Doctoral Thesis

Materials Properties Of Ultra-Thin Silicon Nanowire Arrays Fabricated By EUV Interference Lithography

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MATERIALS PROPERTIES OF ULTRA-THIN SILICON NANOWIRE ARRAYS FABRICATED BY EUV INTERFERENCE LITHOGRAPHY

Daniel FAN
MATERIALS PROPERTIES OF ULTRA-THIN SILICON NANOWIRE ARRAYS FABRICATED BY EUV INTERFERENCE LITHOGRAPHY

A thesis submitted to gain the degree of
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2017
DECLARATION

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Daniel Fan

March 2017
Abstract

Nanowires have attracted much interest due to their materials properties, such as decreased thermal conductivity, enhanced optical absorption, and quantum size effects to name a few. Nanowire structures allow gate-all-around for improved transistor switching behaviour due to better electrostatic control of the nanowire conduction channel. Silicon is a well-established material system with the infrastructure for VLSI capability. Silicon nanowires below 20 nm dimensions can be fabricated by growth methods, which however due to their size and position distributions are difficult to incorporate into devices. For top-down methods, the stand-out replacement of DUV (193 nm) lithography for resolution improvement is lithography using EUV (13.5 nm) light.

This work explores the use of interference lithography combined with coherent EUV light produced by the Swiss Light Source to pattern large-area, well-ordered, periodic structures at very high-resolution. In particular, the interference mask design is investigated. Using a grating line-doubling method, interference patterns of lines and spaces down to 6 nm HP were recorded. Using a ring grating, non-diffracting Bessel beams were demonstrated. The efficiency of achromatic Talbot lithography was also demonstrated. Next, line/space patterns at 22 nm HP were transferred into silicon-on-insulator substrates using plasma etching. HF under-etch was used to release the structures, resulting in ultra-thin, suspended SiNWs.

The thermoelectric properties of these SiNWs were then characterised. SiNWs have been shown by others to have low thermal conductivity due to phonon boundary scattering. In this work, a home-built micro-Raman spectroscopy setup was used to characterise not only the thermal properties of the SiNWs, but also their strain and quantum confinement effects. The thermal conductivity of SiNWs between 10-20 nm width were shown to be between 0.01-1.5 W/m.K, with line-edge-roughness and constrictions playing a role in thermal conductivity reduction. This value is 2 orders of magnitude smaller than bulk silicon. For suspended SiNWs clamped by chromium pads, strain values up to ~2.5% were obtained, indicating a pathway for application of process induced strain to enhance materials properties.
Zusammenfassung


Die thermoelektrischen Eigenschaften dieser SiNWs würden dann charakterisiert. Es wurde gezeigt, dass SiNWs eine geringe Wärmeleitfähigkeit aufgrund der Phonongrenzstreuung aufweisen. In dieser Arbeit wurde ein eigens gebautes Mikro-Raman-Spektroskopie-Setup verwendet, um nicht nur die thermischen Eigenschaften der SiNWs zu charakterisieren, sondern auch ihre Spannungs- und Quanteneinschränkungseffekte. Die thermische Leitfähigkeit von SiNWs zwischen 10-20 nm Linienbreite betrug zwischen 0,5-1 W/m.K, wobei Line-Edge-Rauigkeit und Verengungen scheinbar eine Rolle bei der Wärmeleitfähigkeitsreduktion spielen. Dieser Wert ist um 2 Größenordnungen kleiner als in Silizium-Bulk-Material. Für SiNWs, die durch Cr-Pads geklemmt und freigesetzt wurden, wurden Dehnungswerte bis zu ~2,5% erhalten, was einen Weg für die Anwendung von prozessinduzierter Dehnung zur Verbesserung der Materialeigenschaften anzeigt. Schließlich werden die Messungen der elektrischen Leitfähigkeit und des Seebeck-Koeffizienten vorgestellt.
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<td>BOE</td>
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<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
<td></td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal-oxide-semiconductor</td>
<td></td>
</tr>
<tr>
<td>CPD</td>
<td>Critical point drying</td>
<td></td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
<td></td>
</tr>
<tr>
<td>DOF</td>
<td>Depth-of-focus</td>
<td></td>
</tr>
<tr>
<td>DTL</td>
<td>Displacement Talbot lithography</td>
<td></td>
</tr>
<tr>
<td>DUV</td>
<td>Deep ultraviolet</td>
<td></td>
</tr>
<tr>
<td>e-beam</td>
<td>Electron beam lithography</td>
<td></td>
</tr>
<tr>
<td>EPFL</td>
<td>Ecole Polytechnic Federale de Lausanne</td>
<td></td>
</tr>
<tr>
<td>ETHZ</td>
<td>Eidgenossiche Technische Hochschule, Zurich</td>
<td></td>
</tr>
<tr>
<td>EUV</td>
<td>Extreme ultraviolet</td>
<td></td>
</tr>
<tr>
<td>EUV-IL</td>
<td>Extreme ultraviolet interference lithography</td>
<td></td>
</tr>
<tr>
<td>FEM</td>
<td>Finite element method</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
<td></td>
</tr>
<tr>
<td>high-k</td>
<td>High dielectric constant</td>
<td></td>
</tr>
<tr>
<td>HP</td>
<td>Half-pitch</td>
<td></td>
</tr>
<tr>
<td>HSQ</td>
<td>Hydrogen silsesquioxane</td>
<td></td>
</tr>
<tr>
<td>HVM</td>
<td>High volume manufacturing</td>
<td></td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
<td></td>
</tr>
<tr>
<td>IL</td>
<td>Interference lithography</td>
<td></td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropanol</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>Current-voltage</td>
<td></td>
</tr>
<tr>
<td>LER</td>
<td>Line-edge-roughness</td>
<td></td>
</tr>
<tr>
<td>LMN</td>
<td>Laboratory for Micro and Nanotechnology</td>
<td></td>
</tr>
<tr>
<td>LO</td>
<td>Longitudinal optical</td>
<td></td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-electro-mechanical systems</td>
<td></td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl iso-butyl ketone</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal-oxide-semiconductor field effect transistor</td>
<td></td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperture</td>
<td></td>
</tr>
<tr>
<td>NW</td>
<td>Nanowire</td>
<td></td>
</tr>
<tr>
<td>OD</td>
<td>Optical density</td>
<td></td>
</tr>
<tr>
<td>PAB</td>
<td>Post application bake</td>
<td></td>
</tr>
<tr>
<td>PEALD</td>
<td>Plasma enhanced atomic layer deposition</td>
<td></td>
</tr>
<tr>
<td>PEB</td>
<td>Post exposure bake</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
<td></td>
</tr>
<tr>
<td>PSI</td>
<td>Paul Scherrer Institut</td>
<td></td>
</tr>
<tr>
<td>RCA</td>
<td>Radio Corporation of America</td>
<td></td>
</tr>
<tr>
<td>RCWA</td>
<td>Rigorous coupled-wave analysis</td>
<td></td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
<td></td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive ion etching</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
<td></td>
</tr>
<tr>
<td>SiNW</td>
<td>Silicon nanowire</td>
<td></td>
</tr>
<tr>
<td>SLS</td>
<td>Swiss Light Source</td>
<td></td>
</tr>
<tr>
<td>SOI, sSOI</td>
<td>Silicon-on-insulator, strained silicon-on-insulator</td>
<td></td>
</tr>
<tr>
<td>SSRF</td>
<td>Shanghai Synchrotron Radiation Facility</td>
<td></td>
</tr>
<tr>
<td>TE</td>
<td>Transverse electric</td>
<td></td>
</tr>
<tr>
<td>TM</td>
<td>Transverse magnetic</td>
<td></td>
</tr>
<tr>
<td>TMAH</td>
<td>Tetramethylammonium hydroxide</td>
<td></td>
</tr>
<tr>
<td>TO</td>
<td>Transverse optical</td>
<td></td>
</tr>
<tr>
<td>VHF</td>
<td>Vapour hydrofluoric acid</td>
<td></td>
</tr>
<tr>
<td>VLS</td>
<td>Vapour-liquid-solid</td>
<td></td>
</tr>
<tr>
<td>VLSI</td>
<td>Very large scale integration</td>
<td></td>
</tr>
<tr>
<td>XIL-II</td>
<td>X-ray interference lithography-II beamline</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>Lattice constant</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>Speed of light</td>
<td>299,792,458 m/s</td>
</tr>
<tr>
<td>D_w</td>
<td>Nanowire diameter</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Electric field</td>
<td></td>
</tr>
<tr>
<td>e_i, e_s</td>
<td>Light polarization vectors (incident, scattered)</td>
<td></td>
</tr>
<tr>
<td>ε_{ij}</td>
<td>Strain tensor components</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>Frequency, focal length</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>Mask to sample gap</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Grating side length</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>Planck's constant</td>
<td>4.13567 × 10^{-15} eV.s</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>$h\nu$</td>
<td>Photon energy</td>
<td></td>
</tr>
<tr>
<td>$I$</td>
<td>Intensity</td>
<td></td>
</tr>
<tr>
<td>$J_0$</td>
<td>2D Bessel function of the first kind</td>
<td></td>
</tr>
<tr>
<td>$k$</td>
<td>Wave vector</td>
<td></td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann's constant $1.38065 \times 10^{-23}$ J/K</td>
<td></td>
</tr>
<tr>
<td>$L$</td>
<td>Source to mask length, length of SiNW</td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>Diffraction order</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>Integer, dimensionality</td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>Pattern pitch</td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>Polarisation density</td>
<td></td>
</tr>
<tr>
<td>$p$</td>
<td>Surface roughness parameter</td>
<td></td>
</tr>
<tr>
<td>$P_{den}$</td>
<td>Power density $W/m^2$</td>
<td></td>
</tr>
<tr>
<td>$P_V$</td>
<td>Power absorbed per unit volume $W/m^3$</td>
<td></td>
</tr>
<tr>
<td>$q$</td>
<td>Grating period</td>
<td></td>
</tr>
<tr>
<td>$r$</td>
<td>Radial coordinate</td>
<td></td>
</tr>
<tr>
<td>$R_j$</td>
<td>Raman tensor of phonon j</td>
<td></td>
</tr>
<tr>
<td>$s$</td>
<td>Source size</td>
<td></td>
</tr>
<tr>
<td>$S$</td>
<td>Seebeck coefficient $V/K$</td>
<td></td>
</tr>
<tr>
<td>$s_{ext}$</td>
<td>Source extension size</td>
<td></td>
</tr>
<tr>
<td>$t$</td>
<td>Thickness of SiNW</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature $K$</td>
<td></td>
</tr>
<tr>
<td>$v_g$</td>
<td>Phonon group velocity $m/s$</td>
<td></td>
</tr>
<tr>
<td>$w$</td>
<td>Width of grating field, width of SiNW</td>
<td></td>
</tr>
<tr>
<td>$\omega$</td>
<td>Phonon frequency $cm^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$x, y$</td>
<td>Transverse coordinates</td>
<td></td>
</tr>
<tr>
<td>$z$</td>
<td>Light propagation / longitudinal coordinate</td>
<td></td>
</tr>
<tr>
<td>$z_D, z_A, z_{max}$</td>
<td>Talbot distance; Achromatic Talbot distance; Maximum Achromatic Talbot distance</td>
<td></td>
</tr>
<tr>
<td>$ZT$</td>
<td>Thermoelectric figure of merit</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption factor</td>
<td></td>
</tr>
<tr>
<td>$\alpha_R$</td>
<td>Temperature coefficient of resistance</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{TE}$</td>
<td>Coefficient of linear thermal expansion</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Grüneisen parameter</td>
<td></td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Root-mean-square roughness</td>
<td></td>
</tr>
<tr>
<td>$\Delta\lambda$</td>
<td>Bandwidth</td>
<td></td>
</tr>
<tr>
<td>$\theta$</td>
<td>Diffraction angle</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Thermal conductivity</td>
<td>W/m.K</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength</td>
<td></td>
</tr>
<tr>
<td>( \Lambda )</td>
<td>Phonon mean free path</td>
<td></td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Stress; electrical conductivity</td>
<td>Pa, S/m</td>
</tr>
<tr>
<td>( \tau_B )</td>
<td>Scattering rate</td>
<td></td>
</tr>
<tr>
<td>( \chi )</td>
<td>Electronic susceptibility</td>
<td></td>
</tr>
</tbody>
</table>
1 Introduction

Since the early beginnings of the semiconductor industry, the feature sizes of silicon based devices have been decreasing as guided by Moore’s Law [1], which states that the cost per device halves every 18 months. Currently, that has translated to a device half-pitch (HP) of 18 nm (projected target for 2017) [2]. At this gate length, the classical MOSFET design encounters fundamental limitations in device physics. It appears the scaling laws of Moore are approaching their end.

The objectives towards device research has thus shifted in two ways. Firstly, device dimensions are still being rigorously downscaled to discover and exploit new types of physics as a basis for novel devices such as quantum computers. When a device dimension is smaller than some characteristic length of a carrier existing in the device, for example the phonon mean free path, electron mean free path, or electron de Broglie wavelength, then different physical properties manifest themselves, in this case decreased thermal conductivity, ballistic electron transport, and conductance quantization respectively. For quantum confinement effects in silicon, this means devices with a sub-10 nm length scale [3].

Secondly, variations to the classical transistor device are being explored in numerous ways. By gating not just at one surface of the channel like a traditional MOSFET but at three or even all four surfaces of the channel, electrostatic control is improved, leading to faster switching and lower leakage currents and therefore lower power consumption. By straining the channel material in certain crystallographic directions, the carrier mobility can be enhanced. By using high-k gate dielectrics, gate leakage current can be decreased. In this regard, nanowires offer a geometry that
allows for gate-all-around architectures, strain enhancement, use of high-k dielectrics, and possible optical lasing in a material which has a non-direct band-gap in bulk [4].

Although other material systems have also been pursued, namely GaAs for its high electron mobility and direct band gap, and germanium for its high electron mobility, silicon remains a particularly relevant material for semiconductor devices and nano-devices. It has an excellent native oxide, has a larger bandgap than germanium, is abundant in nature, and its growth with low number of defects is feasible. Furthermore, the processing infrastructure for silicon is well established, with excellent tools for patterning and etching nano-structures.

Silicon nanowires (SiNWs) themselves are a versatile functional material, widely studied and employed as, for example, solar cells [5]–[9], battery anodes [10], [11], micro-electro-mechanical systems (MEMS) [12], chemical and biosensors [13]–[18], thermoelectric harvesters [19]–[21], and transistors [22]–[24], due to changes in materials properties in the micro and nano-scale [3], [25]–[29]. In particular, SiNWs have excellent thermoelectric properties, exhibiting a low thermal conductivity due to increased phonon scattering, high electrical conductivity, and combined with a high Seebeck coefficient, allows efficient thermal energy harvesting [20], [30], [31]. Thermoelectric figures of merit up to $ZT \approx 1$ at room temperature have been reported, compared to the bulk silicon value of $ZT \approx 0.01$ [32].

Until the recent past, SiNWs of very small diameters below 20 nm have been fabricated using growth methods such as vapour-liquid-solid (VLS) growth. Grown SiNWs exhibit a size distribution, making it difficult to fully elucidate size effects. They can also grow in different orientations, making them difficult to incorporate into devices. Their crystallographic orientations and phases are also limited. Similarly, electrochemically etched nanowires have a distribution of sizes and orientations, and must be doped.

Top-down pattern transferred SiNWs show much better order and size tolerances, allowing for incorporation into reliable devices and quantifying their geometry and size related material properties. The state-of-the-art patterning in industry remains at the deep ultraviolet (DUV, 193 nm) wavelength, and combining with immersion and double and quadruple spacer overlays can reach down to 18 nm HP [2]. Directed self-assembly using block-copolymers can reach down to 10 nm feature size but is only semi well-ordered [2]. Nanoimprint lithography is targeted as a next generation patterning technology, but requires another method for fabrication of the template. Superlattice nanowire pattern transfer can achieve down to 10 nm feature sizes but requires extensive preparation of the master stamp and is currently limited to the research lab...
[31]. Electron beam (e-beam) lithography being a serial writing method has low throughput and the resolution is limited by the electron proximity effect [2].

Another candidate technology in industry for producing high-resolution features is lithography using extreme ultraviolet (EUV, 13.5 nm) light [33], [34]. Since the resolution scales with the wavelength, EUV offers an order of magnitude resolution improvement over DUV wavelengths. Efficient EUV optics such as molybdenum/silicon multilayer mirrors are available, while efficient EUV photoresists such as chemically amplified resists and metal-oxide based resists have undergone rapid development and are available down to 16 nm HP. This leaves the EUV source as bottleneck. Current tin plasma based EUV sources are inefficient (~1%) [35], and improvements need to be made before acceptance by industry.

![Fig. 1.1](image)

Fig. 1.1: Progression of minimum feature size produced by photolithography (blue) and progression of the photolithographic wavelength in use (red), showing historic (solid) and targeted (hollow) values [2], [33].

Meanwhile, for further development of EUV photoresists, interference lithography (IL) has proven to be an excellent tool to probe the highest lithographic resolutions. EUV interference lithography (EUV-IL) requires a coherent EUV source. The coherent waves are split into two (or more) beams which are directed to interfere. The interference pattern is recorded in photoresist, being ultra-dense, very high-resolution below 10 nm HP, of good periodic order, with large area and high throughput [36], [37]. The formation of the coherent waves can be accomplished by using diffraction gratings.

In this thesis, EUV patterning technology with respect to mask design and interference patterning schemes will be developed. Ultra-thin high-resolution suspended SiNWs are fabricated using
EUV-IL and their thermoelectric properties characterised. Chapter 2 will describe the design, fabrication, and application of diffraction masks to form different types of EUV beams, including the simplest line/space beam, Bessel beams which are long non-diffracting beams with diameters down to 30 nm, and achromatic Talbot beams which produce self-images of the diffraction grating at high diffraction efficiency. Pattern transfer of these structures into silicon and the subsequent fabrication of ultra-thin suspended SiNWs below 20 nm width are described.

Chapters 3 and 4 describe the thermoelectric characterisation of the SiNW array using Raman spectroscopy. Chapter 3 deals with the measurement theory and equipment setup, while chapter 4 discusses the results with respect to current knowledge of SiNW thermoelectric properties. Chapter 5 gives a summary and outlook on further SiNW characterisation.
2 EUV Interference Lithography

This chapter describes the nano-fabrication method of interference lithography using EUV radiation. The current state-of-the-art patterning methods including the role of EUV are introduced in section 2.1, followed by a presentation of the theory of EUV-IL in section 2.2. High-resolution EUV-IL requires a stable and efficient optical setup, suitable EUV photoresists, and efficient diffraction masks. The design and fabrication of diffraction masks for various interference schemes is described in sections 2.3 to 2.5. The patterning results are discussed in section 2.6 while pattern transfer and fabrication into SiNWs and other functional materials are summarised in sections 2.7 and 2.8.

In this chapter, parts of the work on high resolution patterning using line-doubled iridium grating diffraction mask (parts of sections 2.1 to 2.5) was published under [38]:


where D. Fan performed the simulations, experiments, analysis, and wrote the manuscript and Y. Ekinci suggested the concept and revised the manuscript.

Parts of the sections on Bessel beam lithography (parts of sections 2.1 to 2.5) was published under [39]:

where L. Wang and Y. Ekinci designed the experimental concept, L. Wang fabricated the low-resolution gold mask while D. Fan fabricated the high-resolution nickel mask, and L. Wang and D. Fan performed the lithography. All authors contributed to manuscript writing.

Parts of the sections on achromatic Talbot lithography (parts of sections 2.1 to 2.5) was published under [40]:


where D. Fan performed the simulations and mask fabrication, D. Fan and E. Buitrago performed the lithography and SEM at PSI, and E. Buitrago, S. Yang, Y. Wu, and R. Tai performed the lithography and SEM at SSRF. Y. Ekinci supervised the project. D. Fan wrote the manuscript and all authors revised the manuscript.

Parts of the section on pattern transfer and SiNW plasma etching (section 2.6) was published as a conference paper [41]:


where D. Fan designed and performed the experiment, analysed the data, and wrote the manuscript. All authors revised the manuscript and J. Gobrecht presented the work at the 3M-NANO conference in Taiwan, 2014.

## 2.1 Introduction

### 2.1.1 State-of-the-art patterning

The feature sizes of micro and nano-electronic devices have been steadily decreasing as guided by Moore’s law. Current minimum feature sizes in production are approximately 20 nm for the gate length of a transistor, and feature sizes as low as 7 nm are targeted within the next 15 years. Concurrently, there has been an enormous amount of interest in the nanostructures of various materials and particularly towards potential applications for future electronic devices [2].

The state-of-the-art method for producing high-resolution features with high throughput, suitable for industrial production, uses the DUV wavelength 193 nm. Combined with techniques such as multiple patterning and immersion, features below 20 nm have been patterned. This
technique is reaching its resolution limit in the coming years, and to further extend this downscaling, new top-down patterning methods need to be explored [2]. Candidate technologies include directed self-assembly, nano-imprint lithography, and EUV lithography [33].

EUV lithography, at the source wavelength of 13.5 nm, uses a shorter wavelength compared to DUV to allow a corresponding increase in resolution. EUV lithography is the best industry candidate for producing next generation electronic devices, due to the availability of efficient optics and photoresists [2], [33]. Nonetheless, before EUV lithography is introduced into high volume manufacturing many new EUV resists require development and evaluation [42]. In addition to the challenges of printing resist structures, a significantly challenging step in fabrication of silicon devices is the pattern transfer.

2.1.2  EUV interference lithography

As EUV technology undergoes further research and development to prepare it for industrial use, EUV-IL has been used for the research and development of EUV materials and technologies such as suitable photoresists, since EUV-IL can print the highest resolution patterns possible using photon based sources [36], [38], [43]. Furthermore, EUV-IL is capable of printing high-resolution, well-ordered, highly dense periodic patterns over a large area with high throughput in comparison to other research tools such as e-beam lithography, allowing the fabrication of nanoscale structures for scientific study of, for example, nano-catalysis [44], artificial spin-ice [45], metal nanostructures [46], and quasi-crystallinity [47].

The EUV-IL beamline (XIL-II) at the Swiss Light Source (SLS), Villigen, Paul Scherrer Institut (PSI), is a dedicated beamline for high-resolution patterning using top-down photon based lithography [48], achieving world record resolution of 6 nm HP [38]. Briefly, two or more coherent EUV beams are caused to interfere, and the aerial interference image recorded in photoresist. The beams can be created by using Lloyd's mirrors [49] or diffraction gratings [36].

2.1.3  Bessel beam lithography

Nondiffracting beams have attracted substantial attention since their discovery in the 1980s [50]. Nondiffracting, diffraction-free, or z-independent solutions of the Helmholtz equation are indeed possible for various wave forms, such as Bessel beams, Mathieu beams, and Weber beams [51], [52]. They are defined by the fact that their transverse intensity profile is invariant under free-space propagation. Nondiffracting beams have unique properties such as large depth-of-focus and self-healing of the central core [53], i.e. the central core reconstructs or re-forms after being obstructed, making them attractive for applications such as optical trapping [51], [54], electron
accelerators [55], bioimaging [56], laser ablation [57], and lithography [58], [59]. In particular, Bessel beams are suitable as a serial beam writing tool over surfaces with arbitrary topography.

Approximations to nondiffracting Bessel beams have been experimentally observed by focusing a Gaussian wave with an axicon lens [60], using annular slits in the far field [50], holographic methods [61], by use of metamaterials and nanowire media [62], [63], and by circularly symmetric diffraction gratings [64]. Depending on the synthesis method, the beam can be chromatic or achromatic [60]. It has been shown that Bessel beams can be developed as a limiting case in the family of discrete nondiffracting beams [65]–[68]. One approach for their formation is to use circularly symmetric diffraction gratings.

Such a ring grating was designed and fabricated for EUV. By adapting the approach of diffraction-based EUV-IL [69], multiple-beam interference was used in the limiting case for the generation of a Bessel beam, and its use as a serial beam writing tool is demonstrated, with resolution down to 15 nm spot size.

### 2.1.4 Achromatic Talbot lithography

Achromatic Talbot lithography (ATL), also known as achromatic spatial frequency multiplication, is a very robust, highly efficient, and simple technique to produce dense and high-resolution periodic nanostructures. Patterning capabilities down to 15 nm feature size [44], [70] have been demonstrated. ATL records the summation of the intensities of the self-images of the diffraction grating, i.e., the Talbot images, produced by a broadband EUV source, i.e., most EUV sources. This method is suitable for low intensity or low brightness sources, since the aerial image is generated using the interference from all transmitted diffraction orders and is therefore highly efficient, thereby allowing large-area patterning with high throughput via step-and-repeat exposures [44].

