3D SILICON NANOPHOTONICS

DRIEDIMENSIONALE
NANOFOTONICA IN SILICIUM

Promotiecommissie

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3D SILICON NANOPHOTONICS DRIEDIMENSIONALE NANOFOTONICA IN SILICIUM

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Diana Grishina

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Dit proefschrift is goedgekeurd door:

Prof. Dr. W. L. Vos

In memoriam of
my father Alexander
and
my aunt Kate

Contents

1	Introduction	9
1.1	Photonic crystals	10
1.2	Photonic strength	11
1.3	Realization and probing of photonic crystals	14
2	Single-step etch mask for 3D monolithic nanostructures	27
2.1	Introduction	27
2.2	Fabrication process for the 3D single-step etch mask with built-in alignment	28
2.3	Results and discussion	31
2.3.1	Fabricated structure characterization	31
2.3.2	Structures feasible for fabrication	35
2.4	Conclusions and outlook	38
3	Deep UV lithography on the inclined sidewall of a wafer	43
3.1	Introduction	43
3.2	Experimental results	45
3.2.1	Process flow for V-trench fabrication	45
3.2.2	Spin coating of the sidewalls with photoresist	48
3.2.3	DUV exposure with step-and-scan lithography	49
3.3	Results and discussion	51
3.4	Summary and outlook	54
4	Deep reactive ion etching of silicon	59
4.1	Introduction	59
4.2	General description of deep reactive ion etching	60
4.3	Experimental	61
4.4	Ultra-high aspect ratio nanopores in Si	62
4.5	Advanced two-sided etching for 3D nanofabrication	65
4.5.1	Choice of ICP power	66
4.5.2	Polymer residuals after the Bosch process	70
4.5.3	Process flow transfer to SPTS Pegasus etcher	72
4.6	Summary	72
5	Looking inside 3D photonic nanostructures with X-ray tomography	77
5.1	Introduction	77
5.2	Zoom nanotomography	78
5.2.1	General scheme	78

5.2.2	Phase retrieval	80
5.3	Experimental	86
5.3.1	Samples	86
5.3.2	Experimental setup of beamline	88
5.4	Results and discussions	89
5.4.1	Choice of the phase retrieval algorithm	89
5.4.2	Choice of the resolution	93
5.4.3	Results and discussion on photonic crystals	96
5.5	Summary	102
6	Reflectivity of silicon photonic crystals with and without embedded point defects	109
6.1	Introduction	109
6.2	Optical setup for broadband reflectivity	111
6.3	Reflectivity of 2D silicon photonic crystals	112
6.4	Reflectivity study of 3D silicon photonic band gap crystals	120
6.4.1	Inverse woodpile photonic crystal	120
6.4.2	Reflectivity of 3D inverse woodpile photonic crystal without embedded defects	121
6.4.3	Signature of the cavity resonance in the 3D band gap	125
6.5	Summary	129
7	Outlook	135
A	Background on X-ray wave propagation	139
A.1	Basic equations.	139
A.2	Kirchhoff diffraction	141
A.3	Rayleigh-Sommerfeld diffraction	141
A.4	Fresnel diffraction	142
A.5	Fraunhofer diffraction	143
A.6	Talbot effect for amplitude grating	143
A.7	Talbot effect for a phase grating	145
A.7.1	Numerical calculation in the Fresnel regime.	145
A.7.2	Diffraction using transfer function approach	147
A.8	Diffraction pattern from a 2D centered rectangular grating	150
B	Sample list	155
C	Wave propagation in the birefringent media	159
C.1	Wave propagation in the birefringent media	159
C.1.1	TE polarization	161
C.1.2	TM polarization	161
C.1.3	Reflection and refraction from birefringent medium	162
	Nederlandse samenvatting	167
	Acknowledgements	169

CHAPTER 1

Introduction

Light is everywhere! It is the essence of life on our planet. Light from the sun is the main source of energy for the plants that are at the very bottom of the food chain hence it is the foundation of all life on earth. Daily and nightly changes in the intensity of light are the control factors for many physiological processes in humans and animals bodies. Obviously, light is widely used in society and science [1, 2]. Even the fact that we observe the outside world with our eyes is based on the existence of light and its reflection and refraction from our surroundings. Being limited by the resolution and sensitivity of eyes, mankind creates special devices to obtain the information that is otherwise hidden.

Light is widely used for sensing [3–5]. Sensors that allow us to detect the presence of small molecules or micro organisms in the air, gases, our bodies or environment, which is important for medical or industrial purposes. Nanophotonic sensors are compact, versatile, fast and sensitive [6, 7].

Light has also always attracted great attention due to its fundamental property to have the fastest speed at which information or matter can travel [8]. Thus it is natural to use light for communication that has a great importance for modern society. Already in ancient times light was used for communication in the form of for example lighthouses. The most famous Pharos lighthouse of Alexandria is dated between 280 and 247 BC [9]. But the larger a society grows, the further distances information needs to travel to be communicated. In modern world it is necessary to transmit information as fast as possible over distances of thousands of kilometers. The use of optical circuits for communication started to be a major subject of research in the 19060s and 1970s [10, 11].

Due to the possible integration of optical circuits to the existing electronic devices, silicon stands out as a promising material for optical circuits [12, 13]. In the 1990's silicon optoelectronics started to grow from idea to the realization [14, 15]. Silicon optical phase modulators with the modulation frequency rising from 20 MHz [16] in 1990's to 1 GHz [17] in 2000's. To allow monolithic integration of silicon modulators with electronics on a single silicon substrate it is important to keep the technology compatible with the widely-used complementary metal-oxide-semiconductor (CMOS) processing. Moreover, considering the small size of modern electronic components, in order to match the length scales with it photonic devices have to be of nanometer sizes. Combination of light and silicon at nanometer scale brings us to silicon nanophotonics that is a subject of current thesis. Currently the main application of silicon nanophotonics is to send the signal from one chip to another by optical means, called optical interconnec-

tion [18] and this is being extended to on-chip communication called datacom [19]. Using optical elements allows to benefit in interconnect density, energy and timing [20]. Silicon CMOS-integrated nanophotonics allows to benefit from large total bandwidth with a high number of channels controlled in a wavelength-division multiplexer (WDM) and cost efficiency[21, 22]. Up to date most integrated optics and CMOS processes remain planar and thus two-dimensional (2D). To continue improving the performance and decreasing the costs, higher levels of integration are needed. Three-dimensional (3D) integration is road leading to the future developments. Examples of commercially available integrated circuits with 3D architecture are being offered by world leading companies such as Intel and Micron[23] with a recently announced 3D X-point technology for memory cells and Samsung with 3D vertical NAND (v-NAND) [24].

Besides an increasing commercial interest to push technologies to three dimensions, many fundamental questions arise when the materials are structured in a 3D way. An example of phenomena occurring only in 3D nanostructures is the physics of a full 3D photonic band gap corresponding to a range of frequencies of light are forbidden to propagate in any direction and for any polarization, leading to the ultimate control of spontaneous emission [25], and propagation. Another 3D aspect of light is the so-called “stirring” of light, in other words manipulating the phase space of light [26] that is pursued in the FOM program “Stirring of light!”¹. Current open questions are whether 3D photonic crystals with embedded defects are suitable media for the long awaited experimental observation of 3D Anderson localization of light [28, 29] or even suitable building blocks for 3D integrated circuits [30]. To fulfill these prospects there needs to be a way to fabricate in a CMOS-compatible manner 3D photonic crystals in a large scale to prevent finite size effects and fulfill industrial demands and with good alignment for controlling the geometries. Therefore in this thesis we propose a “wild” idea to provide a CMOS compatible platform to realize truly 3D silicon nanophotonics.

1.1 Photonic crystals

Photonic crystals are ordered composite materials with a periodic change of the refractive index on the scale of the wavelength of light λ [25, 29]. Such a periodicity results in their unique properties in controlling light propagation. At the Bragg condition [31] light that is reflected off the lattice planes in the crystal interferes constructively. The wavelength λ_{Bragg} at which constructive interference of reflected light is equal to

$$n \cdot \lambda_{Bragg} = 2 \cdot n_{eff} \cdot d_{hkl} \cdot \sin \theta \quad (1.1)$$

where n is the diffraction order, n_{eff} is the effective refractive index of the medium, d_{hkl} is the lattice parameter, and θ is the incident angle. A range of frequencies for which light is forbidden to propagate in an infinite crystal due

¹To steer light one needs both advanced wavefront shaping [27] and advanced 3D nanostructures; this dissertation focuses on the latter

to Bragg interference is called a **stop gap**. Constructive interference of the reflected light results in the observed increase of the reflectivity for a range of frequencies that is referred to as a **stop band**. Stop bands for visible light can be observed by eye as shiny and colorful appearance that change its color depending on the viewing angle, as for example natural opals or butterfly wings. In the special case that materials are periodically arranged in all three dimensions there exist a complete 3D **band gap** - a range of frequencies in which light is forbidden to propagate in **all** directions and for **all** polarizations. The term band gap originates from the analogy with semiconductors exhibiting a band gap where no electron states are allowed [32]. The existence of a complete photonic band gap allows photonic crystals to exhibit unique optical properties and novel phenomena in cavity quantum electrodynamics (cQED)[33–35]. Fundamental property of a complete photonic band gap is a suppression of vacuum fluctuations [36]. Such suppression of vacuum fluctuations results in the complete inhibition of spontaneous emission in the band gap of a photonic crystal [36]. Photonic crystals with a complete photonic band gap will also modify blackbody radiation spectrum [37], affect dipole-dipole interactions including Förster transfer [38] and the van der Waals and Casimir forces [39, 40] and provide shielding of quantum computing systems from vacuum fluctuations to make them more robust against vacuum noise [35, 41].

In analogy with doping of semiconductors, introducing intended defects and thus states in a photonic band gap enriches cQED even more. A single point defect in a photonic band gap results in an ultimate 3D cavity that is shielded in all dimensions by a photonic crystal such that there is no direction where light can leak sometimes called a “nano-box” for light [42, 43]. To achieve a high quality factor of a cavity it is needed to surround it with large enough photonic crystal to provide sufficient shielding. The picture becomes even more interesting when there is an array of cavities in the photonic crystal. Light then has a possibility to exist in the multiple tiny “nano-boxes” located inside photonic crystal or we can even “stir” it to hop from one cavity to another, as is depicted in Figure 1.1. The array of point defects inside a complete photonic band gap may be a suitable medium for the experimental observation of 3D Anderson localization of light [29].

1.2 Photonic strength

An important parameter that determines how strongly light interacts with any photonic structure is the photonic strength [44]. The photonic strength is defined as the ratio of the polarizability α of an average scatterer and the average volume per scatterer V :

$$S \equiv \frac{4\pi\alpha}{V} \quad (1.2)$$

For the case of photonic crystals, the photonic strength can be written as [45]:

$$S = 3\phi \frac{m^2 - 1}{m^2 + 2} 3g_{hkl} \quad (1.3)$$

Figure 1.1: Artistic representation of a crystal of cavities inside the 3D photonic crystal. Each cavity is formed as an intersection of smaller pores (green) and a number are lighted in the picture. Light is shown to be “hopping” from one cavity to another as shown with the bright lines which is radically different from free-space propagation of light.

where ϕ is the volume fraction of high refractive index material, g_{hkl} is the structure factor at the dominant reciprocal lattice vector that depends on the geometry of the crystal and m is the refractive index contrast of the high (n_{high}) and low (n_{low}) refractive index materials:

$$m \equiv \frac{n_{high}}{n_{low}}. \quad (1.4)$$

From equation 1.3 it is clear that in order to achieve high photonic strength a large refractive index contrast m is needed. This makes a choice of silicon with the high refractive index $n_{si} = 3.5$ even more attractive for photonic crystal fabrication which is the main choice of this thesis. In practice photonic strength S can be determined from the relative width of the dominant stop band observed in transmission or reflectivity experiments $\Delta\omega$ and the central frequency of the stop band ω_c :

$$S_{exp} \simeq \frac{\Delta\omega_{s.band}}{\omega_c}. \quad (1.5)$$

The central frequency ω_c can be expressed as $\omega_c = \frac{2\pi c}{\lambda_{Bragg}}$, where λ_{Bragg} is the central wavelength of the measured stop band. The photonic strength also defines the length scale L_B called Bragg length for the photonic crystal, which is the exponential decay length of incident light at the central wavelength of the stop band. The Bragg length also provides a typical length scale at which interference of light occurs in a photonic crystal. These two quantities S and L_B are related as

$$L_B = \frac{2d}{\pi S}, \quad (1.6)$$

where d is the spacing between the crystal planes. In order to increase photonic strength there are few approaches. One is to increase volume fraction of high

refractive index material ϕ according to equation 1.3. At the same time it is noted that 100% of high refractive index material will not lead to the high photonic strength as there will be no refractive index contrast. Therefore it is clear that there is an optimal volume fraction.

A second way to improve photonic strength is to choose the crystal geometry that provides wide photonic band gap. Diamond-like structures have attracted particular attention due to their large predicted band gap [46, 47]. The practical realization of diamond-like crystals include woodpiles and inverse woodpiles introduced in Reference [46], spiral diamonds [48] and others. A most promis-

Figure 1.2: The structure of 3D inverse woodpile photonic crystals consists of two identical arrays of pores with radius R that are running in two perpendicular directions X and Z with lattice parameters a and c . The arrays are aligned such that pores running in the Z -direction are centered between rows of pores in the X -direction.

ing type of photonic crystal structure is the inverse woodpile due to its large photonic strength corresponding to a wide relative band width of more than $\frac{\Delta\omega}{\omega_c} = 25\%$ [49, 50]. In this thesis we have chosen to study inverse woodpile photonic crystals whose structure consists of two perpendicular 2D arrays of pores. Each array is a centered rectangular lattice with parameters (a, c) such that $a/c = \sqrt{2}$ corresponding to a cubic diamond $\{hkl = 110\}$ face, as is shown in Figure 1.2. Typical values of the pore radius R and lattice constant a are $R=160$ nm and $a=680$ nm. The pores are aligned such that the pores running in the X -direction are centered between the rows of pores running in the Z -direction. For the inverse woodpile photonic structure the dependence of the volume fraction of Si ϕ on the reduced pore radius R/a is shown in Figure 1.3. By calculation the band diagram for each R/a for inverse woodpile crystal structure we obtain the photonic strength S depending on R/a (Figure 1.4). Figure 1.4 shows the upper and lower edges of the stop gap in the ΓX and ΓZ high symmetry directions and the resulting photonic strength $\frac{\Delta\omega}{\omega_c}$. It is clear from Figure 1.4 that there exist an optimum R/a providing the maximum photonic strength and the widest band gap. The optimum value for the infinite inverse woodpile photonic crystal is found to be $R/a_{opt} = 0.245$ [49, 50]. In this thesis we aim to vary photonic strength by varying the pore radius R/a at constant lattice parameter a .

