deposition of fluorocarbon from the etching process is visible at the top of the pillars making them look wider at the top. Inserts: micrograph of initial lithography pattern. Scale bar: 10 µm
paper, we put forward a more generic approach to tackle the formation of grass using sacrificial structures.

5.2 Material and methods

5.2.1 Proposed method

The model system for this study is an array of widely-spaced pillars with 12 µm diameter and spacing of 50 µm. Such array of pillar can be used as mould for an X-ray gold absorber mask. The spacing of the pillar creates a low aspect ratio which is prone to grass formation. We propose to use sacrificial local geometries to eliminate risk of grass formation. By introducing sacrificial structures, we reduce the spacing which prevent grass formation as explained in the introduction.

Local sacrificial geometries have been used by Docker et al. [127] who described the “waffle” technique on a silicon-on-insulator (SOI) wafer. They demonstrated a method for handling large open areas that otherwise would have remained in a low aspect ratio during the dry etching. To free up large areas surrounding their silicon device, the authors added a matrix of sacrificial square holes (waffle) with dimensions that prevented the Aspect Ratio Dependent Etching (ARDE) effect (i.e. the difference in etch rate for features having different aspect ratio) between the sacrificial “waffle” and the device. They used the notching effect ([128]) at the interface of the buried oxide to release the sacrificial structures.

In this study, we investigated a series of sacrificial structures surrounding some widely-spaced pillars, and as to whether the sacrificial structures complied with these three rules:

1. Be dense enough to avoid grass formation.
2. Should not introduce ARDE effect.
3. Be removable while keeping the integrity of the main structures.

The overall difficulty in using sacrificial structures is to find a pattern that has an identical spacing between the structures to avoid etching rate variation across the surface. Each of the sacrificial structures must be placed at an equal distance from each other. Our proposed manufacturing method is illustrated in Figure 5.2 and requires only a single lithography step, one DRIE step, and one ultrasonic cleaning/removal step. A final oxygen plasma clean for a full removal of the remaining fluorocarbon deposits is optional.

The main modification in the etching recipe was an added short oxygen ashing step. A limitation in the DREM process is the accumulation of fluorocarbon on the top part of the structures, which eventually closes the openings and prevent etching. To circumvent this impasse we added an oxygen plasma ashing step to reduce the FC accumulation. This method, named DREAM for Deposit/ Removal/ Etch/ Ashing/ Multistep, was proposed by the authors of the DREM process, and is described fully in ref. [91]. Following the cyclic DREAM recipe, we used
Figure 5.2: Manufacturing method for reactive ion etching of pillars using an ARDE compensating sacrificial structure design. (1) Photolithography step. (2) Dry etching using optimized DREM process. (3) Isotropic plasma etching to weaken the base of sacrificial structures. (4) Removal of the sacrificial structures in an ultrasonic bath.

two additional none-cyclic steps meant to selectively weaken the sacrificial structures. The parameters for the cyclic silicon anisotropic etching process as well as the parameters for the subsequent steps for weakening of the sacrificial structures are listed in Table 5.1.

Table 5.1: Process parameters for deep reactive ion etching and isotropic etch of the structures

<table>
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<th>Anisotropic etching cyclic phase</th>
<th>Structure weakening</th>
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<td>C4F8 (sccm)</td>
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<tr>
<td>SF6 (sccm)</td>
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<tr>
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<td>8</td>
</tr>
<tr>
<td>Temperature (C)</td>
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<td>-19</td>
</tr>
</tbody>
</table>

Briefly, the method is divided in two distinct phases, (1) a cyclic anisotropic etch phase and, (2) a non-cyclic phase for selective weakening of the sacrificial structures. In the first cyclic etching step, the substrate was exposed to a C4F8 plasma to grow a protective layer of FC. In
the next bottom removal step, an argon plasma at 8 mTorr with high platen power was used to clear the FC at the bottom of the pattern. The third cyclic step was a time-ramped SF$_6$ etching step (ramped from 0.6 s to 1.1 s). The last cyclic step was a 1 s oxygen ashing step to reduce FC accumulation. The cyclic routine was repeated until the desired depth was reached. In the final phase, we passivated the structures for 30 s in C$_4$F$_8$ plasma to ensure good side-wall protection of the pillars to prevent the last isotropic SF$_6$ etch step (meant to weaken the sacrificial pillars) from eroding the silicon pillars.

Finally, the sacrificial structures are removed in an ultrasonic bath of ethanol and rinsed in DI water.

The critical distance at which grass appears depends on the geometry. Figure 5.3 shows SEM images of periodic structures (Ø 12 µm pillars and 3 µm lines) with varying spacing (3, 5, and 7 µm) between structures; the SEM images were selected from a wider range of structures etched using our procedure. At the smallest spacing (3 µm) grass is essentially absent while severe grass formation is seen at 7 µm spacing. At 5 µm spacing faint traces of grass initiation is seen in the interstitial region between the pillars; thus we recommend that spacing between structures should be at most 3 µm for pillars and 6 µm for parallel lines.

### 5.2.2 Sample processing

The samples were processed on 100 mm diameter n-type, 1-20 Ωcm, <100> silicon wafers. The lithography was performed on a 1.5 µm thick image reversal resist (AZ5214e) using a maskless i-line aligner (MLA 100 from Heidelberg Instruments Mikrotechnik GmbH) and a dose of 40 mJ/cm$^2$. The resist was used in image reversal mode. After the exposure, the samples were baked at 110°C for 120 s followed by a flood-exposure with a dose of 210 mJ/cm$^2$. Finally, the samples were developed for 90 s in a TMAH-based solution (AZ 726 MIF - 2.38% TMAH in water) to reveal the pattern. The diameter of the pillars were 9 µm with 27 µm spacing, or 12 µm diameter with 50 µm spacing. The width of the sacrificial structures varied between 1.5 µm and 4 µm depending on the design tested. Prior to etching, the samples were manually cleaved into approximately 1 × 1 cm$^2$ chips, and bonded onto the centre of an alumina coated 100 mm diameter carrier wafer using Galden HT-270 oil. The alumina coating proved to be resistant to the etching plasma, and the carrier wafer could be re-used throughout the experiments. The deep reactive ion etching was done in a SPTS system (DRIE Pegasus), and the resist was used as the masking material. The etching parameters, reported in Table 1, were kept constant throughout the study. After the etching process step and without unloading the sample, we ran a passivation step for 30 s followed by an isotropic etch step to weaken the base of the sacrificial structures. The chips were then unloaded and characterised.

### 5.2.3 Measurement methods

After etching, the chips were manually cleaved in half using a diamond pen. The first half of the chip was placed in an ethanol solution and ultrasonicated for 2 min at low power. The height of the pillars was evaluated from the cross-section using scanning electron microscopy (SEM,
Supra V60 from Zeiss) and the bottom height difference was measured using an optical profiler (OP, PLu Neox 3D from Sensofar). To ensure full access for measurement of the bottom surface morphology, the pillars were mechanically removed prior to the OP measurement. The removal was performed using mechanical rubbing of the surface with a cotton bud. The broken structures, which remained on the surface, were cleaned up using ultrasound. Figure 5.4a shows a schematic cross-section prior to the removal of the sacrificial structures. The cross-section schematic gives an example of the height difference between the base of a sacrificial structure and the base of a pillar; the base of the pillar is used as the reference height. We observed that if the height difference ($\Delta h$) between two adjacent areas exceeded 3 µm, the sacrificial structures were more difficult to remove using the described method. In this case, to successfully remove the sacrificial structures a longer isotropic etch would be needed to weaken the base. However this could also impair the stability of the main pillars. Therefore, in this experiment, we defined an “acceptance window for height difference”, i.e. a bottom height difference in the range between 0 and 3 µm. An OP measurement in the form of a colour-coded height map of the surface is shown in 5.4b, while 5.4C shows the surface height as a line scan extracted from the colour map along the dashed line in 5.4b. The reported bottom height measurements are performed
5.3 Results

In this section, we present the results of 6 series of designs to evaluate the ARDE compensation. The series from 1.x to 3.x have square distribution of circular pillars of 12 µm diameter, spaced with a pitch of 50 µm. The series 4.x has a square distribution of square pillars of 12 µm side length, with a pitch of 50 µm. The series 5.x reports the results of hexagonal pillars of 12 µm width placed in a hexagonal distribution, and spaced with a diagonal pitch of 50 µm. Finally, series 6.x reports the results of circular pillars of 9 µm diameter with hexagonal distribution and 27 µm pitch.

5.3.1 Design #1.0

In the initial design, we used 4 µm diameter sacrificial pillars arranged in concentric rings around the main 12 µm diameter pillars as illustrated in the insert of Figure 5.5a. We etched three samples with 88, 176 and 220 cycles corresponding to pillar heights of approximately 40, 80 and 90 µm, respectively. The height difference at the bottom surface as function of the etched pillar height from the two line scan directions is shown in Figure 5.5a. Figure 5.5a shows that, at least up to 90 µm pillar height, the sacrificial structures perform well with regards to grass formation.
and do not introduce ARDE problems. Both scan directions showed similar bottom height difference, and the standard deviation was negligible. However, occasionally the sacrificial pillars could collapse and stick together or to the main pillars as illustrated in Figure 5.5b. In the latter case, the removal of the sacrificial pillars using an ultrasonic bath became impossible. Therefore, this design did not fulfil the requirement of the sacrificial structures to be removed while keeping the integrity of the main structures. We suggest that the collapse of the sacrificial pillars occurred during unloading of the samples when the chamber is vented. The venting could cause mechanical vibration of the sacrificial pillars, and force them into contact after which they may stick and collapse. If the collapse occurred during etching process, the etch result (ARDE effect, profile, etc.) would have been severely affected, but no such effect was observed.

5.3.2 Designs #2.x

To protect the main pillars against collapse of the sacrificial pillars, we replaced some of the sacrificial pillars of design #1.0 with sacrificial concentric rings. When using concentric rings, the radial spacing between the edge of the main pillar and the edge of the sacrificial ring is constant, which will prevent ARDE within the rings. The sacrificial rings are mechanically more stable and do not collapse. In the design #2.x series, we kept some sacrificial pillars in the interstitial area between the rings, and we tested three different distributions of the sacrificial interstitial pillars. The dimensions of the mask pattern are reported in Table 5.2 and the designs are illustrated in the inserts of Figure 5. The diameter and the pitch of the main pillars remained unchanged at 12\(\mu\)m and 50\(\mu\)m, respectively.

The measured height differences reported in Figure 5.6 showed that designs #2.0 and #2.1 did not satisfy the ARDE requirement. In these two cases, the height difference was above the 3\(\mu\)m threshold and the standard deviation on the height difference was significant. The sacrificial structures could not be removed. The height difference was also quite dependent on the scan.
Table 5.2: Design dimensions of the sacrificial structures for designs #2.x

<table>
<thead>
<tr>
<th>ID</th>
<th>Qty</th>
<th>( \varnothing )</th>
<th>Spacing</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2.0</td>
<td>5</td>
<td>4 ( \mu m )</td>
<td>6.4 ( \mu m )</td>
<td>2 ( \mu m )</td>
</tr>
<tr>
<td>#2.1</td>
<td>5</td>
<td>4 ( \mu m )</td>
<td>6.4 ( \mu m )</td>
<td>2 ( \mu m )</td>
</tr>
<tr>
<td>#2.2</td>
<td>9</td>
<td>4 ( \mu m )</td>
<td>6.4 ( \mu m )</td>
<td>2 ( \mu m )</td>
</tr>
</tbody>
</table>

directions. In designs #2.0 and #2.1, the larger height difference occurred in the interstitial area (scan direction 2) where the distribution of the sacrificial pillars did not sufficiently prevent ARDE. In designs #2.0 and #2.1, the dots did not cover the interstitial area equally, this caused a local gap variation which resulted in strong ARDE as seen in the optical profiler maps illustrated in Figure 5.7a. The height difference was reasonable within the interstitial area and perfectly balanced within the concentric rings. However, between these two zones, the height difference was significant (larger than 3 \( \mu m \)) and caused ultrasonic removal problems.

Figure 5.6: Bottom height measurement for square distribution of circular pillars with combined sacrificial rings and sacrificial dots arranged as illustrated in the inserts for the three designs. All samples were etched for 88, 176, or 220 cycles; for design #2.2 an additional experiment at 320 cycles was included.

Increasing the number of dots from 5 to 9, as done in design #2.2, reduced ARDE, and the bottom height difference remained below our 3 \( \mu m \) threshold across the full pattern. Using this design, it was possible to remove the sacrificial structures while keeping the integrity of the array as seen in Figure 5.7b. This series shows that using sacrificial rings instead of pillars solves the problem of sacrificial pillars sticking to the main structures. The concentric rings compensate nicely for the ARDE inside the rings, however, the interstitial area between the four main pillars remains a zone of difficulty. Design #2.2, is the only successful in this series and fulfils all the requirements.

5.3.3 Designs #3.x

In this design series, the interstitial sacrificial pillars were replaced by an interstitial sacrificial cross in another attempt to reduce the variation in height difference within the interstitial area.
Figure 5.7: (a) optical profiler 3D topography of the bottom surfaces after mechanical removal of the pillars for a etch of 88 cycles, and SEM image of the clean array after ultrasonicication of the sacrificial structures. Scale bar: 20 µm. (b) Widely-spaced arrays of pillars using design #2.2.

The dimensions of the mask patterns are listed in Table 5.3 while inserts in Figure 5.8 show the layouts. The diameter and the pitch of the main pillars remained unchanged at 12 µm and 50 µm, respectively.

Table 5.3: Design dimensions of the sacrificial structures for designs #3.x

<table>
<thead>
<tr>
<th>ID</th>
<th>Interstitial cross pattern</th>
<th>Concentric ring dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length</td>
<td>Width</td>
</tr>
<tr>
<td>#3.0</td>
<td>17 µm</td>
<td>2 µm</td>
</tr>
<tr>
<td>#3.1</td>
<td>27 µm</td>
<td>2 µm</td>
</tr>
<tr>
<td>#3.2</td>
<td>33 µm</td>
<td>2 µm</td>
</tr>
</tbody>
</table>

The height differences reported in Figure 5.8 show that design #3.0 did not satisfy the ARDE requirement. In this design, the length of the cross left large open areas which were etched faster than the surrounding pattern, as seen in OP map in Figure 5.9a.

When increasing the length of the cross from 17 µm to 27 µm like in design #3.1, the height variation in both the scanned directions dropped to a value lower than the 3 µm threshold. Despite having an average height difference below the threshold, removal of the sacrificial structures could not be performed in this case. The 3D optical profiler result revealed that the zones at the four extremities of the cross (red arrow in 5.9a), which were not part of either of the scan direction, were subject to a faster etch. Consequently, the height difference was locally too high and restricted the removal of the outer sacrificial ring. To obtain a better ARDE compensation and perform a clean removal of the sacrificial structures, we extended the length of the cross to
Figure 5.8: Bottom height measurement for square distribution of circular pillars with sacrificial rings and crosses combined. All samples were etched for 88, 176, or 220 cycles; for design #3.2 additional experiments at 320 and 450 cycles were done.