ATL transmission masks were used to perform EUV exposures at 13.5 nm and 8.8 nm illumination wavelengths at two different synchrotron facilities, to study the broadband nature of the method and the used mask as well as to investigate the influence of illumination parameters and experimental arrangements. The experiments were performed at the SLS, PSI, Switzerland [69], and at the Shanghai Synchrotron Radiation Facility (SSRF), P. R. China [71], [72]. ATL was proven to be a simple and robust interference lithography scheme suitable for different wavelengths and for a variety of EUV sources and setups.
2.2 Theory

This section introduces the basic theory of interference lithography using diffraction gratings and various schemes based on diffraction gratings that can be used for interference lithography.

2.2.1 Coherent beams

The basic principle of interference lithography [36] is shown in Fig. 2.1, where two (or more) coherent light waves interfere and this interference pattern is recorded in photoresist. The interference of multiple beams with the same transverse wave vector and with sufficiently large beam size generates periodic and aperiodic aerial images which are nondiffracting. Consider two plane-wave beams with wavelength $\lambda$ converging at a propagation angle of $\theta$ along the z-axis as shown in Fig. 2.1. The beams are placed symmetric to the normal z-axis at a position $r$ from the origin. In this case the beams will interfere when they overlap and form an aerial image. The working distance, thereafter referred to as the gap $g$, between the source plane and the image plane is

$$g = \frac{r}{\tan(\theta)}$$  \hspace{1cm} (2.1)

The total intensity of the image produced by the interference of the coherent beams of the same intensity $I_0$, is

$$I_{total}(x, y) = 2I_0[1 + \cos(\varphi_1(x, y) - \varphi_2(x, y))]$$  \hspace{1cm} (2.2)

For two sources positioned along the x-axis, with the transverse $k$-vector $k_r = k \cdot \sin(\theta)$, the intensity of the aerial image is given as

$$I_{total}(x, y) = 2I_0[1 + \cos(2k_r x)]$$  \hspace{1cm} (2.3)

This represents a sinusoidal line/space pattern with a period $P$ of

$$P = \frac{2\pi}{2k_r}$$  \hspace{1cm} (2.4)

The intensity distribution has no $z$-dependence and is thus nondiffracting.
The two diffracted beams with wave vector \( \mathbf{k} \) interfere to form an aerial image which is recorded in photoresist. The zeroth order undiffracted beam must be blocked by a photon stop to prevent over-exposure of the interference area. Figure adapted from [38].

### 2.2.2 Diffraction grating

Generation of the coherent beams can be accomplished by using Lloyd’s mirrors [73] or diffraction gratings, and requires a coherent source. The benefit of diffraction gratings is that temporal coherence can be relaxed as different wavelengths lead to the same aerial image. Disadvantages include the difficulty in fabrication of diffraction masks with the necessary high-resolution [74], low roughness, and high diffraction efficiency. Using interference lithography, high-resolution periodic patterns can be produced without optics.

For a diffraction grating (Fig. 2.1), the diffraction angle \( \theta \) produced by the grating and the grating period \( q \) are related by the Bragg equation:

\[
q \sin \theta = m \lambda
\]  

2.5
where \( m \) is the diffraction order. Alternatively, the magnitude of the transverse \( k \)-vector can be written as

\[
k_r = 2\pi \frac{m}{q}
\]

Considering Fig. 2.1, the incident beam \( \lambda \) is diffracted by gratings of period \( q \) through an angle \( \theta \), for the diffraction order \( m \), and following Eq. 2.4, 2.5, and 2.6, leads to the interference pattern with the period \( P \) [36]

\[
P = \frac{q}{2m} = \frac{\lambda}{2\sin \theta}
\]

Therefore, the periodicity of the aerial image is half the periodicity of the diffraction grating for the first order diffraction. The absolute limit in resolution, corresponding to a diffraction angle of 90\(^\circ\), is a line/space pitch of \( \lambda/2 \) or HP of \( \lambda/4 \), resulting in about 3.4 nm HP for EUV. At a resolution lower than this wavelength limit, the resolution achievable by interference lithography is directly related to the resolution obtainable for fabrication of the mask diffraction grating (Eq. 2.7).

The location of the aerial interference image is given by the gap \( g \) in Eq. 2.1, where \( 2r \) is the distance between the centre of the two diffraction gratings (Fig. 2.1). The distance \( r \) must be greater than the diffraction grating field area, so that the zeroth order transmitted light through the grating does not overlap the interference area. The zeroth order transmitted light elsewhere is blocked. Note that the optimal gap defined in Eq. 2.1 enables the maximum overlap of two interfering beams and thereby maximizes the total area of the aerial image, but it has no effect on the contrast of the aerial image since IL has infinite depth-of-focus. Finally, the diffraction gratings should lie within the incident beam spot.

### 2.2.3 Bessel beams

One can increase the number of interfering beams at a transverse distance \( r \) from the normal axis (Fig. 2.1). For example, by placing four beams 90\(^\circ\) to each other in a diamond formation, an interference pattern consisting of holes or dots can be formed [75]. Using 6 beams and adjusting the phase difference, periodic patterns such as honeycomb and kagome lattices can be obtained [45]. Using 5 or 8 beams, quasi-periodic patterns are formed [47]. As the number of beams approaches infinity in a ring arrangement (Fig. 2.2a), the aerial image becomes proportional to a zeroth-order 2D Bessel function \( j_0 \) of the first kind [66] with intensity.
where \( r = \sqrt{x^2 + y^2} \) and \( I_M \) is the maximum intensity of the diffracted light. This represents a sharp peak surrounded by rings, not changing along the propagation axis [53]. Again, the aerial image is \( z \)-invariant where the interfering beams overlap. This overlapping region has a certain depth-of-focus (DOF, Fig. 2.1) that equals

\[
DOF = \frac{w}{\tan(\theta)}
\]

where \( w \) is the width of the interfering beams, i.e. the width of the annular ring which forms the effective source. Within the range of the depth-of-focus, the intensity is \( z \)-invariant. As can be seen, the Bessel beam is a special case of \( z \)-independent aerial images formed by the interference of multiple beams that have the same \( k_r \) value. One can create various forms of nondiffracting beams by changing the number of beams and their relative phases [66].

Some of the interesting and useful properties of Bessel beams are their ability to self-heal and their propagation invariant central core. This means that the central core is diffraction resistant and has a steady intensity along the length of the beam, making it suitable for serial beam lithography, as it allows exposure over topographies of varying heights while keeping the beam spot size and intensity constant. For serial beam writing, it is also desirable to have a long central beam core and increased working distance.

It should be noted that the radial wave-vector intensity which defines the aerial image for multiple beam interference, analytically given for line patterns and Bessel beams in Eq. 2.3 and Eq. 2.8, becomes independent of wavelength and depends only on the period of the diffraction grating and diffraction order. Therefore, the use of annular ring gratings enables achromatic Bessel beams. The radius \( r_0 \) of the central core is given as [51]

\[
r_0 = \frac{2.405}{k_r} = \frac{2.405q}{2\pi m}
\]

For example, given a ring grating with period 40 nm, a Bessel spot of approximately 30 nm full-width at half maximum (FWHM) will be produced. The theoretical limit occurs when the diffraction angle becomes 90°, whereby following Eq. 2.5 and 2.10 the Bessel spot would have a
FWHM of ~10 nm at EUV. The depth-of-focus per Eq. 2.9 is dependent on the width of the ring and therefore is practically limited by the spot size of the coherent source. For example, to produce a 15-nm diameter spot using EUV corresponds to a grating with 20 nm period and 42° diffraction angle. For a 1 mm depth-of-focus the width of the annular ring needs to be ~932 μm, and therefore the EUV spot size needs to be at least 2 mm diameter, which is a reasonable number.

Therefore, circular gratings will enable an intense Bessel beam with very narrow waist and much extended depth-of-focus, using broadband sources as compared with Gaussian beams [76]. These properties are particularly advantageous for photolithography. Depth-of-focus is a significant problem in photolithography where the resolution is given as $\lambda/2 \sin \theta$ and the depth-of-focus is $\lambda/\sin^2 \theta$. A nondiffracting beam with large depth-of-focus allows writing of arbitrary structures over topographical surfaces and breaks one of the fundamental trade-offs of photolithography.

![Diagram of Bessel beam and Achromatic Talbot beams](image)

Fig. 2.2: Schemes for (a) Bessel beam diffraction [39] where the incident EUV light is diffracted by a ring grating to form a Bessel beam in the interference region, and (b) Achromatic Talbot diffraction [40] where the broadband self-images of the grating due to interference from all the diffraction orders combine after the achromatic Talbot distance to form a periodic pattern.

### 2.2.4 Achromatic Talbot beams

Talbot first noticed that periodic patterns were produced at fixed distances from a diffraction grating upon which monochromatic coherent light was incident [77]. These patterns are self-
images of the diffraction grating, produced at every integer multiple of the Talbot distance $z_T$ from the mask [78] given by

$$z_T = \frac{2q^2}{\lambda} \quad 2.11$$

where $q$ is the grating period and $\lambda$ is the illumination wavelength as shown in Fig. 2.2b. When the incident light has a spectral bandwidth of $\Delta \lambda$, the Talbot images due to different incident wavelengths overlap at a certain distance $z_A$. This occurs when the Talbot distance of one image due to the minimum incident wavelength equals the Talbot distance of a subsequent image due to the maximum incident wavelength

$$\frac{2nq^2}{\lambda - \Delta \lambda / 2} = \frac{2(n + 1)q^2}{\lambda + \Delta \lambda / 2} = z_A \quad 2.12$$

where $n$ is an integer for every subsequent self-image starting from the grating plane. Solving for $n$, substituting back into Eq. 2.12, and assuming $\lambda / \Delta \lambda$ is much larger than $\frac{1}{2}$ gives the achromatic Talbot distance $z_A$

$$z_A = \frac{2q^2}{\Delta \lambda} \quad 2.13$$

Beyond this distance, self-images of the grating smear and overlap in the $z$-direction and the aerial image becomes $z$-invariant beyond $z_A$ [79]. This is the minimum distance that is needed to obtain a $z$-stationary aerial image. As seen in Eq. 2.13, the bandwidth of the source turns into an advantage by providing an aerial image of very large depth-of-focus. As the self-images are due to the interference from all transmitted diffraction orders, all the transmitted intensity contribute to the aerial image, and therefore exposures are highly efficient in comparison for example to multiple-beam interference lithography.

Furthermore, the whole aerial image can be patterned, giving large-area patterning capabilities in comparison to multiple-beam interference lithography where only the interference patterns due to first or second order diffraction is recorded while the exposed areas due to zeroth order diffraction are not patterned. For a line/space diffraction grating, the resulting line/space pattern has a pitch that is $\frac{1}{2}$ of the mask grating period, while for a dot/hole diffraction grating, the
resulting dot/hole array pattern has a pitch that is $1/\sqrt{2}$ of the mask grating period rotated by 45° [79]. Note that for both dot and hole array diffraction gratings, a dot array is obtained using negative resist.

From the definition of $z_A$ presented above, the grating periodicity and the bandwidth of illumination influences the achromatic Talbot distance. In addition, it should be noted that the aerial image in ATL is a result of interference of diffraction orders from the same grating. As the diffraction orders diverge from each other when moving away from the grating, the overlapping area of diffraction orders and thereby the area of the interference decreases. The diffraction angle $\theta$ of a grating with period $q$ and with illumination wavelength $\lambda$ is calculated by the Bragg equation (2.5). Given the diffraction angle, the field side length $x$ can be calculated from the gap $g$ between mask and sample plane, or vice versa

$$\tan \theta = \frac{G - x}{2g} \quad 2.14$$

where $G$ is the side length of the grating. As the distance of the sample plane from the mask increases, the patterned area $x^2$ approaches zero at the maximum distance

$$z_{max} = \frac{Gq}{2\lambda} \quad 2.15$$

This is valid for small diffraction angles, and is obtained by combining Eq. 2.5 and 2.14.

### 2.3 Mask Design

From Eq. 2.7, the pattern HP on wafer is directly proportional to the diffraction grating period and independent of the wavelength. Therefore, high-resolution diffraction efficient gratings are needed. The obstacles for fabricating these include the choice of grating material, patterning restrictions due to the electron-beam (e-beam) electron proximity effect, and pattern transfer limitations. Firstly, the diffraction efficiency for various grating materials and geometries are simulated, then the fabrication limitations are discussed. The designs of four different diffraction masks are then presented. The optical properties of various materials at $\lambda = 13.5$ nm is shown in Fig. 2.3 for reference.
2.3.1 Diffraction efficiency

The diffraction efficiency of the grating at EUV wavelengths is an important consideration in interference lithography. Sufficient diffracted light must be available such that recording of the aerial image can occur in a reasonable exposure time to mitigate mechanical instabilities. As the wavelength of incident light becomes similar in scale to the diffraction grating period, the scalar approximation of the far-field transmitted image is no longer valid, and to calculate the diffraction efficiency rigorous methods must be used [81]. Boundary effects due to the grating material, such as coupling between $E$ and $H$ fields, polarization effects, and effect of conduction charges, must be considered, and Maxwell's equations must be used fully. Therefore, rigorous coupled-wave analysis (RCWA), a semi-analytical method derived directly from Maxwell's equations, suitable for solving light propagation through periodic media [82], was used. The diffraction efficiency of gratings of various materials, given their refractive indices at EUV [80], was calculated for gratings with different duty cycles and thicknesses up to 200 nm using RCWA [83]. The number of diffraction modes to be calculated was set high enough to ensure convergence of the solution. The maximum diffraction efficiency available for each grating period, for any duty cycle, and grating height up to 200 nm, is plotted in Fig. 2.4. Grating thicknesses above 200 nm were deemed too difficult to fabricate as the large aspect ratios would cause grating collapse.

2.3.2 Fabrication limits

Traditionally, for soft x-ray optics, metals such as gold, chromium, and nickel [84] are used as the grating material. For grating periods above 80 nm such metals are straightforward to pattern transfer via electroplating or reactive ion etching (RIE). Below 50 nm periods however, pattern
transfer into such metals become challenging due to the high-resolutions involved. One alternative is to use very diffraction efficient metals such as molybdenum and record the $2^{nd}$ order interference [85]. Because the $m = 2$ order is used, the patterned pitch has a 4 times magnification and the diffraction grating period can be relaxed. Another alternative method used with success for grating periods between 40 and 80 nm is direct writing of gratings using hydrogen silsesquioxane (HSQ) photoresist by e-beam lithography [74]. HSQ is a high-resolution negative-tone resist which becomes a form of SiO$_2$ after development. Although this greatly simplifies the patterning process, below 40 nm grating period the diffraction efficiency of SiO$_2$ drops significantly (Fig. 2.4).

One way to avoid pattern transfer while still giving high diffraction efficiencies is to use high-resolution photoresists based on highly diffraction efficient materials such as HfO$_2$ [43]. Directly written gratings of HfO$_2$ and SnO$_2$ [86] enables relatively high diffraction efficiencies compared to HSQ (Fig. 2.5). However, with increasing resolution, pattern collapse limits the achievable aspect ratio and thereby limits the diffraction efficiencies. Furthermore, at high-resolutions, the electron proximity effect in e-beam lithography comes into play, and the writing of smooth, high-resolution lines becomes increasingly difficult. The record achievable grating periods at the Laboratory for Micro and Nanotechnology (LMN), PSI, for the various processing methods are listed in Table 2.1 below.

<table>
<thead>
<tr>
<th>Grating material</th>
<th>Process method</th>
<th>Grating period</th>
<th>Half-pitch on wafer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSQ</td>
<td>Direct write e-beam</td>
<td>40 nm</td>
<td>10 nm</td>
<td>Unpublished</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Plasma etching</td>
<td>64 nm</td>
<td>8 nm ($2^{nd}$ order)</td>
<td>[85]</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>Direct write e-beam</td>
<td>28 nm</td>
<td>7 nm</td>
<td>[43]</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>Direct write e-beam</td>
<td>28 nm</td>
<td>7 nm</td>
<td>[86]</td>
</tr>
<tr>
<td>Iridium</td>
<td>Grating line doubling</td>
<td>24 nm</td>
<td>6 nm</td>
<td>[38]</td>
</tr>
</tbody>
</table>

Table 2.1: State-of-the-art resolution in EUV-IL patterning at the XIL-II beamline, LMN, PSI.

To extend the resolution limit of grating fabrication, ion milling can be used as the pattern transfer method into diffraction efficient materials, with the benefit of high anisotropy and relatively stable etch rates for different materials compared to RIE. The disadvantage is that the diffraction grating pattern is still written by e-beam lithography and is thus still susceptible to electron proximity effect.
Fig. 2.4: RCWA simulations of maximum available 1st order diffraction efficiency of various grating materials at different periods, where the maximum efficiency within a grating height up to 200 nm and grating duty cycle of 0-100% is plotted. Graph (a) shows all materials, where the stars represent the minimum achieved grating period and corresponding HP, described in Table 2.1. The diffraction efficiency for evaporated metals (b), spin-on inorganic resists (c), and atomic layer deposition (ALD) metals (d) are separated for clarity. Figure adapted from [38].

2.3.3 Direct write grating masks

The design of direct write masks where the diffraction grating is written by e-beam lithography and no pattern transfer is needed is relatively straightforward [74]. Eq. 2.7 gives the required diffraction grating period and diffraction angle for the targeted HP on wafer, and Eq. 2.1 relates the mask-to-sample gap to the distance between diffraction gratings in the mask plane. This distance should be kept within the EUV spot size, but not be too small such that the zeroth-order light passing through the gratings falls upon the interference area. For practical and accuracy reasons the gap should be kept between 200 to 800 µm.
Simulations show that the diffraction efficiency of HSQ is sufficient down to 10 nm HP on wafer while for SnO$_2$ and HfO$_2$ the diffraction efficiency is reasonable for 5 nm HP on wafer. The process window is also shown to be robust: a reasonable diffraction efficiency is obtained for a range of grating heights and duty cycles which allows some tolerance in the fabrication process.

![Simulations showing diffraction efficiency for different materials](image)

Fig. 2.5: RCWA simulation of diffraction efficiency for direct e-beam written gratings with heights between 0-200 nm and duty cycles between 0-100%. The targeted HP on wafer is indicated on the far right of each row for SiO$_2$ (a), HfO$_2$ (b), and SnO$_2$ (c). SnO$_2$ shows a marked improvement in efficiency, especially at high-resolution.

**2.3.4 High-resolution mask using line-doubling**

Another way to achieve high-resolution gratings is by doubling the grating spatial frequency using atomic layer deposition (ALD) for conformal deposition of a diffraction efficient material. A sparse grating with 25% duty cycle and a period double the targeted mask grating period is written using e-beam lithography in HSQ. Because of the sparseness, e-beam proximity effect becomes less noticeable and smooth lines can be written. Next, conformal deposition of an EUV diffraction efficient material such as iridium, is performed using plasma enhanced atomic layer
deposition (PEALD). Other candidate materials include aluminium oxide (Al₂O₃) which can be deposited very smoothly but has lower diffraction efficiency than iridium, and ruthenium which has higher diffraction efficiency than iridium but cannot be deposited smoothly without extensive process optimization. The top and bottom iridium are removed by ion milling, which is highly anisotropic and therefore leaves only the iridium layer on the sidewalls of the HSQ. The spatial frequency of the original grating lines has therefore been effectively doubled, similar to the spacer technology used in CMOS manufacturing.

Fig. 2.6: Schematic (left) and RCWA simulation (right) of the diffraction efficiency of gratings composed of (a) HSQ lines at 24 nm grating period, (b) 12 nm HSQ lines at 48 nm grating period coated with 12 nm iridium, (c) removal of the top and bottom iridium, and (d) removal of the HSQ to leave iridium lines at 24 nm grating period. The diffraction efficiency progressively improves. Figure adapted from [38].

Simulations of the diffraction efficiency of the various gratings after each processing step are shown in Fig. 2.6, all targeting 6 nm HP on wafer. A purely HSQ grating with 24 nm period gives relatively low diffraction efficiency (Fig. 2.6a). By writing a sparse 48 nm period HSQ grating followed by ALD of iridium, the diffraction efficiency can be improved (Fig. 2.6b). Further ion milling improves the efficiency again (Fig. 2.6c), while removal of the HSQ in between the now opened iridium lines improves the efficiency up to 10% (Fig. 2.6d). Note that the most efficient geometry is for a 25% duty cycle HSQ grating at a height of ~35 nm.

As the ALD process can be optimized to achieve good smoothness, the pattern transfer limitations of electroplating and etching can be avoided, while a highly diffraction efficient material can be used. The limitation of e-beam proximity effect in achieving dense lines is circumvented by
writing a sparse grating. The process window in terms of tolerances in the grating geometry can also be seen to be relaxed (Fig. 2.6): an iridium grating with 40-60% duty cycle and height between 30-40 nm can achieve relatively high diffraction efficiency. Therefore, slight errors in the mask fabrication process can be tolerated.

A summary of the mask design is shown in Table 2.2. The mask-to-sample gap $g$ was kept as small as possible to reduce the blur due to source extension, while being large enough to ensure mechanical positioning tolerances.

<table>
<thead>
<tr>
<th>Target HP on sample wafer ($P/2$)</th>
<th>6 nm</th>
<th>Mask grating HSQ period ($q$)</th>
<th>48 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mask to sample gap ($g$)</td>
<td>150 µm</td>
<td>HSQ width</td>
<td>12 nm</td>
</tr>
<tr>
<td>Distance between gratings ($d$)</td>
<td>204.1 µm</td>
<td>Iridium deposition</td>
<td>12 nm</td>
</tr>
<tr>
<td>Diffraction angle ($\theta$)</td>
<td>34.2°</td>
<td>Grating field size</td>
<td>50 x 50 µm²</td>
</tr>
</tbody>
</table>

Table 2.2: EUV-IL mask design parameters for high-resolution line doubled mask (see Fig. 2.6).

### 2.3.5 Bessel mask

The design of the Bessel beam mask consists of a transmission diffraction ring grating with 300-nm period. The inner diameter is 130 µm and outer diameter 230 µm. This gives a ring width of 100 µm which is less than the inner diameter, thus avoiding zeroth order light overlap into the interference region. The grating period gives a diffraction angle of 2.58° and an optimum gap between mask and sample of 2 mm, as shown in Table 2.3. The central core radius $r_0$ is then calculated to be 115 nm, with a maximum $z$-distance of 2.56 mm between mask and sample as calculated from Eq. 2.1 and 2.10.

<table>
<thead>
<tr>
<th>Gap for 1st order interference</th>
<th>Min value (mm)</th>
<th>Optimal value (mm)</th>
<th>Max value (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>2.00</td>
<td>2.56</td>
<td></td>
</tr>
<tr>
<td>Gap for 2nd order interference</td>
<td>0.72</td>
<td>1.00</td>
<td>1.27</td>
</tr>
</tbody>
</table>

Table 2.3: Bessel beam range for mask with 300 nm period grating.

Simulations of beam propagation were carried out using MATLAB software (R2014a, Mathworks Inc., Natick MA, U.S.A.) and the Bessel beam cross-section in the transverse plane is shown in Fig. 2.7d. Simulations of the application of photoresist dosage thresholds were also performed in MATLAB (Fig. 2.7e). This simulates the recorded image in photoresist for various EUV exposure dosages.

Fig. 2.7f shows a simulation of the Bessel beam propagation for the 300-nm period diffraction ring from 0 to 3 mm in the $z$-direction. The intensity was plotted on a logarithmic scale to better
show the fine structure of the aerial interference pattern, where the Bessel side rings can be clearly seen. The Bessel beam due to the first order diffraction is clearly seen between 1.45 and 2.56 mm. For a perfectly binary grating, the 2nd order diffraction is zero, and therefore no Bessel beam due to 2nd order diffraction was observed in the simulation.

Fig. 2.7: Bessel beam schematic and simulations. (a) Coherent EUV light is diffracted by a ring grating and interfere to form a Bessel aerial image which is recorded. (b) SEM (scale bar = 10 μm) and (c) optical image of the ring grating mask. (d) Simulation of the cross-section of the aerial image. (e) Simulation of photoresist recording by applying a threshold. (f) Simulation of the propagation of the aerial image. Figure adapted from [39].

A second, high-resolution Bessel mask was also fabricated with a ring diameter of 300 μm, ring width of 100 μm, and ring grating pitch of 40 nm. Using Eq. 2.1, 2.5, 2.9, and 2.10 gives a diffraction angle of 19.7°, a mask to sample gap of 418 μm, a depth-of-focus of 279 μm, and a spot size of ~30 nm.