Figure 1.3: Volume fraction of Si ϕ in the inverse woodpile crystal structure as a function of the reduced pore radius R/a .

1.3 Realization and probing of photonic crystals

It is a challenge to realize 3D photonic crystal structures with large photonic strength and desired photonic behavior. A large variety of technique has been used for fabrication of 3D photonic nanostructures [35, 51–53]. One first popular way to fabricate 3D nanostructures is the family of template-assisted methods [54–58]. In these methods, one first assembles a template that is infiltrated with a high refractive index material, followed by removal of the template by calcination or etching. A large variety of templates has been demonstrated, such as artificial opals made from colloidal nanoparticles (usually polymer or silica), polymer photoresist structured by 3D holography [59], or resist structured by direct laser writing (DLW) [60–63]. The geometry of the structures fabricated with DLW is well defined and can be very complex such as for example high-quality photonic crystals made with inversion of woodpile templates shown in Figure 1.5(b) [63], where a nearly complete band gap and remarkable optical properties in transmission and reflection were observed. Nevertheless, subsequent inversion to a high refractive index material introduces undesirable yet unavoidable impurities, roughness, and undesired absorption [64].

A second class of impressive structures are layer-by-layer methods [65–68]. An example of a nano structure fabricated by precise micro-manipulation is shown in Figure 1.5(a). Remarkable results have been reported on the fabrication of woodpile photonic crystal structures with layer-by-layer approach [69, 70]. The main difficulty of layer-by-layer fabrication is the alignment between layers: each

Figure 1.4: Calculated upper (purple) and lower (black) boundaries of the stop gap in ΓX direction for the infinite inverse woodpile photonic crystal. The red curve shows the photonic strength $\frac{\Delta\omega}{\omega}$ extracted from the width of the stop gap.

Figure 1.5: (a) Example of the layer-by-layer fabricated structure from Reference [67]. The structure is a 3D photonic crystal diamond structure made by micro-manipulation in GaAs. The number of layers reaches up to $N = 28$. Image courtesy of T. Tajiri and S. Iwamoto. (b) Example of structure fabricated via inversion of woodpile template made by multiphoton lithography [63]. The image is a cross section made by milling under 45° of a TiO_2 partially infiltrated woodpile. Image courtesy of F. Scheffold.

layer has to be carefully aligned with respect to the previous one so no correlation ensured between layer N and $N + 1$. Therefore it is debatable whether there is a long range order in Z direction. Here we call such an alignment a planar alignment since the layers that are being aligned are in parallel planes. In complementary metal oxide semiconductors (CMOS) industry the parameter

characterizing the planar alignment between two layers is called overlay [71]. For the fabrication of an N -layer thick structure $N-1$ alignment steps are needed with $N-1$ overlay requirements.

In order to avoid a large number of alignment steps a third class of fabrication methods has been proposed, where 3D nanostructures are created by consecutively patterning an etch mask on only two adjacent oblique wafer surfaces with *only* a single alignment step ($n=1$), followed by deep etching [50, 72, 73]. It is important to highlight that in this case the alignment is not planar anymore, as the masks that are aligned with respect to each other are in oblique planes. For the diamond-like photonic crystal under study here, the out-of-plane alignment should be better than 50 nm [50]. In practice an out-of-plane alignment of 15 nm was reached [72]. Nevertheless, even one such out-of-plane alignment step introduces a significant complexity in the fabrication procedure, introducing deviations from perfect alignment and extending the time needed for fabrication. In **Chapter 2** we introduce a novel single-step etch mask approach that allows to fabricate the 3D etch mask on the oblique surfaces with ensured on the design stage alignment. The approach allows flexible design of nearly arbitrary geometries to be patterned on the inclined surfaces with better than 5 nm alignment of features located in different planes with respect to each other. We propose design and realize etch mask for 3D inverse woodpile photonic crystal with and without embedded defects discussed in the later chapters. We also investigate the alignment of the resulting etch mask and prove it to be close to resolution of SEM on the example of a mask for 3D hexagonal crystal lattice.

It is important to push nanofabrication beyond academic facilities and provide fabrication solutions for novel structures that are not only interesting for scientific purposes but also for industry. Recent developments in the field of non-volatile memories are already directed towards the 3D integration [74]. One of the most important industrial requirements to nanofabrication is low cost and high throughput. This can be achieved by using wafer scale fabrication of nanostructures with CMOS compatible techniques. Therefore in **Chapter 3** we propose a possible way to extend the single-step etch mask approach on a wafer scale by means of conventional DUV lithography. The attempts have been made earlier to use highly corrugated surfaces in combination with focused ion beam lithography for nanopatterning such as in the Reference [73]. Nevertheless the minimum feature size achieved in the earlier work stayed in a micrometer scale when the semiconductor industry is steadily moving towards a nanometer feature sizes. In Reference [75] the tilt of the substrate together with the photomask was applied to fabricate 3D microstructures with inclined UV exposure. In this way the microstructures fabricated in the thick layer of negative photoresist first, strongly limited in geometries and second, not transferable into the underlying substrate. Here we propose to employ the conventional UV lithography on the pre-structured silicon substrate to obtain the 3D mask pattern in a single exposure. The substrate is pre-patterned with V-trenches on which photoresist layer is spin coated and DUV exposure is performed. We obtained developed in photoresist features as small as 180 nm located at different depth on the slope of Si V-trenches.

After the etch mask is defined the next step in nanofabrication procedure is pattern transfer from the etch mask to the substrate material. The typical requirements for the pattern transfer are high amplification, reproducibility, small roughness and CMOS compatibility. Pattern transfer is done by a large variety of techniques including anisotropic wet etching [76], electrochemical etching [77], dry (plasma) etching [78] and others [79]. While wet etching of Si allows to fabricate impressive structures with the aspect ratio up to 600 it is fundamentally limited in the geometries of fabricated structures as they are defined by the crystal plane orientations [80]. In the approach of electrochemical etching the advantage is that it allows to etch large volumes [77]. The drawback of it is that when the geometry of the structure becomes complex and multiple etching steps are required, the etchant will pour into already existing structure and inevitably destroy it. To achieve both high aspect ratio etching and flexibility in design allows deep reactive ion etching (DRIE). In DRIE the geometry of the feature and etching selectivity controlled by the etch mask [81]. Most of the reported high aspect ratio structures etched by DRIE are trenches with dimensions in nanometer scale in two directions and large extent in third direction. Great difficulties arise when the etched feature is limited in all three directions such as in case of cylindrical pores. Cylindrical pores are important building blocks both for photonics (including 3D inverse woodpile photonic crystals) and CMOS industry. In this thesis we choose DRIE as the most promising type of etching of 3D photonic nanostructures with high aspect ratio. In **Chapter 4** we describe the process to etch ultra-high aspect ratio nanopores in Si. The example of the high aspect ratio nanopores etched in Si by DRIE and viewed in the cross section by helium ion microscope with unprecedented resolution is shown in Figure 1.6. The aspect ratio achieved in our experiments reaches up to a world record of 42. High aspect ratio nanopores are the building blocks for fabrication of 3D inverse woodpile photonic crystals.

Figure 1.6: High aspect ratio nanopores etching in Si by DRIE and viewed with a helium ion microscope. 1 micron scale bar is shown on the picture.

The optical properties of photonic nanostructures are in essence determined by their complex internal structure that consist of sub-wavelength-scale 3D arrays (periodic, aperiodic, random) of spheres, rods, pores, split-ring resonators, and other structural units [83–85, 108]. Inevitably, a fabricated structure differs from the initial design, both systematically as with structural deformations [50, 86], and statistically as with size polydispersity and random positional disorder [87, 88]. Consequently, the observed performance differs from the expected one. It is therefore critical to assess the structure of a 3D material and verify how well it matches the design. The conventional approach is to perform SEM imaging of the fabricated structures [89]. In spite that it is a non-destructive method and provides high resolution images, it only allows to investigate structure from the outside. Moreover, SEM images are generally of a qualitative nature, that is it is difficult to obtain quantitative structural information. Combining the SEM with micromachining or ion beam milling makes it possible to remove a part of the structure and look inside the structure [90]. The disadvantage of such an approach is that the structure under investigation is inevitably irreversibly destroyed. Among the non-destructive methods of materials investigation the family of X-ray methods stands out. A standard X-ray diffraction patterns provide information about microscopic atomic arrangement but information about mesoscopic structure is missing. Structural information at mesoscopic length scale is accessible by small-angle x-ray scattering. Quantitative data on photonic crystals were notably obtained by our group [91, 92]. This brings us to a field of tomography techniques, which provide a three-dimensional image of a sample [93]. In traditional tomography, the contrast is provided by the sample absorption that is simply related to the brightness of the transmitted image or radiograph. However, since silicon and materials that prevail in nanophotonics and CMOS industry are weakly absorbing, other tomography methods are required. In the **Chapter 5** of this thesis we obtain real space structural information directly from the optical *phase change* of an X-ray beam that propagates through the sample and that depends on the real part of the refractive index. The phase change is quantitatively retrieved from a set of radiographs taken at multiple sample-to-detector distances while rotating the sample (see Methods) [94]. Following a conventional tomographic reconstruction of the retrieved phase maps, the 3D electron density $\rho_e(X, Y, Z)$ is obtained in real space. To achieve nanometer spatial resolution, projection microscopy or zoom tomography is employed [95, 96]. Its main features are that the X-ray beam is focused, and that the sample is placed at a small distance z_s downstream from the focus to collect magnified Fresnel diffraction patterns on the detector [97, 98]. We consider several phase retrieval algorithms and experimental settings to achieve the best reconstruction for our kind of samples. From tomography data we extract important parameters of 3D photonic crystals such as pore radii, pore depth, mutual alignment of the pores and R/a ratio.

Once photonic structure is realized and verified to be matching the design it is time to discover its optical performance. Depending on the functionality of the structure different experiments serve to evaluate its performance [99–101]. The most intriguing feature of 3D photonic crystals is the existence of a 3D photonic

band gap - a range of frequencies for which light is forbidden to propagate in any direction and for any polarization. In the ideal case of an infinite photonic crystal the density of optical states (DOS) as well as local density of states (LDOS) are zero in the band gap [42, 102–104]. In reality though the actual fabricated samples are always finite size and their optical properties differ from the infinite size crystal. Thus it was shown that the LDOS in the band gap of the finite size crystal are non-zero and depend on frequency, position and crystal size [105–107]. Multiple different approaches are used to verify the presence of the complete band gap in a crystal. One method is to probe the LDOS and thus verify the presence of complete photonic band gap is emission measurements since the radiative decay rate of emitters is proportional to LDOS [100, 101]. The accuracy of this method depends strongly on the precision with which the emitter is placed inside the crystal and quantum efficiency of the emitters. Another method is to measure reflected or transmitted light from photonic structure. In the case of stop gap, light with incident k vectors satisfying Bragg condition will be reflected as it cannot propagate inside the crystal. In case of a complete photonic band gap all incident k vectors will be reflected back and in all polarizations. To investigate the photonic behavior of our samples in the **Chapter 6** we choose to perform broadband microscopy reflectivity measurements on fabricated structures. We also study the intriguing polarization behavior of the parent 2D structures of 3D inverse woodpiles by systematically rotating polarization and keeping analyzer parallel or perpendicular to polarizer.

Bibliography

- [1] C. Hyugens (translated by S.P. Thompson, 1912) *Treatise on Light* Project Gutenberg (2005) 9
- [2] Euclid *Optica*, (The English translation is available as: H. E.Burton, *The Optics of Euclid*), J. Opt. Soc. Am. **25** 5 (1945) 9
- [3] S.H. Yun and S.J.J. Kwok *Light in diagnosis, therapy and surgery*, Nat. Biomed. Eng. **1**, 0008 (2017) 9
- [4] Q. Chen, X. Hu, L. Wen, Y. Yu, and D. R.S. Cumming *Nanophotonic Image Sensors*, Small **12**, 4922-4935 (2016) 9
- [5] M.C. Estevez, M. Alvarez, L.M. Lechuga *Integrated optical devices for lab-on-a-chip biosensing applications* Laser Photon. Rev. **6**, 463-487 (2012) 9
- [6] F. Vollmer and S. Arnold *Whispering-gallery-mode biosensing: label-free detection down to single molecules*, Nature Methods **5**, 591-596 (2008) 9
- [7] M. Loncar *Molecular sensors: Cavities lead the way*, Nature Phot. **1**, 565-567 (2007) 9
- [8] A. Einstein *Zur Elektrodynamik bewegter Krper*, Annalen der Physik **17** 891 (1905) 9
- [9] P.A. Clayton, and M.J. Price *The Seven Wonders of the Ancient World*, Routledge, Abingdon (1998) 9
- [10] G.T. Reed *Device physics: The optical age of silicon*, Nature **427**, 595-596 (2004) 9
- [11] R.A. Soref and B.R. Bennett *Electrooptical effects in silicon*, IEEE J. Quant. Electron. **QE-23**, 123129 (1987) 9
- [12] M. Snit, J. van der Tol, and M. Hill *Moore's law in photonics* Laser Photon. Rev. **6**, 1-3 (2012) 9
- [13] J. Orton *The story of semiconductors* Oxford University Press (2004) 9
- [14] R.A. Soref *Silicon-Based Optoelectronics*, Proc. of IEEE **81**, 1687-1706 (1993) 9
- [15] L.Chrostowski, M. Hochberg *Silicon photonics design: from devices to systems*, Cambridge University Press (2015) 9
- [16] C.K. Tang and G.T. Reed *Highly efficient optical phase modulator in SOI waveguides*, Electron. Lett. **31**, 451-452 (1995) 9
- [17] A. Liu, R. Jones, L. Liao, D. Samara-Rubio, D. Rubin, O.Cohen, R. Nicolaescu, and M. Paniccia *A high-speed silicon optical modulator based on a metal-oxidesemiconductor capacitor*, Nature **427**, 615-618 (2004) 9
- [18] G.T. Reed, G. Mashanovich, F.Y. Gardes, and D.J. Thomson *Silicon optical modulators*, Nature Photon. **4**, 518-526 (2010) 10
- [19] P.W. Coteus, J.U. Knickerbocker, C.H. Lam, Y. A. Vlasov *Technologies for*