33 µm in design #3.2. An example of the bottom height difference and the clean array is illustrated in Figure 5.9b.

To evaluate whether design #3.2 could achieve deeper structures, we etched an additional chip with 450 cycles. The measured height for this successful sample was 110 µm, which gave an aspect ratio of 9:1. We observed a slight overetch at the top of the structures due to masking material erosion. The bottom height difference returned a value below 3 µm in both directions, which was still below our threshold. This experiment suggests that using this design could lead to even higher aspect ratio pillars. Just like design #2.2, design #3.2 satisfies all our requirement.

Figure 5.9: (a) optical profiler 3D topography of the bottom surfaces after mechanical removal of the pillars for a etch of 88 cycles, and SEM image of the clean array after ultrasonication of the sacrificial structures. Scale bar: 20 µm. (b) Widely-spaced arrays of pillars using design #3.2
5.3.4 Designs #4.x

In series #4.x, the round pillars were replaced by square pillars of 12\,\mu m side length and 50\,\mu m pitch. We also replaced the sacrificial circular rings with concentric sacrificial square rings. When using square shapes, the size of the interstitial area becomes smaller than when circular structures are used, since the structures and the array then have the same shape. We expect that by reducing the interstitial area we can reduce the difficulty in finding appropriate sacrificial structures. However, when using concentric square instead of concentric circular pillars, it is no longer possible to keep all the distances identical within the concentric square rings. While the distance between two parallel surface is constant (in our case 5.4\,\mu m), the distance at the 4 corners is increased by a factor of $\sqrt{2}$. This will induce a local change in the etch depth at the corners.

We studied the effect of a sacrificial dot in the interstitial area on the bottom height difference. The dimensions of the designs are shown in Table 5.4 while the layouts are illustrated in the inserts of Figure 5.10.

<table>
<thead>
<tr>
<th>Table 5.4: Design dimensions of the sacrificial structures for designs #4.x</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>#4.0</td>
</tr>
<tr>
<td>#4.1</td>
</tr>
<tr>
<td>#4.2</td>
</tr>
</tbody>
</table>

Figure 5.10: Bottom surface height difference for a square distribution of square pillars combined with sacrificial square-rings. All samples were etched for 88, 176, and 220 cycles; for designs #4.1 and #4.2, additional experiments with 320 cycles were performed.

We successfully created widely-spaced arrays of pillars using design #4.0, up to a pillar height of 68\,\mu m, or aspect ratio 5.6:1. The removal of the sacrificial structure was successful despite
the fact that the average bottom height difference was well above our defined window of height acceptance, at least in one of the scan directions. The OP measurement illustrated in Figure 5.11a shows where the height difference was the largest.

In design #4.1 we inserted a 2 µm diameter dot in the interstitial area to evaluate whether it would reduce the ARDE observed in #4.0. Here, the first two runs (88 and 176 cycles) showed an average height difference and a variation, below our 3 µm limit, see Figure 5.10. In these runs, the sacrificial structures could be removed successfully to create widely-spaced arrays of pillars. However, the last two runs (220 and 320 cycles) returned an average height close to, or beyond the acceptance window, with a variation exceeding the 3 µm. In these last two runs, a clean removal of the sacrificial structures could not be performed.

In design #4.2, a larger 3 µm diameter dot was placed in the interstitial area. Figure 5.10 shows that the bottom surface height difference is below the 3 µm threshold at lower pillar height. This low value can also be seen in Figure 5.11a. The height difference eventually increased above the threshold when the pillar height was increased. The removal of the sacrificial structures was impossible already from a pillar height of 58 µm.

Overall, we observed that design #4.0 was better than #4.2 even though the bottom height difference was generally too high. Figure 5.11b illustrated an array of square pillars using this design #4.0. Although seemingly conflicting with the design rule, which states that Δh should be below 3 µm to successfully remove the sacrificial structures, design #4.0, is the only successful design in this series.
5.3.5 Designs #5.x

The interstitial zone between four pillars distributed in a square pattern still proved to be critical. For circular pillars, we showed that a sacrificial cross in the interstice between four pillars gave satisfying results to a depth of more than 100 µm, however a slight change in geometry had large consequences on the observed ARDE. Using square-shaped pillars and square sacrificial ring proved to still be challenging even though the interstitial zone was better in avoiding ARDE. We expect that in using a hexagonal distribution of the pillars instead of a square distribution we would eliminate the interstitial area and therefore reduce the ARDE.

Table 5.5: Design dimensions of the sacrificial structures for designs #5.x

<table>
<thead>
<tr>
<th>ID</th>
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<th>Inner hexagon</th>
<th>Outer hexagon</th>
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<tbody>
<tr>
<td>#5.0</td>
<td>7.5 µm</td>
<td>1.5 µm</td>
<td>15 µm</td>
<td>24.5 µm</td>
</tr>
<tr>
<td>#5.1</td>
<td>7.5 µm</td>
<td>1.5 µm</td>
<td>15 µm</td>
<td>20 µm</td>
</tr>
</tbody>
</table>

We tested two designs with hexagonal pillars distributed in a hexagonal pattern. The width of the hexagonal main pillars was 10 µm, and the horizontal pitch was 50 µm. The dimensions of the sacrificial structures are reported in Table 5.5. Similarly to the square rings, the hexagonal rings will show a change in the spacing at their 6 corners which corresponds to an increase of \( \frac{2}{3} \sqrt{3} \approx 1.15 \). This is closer to the ideal factor 1. It is therefore expected to observe less ARDE at the 6 corners than in the square geometry.

Design #5.0 consisted of a hexagonal ring around the main pillars, surrounded by a continuous honeycomb structure. In this case, the interstitial area is absent since all the lines could be placed at equal distances. The result of the bottom height difference in both scan directions illustrated in Figure 5.12 revealed an average height difference mostly below 1 µm, with very low variation, which suggests that the design is close to ideal in regard to avoiding ARDE. The 3D optical measurement in Figure 5.13a also indicate an ideal ARDE. The main downside of this design rests with the removal of the sacrificial continuous honeycomb, which came off as a single sheet, and partially damaged the main pillars as seen in Figure 5.13b.
In the attempt to reduce the damages caused by the single honeycomb sheet, we added a gap at the interstitial area to facilitate the removal ability. In design #5.1, the gap was created by reducing the side length of the outer hexagonal dimensions. The size of the gap was chosen to be of similar dimensions as in the previous designs tested. The results reported in Figure 5.12 indicate no significant ARDE, up to a pillar height of 63 µm (AR 6.3:1) and sacrificial structures could be removed. However, when etched for 320 cycles, the bottom height difference suddenly increased considerably, which indicates that the ARDE is no longer balanced.
5.3.6 Designs #6.x

As seen with designs series #5.x, the hexagonal distribution offers the least ARDE variation across the pattern due to the significant reduction of the difficult interstitial area. In series #6.x we decided to combine the hexagonal distribution with circular pillars. To do so, we distributed circular pillars in an hexagonal pattern. The pillars were placed closer with a pitch of 27 \( \mu \)m. We used a sacrificial ring around the main pillars with a distance of 5.4 \( \mu \)m from the edge of the pillars. Unlike the square and the hexagonal shape, the distance from the pillar to the edge of the circular ring is not reduced by any geometrical factor. The distance remains constant, which totally avoids ARDE within the ring. The dimensions of the mask patterns are reported in Table 5.6.

The two layouts differed only in the unavoidable interstitial area caused by the circular ring. In design #6.1 we introduced a 2 \( \mu \)m sacrificial dot to reduce ARDE between the interstitial area and the area inside the sacrificial ring.

<table>
<thead>
<tr>
<th>ID</th>
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<th>Spacing</th>
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</tr>
</thead>
<tbody>
<tr>
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<td>0 ( \mu )m</td>
<td>5.4 ( \mu )m</td>
<td>1.5</td>
</tr>
<tr>
<td>#6.1</td>
<td>2 ( \mu )m</td>
<td>5.4 ( \mu )m</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 5.14 shows the bottom height difference for the two designs tested. It is clear that, even with hexagonal distribution, the interstitial area remains an issue with regard to ARDE, as seen in Figure 5.15a design #6.0. A distinct improvement was obtained when a sacrificial dot was inserted as seen in design #6.1. In this latter case, the surface height difference was well below the threshold.

Figure 5.15: (a) optical profiler 3D topography of the bottom surface after mechanical removal of the pillars after 88 cycles of etch, and SEM image of the clean array after ultrasonication of the sacrificial structures. Scale bar: 20 \( \mu \)m. (b) Widely-spaced arrays of pillars using design #6.1
Design #6.1 satisfies our condition to create grass-free widely-spaced pillars with a bottom surface roughness below 3\(\mu\)m. The sacrificial structures were removed easily while keeping the integrity of the main pillars as seen in Figure 5.15b. The maximum height tested and obtained with design #6.1 was 82\(\mu\)m, which led to pillars with 9:1 aspect ratio. Figure 5.15a shows the optical profilometer maps of the bottom surfaces after mechanical removal of the pillars of designs #6.0 and #6.1.

### 5.4 Discussion

The study demonstrates that sacrificial structures can effectively suppress grass formation during DRIE of structures (here widely spaced pillars) that would suffer from severe grass formation if sacrificial structures are omitted. Indeed, all the sacrificial structure designs that were tested resulted in grass-free surfaces. The successful application of this grass-suppression strategy, however, depends on several factors: the stability of the sacrificial structures, the symmetry of the patterns, and good control of ARDE.

Poor stability of the sacrificial structures may prevent removal of the sacrificial structures by post-etching, since they may stick to the main structures, the pillars, as seen with Design #1.0. Too stable sacrificial structures, on the other hand, may prevent damage-free removal of the sacrificial structures as seen with the continuous honeycomb sacrificial structure of Design #5.0.

Sacrificial structures with low enough stability to allow damage-free removal will inevitably leave more or less open interstitial areas (depending on symmetry) that give rise to issues with ARDE control, unless proper sacrificial structures are also added there. These issues are illustrated in
Designs #2.x to #6.x, and are thus present both when pillars and arrays have similar symmetry and when they have different symmetry.

Symmetry is important as illustrated in the completely hexagonal Design #5.0, which is ideal in all aspects except for the too high stability of the sacrificial structure. Here ARDE is very well controlled simply due to the complete absence of interstitial areas.

In fact, based on our findings a simple rule can be set for an ideal symmetry. Every feature should have an identical feature placed at an equal spacing from it. In Figure 5.16 we give some examples of good and bad symmetries, and in Figure 5.17 we propose good candidates for further optimisation of the designs and a generic approach. In a generic approach, the intended structures should always be surrounded by guarding ring that matches the shape as correctly as possible, the rest of the space should be filled in with pillars that prevent ARDE.

![Poor symmetry]

![Good symmetry]

Figure 5.16: Example of geometry exhibiting poor and good symmetry for ARDE compensation

![Figure 5.17: Proposed designs based on ideal symmetry]
5.5 Conclusion

Silicon pillars arrays, used as electroplating mould for X-ray gold absorber may have dimensions which makes them more prone to silicon grass formation. The grass is more often seen when the spacing of the individual pillars is large (i.e. low aspect ratio). The use of sacrificial structures has shown to be beneficial in assisting the DRIE of large areas where the risk of grass formation is increased. In our experiment, we have an array of widely-spaced pillars which encounters this grass formation issue when performing DRIE. By using sacrificial structures, we reduced the spacing surrounding the pillars, and could suppress the formation of grass without the need of fine-tuning the parameters of the recipe.

We have investigated the effect of sacrificial structures as a method to reduce ARDE and avoid formation of grass. All experiments were done using the same DRIE recipe while the geometry of the sacrificial structures was varied. The results are that for pillars distributed in a square pattern, the ARDE significantly impacts the etch rate in the interstitial area between four pillars. Various sacrificial structures were tested in this interstitial area to evaluate and reduce the impact of ARDE. We also showed that the interstitial area problem was reduced significantly with a hexagonal distribution of pillars where perfect symmetry can be obtained. Using the method proposed in this work, we successfully fabricated 9:1 aspect ratio circular pillars, distributed in square and hexagonal pattern.
Chapter 6

Summary and outlook

In this chapter, the overview of the results are presented and possible future improvements are outlined.

6.1 Summary

The experimental work carried out in this thesis proposed improvement to multiple aspects related to the microfabrication of X-ray absorbing optical elements. Amongst the results, we can summarised the following outcomes.

1. Fabrication I: fabrication method for linear silicon/gold grating.

   • A traditional method to manufacture silicon/gold gratings has been simplified. The silicon fluorocarbon can act as sidewalls and top protection of the silicon walls during gold evaporation of the electroplating seed layer at the bottom of the trenches. Since fluorocarbon can be etched away by oxygen plasma, it can be removed after the gold evaporation leaving clean and gold free sidewalls. This method removes the need to create sidewall protection during gold evaporation since it is created in situ during the silicon patterning.

   • Gold plating of HAR silicon trenches is genuinely difficult for AR > 12:1. Sidewall creep and voids are observed. An investigation using different electrolytes with various gold concentrations provided a deeper understanding of the plating behaviour. Concentration of 10 g/L or less resulted in sidewall creep caused by the depletion of the ions in the trenches, which could not be prevented by longer duty cycle. Successful plating could be obtained when using an electrolyte with a gold concentration of 15 g/L, suggesting that the electrolyte concentration is the one of the main causes for sidewall deposition in HAR silicon trenches.

   • Silicon/gold gratings with an aspect ratio 11:1 with features size of 3µm were successfully achieved using this method.
2. Fabrication II: new and simple fabrication method for two-dimensional tungsten grating.

- High aspect ratio hole arrays can be made in bulk tungsten using pulse laser ablation. For each pulse, some material are removed and ejected from the surface until a through hole is made.

- Because of the Gaussian profile of the high-power laser, throughout holes in bulk tungsten can be achieved with a various diameters by adjusting the laser intensity. Two-dimensional tungsten gratings can be fabricated with a thickness of 200 \( \mu \text{m} \) and feature sizes as small as 4.5 \( \mu \text{m} \) using an energy density of 12 J/cm\(^2\), leading to features of close to AR 44:1. The sidewall profile proved to be straight, exhibiting a slope of \(< 2^\circ\). Redeposited material is observed and must be chemically removed.

- Controlling precisely the diameter using solely the beam intensity is difficult and a combination of laser ablation and chemical etch has proved to be the solution. The ablated holes are made significantly smaller than desired, and subsequently widened in a cleaning solution of NH\(_4\)OH and H\(_2\)O\(_2\).