2.3.6 Achromatic Talbot mask

For ATL, the gap $g$ between the mask and the sample plane should be larger than the achromatic Talbot distance $z_A$ but smaller than the maximum distance $z_{max}$ (Fig. 2.2b, Eq. 2.13, Eq. 2.15). The gap should be kept small to maximize the size of the patterned area (Eq. 2.14). For a dot/hole (2D) diffraction grating with period $q = 150$ nm and a field size of $G^2 = 100 \times 100$ μm$^2$, the
calculations for the relevant ATL parameters are given in Table 2.4. The calculations are for EUV beamlines at both the PSI and the SSRF.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>PSI</th>
<th>SSRF $\lambda_1$</th>
<th>SSRF $\lambda_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illumination wavelength</td>
<td>$\lambda$</td>
<td>13.5 nm</td>
<td>13.5 nm</td>
<td>8.8 nm</td>
</tr>
<tr>
<td>Image period (45°)</td>
<td>$P = \frac{q}{\sqrt{2}}$</td>
<td>106 nm</td>
<td>106 nm</td>
<td>106 nm</td>
</tr>
<tr>
<td>Spectral bandwidth</td>
<td>$\Delta\lambda/\lambda$</td>
<td>4%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Monochromatic Talbot distance</td>
<td>$z_T = \frac{2q^2}{\lambda}$</td>
<td>3.3 $\mu$m</td>
<td>3.3 $\mu$m</td>
<td>5.1 $\mu$m</td>
</tr>
<tr>
<td>Achromatic Talbot distance</td>
<td>$z_A = \frac{2q^2}{\Delta\lambda}$</td>
<td>83.3 $\mu$m</td>
<td>111 $\mu$m</td>
<td>170 $\mu$m</td>
</tr>
<tr>
<td>Maximum distance</td>
<td>$z_{max} = \frac{Gq}{2\lambda}$</td>
<td>556 $\mu$m</td>
<td>556 $\mu$m</td>
<td>852 $\mu$m</td>
</tr>
</tbody>
</table>

Table 2.4 Calculations for EUV exposure at the PSI and SSRF using a 2D nickel hole $100 \times 100 \ \mu$m$^2$ ATL mask with 150 nm period (i.e. $G = 100 \ \mu$m, $q = 150 \ \mu$m).

The masks are transmission masks of nickel absorbers on 100-nm-thick Si$_3$N$_4$ membranes. Effectively, the resolution of the pattern is limited by the resolution of the mask. Writing dense, periodic structures using e-beam lithography is challenging due to the electron proximity effect. Electroplating of the dense structures is also difficult, and for nickel, 70 nm feature sizes were achieved with good quality [87]. Aspect ratio is also important as HSQ is used as an electroplating mould. As 200 nm of electroplated nickel is needed to absorb 99.9% of EUV light, for feature sizes below 50 nm this requires aspect ratios greater than 4:1. For HSQ, aspect ratios of 3:1 are generally achievable without the need for pattern collapse mitigation techniques such as critical point drying (CPD).

The exposure efficiency could be further increased by process optimization of the mask fabrication. The grating area was kept small as this was a proof-of-concept work for beamline comparison so that the e-beam writing time was kept relatively short. In essence the grating area can be extended to at most the size of the beam spot. The precision of the exposure area delimitation in the context of step-and-repeat exposures is restricted by the precision of the sample stage. The minimum HP of dot arrays patterned using ATL at PSI is 35 nm with 15 nm dot size, while the theoretical limit approaches 7.5 nm HP using 10.9 nm EUV light [88].

### 2.4 Mask Fabrication

The process flows for fabrication of the various diffraction masks are described in this section. The mask begins with a 100-nm-thick Si$_3$N$_4$ membrane support describe in Table 2.5. For all spin-
coating steps, the mask was placed on a spin-coating chuck with a small droplet of de-ionized (DI) water underneath the mask window for support.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 nm Si₃N₄ on 2-side polished silicon substrate.</td>
<td>Centre of Micro Nano Technology CMi, EPFL.</td>
<td>Thermally grown with low stress optimization.</td>
</tr>
<tr>
<td>3</td>
<td>Optical exposure at 405 nm, 10 s, 60 ml/cm², hard contact.</td>
<td>MA-6 mask aligner, SUSS MicroTec, Garching, Germany.</td>
<td>3 × 3 mm² window with cleave lines for 10 × 10 mm² chips.</td>
</tr>
<tr>
<td>5</td>
<td>Hard bake, 120°C, 10 min.</td>
<td>Präzitherm, Harry Gestigkeit GmbH, Düsseldorf, Germany.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>RIE: CHF₃ 40 sccm, O₂ 3 sccm, pressure 100 mTorr, 20°C, RF power 100 W, ICP power 600 W, 7 min 30s.</td>
<td>Oxford 100, Oxford, U.K.</td>
<td>Etch rate is ~20 nm/min, selectivity of Si₃N₄ to S1813 resist is 1:0.6.</td>
</tr>
<tr>
<td>7</td>
<td>Remove resist in acetone, 10 min, ultra-sonic agitation, followed by isopropanol (IPA), 1 min.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Rinse in DI water, N₂ blow.</td>
</tr>
<tr>
<td>8</td>
<td>KOH (20%) etch, 70°C, until silicon is etched through by visual inspection.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Etch rate is ~50 µm/hr, followed by wash in warm DI water, 5 min, spin dry 3 min.</td>
</tr>
<tr>
<td>9</td>
<td>Spin-coat PMMA, molecular weight 950k, dissolved 4% in ethylactate, 2000 rpm, 45 s. Target = 400 nm. Post application bake, 175°C, 5 min.</td>
<td>PMMA from Allresist GmbH, Strausberg, Germany. Ethylactate from Technic France, Saint-Denis, France. Hotplate from Präzitherm, Harry Gestigkeit GmbH, Düsseldorf, Germany.</td>
<td>Positive tone photoresist for the fabrication of the gold alignment markers to facilitate subsequent e-beam exposures.</td>
</tr>
<tr>
<td>10</td>
<td>E-beam exposure, dose 850 µC/cm², current 10 nA, aperture 400 µm.</td>
<td>VISTEC EBPG 5000+, Jena, Germany.</td>
<td>15 × 15 µm² markers at the corners of the mask window.</td>
</tr>
<tr>
<td>Step</td>
<td>Process</td>
<td>Equipment</td>
<td>Description</td>
</tr>
<tr>
<td>------</td>
<td>---------</td>
<td>-----------</td>
<td>-------------</td>
</tr>
<tr>
<td>11</td>
<td>Development in methyl isobutyl ketone (MIBK) mixed 1:1 with IPA, 60 s.</td>
<td>Technic France, Saint-Denis, France</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Lift-off in acetone.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Overnight soak followed by thorough rinse in DI water, N₂ blow.</td>
</tr>
</tbody>
</table>

Table 2.5 Processing of Si₃N₄ membrane support for diffraction mask.

In general, nickel is used as the photon-stop material as it has an attenuation length of about 15 nm at EUV wavelengths [80], and therefore allows a thinner photon stop and less processing stress on the membrane than gold [84]. The electroplating parameters were optimized [87] to minimize stress on the membrane and ensure relatively homogeneous electroplating across the desired area. For unipolar pulses at 67% duty cycle and current density of ~2.5 mA/cm², the electroplating rate was measured to be ~36 nm/min. Each completed mask was mounted on a stainless-steel mask holder (Fig. 2.8) using poly(methyl methacrylate) (PMMA) and heated to 50°C for solvent removal. The completed assembly was installed in the XIL-II beamline for the interference lithography.

![Fig. 2.8: EUV-IL diffraction mask mounted on a stainless-steel mask holder.](image)

### 2.4.1 Direct write HSQ grating mask

Direct e-beam written HSQ gratings results in SiO₂ based grating material, at a height slightly less than the spin-coated thickness due to resist shrinkage after development. HSQ is an excellent high-resolution photoresist suitable for electron and photon based exposure. The negative tone cross-linking gives HSQ, after development, a profile with slightly positively sloped sidewalls. The SiO₂ based material can be removed by fluorine based etchants but otherwise is very stable. No metallic thin film was used as adhesion/conduction layer on the membrane surface, as the
electron conduction was found to be sufficient for high-resolution writing and minimal sub-field stitching was observed. The process is described in Table 2.6, starting with a 100-nm-thick Si$_3$N$_4$ membrane.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O$_2$ plasma, 150 W, 30 s.</td>
<td>RIE, Plasmalab 80+, Oxford Instruments, U.K.</td>
<td>Surface clean and improve hydrophilicity for better photoresist adhesion.</td>
</tr>
<tr>
<td>2</td>
<td>Spin-coat HSQ XR1541, 5000 rpm, 45 s.</td>
<td>Dow Chemical, Midland, U.S.A.</td>
<td>Negative tone photoresist. Target thickness = 35 nm.</td>
</tr>
<tr>
<td>3</td>
<td>E-beam exposure, dose 12000 to 14000 μC/cm$^2$, current 1 nA, aperture 200 μm.</td>
<td>VISTEC EBPG 5000+, Jena, Germany.</td>
<td>Spot size ~3.5 nm. Grating periods from 44 nm down to 22 nm. For line-doubled mask, period = 48 nm, width = 12 nm.</td>
</tr>
<tr>
<td>4</td>
<td>Development in NaOH buffered solution diluted 1:3 with DI water, 30 s.</td>
<td>Microposit 351, Dow Chemical, U.S.A.</td>
<td>After development, rinse in DI water, dry under N$_2$ blow.</td>
</tr>
<tr>
<td>5</td>
<td>Spin-coat PMMA, molecular weight 950k, dissolved 4% in ethylactate, 2000 rpm, 45 s. Target = 400 nm. Post application bake, 175°C, 5 min.</td>
<td>PMMA from Allresist GmbH, Strausberg, Germany. Ethylactate from Technic France, Saint-Denis, France. Hotplate from Prätzitherm, Harry Gestigkeit GmbH, Düsseldorf, Germany.</td>
<td>Positive tone photoresist for the fabrication of the photon-stop to prevent the transmission of zeroth order light. Previously fabricated alignment markers are used.</td>
</tr>
<tr>
<td>6</td>
<td>E-beam exposure, dose 1000 μC/cm$^2$, current 190 nA, aperture 400 μm.</td>
<td>VISTEC EBPG 5000+, Jena, Germany.</td>
<td>All areas of the mask except the grating areas were exposed.</td>
</tr>
<tr>
<td>7</td>
<td>Development in IPA mixed 7:3 with DI water, 10 s.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Leaves PMMA covering the grating areas on the mask.</td>
</tr>
<tr>
<td>8</td>
<td>Thermal evaporation: 5 nm chromium, 10 nm gold.</td>
<td>BAE 250, Oerlikon Balzers, Liechtenstein.</td>
<td>Chromium adhesion layer, gold electroplating seed layer.</td>
</tr>
<tr>
<td>9</td>
<td>Lift-off in acetone.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Overnight soak plus very light agitation with a small syringe by hand.</td>
</tr>
<tr>
<td>10</td>
<td>Electroplating 400 nm nickel, ~2.5 mA/cm$^2$, 67% duty cycle, unipolar pulses, cycle time 2 s, 7 min, at a rate of ~36 nm/min.</td>
<td>Nickel sulphamate / boric acid bath, Lectro-nic 10-03, Enthone, Trumbull, U.S.A.</td>
<td>Thickness was calculated using the absorption coefficient of nickel at EUV to be sufficient to effectively block EUV light [80].</td>
</tr>
</tbody>
</table>

Table 2.6: Process for direct write grating mask using HSQ.
A process variation whereby the HSQ grating footing is promoted by lightly dosing the areas between the HSQ lines can be undertaken to simplify the fabrication process [89]. In this case, the HSQ footing inhibits electroplating in the areas between the lines while the area outside the grating area undergoes electroplating. Therefore, the central photon stop can be fabricated without e-beam overlay alignment and reduces the number of e-beam steps from 3 (marker fabrication, grating lines, photon stop) to just 1.

### 2.4.2 Line-doubled iridium grating mask

A sparse HSQ base grating is written by e-beam following Table 2.6, at the same thickness. Conformal iridium is deposited and milled to achieve an iridium grating at double the original HSQ period (Table 2.7). PEALD was used because the plasma enhancement between cycles improved surface smoothness and decreased grain size [90], [91].

Fig. 2.9: SEM of 12 nm width 48 nm period HSQ gratings coated with iridium using PEALD. (a) The cross-section of the sparse HSQ lines coated by conformal iridium. (b) Top view shows that the iridium can have a non-negligible grain size. (c) After ion milling the lines become much smoother, and the grating spatial frequency is doubled. Scale bars equal 20 nm. Figure reproduced from [38].

Fig. 2.9 shows the diffraction grating on the mask under scanning electron microscopy (Supra V55, Zeiss, Oberkochem, Germany) after iridium deposition (Fig. 2.9a and Fig. 2.9b) and ion milling (Fig. 2.9c). Firstly, the dimensions of the grating are slightly different from the targeted dimensions. The HSQ lines appear slightly smaller because of the positive slope of the negative-tone resist such that the line is narrower on top, and because of resist shrinkage of ~1 nm after development. The iridium layer looks slightly larger than targeted, due to the increased brightness under SEM inspection, as well as inhomogeneous grain sizes. Nevertheless, as can be seen from simulations, the window of grating dimensions which still allow reasonable diffraction efficiency is sufficiently large, and therefore some errors in the grating geometry can be tolerated.
Care must be taken during ion milling with regards to re-deposition of the etched material. However, Fig. 2.9c shows that ion milling has the benefit of smoothing the sidewalls and grains of the iridium layer, giving much smoother grating lines. Only milled 9 nm of iridium was milled from the line-doubled grating, and the HSQ has not been removed. This is for practical reasons, as the yield for such a mask making process is low, and to avoid pattern collapse of the structure it was decided not to fully etch the iridium lines and perform the HF dip necessary to remove the HSQ. The mask diffraction efficiency can be improved by performing these processes. Future work will include optimization of the mask fabrication process including, for instance, further ion milling to completely remove the remaining top and bottom iridium and removal of the HSQ.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PEALD, precursor iridium(III)</td>
<td>ALD from Picosun, Espoo, Finland. Precursor from abcr GmbH, Karlsruhe, Germany.</td>
<td>Seed time = 3 cycles, rate = 0.243 Å/cycle, target = 12 nm iridium deposition. Plasma enhancement in the ALD cycle improves the surface smoothness and decreases grain size. The coating is conformal.</td>
</tr>
<tr>
<td>2</td>
<td>Argon ion milling, plasma power 150 W, grid voltage 400 V, gun current 4.5 mA, Argon flow rate 8 sccm, 20°C, 9 min.</td>
<td>Ionfab 300Plus, Oxford Instruments, U.K.</td>
<td>Rate = 1 nm/min, target etch = 9 nm of iridium. Anisotropic etch, removes top and bottom iridium whilst leaving sidewall iridium intact.</td>
</tr>
</tbody>
</table>

Table 2.7: Process for grating spatial frequency line-doubling using a sparse HSQ grating written following the process from Table 2.6.

2.4.3 Bessel and achromatic Talbot mask

The Bessel mask consists of electroplated gold grating lines with gold central photon-stop using HSQ as a mould. This is sufficient for the large resolution that is targeted. Further increase in resolution will require different fabrication methods as the resolution of electroplating becomes limited. Similarly, the ATL mask consists of an electroplated nickel hole array around an HSQ mould. In both cases the resolution is also limited by the achievable aspect ratio of the HSQ mould.

Nickel is used because it is an excellent photon-stop material due to its high absorption coefficient at EUV wavelengths and therefore provides high contrast with a relatively smaller thickness
compared to other materials such as gold, thereby relaxing the process parameters and causing less stress on the membrane support. It is also insensitive to surface roughness, as the absorption coefficient becomes relatively constant above a certain thickness.

A second, high-resolution Bessel beam mask with ring grating period of 40 nm was fabricated using HSQ alone, following the same process as the HSQ line grating masks (Table 2.6). E-beam writing strategy of the ring grating structures was optimized using in-house software [92]. For the ATL mask, the theoretical contrast provided by 200 nm thick nickel was calculated to be approximately 70% at 500 μm propagation distance using 4% bandwidth [79]. The calculated background was approximately 18% and the contrast and background is invariant in the z-direction (Fig. 2.10). The fabricated grating was a nickel hole pattern with 150 nm period.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thermal evaporation: 5 nm chromium, 10 nm gold, 8 nm chromium.</td>
<td>BAE 250, Oerlikon Balzers, Liechtenstein.</td>
<td>Chromium adhesion layer, gold electroplating seed layer, and chromium conduction layer to avoid e-beam charging.</td>
</tr>
<tr>
<td>2</td>
<td>Spin-coat HSQ diluted 1:1 with MIBK, 3000 rpm, 60 s.</td>
<td>FOX16, Dow Chemical, Midland, U.S.A. MIBK from Technic France, France.</td>
<td>Target thickness = 250 nm.</td>
</tr>
<tr>
<td>3</td>
<td>E-beam exposure, dose 8000 μC/cm², aperture 400 μm.</td>
<td>VISTEC EBPG 5000+, Jena, Germany.</td>
<td>Circular grating at 300 nm period.</td>
</tr>
<tr>
<td>4</td>
<td>Development in NaOH buffered solution diluted 1:3 with DI water, 120 s.</td>
<td>Microposit 351, Dow Chemical, U.S.A.</td>
<td>After development, rinse in DI water, dry under N₂ blow.</td>
</tr>
<tr>
<td>5</td>
<td>Chromium etch, Cl₂ plasma etcher, 30 s.</td>
<td>BMP Plasmatechnologie, Garching, Germany.</td>
<td>Target etch = 8 nm chromium to reveal gold seed layer.</td>
</tr>
<tr>
<td>6</td>
<td>Electroplating 150 nm gold.</td>
<td>Autronex, Ethone, Trumbull, U.S.A.</td>
<td>Forms grating lines and photon stop.</td>
</tr>
</tbody>
</table>

Table 2.8: Bessel mask fabrication process to achieve gold ring grating with 300 nm period.
Fig. 2.10: ATL simulation showing diagonal intensity profile of the aerial image at a propagation distance of $z = 500 \, \mu m$. The contrast is 70% with an 18% background.

A summary process diagram of the direct write HSQ gratings for line/space masks, and the electroplated gratings using HSQ mould for ring gratings and hole array gratings is shown in Fig. 2.11.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thermal evaporation: 3 nm chromium, 5 nm gold, 3 nm chromium.</td>
<td>BAE 250, Oerlikon Balzers, Liechtenstein.</td>
<td>Chromium adhesion layer, gold electroplating seed layer, and chromium conduction layer to avoid e-beam charging.</td>
</tr>
<tr>
<td>2</td>
<td>Spin-coat HSQ diluted 1:1 with MIBK, 3000 rpm, 60 s.</td>
<td>FOX16, Dow Chemical, Midland, U.S.A.</td>
<td>Target thickness = 250 nm.</td>
</tr>
<tr>
<td>3</td>
<td>E-beam exposure, dose 12000 $\mu C/cm^2$, aperture 400 $\mu m$.</td>
<td>VISTEC EBPG 5000+, Jena, Germany.</td>
<td>Periodic pillar array, pitch 150 nm, diameter 75 nm, field size $100 \times 100 , \mu m^2$.</td>
</tr>
<tr>
<td>4</td>
<td>Development in NaOH buffered solution diluted 1:3 with DI water, 120 s.</td>
<td>Microposit 351, Dow Chemical, U.S.A.</td>
<td>After development, rinse in DI water, dry under N$_2$ blow.</td>
</tr>
<tr>
<td>5</td>
<td>Chromium etch, Cl$_2$ plasma etcher, 10 s.</td>
<td>BMP Plasmatechnologie, Garching, Germany.</td>
<td>Target etch = 3 nm chromium to reveal gold seed layer.</td>
</tr>
<tr>
<td>6</td>
<td>Electroplating 200 nm nickel, ~2.5 mA/cm$^2$, 67% duty cycle, unipolar pulses, cycle time 2 s, 6 min.</td>
<td>Nickel sulfamate / boric acid bath, Lectro-nic 10-03, Enthone, Trumbull, U.S.A.</td>
<td>Forms grating area and photon stop.</td>
</tr>
<tr>
<td>7</td>
<td>Buffered oxide etch (BOE, HF mixed 1:7 with NH$_4$F), 5 min.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Etch rate 1 nm/s, removal of HSQ mould.</td>
</tr>
</tbody>
</table>

Table 2.9: Achromatic Talbot mask fabrication process giving nickel hole array at 150 nm period.
Fig. 2.11: Cross-section schematic of process flow for interference mask fabrication. Left flow describes direct write HSQ gratings: starting with Si₃N₄ membrane (a), HSQ is spin-coated (b) and diffraction gratings patterned by e-beam lithography (c). PMMA is spin-coated (d) and patterned by e-beam (e) to define photon stop regions. Metal is deposited (f) and lifted-off (g) to give an electroplating seed-layer outside the grating areas. Electroplating is performed (h) to create the photon stop. Right flow describes electroplated gratings around an HSQ mould: starting with Si₃N₄ membrane (a), metal thin films are deposited (b) and HSQ is spin-coated (c) and diffraction gratings patterned (d). Chromium is etched (e) to expose the seed-layer which is then electroplated (f). The HSQ mould is removed in BOE (g).

2.5 Patterning

The EUV-IL scheme can be divided into three practical areas: the fabrication of high quality interference masks which was discussed in the previous two sections, the capabilities of the beamline experimental setup, and the characteristics of high-resolution EUV photoresists [42]. In this section the experimental setup and photoresist characteristics will be discussed. The patterning process flow will then be described, and the results for each interference scheme presented.
2.5.1 Beamline setup

EUV radiation was provided by a 3rd generation 2.4 GeV synchrotron source (SLS, PSI, Switzerland). A linear undulator with a periodic arrangement of 22 permanent magnet pairs and adjustable gap can provide a EUV beam with energies between 70 to 500 eV. The broadband EUV beam, with 4% bandwidth ($\Delta\lambda/\lambda$), has high spatial coherence and low emittance [69].

The beam passes through a set of three mirrors to filter the higher harmonics and is spatially filtered through a pinhole of 70 $\mu$m diameter which serves as the effective intermediate source. The beam is polarized along the diffraction gratings, providing the maximum contrast for line/space patterns. The exposure chamber incorporating the mask holder and the sample stage is placed 12 m away from the pinhole, with the beam having a spot size of $1.2 \times 1.8$ mm$^2$ on the mask. A motor with encoder allows accurate movement of the sample stage and adjustment of the mask-to-sample gap. The beamline arrangement is shown in Fig. 2.12.

From the geometrical arrangement of the experimental setup, the blur due to extended source is given by

$$\frac{s_{ext}}{g} = \frac{s}{L}$$

where $s$ is the size of the source, $s_{ext}$ is the size of the source extension on sample wafer, $L$ is the distance from source to mask, and $g$ is the distance from mask to sample wafer. At $\lambda = 13.5$ nm incident wavelength, for $g = 550$ $\mu$m, the blur is $\sim 3$ nm, while for $g = 150$ $\mu$m, the blur is $\sim 1$ nm. Although for the ATL mask producing patterns with period of 106 nm, a few nm of blur is relatively small and would not affect the resolution, this amount of blur is not negligible for targeted HP resolutions below 10 nm. The system blur due to source extension can be decreased by using a smaller pinhole at the intermediate focus. This would however lower the available flux and thereby increase exposure times, causing the exposure to be more sensitive to mechanical instabilities.
Therefore, for beamlines with a similar arrangement as the SLS and SSRF, where the effective source size is much smaller than the source to mask distance, the source extension introduces a blur of approximately a few nm. The effect of source extension becomes a limiting factor for plasma sources, where the source must be placed closer to the mask due to efficiency problems. Finally, note that the damping and settling of mechanical vibrations plays a role in resolution improvement and limitations.

### 2.5.2 EUV photoresists

For photoresists, their homogeneous application, adhesion, and process optimization, become critically important. State-of-the-art EUV photoresists require a balanced trade-off between critical dimension, line-edge-roughness (LER), and sensitivity. Factors such as acid diffusion in chemically amplified resists [42] and shot noise [93] in general can limit the resolution and LER. A detailed study of EUV photoresists is beyond the scope of this work.

One trade-off relevant to this work is between the pattern resolution due to pattern collapse and LER. For very high-resolution gratings the aspect ratio needs to be low enough to avoid pattern collapse. This means that the resist thickness needs to become thinner and thinner, causing increased LER due to backscattering from the substrate. Pattern collapse mitigation such as CPD is needed to increase the resolution. Another resist trade-off is in the etching properties. The photoresist needs to have sufficient etching selectivity against the substrate (in this case silicon) to achieve acceptable pattern transfer. This will be discussed further in section 2.6.