- exascale systems* IBM J. Res. & Dev. **55** 14 (2011) 10
- [20] D.A. B. Miller *Device Requirements for Optical Interconnects to Silicon Chips* Proc. of IEEE **97**, 1166-1185 (2009) 10
- [21] Yu. Vlasov *Silicon CMOS-Integrated Nano-Photonics for Computer and Data Communications Beyond 100G* IEEE Comm. Mag. **12**, S67-S71 (2012) 10
- [22] J. Leuthold, C. Koos, and W. Freude *Nonlinear silicon photonics* Nature Photon. **4**, 535-544 (2010) 10
- [23] <https://www.micron.com/about/our-innovation/3d-xpoint-technology> Micron press release 17.04.2017 10
- [24] <http://www.samsung.com/semiconductor/products/flash-storage/v-nand/> Samsung brochure 20.06.2016 10
- [25] E. Yablonovitch *Inhibited spontaneous emission in solid-state physics and electronics* Phys. Rev. Lett. **58**, 2059-2062 (1987) 10
- [26] O. S. Ojambati *Stirring the propagation and the absorption of light in complex nanophotonic systems* PhD thesis (2016) 10
- [27] A. P. Mosk, A. Lagendijk, G. Lerosey, and M. Fink *Controlling waves in space and time for imaging and focusing in complex media (Review)* Nature Photon. **6**, 283-292 (2012) 10
- [28] D.S. Wiersma *Disordered photonics* Nat. Phot. **7** 188-196 (2013) 10
- [29] S. John *Strong localization of photons in certain disordered dielectric superlattices* Phys. Rev. Lett. **58**, 2486-2489 (1987) 10, 11
- [30] K. Ishizaki, M. Koumura, K. Suzuki, K. Gondaria, and S. Noda *Realization of three-dimensional guiding of photons in photonic crystals* Nature Photon. **7** 133-137 (2013) 10
- [31] W.L. Bragg *Diffraction of short electromagnetic waves by a crystal*, Proc. Camb. Phil. Soc. **17**, 43 (1913) 10
- [32] C. Kittel *Introduction to Solid State Physics* John Wiley & Sons (2005) 11
- [33] S. John *Quantum electrodynamics of localized light* Physica B: Phys. of Cond. Matt. **175** 87-95 (1991) 11
- [34] S. John *Frozen light* Nature **390**, 661-662 (1997) 11
- [35] M. Ghulinyan and L. Pavesi L (eds) *Vos W and Woldering L ch 8 Cavity quantum electrodynamics with three-dimensional photonic band gap crystals* (Cambridge: Cambridge University Press) (2015) 11, 14
- [36] S. Haroche *Cavity quantum electrodynamics: Fundamental systems in quantum optics* North Holland, Amsterdam (1992) 11
- [37] J. G. Fleming, S. Y. Lin, I. El-Kady, R. Biswas, and K. M. Ho, *All-metallic three-dimensional photonic crystals with a large infrared bandgap*, Nature **417**, 52 (2002) 11
- [38] C. Blum, N. Zijlstra, A. Lagendijk, M. Wubs, A. P. Mosk, V. Subramaniam, and W. L. Vos *Nanophotonic control of the forster resonance energy transfer efficiency*, Phys. Rev. Lett. **109**, 203601 (2012) 11
- [39] G. Kurizki and A. Genack *Suppression of molecular interactions in periodic dielectric structures*, Phys. Rev. Lett. **61**, 2269 (1988) 11
- [40] M. I. Antonoyiannakis and J. B. Pendry *Electromagnetic forces in photonic crystals*, Phys. Rev. B **60**, 2363 (1999) 11

-
- [41] W.H. Zurek *Decoherence and the transition from quantum to classical* Phys. Today **44**, 36 (1991) 11
 - [42] J.D. Joannopoulos, S.G. Johnson, J.N. Winn, and R. D. Meade *Photonic crystals: molding the flow of light* Princeton university press (2008) 11, 19
 - [43] L. A. Woldering, A. P. Mosk, and W. L. Vos *Design of a 3D photonic band gap cavity in a diamond-like inverse woodpile photonic crystal* Phys. Rev. B **90**, 115140: 1-9 (2014) 11
 - [44] W. L. Vos, R. Sprik, A. van Blaaderen, A. Imhof, A. Lagendijk, and G. H. Wegdam, *Strong effects of photonic band structures on the diffraction of colloidal crystals*, Phys. Rev. B **53**, 16231 (1996) 11
 - [45] M. Megens *Structure and fluorescence of photonic colloidal crystals* Ph.D. thesis, University of Amsterdam (1999) 11
 - [46] K. M. Ho, C. T. Chan, C. M. Soukoulis, R. Biswas, and M. Sigalas *Photonic band gaps in three dimensions: new layer-by-layer periodic structures*, Solid State Comm. **89**, 413 (1994) 13
 - [47] M. Maldovan and E. L. Thomas *Diamond-structured photonic crystals*, Nature Mat. **3**, 593 (2004) 13
 - [48] A. Chutinan and S. Noda *Spiral three-dimensional photonic band-gap structure*, Phys. Rev. B **57**, R2006 (1998) 13
 - [49] R. Hillebrand, S. Senz, W. Hergert, and U. G'osele *Macroporous silicon-based three-dimensional photonic crystal with a large complete band gap*, J. Appl. Phys. **94**, 2758 (2003) 13
 - [50] L.A. Woldering, A.P. Mosk, R.W. Tjerkstra, and W.L. Vos, *The influence of fabrication deviations on the photonic band gap of three-dimensional inverse woodpile nanostructures*, J. Appl. Phys. **105**, 093108: 1-10 (2009). 13, 16, 18
 - [51] C. López *Materials Aspects of Photonic Crystals*, Adv. Mater **15**, 1679-1704 (2003) 14
 - [52] J.F. Galisteo-López, M. Ibisate, R. Sapienza, L.S. Froufe-Pérez, Á. Blanco , and C. López *Self-Assembled Photonic Structures*, Adv. Mater **23**, 30-69 (2010) 14
 - [53] M. Ghulinyan, and L. Pavesi (eds) *Light Localisation and Lasing: Random and Quasi-Random Photonic Structures* (Cambridge: Cambridge University Press) (2015) 14
 - [54] Yu. A. Vlasov, B. Xiang-Zheng, C.S. James, and D.J. Norris *On-chip natural assembly of silicon photonic bandgap crystals*, Nature **414**, 289-293 (2001) 14
 - [55] P. Braun *Materials Chemistry in 3D Templates for Functional Photonics* Chem. Mater **26**, 277-286 (2014) 14
 - [56] A. Imhof, D.J. Pine *Ordered macroporous materials by emulsion templating*, Nature **389**, 948-951 (1997) 14
 - [57] B.T. Holland, C.F. Blanford, and A. Stein *Synthesis of macroporous minerals with highly ordered three-dimensional arrays of spheroidal voids*, Science **281**, 538-540 (1998) 14
 - [58] J.E.G.J. Wijnhoven and W.L. Vos 1998 *Preparation of photonic crystals made of air spheres in titania*, Science **281**, 802-804 (1998) 14
 - [59] M. Campbell, D.N. Sharp, M.T. Harrison, R.G. Denning, and A.J. Turberfield *Fabrication of photonic crystals for the visible spectrum by holographic*

- lithography*, Nature **404**, 53-56 (2000) 14
- [60] H.B. Sun, S. Matsuo, H. Misawa *Three-dimensional photonic structures archived with two-photon-absorption photopolymerization of resin* Appl. Phys. Lett **74**, 786-788 (1999) 14
- [61] B.H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Heikal, S.M. Kuebler, I.Y. Sandy Lee, D. McCord-Maughon, J. Qin, H. Rckel, M. Rumi, X.L. Wu, S.R. Marder, and J.W. Perry *Two-photon polymerization initiators for three-dimensional optical data storage and microfabrication* Nature, **398** 51-54 (1999) 14
- [62] M. Deubel, M. Wegener, A. Kasao, and S. John *Direct laser writing and characterization of Slanted Pore Photonic Crystals*, Appl. Phys. Lett, **85** 1895-1897 (2004) 14
- [63] C. Marichy, N. Muller, L.S. Froufe-Pérez, and F. Scheffold, *High-quality photonic crystals with a nearly complete band gap obtained by direct inversion of woodpile templates with titanium dioxide*, Sci. Rep. **6**, 21818: 1-8 (2015) 14, 15
- [64] J.E.G.J. Wijnhoven, L. Bechger, and W.L. Vos *Fabrication and Characterization of Large Macroporous Photonic Crystals in Titania*, Chem. Mater. **13**, 4486-4499 (2001) 14
- [65] J.G. Fleming and S.Y. Lin *Three-dimensional photonic crystal with a stop band from 1.35 to 1.95 m*, Opt. Lett. **24**, 49-51 (1999) 14
- [66] S. Ogawa, M. Imada, S. Yoshimoto, M. Okano, and S. Noda 2004 *Control of light emission by 3D photonic crystals*, Science **305**, 227-229 (2004) 14
- [67] T. Tajiri, S. Takahashi, Y. Ota, J. Tatebayashi, S. Iwamoto, and Y. Arakawa *Demonstration of a three-dimensional photonic crystal nanocavity in a 110-layered diamond structure*, Appl. Phys. Lett. **107**, 071102 (2015) 14, 15
- [68] S. Iwamoto, S. Takahashi, T. Tajiri, and Y. Arakawa *Semiconductor Three-Dimensional Photonic Crystals with Novel Layer-by-Layer Structures*, Photonics **34**, 34 (2016) 14
- [69] S. Ogawa, K. Ishizaki, T. Furukawa, and S. Noda *Spontaneous emission control by 17 layers of three-dimensional photonic crystals*, Electronics Lett. **44**, 377-378 (2008) 14
- [70] S. Noda, K. Tomoda, N. Yamamoto, and A. Chutinan *Full three-dimensional photonic bandgap crystals at near-infrared wavelengths*, Science **289**, 604-606 (2000) 14
- [71] H.J. Levinson *Principles of Lithography* (Bellingham: SPIE Press) p 363 (2001) 16
- [72] R.W. Tjerkstra, L.A. Woldering, J.M. van den Broek, F. Roozeboom, I.D. Setija, and W.L. Vos *A method to pattern masks in two inclined planes for three-dimensional nano- and microfabrication* J. Vac. Sci. Technol. B **29**, 061604: 1-8 (2011) 16
- [73] M. Erdmanis, P. Sievil, A. Shah, N. Chekurov, V. Ovchinnikov, and I. Tittonen *Focused ion beam lithography for fabrication of suspended nanostructures on highly corrugated surfaces* Nanotechnology **25**, 335302 (2014) 16
- [74] Y. Fujisaki *Review of Emerging New Solid-State Non-Volatile Memories* Jpn. J. Appl. Phys. **52**, 040001:1-11 (2013) 16

-
- [75] M. Han, W. Lee, S.-K. Lee, S.S. Lee *3D microfabrication with inclined/rotated UV lithography* Sens. and Act. A: Phys. **111**, 14-20 (2004) 16
 - [76] K. E. Bean *Anisotropic etching of silicon*, IEEE Transactions of Electron Devices **25**, 1185 (1978) 17
 - [77] J. E. A. M. van den Meerakker, R. J. G. Elfrink, F. Roozeboom, and J. F. C. M. Verhoeven *Etching of deep macropores in 6in. Si wafers*, J. Electrochem. Soc. **147**, 2757 (2000) 17
 - [78] F. Marty, L. Rousseau, B. Saadany, B. Mercier, O. Francais, Y. Mita, and T. Bourouina *Advanced etching of silicon based on deep reactive ion etching for silicon high aspect ratio microstructures and threedimensional micro- and nanostructures*, Microelectronics Journal **36**, 673 (2005) 17
 - [79] Y.Nishi and R.Doering *Handbook of Semiconductor Manufacturing Technology* Marcel Dekker. New York, (2000) 17
 - [80] B. Wu, A. Kumar, and S. Pamorthy *High aspect ratio silicon etch: A review* J. Appl. Phys. **108**, 051101 (2010) 17
 - [81] A. A. Ayón, K. S. Chen, K. A. Lohner, S. M. Spearing, H. H. Sawin, and M. A. Schmidt *Deep reactive ion etching of silicon* Mater. Res. Soc. Symp. Proc., vol. 546, pp. 5161, 1999 17
 - [82] C.M. Soukoulis, M. Wegener, *Nature Photon* **5**, 523 (2011) 18
 - [83] J.K. Gansel *et al.*, *Science* **325**, 1513 (2009) 18
 - [84] J.E.G.J. Wijnhoven, W.L. Vos, *Science* **281**, 802 (1998) 18
 - [85] S. Noda, K. Tomoda, N. Yamamoto, A. Chutinan, *Science* **289**, 604 (2000) 18
 - [86] S.H. Fan, P.R. Villeneuve, J.D. Joannopoulos, *J. Appl. Phys* **78**, 1415 (1995). 18
 - [87] S. Hughes, L. Ramunno, J.F. Young, J.E. Sipe, *Phys. Rev. Lett.* **94**, 033903 (2005) 18
 - [88] A.F. Koenderink, A. Lagendijk, W.L. Vos, *Phys. Rev. B* **72**, 053102 (2005). 18
 - [89] D. McMullan *Scanning electron microscopy* Science **17**, 175-185 (1995) 18
 - [90] J. Goldstein, D.E. Newbury, D.C. Joy, C.E. Lyman, P. Echlin, E. Lifshim, L. Sawyer, and J.R. Michael *Scanning Electron Microscopy and X-ray Microanalysis* (Springer science + business media, New York, 2003) 3rd Edition 18
 - [91] J. E. G. J. Wijnhoven, L. Bechger, and W. L. Vos *Fabrication and characterization of large macroporous photonic crystals in titania* Chem. Mater. **13** 4486-4499 (2001) 18
 - [92] M. Megens, and W. L. Vos *Particle excursions in colloidal crystals* Phys. Rev. Lett. **86**, 4855-4858 (2001) 18
 - [93] B. Pollak *Experiences with Planography* Dis Chest **24**, 663-669 (1953) 18
 - [94] S. Zabler, P. Cloetens, J.-P. Guigay, J. Baruchel, and M. Schlenker, *Optimization of phase contrast imaging using hard x rays* Rev. Sci. Instrum. **76**, 073705:1-7 (2005) 18
 - [95] C. S. Schroer, J. Meyer, M. Kuhlmann, B. Benner, T. F. Gunler, B. Lengeler, C. Rau, T. Weitkamp, A. Snigirev, and I. Snigireva, *Nanotomography based on hard x-ray microscopy with refractive lenses* Appl. Phys. Lett. **81**, 1527-1529