- A tungsten grating fabricated using laser ablation was used in an edge illumination phase-contrast imaging setup using 50 keV X-ray source. Differential and absolute phase-contrast images of organic material were successfully obtained with a high level of detail.

3. Fabrication III: fabrication method for grass-free silicon mould for two-dimensional X-ray absorbing mask.

- In many cases, silicon grass is an unwanted effect which is a consequence of micro-masking material present on the silicon surface, which develops into needle-like structures during silicon dry etching. This effect is particularly seen in low aspect ratio structures such as widely spaced pillar arrays. It has been demonstrated that grass can be suppressed in the low aspect ratio areas by adding sacrificial structures which reduces the micro-masking. The sacrificial structures are made weaker by applying a final isotropic etch which weakens their base, allowing for an easy removal in an ultrasonic bath.

- The design of the sacrificial structures must lead to HAR structures to prevent the development of grass. In addition, the design should also have sufficient symmetry to reduce ARDE effect. Poor symmetry of the sacrificial structures will cause spatially varying etch rate which consequently lead to difficulties in the removal process.

- Square distribution of circular-shaped pillars will always have an interstitial area which are difficult to cover with symmetrical sacrificial structures.

- The best symmetry which induces the least ARDE effect is obtained with hexagonal distribution of hexagonal-shaped pillars and honeycomb sacrificial structures.

- Based on these observations a generic design, independent of the shape of the pattern, is proposed. The design combined a sacrificial ring around the main structures, surrounded by evenly distributed sacrificial small pillars. With sufficient symmetrical distribution, the small pillars cause no ARDE effect.
6.2 Further research

The results reported in this thesis have made a contribution toward a better understanding of the challenges when fabricating X-ray absorbing elements. We were able to document a number of observations and address microfabrication issues. However, like all research, there are limitations which can offer opportunities for further studies.

The accumulation of fluorocarbon proposed in the first fabrication method, successfully acts as shadow mask and lift-off layers for gold evaporation of the electroplating seed layer inside the trenches. This method was applied to manufacture absorbing gratings with AR 11:1, and some of our experimental tests also showed satisfactory results with AR 13:1. However, the literature related to the microfabrication of X-ray absorbing linear gratings often used AR ≈ 12:1 as the rough limit for gold electroplating. It is therefore uncertain if deeper structures can show similar successful outcomes using this technique. The evaporation of the gold layer inside the trenches may ultimately be a limiting factor, and the electroplating may show ion depletion behaviour for deeper structures which need to be investigated. Improvements of the fabrication process could be made by, for example

- Having a deeper understanding of the gold electroplating dynamics, chemical reaction and electric potential in the silicon trenches could provide with knowledge that can help to address more efficiently some of the plating difficulties.
- Performing a systematic comparison with an increasing concentration and various aspect ratio trenches, to empirically observe when the plating follows strictly a bottom-up filling.

Patterning tungsten using laser ablation and chemical etching has the advantage of using only two fabrication process steps, making it a very simple method to manufacture absorbing X-ray optical elements. Despite the simplicity, this technique remains slow, and doubling the active area dimension, or hole density, will scale the time with a factor $2^2$. The time factor makes it an obvious limitation for large-scale production. Some optimisation of the process parameter could lead to more effective fabrication process. Some of which could for example be

- Reducing the number of pulses. The number of pulses used to drill the throughout holes was somewhat chosen arbitrarily, since the time factor was not an issue, and the hole diameter was not influenced by the number of pulses. We used 10,000 pulses for the manufacturing of the tungsten mask. However recent experiments have shown that 7,000 pulses were already enough to drill through holes in 200μm tungsten, which would already reduce the process time by 30%. Combining higher power and lower number of iterations could potentially reduce even further the process time.
- Modifying dynamically the focus position as the depth increases. In the presented experiment, the laser beam was focused at the surface of the sample prior the ablation. This position was not modified during the drilling process. Thus, a change in energy density is to be expected with the increasing depth, certainly leading to lower etch rates. Due to the non-linearity of the etch rate inside the hole, it is difficult to predict how the focal point should be moved. Investigating the etch rate of the material in different aspect ratio hole
could lead to a better understanding of the material removal dynamic and possibly faster etch rate since the focal point could be modified.

Finally, the proposed method to suppress the silicon grass formation in wide areas with low aspect ratio has proved successful. Based on the observed results, we proposed a generic design, following an ideal symmetry, which can potentially be applied to all shapes and distribution. However, some points need to be considered.

- This design has not been tested for complete X-ray grating fabrication in this project and it is reasonable to expect that other potential issues arise, particularly at a very high aspect ratio.

- The proposed sacrificial rings around the main features form tubes as the etch depth increases. The highest structure we tested was approximately 110 µm and the tubes could easily be removed. However, it is reasonable to expect that taller tubes may stick to the main structures upon removal, and may be impossible to remove. Discontinued rings could potentially be an alternative to avoid this issue, providing that symmetry is kept.
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Appendix A

List of publications

A.1 Publication 1: Laser ablation of high-aspect-ratio hole arrays in tungsten for X-ray applications.

My contributions
• Literature review conducted • Research objective and specific research question developed • Evaluation of the laser capability and limits • Research methodology established • Case study developed for reaching objectives • Sample fabrication • Analysis of data and interpretation of results • Tables and figures developed • Wrote first draft of the complete manuscript
Laser ablation of high-aspect-ratio hole arrays in tungsten for X-ray applications

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\begin{abstract}
Periodic two-dimensional tungsten X-ray optical gratings were fabricated using a combination of pico-second laser ablation and wet chemical etch. A 200\,μm thick cold-rolled sheet of tungsten (99.97\%) was used as the base material for the fabrication of a 1.5 × 1.5 cm\textsuperscript{2} periodic grating with an array of circular holes of approximately 12.1 aspect ratio. The laser parameters were optimized to obtain through-hole diameters slightly smaller than the desired final dimension. Subsequent wet etching was used to precisely control the diameter of through-holes. The through-hole profile was characterized using scanning electron microscopy (SEM) and showed a slight conical shape with a slope of 1.3\%. The two-dimensional tungsten absorption grating was successfully tested in an X-ray phase-contrast imaging setup. The method has proven to have some relevant benefits, such as good reproducibility and a fairly easy fabrication due to few manufacturing steps.
\end{abstract}

1. Introduction

X-ray absorption imaging has been used extensively in medical diagnosis since its discovery in the late 19th century. Today, this form of imaging is widely applied also to other areas of research and technology, such as airport security, food industry or laboratory research equipment \cite{1,2,3}; making it a valuable imaging technique. While X-ray absorption imaging gives high contrast images with absorbing materials like bones and metal, it has severe limitations when imaging weakly absorbing heterogeneous samples. In these cases, it becomes difficult to differentiate between two similar media, and thus the overall contrast of the image is significantly reduced. An alternative to overcome this limitation is to take advantage of the dispersive contribution \(\delta\) of the refractive index \((n = 1 - \delta + i \beta)\) of the sample material. Conventional X-ray absorption imaging relies exclusively on the absorptive contribution \(\beta\) of a material, and ignores the dispersive aspect. However, for weakly absorbing materials, the dispersive contribution can be several orders of magnitude higher than that of the absorptive contribution. The dispersion causes a phase-shift of the transmitted light, which, once recorded, can be used to enhance the contrast of the final image. The method relies on measurement of the deflection of light in the propagation direction caused by the refraction of the object being imaged as illustrated in Fig. 1.

During the last fifteen years, several phase-contrast imaging techniques, using X-ray laboratory sources, have shown a potential for circumventing the limitations of standard absorption imaging; hence allowing the discrimination between similar tissues using clinical-size setups \cite{4,5,6}. The main optical elements of these setups are the gratings, whose precision and high aspect ratio (HAR) play a significant role in the final image quality.

To ensure a high X-ray contrast image, the gratings are made of heavy absorbing material (high atomic number \(Z\) and high density \(\rho\) ), with a high aspect ratio structure (often above 10:1). In our setup, the grating pattern is a periodic two-dimensional grid of 12,μm holes with a period of 100 μm over an active area of 1.5 × 1.5 cm\textsuperscript{2}, which acts as an absorbing mask. In the state-of-the-art fabrication process of these absorption gratings, gold is often preferred as the heavy absorber element. Gold is an almost ideal absorber for X-rays and can easily be electroplated. In these cases, the metal is micro-cast or electroplated into periodic scaffold templates, prepared using deep reaction ion etching (DRIE) or wet etching of silicon \cite{7,8,9}.

Other fabrication approaches using a combination of lithography, electroplating and moulding (LIGA) processes have also been reported \cite{10,11}. However, to achieve a complete absorber grating with these conventional methods, either several fabrication steps or costly steps (such as synchrotron radiation based lithography in the case of LIGA)
must be performed; hence, increasing the complexity, and the cost of the final device and limiting the opportunity for mass production.

In this work, we propose to use tungsten as an alternative to gold. The density and atomic number of tungsten (19.25 g/cm³, 74) is comparable to those of gold (19.3 g/cm³, 79) and thus similar HAR holes are required to get comparable X-ray absorption contrast as shown in Table 1, where key parameters for potential absorber materials are listed. For good X-ray absorbers, both the atomic number and the density should be high. Table 1 shows that approximately 205 μm W will absorb 90% of the incoming intensity of a 50 keV beam. To achieve a similar absorption only 167 μm of gold (Au) is required, however at significantly larger material costs when considering large area gratings. The same applies for Iridium (Ir) and Platinum (Pt) which are rare and expensive materials. Cheaper materials like Tantalum (Ta), Bismuth (Bi) and Lead (Pb) require larger thicknesses to achieve similar absorption, thus increasing the already difficult-to-achieve high aspect ratio of the grating. Patterning directly on a tungsten substrate allows for reducing the number of fabrication steps. The fabrication of tungsten gratings for X-ray optical elements using reactive ion etching has previously been reported [12,13]. However, this technique is, to our knowledge, limited to aspect ratios lower than 10 in tungsten thin films.

In order to pattern higher aspect ratio holes in tungsten we use a picosecond laser. By using laser ablation of tungsten we can pattern deeper holes and obtain larger aspect ratios. Ultra-short pulse lasers have already shown the ability to micromachine a wide range of metals and ceramics with a high degree of precision [14-16]. In our fabrication process, each pulse removes some material until a through-hole of a few micrometres in radius is formed. The through-hole is then widened to the desired diameter by wet chemical etching. Laser ablation of tungsten is a serial fabrication process which prevents high throughput and has a lower pattern resolution, as compared to conventional photolithography methods. However, this presented method has the advantage of requiring only very few processes steps, uses a cheaper material and does not use hazardous chemicals such as gold cyanide, which is the preferred electrolyte for Au plating; less harmful electrolytes exist but they suffer from poor shelf life. Furthermore, since the tungsten hole grating is a single material structure it might be easier to curve the grating to the radius of curvature needed to overcome the natural beam divergence of the light source in case a larger field of view is desirable.

### Table 1

Properties of common X-ray absorber metals. The atomic number Z, the atomic weight A, and the mass density ρ, the attenuation length \( L_{\text{att}} \) (1/e attenuation) as well as the required absorber thickness \( d_{\text{req}} \) for 90% attenuation at 50 keV are listed. Values were calculated using ref. [17]. All elements are assumed pure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number Z</th>
<th>Atomic weight A</th>
<th>Density ρ (g/cm³)</th>
<th>At 50 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Attenuation length (μm)</td>
</tr>
<tr>
<td>W</td>
<td>74</td>
<td>183.84</td>
<td>19.25</td>
<td>89.0</td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
<td>196.97</td>
<td>19.30</td>
<td>72.4</td>
</tr>
<tr>
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<td>16.65</td>
<td>107.4</td>
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<td>192.22</td>
<td>22.56</td>
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<tr>
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<td>21.45</td>
<td>69.1</td>
</tr>
<tr>
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<td>11.34</td>
<td>114.0</td>
</tr>
<tr>
<td>Bi</td>
<td>83</td>
<td>208.98</td>
<td>9.78</td>
<td>127.6</td>
</tr>
</tbody>
</table>

### 2. Material and methods

The base materials for the grating were 10 x 10 cm² cold-rolled sheets of tungsten (99.97% from Plansee AG, Germany) with thickness of 200 ± 35 μm and 50 ± 6 μm, respectively. The sheets were first diced in 2 x 2 cm² chips for this study. The thermal ablation of the pattern was carried out using a Nd:YVO4 picosecond laser from Lumentum Operations LLC, mounted in a microSTRUCT vario system (3D Micromac AG, Germany). The system generates pulses at a wavelength of 1064 nm with a pulse duration of 10 ps. The wavelengths of 532 nm and 355 nm are obtained by a second and third-harmonic generator. In this study, only the 355 nm wavelength was used since it exhibits the smallest spot size, and allows for the highest resolution. The beam diameter \( (2w_0) \) at 1/e² of the Gaussian beam profile was evaluated using the method described by J. M. Liu [18]. The details of the laser characteristics and process parameters used are reported in Table 2.

The tungsten 2 x 2 cm² chip was placed on the vacuum chuck of the tool under ambient atmosphere and pressure, and the focal position of the laser was set at the surface of the workpiece using the embedded camera. During processing, the sample remained stationary while the beam was guided in the x-y direction using piezo-mounted mirrors as illustrated in Fig. 2a. The desired pattern was created using a Visual Basic Script (VBS), and consisted of a matrix of 150 x 150 dots spaced with a pitch of 100 μm and aligned to the centre of the chip. For ultra-
short pulses, such as from pico- and femtosecond lasers, the pulse length is shorter than the time required to heat the material ion lattice. In this case, the material is vaporized in the form of droplets and ejected out of the material by the pressure produced in the overheated liquid formed at the interface between the plasma and the metal as illustrated in Fig. 2b [19].

Although the diameter of the spot size (Fig. 3a) at 1/e^2 (13.5%) of the intensity is 10 μm, it was possible to obtain through-holes with diameters from 2 to 8 μm by reducing the intensity as illustrated in Fig. 3b. The removal of material takes place when the incident energy density of the beam is larger than the ablation threshold of the material. Thus, reducing the peak intensity to a value near the ablation threshold allows material removal while insuring opening diameters below the beam-width. However, reducing the intensity also affects the ablation rate, and therefore a trade-off between processing time and resolution has to be struck.