A hafnium based resist from Inpria Corp. and hydrogen silsesquioxane (HSQ), which is based on silicon dioxide, were used. Both resists are known for their high-resolution patterning by EUV and e-beam lithography [43], [74]. HSQ in particular represents the state-of-the-art in high-resolution patterning. However, it has very low sensitivity and is therefore unsuitable for industrial applications. The relatively long exposure times can become susceptible to vibrations.
Further, HSQ is particularly sensitive to humidity, temperature, and age, and incorrect handling can contribute towards sub-optimal results. Inpria resist has volatile performance behaviour due to limited shelf life and very stringent processing requirements.

2.5.3 Patternning process

The process flow for EUV-IL patterning using three different types sample surface preparation is described in Table 2.10 and using three different types of photoresist described in Table 2.11. Table 2.13 and remains similar for the various IL schemes. The beam flux is measured by a diode and for a given dose the shutter time is automatically calculated. The sample to be patterned is either p-type 550-μm-thick (100) single side polished silicon wafer or p-type 750-μm-thick (100) single side polished silicon-on-insulator (SOI) chip, with an 88-nm thick silicon device layer on top of a 145-nm thick buried oxide (BOX) layer (SOITEC, Bernin, France). The device layer was thinned down to ~20 nm by thermal oxidation and subsequent etching in BOE (HF 1:7 NH₄F).

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TMAH dip, 60 s, DI water rinse, 60 s, N₂ blow, then bake at 180°C, 5 min.</td>
<td>MF26A, Dow Chemical, Midland, U.S.A.</td>
<td>Surface clean and improve hydrophilicity for better photoresist adhesion.</td>
</tr>
<tr>
<td></td>
<td>Bake at 250°C, 5 min.</td>
<td>Präzitherm, Harry Gestigkeit GmbH, Düsseldorf, Germany.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Light O₂ plasma, 100 sccm, 60 s.</td>
<td>BMP Plasmatechnologie, Garching, Germany.</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.10: Three different sample surface preparation processes to improve hydrophilicity, promote photoresist adhesion, and to clean the surface.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>Spin-coat HSQ diluted 1:1 with MIBK solvent, 2500 rpm, 45 s.</td>
<td>XR1541, Dow Chemical, Midland, U.S.A.</td>
<td>Negative-tone photoresist for a target thickness of ~20 nm.</td>
</tr>
<tr>
<td>3a</td>
<td>Exposure at 92 eV (13.5 nm), dose between 100 ml/cm² to 8000 ml/cm².</td>
<td>XIL-II beamline, SLS, PSI.</td>
<td>Photon flux is ~30 mW/cm² giving exposure times between 3 s to 4 min.</td>
</tr>
<tr>
<td>4a</td>
<td>Development of HSQ patterns using NaOH buffered solution diluted 1:3 with DI water, 30 s.</td>
<td>Microposit 351, Dow Chemical, Midland, U.S.A.</td>
<td>Followed by rinse under DI water, 60 s, and N₂ blow dry.</td>
</tr>
</tbody>
</table>

Table 2.11: EUV-IL patterning process using thin HSQ to give highest resolution.
<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>Spin-coat undiluted HSQ 5000 rpm, 45 s.</td>
<td>XR1541, Dow Chemical, Midland, U.S.A.</td>
<td>Negative-tone photoresist for a target thickness of ~35 nm.</td>
</tr>
<tr>
<td>3b</td>
<td>Exposure as per Table 2.11.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>Development of HSQ patterns using TMAH at 25% concentration, 60 s.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Followed by rinse under DI water, 60 s, and N₂ blow dry.</td>
</tr>
</tbody>
</table>

Table 2.12: EUV-IL patterning process using TMAH developer to give good sensitivity and therefore quicker exposure times.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2c</td>
<td>Spin-coat Inpria HfO₂ resist, 5000 rpm, 45 s, PAB 80°C, 180 s.</td>
<td>XE2015J, Inpria corp., Corvallis, U.S.A.</td>
<td>Negative-tone photoresist for a target thickness of ~25 nm.</td>
</tr>
<tr>
<td>3c</td>
<td>Exposure as per Table 2.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td>Development of Inpria patterns: PEB 80°C, 60 s, TMAH 25%, 30 s, hard-bake 250°C, 5 min.</td>
<td>XE2015J, Inpria corp., Corvallis, U.S.A.</td>
<td>Followed by rinse under DI water, 60 s, and N₂ blow dry.</td>
</tr>
</tbody>
</table>

Table 2.13: EUV-IL patterning process using Inpria photoresist to give high-resolution and high sensitivity together with high etching selectivity.

HSQ thinner than ~20 nm is difficult to achieve as higher spin speeds were shown to result in inhomogeneous resist layer thickness or even complete lack of adhesion. For development, it has been shown that TMAH development leads to more sensitivity (i.e. less EUV dose) whereas NaOH based salty developer enables higher resolution than that of the TMAH developer.

### 2.5.4 Results: line/space patterns

The patterned samples were inspected using scanning electron microscope (SEM) at an acceleration voltage of 1kV and working distance of 3.5 mm (Supra V55, Zeiss, Oberkochem, Germany). Using the HSQ based EUV-IL mask, patterning down to 11 nm HP lines on HSQ with 351 developer (Fig. 2.13) at an EUV dose on mask of 1550 mJ/cm² was achieved. Note that this is the dose on the mask, which is roughly 3 times more than the dose on the wafer. At such high-resolution, transmission mask quality becomes more apparent, and this has a direct influence on pattern transfer. Patterning down to 14 nm HP lines using HSQ with TMAH 25% developer at an EUV dose of 500 mJ/cm² on mask (Fig. 2.13) was also achieved. These lines showed much higher LER, and were in general of lesser quality. For Inpria’s hafnium based resist, patterning down to
14 nm HP lines at an EUV dose of 475 mJ/cm² on mask (Fig. 2.13) was achieved. Below this resolution, LER became a problem, and pattern collapse was also observed (Fig. 2.14).

For the iridium based IL mask, the results are shown in Fig. 2.15. Line/space patterns with 6 nm HP were resolved in HSQ at an aspect ratio of approximately 3:1, although bridging and collapse was evident. The mask incorporated only this HP due to the fabrication process, which can be optimized to only a single HP. The exposure dose was 7500 mJ/cm² on mask corresponding to 125 s of exposure time. Although the pattern is well-resolved, it shows significant bridging between the lines and partial pattern collapse. It seems that the resolution limit is being approached.

![Fig. 2.15: SEM images of line/space patterns fabricated using EUV-IL via the same HSQ diffraction grating mask for dose comparison. The photoresists used include (a) chemically amplified resist (JSR, Japan), (b) and (c) HSQ, and (d) Inpria HfO₂ based resist. Patterns down to 11 nm HP were resolved cleanly using HSQ. Note that the dose values are for the dose on mask which is typically three times more than the dose on wafer.](image)

This could be due to a variety of reasons including mask fabrication (e.g. LER of the mask), resist processing (pattern collapse, resolution limit of the resist), or tool limitations (e.g. mechanical
instabilities during the exposure). At this point it is difficult to isolate the root cause of the problem because masks fabricated using this method can only target one HP, making it difficult to compare with different resolution patterns on the same mask, to determine if there are mask defects. Moreover, there is no immediate possibility of comparing results with any other resist or tool, since both HSQ and the XIL-II tool have the best performance in terms of resolution.

Fig. 2.14: SEM micrograph of 14 nm HP lines patterned in Inpria using EUV-IL showing collapse of the lines. Scale bar corresponds to 100 nm. Figure reproduced from [41].

Fig. 2.15: SEM of 6 nm HP resolved line/space pattern using EUV-IL via an iridium line-doubled diffraction mask. Scale bar = 100 nm. Inset scale bar = 10 nm. Figure reproduced from [38].

Such a feature size of 6 nm HP represents ~12 atoms of silicon in width, and is well within the quantum regime where quantum effects play an important role in device physics. For EUV-IL, 6 nm HP is close to the theoretical limit of ~3.5 nm HP for this scheme. The result is an improvement on the previous 7 nm HP patterning using Inpria based photoresist as the mask grating [43], and to the best of the author’s knowledge, represents the highest resolution achieved to date using photolithography.
2.5.5 Results: Bessel beams

Fig. 2.16 shows the developed images of the recorded Bessel beam using SEM. In Fig. 2.16a, exposures with different doses on the right and the simulated image on the left are shown. The recorded intensity as the dose is increased agrees well with the simulations. For smaller doses, only the central beam is recorded. With increasing dose, more and more of the side rings become exposed. This corresponds well with simulation of the Bessel beam sectional profile (Fig. 2.16a, left). The top exposure in Fig. 2.16a corresponds to a dose of 12 mJ/cm² (i.e. dose on mask), while the first side ring appears at 23 mJ/cm². This gives the exposure latitude of the Bessel spot such that no side rings are present (i.e. 11 mJ/cm²). All doses are dose on mask, while the dose on wafer is typically one third the dose on mask. The FWHM of the central beam at high dose was measured to be approximately 223 nm diameter, in comparison with the theoretical 230 nm.

Fig. 2.16: Simulations and SEM images of Bessel beam recorded in HSQ. (a) Simulation (left) and experimental (right) of Bessel beam at various thresholds/doses. The experimental doses (dose before the grating) in HSQ from top to bottom are 12.1, 23.1, 39, 74, and 124.9 mJ/cm², and match well with simulation. Scale bar is 1 µm. Fluctuations in the simulation are due to simulation mesh size. (b) Simulation of Bessel beam intensity showing artefacts and proximity effect due to side rings. (c) Applying a threshold by changing the resist dosage can mitigate the problem. (d) Experimental exposure in HSQ, scale bar = 300 nm. The dark central region in the spots is due to difference in electron scattering between flat areas and edges under SEM, and is an artefact of the SEM micrograph. (e) Exposed pattern at various gap distances. Figure reproduced from [39].
Although, by using the correct dose, a single Bessel spot could be obtained, it may be possible that a line of such Bessel spots would exhibit a proximity effect at the central spots (Fig. 2.16b-d) due to dosage contribution from neighbouring Bessel beams. Fig. 2.16b shows a simulation of the image of a row of Bessel beams, with the side ring intensities quite apparent. To mitigate these artefacts, a high contrast photoresist can be used which captures the central beam spot but is insensitive to the lower intensity side rings. By applying a threshold which simulates resist sensitivity (Fig. 2.16c) the Bessel beam exposure dosage which gives only a central spot and where the side rings are not recorded can be determined.

By patterning in HSQ (Fig. 2.16d), the exposure of the Bessel beam central spot without the surrounding artefacts was observed, in accordance with the simulations. This allows identification of the maximum dosage and depth-of-focus while still giving single spot exposure. However, it can be seen in Fig. 2.16c and Fig. 2.16d, that the middle spots are larger than the side spots. This is due to the contribution of the side rings of neighbouring Bessel beams to the dosage in the spot area. Although the side rings themselves are not recorded, their intensities nevertheless contribute to the exposure dose in the spot areas. This is analogous to the proximity effect in electron beam lithography, where secondary electrons cause resist exposure in unwanted areas, setting limitations in writing dense patterns. To mitigate this problem and ensure minimum side-ring intensity, careful adjustment of the dosage or proximity error correction is needed.

The EUV-IL exposures for various gaps are shown in Fig. 2.16e. The Bessel beam cross-section is clearly shown for gaps 1.5 mm, 2 mm, and 2.5 mm, which corresponds to the beam formed by 1st order interference. The central spot and two side rings have almost the same shape and intensity for these three gaps, which shows that the Bessel beam is nondiffracting within the calculated minimum to maximum range as per Table 2.3. A smaller Bessel beam was also observed at a gap of 1 mm, which corresponds to the location of the optimal distance to observe a beam due to 2nd order interference. Although from the simulation in Fig. 2.7f, no beam due to 2nd order interference is predicted for a perfectly binary grating, the fabricated grating is not perfectly binary, and therefore some increase in the 2nd order diffraction efficiency is expected. As predicted, the beam size is much smaller, and in fact the beam spot is one half the FWHM of the beam spot due to 1st order interference, as per Eq. 2.10. These exposures show that Bessel beam formation using the transmission ring grating approach agrees well with theory.

The use of the Bessel beam as a serial EUV beam writer was also demonstrated. The beam spot shape and intensity is well repeatable, as seen in Fig. 2.17. The variability comes from inaccuracies in the sample stage, which would be alleviated by using a precise, laser-
interferometer controlled stage. This shows the ability of using Bessel beams to write arbitrary, nano-sized structures, across varying topographies. Since it is a serial writing method the throughput is limited, although large arrays of Bessel beams could be used to increase throughput (Fig. 2.17).

Fig. 2.17: (Left) Bessel beam as a serial lithography tool. Due to its large depth of focus and self-healing properties Bessel beams can be used to write structures over changing topographical surfaces. (Right) Serial beam writing using Bessel beam array formed from EUV light. The 53 spots were written in 39.75 s using a beam flux of 4 mW/cm². Top scale bar is 100 μm. Inset scale bar is 10 μm. Figure reproduced from [39].

Finally, high-resolution dots with 30 nm diameter were exposed, with the results shown in Fig. 2.18. An exposed dot of 30 × 20 nm² size was found in the middle of the exposure field as expected. The mask-to-sample gap distance was 550 μm which is within the range of the calculated depth-of-field for 1st order interference Bessel beam. The dose was 268 mJ/cm² (dose on mask) which is ten times higher than the dose required for the gold-based ring grating of 300 nm period. This is due to losses in diffraction efficiency in the HSQ material at 40 nm pitch and EUV wavelength.

There are several reasons which might explain why the dot shows astigmatism and not of an ideal shape, and why such an experiment is currently difficult to perfect. Firstly, at such high-resolutions the diffraction efficiencies of the ring grating at different positions of the grating will be different due to the polarization of the incident light. The EUV beam that was used was linearly polarized, meaning that diffraction efficiencies from the ring grating at positions on the vertical axis will be slightly different compared to the horizontal axis. Adjustment of the duty cycle of the ring grating at various positions along the ring will be needed to ensure that linearly polarized light is diffracted with equal intensity at all positions. The diffraction angle for 40 nm pitch
gratings is 19.7°. At such high diffraction angles combined with the linearly polarized nature of the light, the interference intensities due to diffraction from various parts of the ring will be different. Therefore, compensation for polarization effects will be needed in future ring grating designs.

Fig. 2.18: SEM image of a 30 × 20 nm² lithographic mark in HSQ exposed by interference of diffracted EUV beams from a 40-nm period HSQ ring grating. Scale bar is 20 nm. Inset: SEM image of the HSQ ring grating with nickel photon stop on a Si₃N₄ membrane. Scale bar is 100 μm.

Secondly, for high-resolution features of 30 nm dot size, the mask to sample gap is much smaller and the exposure is more sensitive to mask inhomogeneity, beam inhomogeneity, mechanical vibrations and drift, and sample stage and mask holder positioning tolerances. Adhesion of the photoresist on the sample surface can also become a problem at such high-resolution. Bessel beam diffraction masks are also very challenging to fabricate. For a 30 nm spot the ring grating period required was 40 nm and any defects or inhomogeneity in the mask would be amplified on the sample. The technology to fabricate high-resolution gratings using e-beam lithography is constantly being improved and 40-nm period gratings in HSQ represent the resolution limit, for lines with reasonable LER, at the LMN, PSI. Lastly, a 30-nm sized dot is quite difficult to find on a sample for SEM inspection. The position tolerance for our interference lithography sample stage is ± 500 nm. An improved sample stage such as a piezo-actuated stage or laser-interferometer controlled stage would improve the placement of such lithography marks.

2.5.6 Results: ATL dot array

SEM inspection of the developed samples show a minimum feature size of 20 nm over an exposure area of 43 μm width (Fig. 2.19d-f). The resulting feature sizes can be controlled by changing the dose from 600 to 800 mJ/cm² (i.e. dose on mask). Higher doses showed oval dots
and astigmatism. The observed field area of $43 \times 43 \, \mu m^2$ was slightly smaller than expected from calculations given a mask-to-wafer gap of 275 $\mu m$ and a mask field area of $100 \times 100 \, \mu m^2$, calculated to be 50 $\mu m$ on wafer. This discrepancy may be due to errors in measurement of the mask thickness and silicon wafer thickness. The gap back-calculated from the measured field area of $43 \times 43 \, \mu m^2$ is 318 $\mu m$.

Fig. 2.19: SEM images of the exposed patterns after development at the SSRF (a-c) and at PSI (d-f). In all cases the dot array has pitch 106 nm. (a) Dose 400 mJ/cm$^2$, dot size 20 nm. (b) Dose 670 mJ/cm$^2$, dot size 48 nm. (d) Dose 600 mJ/cm$^2$, dot size 20 nm. (e) Dose 800 mJ/cm$^2$, dot size 40 nm. The measured exposure area was (c) 32 $\mu m$ at SSRF and (f) 43 $\mu m$ at PSI. Scale bars for (a-b) and (d-e) equals 200 nm. Scale bars for (c) and (f) equals 10 $\mu m$. All doses are dose on mask. Figure reproduced from [40].

Although the distance between the wafer and the mask can be controlled by a mask motor at PSI, the setup at the SSRF does not permit the exact positioning of the mask, making direct comparison of the resulting exposed patterns difficult as different settings had to be used to test the performance of the mask. As can be seen from Fig. 2.19, the achievable contrast for the different experiments is similar. An absolute direct comparison of the lithographic performance between the two is not possible because of the dissimilarities between the two different IL setups and
infrastructure available to each lab. Nevertheless, because the contrast was comparable between the different beamlines and beamline arrangements, this shows that the two beamlines have a similar and comparable performance, and that high-resolution periodic patterning was achieved at both synchrotron radiation facilities.

2.6 Pattern transfer

Once the high-resolution, ultra-dense, large-area periodic patterns are printed, it remains to transfer the pattern into a functional material. The focus is on silicon nanowires, although metal deposition and lift-off to produce metal nanowires and dot arrays is also interesting for studying plasmonics, catalysis, and sensing.

2.6.1 Plasma etching: silicon nanowires

The recorded line/space patterns were transferred into a SOI substrate using reactive ion etching with inductively coupled plasma (RIE-ICP, Oxford100, Oxford, U.K.). RIE uses plasma formed from the etchant gas and accelerates these reactive ions towards the sample using an electric field. Therefore, not only is the sample chemically etched by the etchant gas, but is also physically etched through sputtering. The addition of an inductive coil allows separate control of the plasma density and the forward power, and therefore better control of the degree of chemical and physical etching and thus the etching profile. By using a passivation gas, the sidewalls can be protected from chemical etching, thus resulting in a highly anisotropic etch [94] (Fig. 2.20).

![Fig. 2.20: Schematic of RIE-ICP etching with simultaneous etching and passivation. (a) Passivation gas protects the surface from chemical attack. (b) Directional sputtering etches the bottom of the trench with the side-walls protected. (c) Chemical etching of the now open trench bottom. All reactants and products must be transported through the nano-channel. Figure reproduced from [41].]

Using an etching recipe consisting of SF\(_6\) gas as the etchant and C\(_4\)F\(_8\) gas for passivation of the sidewalls, first, C\(_4\)F\(_8\) forms a protective polymer layer on all surfaces, side and bottom. Then, the bottom surface is sputtered by physical etching. The open bottom surface is then chemically
etched by SF$_6$ while the sidewalls are passivated. These processes occur simultaneously where the reacting ions and the reaction product need to enter and simultaneously leave the etched area, respectively (Fig. 2.20). For highly dense, very small structures, where the distance between sidewalls is small and space for reacting ions and etched ions to enter and leave is limited, optimization of the processing parameters, including chamber pressure, sample temperature, gas flow, and platen and coil power, become critical [95].

![Fig. 2.21: Cross-section SEM image of SiNWs etched into SOI sample using RIE-ICP and HfO$_2$ (Inpria) etching mask with resolution of (a) 14 nm HP, (b) 16 nm HP, and (c) 14 nm HP.](image)

For HfO$_2$ (Inpria) patterns, 14 nm HP SiNWs were obtained with ~1:1 aspect ratio and square cross-sectional profile etched into SOI substrate (Fig. 2.21). This result was obtained with the parameters listed in Table 2.14. The Inpria photoresist was spin-coated at 5000 rpm resulting in a thickness of ~15 nm after exposure. This Inpria resist showed very good etching selectivity against silicon for these etchants. However, the problem then comes that the selectivity is too good, and it becomes difficult to remove the leftover resist, or ‘scum’, between the lines, which can cause roughness at the bottom and sidewalls (Fig. 2.22a-b). The very good selectivity also means that LER is directly transferred into the substrate below, without any smoothing effects. Therefore, a pre-treatment of medium power argon plasma sputtering for 15 s (Table 2.14) was used to de-scum between the patterned lines.

<table>
<thead>
<tr>
<th>Resist mask / process</th>
<th>ICP etching parameters</th>
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<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
</tr>
<tr>
<td>Inpria</td>
<td>0</td>
</tr>
<tr>
<td>HSQ (1)</td>
<td>20</td>
</tr>
<tr>
<td>HSQ (2)</td>
<td>0</td>
</tr>
<tr>
<td>Inpria de-scum</td>
<td>20</td>
</tr>
</tbody>
</table>
Table 2.14: RIE-ICP etching parameters for silicon using various masks. The etch-rate was between 1-2 nm/s while the selectivity of silicon varied between ~1.5 against HSQ and ~3 against Inpria.

The optimal C₄F₈ gas flow was found and is listed in Table 2.14 with some tolerance in the values for the Inpria mask. For lower flows, there was an increase in bowing due to insufficient protection of the sidewalls. For higher flows, the etch rate decreased and the profile became more rounded, possibly due to over passivation (Fig. 2.22). However, since the effects of RIE-ICP parameters are linked, a more systematic study of all the parameters is required.

For pattern transfer using HSQ resist, the etching selectivity of HSQ against silicon was found to be low. This is expected since HSQ after exposure and development is chemically almost pure SiO₂ which is known to have a limited selectivity against silicon in SF₆ based RIE processes. The modulation pattern in the HSQ resist for high-resolution lines below 14 nm HP is transferred to the substrate via RIE etching. Because of the low selectivity, the cross-section of the resulting nanowires is rounded instead of square-shaped. SiNWs with square cross-sectional shape down to 16 nm HP (Fig. 2.23) were obtained.

Fig. 2.22: Cross-section SEM images of 16 nm HP etched SiNWs on an SOI substrate. (a) Using Inpria HfO₂ resist as mask, roughness is transferred into the silicon due to the high selectivity of HfO₂. (b) After a short argon de-scum of the Inpria material, the resulting SiNWs are smoother. (c-e) SiNWs etched using Inpria HfO₂ resist mask for various C₄F₈ flow rates: (c) 50 sccm; (d) 60 sccm; (e) 70 sccm. All scale bars equal 20 nm. Figure adapted from [41].
Finally, note that cleanliness of the plasma chamber is very important, and striking and running the plasma with a dummy wafer for a few minutes to ‘pre-condition’ the plasma chamber drastically improves plasma and etching stability. If the plasma chamber is not pristine, dirt on the chamber sealing may cause an unstable plasma, in which case slightly increasing the chamber pressure while lowering the temperature can achieve similar etching profiles for HSQ (Table 2.14). The etch rate for silicon is $\sim 1$ nm/s, and for a device layer of $\sim 25$ nm the etching time was set to 30 s taking into consideration the initial plasma striking time.

### 2.6.2 Deposition and lift-off: metal nanowires

Besides silicon, other nano-patterned materials may be of interest for example for scientific study of nano-catalysis, nano-magnetism, or plasmonics. Of these, metal nano-structures are of particular interest. Since metal etching at high-resolution is very challenging, one complementary method is metal deposition followed by lift-off. This involves applying two layers of photoresist: one, a thick sacrificial layer for lift-off, typically PMMA, and on top of this a high-resolution resist such as HSQ for patterning. Once the HSQ is patterned by EUV, the pattern is transferred into the PMMA by directional oxygen plasma. The chosen metal is then deposited and the PMMA dissolved in solvent to lift-off the unwanted metal. Using this method chromium/gold nanowires down to 16 nm HP have been achieved [46].