- (2002) 18
- [96] C. A. Larabell and M. A. L. Gros, *X-ray Tomography Generates 3-D Reconstructions of the Yeast, *Saccharomyces cerevisiae*, at 60-nm Resolution* Mol. Biol. Cell **15**, 957-962 (2003) 18
 - [97] R. Mokso, P. Cloetens, E. Maire, W. Ludwig, and J.-Y. Buffire, *Nanoscale zoom tomography with hard x rays using Kirkpatrick-Baez optics* Appl. Phys. Lett. **90**, 144104 (2007) 18
 - [98] P. Cloetens, W. Ludwig, J. Baruchel, D. van Dyck, J. van Landuyt, J.P. Guigay, and M. Schelenker, *Holotomography: Quantative phase tomography with micrometer resolution using hard synchrotron radiation x rays*, Appl. Phys. Lett. **75**, 2912 (1999) 18
 - [99] S. Takayama, H. Kitagawa, Y. Tanaka, T. Asano, and S. Noda, *Experimental demonstration of complete photonic band gap in two-dimensional photonic crystal slabs* Appl. Phys. Lett. **87**, 061107 (2005) 18
 - [100] A. F. Koenderink, L. Bechger, A. Lagendijk, and W. L. Vos, *An experimental study of strongly modified emission in inverse opal photonic crystals* Phys. Stat. Sol. (A) **197**, (2003) 648-661 18, 19
 - [101] P. Lodahl, A. F. van Driel, I. S. Nikolaev, A. Irman, K. Overgaag, D. Vanmaekelbergh, and W. L. Vos, *Controlling the dynamics of spontaneous emission from quantum dots by photonic crystals* Nature **430**, (2004) 654-657 18, 19
 - [102] Z.Y. Li and Y. Xia *Optical photonic band gaps and the Lamb shift*, Phys. Rev. A, **63**, 043817 (2001) 19
 - [103] K. Bush and S. John *Photonic band gap formation in certain self-organizing systems*, Phys. Rev. E, **58**, 3896 (1998) 19
 - [104] C.M. Soukoulis *Photonic band gap materials: "semiconductors" of the future?*, Phys. Scr. T **66**, (1996) 146-150 19
 - [105] M. D. Leistikow, A. P. Mosk, E. Yeganegi, S. R. Huisman, A. Lagendijk, and W. L. Vos *Inhibited spontaneous emission of quantum dots observed in a 3D photonic band gap*, Phys. Rev. Lett. **107**, 193903: 1-5 (2011) 19
 - [106] D. P. Fussell, R. C. McPhedran, and C. Martijn de Sterke *Three-dimensional Greens tensor, local density of states, and spontaneous emission in finite two-dimensional photonic crystals composed of cylinders*, Phys. Rev. E **70**, 06608 (2004) 19
 - [107] E. Yeganegi, A. Lagendijk, A.P. Mosk, and W.L. Vos *Local density of optical states in the band gap of a finite one-dimensional photonic crystal* Phys. Rev. B **89**, (2014) 045123: 1-10 19
 - [108] C.M. Soukoulis, and M. Wegener, *Past achievements and future challenges in the development of three-dimensional photonic metamaterials*, Nature Photon **5**, 523 (2011) 18

CHAPTER 2

Single-step etch mask for 3D monolithic nanostructures

We present a method to fabricate a 3D mask that allows to etch three-dimensional monolithic nanostructures by using only CMOS-compatible processes. The mask is written in a hard-mask layer that is deposited on two adjacent inclined planes of a Si wafer. By projecting in a single step two different 2D patterns within one 3D mask on the two inclined planes, the mutual alignment between the patterns is ensured. After the mask pattern is defined, the etching of deep pores in two oblique directions yields a three-dimensional structure in Si. As a proof of concept we demonstrate 3D mask fabrication for three-dimensional diamond-like photonic band gap crystals in silicon. The fabricated crystals reveal a broad stop gap in optical reflectivity measurements. We propose how 3D nanostructures with five different Bravais lattices can be realised, namely cubic, tetragonal, orthorhombic, monoclinic, and hexagonal, and demonstrate a mask for a 3D hexagonal crystal. We also demonstrate the mask for a diamond-structure crystal with a 3D array of cavities. In general, the 2D patterns on the different planes can be completely independently structured and still be in perfect mutual alignment. Indeed, we observe an alignment accuracy of better than 3.0 nm between the 2D mask patterns on the inclined planes, which permits one to etch well-defined monolithic 3D nanostructures.

2.1 Introduction

In this chapter we present a new fabrication method for monolithic 3D nanostructures. The key step is to define and make a single step etch mask on two inclined planes *simultaneously* with an out-of-plane alignment ensured at the design stage. As an example for a single step etch mask, we realise a pattern that yields a (110) plane of a cubic inverse woodpile structure on one surface and $(1\bar{1}0)$ plane on a perpendicular adjacent surface. We describe the fabrication process of such a so-called “3D mask”, as well as the subsequent etching process to fabricate 3D photonic band gap crystals with diamond-like inverse woodpile structure (see Figure 2.1). We investigate the ensured alignment at the design stage by

carefully characterizing the realised structures on the inclined planes. We study nanophotonic behaviour of the fabricated crystal by reflectivity measurements. We discuss other 3D structures that are feasible using our method such as disordered structures and different 3D Bravais lattices; as a proof of principle, we demonstrate a 3D mask for a hexagonal 3D nanostructure, and a 3D cavity array. Finally we discuss the use of various lithography techniques with our method.

Figure 2.1: SEM image of a monolithic 3D photonic band gap crystal fabricated in Si using a single step etch mask. The crystal has the inverse woodpile structure with a cubic diamond-like symmetry that consists of two sets of perpendicular pores. The top surface in the image is the (110) crystal plane and the perpendicular surface at the bottom is the $(\bar{1}10)$ crystal plane. The scale bar is shown in the image. The typical radius of the pore is $R=160$ nm and the lattice constant $a=680$ nm.

2.2 Fabrication process for the 3D single-step etch mask with built-in alignment

The generic scheme to fabricate a 3D etch mask on two inclined planes is shown in Figure 2.2. First, the hard mask material that serves as an etch stop is deposited on two inclined planes, see Figure 2.2(a). Next, the desired pattern is written onto the oblique surfaces, as shown in Figure 2.2(b). The projection is made from a side such that both inclined planes can be reached. The projected pattern consists of two parts: pattern a , designed for one surface and pattern b , designed for the second surface. We emphasize that our method allows for a complete freedom to independently design the two patterns a and b . In Figure 2.2(b) the two patterns are designed to be similar and in Figure 2.7(b) and (c) examples are given where patterns on oblique planes are designed to be different. The two patterns are written in one projection and are therefore by design in perfect mutual alignment. Mask apertures for subsequent etching are opened during the third step of the mask fabrication process (Figure 2.2(c)).

The fact that the pattern is projected on a non-normal surface must be taken into account in the pattern design. The pattern is designed in such a way that

Figure 2.2: Scheme for the single step etch mask fabrication on two perpendicularly inclined planes. a) Deposition of a hard mask layer on two inclined planes of a Si wafer. b) Patterning of mask layer in one step on both planes - projection of single 2D mask on 3D surface. Patterns for both perpendicular planes are written in one projection and therefore alignment is ensured. c) Apertures are opened in the mask layer to obtain an etch mask for two intersecting 2D structures that yield the desired 3D structure.

after projection on the inclined planes it yields the desired structure. As is shown in Figure 2.2(b), the x' and y' coordinates in the design plane differ from the x and y coordinates on the sample surface.

We demonstrate our fabrication process using as an example a 3D cubic diamond-like photonic band gap crystal made from silicon. Due to its physical properties silicon plays an important role both in optics and electronics. As a material that is widely used in research and manufacturing, silicon is widely available, cheap, and has a very high purity. Among the diamond-like photonic band gap structures [2] we chose the inverse-woodpile photonic crystal. Inverse-woodpile photonic crystals deserve particular attention in view of the broad band gap with relative width ($\Delta\omega/\omega_c$) of more than 25% [1, 3, 4]. These crystals consist of two mutually perpendicular rectangular arrays of cylindrical pores etched in a high refractive index material. Conceptually the fabrication of an inverse-woodpile structure is easy, although its fabrication remains a challenge due to the required

Figure 2.3: Geometry of the pattern that is projected on two inclined planes. The structure is designed to consist of two centred rectangular arrays shifted with respect to each other by $x' = c'/4$ such that after being projected on two 45° inclined surfaces it gives the (110) and $(1\bar{1}0)$ faces of a cubic inverse woodpile photonic crystal with lattice parameters $a = \sin 45^\circ \times a'$ and $c = c'$. The basic building blocks are designed to be elliptical, in order to yield circles on the mask after projection. The dashed line delimits the top part of the pattern (pattern *a*) that is projected on one surface of the wafer and the bottom part (pattern *b*) that is projected on the second surface.

precise alignment of the perpendicular sets of pores [5, 6, 24].

We start the fabrication procedure from a single crystalline Si wafer. We fabricated the 3D etch mask on two polished adjacent perpendicular surfaces of the wafer. In the first step we deposited a 50 nm thick Cr layer that serves as a hard mask material on two adjacent planes of a wafer (Figure 2.2(a)). We choose Cr as a hard mask material due to its sustainability to SH_6 etching [7], but other possible mask materials such as SiN or SiC are also compatible with our method. The deposition of Cr is done in a home-built sputtering machine and takes around 4 minutes for a 50 nm thick layer.

The patterning of the etch mask can be performed using several types of lithography [8] such as e-beam, focused ion beam (FIB), deep UV (DUV) step-and-scan, or nanoimprint. Since the patterning of the etch mask is performed under an angle θ , the depth of focus F of a lithography tool will limit the mask size along the y -direction (Figure 2.2(b)) to $\Delta y = F / \sin \theta$. E-beam lithography tools and FIB may be refocused during patterning and thus the depth of focus can be extended to the desired value [9, 10]. For DUV lithography the depth of focus (DOF) and the lateral resolution that is also called critical dimension (CD) depend on the wavelength of UV source λ , numerical aperture of the illumination lens NA and technological factors k_1 , k_2 : $CD = k_1 \frac{\lambda}{NA}$, $DOF = k_2 \frac{\lambda}{NA^2}$. For photonic applications considered here the length scales are in the order of the wavelength of light which is much larger (about $20\times$) than typical length scale in electronic integrated circuits and therefore more than a micron-sized depth of focus may be expected. In case of nanoimprint lithography (NIL) the stamp can be fabricated using e-beam lithography and later transferred into a conformal mask pattern as described for example in Ref. [11]. In our case we had focused ion beam (FIB) milling equipment at our disposition to project the mask and open the apertures. We placed a sample in a FEI Nova 600 Nanolab FIB chamber under 45° angle

with respect to the ion beam gun so that both adjacent planes of the wafer can be reached (Figure 2.2b).

The design of a single pattern that is projected on two adjacent planes consists of two parts as shown in Figure 2.3: pattern *a* intended for one plane and pattern *b* intended for the second plane. In our case the planes are orthogonal to each other and aligned at 45° angle with respect to the ion beam gun in *y* direction (Figure 2.2(b)). In the pattern design it is taken into account that projection of the pattern is made under an angle $\theta = 45^\circ$ to the planes, meaning that x' and y' coordinates in the pattern design are related to the x and y coordinates on a surface of fabricated mask as following: $x' = x$ and $y' = y/\sin\theta$. In order to form a cubic diamond-like structure inside the silicon wafer we patterned each plane of the wafer with a centred rectangular array of holes with lattice parameters a and c , where $\frac{a}{c} = \sqrt{2}$ to fulfil the criterion for a cubic crystal. Arrays of holes for two surfaces are shifted by $c/4$ in the x -direction. The pattern is shown in Figure 2.3 and yields (110) and ($\bar{1}\bar{1}0$) crystal planes on a surface of a wafer. The mask pattern is projected on both planes in one step. Since the two patterns intended for different planes are contained in one image, the alignment between them is ensured. A patterning of a 3D mask consisting of two arrays of 30 by 30 holes each takes 7 minutes.

After the etch mask is created, the next step is to etch deep pores inside Si through the openings. Etching can be done using a variety of techniques [12] such as reactive ion etching (RIE) [13], cryogenic etching, wet etching, photo-electrochemical etching [14, 15], or other types of etching depending on a desired structure and mask material. Nanopores are first etched in one direction, then the sample is rotated by 90° and pores are etched in the second perpendicular direction. We etched deep nanopores using deep reactive ion etcher (DRIE) Adixen AMS 100SE as described in reference [13]. It has been shown earlier that the air-silicon interface deflects ions by only a small angle [6]. Moreover for diamond-like inverse woodpile 3D photonic crystal it has been shown that its band gap is robust to deviations of the pore directions [16]: even with misalignments as large as 5° , the relative band gap width is only reduced from 24% to 21%. Since we etch both sets of pores one after another we introduce an additional oxygen plasma cleaning step after etching each set of pores. The cleaning step is needed to remove the protective polymer layer remaining after the etching process into the front surface of the sample.