Preliminary experiments verified that both the size and shape of the ablated material were affected by the beam power, the number of pulses as well as the laser repetition rate, thus accurate control of the through-hole diameter by controlling the beam intensity proved difficult. Moreover, the holes were often obstructed by re-deposited material consisting of non-volatile tungsten containing particles. The redeposition of material during laser ablation also proved difficult to control and impossible to eliminate completely. To overcome these problems, we chose to combine laser ablation of through-holes (with diameters below target) with a wet chemical etching for removal of redeposited material as well as fine tuning of the through-hole diameter. This approach was crucial for achieving well-controlled through-hole diameter and obstruction free through-holes and thus high signal-to-noise ratio (SNR) during X-ray imaging. Wet chemical etching for removal of redeposited and widening of through-holes was done in an aqueous solution of 1:2 mixture of NH₄OH (29% by weight of NH₃ in water) and H₂O₂ at 20 °C in an ultrasonic bath. The tungsten etch rate in this solution was measured to be 0.5 ± 0.3 μm/min, which allows for decent control of the final through-hole diameter by timed wet etching. An increase in temperature to 40 °C revealed an etch rate of 1.1 ± 0.2 μm.

3. Results and discussion

Fig. 4 illustrates a hole filled with redeposited material before and after chemical cleaning/etching at 40 °C. The holes in this sample were made using 1400 pulses per hole on a 50 μm thick tungsten foil. Redeposited material was not visible in all holes, and could also be trapped deep within the through-hole itself. Dark-field optical microscopy images (not shown here) easily revealed whether the holes were clear of redeposited material or not. Note, since the holes are not perfectly circular, the diameter of the circumscribed circle is reported (yellow dashed circles in Fig. 4). Evaluation of the aspect ratio for the 50 μm thick sample was made using the largest diameter of the through-hole, namely the entrance hole. The average entrance diameter of the drilled hole is 2.7 ± 0.4 μm which leads to an aspect ratio of 18.5:1.
however a considerable amount of redeposited material was trapped in most of the holes and thus cleaning was necessary.

To further characterize the profile and aspect ratio of the ablated holes, we produced a similar sample using the same fabrication parameters, but now in a 200 μm thick tungsten sheet. The sample used for the characterization was an array of 80 × 50 holes with 100 μm pitch and was subsequently diced diagonally through the array of holes in order to increase the probability to have a number of holes diced through the middle. The dicing step was done using an automatic dicing saw (Disco Dicer DAD321) and imaged using scanning electron microscopy (SEM). To allow for a clean image of the cross-section, the sample underwent a short 30 s cleaning in the etch solution at 20 °C in order to remove the redeposited material without influencing the overall shape of the holes too much. In total, 3 holes along the diagonal dicing line were cut in their middle and they allowed for a measurement of the side-wall profile. The results, illustrated in Fig. 5a,b, reveal a conical shape of the hole throughout the thickness, with a slope of 1.3 ± 0.2%. Due to the nature of the cold-rolled tungsten foil fabrication, the top layers of the metal de-laminated during the dicing process. To evaluate the aspect ratio we used the diameter of the larger entrance holes prior to dicing. Since the holes are not completely circular, circumscribed circles were fitted to SEM images of the holes on the top of the samples. The average diameter of the entrance holes was 15.7 ± 0.6 μm which gives an aspect ratio of 12.7:1. The exit holes show an average diameter of 9.4 ± 0.3 μm, which is in agreement with the measured slope after dicing.

Finally, to verify the ability of the tungsten grating to perform X-ray phase-contrast imaging, we tested a h = 200 μm thick tungsten grating of 1.5 × 1.5 cm² active area (Fig. 5c), with exit holes of diameter Ø = 12.3 ± 0.1 μm (Fig. 5d), and a chosen pitch of p = 100 μm. A series of samples were imaged using a single mask phase contrast imaging setup, as illustrated in Fig. 1 and described in [20] using a tungsten X-ray source operating at 50 kV. The technique uses the single absorption tungsten mask to cut the X-ray beam into multiple beamlets (micron size X-ray beams). The sample affects the beamlets through a reduction of their intensity due to absorption, a shift in position due to refraction, and broadening of the beamlets intensity distribution due to X-ray scattering. By identifying each beamlets photon distribution, it is possible to obtain a traditional absorption image, a phase contrast image (refraction), and a
dark field image (scattering) of the sample in a single acquisition. The beam-let intensity distribution is analyzed at the X-ray detector, by using single photon counting techniques described in ref. [20]. An example of an imaged moth is shown in Fig. 6. Here an absolute 2D differential phase-contrast image is compared to a standard absorption image taken with the same X-ray dose, and the improvement in image quality with phase contrast imaging is striking. Whether this method is comparable to that of gold electroplated gratings, with regards to image quality is subject to further investigations. The small variations in the wall profile of the holes, which are seen in the SEM images, were not observed to affect the final X-ray phase contrast images. It is estimated that the small contribution to the final beam-let intensity distribution measured on the detector from these variations is insignificant compared to the effect of the X-ray source spot size ($\sigma = 5 \mu m$), and the non-uniform detector response described in ref. [20]. Nevertheless, this experiment demonstrates that laser ablation of tungsten is a viable technology for the manufacturing of HAR microstructures with the aforementioned dimensions.

4. Conclusion

Our experiment has demonstrated the successful fabrication of two-dimensional $1.5 \times 1.5 \text{cm}^2$ periodic tungsten gratings using a combination of pico-second pulse laser ablation and chemical etch. Through-holes with a pitch of 100 $\mu m$ and diameter of 12.3 $\mu m$ were successfully micro-structured with an aspect ratio of 12.7:1 in 200 $\mu m$ thick bulk tungsten foils. The diameter of the holes was fine-tuned using a chemical etch solution based on hydrogen peroxide and ammonium hydroxide. We characterized the profile of the periodic pattern using electron microscopy and tested the grating on a phase-contrast imaging system. The characterization of cross-sectioned holes demonstrated a side wall slope of 1.3 $\pm$ 0.2%. The experimental X-ray images obtained showed a large amount of detail that could not be resolved with standard absorption X-ray imaging. The reported results open the way to a simple method to pattern high aspect ratio holes in bulk tungsten. We are convinced that, despite the long processing time this method is nonetheless a viable method for creating absorbing gratings for X-ray phase-contrast imaging without the use of any hazardous or expensive wet chemical processes. Furthermore, we consider that the possibility to curve a tungsten grating to a preferred radius of curvature can pave the way for larger field of view gratings without the need of tiling smaller gratings together.

Acknowledgement

The authors acknowledge the Innovation Fund Denmark for its financial contribution.

References


A.2 Publication 2: Deep reactive ion etching of ‘grass-free’ widely-spaced periodics 2D arrays, using sacrificial structures.

My contributions

- Literature review conducted
- Research objective and specific research question developed
- Research methodology established
- Case study developed for reaching objectives
- Sample fabrication
- Analysis of data and interpretation of results
- Tables and figures developed
- Wrote first draft of the complete manuscript
Deep reactive ion etching of ‘grass-free’ widely-spaced periodic 2D arrays, using sacrificial structures

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ARTICLE INFO

Keywords:
- ARDE
- Plasma etching
- Periodic structures
- High aspect ratio
- Sacrificial structures
- Silicon patterning

ABSTRACT

We fabricated two-dimensional arrays of periodic, widely-spaced pillars using deep reactive ion etching of silicon. To avoid the formation of micro-grass in the large open areas we used sacrificial structures surrounding the widely-spaced pillars. The use of sacrificial structures results in a denser pattern where the formation of grass is less likely to happen. We were able to remove the sacrificial structures without damaging the main array of pillars by using a modified Bosch process. The roughness remaining after removal of the sacrificial structures was evaluated using optical profilometry. Using this method, we were able to pattern grass-free arrays of widely-spaced 12 μm diameter pillars of 9:1 aspect ratio, with hexagonal and square distributions.

1. Introduction

Anisotropic etching of silicon using deep reactive ion etching (DRIE) is among the key technologies for fabrication of microstructures for a wide range of applications [1–3]. DRIE processes are often based on the cyclic Bosch process [4]. This process is a two-phase procedure comprising a passivation phase and an etch phase. First, a fluorocarbon (FC) sidewall protection (i.e. passivation phase) is deposited to protect the substrate against etching. Second, the etching phase ideally first removes the protection on horizontal surfaces and then proceeds to etch silicon. The deposition/etching steps are cyclically repeated and this results in a highly anisotropic etching process, alas with significant sidewall scallops. Process control and sidewall morphology can be improved significantly when the Bosch process is modified to a three-phase process: a FC deposition phase, a removal phase that erodes away the FC on horizontal surfaces and a less aggressive etch phase that etches silicon. This three phase procedure, described in [5], is known as DREM (Deposit/Removal/Etch/Multistep).

A critical issue during anisotropic etching of silicon using DRIE is the formation of needle-like structures also known as grass or black silicon. The grass formation is caused by all sorts of micro masking present on the silicon surface. The extrinsic sources of these micro masks are various, such as native oxide or dust on the surface prior to etching [6]. But, micro masking can also occur in the vacuum chamber during the etching process itself. This intrinsic micro masking can either be due to re-deposition of the masking material sputtered by the incoming high energy ions, or from remaining passivation of the surface [7], or from particulates originating from the chamber walls.

The formation of grass is often more pronounced in larger open areas with low aspect ratio than in narrow features with high aspect ratio. This effect is particularly seen when the micro masking originates from the passivation of the surface. Here, the thickness of the passivation layer plays a significant role. In the large spaced areas, where the aspect ratio remains low during the whole etching process, the structures will receive more fluorocarbon species because the cone of incoming fluorocarbon species is wider (Fig. 1A (1)). As a consequence, residues will build up thicker than in higher aspect ratio. Thus, during the subsequent removal step, parts of the passivating film may remain on the surface (Fig. 1A (2)) causing micro masking when the removal is insufficient on the bottom surface. This results in the formation of particulates during the etching (Fig. 1A (3)). The particulates will become taller with the increasing number of cycles and will eventually turn into grass (Fig. 1A (4)). On the other hand, the deposited fluorocarbon quickly becomes thinner in the narrow spaces as the aspect ratio increases, whereas the removal (which is ideally purely directional), will not decrease as much, thereby ensuring a clean removal of the bottom surface passivation layer after each cycle.

It has been repeatedly demonstrated that parameters such as temperature, ICP power loading and pressure can affect the roughness in large open areas [8–10]. When the right balance is struck between the parameters, it is possible to obtain a grass-free bottom surface. However, fine-tuning of the etching parameters is often specific to the reactor in which the recipe was optimized. Therefore, a successful recipe is not necessarily working when applied to another reactor, which may
have a different geometry or may show what we call a “memory effect” [11] (i.e. contamination of the chamber due to previous usage). More importantly, even minor changes in the mask layout used might have large effect on grass formation. Therefore, in this paper, we put forward a more generic approach to tackle the formation of grass using sacrificial structures.

2. Proposed method

The model system for this study is an array of widely-spaced pillars, which is used as an electroplating mold for an X-ray Au absorber grating, which is a critical optical element in an X-ray phase contrast imaging setup [12]. We propose to use sacrificial local geometries to achieve grass-free widely-spaced pillar arrays where the spacing is still too large to eliminate the risk of grass formation. By introducing sacrificial structures, we reduce the spacing which prevent grass formation as explained in the introduction.

Local sacrificial geometries have been used by Docker et al. [13] who described the “waffle” technique on a silicon-on-insulator (SOI) wafer. They demonstrated a method for handling large open areas that otherwise would have remained in a low aspect ratio during the dry etching. To free up large areas surrounding their silicon device, the authors added a matrix of sacrificial square holes (waffle) with dimensions that prevented the Aspect Ratio Dependent Etching (ARDE) effect (i.e. the difference in etch rate for features having different aspect ratio) between the sacrificial “waffle” and the device. They used the notching effect ([14]) at the interface of the buried oxide to release the sacrificial structures.

In this study, we investigated a series of sacrificial structures surrounding some widely-spaced pillars, and as to whether the sacrificial structures complied with these three rules:

1. Be dense enough to avoid grass formation.
2. Should not introduce ARDE effect.
3. Be removable while keeping the integrity of the main structures.

The overall difficulty in using sacrificial structures is to find a pattern that has an identical spacing between the structures to avoid

Fig. 1. Illustration of the grass formation during DRIE process. A: Deposition step, a thicker FC layer deposits in large open area. (2) Removal step, intended for removal of FC on horizontal surfaces. (3) Etching step, the remains of the thicker FC layer in larger areas create micro-masking during the etch step. (4) Formation of grass due to micro masking in large open area. B: (left) Electron micrograph showing grass formation in large open areas around Ø12 μm pillars. (right) Electron micrograph showing the absence of grass between the same Ø12 μm pillars surrounded by Ø4 μm pillars. Deposition of fluorocarbon from the etching process is visible at the top of the pillars making them look wider at the top. Inserts: micrograph of initial lithography pattern. Scale bar: 10 μm.
etching rate variation across the surface. Each of the sacrificial structures must be placed at an equal distance from each other. Our proposed manufacturing method is illustrated in Fig. 2 and requires only a single lithography step, one DRIE step, and one ultrasonic cleaning/removal step. A final oxygen plasma clean for a full removal of the remaining fluorocarbon deposits is optional.

The main modification in the etching recipe was an added short oxygen ashing step. A limitation in the DREM process is the accumulation of fluorocarbon on the top part of the structures, which eventually closes the openings and prevent etching. To circumvent this impasse we added an oxygen plasma ashing step to reduce the FC accumulation. This method, named DREAM for Deposit/Removal/ Etch/ Ashing/Multistep, was proposed by the authors of the DREM process, and is described fully in ref. [15]. Following the cyclic DREAM recipe, we used two additional non-cyclic steps meant to selectively weaken the sacrificial structures. The parameters for the cyclic silicon anisotropic etching process as well as the parameters for the subsequent steps for weakening of the sacrificial structures are listed in Table 1.

Briefly, the method is divided in two distinct phases, (1) a cyclic anisotropic etch phase and, (2) a non-cyclic phase for selective weakening of the sacrificial structures. In the first cyclic etching step, the substrate was exposed to a C₄F₈ plasma to grow a protective layer of FC. In the next bottom removal step, an argon plasma at 8 mTorr with high platen power was used to clear the FC at the bottom of the pattern. The third cyclic step was a time-ramped SF₆ etching step (ramped from 0.6 s to 1.1 s). The last cyclic step was a 1 s oxygen ashing step to reduce FC accumulation. The cyclic routine was repeated until the desired depth was reached. In the final phase, we passivated the structures for 30 s in C₄F₈ plasma to ensure good side-wall protection of the pillars to prevent the last isotropic SF₆ etch step (meant to weaken the sacrificial pillars) from eroding the silicon pillars.

Finally, the sacrificial structures are removed in an ultrasonic bath of ethanol and rinsed in DI water.

The critical distance at which grass appears depends on the geometry. Fig. 3 shows SEM images of periodic structures (Ø12 μm pillars and 3 μm lines) with varying spacing (3, 5, and 7 μm) between structures; the SEM images were selected from a wider range of structures etched using our procedure. At the smallest spacing (3 μm) grass is essentially absent while severe grass formation is seen at 7 μm spacing. At 5 μm spacing faint traces of grass initiation is seen in the interstitial region between the pillars; thus we recommend that spacing between structures should be at most 3 μm for pillars and 6 μm for parallel lines.