### 2.7 SiNW fabrication

After pattern transfer, further processing is required to accurately measure the material properties of the SiNWs. First, suspended SiNW arrays are described, followed by electrically contacted SiNWs.
2.7.1 Suspended SiNW arrays

As will be described in Chapter 3, SiNWs can be used as a transistor channel material, and suspended SiNWs allow for gate-all-around structures for better electrostatic control of the channel, improving the leakage current and sub-threshold swing. Further, suspended SiNWs allow for more accurate measurement of their thermoelectric properties, as they are better insulated from their surroundings and accurate thermal measurements can be taken. SiNWs have been shown to have excellent thermoelectric characteristics, with high electrical conductivity combined with low thermal conductivity to give thermoelectric coefficients of $ZT \approx 0.6$ at room temperature [32].

In the recent past, ultra-thin SiNWs have typically been fabricated using either bottom up methods [5], [26], [27], [96]–[103] such as VLS growth, or by chemical etching [32], [96], [104]–[109]. Both methods result in SiNWs with large distribution of sizes and orientations, making them difficult to incorporate into devices as well as extract materials characteristics. Top-down patterned SiNW arrays have on the other hand been limited by lithography resolution or sparseness of the array. The SiNWs fabricated in this work is highly dense, giving good signal-to-noise ratio; is ultra-thin, from 20 nm width down to 8 nm width; and is well-ordered, so that the interpretation of the measurement becomes simpler.

![Fig. 2.24: Schematic of suspended SiNW arrays.](image)

(a) The SiNWs are etched, clamped by metal, and then released. (b) The SiNW pads are patterned first by metal lift-off, then the whole device structure is etched, followed by release. (c) A cartoon of the procedure, where large pads are defined and the SiNWs joining them are released.

The schematic for suspended SiNW array fabrication is shown in Fig. 2.24. As the etched SiNWs are on top of a 140-nm-thick BOX, they can be clamped at both ends and the BOX under-etched to release the suspended structure (Fig. 2.24c). Two methods for clamping are presented: one, the etched SiNWs are patterned again with large pads using e-beam lithography and PMMA photoresist, chromium metal is deposited on top and then lifted-off to reveal SiNWs covered by chromium pads at two ends (Fig. 2.24a).
Fig. 2.25: SEM images of suspended SiNW arrays clamped by chromium pads viewed from 30° tilt angle. Scale bars are 300 nm. (a) Width 20 nm at 22 nm HP, with lengths up to 1 µm. (b) If the SEM inspection is not careful (i.e. too high acceleration voltage or too close working distance) the SiNWs can become charged and stick together. Stiction can be observed in action during the SEM scan in the far left and far right of the image (circled).

Two, before SiNW etching, the HSQ lines are patterned again with large pads using e-beam lithography and PMMA photoresist, chromium metal is deposited on top and then lifted-off, and finally the device is etched to result in SiNWs connected monolithically to bulk silicon pads, with a covering of chromium on top of the silicon pads (Fig. 2.24b). The chromium metal is used to discharge the structure during SEM inspection (Fig. 2.25). In the first case, the result is a SiNW array clamped by chromium metal pads, and in the second case the result is a SiNW array joined monolithically to bulk silicon pads, with chromium metal on top of the silicon pads. The two processes are described in Table 2.15, and example SEMs of SiNWs clamped by chromium pads is shown in Fig. 2.25 and Fig. 2.26c, while those joined monolithically to bulk silicon are shown in Fig. 2.26a and Fig. 2.26b.

Next, the BOX is under-etched by isotropic HF-based etching. Again, two methods can be used: one, a wet buffered oxide etch (BOE, HF 1:7 NH₄F) and two, vapour HF (VHF). Using wet BOE can cause stiction between the SiNWs during drying due to capillary forces. CPD can be used to mitigate stiction but increases the LER (Fig. 2.26b), while liquids can be avoided altogether by using VHF (Fig. 2.26a). SiNWs released by VHF and BOE alone show smooth surface roughness
while SiNWs undergoing CPD are much rougher (Fig. 2.26). The release processes are summarised in Table 2.16.

Fig. 2.26: Top-down SEM images of suspended SiNW arrays. (a) Width 18 nm, 22 nm HP SiNWs released by VHF with silicon pads. (b) Width 16 nm, 22 nm HP SiNWs released by BOE with CPD and silicon pads. (c) Width 6.5 nm, 16 nm HP SiNWs after undergoing 2 thinning procedures of Piranha dip 10 min, followed by BOE etch 10 s, released by BOE and clamped by chromium pads.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Equipment</th>
<th>Description</th>
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<tbody>
<tr>
<td></td>
<td>Start with HSQ patterned SOI sample.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Spin-coat PMMA 950k in 4% ethylactate, 2000 rpm, 45 s, post-application bake 175°C, 5 min.</td>
<td>PMMA from Allresist GmbH, Strausberg, Germany. Ethylactate from Technic France, Saint-Denis, France.</td>
<td>Positive tone photoresist. Target thickness = 400 nm.</td>
</tr>
<tr>
<td>2</td>
<td>E-beam exposure, dose 850 μC/cm², aperture 400 μm.</td>
<td>VISTEC EBPG 5000+, Jena, Germany.</td>
<td>Pad areas of 20 x 10 μm², between 0.2-1 μm apart.</td>
</tr>
<tr>
<td>3</td>
<td>Development in IPA mixed 3:7 with DI water, 20 s.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Followed by IPA dip 20 s, N₂ blow-dry. Leaves pad areas open, PMMA elsewhere.</td>
</tr>
<tr>
<td>4</td>
<td>Thermal evaporation: 75 nm chromium.</td>
<td>BAE 250, Oerlikon Balzers, Liechtenstein.</td>
<td>Anchoring pads.</td>
</tr>
<tr>
<td>5</td>
<td>Lift-off in acetone.</td>
<td>Technic France, Saint-Denis, France.</td>
<td>Overnight soak. Sonication 2 min.</td>
</tr>
</tbody>
</table>
Table 2.15: Suspended SiNW anchoring pad fabrication process. The asterisked item (*) can be done either at the start of the process to obtain chromium clamped SiNWs (Fig. 2.24a) or at the end to obtain SiNWs monolithically joined to bulk silicon pads (Fig. 2.24b).

Finally, the suspended SiNWs can be further thinned down using oxidation and etching cycles. The SiNW array can be dipped in Piranha solution (H$_2$SO$_4$ 1:2 H$_2$O$_2$) to oxidise the surface, consuming ~1-2 nm of silicon per dip. The oxide is then removed in BOE. Repeating these two steps allows further thinning of the SiNWs, as summarised in Table 2.16. Widths of down to ~6.5 nm have been achieved using this procedure (Fig. 2.26c).

Table 2.16: Processes for (a) suspended SiNW release from the BOX and (b) SiNW thinning.

Steps (b1) and (b2) can be repeated for progressive thinning.

### 2.8 Summary

EUV-IL is a method to produce high-resolution periodic patterns with high throughput. Critical parameters for achieving high-resolution features include the mechanical arrangement of the setup, photoresist characteristics, and diffraction mask quality. The diffraction mask gratings must also be high-resolution and made of diffraction efficient material, making their fabrication challenging.

Diffraction gratings with various pitches, thicknesses, and materials were simulated using RCWA to calculate the maximum efficiency. A mask design where HSQ lines were written using e-beam at a relaxed pitch followed by conformal ALD of iridium and anisotropic ion milling to leave only...
iridium on the sidewalls of the HSQ lines was implemented. This resulted in the recording of line/space interference patterns down to a record 6 nm HP in HSQ resist. For more relaxed line/space patterns between 10-25 nm HP, masks composed of direct write e-beam HSQ gratings was sufficient.

Other EUV-IL schemes were also explored. Achromatic Talbot lithography was shown to be a robust method for producing periodic dot patterns of 20 nm dot size and 106 nm period with very high throughput at two different beamline facilities. Bessel beam lithography was shown to be able to write arbitrary patterns over surfaces of varying height and curvature due to the large depth-of-focus and self-healing nature of the small (20 × 30 nm²) beam spot.

Optimization of the plasma etching process allowed pattern transfer of line/space HSQ patterns into silicon down to 16 nm HP, resulting in the fabrication of SiNWs with 16 nm HP and widths between 10 – 20 nm per the patterning dose. These SiNW structures can be fabricated on SOI substrates, with e-beam defined anchoring pads and released by under-etching the BOX. This resulted in suspended SiNWs down to 16 nm HP, widths down to 6 nm following SiNW oxidation and oxide removal, and aspect ratios up to 1:80.
3 Characterisation Methods and Models

This chapter describes SiNW characterisation methods, in particular their thermoelectric properties. Measurement of strain and quantum confinement will also be discussed. Following a brief survey of nano-characterisation techniques, Raman spectroscopy will be presented as the main characterisation tool. This includes the theory and application to nanostructures and the measurement setup and calibration. A section on the thermal and optical modelling of suspended SiNWs follows as preparation for measurement interpretation. Parts of section 3.3 will be submitted for publication as supplementary information for the article.

- D. Fan, H. Sigg, R. Spolenak, Y. Ekinci, “Strain and thermal conductivity in ultra-thin suspended silicon nanowires,” to be submitted.

where D. Fan performed the simulations and analysis and all authors suggested concepts and revised the supplementary information.

3.1 Characterisation methods

Measurement of the thermal and electrical transport properties of nanowires are strongly dependent on the sample configuration. Single nanowires require very sensitive, highly localised methods, and accurate placement of the probe and nanowire, involving complicated fabrication and placement techniques. On the other hand, nanowire arrays need to be well-ordered or the measurement signal needs to be deconvoluted from the averaging effect of an array of nanowires of various sizes, dimensions, orientations, and placements. Table 3.1 lists a summary of the major SiNW characterisation techniques, available for both single nanowires and nanowire arrays.
SiNW materials properties are also highly dependent on their fabrication method. VLS growth SiNWs can achieve single-digit-nm diameters, however their size and orientation distributions between nanowires and along the nanowire itself can be large. Further, they are difficult to precisely place and therefore difficult to incorporate into devices. The available crystal orientations are also restricted. Similarly, electrochemically etched nanowires can have a size and orientation distribution, making the analysis of their properties more complicated. Top-down fabricated SiNWs such as via lithography and etching allow precise placement and size and orientation control but have not regularly reached sub-10-nm dimensions, as the feature size has been limited by the optical lithography wavelength.

<table>
<thead>
<tr>
<th>Method</th>
<th>Measurement</th>
<th>Advantages / disadvantages</th>
</tr>
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<tbody>
<tr>
<td>4-point probe on substrate</td>
<td>Electrical: IV curve. Thermal: Wiedemann-Franz law for metal NWs, AC methods such as the 3-ω method, Harman technique.</td>
<td>Easier fabrication of contacts. Needs thermally insulating substrate and environment.</td>
</tr>
</tbody>
</table>

Table 3.1: Summary of standard nanowire characterisation methods for measurement of thermal and electrical transport.

### 3.2 Raman spectroscopy

Inelastic scattering of sunlight in various liquids was first observed by Raman [110]. A small amount of the incident light is inelastically scattered to either longer (Stokes) or shorter (anti-Stokes) wavelengths. The difference in wavelength represents the vibrational energy of the chemical bond which is participating in the scattering process. Thus, Raman spectroscopy has become a versatile, non-destructive, and standard method for materials characterisation, probing a materials' chemical composition, structure, thermal properties, strain, quantum confinement, and phonon dispersion. Together in confocal or tip-enhanced arrangements, Raman spectroscopy can probe the properties of nanostructures at submicron resolution.
3.2.1 Theory

During the scattering process, a photon with energy $h\nu$ and wave-vector $k$ excites the system from an initial state to an excited state. The system then emits a photon with energy $h\nu'$ and wave-vector $k'$ and the system energy drops from the excited state to the final state. If the initial and final states are the same, the incident and scattered light are equal, giving elastic or Rayleigh scattering. If the final state is different from the initial state, the incident and scattered light are different, giving inelastic or Raman scattering (Fig. 3.1a). Scattered light which has lower energy is related to the creation of an excited state, otherwise known as Stokes scattering. Scattered light with a higher energy means the annihilation of an excited state, i.e. anti-Stokes scattering (Fig. 3.1b).

![Diagram of scattering processes](image)

**Fig. 3.1:** Schematic of (a) various scattering processes where arrows represent energy transitions and lines represent energy states, (b) spectrum showing difference in wavelength between Raman scattered light and incident light, and (c) coordinate system of the measurement showing microscope objective and laser probe focused on a sample.

The states of the system can be related to the quantized lattice vibrations in a crystal (phonons) or the vibrational modes of a molecule. Scattered light is related to the polarisation density $P$ of the scatterer,

$$P = \chi E$$  \hspace{1cm} (3.1)

where $E$ is the incident electric field and $\chi$ is the electric susceptibility. If $\chi$ is a time-dependent quantity such as a phonon, it can modulate the incident light into frequency sidebands, i.e. the Stokes and anti-Stokes shifts.
The probability of Stokes and anti-Stokes scattering are different because of the different population levels of the two energy levels (ground and excited states) at a certain temperature $T$. Therefore, by measuring the Stokes and anti-Stokes intensities, the temperature of the system can be calculated. The scattering intensity $I$ depends on the polarisation vectors of the incident $e_i$ and scattered $e_s$ light, given by

$$I = C \sum_j |e_i \cdot R_j \cdot e_s|^2 \quad 3.2$$

where $C$ is a constant and $R_j$ is the Raman tensor of the phonon $j$. The Raman tensors are derived for each of the 32 crystal classes using group theory considerations [111]–[113]. For silicon in the crystal coordinate system $x = <100>, y = <010>, z = <001>$, the Raman tensors are given as

$$
R_x = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix};
R_y = \begin{pmatrix}
0 & 0 & 1 \\
0 & 0 & 0 \\
1 & 0 & 0
\end{pmatrix};
R_z = \begin{pmatrix}
0 & 1 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix} \quad 3.3
$$

Combining Eq. 3.2 and 3.3, for backscattering from a (001) surface, only the $z$-polarised phonon (the longitudinal optical or LO phonon) can be observed. Meanwhile, the transverse optical (TO) phonons cannot be observed. However, by using a high numerical aperture (NA) objective, incident light can be directed at an angle to excite components other than the (001) surface. In this case TO phonons can be observed [114].

### 3.2.2 Raman measurements of SiNWs

Extensive Raman work has been done on SiNWs, where the Raman peak shift and shape can be related to strain, thermal effects, and confinement effects [21], [31], [32], [96]–[109], [115]–[120]. The largest and most common contributor to Raman peak shift and broadening are thermal effects such as those due to local laser heating or insufficient thermal contact between SiNW and substrate [119]. Temperature $T$ can be calculated from the Stokes/anti-Stokes intensities ($I_S$, $I_{AS}$) by [96]

$$
\frac{I_S}{I_{AS}} = C \left( \frac{\omega_S}{\omega_{AS}} \right)^3 \exp \left( \frac{\hbar \omega}{k_B T} \right) \quad 3.4
$$
where $\omega_S$ and $\omega_A$ are the Stokes and anti-Stokes photon frequencies respectively, $\omega$ is the phonon frequency, $C$ is a constant determined by the absorption constants and Raman cross-sections, and $k_B$, $h$, and $c$ are the constants of Boltzmann, Planck and the speed of light respectively.

Independent of intensity, the temperature dependent part of the Raman peak shift at room temperature can be approximated by the linear relation [96]

$$\frac{d\omega}{dT} \approx -3\omega_0\gamma \alpha_{TE} + \frac{k_B}{h\omega_0} \left[ 4A + 9B \right]$$

where $T$ is the temperature, $\alpha_{TE}$ is the coefficient of linear thermal expansion, $\gamma$ is the Grüneisen parameter, $\omega_0$ is the optical phonon frequency at the zone centre ($\Gamma$-point), and $A$ and $B$ are the cubic and quartic harmonic constants respectively. Therefore, for bulk silicon, the Stokes/anti-Stokes peak position can be related to temperature using the relation $\frac{d\omega}{dT} = -0.024 \text{ cm}^{-1}/\text{K}$ [121], [122].

Due to the conservation of momentum, only the $\Gamma$-point phonons participate in the scattering. For the silicon crystal, the optical branch phonons (TO and LO) are degenerate at the $\Gamma$-point with an energy of approximately 520 relative wavenumbers (rel. cm$^{-1}$). For nanostructures where some dimension is below the phonon de Broglie wavelength, the phonon is then confined. From Heisenberg’s uncertainty principle, the phonon momentum becomes broadened and phonons away from the $\Gamma$-point can participate in the scattering process. For SiNWs below 15 nm, this quantum confinement effect causes peak shifts and asymmetric peak broadening [123]–[125].

The effect of stress on the frequencies of the three optical modes can be found by using the phonon deformation potentials ($p$, $q$, and $r$) of silicon and the secular equation

$$\begin{vmatrix}
  p\varepsilon_{11} + q(\varepsilon_{22} + \varepsilon_{33}) - \lambda & 2r\varepsilon_{12} & 2r\varepsilon_{13} \\
  2r\varepsilon_{12} & p\varepsilon_{22} + q(\varepsilon_{33} + \varepsilon_{11}) - \lambda & 2r\varepsilon_{23} \\
  2r\varepsilon_{13} & 2r\varepsilon_{23} & p\varepsilon_{33} + q(\varepsilon_{11} + \varepsilon_{22}) - \lambda
\end{vmatrix} = 0 \quad 3.6$$

where $\varepsilon_{ij}$ are the strain tensor components. Therefore strain, depending on the crystal direction, can be related to peak shifts for the different optical mode phonons [113], [114], [126]. For uniaxial stress $\sigma$ in the $<100>$ direction and Raman scattering in the backscattering arrangement on a (001) surface, the Raman peak shift is

78
\[ \Delta \omega = -2 \times 10^{-9} \sigma \]  

where \( \Delta \omega \) is in \( \text{cm}^{-1} \) and \( \sigma \) in units of \( \text{Pa} \). Similarly, in the \( <110> \) direction

\[ \Delta \omega = -3 \times 10^{-9} \sigma \]

For compressive stress this equates to an increase in the Raman frequency shift while tensile stress will cause a decrease.

Combining a phonon confinement model based on bond polarizability [125] and a simple uniaxial strain model [118], the Raman shift due to quantum confinement and uniaxial elastic strain for a SiNW is

\[ \Delta \omega = -D \left( \frac{a_0}{D_w} \right)^{\beta} - n \gamma \omega_0 \frac{a - a_0}{a_0} \]  

where \( \Delta \omega \) is the phonon shift from the optical phonon frequency at the zone centre, \( a_0 \) is the bulk silicon lattice constant, \( a \) is the silicon nanowire lattice constant, \( D_w \) is the SiNW diameter, \( n \) is the dimensionality (for SiNWs \( n = 1 \)), and \( D = 20.92 \) and \( \beta = 1.08 \) are fitting parameters. \( D_w \) can be replaced for a SiNW with rectangular cross-section (width \( w \), height \( t \)) with the effective size

\[ D_w = \frac{2\sqrt{wt}}{\sqrt{\pi}} \]

Much of the work done using Raman on SiNWs has been on chemically synthesized or chemically etched SiNWs, which typically exhibit a size, position, and orientation distribution. Therefore, the Raman spectra requires further deconvolution to account for these geometric distributions within the laser probe spot [127].

Finally, the absorption depth of silicon versus wavelength of incident light is plotted in Fig. 3.2. It shows that for high surface sensitivity and good light absorption for ultra-thin SiNWs below 20 nm, the incident wavelength should be below about 365 nm in the deep UV. Longer wavelengths not only penetrate deeper into the substrate, but since depth-of-focus is proportional to \( \lambda \), the interaction depth of the focal point for longer wavelengths is also much larger. This gives a large bulk silicon Raman signal which may overwhelm the subtle Raman peaks of the ultra-thin SiNWs.
3.2.3 Measurement setup and calibration

The fabricated specimens were measured using a home-built micro-Raman spectroscopy setup based on a 405-nm single-mode continuous wave laser (405L-21, Integrated Optics, Vilnius, Lithuania). The wavelength was chosen to achieve maximum surface sensitivity whilst still being able to use standard microscope objectives and optics. Preliminary measurements using a 532-nm laser and 442-nm laser show that the SiNW Raman peak becomes progressively prominent as the wavelength decreases. For the 532-nm laser, the SiNW Raman signal is so small compared with the substrate that it only manifests itself as a slight peak asymmetry and broadening (Fig. 3.3).

![Graph showing absorption depth versus wavelength for silicon](image)

Fig. 3.2: Absorption depth versus wavelength for silicon [128].

![Graphs showing SiNW on silicon substrate Stokes peak](image)

Fig. 3.3: SiNW on silicon substrate Stokes peak for (a) 532 nm incident light and (b) 442 nm incident light. For shorter wavelengths, the SiNW Raman signal becomes stronger and the peak more prominent.

An inverted microscope (Leica DMI5000 M, Wetzlar, Germany) was used as the sample stage, together with a 100× objective, NA = 0.9. This was followed by a 405-nm notch filter to allow both
Stokes and anti-Stokes detection, then a 40 µm slit entrance onto an 1800 lines/mm spectrograph (Acton SP500i, Princeton Instruments, U.S.A.). The light was recorded by a single-photon CCD camera (EmCCD, ProEM 1600², Princeton Instruments, U.S.A.) and controlled using WinSpec software (WinSpec/32 v 2.6.19.0, Princeton Instruments, U.S.A.). The camera and spectrograph arrangement resulted in a measurement resolution of 0.015 nm. Summation of three 30 s exposures was sufficient to achieve acceptable signal-to-noise ratio, and the laser power was measured at the sample using a power meter (Fieldmaster, Coherent, Santa Clara, U.S.A.). Two half-wave plates at the entrance and exit of the microscope allowed polarization dependent measurements. The experimental arrangement is shown in Fig. 3.4 with the equipment details described in Table 3.2.

Calibration of the spectrograph was performed using the known emission lines in a standard argon lamp. The laser light through a 100×, NA = 0.9 objective, was then scanned in the x-direction on a piece of cleaved silicon crystal. The intensity was measured for each stage position, with the position marked when the light was 10% and 90% of maximum, for various laser powers between 50 µW to 1.5 mW. The spot size was thus calculated to be 1.78 ± 0.3 µm. Next, white light was applied into the spectrograph and recorded by the CCD camera, with and without Raman filter. The two spectra were divided upon each other to obtain an intensity correction factor. The transmission of the Raman filter in the Stokes and anti-Stokes regions are different and thus the intensity must be corrected. Finally, a measured power range between 0 and 175 µW fell on the sample, i.e. a power density of up to ~70 µW/µm².
<table>
<thead>
<tr>
<th>Item</th>
<th>Equipment</th>
<th>Manufacturer</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Laser $\lambda = 405$ nm</td>
<td>Integrated Optics, Vilnius, Lithuania.</td>
<td>Single mode up to 10 mW</td>
</tr>
<tr>
<td>(b)</td>
<td>Bandpass filter 405 nm</td>
<td>Iridian Spectral Tech., Ottawa, Canada.</td>
<td>For cleaning the laser line</td>
</tr>
<tr>
<td>(c)</td>
<td>Broadband dielectric mirror</td>
<td>Edmund Optics, York, U.K.</td>
<td>For beam adjustment</td>
</tr>
<tr>
<td>(d)</td>
<td>$\lambda/2$-wave plate</td>
<td>Edmund Optics, York, U.K.</td>
<td>For polarization adjustment</td>
</tr>
<tr>
<td>(e)</td>
<td>Broadband dielectric mirror</td>
<td>Edmund Optics, York, U.K.</td>
<td>For beam adjustment</td>
</tr>
<tr>
<td>(f)</td>
<td>Pinhole</td>
<td>Edmund Optics, York, U.K.</td>
<td>For beam alignment</td>
</tr>
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<td>(g)</td>
<td>Lens</td>
<td>Edmund Optics, York, U.K.</td>
<td>For beam alignment</td>
</tr>
<tr>
<td>(h)</td>
<td>Pinhole</td>
<td>Edmund Optics, York, U.K.</td>
<td>For beam alignment</td>
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<td>For beam alignment</td>
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<tr>
<td>(j)</td>
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<td>Edmund Optics, York, U.K.</td>
<td>For beam alignment</td>
</tr>
<tr>
<td>(k)</td>
<td>Inverted microscope</td>
<td>Leica DMIS5000 M, Wetzlar, Germany.</td>
<td>For sample placement and micro-Raman using 100x, NA = 0.9 objective</td>
</tr>
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<td>Edmund Optics, York, U.K.</td>
<td>For beam alignment</td>
</tr>
<tr>
<td>(m)</td>
<td>$\lambda/2$-wave plate</td>
<td>Edmund Optics, York, U.K.</td>
<td>For beam alignment</td>
</tr>
<tr>
<td>(n)</td>
<td>Notch filter OD6, 405 nm</td>
<td>Edmund Optics, York, U.K.</td>
<td>For beam alignment</td>
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<td>(o)</td>
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<td>Demagnification 3×</td>
</tr>
<tr>
<td>(p)</td>
<td>Lens spherical f = 50 mm</td>
<td>Edmund Optics, York, U.K.</td>
<td>Demagnification 3×</td>
</tr>
<tr>
<td>(q)</td>
<td>Adjustable slit, 40 $\mu$m</td>
<td>Edmund Optics, York, U.K.</td>
<td>Resolution vs collection time</td>
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<td>Shutter</td>
<td>Edmund Optics, York, U.K.</td>
<td>For high-resolution at 0.015 nm per pixel.</td>
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<tr>
<td>(s)</td>
<td>Spectrograph 1800 lines/mm</td>
<td>Edmund Optics, York, U.K.</td>
<td>For high-resolution at 0.015 nm per pixel.</td>
</tr>
<tr>
<td>(t)</td>
<td>CCD camera</td>
<td>ProEM 1600$^2$, Princeton Instruments, U.S.A.</td>
<td>Single photon detection. Pixel size = 16 $\mu$m.</td>
</tr>
</tbody>
</table>

Table 3.2: Details of optical elements for Raman spectroscopy setup shown in Fig. 3.4.
Fig. 3.5: Left, scan of a piece of cleaved silicon at a laser power of 1 mW to find the laser spot size (1.78 µm). Right, intensity of broadband lamp with and without Raman filter to find the intensity correction factor.