2.3 Results and discussion

2.3.1 Fabricated structure characterization

The result of patterning a 3D etch mask in a single step is shown in Figure 2.4. Figure 2.4(a) shows four 3D masks in a row on the edge of a Si wafer. Each of the 3D masks was written in one step and consists of (110) and ($\bar{1}\bar{1}0$) crystal planes of the cubic inverse woodpile crystal. The number of 3D mask structures written along the edge of a Si wafer is only limited by the size of the wafer. The maximum width in the x -direction of a single structure that is written in one

step is determined by the horizontal field of view of the lithography tool which is in our case a FIB setup. In this study the horizontal field of view was $12.8\mu\text{m}$ as set by the magnification of $10000\times$. By decreasing the magnification or stitching the fields of view, it is possible to increase the size of a continuous structure in the x direction. Thus, we may effectively consider the four closely spaced 3D patterns in Figure 2.4(a) as one large $L_x = 40\mu\text{m}$ sized nanostructure. The size in the y -direction is limited by the depth of focus of the tool and can be extended by performing for example multiple milling runs at different depths.

Figure 2.4: a) Overview of a Si wafer with four 3D etch masks milled in one step. The coordinates (x,y) are indicated. b) Side view on one of the mask patterns. The dashed line in the middle indicates the 90 degree edge of the Si wafer. c) Zoom-in on one surface of a mask pattern. a and c are lattice parameters with $\frac{a}{c} = \sqrt{2}$. Scale bars are shown in each image.

Figure 2.4(b) shows one complete mask patterned on both wafer planes. Above the dashed red line there is a surface that contains pattern a corresponding to a (110) crystal plane of the targeted photonic crystal. Below the dashed line there is a perpendicular surface that contains pattern b corresponding to a $(1\bar{1}0)$ crystal plane. The design for this mask shown in Figure 2.3 is such that centres of the apertures in pattern b are shifted by $\Delta x = a/4$ to be exactly in the middle between apertures of pattern a . The lower surface of the wafer has some deep

lines that are the result of manual polishing (and which slightly reduce the quality of the mask layer on that side. Fortunately, the effect of such lines was found to be insignificant in subsequent processing, although it may introduce optical scattering.

Figure 2.5: The out-of-plane alignment defined as a deviation Δx of the position of an aperture in pattern *a* relative to an aperture on the oblique plane in pattern *b*. The data were taken on the pattern shown in Fig. 9. (a) Circles show measurements taken for four pairs of apertures close to the wafer edge; apertures in pattern *a* are located at $y = 1.42 \mu\text{m}$ and in pattern *b* at $y = -1 \mu\text{m}$. Squares show measurements for four pairs of apertures further from the edge; in pattern *a* at $y = 1.42 \mu\text{m}$ and in pattern *b* at $y = -5.42 \mu\text{m}$. (b) Out-of-plane alignment averaged over four pairs of apertures Δx within one structure is shown for four different structures. In both figures error bars represent the resolution of the SEM.

Since patterns *a* and *b* are located on oblique planes we characterize the alignment between patterns *a* and *b* that we refer to as the out-of-plane alignment. We foresee two sources of possible misalignment: first, the sample may be placed under an angle different from 45° during the mask projection step (Figure 2.2(b)), second, the mask pattern can be rotated with respect to the edge of the sample. In the first case the sample tilt is precisely set by a positioning stage and controlled with SEM image, therefore we expect the tilt alignment to be always better than a few degrees. For a misalignment by 2° the dimensions of a projected pattern result in a structural strain of only 3%. In the second case if the projected pattern is rotated with respect to the wafer edge by an angle δ , the apertures located at a distance y from the edge will be displaced by $\Delta x = y \cdot \sin \delta$ from their designed positions. In practice we expect the angular misalignment to be less than $\delta = 2^\circ$, which is sufficiently small to realise bonafide 3D nanostructures.

To characterize the out-of-plane alignment we digitally take the grey value cross-sections from the SEM images through a row of apertures. First we select an aperture in pattern *a* and take a grey value cross section from the SEM image to define its central position. Then we select an aperture in pattern *b*, take a grey value cross-section to define its position and compare the relative position

Δx of these two apertures. In this way we determine a mutual alignment of the apertures located on inclined planes. In Figure 2.5(a) we have collected two sets of data for the structure shown in Figure 2.8. In the 1st set indicated as circles we plot the out-of-plane alignment between pairs of apertures where one aperture in pattern *a* is taken in the row at a distance $y = 1.4 \mu\text{m}$ from the edge and the second aperture in pattern *b* is taken in the row at a distance $y = -1 \mu\text{m}$ from the edge. From the data we conclude that the deviation of apertures positions from the design is within the error bar of SEM accuracy. To verify the alignment over further distances from the edge, in the 2nd set of alignment data, shown as squares in Figure 2.5(a), we take the second aperture in pattern *b* in a row located at $y = -5.42 \mu\text{m}$ and compare their positions to the same apertures in pattern *a* as before. We see that the out-of-plane alignment stays within the resolution of SEM for both sets of data, independent of the distance from the edge, thus providing an upper boundary of 0.05° for rotational misalignment discussed earlier. We find here the deviation from the designed structure (Figure 2.3) to be at most 5 nm. In Figure 2.5(b) we plot the out-of-plane alignment data $\overline{\Delta x}$ that are averaged over four pairs of apertures within one structure for four different structures (as illustrated, e.g., in Fig. 4(a)). It is seen that the average over a mask varies between $\overline{\Delta x} = 2.3 \text{ nm}$ and $\overline{\Delta x} = 4.3 \text{ nm}$ with a mean of 3.0 nm. The error bars in both Figures 2.5 (a) and 2.5(b) indicate the typical accuracy of $\pm 4 \text{ nm}$ of the scanning electron microscope. Thus, we conclude that the out-of-plane alignment data are mostly determined by the SEM error and are better than 3.0 nm. Therefore, the out-of-plane alignment for individual apertures is consistent with zero deviation, in agreement with the starting point of our 3D mask method that the two oblique pattern have built-in mutual alignment.

Figure 2.4c shows a zoom-in to the front surface of a wafer. We see that the elliptical apertures in the pattern design (see Figure 2.3) have been correctly projected to become circular apertures with the diameter of 273 nm on the sample surface. From Figures 2.4 and 2.5 we conclude that we have successfully fabricated a desired 3D mask structure on two inclined planes. We emphasize that the alignment between the patterns on two inclined planes is ensured at the design stage since both patterns are written in one projection and is within the resolution of SEM.

After etching of deep pores in silicon in two perpendicular directions, we have sacrificed one crystal in order to view the internal structure of the sample by milling it with a focused ion beam. Figure 2.6(b) shows a schematic representation of the cut and a surface plane that is open for viewing. The cut was made under 45° angle to both planes. Since the pore depth is finite, starting at a certain depth in the structure the perpendicular pores will not overlap inside the crystal. Pores that are far from the edge of a wafer are not deep enough in order to reach the corresponding perpendicular pore, see green line in Figure 2.6(c). Therefore we expect to see a region inside the crystal closer to the edge where pores overlap and form a 3D structure. Further from the edge we expect a region where the structure will be two dimensional. The SEM image of a crystal cross section is shown in Figure 2.6(a). We see that using a single step etch mask deep pores were successfully etched in silicon. Pores etched in both perpendicular

Figure 2.6: (a) The fabricated 3D diamond-like photonic crystal that was opened up by focused ion beam milling. Scale bar is shown in the picture. (b) Schematic representation of how a cross-section is milled on a fabricated sample. The cut is made at 45° to the side of silicon bar. Dashed lines indicate the pore geometry. (c) Schematic cross-section that illustrates how limited pore depth appears on the milled structure. The black line shows where pores overlap with each other and the green line shows the depth beyond which the arrays of pores are two dimensional. (colour online)

directions form a 3D diamond-like structure in the bulk. Far from the surface of the Si wafer the pores are not overlapping. In the present case, the depth of the pores is determined to be $4\text{ }\mu\text{m}$ deep with an aspect ratio (depth to width ratio) of 14. The size of the fabricated photonic crystal is limited by the depth of the pores in the silicon [13]. We conclude from the cross-section that single step etch mask with ensured alignment allows us to fabricate a 3D monolithic nanostructure in bulk silicon.

2.3.2 Structures feasible for fabrication

There is a large variety of structures that can be fabricated using the presented technique. In general mask patterns projected in one step on inclined planes have an arbitrary structure and still be in perfect alignment with respect to each other. We consider 3D Bravais lattices that can be created with the described fabrication process. Using different pattern designs, it is possible to achieve structures with five Bravais lattice systems: cubic, monoclinic, orthorhombic, tetragonal and hexagonal. In Figure 2.7(a) on a left side is shown the simple cubic lattice. On the right side there is a pattern design for the fabrication

of a simple cubic structure, where all lattice parameters are equal ($a=b=c$). Taking into account that the pattern is projected on a $\theta = 45^\circ$ inclined planes, in the design $a' = a/\sin 45^\circ$, $c' = c/\sin 45^\circ$ and $b' = b$. This design consist of two rectangular arrays of apertures aligned with no shift with respect to each other. For completeness we note that this design for a cubic structure is not unique, as many different designs are feasible. In particular, the mask design presented in Figure 2.3 confirms that there are multiple possible designs for cubic structure, notable depending on the type of cubic symmetry (simple versus face centred). Figure 2.7(b) shows a simple tetragonal structure on the left side and the design pattern for realisation of such structure on two perpendicular planes on the right side. In case of tetragonal structure $a=b \neq c$, therefore in the design pattern $c' \neq a'$. That means that the complete mask pattern for a tetragonal structure consist of two different rectangular arrays of apertures, one with lattice parameters a' and b' and other one with parameters c' and b' . Figure 2.7(c) shows the orthorhombic structure on the left and the corresponding design pattern on the right. For an orthorhombic structure $a \neq b \neq c$, which means that in the design pattern all lattice parameters are different. Hence the complete design consist of two different rectangular arrays of apertures with parameters a', b' and c', b' . In Figure 2.7(d) on the left side the monoclinic structure is shown, where $a=b \neq c$ and the angle between two lattice vectors is $\alpha \neq 90^\circ$. In the pattern design this means that the rows of apertures are shifted with respect to each other so that the angle between vectors a', b' and c', b' is $\alpha' = \alpha/\sin 45^\circ$. In Figure 2.7(e) the hexagonal structure is shown on the left side and the pattern design on the right side. The structure consist of two hexagons shifted with respect to each other. Lattice parameters are $a=b \neq c$ and lattice angle $\alpha = 120^\circ$. The pattern design consist of two completely different patterns. Pattern a is similar to the well known hexagonal graphene-like pattern [18], whereas pattern b has a rectangular array of apertures. Due to projection on the inclined planes the lattice parameters in the design are $a' = a/\sin 45^\circ$, $c' = c/\sin 45^\circ$ and $b' = b/\cos \alpha'$, where $\alpha' = \alpha/\sin 45^\circ$. The hexagonal mask has been realized in Cr on a Si wafer by means of a fabrication procedure described earlier in this article and is shown in Figure 2.8. The red dashed line shows the 90° edge of a wafer. The top side on the picture is the (0001) crystal surface of hexagonal structure and the bottom side is a (1010) crystal plane. The 3D mask for this hexagonal structure shows clearly the flexibility of fabrication method to realise structures with independent patterns on inclined surfaces with an unprecedented out-of-plane alignment better than 5 nm. All described 3D structures, except cubic, are predicted to reveal sub-Bragg diffraction [19] which makes them interesting subject for optical study, moreover, simple cubic and hexagonal structures have been predicted to reveal 3D band gaps [20, 21].

Besides different periodic structures it is possible to fabricate masks that yield non-periodic three-dimensional structures or periodic structures with controlled defects. An interesting example is the fabrication of a 3D photonic band gap crystal with a cavity inside. The geometry of cavity described in Reference [22] can be straightforward realised with the presented fabrication method by making two apertures for crossing pores on oblique planes smaller. Moreover,

Figure 2.7: Pattern designs for different lattice systems fabrication. The 3D scheme of the structure is shown on the left and corresponding pattern for etch mask is on the right. (a) Cubic (b) Tetragonal (c) Orthorhombic (d) Monoclinic (e) Hexagonal

it is possible to realize an array of such cavities in a 3D photonic crystal. In Figure 2.9 the mask pattern for an array of $2 \times 2 \times 4$ cavities in 3D photonic crystal is shown. The resulting 3D array of band-gap cavities would represent the photonic version of the Anderson tight-binding model [23] that may reveal intricate nanophotonic phase transitions for light. Another example is the fabrication of three-dimensional disordered or aperiodic structures. In this case patterns a and b can be arrays of randomly distributed apertures or incommensurable lattices [25].

Since patterns a and b are independent from each other, it is also possible to fabricate functionally different components on inclined planes. Figure 1 in Reference [24] shows an illustration of a suggested chip consisting of two integrated circuits on adjacent planes that are interconnected. Using the presented fabrication method it is possible to make interconnection between different integrated circuits with ensured alignment. In addition, it is possible to project optically functional device on one surface and electronic components on the other surface. Such architecture greatly increases density of components on chip, makes interconnections between them easier and gives a possibility to spatially separate optics and electronics on chip.

The limitation for a number of possible structures comes from the subsequent silicon etching step. So far we assume that etching is always done with pores direction normal to the surface of the sample. Nevertheless there are examples where etching under an angle has been demonstrated [26] which can further increase the number of feasible structures.

Figure 2.8: SEM image of a mask for hexagonal 3D crystal fabrication. The dashed line shows the 90° edge of a wafer. Top side is a (0001) crystal plane of hexagonal structure and the bottom side is a (1010) crystal plane. The scale bar is shown on the picture.

Figure 2.9: SEM image of a mask for an array of $2 \times 2 \times 4$ cavities in 3D photonic band gap crystal. Smaller pores that form cavities inside a structure are marked with red circles. (colour online)

2.4 Conclusions and outlook

In summary, a novel method has been proposed to fabricate a three-dimensional etch mask in one step with built-in alignment. The out-of-plane alignment between structures on to oblique adjacent planes has been characterized by means of deviation from the designed structure. The out-of-plane alignment has been found to be better than 3.0 nm. A three-dimensional band gap photonic crys-

tal with an inverse woodpile structure has been realized using a mask that we propose. The masks designs for 3D nanostructures with five different Bravais lattices, namely cubic, tetragonal, orthorhombic, monoclinic, and hexagonal has been shown. The mask for 3D hexagonal structure and for a 3D array of cavities had been realised on a Si wafer.