### 3. Materials and methods

#### 3.1. Sample processing

The samples were processed on 100 mm diameter n-type, 1–20 Ωcm, (100) silicon wafers. The lithography was performed on a 1.5 μm thick image reversal resist (AZ5214e) using a maskless i-line aligner (MLA 100 from Heidelberg Instruments Mikrotechnik GmbH) and a dose of 40 mJ/cm². The resist was used in image reversal mode. After the exposure, the samples were baked at 110°C for 120 s followed by a

<table>
<thead>
<tr>
<th>Process parameters for deep reactive ion etching and isotropic etch of the structures.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anisotropic etching cyclic phase</strong></td>
</tr>
<tr>
<td><em>Deposition</em></td>
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<tr>
<td>C₄F₈ (sccm)</td>
</tr>
<tr>
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</tr>
<tr>
<td>Ar (sccm)</td>
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<tr>
<td><strong>Platen power (W)</strong></td>
</tr>
<tr>
<td><strong>Pressure (mTorr)</strong></td>
</tr>
<tr>
<td><strong>Temperature (C)</strong></td>
</tr>
</tbody>
</table>

![Fig. 2. Manufacturing method for reactive ion etching of pillars using an ARDE compensating sacrificial structure design. (1) Photolithography step. (2) Dry etching using optimized DREM process. (3) Isotropic plasma etching to weaken the base of sacrificial structures. (4) Removal of the sacrificial structures in an ultrasonic bath.](image1)

![Fig. 3. SEM images of etched periodic structures (pillars and lines) with varying distance between the pillars or lines (a) 3 μm spacing. (b) 5 μm spacing and (c) 7 μm spacing. The yellow arrows indicate the smallest distance. Note the grass formation at 7 μm spacing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image2)
flood-exposure with a dose of 210 mJ/cm². Finally, the samples were developed for 90 s in a TMAH-based solution (AZ 726 MIF - 2.38% TMAH in water) to reveal the pattern. The diameter of the pillars were 9 μm with 27 μm spacing, or 12 μm diameter with 50 μm spacing. The width of the sacrificial structures varied between 1.5 μm and 4 μm depending on the design tested. Prior to etching, the samples were manually cleaved into approximately 1 × 1 cm² chips, and bonded onto the centre of an alumina coated 100 mm diameter carrier wafer using Galden HT-270 oil. The alumina coating proved to be resistant to the etching plasma, and the carrier wafer could be re-used throughout the experiments. The deep reactive ion etching was done in a SPTS system (DRIE Pegasus), and the resist was used as the masking material. The etching parameters, reported in Table 1, were kept constant throughout the study. After the etching process step and without unloading the sample, we ran a passivation step for 30 s followed by an isotropic etch step to weaken the base of the sacrificial structures. The chips were then unloaded and characterised.

3.2. Measurement methods

After etching, the chips were manually cleaved in half using a diamond pen. The first half of the chip was placed in an ethanol solution and ultrasonicated for 2 min at low power. The height of the pillars was evaluated from scanning electron microscopy (SEM, Supra V60 from Zeiss) and the bottom height difference was measured using an optical profiler (OP, Plux Neox 3D from Sensofar). To ensure full access for measurement of the bottom surface morphology, the pillars were mechanically removed prior to the OP measurement. The removal was performed using mechanical rubbing of the surface with a cotton bud. The broken structures, which remained on the surface, were cleaned up using ultrasound. Fig. 4A shows a schematic cross-section prior to the removal of the sacrificial structures. The cross-section schematic gives an example of the height difference between the base of a sacrificial structure and the base of a pillar; the base of the pillar is used as the reference height. We observed that if the height difference (Δh) between two adjacent areas exceeded 3 μm, the sacrificial structures were more difficult to remove using the described method. In this case, to successfully remove the sacrificial structures a longer isotropic etch would be needed to weaken the base. However this could also impair the stability of the main pillars. Therefore, in this experiment, we defined an “acceptance window for height difference” i.e. a bottom height difference in the range between 0 and 3 μm. An OP measurement in the form of a colour-coded height map of the surface is shown in 4B, while 4C shows the surface height as a line scan extracted from the colour map along the dashed line in 4B. The reported bottom height measurements are performed on an average of six measurements across each scan direction.

4. Experiments

In this section, we present the results of 6 series of designs to evaluate the ARDE compensation. The series from 1.x to 3.x have square distribution of circular pillars of 12 μm diameter, spaced with a pitch of 50 μm. The series 4.x has a square distribution of square pillars of 12 μm side length, with a pitch of 50 μm. The series 5.x reports the results of circular pillars of 12 μm diameter. The series 6.x reports the results of hexagonal pillars of 12 μm width placed in a hexagonal distribution, and spaced with a diagonal pitch of 50 μm. Finally, series 6.x reports the results of circular pillars of 9 μm diameter with hexagonal distribution and 27 μm pitch.

4.1. Design #1.0

In the initial design, we used 4 μm diameter sacrificial pillars arranged in concentric rings around the main 12 μm diameter pillars as illustrated in the insert of Fig. 5A. We etched three samples with 88, 176 and 220 cycles corresponding to pillar heights of approximately 40, 80 and 90 μm, respectively. The height difference at the bottom surface as function of the etched pillar height from the two line scan directions is shown in Fig. 5A. Fig. 5A shows that, at least up to 90 μm pillar height, the sacrificial structures perform well with regards to grass formation and do not introduce ARDE problems. Both scan directions showed similar bottom height difference, and the standard deviation was negligible. However, occasionally the sacrificial pillars collapsed and stick together or to the main pillars as illustrated in Fig. 5B. In the latter case, the removal of the sacrificial pillars using an ultrasonic bath became impossible. Therefore, this design did not fulfill the requirement of the sacrificial structures to be removed while keeping the integrity of the main structures. We suggest that the collapse of the sacrificial pillars occurred during unloading of the samples when the chamber was vented. The venting could cause mechanical vibration of the sacrificial pillars, and force them into contact after which they may stick and collapse. If the collapse occurred during etching process, the
etch result (ARDE effect, profile, etc.) would have been severely affected, but no such effect was observed.

4.2. Designs #2.x

To protect the main pillars against collapse of the sacrificial pillars, we replaced some of the sacrificial pillars of design #1.0 with sacrificial concentric rings. When using concentric rings, the radial spacing between the edge of the main pillar and the edge of the sacrificial ring is constant, which will prevent ARDE within the rings. The sacrificial rings are mechanically more stable and do not collapse. In the design #2.x series, we kept some sacrificial pillars in the interstitial area between the rings, and we tested three different distributions of the sacrificial interstitial pillars. The dimensions of the mask pattern are reported in Table 2 and the designs are illustrated in the inserts of Fig. 5. The diameter and the pitch of the main pillars remained unchanged at 12 μm and 50 μm, respectively.

The measured height differences reported in Fig. 6 showed that designs #2.0 and #2.1 did not satisfy the ARDE requirement. In these two cases, the height difference was above the 3 μm threshold and the standard deviation on the height difference was significant. The sacrificial structures could not be removed. The height difference was also quite dependent on the scan directions. In designs #2.0 and #2.1, the larger height difference occurred in the interstitial area (scan direction 2) where the distribution of the sacrificial pillars did not sufficiently prevent ARDE. In designs #2.0 and #2.1, the dots did not cover the interstitial area equally, this caused a local gap variation which resulted in strong ARDE as seen in OP map in Fig. 7A. The height difference was reasonable within the interstitial area and perfectly balanced within the concentric rings. However, between these two zones, the height difference was significant (larger than 3μm) and caused ultrasonic removal problems.

Increasing the number of dots from 5 to 9, as done in design #2.2, reduced ARDE, and the bottom height difference remained below our 3 μm threshold across the full pattern. Using this design, it was possible to remove the sacrificial structures while keeping the integrity of the array as seen in Fig. 7B. This series shows that using sacrificial rings instead of pillars solves the problem of sacrificial pillars sticking to the main structures. The concentric rings compensate nicely for the ARDE inside the rings, however, the interstitial area between the four main pillars remains a zone of difficulty. Design #2.2, is the only successful in this series and fulfills all the requirements.

4.3. Designs #3.x

In this design series, the interstitial sacrificial pillars were replaced by an interstitial sacrificial cross in another attempt to reduce the variation in height difference within the interstitial area. The dimensions of the mask patterns are listed in Table 3 while inserts in Fig. 8 show the layouts. The diameter and the pitch of the main pillars remained unchanged at 12 μm and 50 μm, respectively.

The height differences reported in Fig. 8 show that design #3.0 did not satisfy the ARDE requirement. In this design, the length of the cross left large open areas which were etched faster than the surrounding pattern, as seen in OP map in Fig. 9A.

When increasing the length of the cross from 17 μm to 27 μm like in design #3.1, the height variation in both the scanned directions dropped to a value lower than the 3 μm threshold. Despite having an average height difference below the threshold, removal of the sacrificial structures could not be performed in this case. The 3D optical profiler result revealed that the zones at the four extremities of the cross (red arrow in 9A), which were not part of either of the scan direction, were subject to a faster etch. Consequently, the height difference was locally too high and restricted the removal of the outer sacrificial ring. To obtain a better ARDE compensation and perform a clean removal of the sacrificial structures, we extended the length of the cross to 33 μm in design #3.2. An example of the bottom height difference and the clean array is illustrated in Fig. 9B.

To evaluate whether design #3.2 could achieve deeper structures, we etched an additional chip with 450 cycles. The measured height for this successful sample was 110 μm, which gave an aspect ratio of 9:1. We observed a slight overetch at the top of the structures due to masking material erosion. The bottom height difference returned a value below 3 μm in both directions, which was still below our threshold. This experiment suggests that using this design could lead to even higher aspect ratio pillars. Just like design #2.2, design #3.2 satisfies all our requirement.

4.4. Designs #4.x

In series #4.x, the round pillars were replaced by square pillars of 12 μm side length and 50 μm pitch. We also replaced the sacrificial

![Fig. 5. A: Bottom height difference in directions 1 (lateral) and 2 (transverse) of the pillar sacrificial structure. The resist pattern and the scan directions are illustrated in the upper right corner. B: SEM image of sacrificial pillars collapsed after unloading from the DRIE tool. The pillar are covered with fluorocarbon caused by the cyclic dry etching process.](image-url)
circular rings with concentric sacrificial square rings. When using square shapes, the size of the interstitial area becomes smaller than when circular structures are used, since the structures and the array then have the same shape. We expect that by reducing the interstitial area we can reduce the difficulty in finding appropriate sacrificial structures. However, when using concentric square instead of concentric circular pillars, it is no longer possible to keep all the distances identical within the concentric square rings. While the distance between two parallel surfaces is constant (in our case 5.4 μm), the distance at the 4 corners is increased by a factor of $\sqrt{2}$. This will induce a local change in the etch depth at the corners.

We studied the effect of a sacrificial dot in the interstitial area on the bottom height difference. The dimensions of the designs are shown in Table 4 while the layouts are illustrated in the inserts of Fig. 10.

We successfully created widely-spaced arrays of pillars using design #4.0, up to a pillar height of 68 μm, or aspect ratio 5.6:1. The removal of the sacrificial structure was successful despite the fact that the average bottom height difference was well above our defined window of height acceptance, at least in one of the scan directions. The OP measurement illustrated in Fig. 11A shows where the height difference was the largest.

In design #4.1 we inserted a 2 μm diameter dot in the interstitial area to evaluate whether it would reduce the ARDE observed in #4.0. Here, the first two runs (88 and 176 cycles) showed an average height difference and a variation, below our 3 μm limit, see Fig. 10. In these runs, the sacrificial structures could be removed successfully to create widely-spaced arrays of pillars. However, the last two runs (220 and 320 cycles) returned an average height close to, or beyond the acceptance window, with a variation exceeding the 3 μm. In these last two runs, a clean removal of the sacrificial structures could not be performed.

In design #4.2, a larger 3 μm diameter dot was placed in the interstitial area. Fig. 6 shows that the bottom surface height difference is below the 3 μm threshold at lower pillar height. This low value can also be seen in Fig. 11A. The height difference eventually increased above the threshold when the pillar height was increased. The removal of the sacrificial structures was impossible already from a pillar height of 58 μm.

Overall, we observed that design # 4.0 was better than #4.2 even though the bottom height difference was generally too high. Fig. 11B illustrated an array of square pillars using this design #4.0. Although

![Fig. 6. Bottom height measurement for square distribution of circular pillars with combined sacrificial rings and sacrificial dots arranged as illustrated in the inserts for the three designs. All samples were etched for 88, 176, or 220 cycles; for design #2.2 an additional experiment at 320 cycles was included.](image)

![Fig. 7. A: optical profiler 3D topography of the bottom surfaces after mechanical removal of the pillars for a etch of 88 cycles, and SEM image of the clean array after ultra-sonication of the sacrificial structures. Scale bar: 20 μm. B: Widely-spaced arrays of pillars using design #2.2.](image)

<table>
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</tr>
<tr>
<td>#3.1</td>
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<td>2 μm</td>
</tr>
<tr>
<td>#3.2</td>
<td>33</td>
<td>2 μm</td>
</tr>
</tbody>
</table>
seemingly conflicting with the design rule, which states that $\Delta h$ should be below 3 $\mu$m to successfully remove the sacrificial structures, design #4.0, is the only successful design in this series.

5. Design #5.x

The interstitial zone between four pillars distributed in a square pattern still proved to be critical. For circular pillars, we showed that a sacrificial cross in the interstice between four pillars gave satisfying results to a depth of more than 100 $\mu$m, however a slight change in geometry had large consequences on the observed ARDE. Using square-shaped pillars and square sacrificial ring proved to still be challenging even though the interstitial zone was better in avoiding ARDE. We expect that in using a hexagonal distribution of the pillars instead of a square distribution we would eliminate the interstitial area and therefore reduce the ARDE.

We tested two designs with hexagonal pillars distributed in a hexagonal pattern. The width of the hexagonal main pillars was 10 $\mu$m, and the horizontal pitch was 50 $\mu$m. The dimensions of the sacrificial structures are reported in Table 4. Similarly to the square rings, the hexagonal rings will show a change in the spacing at their 6 corners which corresponds to an increase of $\sqrt{3} \approx 1.15$. This is closer to the ideal factor 1. It is therefore expected to observe less ARDE at the 6 corners than in the square geometry.

Design #5.0 consisted of a hexagonal ring around the main pillars, surrounded by a continuous honeycomb structure. In this case, the interstitial area is absent since all the lines could be placed at equal distances. The result of the bottom height difference in both scan directions illustrated in Fig. 12 revealed an average height difference mostly below 1 $\mu$m, with very low variation, which suggests that the design is close to ideal in regard to avoiding ARDE. The 3D optical measurement in Fig. 13A also indicate an ideal ARDE. The main downside of this design rests with the removal of the sacrificial continuous honeycomb, which came off as a single sheet, and partially damaged the main pillars as seen in Fig. 13B.