3.3 Thermal model of suspended SiNW array

3.3.1 Model and geometry

The suspended SiNW array structure under investigation is shown in Fig. 3.6. The suspended SiNWs are either connected monolithically to large silicon pads at both ends or clamped by metal at both ends. In the first case, the silicon pads are 20 nm thick, 10 µm long, and 20 µm wide. Underneath the silicon pads is 140-nm-thick SiO₂. On top of the silicon pads is 75-nm-thick chromium. Between the pads the suspended SiNWs are typically 570-nm-long and vary in width between 10 to 20 nm. The SiNW widths and LER were measured by SEM combined with image analysis software (SuMMIT, Lithometrix). The SiNW thickness was measured to be 20 nm ± 5% via cross-sectional SEM image (Fig. 3.7). Below the SiNWs is 140-nm-thick air gap while the whole assembly sits on top of a 750-µm-thick silicon handle wafer. The SiNW cross-sections can vary between rectangular to trapezoidal (Fig. 3.7).
Fig. 3.6: (a) Schematic of suspended SiNW array where the SiNWs are connected monolithically to silicon pads. These pads have silicon oxide below and chromium metal above. The whole arrangement sits on top of a silicon handle wafer. The inset shows modelling of constrictions for FEM analysis. (b) SEM image at tilted angle of suspended SiNW array.

Fig. 3.7: SEM cross-section image of SiNW anchoring pad. Left: thickness was measured with an error of ~5%. The undercut of etched BOX can be observed. Right: nanowire region. The SiNWs are in/out of plane. In the bottom left are collapsed SiNWs which have trapezoidal shape with dimensions of 19 × 19 nm². The holes are the EUV-IL patterned HSQ lines which are transferred into the silicon device layer via RIE.

A simple model for the heat generation and transport is shown in Fig. 3.8. Since the laser spot size (1.78 µm) is much larger than the SiNW length (570 nm) the incident laser intensity along the SiNW is assumed to be homogeneous and thus heat is generated homogeneously by laser irradiation along the SiNWs. Using finite element method (FEM) simulations the primary heat transport is along the SiNW and into the large anchoring pads at both ends.
Fig. 3.8: Schematic side-view of suspended SiNW with incoming laser light. The suspended SiNW is homogeneously heated by laser irradiation as the laser spot is much larger than the suspended region. Heat conduction occurs along the nanowire in the direction of the large anchoring pads on each side.

Therefore, the system can be described by the 1D heat equation, in the steady-state, with a constant rate of heat generation per unit volume [57]

\[
\frac{d^2 T}{dx^2} = -\frac{P_v}{\kappa}
\]

where \( T \) is the temperature, \( x \) is the position along the SiNW, \( P_v \) is the power absorbed per unit volume in the SiNW which heats the structure, and \( \kappa \) is the thermal conductivity. The solution, for symmetric boundary conditions where the temperature at both ends of the SiNW is the same (\( T_0 \)), is

\[
T(x) = \frac{P_vL^2}{8\kappa} \left( 1 - \frac{4x^2}{L^2} \right) + T_0
\]

where \( L \) is the SiNW length. The average temperature of the SiNW is then

\[
T_{avg} = \frac{1}{L} \int_{-L/2}^{+L/2} T(x) \, dx = \frac{1}{L} \int_{-L/2}^{+L/2} \left( \frac{P_vL^2}{8\kappa} \left[ x - \frac{4x^3}{3L^2} \right]_{-L/2}^{+L/2} + T_0 \right)
\]

which simplifies to
where \( T_{\text{avg}} \) is measured by Raman scattering and \( T_0 \) is the boundary condition calculated by FEM to be fixed under certain conditions (see section 3.3.3).

### 3.3.2 Power absorption simulations (RCWA)

The absorbed power was calculated by measuring the laser power at the objective, measuring the spot size, and calculating the power absorption factor in the SiNW thin film array. Since the SiNW array is periodic, rigorous coupled-wave analysis (RCWA) [82] could be used, a semi-analytical method based on Maxwell’s equations to fully solve the light absorption in the nanostructures (Fig. 3.9), at the laser wavelength of 405.3 nm. The absorption factor was constant for the nanowire dimensions under investigation: roughly 0.06 for SiNW thicknesses between 15 and 25 nm, widths between 10 and 20 nm, and under-etch between 100 to 140 nm. Material properties were obtained for silicon [128], silicon oxide [130], and chromium [131] from standard references.

The laser power absorbed per unit volume in the SiNW array is:

\[
P_V = \frac{\alpha P_{\text{den}}}{D.C.}
\]

where \( P_{\text{den}} \) is the power density of the laser spot at the sample plane, \( \alpha \) is the absorption factor calculated by RCWA for each SiNW width, and \( D.C. \) is the duty cycle of the SiNW array. Duty cycle is incorporated as it is assumed that most light is absorbed in the SiNW and the absorption of the surrounding air is negligible. Since it is also assumed that heat transport is in one direction along the SiNW only (it is shown in section 3.3.3 that radiation and convection are negligible), then the thermal conductivity of a single SiNW is the total thermal conductivity of the array divided by the number of parallel, irradiated SiNWs.

The error in thickness measurement using SEM is around \( \pm 5\% \) \((\pm 1 \text{ nm})\). The consequent error in \( \alpha \) is \( \pm 3\% \). The error in power measurement is \( \pm 2\% \) while the error in spot size measurement is \( \pm 3\% \). Finally, the error in SiNW width measurement by SEM is \( \pm 5\% \), giving a total error in power absorption of approximately \( \pm 20\% \).
Fig. 3.9: RCWA calculations of absorption $\alpha$ at $\lambda = 405$ nm and under-etch $= 140$ nm for suspended SiNWs with 44 nm pitch and variable width and thickness. (a) Reflection and (b) absorption in the TE mode for SiNWs with variable widths and thicknesses. (c) Thickness $= 20$ nm and (d) width $= 15$ nm for various widths and thicknesses respectively. The absorption does not vary greatly over the range of interest. (e) Variable incident wavelength. The wavelength used is 405 nm due to availability of optical components, although using shorter wavelength light would result in greater absorption and stronger Raman signal. (f) Versus degree of under-etch, the absorption is relatively constant if the degree of under-etch is varying in the range of interest.
3.3.3 Heat transport simulations (FEM)

The FEM software package COMSOL Multiphysics (Stockholm, Sweden) was used to model and calculate heat transport in the SiNW array. The far edges of the pads were assumed to be at room temperature (293.15 K) while other surfaces were made thermally insulating. Standard materials properties were used while the thermal conductivity of the SiNWs was varied and the average temperature calculated.

Fig. 3.10: Schematic of FEM model where the boundaries in blue are set to room temperature 293.15 K. Top inset shows the SiNW array with the heat generation area. Bottom inset shows the different layers of materials.

For heat transfer between nanowires in the array, note that the measured dependency between laser power and Raman shift appears to be linear, and combined with Eq. 3.5, shows radiation is negligible since radiation scales to $T^4$. Convection was also found to be negligible as follows: SiNW arrays at 44 nm pitch, 20 nm width, and 570 nm length were simulated, with the ends set to room temperature, and the array either surrounded by air or vacuum. The heat generation was set either to the realistic RCWA adjusted value of $2 \times 10^{14} \text{W/m}^3$ or to the maximum possible $3 \times 10^{15} \text{W/m}^3$ assuming all incident power is absorbed. The simulation results for maximum change in temperature is shown in Table 3.3. The temperature rise most accurately reflecting experimental values was for SiNWs with the calculated heat generation and surrounded by vacuum. Therefore, convection is negligible.
Surrounded by air | Surrounded by vacuum
--- | ---
Heat generation = $2 \times 10^{14}$ W/m$^3$ | 0.21 K | 12 K
Heat generation = $3 \times 10^{15}$ W/m$^3$ | 3.09 K | 180.2 K

Table 3.3: COMSOL simulation results of maximum temperature rise in SiNW array surrounded by different mediums and with different heat generation.

For heat transfer along the SiNW, there are two cases: a) SiNW connected monolithically to silicon bulk; b) SiNW clamped by chromium. The test structure parameters are as follows: $L = 580$ nm, $w = 15$ nm, $t = 25$ nm, heat generation = $2 \times 10^{14}$ W/m$^3$, $\kappa$ set to 1 W/m.K, and the SiNWs connected to 25 nm thick bulk silicon. Three cases were tested: the SiNW array pads were connected to SiO$_2$ (BOX) below, SiNW array and pads floating on air, and SiNW array and pads isolated in vacuum. The last case represents the worst-case heat transfer, where heat can only be transported through the bulk silicon pads away from the SiNW array.

For all three cases, the maximum temperature in the middle of the SiNWs was 308 K while the end temperatures of the SiNW where they connect to the bulk silicon were all at 293 K. This shows that the boundary conditions are pinned to room temperature at either end and any under-etching of the BOX has no effect on the boundary conditions.

Next, the SiNW array was clamped by chromium, and an air-gap was slowly introduced between the chromium and the SiNWs. The test structure parameters were same as before, while the air-gap surrounding the SiNWs was increased. The result is that as the air-gap increased both the maximum temperature and the boundary temperature increased. The thermal contact resistance is therefore dramatically raised at the ends of the nanowire (Fig. 3.11). Since the air-gap is unknown, the thermal resistance is unknown and cannot be modelled. Therefore, since the boundary condition is now unknown, $\kappa$ cannot be accurately determined from the measured temperature.

In summary, heat transfer in suspended SiNWs can be modelled by conduction along the nanowire alone. For SiNWs connected monolithically to bulk silicon the boundary condition can be considered pinned to room temperature and thus the thermal conductivity can be measured and calculated. For SiNWs clamped by chromium the boundary conditions are unknown and thus the thermal conductivity cannot be known.
Fig. 3.11: (a) Schematic of SiNW under-etch by HF. (b) SEM of SiNW clamped by chromium and released by BOE, where air-gap is apparent due to under-etching of chromium oxide. (c) COMSOL simulation of the temperature for SiNWs connected to silicon (top) and chromium with an air-gap (bottom). In the latter case the temperature at the boundary condition is unknown.

3.3.4 Sensitivity analysis of heat transport (FEM)

Variability in the SiNW geometry, anchoring pad geometry, and laser spot power and position, can all cause variability in the heat transport. It is necessary to understand how variations in the experimental arrangement can influence the resulting thermal conductivity of the SiNW. These variations were simulated using FEM and the changes in temperature and thermal conductivity calculated, for monolithically connected SiNWs.

For anchoring pad size, the ideal case is for infinite size pads with room temperature at the infinite boundary. The pad width was kept constant at 20 µm, while the length was varied from 1 to 20 µm. It was found that temperature for 10 µm length pads was sufficiently close to the asymptotic value and any further variations in pad length did not affect the temperature.

It was noticed via SEM that the SiNWs often had pinched or constricted connections to the anchoring pads. This occurred due to processing variations. A 20-nm-wide SiNW was modelled, with constricted regions 20 nm long and varying between 4 to 20 nm introduced at the ends of
the SiNW. All regions had the same nominal $\kappa$. The variation in temperature over the region of interest was $\pm$ 0.5 K, possibly only due to the contact area between the regions. This represents an error in $\kappa$ of around $\pm$ 3-4%. If $\kappa$ is different between the constriction and SiNW, the effect is negligible since the thermal resistance of the wire is much larger, due to its length, than the constricted areas, and the wire therefore dominates heat transport.

The laser spot position was varied along the SiNW. The Gaussian shape of the beam was not considered. Since the SiNWs are typically ~600 nm long, if the spot is 1 $\mu$m away the Raman signal is negligible. Therefore, the maximum variation in temperature due to variation in laser spot position is $\pm$ 0.2 K. In all three cases above, the SiNW boundary temperature remained fixed and was insensitive to variations. Therefore, the power-temperature relationship is dominated by the SiNW and not the pad.

![Simulation of temperature with varying pad length for SiNW width = 20 nm. At 10 $\mu$m pad length the temperature is relatively stable and insensitive to pad length changes.](image)

Finally, the cross-sectional shape was changed from rectangular ($w = 16$ nm, $t = 20$ nm), to trapezoidal (bottom $w = 16$ nm, top $w = 10$ nm, $t = 20$ nm), to simulate fabricated samples where variations in pattern transfer result in etching profiles of SiNWs with markedly sloped sidewalls. For a test heat generation of $5 \times 10^{14}$ W/m$^3$, and $\kappa = 0.8$ W/m.K, the difference in $\Delta T$ was found to be an increase of 2.2%. Variations in cross-sectional shape would also result in variations in power absorption. Although this was not studied in detail, estimates from Fig. 3.9 indicate that variations in $\alpha$ due to cross-sectional shape would not be significant.
Fig. 3.13: Simulations of temperature for SiNW with width = 20 nm and varying constriction widths. In the range of constriction widths of interest (~ 80%) the temperature varies by at most ± 4%.

Fig. 3.14: FEM simulations of temperature in a SiNW with width = 20 nm as the spot position is varied. The variation in temperature is small, a few tenths of a degree Kelvin (± 1%), and when the temperature increases the spot is far enough away from the SiNW such that the Raman scattering would be too small to detect.

In all cases above, the boundary temperatures were pinned as the power varied. Therefore, any change in measured temperature is known to be a result of the SiNW heat transport and not the pad heat transport, and κ could be determined. The total variability in temperature combining all the above factors was ± 8%. The error in $P_V$ was around ± 20% while the SiNW length was measured via SEM to have an error of ± 1%. This gives a total error in κ of ~ ± 30%.

For example, take a SiNW array with the following SEM measurements of dimensions: $w = 14$ nm, $t = 20$ nm, $L = 580$ nm. RCWA simulations show a power absorption factor of $\alpha = 0.07$. The laser
power was varied and the Raman signal recorded for each incident power. Each Raman spectra was interpreted to provide an average temperature $T_{\text{avg}}$ of the SiNW array. This power-temperature dependency was linearly fitted to show a change in temperature of 16 K for a power density of 68.7 $\mu$W/um$^2$, i.e. a heat generation of $7.56 \times 10^{14}$ W/m$^3$.

Although the boundary temperature $T_0$ is unknown, FEM simulations showed that for monolithically connected SiNWs $T_0$ is essentially pinned and does not vary (whereas for clamped SiNWs $T_0$ can vary considerably per the degree of under-etch, which is unknown). It is assumed that the far edges of the anchoring pads are at room temperature.

The simulation inputs are therefore: boundary condition at far edge of pads, heat generation and dimensions as described above. The input variables are $\kappa$ of the SiNWs and the heat generation per unit volume $P_V$, while the output is $T_{\text{avg}}$. The $\kappa$ was changed iteratively until a temperature matching the measured Raman temperature was obtained. This gave a $\kappa$ in this example of $\kappa = 1.32$ W/m.K, with an error of $\pm 0.4$ W/m.K ($\pm 30\%$).
4 Materials Properties of SiNWs

Well-ordered, large area, suspended SiNW arrays at 22 nm HP and widths between 9 and 24 nm on a lightly p-doped, (100), 20-nm-thick SOI substrate were fabricated (see Chapter 2). The thermal properties of the suspended nanowires were measured using Raman spectroscopy. Different methods of SiNW anchoring and under-etch release were tried to observe the impact of the processing method on materials properties. A summary of the different types of samples is listed in Table 4.1.

SEM images of typical structures were used for measurement of width and LER and shown in Fig. 4.1. SiNW arrays clamped by chromium metal and released by BOE are shown in Fig. 4.1c, SiNW arrays monolithically connected to bulk silicon pads and released by VHF in Fig. 4.1d, and SiNW arrays monolithically connected to bulk silicon pads and undergoing Piranha oxidation and BOE etching for decreasing the width followed by CPD shown in Fig. 4.1e.

Parts of this chapter will be submitted for publication as the article

- D. Fan, H. Sigg, R. Spolenak, Y. Ekinci, “Strain and thermal conductivity in ultra-thin suspended silicon nanowires,” to be submitted.

where D. Fan performed the simulations, fabrication, experiment, and analysis, H. Sigg and R. Spolenak suggested the experimental concept, and all authors revised the manuscript.
Fig. 4.1: Schematic of suspended SiNWs with anchoring pads composed of chromium clamping metal (a), and monolithically connected silicon pads (b). SEM images of suspended SiNWs with (c) chromium clamping metal and structure release by BOE under-etch (LER ~ 2 nm), (d) monolithic silicon pads and release by VHF (LER ~ 2 nm), and (e) monolithic silicon pads and release by BOE followed by CPD for width thinning (LER ~ 4 nm).

<table>
<thead>
<tr>
<th>Anchoring methods</th>
<th>Release methods</th>
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<tbody>
<tr>
<td><strong>Si</strong>: SiNWs monolithically connected to large silicon pads at both ends. On top of the silicon pads is 75 nm of chromium for discharging during SEM inspection. Constrictions can appear at the ends due to the etching process.</td>
<td><strong>VHF</strong>: vapour hydrofluoric acid uses HF in the vapour phase to etch the BOX without causing stiction. The resulting LER is typically low.</td>
</tr>
<tr>
<td><strong>Cr</strong>: SiNWs are etched first and then clamped by metal deposition at both ends. There are no constrictions at the ends. However, since the SiNWs in the anchoring area have an interface between the metal above and the oxide below, an air-gap may form during release etching.</td>
<td><strong>BOE</strong>: buffered oxide etch (HF 1:7 NH₄F) in liquid state to etch the BOX. The specimen is placed in IPA last for quick drying. The yield is low due to stiction from capillary forces during drying. The LER is also low.</td>
</tr>
<tr>
<td></td>
<td><strong>CPD</strong>: involves Piranha oxidation for width reduction and BOE, while the last step is critical point drying to avoid stiction. The LER is high.</td>
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Table 4.1: Suspended SiNW fabrication variations and the resulting properties.
4.1 Preliminary Raman measurements

The incident polarization dependency of the Raman peak intensity was measured using a half-wave plate before the sample for the incident polarization and a half-wave plate combined with Glan-Thompson filter after the sample to select a scattered polarization and then match the spectrograph grating polarization response for maximum intensity. Here, 0° is the TE mode (polarization aligned along the nanowire).

Due to the dielectric mismatch between SiNW and air, a large polarization anisotropy is exhibited where both SiNW and substrate peaks are polarization dependent (Fig. 4.2, left), evidence that the Raman signal is produced by the SiNWs. By tuning the polarization both SiNW and substrate peaks can be observed at equal intensity, allowing for better peak fitting (Fig. 4.2, left inset). The Raman peak of the suspended SiNW array was also recorded whilst scanning the focus position. The SiNW and substrate peaks are both clearly visible only in the surface region (Fig. 4.2, right), further evidence that the signal is produced by the SiNWs.

![Fig. 4.2: Left: polarisation dependency of Raman intensity on SiNW sample. Right: focus dependency of Raman intensity on SiNW sample. All intensity scales are arbitrary.](image)

For three representative SiNW samples, the Raman spectra were recorded for various laser powers, the Stokes/anti-Stokes intensities \( I_S, I_{AS} \) were measured, and the temperature was calculated (Fig. 4.3) using Eq. 3.4 (the relevant equations from Chapter 3 are repeated in Table 4.2).
\[ \frac{I_S}{I_{AS}} = C \left( \frac{\omega_S}{\omega_{AS}} \right)^3 \exp \left( \frac{h \omega}{k_B T} \right) \]

\[ \frac{d\omega}{dT} \approx -3\omega_0 \gamma_{TE} + \frac{k_B}{h \omega_0} [4A + 9B] \]

\[ \Delta \omega = -D \left( \frac{a_0}{D_w} \right)^\beta - n \gamma \omega_0 \frac{a-a_0}{a_0} \]

\[ D_w = \frac{2 \sqrt{\omega l}}{\sqrt{\pi}} \]

\[ \kappa = \frac{P_v L^2}{12 (T_{avg} - T_0)} \]

\[ P_v = \frac{\alpha P_{den}}{t \times D.C.} \]

<table>
<thead>
<tr>
<th>Equation</th>
<th>#</th>
<th>Parameters</th>
</tr>
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<tbody>
<tr>
<td>[ \frac{I_S}{I_{AS}} = C \left( \frac{\omega_S}{\omega_{AS}} \right)^3 \exp \left( \frac{h \omega}{k_B T} \right) ]</td>
<td>3.4</td>
<td>- Stokes and anti-Stokes intensities ( (I_S, I_{AS}) ); - Stokes and anti-Stokes photon frequencies ( (\omega_S, \omega_{AS}) ); - Phonon frequency ( (\omega) ); - Constant from absorption cross-section ( (C) ); - Boltzmann constant ( (k_B) ); - Planck constant ( (h) ); - Speed of light ( (c) ); - Temperature, average temperature ( (T, T_{avg}) ); - Boundary temperature ( (T_0) ); - Coefficient of linear thermal expansion ( (\alpha_{TE}) ); - Grüneisen parameter ( (\gamma) ); - Optical phonon frequency, zone centre ( (\omega_0) ); - Cubic &amp; quartic harmonic constants ( (A &amp; B) ); - Length, width, and thickness ( (L, w, and t) ); - Diameter ( (D_w) ); - Phonon shift from ( \omega_0 (\Delta \omega) ); - Bulk silicon &amp; SiNW lattice constant ( (a_0 &amp; a) ); - Dimensionality ( (n, for SiNWs n = 1) ); - Fitting parameters ( D = 20.92 ) and ( \beta = 1.08 ); - Power absorbed per unit volume ( (P_v) ); - Thermal conductivity ( (\kappa) ); - Power density ( (P_{den}) ); - Absorption factor ( (\alpha) ); - Duty cycle ( (D.C.) ).</td>
</tr>
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Table 4.2: Relevant equations for Raman analysis repeated from Chapter 3 for readability.

The calculated temperatures using Eq. 3.4 were plotted as solid data points in Fig. 4.3 and linearly fitted by solid lines. The Raman spectra was obtained at small laser power, increasing the laser power, then going back to small laser power to observe any hysteresis or phase change in the material. It was observed that at ~500 K the Raman spectra changed and the original low power spectra could not be reproduced, indicating a phase change or breakage in the material. These data points were therefore ignored in the linear fit (Fig. 4.3, bottom, arrows). The linear fit was adjusted for parameter \( C \) in Eq. 3.4 so that the zero-power intercept was at room temperature.
Fig. 4.3: Top: example laser power dependent Raman spectra of suspended SiNWs with the dotted lines highlighting the SiNW Raman peak shift as laser power is varied. Bottom: measurement of temperature using Stokes/anti-Stokes peak intensities (solid) and Raman peak shift (hollow, dotted). The data points highlighted by arrows were ignored in the fitting due to hysteresis – as the laser power was cycled high and then low, the original low power spectra could not be recovered, possibly due to materials changes caused by high temperatures.