The presented method allows fabrication of 3D nanostructures that enable exciting prospects in nanophotonics including the pursuit of cavity resonances in 3D photonic band gap crystals [22] and 3D Anderson localization of light in photonic crystals [23, 27]. The next step for further development of the single-step etch mask technique is to broaden it to different types of lithography discussed earlier. DUV lithography is particularly interesting since it is widely used in CMOS industry and therefore opens new possibilities notably for 3D photonic integrated circuits [28, 29]. Also, patterning of inclined planes with accurate alignment allows one integrate on-chip different functional devices: for example an optical device on one surface and an electronic device on adjacent surface. We therefore foresee novel applications of our method in opto-electronics, integrated photonics and sensing.

Bibliography

- [1] Woldering L A, Mosk A P, Tjerkstra R W and Vos W L 2009 The influence of fabrication deviations on the photonic band gap of three-dimensional inverse woodpile nanostructures *J. Appl. Phys.* **105** 093108 29
- [2] Maldovan M and Thomas E L 2004 Diamond-structured photonic crystals *Nature Mater.* **3** 593-600 29
- [3] Ho K M, Chan C T, Soukoulis C M, Biswas R and Sigalas M 1994 Photonic band gaps in three dimensions: New layer-by-layer periodic structures *Solid State Comm.* **89** 413-416 29
- [4] Hillebrand R, Senz S, Hergert W and Gösele 2003 Macroporous-silicon-based three-dimensional photonic crystal with a large complete band gap *J. Appl. Phys.* **94** 2758 29
- [5] L.A. Woldering, A.P. Mosk, R.W. Tjerkstra, and W.L. Vos, *The influence of fabrication deviations on the photonic band gap of three-dimensional inverse woodpile nanostructures*, *J. Appl. Phys.* **105**, 093108: 1-10 (2009). 30
- [6] van den Broek J M, Woldering L A, Tjerkstra R W, Segerink F B, Setija I D and Vos W L 2012 Inverse-woodpile photonic band gap crystals with a cubic diamond-like structure made from single-crystalline silicon *Adv. Func. Mat.* **22** 25-31 30, 31
- [7] Williams K R, Gupta K and Wasilik M 2003 Etch Rates for Micromachining ProcessingPart II *J. Microelectromech. Syst.* **12** 761-778 30
- [8] Imboden M and Bishop D 2014 Top-down nanomanufacturing *Physics Today* **67** 45-50 30
- [9] Grivet P 1972 *Electron optics* (Oxford: Pergamon Press) p 505 30
- [10] Dwir B, Utke I, Kaufman D and Kapon E 2000 Electron-beam lithography of V-groove quantum wire device *Microelectron. Eng.* **53** 295-298 30
- [11] Smith C L C, Desiatov B, Giykmann I, Fernandez-Cuesta I, Levy U and Kristenses A 2012 Plasmonic V-groove waveguides with Bragg grating filters via nanoimprint lithography *Opt. Express* **20** 5696-5706 30
- [12] Banquiu W, Kumar A and Pamarthy S 2010 High aspect ratio silicon etch: A review *J. Appl. Phys.* **108** 051101 31
- [13] Woldering L A, Tjerkstra R W, Jansen H V, Setija I D and Vos W L 2008 Periodic arrays of deep nanopores made in silicon with reactive ion etching and deep UV lithography *Nanotechnology* **19**145304:1-11 31, 35
- [14] Schilling J, Müller F, Matthias S, Wehrspohn R B, Gösele U and Busch K 2001 Three-dimensional photonic crystals based on macroporous silicon with modulated pore diameter *Appl. Phys. Lett.* **78** 1180 31
- [15] Föll H, Christophersen M, Carstensen J and Hasse G 2002 Formation and

- application of porous silicon *Mat. Sci. Eng. R* **39** 93-141 31
- [16] Schilling J and Scherer A 2005 3D photonic crystals based on macroporous silicon: Towards a large complete photonic bandgap *Photonics Nanostruct. Fundam. Appl.* **3** 90-95 31
- [17] Huisman S R, Nair R V, Woldering L A, Leistikow M D, Mosk A P and Vos W L 2011 Signature of a three-dimensional band gap observed on silicon inverse woodpile photonic crystals *Phys. Rev. B* **83** 205313: 1-7
- [18] Geim A K and Novoselov K S 2007 The rise of graphene *Nature Mater.* **6** 183-191 36
- [19] Huisman S R, Nair R V, Hartsuiker A, Woldering L A, Mosk A P and Vos W L 2012 Observation of sub-Bragg diffraction of waves in crystals *Phys. Rev. Lett.* **108** 083901 36
- [20] Cassagne D, Jouanin C and Bertho D 1996 Hexagonal photonic-band-gap structures *Phys. Rev. B* **53** 36
- [21] Sözüer S and Haus J W 1993 Photonic bands: simple-cubic lattice *J. Opt. Soc. Am. B* **2** 296-302 36
- [22] Woldering L A, Mosk A P and Vos W L 2014 Design of a 3D photonic band gap cavity in a diamond-like inverse woodpile photonic crystal *Phys. Rev. B* **90** 115140 36, 39
- [23] Anderson P W 1958 Absence of Diffusion in Certain Random Lattices *Phys. Rev* **109** 1492 37, 39
- [24] Tjerkstra R W, Woldering L A, van den Broek J M, Roozeboom F, Setija I D and Vos W L 2011 A method to pattern masks in two inclined planes for three-dimensional nano- and microfabrication *J. Vac. Sci. Technol. B* **29** 061604: 1-8 30, 37
- [25] Ghulinyan M and Pavesi L (eds) 2015 *Ledermann A, Renner M and von Freymann G* ch 7 *Three-dimensional photonic quasicrystals and deterministic aperiodic structures* (Cambridge: Cambridge University Press) 37
- [26] Suzuki K, Kitano K, Ishizaki K and Noda S 2014 Three-dimensional photonic crystals created by single-step multi-directional plasma etching *Opt. Expr.* **22** 17100-17106 37
- [27] John S 1987 Strong localization of photons in certain disordered dielectric superlattices *Phys. Rev. Lett.* **58** 2486-2489 39
- [28] Chutinan A, John S and Toader O 2003 Diffractionless Flow of Light in All-Optical Microchips *Phys. Rev. Lett.* **90** 123901 39
- [29] Ishizaki K, Koumura M, Suzuki K, Gondaira K and Noda S 2013 Realization of three-dimensional guiding of photons in photonic crystals *Nature Photon.* **7** 133-137 39

CHAPTER 3

Deep UV lithography on the inclined sidewall of a wafer

In this chapter we present an original method to use conventional deep-UV step and scan lithography in combination with a pre-structured substrate to pattern monolithic 3D nanostructures in only one step, with ensured out-of-plane alignment [1]. For the proof-of-concept demonstration of the method we start with a silicon wafer structured with V-shaped trenches. Following the photoresist spin coating on the sidewall of the V-trenches, a deep UV exposure is performed to pattern the resist on the inclined *sidewall* of the Si. Thus apertures developed on the sidewall are located at different depths with respect to the Si wafer surface and therefore form the basis of a 3D structure made by etching. Apertures with diameter between 180 and 500 nm were successfully exposed up to 1.8 μm deep on a silicon sidewall.

3.1 Introduction

Current fabrication technology in semiconductor industry is steadily developing and expanding in the direction of three-dimensional (3D) architectures. A large progress towards 3D architectures was achieved in the area of non-volatile memories driven by the increase of memory capacity while going from 2D to 3D architecture [2]. Modern flash memories, such as BiCS ("bit cost scalable") and NAND are already 3D structures [3, 4]. A large demand for 3D nanostructures also arises in microelectrochemical (MEMS) or nanoelectromechanical (NEMS) technology [5, 6] where the structures typically have a very complex 3D geometry and are produced in a multiple-step layer-by-layer fabrication processes (that are in themselves planar steps). Besides an increasing commercial interest to push technologies to three dimensions, many new fundamental questions arise when the materials are structured in a 3D way. An example of a phenomena occurring only in 3D nanostructures is the full photonic band gap meaning that for a range of frequencies light is forbidden to propagate in any direction and for any polarization leading to the ultimate control of spontaneous emission [7]. Current open questions are whether 3D photonic crystals with embedded defects are suitable media for the long awaited experimental observation of 3D Anderson localization of light [9] or even suitable building blocks for 3D photonic integrated circuits

(so-called PICs) [8]. To answer those questions there needs to be a way to fabricate in a CMOS-compatible manner 3D photonic crystals in a large scale to prevent finite size effects and fulfill industrial demands and with good alignment for controlling the geometries.

Despite the rapidly growing attention to 3D architectures, the platform for their fabrication are at this time purely two dimensional (2D). The most common way for industrial fabrication of 3D structures is layer-by-layer fabrication [10]. In this approach each layer is fabricated separately as a two-dimensional structure and all layers are stacked to form the 3D structure. An obvious issue in this approach is overlay: the alignment of every layer to the previous one. Thus, for fabrication of N layered structure one needs $N - 1$ alignment steps. Every alignment step introduces errors in the structure and moreover slows down the fabrication speed and thus the overall throughput of the fabrication process. A second issue in the layer-by-layer approach is interconnections between layers [11]. Some components that need to be connected to each other may often be located in different layers and thus the interconnection between them is complicated. On the other hand, features that are located close to each other within one layer have the problem of electrical and optical cross talk. Solving these problems is possible if the entire structure is built in a non-planar way such as, for example, feasible in the fast-rising multiphoton lithography also known as direct laser writing (DLW) [12]. The main current disadvantage of DLW is that fabrication is currently processed with polymer materials that are not typically used in optical or electronics. Thus in order to fabricate optically or electronically active device one needs to employ additional processing steps such as multiple infiltrations and calcinations that usually reduce the quality of the resulting structure by introducing the impurities, structural cracks, incomplete filling, see e.g. References [13, 14].

In this Chapter we introduce a novel concept for 3D nanofabrication using conventional UV lithography on a non-planar substrate. We propose to start fabrication process of 3D structures immediately from a non-planar pre-structured Si wafer and describe a process flow for making an etch mask on the inclined sidewalls of the wafer. The etch mask on the inclined sidewalls allows to directly etch structures in different depths of the wafer to form a 3D architecture. The wafer is pre-structured to differ from the planar geometry as shown in Figure 3.1(1). For the proof-of-principle experiment we choose to start from V-shaped trenches on a Si wafer. The dimensions of the trenches can be varied depending on the required applications.

The next step for lithographic process is covering of the substrate with back anti-reflection coating (BARC) and photoresist as shown in Figure 3.1(2). Since the aim is to perform lithography on a sidewall, it is important that the sidewall of the trenches is covered with the photoresist homogeneously. After the sidewall is covered with photoresist, features can be exposed at different depths of the sidewall. Being exposed at different depths features are thus located in different planes with respect to each. As indicated with the black dashed line in Figure 3.1(3), the center of the aperture on the left sidewall is located in between the apertures on the right sidewall to form a 3D structure. Notably even when

Figure 3.1: Concept of our lithography process for a 3D etch mask. The process starts with a pre-structured silicon wafer (1) with V-shaped trenches with width w and depth d that are made by standard cleanroom technologies. (2) The layer of photoresist is spin coated on the wafer and covers the sidewall of the trench to form a homogeneous layer. (3) Exposure of the features on the sidewall. Features are located on different Z -depths from the top of the trench and therefore are in different (x, y) planes. As indicated with the black dashed line the center of the aperture on the left sidewall is intentionally in between the apertures on the right sidewall.

being located in different planes features are in perfect alignment with respect to each other since they are initially designed and projected as one image. Thus with just a single UV exposure on the pre-structured substrate, we realize a mask for etching in two non-parallel directions that allow to achieve a fully 3D structure.

3.2 Experimental results

3.2.1 Process flow for V-trench fabrication

To fabricate pre-structures silicon wafer with V-trenches as shown in Figure 3.1 we have designed a CMOS compatible process flow consisting of 7 steps that are schematically shown in Figure 3.2) and listed with detailed of process parameters in Table 3.1. In this process flow we use KOH anisotropic wet etching of Si to etch long trenches with well-defined sidewalls and inclination [15]. We start with a (100) silicon wafer covered with SiN layer that serves as a hardmask material for KOH etching (Figure 3.1, step 1). In the second step the photoresist layer is spin coated on top of the wafer. In order to etch trenches in a Si wafer using KOH

Figure 3.2: Schematic fabrication process for V-trenches on Si wafer. The detailed description of each fabrication step is given in Table 3.1.

wet etching [15] one needs to align the array of rectangles in the mask material parallel to the $\langle 110 \rangle$ direction of the wafer. Thus special care has to be taken to carefully align the array of rectangles that are exposed in photoresist with respect to Si crystal planes. The alignment of the rectangles can be done either manually or by using standard procedure involving the fan alignment pattern described in reference [16, 17]. After exposure and development of the pattern in photoresist it is transferred into SiN layer (step 3). The transfer is done by reactive ion etching (RIE) of SiN with parameters listed in Table 3.1. The etching time is chosen to be slightly shorter than needed to completely etch away SiN layer in order to prevent unwanted etching of Si underneath SiN. Therefore after stripping of photoresist with oxygen plasma (Step 4), a thin layer of SiN is still left in the lines that are supposed to be open. To completely remove both this layer as well as the native silicon oxide layer underneath a short wet etching in hot 50% HF is applied (Step 6). The seventh step is anisotropic etching of the trenches in Si. KOH wet etching is chosen for anisotropic Si etching due to its known large ratio between etch rates of (110) and (111) Si crystal planes [20]. The wafer with SiN mask is placed in the KOH solution. Etching of the long lines parallel to $\langle 110 \rangle$ direction in silicon wafer results in the grooves with 54.7° inclined sidewall [16] as shown in the Figure 3.2(7). The etching time in KOH defines the depth of the resulting trenches. After 6 minutes of etching the depth of the trenches will be $6 \mu\text{m}$ [21] meaning that the trenches with a width of more than $w = 8.76 \mu\text{m}$ will have flat bottom (see Figure 3.2(7)). The optical microscope image of the resulting trenches on Si wafer is shown in Figure 3.3. The blue layer on the image is the remaining SiN mask layer. Bottom of the

Step	Description	Comments
Start	(100) Silicon wafer	
1	100 nm of silicon nitride deposition	Serves as an etch mask
2	Photoresist spin coating $1.7 \mu m$	For pattern transfer to SiN
3	UV lithography exposure and development	Array of rectangles parallel to the $\langle 110 \rangle$ crystal plane
4	RIE of SiN CHF_3 : 5 sccm O_2 : 5 sccm Pressure: 10 mTorr Time: 1 min 50 sec	Pattern transfer from photoresist to SiN
5	Photoresist stripping	
6	Hot HF 50%: 2 min 50 sec	To remove remaining SiN and native oxide
7	KOH 25%: 6 minutes Temp.: $75^\circ C$	Anisotropic etching of Si

Table 3.1: The process flow for V trenches fabrication on Si wafer

trenches are visible sharp since the microscope is focused on the bottom. The sidewall of the trenches is seen blurred since it is going in depth out of the focus range of the optical microscope.