In the attempt to reduce the damages caused by the single honeycomb sheet, we added a gap at the interstitial area to facilitate the removal ability. In design #5.1, the gap was created by reducing the side length of the outer hexagonal dimensions. The size of the gap was chosen to be of similar dimensions as in the previous designs tested. The results reported in Fig. 12 indicate no significant ARDE, up to a pillar
height of 63 μm (AR 6.3:1) and sacrificial structures could be removed. However, when etched for 320 cycles, the bottom height difference suddenly increased considerably, which indicates that the ARDE is no longer balanced.

6. Designs #6.x

As seen with designs series #5.x, the hexagonal distribution offers the least ARDE variation across the pattern due to the significant reduction of the difficult interstitial area. In series #6.x we decided to combine the hexagonal distribution with circular pillars. To do so, we distributed circular pillars in an hexagonal pattern. The pillars were placed closer with a pitch of 27 μm. We used a sacrificial ring around the main pillars with a distance of 5.4 μm from the edge of the pillars. Unlike the square and the hexagonal shape, the distance from the pillar to the edge of the circular ring is not reduced by any geometrical factor. The distance remains constant, which totally avoids ARDE within the ring. The dimensions of the mask patterns are reported in Table 6.

The two layouts differed only in the unavoidable interstitial area caused by the circular ring. In design #6.1 we introduced a 2 μm sacrificial dot to reduce ARDE between the interstitial area and the area inside the sacrificial ring.

Fig. 14 shows the bottom height difference for the two designs tested. It is clear that, even with hexagonal distribution, the interstitial area remains an issue with regard to ARDE, as seen in Fig. 15A design #6.0. A distinct improvement was obtained when a sacrificial dot was inserted as seen in design #6.1. In this latter case, the surface height difference was well below the threshold.

Design #6.1 satisfies our condition to create grass-free widely-spaced pillars with a bottom surface roughness below 3 μm. The sacrificial structures were removed easily while keeping the integrity of the main pillars as seen in Fig. 15B. The maximum height tested and obtained with design #6.1 was 82 μm, which led to pillars with 9:1

Table 5
Design dimensions of the sacrificial structures for designs #5.x.

<table>
<thead>
<tr>
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<th>Side length</th>
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<td>1.5 μm</td>
</tr>
<tr>
<td>#5.1</td>
<td>7.5 μm</td>
<td>1.5 μm</td>
</tr>
</tbody>
</table>
aspect ratio. Fig. 15A shows the optical profilometer maps of the bottom surfaces after mechanical removal of the pillars of designs #6.0 and #6.1.

Table 6

<table>
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<tr>
<th>ID</th>
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<th>Concentric circle dimensions</th>
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</thead>
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<td>Spacing</td>
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</tr>
<tr>
<td>#6.1</td>
<td>2 μm</td>
<td>5.4 μm</td>
</tr>
</tbody>
</table>

7. Discussion

The study demonstrates that sacrificial structures can effectively suppress grass formation during DRIE of structures (here widely spaced pillars) that would suffer from severe grass formation if sacrificial structures are omitted. Indeed, all the sacrificial structure designs that were tested resulted in grass-free surfaces. The successful application of this grass-suppression strategy, however, depends on several factors: the stability of the sacrificial structures, the symmetry of the patterns, and good control of ARDE.

Poor stability of the sacrificial structures may prevent removal of the sacrificial structures by post-etching, since they may stick to the main structures, the pillars, as seen with Design #1.0. Too stable sacrificial structures, on the other hand, may prevent damage-free removal of the sacrificial structures as seen with the continuous honeycomb sacrificial structure of Design #5.0.

Sacrificial structures with low enough stability to allow damage-free removal will inevitably leave more or less open interstitial areas (depending on symmetry) that give rise to issues with ARDE control, unless proper sacrificial structures are also added there. These issues are illustrated in Designs #2.x to #6.x, and are thus present both when pillars and arrays have similar symmetry and when they have different symmetry.

Symmetry is important as illustrated in the completely hexagonal Design #5.0, which is ideal in all aspects except for the too high stability of the sacrificial structure. Here ARDE is very well controlled simply due to the complete absence of interstitial areas.

In fact, based on our findings a simple rule can be set for an ideal symmetry. Every feature should have an identical feature placed at an equal spacing from it. In Fig. 16 we give some examples of good and bad symmetries, and in Fig. 17 we propose good candidates for further optimisation of the designs and a generic approach. In a generic approach, the intended structures should always be surrounded by
Fig. 14. Bottom surface height measurement for hexagonal distribution of circular pillars with sacrificial rings; design #6.1 also has sacrificial dots, which are missing on design #6.0 as seen in the inserts. All samples were etched for 88, 176 and 220 cycles; for design #6.1 an additional experiment with 320 etch cycles was done.

Fig. 15. A: optical profiler 3D topography of the bottom surface after mechanical removal of the pillars after 88 cycles of etch, and SEM image of the clean array after ultra-sonication of the sacrificial structures. Scale bar: 20 μm. B: Widely-spaced arrays of pillars using design #6.1.

Fig. 16. Example of geometry exhibiting poor and good symmetry for ARDE compensation.

Fig. 17. Proposed designs based on ideal symmetry.
guarding ring that matches the shape as correctly as possible, the rest of the space should be filled in with pillars that prevent ARDE.

8. Conclusion

The use of sacrificial structures has shown to be beneficial in assisting the DRIE of large areas where the risk of grass formation is increased. In our experiment, we have an array of widely-spaced pillars which encounters this grass formation issue when performing DRIE. By using sacrificial structures, we reduced the spacing surrounding the pillars, and could suppress the formation of grass without the need of fine-tuning the parameters of the recipe.

We have investigated the effect of sacrificial structures as a method to reduce ARDE and avoid formation of grass. All experiments were done using the same DRIE recipe while the geometry of the sacrificial structures was varied. The results are that for pillars distributed in a square pattern, the ARDE significantly impacts the etch rate in the interstitial area between four pillars. Various sacrificial structures were tested in this interstitial area to evaluate and reduce the impact of ARDE. We also showed that the interstitial area problem was reduced significantly with a hexagonal distribution of pillars where perfect symmetry can be obtained. Using the method proposed in this work, we successfully fabricated 9:1 aspect ratio circular pillars, distributed in square and hexagonal pattern.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors acknowledge the Innovation Fund Denmark for financial support.

References

A.3 Publication 3: Virtual subpixel approach for single-mask phase-contrast imaging using Timepix3

My contributions

• Engaged in discussions of the experimental setup and the design of the absorption grating
• Developed the fabrication process for the absorption grating
• Fabrication of the absorption grating used in the experiments
• Provided photograph and SEM images used in the article
• Revised the manuscript.
Virtual subpixel approach for single-mask phase-contrast imaging using Timepix3


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ABSTRACT: X-ray phase contrast imaging provides a method to distinguish materials with similar density and effective atomic number, which otherwise would be difficult using conventional X-ray absorption contrast. In recent years, multiple methods have been developed to acquire X-ray phase contrast images using incoherent laboratory sources. The single mask edge illumination setup has been demonstrated as a possible candidate for large scale applications due to its relaxed restrictions on longitudinal coherence and mask alignment, and for its ability to do bi-directional phase contrast images in a single sample exposure. Unfortunately, the single mask edge illumination setup’s refraction sensitivity, and thereby signal to noise, is limited by detector artifacts. Furthermore, it requires multiple exposures to perform dark-field imaging, a method that enables imaging of micro-structures smaller than the image resolution.

1Corresponding author.
We propose using an Advapix detector with Timepix3 pixel-readout chip in a single mask imaging setup to improve signal to noise ratio in phase contrast images. This is achieved using the Timepix3 chip’s ability to simultaneously acquire fast time of arrival and time over threshold measurement of single photon events, which enables sub-pixel identification of individual photons. In this paper, we demonstrate that signal to noise ratio can be improved by at least $67 \pm 5\%$ using subpixel identification of single photons compared to conventional acquisitions methods. Thereby the required sample dose can be reduced considerably. This shows that there is a great potential in using Timepix3 chip to improve x-ray phase contrast imaging. Further, the results indicate the possibility for dark field imaging in a single sample exposure using Timepix3 in a single mask edge illumination setup.

**Keywords:** Data processing methods; Inspection with x-rays; X-ray detectors; X-ray radiography and digital radiography (DR)
Contents

1 Introduction  
2 Single Mask Edge Illumination  
3 Subpixel positioning with Timepix3 chip  
4 Discussion and outlook

1 Introduction

X-ray Phase Contrast (XPC) imaging has drawn much attention for its ability to image biological samples with a considerably lower sample dose than conventional X-ray absorption imaging. This is achieved by using X-ray refraction as image contrast, which in particular gives a high sensitivity for light materials with low effective atomic number. Multiple techniques have been developed over the last two decades to implement XPC imaging for laboratory sources [1–6]. All of these techniques are multi-modal, making it possible to acquire absorption and XPC images simultaneously as well as dark field images of objects smaller than the image resolution [7–9].

The Double Mask Edge illumination (DM-EI) XPC imaging technique [2] has already been applied for large scale applications [10]. The technique’s major advantages are its eased restriction on mask alignment, low sample dose, and ability to use the entire energy spectrum of a conventional laboratory source [11]. DM-EI is a non-interferometric technique that uses a pre-sample mask to create beamlets and a detector mask to analyze the beamlet’s position. By scanning the detector mask, the beamlets’ intensity distributions are obtained. A minimum of two steps is required to detect a phase shift of the beamlets due to a sample and three steps to get a dark field image [9]. DM-EI is commonly only implemented with refraction sensitivity along one direction as two-directional sensitivity requires complicated masks and at least three steps of the detector mask [12].

To overcome the above problems of the DM-EI setup, single mask techniques have been developed. Here, the detector mask is removed and the beamlets’ position are analyzed with the detector directly. Two approaches exist: the beam-tracking technique [5], where the detector pixels are sufficiently smaller than the beamlet, and the Single Mask Edge Illumination (SM-EI) technique, where the pixel borders constitute the analyzing edges of the setup [3]. The latter shows promising result for XPC imaging when compared to the DM-EI setup. The setup has high refraction sensitivity, as a small movement of the beamlet causes a large shift in intensity between the illuminated pixels, and two-directional sensitivity can be obtained in a single sample exposure using a two-dimensional pre-sample mask [13]. Unfortunately, its performance is limited by charge sharing in the detector [14], and it is not possible to obtain dark field images in a single exposure.

We propose that photon counting detectors with the Timepix3 pixel-readout chip, developed by the Medipix consortium, could minimize the limitation of the SM-EI method originally developed
by Krejci et al. [13]. This is possible due to the Timepix3 chip’s data-driven readout architecture which enables the measurement of the excited charge distribution in the detector of each individual photon at a hit rate of 40 Mhits/s/cm² [15]. By analyzing the measured charge distribution, it is possible to identify each photon’s sub-pixel position [16], making it possible to decrease the effective pixel size. In this paper, we focus on the use of photon sub-pixel positioning to improve signal to noise ratio in XPC images acquired with a SM-EI setup.

2 Single Mask Edge Illumination

The SM-EI setup employed at the Technical University of Denmark (DTU) is shown in figure 1a. The setup uses a Hamamatsu Photonics L12161-07 micro focus X-ray source, which for the experiments presented in this paper was set to a source spot size of 5 µm, $U = 50$ kV, and $I = 67$ µA. An absorption mask is placed $Z_{XM}$ from the source. The absorption mask was made with laser ablation of a 200 µm thick Tungsten (W) foil and is designed with a two-dimensional array of holes with a diameter $12.3 \pm 0.1$ µm and a pitch of 100 µm as illustrated in figure 1(b-c) [17]. An Advapix detector with a Timepix3 pixel-readout chip, 1 mm Silicon sensor, and 55 µm pixel size, is placed $Z_{MD}$ from the mask. By adjusting $Z_{MD}$, the beamlets that pass through the mask has a spacing equal to an integer number of pixels at the detector. Through translation of the detector in the two directions perpendicular to the X-ray beam, the mask is aligned with the detector such that the beamlets hit the pixel corners. The sample is placed between mask and detector at $Z_{SD}$ from the detector.

The SM-EI technique allows for retrieval of a bi-directional phase images in a single shot. The XPC image is acquired by finding the shift of each beamlet

$$\Delta S = S_{\text{Sample}} - S_0,$$

where $S_{\text{Sample}}$ and $S_0$ is the beamlet’s position with and without a sample respectively. The beamlet’s position is found through a weighted mean of the intensity $I_p$ in the $M$ pixels surrounding
Figure 2. Bi-direction XPC image of 4 crossed nylon wires using the horizontal $\Theta_x$ (a) and vertical $\Theta_y$ (b) refraction angle of the X-ray beamlets as contrast. The color scale (left) is given in $\mu$rad. The refraction signal in the two directions can can be combined in an HSV color image (c), where the color shows the direction of the refraction and brightness the amplitude of the refraction angle.

the illuminated corner

$$S = \frac{\sum_{p=1}^{M} P_p I_p}{\sum_{p=1}^{M} I_p},$$  \hspace{1cm} (2.2)

where $P_p$ is the pixel position. The refraction angle of the beamlet passing through a sample along the horizontal $x$ and vertical direction $y$ is then given by

$$\Theta_x = \tan^{-1} \left( \frac{\Delta S_x}{Z_{SD}} \right) \quad \text{and} \quad \Theta_y = \tan^{-1} \left( \frac{\Delta S_y}{Z_{SD}} \right).$$  \hspace{1cm} (2.3)

An image of 4 crossed wires acquired with the setup at DTU is shown in figure 2. The image was obtained by raster scanning the sample in 6 x 6 steps with a step size of 20 $\mu$m to obtain higher resolution than the mask pitch. As clearly shown by the HSV color-plot in figure 2c, the bi-directional sensitivity allows for clear detection of all wires, which is difficult using the refraction along horizontal or vertical direction alone (figure 2a-b).

3 Subpixel positioning with Timepix3 chip

Charge sharing between detector pixels can induce a current in multiple adjacent pixel’s electrodes. When the current induced in an electrode is higher than the triggering threshold, it will be registered as an event. By recording the current’s Time over Threshold (ToT) in the electrode, the energy deposited in that pixel can be found [18]. The Timepix3 chip is capable of reading both Time over Threshold (ToT) as well as the Time of Arrival (ToA) at a resolution of 1.56 ns for each single event. This enables the possibility to identify clusters of events belonging to the same photon interaction. The ToT measurement, and hence the amount of energy deposited in each pixel, can then be used to find the position of the photon interaction [16]

$$R_{ph} = \frac{\sum_{e=1}^{N} P_e E_e}{\sum_{e=1}^{N} E_e},$$  \hspace{1cm} (3.1)

where $P_e$ and $E_e$ are the pixel position and the deposited energy of the $e$’th event, and $N$ is the total number of events in the cluster of pixels triggered by the photon.
Figure 3. Image of a single beamlet acquired using different data processing methods (a), with horizontal and vertical profiles of the beamlets’ distribution shown for selected methods (b). The image signal has been normalized to the standard deviation in the non illuminated pixels. The lines mark pixel borders.