Similarly, the Stokes/anti-Stokes peak positions for each laser power was related to a temperature using the bulk silicon relation of $\frac{d\omega}{dT} = -0.024 \text{ cm}^{-1}/\text{K}$ [121], [122], independent of intensity, where the temperature dependent part of the Raman peak shift at room temperature can be approximated by the linear relation of Eq. 3.5. The Raman measurements were fitted by Lorentzian peak profiles (OriginPro 2016G, OriginLab, Northampton, U.S.A.). The temperature calculated using this method, i.e. per the Stokes peak shift, are plotted as hollow data points in Fig. 4.3 and linearly fitted by dotted lines. These two independent measurements of temperature agree well, similar to the work by Doerk et al. [96] who found the same bulk silicon relation of Raman peak shift to temperature for electrochemically etched SiNWs down to 50 nm diameter. Doerk et al. suggested that, as per Eq. 3.5 and considering the matching measurements of temperature, the anharmonic constants for SiNWs remain bulk-like, an indication that lattice anharmonicity is not modified compared with bulk values. Similarly, from the first term of Eq. 3.5,
the Grüneisen parameter is bulk-like, and the bulk silicon value can be taken, i.e. \( \gamma \approx 0.98 \) [121], [132]. For subsequent measurements of temperature where the anti-Stokes intensity is insufficient for accurate calculation of temperature, the relation \( \frac{d\omega}{dT} = -0.024 \text{ cm}^{-1}/\text{K} \) can be used.

Assuming for the temperature ranges being investigated that the thermal conductivity is approximately constant, then per Eq. 3.5 and 3.14, the laser power dependent Raman peak shift can be fitted linearly, shown in Fig. 4.4 for a few SiNW examples. The slope can be related to thermal conductivity while the zero-power intercept represents the Raman peak shift in the absence of any thermal effects and is thus composed of quantum confinement effects and uniaxial elastic strain [133] (Eq. 3.6).

Fig. 4.4: (a) Example laser power dependent Stokes peak shift for a variety of SiNWs processed using different methods. The SiNWs are either joined monolithically to bulk silicon pads or clamped by chromium metal and released by either vapour HF (VHF), wet buffered oxide etch (BOE), or wet buffered oxide etch combined with critical point drying (CPD). The data points highlighted by arrows were ignored in the fit due to hysteresis of the Raman spectra, indicating materials phase changes possibly due to the high temperatures. (b) Example Raman spectra of SiNW arrays versus increasing laser power.
4.2 Strain and quantum confinement

The bulk silicon Raman shift for the anchoring pads and the substrate was measured to be 519.75 cm\(^{-1}\). Taking this as the zone centre phonon frequency \(\omega_0\), the quantum confinement was calculated using the first term of Eq. 3.8 and plotted against width in Fig. 4.5 (dotted line). Any subsequent zero-laser-power Raman peak shift is therefore due to uniaxial elastic strain, described by the second term in Eq. 3.8. Raman back-scattering from a (001) silicon surface allows only the LO mode to be observed [113], although using a high NA objective with small spot size allows measurement of the two TO modes as well [114]. Although Tarun et al. showed that pre-strained SiNWs retain a complex strain distribution when patterned on oxide [114], here only uniaxial strain is expected to remain after suspension of the SiNWs whereby the free surfaces of the SiNW are allowed to relax. Gridlines for uniaxial elastic strain in intervals of 0.5% are plotted in Fig. 4.5 in blue.

The zero-laser-power Raman peak shift for various SiNW arrays is plotted against width (Fig. 4.5). Clearly, the difference in nanowire anchoring plays an important role. For SiNWs anchored and joined monolithically to the bulk silicon (solid data points), the Raman shift is small and close to the bulk silicon value for all widths in the range from 10 to 20 nm. A slight downward trend as the width decreases correlates well with quantum confinement effects. A consistent elastic strain of approximately 0.1% is apparent. For SOI substrates the silicon device layer might be slightly pre-strained due to the processing method. The release of the biaxial strain in one in-plane direction can affect the uniaxial strain in the orthogonal direction, a technique used on heavily pre-strained substrates to fabricate strained nanowires [134]. Although no significant Raman shift for the bulk silicon device layer was observed, this could be due to the thinness of the layer and the \(\text{SiO}_2\) beneath. Therefore, the biaxial strain of the bulk silicon device layer might not be detectable. It has also been reported that oxidising the nanowire shell can impart stress along the nanowire [109], [116]. For the SiNWs released by VHF and BOE the scatter in strain is small, since the size of the native oxide shell is consistent. For SiNWs undergoing CPD (solid triangles, Fig. 4.5), the surface roughness is large, resulting in different thicknesses of oxide shell along the nanowire which may impart different types of stresses, thereby causing inconsistent strain.

For SiNWs clamped by thermally evaporated metal (hollow data points, Fig. 4.5), the Raman shift and hence strain is significant, in some cases up to 2.3%. Direct metal deposition represents another method for electrical contacting of ultra-thin SiNWs. The variability in the strain is large, and for SiNWs released by BOE under-etching (hollow circles, Fig. 4.5), the strain varies significantly over a small width range. One possible explanation for the increased strain in SiNWs which are clamped is thermal expansion of the SiNW structure during thermal evaporation of the
metal, which then clamps the SiNW and thus keeps it strained after the sample has cooled. Although variability is an issue, this has important consequences for strain engineering of materials, for example, for carrier mobility enhancement in transistor devices [135] and enhanced optical properties [4]. By using an unstrained substrate and etching nm-sized features and applying heat to thermally expand the material, one can achieve significant strain. Currently, strain engineering typically involves using pre-strained substrates which are epitaxially grown or wafer-bonded and which can be expensive [136].

Fig. 4.5: SiNW width versus extrapolated zero laser power Stokes shift. Estimate of the quantum confinement component (black dotted line) and the uniaxial elastic strain (blue dashed lines) are plotted. Monolithically connected SiNWs (solid) have low strain. Metal clamped SiNWs (hollow) exhibit high and variable process induced strain. Very rough SiNWs (solid triangle) have low but variable strain, possibly due to variable oxide formation.

4.3 Thermal transport

The suspended SiNWs were assumed to be homogeneously heated by the laser. The thermal contact resistance was modelled using FEM, showing that SiNWs monolithically connected to bulk silicon pads have their boundary conditions essentially pinned to room temperature (see section 3.3). The heat equation with room temperature boundary conditions was then applied to find the average temperature across the nanowire array, and subsequently an expression for the
thermal conductivity. The absorbed power was calculated using RCWA for the suspended SiNW array. For each absorbed power, a measure of the temperature of the system thus gives the thermal conductivity.

4.3.1 Thermal conductivity of SiNW arrays

For bulk silicon, the measured change in temperature was small, and the thermal conductivity was measured to be \( \sim 150 \, \text{W/m.K} \), as expected following standard measurements in literature. For SiNWs the thermal conductivity was measured to be in the range of 0.4 to 1.5 W/m.K which is more than 2 orders of magnitude lower than the bulk value. For SiNWs connected to bulk silicon anchor pads and released using various methods, \( \kappa \) is plotted against the width in Fig. 4.6. The LER was measured using SEM analysis software to be \( \sim 2 \, \text{nm} \) for SiNWs released by VHF and BOE, and between 3.4 to 4.6 nm for SiNWs undergoing Piranha thinning and CPD. There does not appear to be strong width dependence of \( \kappa \) in this width range.

![Thermal conductivity versus width for SiNWs from various references and produced in this work. A model of the thermal conductivity due to purely diffusive scattering (Casimir limit) is shown as the solid line. For e-beam defined SiNWs with rectangular cross-section, the effective diameter was calculated using Eq. 3.9 for better comparison.](image)

For SiNWs released using VHF, giving smooth sidewalls, the thermal conductivity is approximately \( 1 \pm 0.5 \, \text{W/m.K} \). For the rougher SiNWs, \( \kappa \) is approximately \( 0.1 \pm 0.05 \, \text{W/m.K} \). For SiNWs clamped by chromium, the thermal conductivity could not be calculated because an air-gap formed between the SiNW and the metal pad, resulting in an unknown boundary condition (see section 3.3). Overall, the decrease in \( \kappa \) for the SiNW array agrees well with the trend of
decreasing $\kappa$ versus width reported by a variety of studies of SiNWs synthesised by various methods (Fig. 4.6) [31], [32], [103], [107]–[109], [117], [137]–[140]. The degree of scatter in the data is approximately ± 50%, slightly larger than simulations which show sensitivity errors of ~ ± 30%.

### 4.3.2 Phonon scattering mechanisms

For metals, heat transport is mediated by electrons while for insulators and semiconductors, heat transport is mediated mainly by phonons [141]. Using Matthiessen's rule, the total phonon scattering rate is the sum of intrinsic, boundary, crystal defect (such as grain boundary), phonon-electron, and impurity scattering rates, and the quantum confinement effect where the phonon dispersion itself is modified. Since the SiNWs are above 10 nm in size, confinement effects are negligible (Eq. 3.6). Since the SiNWs are etched from bulk crystalline silicon, grain boundary scattering is expected to be minimal. Since the SiNWs have low doping, the phonon-electron and impurity scattering will also be minimal at room temperature.

Furthermore, it was shown earlier in section 4.1 that lattice anharmonicity was not modified and therefore did not play a role in the decrease in thermal conductivity in SiNWs, supporting the work by Doerk et al. [96]. Therefore, the intrinsic scattering is bulk-like. From the work by Hochbaum [32], Li [103], and others, the temperature dependence of $\kappa$ near room temperature for SiNWs with small widths is relatively constant. In this work, the measured temperatures of suspended SiNWs with low LER ranged from room temperature up to ~325 K, such that it can be assumed that $\kappa$ is constant in this temperature range. The best fit of Stokes shift (which is proportional to temperature) versus laser power is linear, also indicating that $\kappa$ is constant over this temperature range since $\frac{dP}{dT}$ is proportional to $\kappa$ (Eq. 3.14).

For SiNWs with high LER, the temperatures measured ranged up to ~500 K, and the temperature dependence of $\kappa$ must be taken into consideration. At these higher temperatures, phonon-phonon scattering becomes important, and $\kappa$ decreases as temperature increases, a signature of phonon-phonon scattering processes [142]. Over the larger temperature range, the best fit of Stokes shift versus laser power is a concave quadratic (i.e. $\frac{d\kappa}{dT} \sim \frac{d^2P}{dT^2} < 0$) showing that $\kappa$ decreases as $T$ increases (Fig. 4.7). Therefore, for SiNWs with high LER, only the measurements at low power were fitted linearly and the rest discarded from the fit in order to find the room temperature $\kappa$. 

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Fig. 4.7: Laser power dependent Stokes shift for three example SiNWs released by BOE. At higher powers, the measured temperatures can reach up to 450 – 500 K, and $\kappa$ might not be constant. These data can be fitted with quadratic functions, showing that $\kappa$ is roughly linearly decreasing as $T$ increases. Therefore, phonon-phonon scattering is significant.

Finally, Murphy et al. [117] showed that strain did not modify the thermal conductivity for SiNWs in the <111> direction, but bulk ion implantation had a large effect on thermal conductivity. It is also shown in this work (section 4.3.4) that strain of SiNWs in the <110> direction did not affect $\kappa$. Therefore, the room temperature $\kappa$ for the SiNWs in this work is mediated mainly by boundary scattering.

4.3.3 Temperature hysteresis

The laser power was cycled from low power to the next higher power level and then back down again to observe changes in the Raman spectra. Above $\sim$500 K, the low power Raman spectra could not be recovered, indicating some materials phase change. For example, in Fig. 4.8, above a certain laser power an intermediate Raman peak appears. This can be correlated to the SEM image which shows breakage of the nanowires and therefore some strain relaxation. Oxidation of the nanowires can also occur. Thus, Raman data after which the low power Raman spectra could not be recovered was discarded.
Fig. 4.8: (a) SEM of broken suspended SiNWs due to overheating. (b) As the laser power increases the Raman spectra exhibits an intermediate peak, possibly due to the broken nanowires or other materials changes such as oxidation.

4.3.4 Effect of strain on thermal conductivity

Strained suspended SiNWs in the <110> direction were fabricated using a pre-strained SOI substrate (sSOI) with the SiNWs monolithically connected to the bulk silicon pads and released by VHF. The uniaxial elastic strain was measured by Raman to be approximately 0.75% compared with the unstrained SiNWs with ~0.15% strain. The thermal conductivity of the strained SiNWs were measured to be similar in value to the unstrained SiNWs of between 0.3-1 W/m.K. Strained SiNWs that did not exhibit constrictions at the ends, due to processing variations, had slightly larger thermal conductivities up to 2.5 W/m.K (Fig. 4.9). In this preliminary trial, no chromium metal was deposited, and therefore the RIE plasma etching was relatively homogeneous. Also, the strain dependence and width dependence of the thermal conductivity for strained SiNWs show no clear trends (Fig. 4.9a-b). The main cause of changes in $\kappa$ are the presence of constrictions. This supports the tentative conclusion that homogeneous uniaxial elastic strain does not play a role in the thermal conductivity of <110> SiNWs, similar to the study by Murphy et al. for <111> strained SiNWs [117].
Fig. 4.9: (a) Uniaxial elastic strain versus thermal conductivity for suspended SiNWs connected monolithically to bulk silicon pads. The strained SiNWs were fabricated from pre-strained SOI substrates. Depending on the placement of metal pads for discharging during SEM inspection, the SiNWs exhibited either constrictions at the ends (metal pads, solid) or no constrictions (no metal pads, hollow). (b) Effective SiNW diameter (Eq. 3.9) versus thermal conductivity for strained and non-strained SiNWs, with legend as per (a). (c) Strained 11 nm wide SiNWs with constrictions. (d) Strained 17 nm wide SiNWs without constrictions. Scale bars equal 200 nm.

4.3.5 Boundary scattering in SiNWs

As the size of nanowires decreases below the phonon mean free path for silicon (~300 nm at room temperature), boundary scattering begins to dominate phonon transport. In the Casimir limit where the boundary scatters completely diffusively, the relative reduction in thermal conductivity due to boundary and intrinsic scattering is [21]

\[
\frac{k_{\text{SiNWs}}}{k_{\text{bulk}}} \approx \left(1 + \frac{\Lambda}{D_w}ight)^{-1}
\]

where \( \Lambda \) is the phonon mean free path in bulk and \( D_w \) is the nanowire diameter for circular nanowires, which represents the phonon mean free path in SiNWs. The phonon mean free path can be decomposed following Matthiessen’s rule into different scattering mechanisms.
\[
\frac{1}{\Lambda} = \frac{1}{\Lambda_B} + \frac{1}{\Lambda_{ph-ph}} + \frac{1}{\Lambda_{im}} + \frac{1}{\Lambda_{ph-el}}
\]

where \(\Lambda_B\), \(\Lambda_{ph-ph}\), \(\Lambda_{im}\), and \(\Lambda_{ph-el}\) are the mean free paths due to boundary, phonon-phonon, impurity, and phonon-electron scattering, respectively. For rectangular nanowires with thickness \(t\) and width \(w\), the effective diameter can be defined by Eq. 3.9. The thermal conductivity versus width using this model is plotted (solid line) in Fig. 4.6. The experimental values measured on VLS grown circular SiNWs by Li et al. [103] agree well with the model. Rectangular shaped SiNWs fabricated by lithography definition and RIE as well as electrochemically etched SiNWs, show a \(D_w^2\) dependency, i.e. scaling to the nanowire cross-sectional area. Electrochemically etched SiNWs are typically doped, and impurity scattering may be a cause of lower thermal conductivity. Lithography defined SiNWs can thus better isolate the effect of boundary scattering.

The boundary scattering rate \(\tau_B^{-1}\) can be expressed as [143]

\[
\tau_B^{-1} = \frac{v_g (1 - p)}{D_w (1 + p)}
\]

where \(v_g\) is the phonon group velocity, \(D_w\) is the diameter, and \(p\) is the surface roughness parameter (\(p = 1\) for smooth, \(p = 0\) for very rough). In the diffuse scattering limit (the Casimir limit), \(p = 0\) and Eq. 4.1 is produced. If the phonon wavelength is much larger than the surface roughness the phonons are reflected specularly and there is no effect on thermal conductivity. If the phonon wavelength is similar to the surface roughness the phonons are scattered diffusely and lowers the probability of phonon transport and hence the thermal conductivity. If the phonon wavelength is much smaller than the surface roughness they can be backscattered, giving much lower thermal conductivities than pure diffusive scattering from the surface.

For example, SiNWs fabricated by Hochbaum et al. [32], Lim et al. [144], and Feser et al. [139] have a very rough surface and exhibit much lower thermal conductivities than the purely diffuse scattering model. Alternatively, Heron et al. [140] showed that very long wavelength phonons can be backscattered in SiNWs with serpentine structures, which can be viewed as structures that have a ‘roughness’ or discontinuity feature much larger than the phonon wavelength of interest. Therefore, in the case of extremely rough nanowires where the SiNW is so rough it can be viewed as a row of connected nanocrystals, backscattering becomes important. This increases the scattering rate beyond that predicted by the Casimir limit and could be possibly described phenomenologically by allowing \(p < 0\) as suggested by Moore et al. [145]. Indeed, the Monte Carlo
simulations by Moore et al. [145] show that if there is significant backscattering at the boundary, \( \kappa \) can be much less than the Casimir limit. This applies when roughness is not randomly distributed such that backscattering becomes significant.

For silicon at room temperature, the phonon wavelength is approximately 1-2 nm. Therefore, roughness in the order of 1-2 nm will scatter phonons diffusely. However, the phonon spectrum is also quite broad, and thus phonons of different wavelengths will be scattered by the boundary differently [144], [146], [147]. The data points in Fig. 4.6 show the thermal conductivity of SiNWs with a relatively smooth surface (LER ~ 2 nm) and rougher surface (LER ~ 4 nm). Although the LER is much smoother compared to those SiNWs studied by Hochbaum et al., the thermal conductivity is similarly much lower than predicted by the diffuse boundary scattering model. One reason might be because the ends of the nanowires are pinched, causing a slight constriction. This is possibly due to the fabrication process: the SiNWs are patterned and the metal pads are patterned on top. The whole structure is then etched using plasma etching, where the presence of the metal can modify the local electric field causing over-etching at the ends of the SiNWs. These constrictions can act like the serpentine structures studied by Heron, i.e. scatter the long-range phonons.

For SiNWs undergoing CPD, the thermal conductivity is much lower due to the much rougher surface, in addition to the constrictions at the ends of the SiNWs. This also supports the work by Lim et al. who showed strong dependence of \( \kappa \) on the SiNW roughness and phonon spectrum, while the dependency on diameter was not as strong [144]. It is clear from Fig. 4.6 that roughened SiNWs exhibit thermal conductivities below the Casimir limit, and scattering models must consider the full phonon spectrum and scattering behaviour at each phonon frequency.

Fractal geometry, a way to describe a repeating pattern (e.g. roughness) at every length scale (e.g. for phonons of different wavelengths), would be one suitable way to treat such scattering, as calculated by Lü for copper and tungsten damascene structures [148]. Using perturbation theory, Martin et al. [149] showed a \((D_w/\Delta)^2\) dependence of \( \kappa \), rather than the linear dependence of \( \kappa \) on \( D_w \) described in 4.1, where \( \Delta \) is the root-mean-square roughness of the SiNW. The onset of this change in \( D_w \) vs. \( \kappa \) dependence occurs at higher \( D_w \) as roughness increases. As mentioned earlier, rectangular shaped SiNWs and rough SiNWs show a \( D_w^2 \) dependency of \( \kappa \), supporting this model.

Apart from roughness considerations in terms of geometry, boundary scattering behaviour can also highly depend on the surface treatment [150]. Glynn et al. [151] studied roughness of SiNWs using transmission electron microscopy, showing that the roughness features themselves may be intrinsically different from the rest of the SiNW, thereby introducing new scattering mechanisms.
Finally, the cross-sectional shape of the nanowires and the crystal orientations of the surfaces may have a role in boundary scattering which needs to be further explored [152].
5 Conclusions and Outlook

In contrast to the atomistic approach, a simple macroscopic view of materials properties is shown in Fig. 5.1. Each materials property can undergo a reversible process and can be coupled to each other in a reversible way [153]. The atomistic and macroscopic experimental approaches for nanostructured materials are both important and complementary, and extremely challenging in both cases.

Fig. 5.1: Reversible, steady state macroscopic materials properties and their couplings.

For the atomistic approach, precise control over atoms, their placement, and their chemical bonds is important [154]. For the macroscopic approach, a large ensemble of nanostructures which are
as close to identical as possible is required. Many important studies of nanostructures in the past have been on ensembles of nanostructures which have a considerable size, geometry, and orientation distribution. Isolating the size, geometry, and orientation of nanostructure ensembles allows more accurate elucidation of materials properties, with the benefit of better signal-to-noise ratio and ease of experimental arrangement.

Secondly, from a technological point of view, the push from science to technology is strongly driven by economic factors. For example, the basic principles of photolithography and fabricating silicon components were developed in the 1940s and 1950s, but it was only when Moore [1] realised in 1965 that the cost of each component was decreasing exponentially and that economy of scale could be realised that silicon technology became ubiquitous. The result was the information revolution beginning in the 1980s and continuing through to today.

5.1 EUV-IL as an enabling technology

EUV-IL is an excellent and well-developed platform to investigate nano-scale phenomena down to 16 nm HP and 10 nm widths. Patterning down to 10 nm HP is regularly obtainable. The challenge is pattern transfer of developed photoresist into functional materials. Pattern transfer down to 16 nm HP into silicon was demonstrated, and further decreases in resolution will require creative approaches as well as process optimization, but is very feasible. Fabrication of suspended structures and contacts are standard processes in the clean-room. Therefore, it is expected that single-digit-nm structures will be achieved in the coming years, with excellent reproducibility and tight size and position tolerances which are characteristic of photolithography and EUV-IL.

Such suspended SiNW arrays are excellent model systems to study a wide variety of materials properties (Fig. 5.1). EUV-IL enables large ensembles for macroscopic studies, complementary to the many atomistic studies of nanostructures. Nano-structured materials are incredibly exciting future functional materials that can be precisely engineered and tuned. Deep understanding of these device building blocks could be instrumental for the future technological landscape, while EUV-IL is a leading, and industrially capable, enabler for nano-devices in the near future.

5.1.1 High-resolution patterning

EUV photolithography uses a shorter wavelength compared to current DUV photolithography (13.5 nm vs. 193 nm) to produce nano-size features. Using diffraction gratings to form interference patterns, very high-resolution, large-area, periodic patterns with excellent reproducibility and strict size and position tolerances can be produced, at high throughput. This
satisfies the scientific requirement of fabricating nanostructure ensembles with tight tolerances, as well as industrial requirements of economy and throughput.

In this work, HSQ line/space patterns down to 11 nm HP and Inpria patterns down to 14 nm HP with excellent LER and precise critical dimension were produced regularly, using diffraction masks composed of HSQ gratings. Further decrease in HP using HSQ gratings was not possible due to drastic loss in diffraction efficiency. Alternative mask designs were developed with the help of RCWA simulations, and an approach based on doubling the spatial frequency of the grating lines using ALD of iridium on a HSQ mould was used. The resolution limit achieved was 6 nm HP, although with high roughness. The resolution limit could be due to the mask, resist, resist processing, or tool limits. Achieving higher resolution becomes more difficult due to a combination of lower diffraction efficiencies (and thus longer exposure times), the effect of source extension onto the image, and diffraction gratings having higher required tolerances.

Using the current technology EUV-IL mask technology can be improved several ways. It was shown that high diffraction efficient materials are vital below 7 nm HP (i.e. ALD suitable materials such as iridium and ruthenium, see Fig. 2.3). Optimization of ruthenium ALD is the next step to improving mask efficiency, as ruthenium has much higher diffraction efficiency than iridium. Standard ALD deposited ruthenium has large grain size (up to 30 nm) and is not suitable for high resolution grating fabrication. One approach is to use plasma enhancement incorporating, for example, ammonia plasma [155] or oxygen plasma, of which there is currently little information. Plasmas break the surface passivating hydrogen bonds allowing easier deposition onto the now dangling bonds.

Secondly, the ALD deposited grating can have its top and bottom coatings fully removed by ion milling, and the HSQ mould etched away together with critical point drying to avoid pattern collapse. This would improve diffraction efficiency. Ion milling itself is a suitable strategy for pattern transfer of high resolution nano-structures. For example, many materials have a very high ion milling selectivity against carbon, and using a carbon based hard-mask or carbon based photoresist would allow excellent transfer of nano-structures into a variety of EUV-IL suitable materials.

Thirdly, super-lattices deposited by ALD themselves can be used as diffraction gratings. For example, starting with a µm sized suspended block such as Si₃N₄ as a starting template, successive ALD cycles of alternating and EUV contrasting materials (e.g. Al₂O₃ and ruthenium) allow nm precision control over grating formation. The sidewall super-lattices on either side of the template block would then form the gratings necessary for high resolution interference. RCWA
simulations would allow a variety of such structures to be studied for their optical and beam guiding properties. Another way to improve grating efficiency is to fabricate blazed gratings using grayscale lithography, combined with multilayers to specifically target the EUV wavelength [156]. Changing the support material from Si₃N₄ to a less EUV absorptive material such as silicon would also enhance diffraction efficiency, with the added benefit of improving mechanical stability of the support as it can be made thicker. Finally, free standing grating lines without support might offer further efficiency improvements.