Figure 3.3: Optical microscope image of the trenches etched in silicon. Blue covering is the SiN etch mask. The width of the trenches is $w = 15 \mu m$. The $20 \mu m$ scale bar is shown on the picture.

3.2.2 Spin coating of the sidewalls with photoresist

After the trenches are formed the next step for UV lithography is the coating of the substrate consecutively with back anti-reflection coating (BARC) and photoresist. For the proof-of-principle experiment we require photoresist layer to have homogeneous withing 10 nm thickness along the area of exposure. In case of the flat substrate spin coating method is typically used to apply BARC and photoresist coatings. Alternative ways to coat the substrate are for example spray coating, dip coating or roll coating [18]. For the proof-of-principle experiment we choose spin coating as it is the most commonly used method. In a spin coating process the coating material is applied to the center of the rotating substrate. Fast spinning of the substrate ensures an even distribution of the coating along the substrate from the center to the edges. Although this method works well in case of a flat substrate it requires optimization in order to be applied for the non flat substrate such as Si with V-trenches. The experiments for optimization of the spin coating recipe were performed both in University of Twente Nanolab and in Nanolab of Technical University of Eindhoven (TU/e). In the University of Twente the coating experiments were performed on a Primus SB15 spin coater and in the TU/e the coating was applied using JDS-Uniphase Primer-oven system. The target of the experiments was to identify the thickness of the photoresist on the sidewall of the trenches on the Si wafer at different spin coating speeds and verify that homogeneous layer of photoresist is formed on the slope of a sidewall. For this experiment wafers were prepared according to the process flow described in section 3.2.1 consisting of the trenches with widths varying from 15 to 100 μm . After the spin coating wafers were cleaved and viewed with SEM in the cross section to identify the thickness of the photoresist layer on the sidewalls. The pieces of the wafer chosen for the viewing were typically located in the central part of the wafer. The left sidewall and the right sidewall of the trench in a cross section are shown in the Figure 3.4(a). To verify the thickness along the slope of the sidewall multiple measurements were taken at different points. At 5 different positions on the slope of the sidewall photoresist thickness varied as little as 256 nm and 263 nm on *both* the left and the right sidewall. The important conclusion from this measurements is that the photoresist thickness is homogeneous on both sidewalls of the trench to within 7 nm along 2.6 microns of the slope which is sufficient for our proof-of-principle experiment.

Similar measurements were performed on the cross sections of the trenches with different widths and for wafers that were coated with two different spinning speeds: 4000 rpm and 3000 rpm. The photoresist thickness measured at the half depth of the slope depending on the width of the V-trenches is plotted in the Figure 3.4(b). For both coating speeds there is a clear increase in the photoresist thickness with the increase of the trench width. This means that by designing trenches with different widths on the same wafer it is possible to achieve different resist thicknesses on the sidewalls depending on the requirements for the further processing. At the same time by varying the speed of the spin coating it is also possible to get different photoresist thicknesses on the sidewalls of the trenches. Thus there are two ways to achieve targeting resist thickness on the sidewall of

the silicon wafer: first is to design trench width with respect to the given spin coating speed and second is to optimize the spinner speed to the given width of the trenches. This flexibility allows to vary the thickness of the targeted photoresist coating at multiple steps during fabrication process starting from the design of the pre-structured substrate and till the last moment before the spin coating. For our further exposure the targeted resist thickness was chosen to be 225 nm. Given the targeted resist thickness for the DUV exposure we choose to have a substrate pre-structured with V-trenches with the range between 20 μm and 40 μm and spin coated with 3000 and 2500 rpm.

Figure 3.4: (a) SEM image of photoresist spin coated on the left and right sidewalls of the V-trench. The corresponding resist thickness measured at different points on the sidewall is indicated on the figure. The thickness of photoresist is similar on both sidewalls. The scale bar is shown on the image. (b) Thickness of the photoresist on a sidewall depending on a width of the V-trench. Red line shows the resist thickness spin coated at 3000 rpm, black line shows the resist spin coated at 4000 rpm. The error bar indicates the

3.2.3 DUV exposure with step-and-scan lithography

For the exposure experiment we prepared two sets of wafers with V-trenches. Each set of wafers had trenches with depth varying from 20 to 40 μm . One set of wafers was spin coated with 3000 rpm spinning speed and the second set of wafers was coated with 2500 rpm spinning speed. The process flow for the coatings of the wafer is shown in Table 3.2. Each wafer was first coated with BARC, then with photoresist and last with top coating. The exposures of the

photoresist on the sidewalls of Si wafer were performed with the ASML PAS 5500/1100B stepper located in the TU/e NanoLab ¹. The stepper is equipped with a 193 nm ArF laser and 0.75 NA lens providing 90 nm nominal spatial resolution. The exposure dose during the experiments was set to 25 mJ/cm². The layout of each wafer is made in such a way that there is a flat area in the middle of the wafer without any V-trenches that is used for leveling in the stepper. Since our target is to expose apertures in depth on the inclined sidewall of the silicon wafer we set the nominal focus of the stepper to be 500 nm *below* the flat wafer level.

Step	Description	Parameters	Comments
1	Silicon wafer		Pre-structured with V-trenches with 15 to 40 μm width (Table 3.1)
2	Prime		HMDS
3	Chill	21°C for 60 sec	
4	Bottom anti reflection coating BARC 1c5d		$38 \pm 3\text{nm}$
5	Bake	200°C for 90 sec	
6	Chill	21°C for 60 sec	
7	Photoresist TARFP6111		$225 \pm 5\text{nm}$
8	Soft bake	125°C for 90 sec	
9	Chill	21°C for 30 sec	
10	Top coat TCX041		$90 \pm 3\text{nm}$
11	Soft bake	90°C for 60 sec	
12	Chill	21°C for 30 sec	
13	Exposure	25 mJ/cm ²	
14	Developing OPD5262		
15	Rinsing		
16	Hard bake	160°C for 90 sec	

Table 3.2: The process flow for the coating and exposure of silicon wafers using ASML PAS 5500/1100B stepper.

For the exposure of the apertures on the sidewalls of the V-trenches a special reticle was designed and bought by us. Our target is to expose circular apertures on the sidewalls that are inclined with 54.7° with respect to the flat surface of the wafer (see Figure 3.2(7)). In order to get circles on the inclined surface one needs to project ellipses from above in the same way as it is done in the single step etch mask described in in chapter 2 section 2.2. Thus the design of the reticle consist of large fields of ellipses that result in the circular apertures on the

¹It is a pleasure to thank Robert van der Laar, Jeroen Bolk, Kevin Williams, Huub Ambrosius and Meint Smit from TU/e for their advice and assistance in photoresist spin coating and DUV exposures and Eddy van der Heijde, Jo Finders and Arie den Boef from ASML for their help with DUV exposures.

slope of the sidewalls. The small extraction from the reticle is shown in Figure 3.5. Elliptical apertures to be exposed in a photoresist are shown in blue. The arrangement of the apertures is centered rectangular with ratio $c/a = \sqrt{2}$. The size of the apertures varies across the reticle but the ratio c/a is kept constant. By

Figure 3.5: Detail of our new reticle design. The layout consists of large arrays of ellipses designed to appear as circles on the inclined slope. Apertures are arranged in a centered rectangular lattice with ratio $c/a = \sqrt{2}$. Scale bar of 1 micron is shown on the picture.

design, the apertures on the sidewall have a range of the diameters from 100 nm to 1000 nm. The apertures are designed to form the centered rectangular lattice that is suitable for fabrication of for example 3D photonic band gap crystals (see Chapter 2, Figure 2.3). For the proof of principle experiment we aim to project apertures on anywhere on the sidewalls. To make it easier to find apertures in SEM after exposure we fill the entire wafer with apertures. Since there are slight variations in the photoresist thickness along the sidewall we expect exposure to be successful at the point of the slope where resist thickness will be matching the dose, focus depth and aperture size.

3.3 Results and discussion

After the exposure all wafers were viewed with a critical dimensions SEM (CD SEM) Hitachi S-9920 to evaluate the exposure. The typical CD SEM image of the photoresist layer on the sidewalls of the wafers spin coated with 3000 rpm after the exposure and development is shown in Figure 3.6. Wafers that were spin coated with 3000 rpm speed did show neither individual apertures on the slopes of the sidewalls nor on the flat parts of the wafer.

The flat top of the V-trench is on the left side of the image and the sidewall is going downhill from right to left. It can be seen that there are traces of apertures on the sidewall of the trench however the geometry of single apertures was lost likely due to the mismatch of the exposure dose and photoresist thickness .

Figure 3.6: Typical exposure and development result on the wafers coated with 3000 rpm spinning speed. Traces of rows of apertures are visible on the slope of the trench. The geometry of individual apertures was lost likely due to the mismatch of the exposure dose and photoresist thickness.

However wafers that were spin coated with 2500 rpm were exposed and developed successfully. Figure 3.7 shows the CD SEM images of the wafer that was coated with 2500 rpm speed. In Figure 3.7(a) the top of the trench is on the right and the slope of the sidewall is going down from right to left. It is clearly seen that apertures of 509 nm size are fully open in the photoresist layer. Below the first row of apertures there is seen a signature of the second row of apertures though apertures from the second row are seen less clear. We associate it with the fact that second row of apertures is located deeper on the slope thus further from the nominal focus of the exposure. Nevertheless for the proof of principle experiment even not fully developed apertures we count as a successful exposure. In Figure 3.7(b) another exposure and development on the slope of the sidewall is shown. The flat top of the wafer is on the left side and the sidewall slope is on the right side. The size of the fully developed aperture here is 412 nm. There are two other rows of apertures apparent deeper down on the slope. Figure 3.7(c) shows exposure and development of apertures on another V-trench. In this case the right side of the trench is shown in order to prove that successful exposures are possible on both sides of the V-trenches. Here the flat top part of the wafer is on the right side and the slope downhill is on the left side. The size of the open in photoresist aperture is 470 nm. Figure 3.7(d) shows the smallest apertures that was found open on the wafers. Here the size of the apertures here is 180 nm. Typically as feature size decreases their sensitivity to the focus errors increase

Figure 3.7: Apertures open in the photoresist on a sidewall of Si V-trench. (a) The flat top of the trench is on the left side and the sidewall is on the right side. A row of apertures is clearly visible to be developed on the sidewall close to the top surface. The size of each aperture is 509 ± 5 nm. One more row of apertures is less clearly seen deeper towards the bottom of the trench. (b) A row of apertures is open in the photoresist close to the top surface of the trench. The size of each aperture is around 412 ± 5 nm. Two more rows of apertures are visible deeper on the sidewall. (c) A row of apertures with 470 ± 5 nm size is seen on the right side of the trench. We show here another side of the trench to indicate that successful exposure and development are possible on both sides of the trenches. (d) A row of apertures with the smallest size that was found on the wafer are seen on the sidewall. The size of each aperture is 180 ± 5 nm.

dramatically [23]. Thus it is reasonable that the smallest apertures are exposed best close to the nominal focal planes.

To evaluate the exposures in depth on the sidewall of V-trenches we measured the depth of the furthest open aperture of each size on the slope. The maximum depth at which we can still see the signatures of open apertures we call here maximum depth of exposure in order to not confuse with conventional definition

Figure 3.8: The maximum depth of exposure achieved on the sidewall of Si wafer depending on the aperture size. The purple dashed line indicates the nominal depth of the focus during the exposures. The dose during the exposure was 25 mJ/cm^2 . Black dashed dotted line has a slope 0.45, as a guide to the eye.

of depth of focus [23]. Figure 3.8 shows the maximum depth of exposure observed for apertures of each size. The largest apertures of around 500 nm were exposed up to $1.18 \mu\text{m}$ down on the slope of the sidewall whereas the smallest apertures of 180 nm were successfully exposed at the maximum depth of 450 nm . It is clearly seen that the maximum depth of exposure is larger for the large apertures which agrees with similar trend for the exposures on the flat wafers.

3.4 Summary and outlook

We have demonstrated first experiments for DUV lithography on the sidewall of Si trenches. We developed a process flow for pre-structuring Si wafers with V-trenches for further DUV exposures. We showed that spin coating of photoresist on highly corrugated non planar substrate provides homogeneous coverage of the sidewalls with photoresist. The photoresist thickness on the sidewalls of V-trenches was found to vary within 7 nm over the depth of $2.6 \mu\text{m}$. We demonstrated exposure and development of apertures with diameters between 180 and 509 nm on located on the sidewalls of Si trenches. We found the maximum depth of focus for each aperture size. Apertures with largest size of 509 nm are located on the maximum depth of $1.18 \mu\text{m}$. The smallest exposed and developed apertures are the apertures with 180 nm and the corresponding maximum depth of focus is found to be 449 nm . In our experiments we observed only one row

of apertures to be fully exposed and developed on the sidewall. While one row of apertures is not sufficient to fabricate a 3D photonic crystal, the required 4 to 5 rows (from Equation 1.6 we derive $L_{Bragg} \approx 3.2d$, where d is a lattice spacing) could be achieved by for example consecutive lithography imaging on consecutive depths. In order to improve fabrication process care needs to be taken in the design of the trenches since photoresist thickness on the sidewalls depends on the width of the trench and should be optimized. A special reticle with apertures that will be aligned with respect to the trenches on located exactly on the slope will also help in achieving better exposure results. A process flow needs to be designed to transfer the pattern from photoresist to silicon. This can be done with deep reactive ion etching. This results open a number of new opportunities for 3D nanofabrication by means of conventional DUV lithography such as for example possibility to fabricate wafer scale 3D photonic band gap crystals with seemingly *endless* length along the trenches or hybrid functional nanostructures such as photonic integrated circuits (PIC) in close proximity to e.g. memory circuits or electronic data processing circuits.