Close to a pixel border, the probability of charge sharing increases and hence the number of pixels that are triggered per photon. In order to obtain a best estimate of the single photon position, a high number of triggered pixels is desired [16]. The probability of charge sharing is maximized by adjusting the position of the detector such that beamlets hit the pixel corners.

Using Advacam developed interface software Pixet, each photon’s position is calculated and afterwards all photons are binned into \((n \times n)\) virtual “subpixels” per pixel. We will compare the results of subpixel rebinning the photons to the more conventional integrated ToT (iTToT), where the ToT is integrated across all events in every pixel, and event count (Event), where just the number of events in each pixel is summed regardless of deposited energy. To avoid experimental variation affecting the comparison, all experiments are conducted with data being saved in a raw data format. For each event, pixel position, ToA, and ToT are recorded. After acquisition, the different processing methods are applied to the raw data. For all methods, the conversion of ToT into energy developed by Jakubek [18] has been employed. Only single photons causing clusters equal to or larger than two pixels are included for the subpixel methods. In principle, it is necessary to have at least 3 events per single photon cluster in order to determine a single photon’s position in the pixel plane, however, the ensemble average of all photons’ position was found to be more precise by also including two pixel clusters.

In figure 3, we show how subpixel rebinning can be used to resolve the distribution of a single beamlet hitting the corner of 4 pixels. For this measurement, we used \(Z_{MD} = 513\ \text{mm}\) and \(Z_{SD} = 315\ \text{mm}\). Including only the geometric expansion of the beamlets due to the fan-beam setup and assuming a gaussian beamlet shape, this geometry would result in the beamlets having an expected FWHM at the detector of \(\phi \sim 27\ \mu\text{m}\). As seen in figure 3, using subpixel identification of each photon increases the Signal to Noise Ratio (SNR).

To evaluate the accuracy and precision of the beamlet’s position for different data processing methods, a single beamlet was moved across the detector. The beamlet was made with a pinhole mask with similar holesize as the 2D mask. The mask was scanned, moving the beamlet across the detector in \(10 \times 20\) points in horizontal and vertical direction, respectively, with a spacing of \(20\ \mu\text{m}\) between the points in both directions. The detector was tilted by \(\sim 1^\circ\) as compared to the movement the beamlet scan. When projecting the scan into a single pixel, the tilt ensures that the entire area of the pixel is covered with a spacing of \(2 - 5\ \mu\text{m}\) between the beamlet’s center positions.
Figure 4. Comparison of expected $S_E$ and measured $S_M$ position using different readout methods as the beamlet is scanned across the detector. The scan covers 10 × 20 position across the detector (a). A zoom in on 2 × 2 pixels (center to center) illustrates the difference between $S_E$ (black stars) and $S_M$ (colored symbols) for the tree methods (b). The black lines show the pixel borders. The difference in measured and expected horizontal position $\Delta S_x = S_{x,M} - S_{x,E}$ is shown as function of $S_{x,E}$ projected into a single pixel (c). The color scale is given in μm and the red scale bar shows the pixel position in μm. The difference between measured $R_M$ and expected $R_E$ distance to the nearest corner (d) can be fitted with $F(R_E)$ given in eq. (3.2) (black curves) and the standard deviation $\sigma_R$ of the distribution of data points around $F(R_E)$ calculated for $R_E < 15$ μm (e).

In figure 4, we compare the beamlets’ measured position $S_M$, estimated by the different processing method, to the expected beamlet position $S_E$. We determine $S_E$ assuming a fixed beamlet spacing of 20 μm and an average across all position $\bar{S}_E = \bar{S}_{iToT}$, where $\bar{S}_{iToT}$ is the average of all the beamlet’s position found with iToT data processing method. By subtracting the expected position of the beamlet from the position estimated by the different method $S_M$, the detector response can be evaluated. As seen from figure 4c, the different ways of processing the data affect the detector response differently. The iToT seems to predict the beamlet position most accurately with smallest difference between the measured and expected position, generally tending to push the beamlet’s predicted position towards the center of the pixel. It is seen clearly from both figure 4b and 4c, that rebinning into a single pixel after subpixel localizing each individual photon seems to over predict the beamlet’s proximity to the pixel centers. Opposite, rebinning into a 2 × 2 subpixel grid, decreasing the virtual pixel size to 27.5 μm, seems to push the predicted position of the beamlets towards the corners.

The same behavior is clearly seen in the average distance to the nearest corner, shown in figure 4d. Here, the single pixel rebinning over-predicts the position of the beamlet with more than 15 μm towards the beam center at a distance of 15 μm from a corner. However, the figure also seems to indicate that the variation of the points is smaller for the 2 × 2 subpixel binned data than the others. This is quantified through fitting

$$F(R_E) = A \sin \left( \frac{R_M - R_E}{2\pi/D} \right),$$

where $D = 77.8$ μm is the diagonal of the pixel, and $A$ is the variable amplitude. As a measure of the precision, we calculate the standard deviation of the measured radius distribution $\sigma_R$ around
Figure 5. XPC image of a 300 μm thick nylon wire. The effect of different processing methods on the XPC images of a wire (a). The green lines mark the XPC profiles of the wire shown in (b) where the blue and red markers illustrate the maximum refraction signal in the two directions. For the different methods we calculate the standard deviation of the background XPC image $\sigma_0$ (c), mean maximum refraction across both direction $\Theta_{\text{max}}$ (d), and the signal to noise ratio $\Gamma = \Theta_{\text{max}}/\sigma_0$ (e).

$F(R_E)$ at $R_E < 15 \mu m$. We do so for 3 different distances of $Z_{\text{MD}}$ corresponding to three different sizes of the beamlet onto the detector $\text{FWHM}_{\text{Beam}}$. The results are presented in figure 4e and show that rebinning into subpixels ($2 \times 2$) seems to give a much more precise measure of the beamlet’s position than any of the two other methods at small beamlet sizes (small $Z_{\text{MD}}$). As $\text{FWHM}_{\text{Beam}}$ is increased, the precision of the beamlet’s position is decreased. When $\text{FWHM}_{\text{Beam}}$ approaches the size of the pixel, the effect of using subpixel positioning disappears.

The above implies that a more precise positioning of the beamlet can be achieved using the subpixel methods. To evaluate the effect of this on the XPC sensitivity, a 300 μm thick nylon wire was measured at $Z_{\text{SD}} = 190 \text{ mm}$, $Z_{\text{MD}} = 358 \text{ mm}$, and $Z_{\text{XM}} = 289 \text{ mm}$. At this geometry, the beamlets were hitting every fourth pixel corner. The phase shift along the entire profile of the wire was measured through raster scanning the sample in $7 \times 2$ steps along the horizontal (perpendicular to the wire) and vertical direction respectively. The exposure time was set to 15 s for each measurement point. The results of this experiment is shown in figure 5. It is clearly seen from the XPC images and profiles of the wire in figure 5(a-b), that the phase shift prediction is largely affected by the accuracy of the beamlet’s position. Most clearly seen from the different prediction of peak refraction, where the large inaccuracy of the $(1 \times 1)$ subpixel results in a much larger prediction of refraction angle. Similarly, there is a discrepancy between the other data processing methods.
To quantify this, we calculate the standard deviation of the background signal \( \sigma_\theta \) within the white rectangle in figure 5a and the average maximum absolute refraction \( \Theta_{\text{max}} \) along the whole wire. The result can be seen in figure 5(c-d), where the over-prediction of refraction from (1 \times 1) subpixel rebinning is clearly seen in both \( \Theta_{\text{max}} \) and \( \sigma_\theta \) values. Furthermore, it is generally observed that the refraction angle is predicted differently for each method.

To compare the different methods, we use the ratio \( \Gamma = \Theta_{\text{max}} / \sigma_\theta \) as a measure of signal to noise ratio in the images. The result is plotted in figure 5e and shows that \( \Gamma \) is maximized when using (2 \times 2) subpixels. The difference between iToT and (2 \times 2) subpixel is 67 ± 5 %. It is noted, that increasing the distance \( Z_{\text{MD}} \) so that the beamlet hit every 5th, 6th, or 7th pixel decreases the gain from using subpixel to below 20 %.

4 Discussion and outlook

We have in this paper demonstrated that using Timepix3 chip for SM-EI XPC imaging could improve the technique’s sensitivity significantly. In figure 5, it is seen in the peak refraction angle to background noise ratio \( \Gamma \) increases with 67±5 % when using (2 \times 2) subpixel compared to the normal charge integrating iToT. However, the result was found largely dependent on the setup’s geometry. Assuming that \( \Gamma \) is proportional to the square root of the acquisition time, the (2 \times 2) subpixel method could reduce the sample exposure time to 36 % of what is needed for the iToT method.

It was shown in figure 4 that subpixel data processing methods greatly reduced the accuracy of the beamlet’s measured position through a systematic shift compared to the expected. We suspect that it is the systematic inaccuracy that affects the measured \( \sigma_\theta \) and \( \Theta_{\text{max}} \) in figure 5. Similarly, data processing artifacts are likely causing the substantial decrease in \( \Gamma \) when using more than (4 \times 4) rebinning in figure 5. The tendency of inaccurate measurements of beamlet position should be correctable with models of data processing artifacts. If these inaccuracies were properly accounted for, we expect \( \Theta_{\text{max}} \) to be the same for all methods, and the difference between the methods to be seen solely in \( \sigma_\theta \).

The sensitivity of the XPC imaging setup is determined by the measurement precision of the refraction angle of each beamlet, which is controlled by the precision of the change in beamlet position on the detector.

Figure 4 shows that the precision is significantly better when using (2 \times 2) subpixel positioning for the beamlet placed close to a corner as compared to iToT method. We demonstrated that the best precision of the beamlet’s position was 0.9 ± 0.1 µm using (2 \times 2) subpixel method. For this experiment, the mask was translated with Newport IMS500CC translation stages in both direction. The accuracy of the motors, measured as the minimum to maximum deviation of the desired position (not standard deviation) across the full travel length (500 mm) is expected to be 3 µm for both directions. Furthermore, the motor has an expected 1 standard deviation bi-directional reproducibility of 0.5 µm. Therefore, the precision of 0.9 ± 0.1 µm is most likely dominated by imprecise motor translation.

In comparison, the precision of the beamlets’ measured movement in the XPC images in figure 5 is significantly better than the above. \( \sigma_\theta \) in the XPC image was for iToT found to be \( \sigma_{\Theta, \text{iToT}} = 2.4 \) µrad, which corresponds to an uncertainty on the beamlet’s measured position of \( \sigma_{\Delta x, \text{iToT}} = 0.49 \) µm on the detector.
The expected error on the mean of the actual beamlet position due to statistical variation is given by 
\[ \sigma_{S_x} = \frac{\text{FWHM}_{\text{Beam}}(2\sqrt{2\ln(2)})^{-1}}{\sqrt{N}}, \]
assuming a Gaussian beam distribution. \( N \sim 3000 \) is the number of photons in each beamlet, found from the number of excited clusters per beamlet. At \( Z_{\text{MD}} = 358 \text{ mm} \), we expect \( \text{FWHM}_{\text{Beam}} = 27 \text{ \mu m} \), which results in \( \sigma_{E,S_x} = 0.21 \text{ \mu m} \). Assuming a low absorbing sample (the same number of photons with and without a sample) this gives an uncertainty on the beam positioning of \( \sigma_{\Delta S_x,E} = \sqrt{2} \sigma_{S_x,E} = 0.30 \text{ \mu m} \). Assuming that the entire change in \( \Gamma \) is due to a change in uncertainty of the measured refraction, \( \sigma_{\theta} \) could decrease with as much as 67 % when using the \((2 \times 2)\) subpixel method, making \( \sigma_{\Delta S_x,(2\times2)} \sim 0.3 \text{ \mu m} \). \( \sigma_{\theta} \) found in this experiment, therefore, seems to be at the limit of statistical variation in the actual beamlet position. The actual beamlet position is controlled by the aperture size of the mask, the source size, \( Z_{\text{MD}}, Z_{\text{SD}} \), and the number of photons through each hole (the product of photon flux and count time). If the beamlet size is the dominating contributor to \( \sigma_{\theta} \), decreasing the aperture size would increase the XPC sensitivity as function of sample exposure. However, more experiments are required to determine the lower limit of the angular resolution of the SM-EI technique using subpixel methods.

The SM-EI XPC setup presented in this paper shows great potential for further development using the increased information obtained with subpixel positioning of the photon. Firstly, the present setup uses a mask with 100 \( \mu \)m pitch, and hence it was necessary to raster scan the sample to obtain information of the entire sample as done for the nylon threads in figure 2. Using subpixel positioning, it should be possible to acquire XPC images even if the beamlets hit every corner as long as \( \text{FWHM}_{\text{Beam}} \) is kept significantly smaller than the pixel size. Secondly, the ability to resolve the beamlet’s shape with multiple points as shown in figure 3, should enable dark field imaging as demonstrated with the beam tracking techniques (using a single mask and a high resolution detector) [5]. Future work will investigate the possibility to use the Timepix3 chip to acquire dark field images in a single sample exposure.

Acknowledgments

The authors acknowledge Innovation Fund Denmark and the EUROSTARS programs for financing their research work, and acknowledge the MEDIPIX collaborations who are responsible for the development of the Timepix3 ASIC used in this work.

References


A.4 Publication 4: Single-shot, omni-directional x-ray scattering imaging with a laboratory source and single-photon localization

My contributions

• Engaged in discussions of the experimental setup and the design of the absorption grating
• Developed the fabrication process for the absorption grating • Fabrication of the absorption grating used in the experiments • Provided photograph and SEM images used in the article • Revised the manuscript.
Single-shot, omni-directional x-ray scattering imaging with a laboratory source and single-photon localization

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Received 25 October 2019; revised 12 December 2019; accepted 23 December 2019; posted 24 December 2019 (Doc. ID 381420);
published 14 February 2020

Omni-directional, ultra-small-angle x-ray scattering imaging provides a method to measure the orientation of micro-structures without having to resolve them. In this letter, we use single-photon localization with the Timepix3 chip to demonstrate, to the best of our knowledge, the first laboratory-based implementation of single-shot, omni-directional x-ray scattering imaging using the beam-tracking technique. The setup allows a fast and accurate retrieval of the scattering signal using a simple absorption mask. We suggest that our new approach may enable faster laboratory-based tensor tomography and could be used for energy-resolved x-ray scattering imaging. © 2020 Optical Society of America

https://doi.org/10.1364/OL.381420

The measurement of ultra-small-angle x-ray scattering from sub-resolution sample structures is in x-ray imaging commonly referred to as the dark-field contrast [1,2]. The dark-field contrast has potential both in non-destructive testing [3] and medical [4] applications as it enables the detection of microstructures smaller than the effective image resolution.