For high resolution EUV photoresists, current trends are toward chemically amplified resists [42] and metal-organic resists [93], [157]. Beyond photoresist chemistry, photoresist adhesion and noise need to be improved. Depending on the photoresist, adhesion promoters, under-layers, and surface treatments might be needed. Surface treatments other than the ones described in chapter two include hexamethyldisilazane (HMDS) application, TI prime application, HF dip, Piranha dip, RCA cleaning, and annealing in forming gas. All procedures desorb water and passivate the surface to prevent further moisture and contaminant build-up. Under-layers (single and multilayers) may also suppress electron backscattering and thus decrease LER and decrease proximity effect [158].

The extension of the intermediate source onto the image plane can be decreased several ways. By improving photoresist sensitivity, the spatial filtering pinhole can be made smaller which decreases the size of the effective source but reduces light flux. For line/space patterns, instead of a pinhole, a slit can be used as the effective source, parallel to the direction of the diffracting grating lines so that although flux is maintained, the influence of the effective source in the critical direction along the diffraction plane is minimized. The mask to sample gap can be made smaller. For example, by electroplating a g = 50 µm frame around the support membrane, the blur can be reduced by a third cf. the line-doubled iridium mask presented in this work which targeted g = 150 µm.

Fig. 5.2 shows the resolution limit of the interference lithography tool at the SLS, PSI. Steady process has been made for producing high-resolution patterns, giving access to high contrast, high-resolution, and well-defined aerial images for the early development of photoresists for EUV lithography. Photolithography at 6 nm HP marks a new record, which is a remarkable achievement. This corresponds in width to ~12 silicon atoms or ~18 silicon oxide molecules. It is a significant demonstration that EUV photons can achieve such a resolution and there is no fundamental limiting factor in terms of materials and photochemistry. The secondary electron blur for EUV is estimated to be 1 to 3 nm [159]. If this is about 3 nm, the ultimate limit in photolithography has been reached. If the secondary electron blur is lower, the resolution might
be further increased down to 5 nm HP. For high volume manufacturing (HVM), EUV scanners with 0.55 NA optics might be able to achieve 6 nm HP resolution [160]. This requires suitable photoresists with much higher sensitivity than that of HSQ.

Fig. 5.2: Minimum line/space HP resolved by EUV-IL at the XIL-II beamline, SLS, PSI. Figure reproduced from [38].

Beyond this resolution, the wavelength should be reduced, such as patterning with BEUV (beyond EUV, 6.5 nm wavelength) and with soft x-rays [74]. The advantage of reduced wavelength comes with significant technological challenges. Moreover, secondary electron blur will increase with further decrease in wavelength. One feasible option would be to decrease the wavelength to 12.5 nm, which is very close to the absorption edge of silicon (12.5 nm, 100 eV). This wavelength provides 7% improvement in resolution for the same NA and without changing materials for the resists or optics. In case free electron lasers (FELs) are used for HVM in future as proposed [161], this wavelength, which can be called EUV+, would provide a feasible improvement in resolution without any change except changes in the period of the molybdenum/silicon multilayers which also have a high reflectivity [80]. Beyond this limit, top-down resolution can be pushed further using pattern multiplication techniques such as directed self-assembly and line doubling.

5.1.2 Bessel beams

Formation of a Bessel beam down to 20 × 30 nm² spot size with EUV light using a transmission ring grating was demonstrated. For various gaps, the recorded pattern intensity corresponds well with theoretical Bessel beam propagation. By varying the exposure dose, the beam intensity profile can be adjusted. This is important for applications in beam writing where the correct dose
is needed to avoid artefacts, proximity effect, and unwanted exposure of side-rings. Beam writing was also demonstrated showing good reproducibility, and accuracy could be increased by using a more precise sample stage.

Compared to Fresnel zone-plate lithography which is a similar scheme, Bessel beam lithography can produce similar spot sizes but with a much larger depth-of-focus [162], overcoming one of the main trade-offs in traditional photolithography of resolution versus depth-of-focus. Using our current technology as described in this work, a Bessel spot of \(~15\) nm diameter with a depth-of-focus of \(~1\) mm would be achievable. Bessel beams show good promise as a serial beam writing tool for arbitrary nanostructures over changing surface topographies and curved surfaces, for example as an alternative to nanoimprint lithography [163], and as micro-lens arrays [164] for patterning spray-coated curved surfaces. A Bessel beam array could be used to increase throughput, similar to current e-beam array schemes.

Applications of Bessel beam lithography and Fresnel zone-plate lithography include not only serial writing of arbitrary nano-structures, but also for example functionalizing surfaces with arbitrary patterns for biological or chemical sensing and applications. Both schemes represent a photon based alternative to electron and ion based serial beam writing. Bessel beam lithography has the added feature over Fresnel zone-plate lithography of having a long central core, allowing the clearance of thick photoresist to produce moulds for electroplating high aspect ratio nano-structures. For example, \(\lambda = 5\) nm light with its longer absorption depth in PMMA was used to produce gold nano-pillars of \(80\) nm diameter and \(160\) nm height using a dot/hole interference mask [74]. This could be accomplished using Bessel beams to produce arbitrary high aspect ratio structures. By varying the dose, different thicknesses of photoresist can be cleared resulting in 3-dimensional structures [165]. Using the long central core, Bessel beam lithography could produce structures of varying heights at higher resolution and aspect ratios than current two-photon or e-beam methods.

Bessel beams are one type of nondiffracting beam. Others include vortex or spiral beams, characterised by a phase singularity in the centre of the resulting aerial wavefront [166]. Such beams could have applications as optical tweezers and especially in interferometry [167], where elevations and depressions can be distinguished in the sample by their spiral interferogram, extending the range of EUV metrology tools. Airy beams are self-accelerating nondiffracting beams where the asymmetric beam appears to curve to one transverse direction during propagation [168]. These have not yet been implemented at EUV, but again might find application as a lithography tool. For example using an abruptly autofocusing wave composed of Airy beams
A defined volume can be exposed in thick photoresist, similar to two-photon lithography at optical wavelengths which allow fabrication of true 3-dimensional structures.

### Achromatic Talbot lithography

Achromatic Talbot lithography (ATL) was performed at PSI and at the SSRF with the same mask. Periodic dot arrays with 20 nm feature size at 106 nm pitch were produced using HSQ resist exposed at 13.5 nm and 8.8 nm illumination wavelengths. A 3% bandwidth at SSRF in comparison to 4% bandwidth at PSI means that the achromatic distance is larger at SSRF which in turn reduces the size of the patterned area and increases the minimum achievable feature size. ATL has been proven to be a robust method for use in different types of EUV beamlines at different wavelengths and conditions, requiring only a broadband EUV source, as well as producing high-density, high-resolution periodic nanostructures with high throughput. This allows ATL to be a relatively accessible, cheap, robust, and efficient method to produce periodic patterns. For example, periodic iron nanodot arrays were fabricated using ATL to study nano-catalysis and hydrogen spillover [44]. ATL would be suitable as an EUV diagnostic tool due to its excellent reproducibility and relatively high-resolution, and is ideal for large area patterning by step-and-repeat processes.

Another way broadband sources can be used in interference lithography is to use a grating beam-splitter to first produce two divergent beams which are then diffracted back to interfere, however with lower efficiency than ATL. Complementary to ATL, displacement Talbot lithography (DTL) uses the same effect of summing together Talbot images of the transmission mask, but instead by monochromatic illumination and then moving the sample through one Talbot distance in the z-direction. The image is then a convolution of the transmission function with itself [170]. Similarly, since ATL is in the temporal domain, if the ATL image is the autocorrelation of the transmission function with itself, the power spectral density of the source can be recovered. This will need both theoretical and experimental confirmation.

### Nano-devices patterned by EUV-IL

EUV-IL has proven to be a versatile method to produce well-ordered arrangements of nanostructures. For example, kagome lattice patterns [45] of magnetic materials could be used to study mesoscopic magnetic phenomena such as artificial spin ice. Dense metal aluminium nanowires have been fabricated as wire-grid polarizers [171]. Photonic quasicrystals can be fabricated using EUV-IL [47] to study a rich range of interesting optical phenomena [172].
Pattern transfer into metal nanostructures is typically done by a lift-off process, requiring high aspect ratio patterns. For pattern transfer into semiconductors, plasma etching is used. Plasma etching of 14 nm HP line/space patterns into SOI substrates was optimised using RIE-ICP and a simultaneous side-wall passivation and bottom etching scheme. Etch rates of 1 nm/s were achieved, giving excellent control over the etching process. The photoresist itself was used as the etch mask, although the selectivity was low (~1.6:1 for Si against HSQ). Further, a trade-off appears where photoresist thickness should be small for high-resolution patterning to avoid pattern collapse, but of sufficient thickness to act as an etching mask. This limits the pattern resolution that can be etched.

Future schemes for pattern transfer into semiconductors can be approached in several ways. An intermediate hard mask could be used between photoresist and substrate. This would require excellent pattern transfer schemes into the hard mask. For example, the current standard chromium hard mask may not be suitable for sub-10-nm features because Cl₂ etching is isotropic, and would require stringent control and ultra-thin hard-mask. Alternatively, spin-on carbon might be a suitable hard mask for ion milling since most materials, such as silicon, have high ion milling selectivity against carbon. The initial pattern transfer into the carbon mask can be done using O₂ plasma.

Large, high-resolution periodic patterns, as mentioned earlier, are eminently suitable for many types of materials characterisation techniques, due to its high signal-to-noise ratio. But periodic patterns can form useful devices as well. For example, nanowire crossbar arrays composed of metal – metal oxide – metal nanowire layers have been used as resistive memory structures, allowing high density of addressable junction locations [173]. Large area metal nanowires have been used as UV polarizers [171] and x-ray optical elements as well as aluminium nanodots for surface enhanced UV Raman substrates [174].

Periodic patterns can also be used as templates for other nanofabrication schemes. For example, as a template for VLS grown nanowires, defining the exact geometry of the template can allow precise control over the growth process. The crystal phase and composition of VLS nanowires are highly dependent on the catalytic droplet such as its contact angle and doping [175], [176]. Therefore, a precise template can control the resulting nanowire morphology. Similarly, templates for directed self-assembly [177] and nanoimprinting [171], [178] can be made. This would extend high-resolution pattern transfer from metals and semiconductors into materials such as polymers, colloids, and gels.
Following patterning and etching, suspended SiNWs were fabricated by e-beam definition of anchoring pads or by clamping down the SiNWs with deposited metal. After release of the BOX via BOE, suspended SiNWs were produced with widths typically between 10 and 20 nm. SiNWs down to 6.5 nm width and 16 nm HP were fabricated by successive oxidation of the SiNW shell and removal of the oxide, although yield was low due to stiction caused by capillary forces.

Such suspended structures are interesting for a variety of applications where nano-mechanics plays a role, since the structure is mechanically 'free' to move. Following Fig. 5.1, mechanical properties can be coupled with optics to give cavity opto-mechanics, for example in driving or detecting mechanical resonances using optics [179] or active optic cooling of the mechanical sensor [180]. This is especially suitable for sensing applications where functionalised mechanical resonators attract the target species and shift the resonance frequency, allowing measurement in the zeptogram range [181]–[183]. The light field can also be used to drive the cavity to study non-linear and chaotic behaviour.

In terms of piezoelectricity, significant process induced elastic strain was shown for SiNWs that were etched first and then clamped down by thermally evaporated metal, possibly due to thermal expansion of the SiNW during the deposition process. This has important implications in strain engineering since strain causes carrier mobility enhancement for certain crystal orientations in silicon [135]. It may be possible to control SiNW strain through the fabrication process which gives more flexibility in fabricating transistor devices.

Further, when the mechanical resonance matches the electrical signal frequency, the electrical signal can be modulated. These micro-resonators have been widely studied as radio-frequency elements such as filters and switches [184]. The dimensions of the SiNWs produced in this work would allow operation up to the GHz range. By using lighter materials such as carbon nanotubes with position controlled by an EUV-IL template pattern, THz frequencies can be reached [185].

Finally, suspended SiNWs offer their entire surface area to the environment. For transistors, this allows gate-all-around conduction channels which can be combined with high-k dielectrics to improve electrostatic control of the conduction channel [23]. For biosensors, a large functionalised surface area improves signal-to-noise ratio [186]. The high pattern density and precise arrangement of nanostructures enabled by EUV-IL is the key technology for realising such devices.
5.3 Suspended SiNW thermoelectric devices

5.3.1 The thermoelectric effect

When a temperature gradient is applied across a material, a voltage can appear. This is the thermoelectric effect, first observed by Seebeck and Peltier. The efficiency with which this material can produce thermoelectric power is described by the figure of merit:

\[ ZT = \frac{\sigma S^2 T}{\kappa} \]  

where \( \sigma \) is the electrical conductivity, \( S \) is the Seebeck coefficient, \( T \) is the temperature, and \( \kappa \) is the thermal conductivity. Therefore, for efficient thermoelectric power, high \( \sigma \), high \( S \), and low \( \kappa \) is required (i.e. phonon glass and electron crystal [187]). For bulk materials, the three parameters are typically coupled and trade-offs occur when optimizing one parameter over another [188].

Semiconductors are ideal thermoelectric materials, and some of the best performing bulk thermoelectric materials include Bi\(_2\)Te\(_3\) (\( ZT \sim 0.8 \)) and PbTe (\( ZT \sim 1.5 \)) [188]. To further engineer improvements in \( ZT \), two main approaches can be taken. One, create alloys incorporating point defects, vacancies, rattling structures, dopants, and superlattice structures and two, create nanocomposites. In both cases the goal is the same, to decrease the thermal conductivity by scattering phonons while retaining high electrical conductivity. Nano-structures therefore allow a degree of decoupling between the parameters in \( ZT \).

Semiconductors with ‘heavy’ carriers such as Bi\(_2\)Te\(_3\), Bi\(_2\)Se\(_3\), and PbTe have excellent \( ZT \), but are difficult to fabricate into nanostructures. Silicon and SiGe on the other hand are well supported by extensive nanofabrication techniques. Much work has been done on SiNW thermoelectric properties from theory [30] to experiment [31], [32]. The main approach has been to use the increased boundary scattering to further decrease \( \kappa \). If the nanostructure dimensions are small enough, quantum confinement will lead to band warping and carrier effective masses to become heavier, resulting in higher \( S \). The disadvantage of nanostructures is that electrical conduction is typically lower, possibly due to increased boundary scattering of the charge carriers [189]. Much of the work on SiNW thermoelectric properties have been done on ensembles of nanowires with considerable size and geometry distributions, in the region of 50 to 100 nm diameter. By using EUV-IL, SiNWs with precise geometry tolerances and widths below 20 nm could be studied.
5.3.2 SiNW boundary scattering for low $\kappa$

The thermal conductivity of suspended SiNWs below 20 nm width was measured using the Stokes/anti-Stokes intensity ratios which matched well with the independent measurement of applying the bulk silicon temperature dependency of the Stokes peak shift. This shows that intrinsic scattering is unmodified from the bulk. Strain also did not influence thermal conductivity. Since the SiNW specimens were only lightly doped, the electronic contribution to thermal conductivity was negligible. Therefore, phonon boundary scattering is the dominant mechanism for reduced thermal transport in this case. Thermal conductivities in the range of 0.1 to 1.5 W/m.K were found, significantly lower than the bulk thermal conductivity and lower than results by other investigators.

The thermal conductivities are also much lower than expected using a diffuse boundary scattering model. Not only does LER play a role in further increasing the rate of boundary scattering, but also that longer range phonons can be scattered by constrictions at the ends of the nanowires. Since the phonon spectrum is broad, different types of phonons need to be scattered by different types of boundary features to fully minimise $\kappa$. By considering backscattering of phonons by constrictions and roughness of different size orders, $\kappa$ can decrease below the Casimir limit [145]. One possible way to quantify and model the interaction between the broad phonon spectrum and surface roughness is studying the fractal geometry of the SiNW.

Pan et al., Glynn et al., and Zhou et al. have shown that surface modification [150], [151] and nanowire cross-sectional shape [152] are also important factors in decreasing $\kappa$. For high surface-to-volume ratio nanowires at sub-10-nm widths, the surface plays a considerable role in boundary scattering [190]. It remains therefore to repeat room temperature measurement of $\kappa$ for highly doped n- and p-type SiNWs, in the different crystal directions, with different surface terminations. Phonon polarisation can be studied by using a high NA objective and a polariser to isolate the TO modes. This can be measured for SiNWs with different cross-sectional shapes to investigate confinement effects.

The scattering of different wavelength phonons can be studied by isolating one type of surface roughness, for example constrictions which scatter long range phonons. Maire et al. [191] recently showed semi-ballistic transport in SiNWs at 4 K. Johnson et al. [192] showed room temperature semi-ballistic transport of long wavelength phonons in silicon membranes. Although the SiNWs in this work were typically around 580-nm-length, measurements on shorter SiNWs may indicate semi-ballistic phonon transport, as the thermal conductivity is length dependent (Fig. 5.3). This may be caused by the longer wavelength phonons being scattered at the
constrictions, which only occur at both ends of the SiNW. The distance between scattering constrictions is thus SiNW length dependent, indicating ballistic transport of the long wavelength phonons between the constrictions. By investigating $\kappa$ using these different types of scattering features, the dominant heat-carrying phonon wavelength(s) can be determined.

![Graph showing $\kappa$ versus SiNW length](image)

Fig. 5.3: Measurement of $\kappa$ versus SiNW length for SiNWs released by VHF (solid) and BOE (hollow), and connected monolithically to silicon pads. For diffusive heat transport, $\kappa$ is constant. For ballistic heat transport, $\kappa$ is length dependent.

### 5.3.3 SiNW electronic filtering for high $S$

As already mentioned, nanowires can have increased $S$ when quantum confinement warps the band structure resulting in carriers with heavier effective masses. Another approach is to filter carriers by placing heterojunction barriers which allow thermionic emission of only high energy carriers. Although this would slightly decrease electrical conductivity, the carriers contributing to conduction would all have high energy, thus increasing the chemical potential difference and subsequently $S$ [193]. For monolithically connected SiNWs, depending on the surface terminations, the bandgap of the SiNW region can be larger than the bulk pad region [194]. For SiNWs with constrictions at both ends where the constriction is a sizeable amount, the constriction can have even larger bandgap, thus forming an energy barrier for electronic filtering. This might be one reason why SiNWs have larger $S$ values compared with bulk silicon. Therefore, due to quantum confinement, the band gap can be varied between neighbouring regions using the one, monolithic material.

Preliminary measurements of $S$ in air are show below in Fig. 5.4. Two nickel wires were patterned on SiNW arrays arranged in different crystal directions, with one wire acting as a heater via Joule heating by a current source and the other as a thermometer. The resistance of both wires was measured and translated into temperature using the temperature coefficient of resistance for nickel and the formula.
\[ \Delta R = 1 + \alpha_R \Delta T \]

where \( R \) is electrical resistance, \( T \) is temperature, and \( \alpha_R \) is the temperature coefficient of resistance (for nickel, \( \alpha_R = 0.005866 \)). Although the resulting \( S \) were similar in value to bulk silicon (\( S = -440 \mu V/K \)), the scatter in \( S \) was very large, and measurement confidence is therefore low. Seebeck measurements can be very tricky due to the small voltages and temperature fluctuations involved, and further investment in infrastructure might be required for more accurate measurements.

Fig. 5.4: Measurements of Seebeck coefficient for SiNWs arranged in different crystal directions using two lithography defined nickel wires acting as heater and temperature sensor.

5.3.4 SiNW strain for high \( \sigma \)

Nanowires are known to have decreased electrical conductivity due to increased boundary scattering of the carriers [195]. Furthermore, carrier concentrations for optimum \( ZT \) range between \( 10^{19} \) to \( 10^{20} \) cm\(^{-3}\). Doping is one approach that may increase \( \sigma \), but although doping can introduce scattering centres which decrease \( \kappa \), the electronic contribution to \( \kappa \) increases per the Wiedemann-Franz law

\[
\frac{\kappa_{el}}{\sigma} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 T
\]

where \( e \) is the charge of an electron and \( \kappa_{el} \) is the electronic contribution to the thermal conductivity. At room temperature, this ratio is \( 7.15 \times 10^{-6} \) W\( \Omega \)/K, so for low doped silicon (e.g.
$10^{15}$ boron atoms cm$^{-3}$, $\kappa_{el} \approx 5.3 \times 10^{-5}$ W/m.K which is negligible. For high doped silicon (e.g. $10^{20}$ phosphorus atoms cm$^{-3}$), $\kappa_{el} \approx 0.89$ W/m.K, a significant amount. Therefore, the measurement of room temperature $\kappa$ for highly doped SiNWs is the next immediate step towards characterising SiNW thermoelectric devices.

Another approach is to apply strain to increase carrier mobility and thereby $\sigma$. Homogeneous uniaxial elastic strain has been shown not to affect $\kappa$, and therefore is another decoupled parameter that can be used to tune $\sigma S^2$ without trade-off against $\kappa$. Strain can be applied to nanostructures by thermal expansion and clamping with metal, followed by cooling, for example.

The electrical characterisation of ultra-thin SiNWs remains challenging. The key is good electrical contact of the SiNWs and gate materials with minimal leakage current. Aluminium, the traditional material for silicon contacts, spikes into silicon and therefore is unsuitable for ultra-thin materials. Nickel is an excellent contact material which forms stable NiSi after low temperature annealing. For gate materials, high-k materials are needed to avoid leakage current while retaining electrostatic channel control. Materials such as HfO$_2$ have been recently investigated for ultra-thin gate-all-around structures [196]. Further, the role of crystal orientation of SiNW surfaces and the termination of surface bonds can play a significant role in boundary scattering.

5.3.5 SiNW estimate of ZT

SiNWs are ideal structures which allow the tuning of thermoelectric properties. By increasing the surface-to-volume ratio, phonon boundary scattering dominates thermal transport. Different sizes of roughness can scatter different wavelengths of phonon. Surface terminations and surface orientations are also expected to play a major role in boundary scattering. In the orthogonal direction, SiNWs can form heterojunctions which filter carriers such that only high chemical potential carriers are transported, thereby maximising $S$. By straining SiNWs and modifying the band structure, mobility and conductivity can be increased without change to $\kappa$.

In this work, a typical suspended SiNW with dimensions $15 \times 20$ nm$^2$ and 550 nm length was shown to have an average $\kappa \approx 1$ W/m.K. The Seebeck coefficient could be estimated to be approximately $S \approx -1000$ µV/K. This would indicate $ZT \approx 0.002$ for low doped SiNWs and $ZT > 1$ for highly doped SiNWs. The next step is thus to measure the same parameters $\kappa$ and $S$ for heavily doped SiNWs. It has been shown by Hochbaum et al. [32] that heavily doped electrochemically etched SiNWs also exhibit very low $\kappa$. Therefore, it is reasonable to expect that EUV-IL fabricated doped SiNWs would also retain low $\kappa$ since boundary scattering effects increase as SiNW size decreases. This would result in SiNWs with $ZT > 1$. 

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Appendix

Scientific contributions produced during this project (Swiss National Science Foundation, SNF: 200021_143969), together with the author’s resume, is listed below. Parts of this thesis were taken from the publications below, with modifications.

List of Publications


Conference Contributions

- **Nov 2016:** Materials Research Symposium, Boston, U.S.A. (Oral presentation)
- **Aug 2016:** Low Dimensional Structures & Devices, Maya Riviera, Mexico (Oral presentation)
- **May 2016:** Swiss Nano Convention, Basel, Switzerland (Poster)
- **Apr 2016:** IEEE NEMS, Sendai, Japan (Oral presentation)
- **Apr 2015:** CSTIC, Shanghai, China (Oral presentation)
- **Oct 2014:** IEEE 3M NANO, Taipei, Taiwan (Oral presentation)
- **Sep 2014:** Micro Nano Engineering, Lausanne, Switzerland (Poster)
- **May 2014:** Swiss Nano Convention, Brugg, Switzerland (Poster)

Awards

- **Aug 2016:** Low Dimensional Structures and Devices, Maya Riviera, Mexico – **Best Talk**
- **Oct 2014:** IEEE 3M NANO, Taipei, Taiwan – **Best Paper**
- **Sep 2014:** Micro Nano Engineering, Lausanne, Switzerland – **Best Poster**