The dark-field contrast measures the increase in x-ray beam divergence due to a non-resolved x-ray phase shift by sample micro-structures [5]. The signal is retrieved with multi-modal imaging techniques, which typically measure the conventional attenuation contrast simultaneously with the dark-field and the differential phase contrast (DPC) perpendicular to the beam propagation direction. Anisotropic microstructures in a sample will cause a highly directional dark-field signal, which in general is strongest when orthogonal to the average microstructure orientation [6]. However, the first multi-modal imaging techniques, such as the grating interferrometer (GI) [1] and edge illumination (EI) setups [2], could only retrieve the scattering strength along one direction. For directional dark-field sensitivity, conventional EI and GI required advanced two-dimensional optics and additional sample exposures [7,8].

Single-shot, omni-directional dark-field imaging was demonstrated using an advanced 2D phase grating, a high-resolution detector, and synchrotron radiation [9]. Recently, this interferometric method was generalized to laboratory sources [10]. Single-shot here refers to the measurement of DPC and dark-field signals in a single acquisition without the movement of gratings or masks. Previously, the speckle-tracking (ST) technique has also demonstrated single-shot, omni-directional dark-field images using a laboratory source and a random mask [11]. However, the quality of the retrieved dark-field signal from the ST method is debated and may have contributions from effects other than micro-structure scattering [12,13]. Furthermore, the ST technique needs long exposures to retrieve a dark-field signal due to the need for high-resolution images of the speckle pattern [14].

The beam-tracking (BT) technique is yet another alternative for single-shot dark-field imaging. The technique uses a single, simple absorption mask to generate mutually incoherent x-ray beams. BT has been shown to render the dark-field signal more accurately than the random-mask technique [13], and it imposes less restriction on the longitudinal coherence and setup geometry than the phase-grating methods [15]. However, the BT technique has only been shown as capable of single-shot retrieval of one-dimensional dark-field signals so far.

In this Letter, we demonstrate, to the best of our knowledge, the first single-shot, omni-directional dark-field image using the BT technique. We employ the photon-counting, energy sensitive Adnapix detector with the novel Timepix3 chip [16], developed by the Medipix consortium. The chip is capable of subpixel localization of single-photon events, which enables the use of the Adnapix detector in a compact BT setup [15] despite...
the relatively large 55 µm pixel pitch. The subpixel localization of single photons has previously been applied to GI using the analog readout MÖNCH detector [17], but we are, to the best of our knowledge, the first to apply this approach in dark-field imaging using a photon-counting detector.

Figure 1 shows our BT setup. We use a Hamamatsu Photonics L12161-07 micro-focus source with a Tungsten target. The source was operated at 3.35 W with a source size < 5 µm and U = 50 kV. The measured mean energy at the detector was 14 ± 0.5 keV. The beam is shaped into x-ray beamlets (small x-ray beams) by an absorption mask placed at \( Z_{\text{SM}} = 400 \text{ mm} \) from the source. The absorption mask has a periodic array of cylindrically shaped apertures with a 100 µm pitch. It was made from a 200-µm-thick tungsten foil and fabricated with a combination of wet chemical etching and pico-second laser ablation, as described in details in Ref. [18]. The apertures are slightly conical with the exit and entrance hole diameter of \( \emptyset = 9.4 \pm 0.3 \) µm and \( \emptyset = 15.7 \pm 0.6 \) µm, respectively. The transmission through the 200 µm tungsten is estimated to be less than 1% for x-rays with energy below 30 keV. With photons above 30 keV constituting less than 5% of the source spectrum at the detector without a mask, the pre-sample mask is to good approximation fully absorbing.

With the Timepix3 chip’s fast time-stamping, each absorbed photon can be accurately localized below the pixel size at a hit rate of up to 40 Mhits s\(^{-1}\) cm\(^{-2}\) [16] by measuring the charge sharing distribution for each event [19]. In practice, the recorded photon subpixel positions are rebinned into virtual subpixels, and the beamlets’ intensity distribution can afterward be analyzed at a resolution smaller than the physical pixel size. The use of the virtual subpixels for BT is described in details in Ref. [20], where it was used for directional DPC imaging. The absorption mask is aligned such that the beamlets hit in the corners between pixels to increase the photon localization precision [20], making our setup similar to the single-mask edge-illumination technique [21]. For the presented setup, the mask to detector distance is set to \( Z_{\text{SD}} = 480 \text{ mm} \), and the mask is aligned such that every fourth pixel corner of the detector is illuminated.

The sample is placed at \( Z_{\text{SD}} = 290 \text{ mm} \) from the detector. By comparing the shape of the beamlets with and without sample, the presence and orientation of a scattering signal can be identified. The intensity distribution of the beamlets with a sample can be described as a convolution of the beamlets’ shape without a sample \( i_0 \) and the sample’s scattering function \( s \) through [15]

\[
i(x, y) = i(i_0 \ast s)(x - \Delta x, y - \Delta y),
\]

where \( i_0 \) is determined by the setup and can be described as a convolution of the mask aperture and the projected source size. \( \Delta x \) and \( \Delta y \) are the refraction distance perpendicular to the beamlet’s propagation directions at the detector, and \( i \) is the transmission through the sample. A analysis of the sample scattering function [5] relates the moments of \( s \) to the differential phase signal from sub-resolution micro-structures and shows that similar information is accessible from both coherent and incoherent techniques such as GI and BT, respectively.

The beamlets’ full width at half maximum (FWHM) at the sample and detector are expected to be \( \sim 20.5 \) µm and \( \sim 39.8 \) µm, respectively, taking into account the geometrical magnification and source blurring of the mask’s entrance hole. This is within the uncertainty of the measured FWHM of beamlets at the detector of 44 ± 3 µm. The size at the detector means that the beamlets can be sufficiently resolved using a rebinning of 2 x 2 virtual pixels per physical pixel. A rebinning of 2 x 2 virtual pixels has been shown to be the most accurate for DPC retrieval [20].

The shape of each beamlet’s intensity distribution may be quantified by calculating its moments \( M^n \), where \( m \) is the order of the moment. The moments along the horizontal direction is with a sample given by

\[
M_0 = \sum_{n=1}^{N} i(n),
\]

\[
M_x = \frac{\sum_{n=1}^{N} x(n)i(n)}{M_0},
\]

\[
M_x^m = \left( \frac{\sum_{n=1}^{N} (x(n) - M_x)^m i(n)}{M_0} \right) \quad \text{for } m \geq 2,
\]

and similarly for the first and second moments along the vertical direction \( y \). \( M_0 = I \) is equal to the summed intensity of the beamlet with a sample. \( M_x \) and \( M_y \) are the beamlet’s center of mass \((\langle x \rangle, \langle y \rangle)\), and the second-order moment is the same as the variance of the intensity distribution with \( \sigma_x^2 = M_x^2 - \langle x \rangle^2 \) and \( \sigma_y^2 = M_y^2 - \langle y \rangle^2 \). The covariance of the intensity distribution can likewise be calculated using

\[
\sigma_{xy} = \left( \frac{\sum_{n=1}^{N} (x(n) - M_x)(y(n) - M_y)i(n)}{M_0} \right).
\]

A similar analysis is done for the beamlet’s intensity distribution without a sample, \( i_0 \). In non-directional multi-modal imaging, a common assumption is that both \( i_0 \) and \( i \) are Gaussian distributions [2,7,15]. Similarly, we will assume that \( i_0(x, y) \) and \( s(x, y) \) can be represented by multivariate normal distributions with covariance matrices \( \sum_{i=0}^{\infty} \) and \( \sum_s \). Assuming a perfectly absorbing mask, the covariance matrix of the scattering function can hence be found from

\[
\sum_s = \sum_0 - \sum_{i_0} = \begin{pmatrix}
\Delta \sigma_x^2 & \Delta \sigma_{xy} \\
\Delta \sigma_{xy} & \Delta \sigma_y^2
\end{pmatrix},
\]

where \( \Delta \sigma_x^2 = \sigma_x^2 - \sigma_x^2_{i_0} \) is the difference between the beamlet’s horizontal variance with and without a sample. The difference
in vertical variance, $\Delta \sigma_y^2$, and covariance, $\Delta \sigma_{yx}$, is calculated similarly. The directional refraction is likewise found from the change in the beamlet’s center of mass, and the transmission from $t = I/I_0$. The primary scattering signal is defined as the magnitude and direction of the largest variance of $s(x, y)$. This is equal to the biggest eigenvalue of $\sum_S$ and the direction of the corresponding eigenvector.

A Kevlar fiber loop was imaged to validate the scattering retrieval method. Figure 2 shows a dark-field image of the Kevlar loop with a resolution of $\sim 20 \, \mu m$, which was retrieved through raster scanning the sample in a $7 \times 7$ grid. Each sample position was measured for 30 s. The retrieved scattering function is rendered in an HSV color scheme with the Hue given by the orientation of $\sum_S$ primary eigenvector, constant Saturation, and Value equal to the corresponding eigenvalue, $\Delta \sigma_2^2$. The Kevlar fiber is spun from Kevlar filaments of $12 - 15 \, \mu m$ in diameter, which means that the individual filaments are smaller than the size of the beamlets at the sample. The filaments should cause a broadening of $s(x, y)$ perpendicular to the fiber’s orientation, which is also observed in Fig. 2.

Three hard wood sticks from the non-coated end of wooden matches were imaged in a $6 \times 6$ grid scan for 30 s at each position to validate the angular precision of our technique. Hard wood is a well-known sample for multi-modal imaging as it contains structures at different-length scales [15]. From computed tomography of the wooden matches, it was found that it has large vessels ranging from $50 \, \mu m$ to $100 \, \mu m$ in diameter and smaller fibers with diameter ranging from $5 \, \mu m$ to $25 \, \mu m$. Both are oriented along the same direction. The sticks were placed in three different orientations, as seen from the radiographic attenuation image of the sticks in Fig. 3(a). The scattering from the wooden matches is expected to be caused primarily by the fibrous structure. Hence, the orientation of the fibers can be found from the normal to the scattering signal. As illustrated in Fig. 3(b), the normal to the scattering function almost points along the wooden match.

To quantify the accuracy of the measured scattering angle, the orientation of the normal to the scattering signal is compared to the angle of the hardwood vessels identified in the attenuation image. The result is shown in Table 1. The predicted fiber angles from the dark-field signal scan are within two standard deviations of the angle found from the vessel’s orientation.

A butterfly was imaged to illustrate the usefulness of multi-modal imaging with directional sensitivity. The butterfly was chosen as it contains multiple different features with different-size scales. This sample was scanned in a $7 \times 7$ grid with an exposure time of 15 s per position. In Fig. 4, the butterfly’s head and part of its thorax are shown using the attenuation contrast, omni-directional DPC, and omni-direction dark-field contrast.

The omnidirectional DPC is found by the method presented in Ref. [20]. To optimize the image contrast of the thin butterfly (the thickest part is $\sim 2 \, mm$), the Timepix3’s spectral sensitivity was used to include only photons around the tungsten $L_\alpha$ emission line ($E_\gamma, \in [5, 12.2] \, KeV$). Attenuation, DPC, and dark-field contrast all decrease with energy [5,15], and hence the lower energy x-rays have greater contrast for low-absorbing samples.

It is clearly seen from Fig. 4 how the hairy structures on the legs and the region between the butterfly’s head and thorax provide a strong directional scattering signal. A similar result was found by Kagias et al. [9] using their synchrotron-based dark-field imaging technique. Fig. 4 also shows how the DPC image provides an increased contrast for thin-sample features with low absorption, eg, the butterfly’s antennae.

The Timepix3 chip’s energy sensitivity may not only be used to increase the image contrast as above, but also for actual energy-resolved dark-field imaging. We anticipate that energy resolved dark-field imaging could help mitigate artifacts observed in a polychromatic x-ray dark-field signal caused by beam hardening and spectral broadening of macroscopic refraction signals [15].
By using a geometrically flexible and simple setup with no constraints on spectral coherence, the single-shot, omni-directional BT method presented in this letter has similar advantages as the ST method. BT should, however, retrieve a more accurate scattering signal than ST [13]. In addition, our BT setup even seems to obtain relatively fast images when comparing the exposure time, resolution, and source specifications reported in this letter to an $\sim$180 $\mu$m resolution at the 1 min exposure using a 30 W source at 50 kVp reported for omni-directional ST method [11]. On the other hand, it should be noted that ST directly obtains a full-field image, whereas our BT method needs a $(7 \times 7)$ grid scan of the sample to obtain full-field images, although with an $\sim$20 $\mu$m resolution. Faster full-field imaging could be achieved by decreasing the mask pitch to 50 $\mu$m, which would still provide well-spaced beamlets. The mask pitch may be reduced even further by using a multi-Gaussian-fitting approach to extract weak scattering signals from overlapping beamlets [22].

The setup’s field of view may be increased by combining multiple Timepix3 chips or, if energy-sensitivity is not required, using a larger, high-resolution flat-panel detector. Furthermore, the relationship between the setup’s geometry and the dark-field contrast should be studied in detail, to understand how the setup’s angular sensitivity could be improved.

The BT technique has been previously demonstrated to enable tomographic reconstruction of dark-field signal using a polychromatic source [23]. Using tensor tomography, our setup may be employed to reconstruct a three-dimensional tomogram with three-dimensional scattering tensor information in each voxel. Tensor tomography has previously been applied in traditional GI setups with one-dimensional dark-field sensitivity, where it required three rotation axes [24]. We expect that our omni-directional dark-field technique makes one axis redundant and that it could be used similarly to the three-dimensional small angle x-ray scattering (SAXS) technique, where tensor tomography is performed using only two rotation axes [25].

In conclusion, in this Letter, we present the first single-shot, omni-directional dark-field setup using the BT method. Our results demonstrate that fast and accurate directional scattering images can be acquired using a simple, regular absorption mask. Furthermore, our results are, to the best of our knowledge, the first demonstration of single-photon localization for dark-field imaging using a photon-counting detector. This allows for detectors with a larger pixel size to be used in BT, as well as energy-resolved dark-field imaging, which may be useful for mitigating artifacts in the retrieved scattering signal triggered by the use of polychromatic illumination.

**Funding.** Innovationsfonden (CIL2018).

**Disclosures.** DT: Advacam s.r.o. (E), JJ: Advacam s.r.o. (I, E).

**REFERENCES**