Bibliography

- [1] D.A. Grishina, C.A.M. Harteveld, L.A. Woldering, and W.L. Vos, *Method to make a single-step etch mask for 3D monolithic nanostructures*, Nanotechnology **26**, 505302 (2015)
- [2] Y. Fujisaki *Review of Emerging New Solid-State Non-Volatile Memories* Jpn. J. Appl. Phys. **52**, 040001:1-11 (2013) 43
- [3] H. Tanaka, M. Kido, K. Yahashi, M. Oomura, R. Katsumata, M. Kito, Y. Fukuzumi, M. Sato, Y. Nagata, Y. Matsuoka, Y. Iwata, H. Aochi, and A. Nitayama *Bit Cost Scalable Technology with Punch and Plug Process for Ultra High Density Flash Memory* Proc. Int. Symp. VLSI Technology, 14 (2007) 43
- [4] S. Whang, K. Lee, D. Shin, B. Kim, M. Kim, J. Bin, J. Han, S. Kim, B. Lee, Y. Jung, S. Cho, C. Shin, H. Yoo, S. Choi, K. Hong, S. Aritome, S. Park, and S. Hong *Novel 3-Dimensional Dual Control-Gate with Surrounding Floating-Gate (DC-SF) NAND Flash Cell for 1Tb File Storage Application* IEDM Tech. Dig. **10**, 668-671 (2010) 43
- [5] F. Niklaus, M. Lapisa, S.J. Bleiker, V. Dubois, N. Roxhed, A. C. Fischer, F. Forsberg, G. Stemme, D. Grogg, M. Despont *Wafer-level heterogeneous 3D integration for MEMS and NEMS* LTB-3D, 247-252 (2012) 43
- [6] V.Ya. Prinz, V.A. Seleznev, A.V. Prinz, and A.V. Kopylov *3D heterostructures and systems for novel MEMS/NEMS* J. Micromech. Microeng. **20** 015021:1-11 (2010) 43
- [7] E. Yablonovitch *Inhibited spontaneous emission in solid-state physics and electronics* Phys. Rev. Lett. **58**, 2059-2062 (1987) 43
- [8] K. Ishizaki, M. Koumura, K. Suzuki, K. Gondaria, and S. Noda *Realization of three-dimensional guiding of photons in photonic crystals* Nature Photon. **7**133-137 (2013) 44
- [9] S. John *Strong localization of photons in certain disordered dielectric superlattices* Phys. Rev. Lett. **58**, 2486-2489 (1987) 43
- [10] A. Todorci-Sanial and C.S. Tan *Physical design for 3D integrated circuits* CRC Press (2016) 44
- [11] V. Kumar, H. Oh, X. Zhang, L. Zheng, M. S. Bakir, and A. Naeemi *Impact of On-Chip Interconnect on the Performance of 3-D Integrated Circuits With Through Silicon Vias: Part I* IEEE Trans. Electron Devices **63**, 2503-2509 (2016) 44
- [12] M. Deubel, G. von Freymann, M. Wegener, S. Pereira, K. Busch, and C.M. Soukoulis *Direct laser writing of three-dimensional photonic-crystal templates for telecommunications* Nat. Mater. **3** 444-7 (2004) 44
- [13] J. E. G. J. Wijnhoven, L. Bechger, and W. L. Vos *Fabrication and charac-*

- terization of large macroporous photonic crystals in titania Chem. Mater. **13** 4486-4499 (2001) 44
- [14] L. Bechger *Synthesis and Fluorescence of Opal & Air-Sphere Photonic Crystals*, PhD thesis (2003) 44
- [15] M. Elwenspoek, H.V. Jansen *Silicon micromachining (Cambridge Studies in Semiconductor Physics and Microelectronic Engineering)* Cambridge University Press, 1999 45, 46
- [16] T.D. James, G. Parish, K.J. Winchester, and C.A. Musca *A crystallographical alignment method in silicon for deep, long microchannel fabrication* J. Micromech. Microeng. **16**, 2177-2182 (2006) 46
- [17] W.-H. Chang and Y.-C. Huang *A new pre-etching pattern to determine h110i crystallographic orientation on both (100) and (110) silicon wafers* Microsys. Technol. **11**, 117-128 (2005) 46
- [18] S. Franssila *Introduction to Microfabrication* John Wiley & Sons, Ltd (2004) 48
- [19] D.L. Kendall *On etching very narrow grooves in silicon* Appl. Phys. Lett. **26**, 195-198 (1975)
- [20] K. Sato, M. Shikida, Y. Matsushima, T. Yamashiro, K. Asaumi, Y. Iriye, and M. Yamamoto *Characterization of orientation-dependent etching properties of single-crystal silicon: effects of KOH concentration* Sens. Actuators A **64**, 87-93 (1998) 46
- [21] W.R. Runyan and K.E. Bean *Semiconductor Integrated Circuit Precessing Technology* Reading, MA: Addison-Wesley (1990) 46
- [22] W. M. Moreau *Semiconductor Lithography Principles, Practice, and Materials* Plenum Press. New York (1988)
- [23] C.A. Mack *Fundamental Principles of Optical Lithography: The Science of Microfabrication* John Wiley & Sons, Ltd (2007) 53, 54

CHAPTER 4

Deep reactive ion etching of silicon

We present advanced nanofabrication process realized in two steps on two inclined surfaces of a silicon wafer. Such process is required for the fabrication of 3D nanostructures in silicon. We discuss here Cr hard mask deposition and milling on two faces of silicon wafer as well as deep reactive ion etching (DRIE) process required for successful fabrication of 3D nanostructures. We fabricate 3D inverse woodpile photonic band gap crystals using our single step Cr etch mask discussed in details in the previous chapter and DRIE process described here. We also present nanopores with the highest reported aspect ratios etched by means of DRIE in silicon: the etched structures have a diameter of 510 nm and a depth of 21.5 microns resulting in a high aspect ratio of 42. The advances in the etching of deep pores in silicon offers exciting opportunities for both two-dimensional and three-dimensional silicon fabrication in the areas of photonic crystals, sensing, solar cells, high-frequency electronics and many others.

4.1 Introduction

Since silicon is the main material in modern CMOS industry, its processing attracts particular attention [1]. Growing attention for three-dimensional devices requires creative approaches in their fabrication. One of the challenges related to the increasing dimensionality of the devices is the fabrication of structures in silicon with high aspect ratio. One of the most used tools for high aspect ratio (HAR) structures fabrication in silicon is deep reactive ion etching (DRIE) [2]. In order to form a three-dimensional structure it is necessary to perform etching in multiple directions. This can be done by simultaneous multidirectional etching with the control over the ion sheath as shown in Reference [9]. Even though there are successfully fabricated photonic crystals using this approach, a strong limitation on the size of fabricated structure to 2 lattice periods may prevent the formation of the complete band gap. Moreover, there is a strong limitation on the geometry of fabricated structure since one and the same mask is necessarily used for etching in different directions. Another approach for multidirectional etching is shown in Reference [10] with the use of Faraday cage around the sample in the etching chamber. The cage provides the equipotential surface for the etching plasma ensuring that ions propagate normal to its surface. Such an approach

requires a significant modification to the etching chamber and extensive simulations of the cage angle, mesh size and the sample placement. Thus for fabrication of our structure of inverse woodpile (see Chapter 1, Figure 1.2) consisting of two perpendicular array of pores we choose to perform etching in two steps with 90 deg rotation of the sample in between. The first successes in this respect were reported by van der Broek et. al. [11] and here we extend this approach to much deeper pores and new two-step etch mask.

4.2 General description of deep reactive ion etching

Deep reactive ion etching is a dry plasma type of etching [2]. While DRIE can be performed with many various types of etching gases, in this Chapter we choose SF_6 gas as an etchant for Si, and O_2 for cleaning. The schematic of the etching chamber is shown in Figure 4.1. The pressure in the chamber is regulated by vacuum pumps and valves. The gas flow that is fed to the chamber is regulated with the entry valves. For stability and temperature control the helium backside cooling is provided. For high aspect ratio etching the chamber is typically featured with capacitive coupled plasma source (CCP) and inductively coupled plasma source (ICP) for separate control of ion energy and ion density respectively (Figure 4.1). The ICP plasma source generates plasma remotely and CCP generator is coupled to the lower electrode to induce the DC bias. Hence the ion density is controlled by ICP power and ion energy is controlled by CCP power supply. High ion densities increase the directionality of the etching but at the same time due to the ions collisions the angular distribution of ions leads to the unwanted sidewall erosion. The composition of the plasma in the chamber is very complex but generally in case of SF_6 etchant it contains $F\cdot$ radicals and SF_x^+ ions [3]. The radicals are not influenced by the electric field in the chamber and thus do not have a preferable direction of movement. The directionality of the etching is employed by the ions that are directed towards the lower electrode by the electric field (see Figure 4.1). If the applied electric field is high then physical sputtering of the material from the surface may occur. Micro-masking effects appearing due to the physical sputtering [4] may also contribute to the sidewall erosion. The etching process that is used in this Chapter for the fabrication of deep structures in silicon is the two-step Bosch process [8]. In this process the etching step and the protective deposition step are continuously alternated. During the deposition step a passivation gas is entered into the reaction chamber, in our case it is C_4F_8 . From the C_4F_8 plasma a protective layer of polymer is deposited over the whole surfaced present in the chamber including sidewalls and bottom of the etched structures. During the next etching step the protective layer is removed from the horizontal surfaces due to the vertically directed ions bombardment. Thus passivation layer protects the sidewalls and ensures high aspect ratio etching. Careful manipulation of both etching and deposition steps duration, gas flows and powers of the plasma sources is required to achieve deep structures without significant sidewalls erosion. The maximum depth of the structure that can be etched with the Bosch process depends on the opening in

Figure 4.1: The schematic picture of a DRIE chamber with inductively coupled plasma source (ICP) and capacitively coupled plasma source (CCP). Vacuum pumps and entry valves regulate the pressure and the flow of etchant gas. The plasma consisted of ions and radicals is generated by the ICP plasma source and ions are accelerated towards the sample (gray ellipsoid) by CCP plasma source. Helium backside cooling provides temperature regularization of the substrate. The figure is adopted from the Reference [7].

the etch mask through which the etching is occurring. In the case of pores the maximum depth of the etched pore will depend on the pore diameter thus to characterize the etching process we will use aspect ratio rather than pore depths. The maximum aspect ratio that is possible to achieve with Bosch process is limited due to the changes in ions angular distribution in the depth of the etched structure and the difficulty for the etching gas to penetrate deeper in the pores.

4.3 Experimental

In this Chapter we study DRIE etching with Bosch process performed on two etching machines - Adixen Alcatel AMS100SE (from now on shortly referred to as Adixen) and SPTS Pegasus etching machine (referred to as SPTS). Due to the differences in two machines the optimized recipes for etching deep pores in Si will be listed separately for each machine. We use single crystalline silicon $\langle 110 \rangle$ p-type wafer as a substrate to be etched. For fabrication of 3D photonic crystals small Si bars are etched from the substrate such that there are two perpendicular surfaces open for etching. Both perpendicular surfaces are covered with 50 nm layer of sputtered Cr that is used as a hard mask material. We define the apertures in the etch mask for 3D photonic crystal fabrication by means of focused ion beam lithography as described in the Chapter 2. For the

test of etching parameters we use flat Si wafers with Cr etch mask patterned with centered rectangular array of apertures by means of DUV lithography. The pattern is chosen such that the wafer always cleaves through a set of pores and thus is referred to as an “easy cleave” pattern. The pattern design has 84.5 deg angle between the axis of the primitive lattice. The details of the “easy cleave” pattern can be found in Reference [7]. For the test of parameters wafer with 2D pattern is cleaved into small pieces that are then places in the etching chamber on top of a dummy wafer. Si bars for etching of 3D photonic crystals are placed on the dummy wafer as well. Since DRIE etching is known to have the load effect [4] such that the etch rate depends on the amount of the surface that is being etching it is important to control the amount of surface that is etched. Thus we need to coat the silicon surface of a dummy wafer. To do so a dummy silicon wafer is always covered with a photoresist layer according to the recipe in the Table 4.1. For better temperature conductivity between the sample and dummy wafer a droplet of a vacuum oil is applied underneath the sample.

Step	Comments
Primer spin coating	HMDS
Photoresist coating	Olin OIR 907-17
Baking	T=120 C for 3 min

Table 4.1: The process flow for the coverage of dummy wafer with the photoresist

4.4 Ultra-high aspect ratio nanopores in Si

2D arrays of deep pores are the building blocks for 3D inverse woodpile photonic crystal structures (see Chapter 1 Figure 1.2) that are discussed in this thesis. To maximize the size of the 3D structure it is necessary to make pores as deep as possible. Moreover for the good optical performance the sidewall erosion should be minimized to reduce undesirable light scattering in the structure. Thus care needs to be taken of this two parameters. Let us first consider the sidewall erosion present in the pores after the etching. Bosch process is known to have a systematic roughness arising from the cycling nature of the etching process. Such roughness is a sequence of rims and is shown closely on the top inset in Figure 4.2. This type of erosion is commonly referred to as a scallop in literature[5]. The scallop is typically more pronounced in the top part of the etched structure as can be seen from Figure 4.2 and this is because the top part of the etched structure is experiencing larger number of etching cycles. The top part scallop present in the Figure 4.2 is periodic with periodicity around 180 nm and thus we expect it to have small influence on the scattering of light of wavelengths within the range of our interest (λ from 800 nm to 2500 nm). The lower inset in Figure 4.2 shows the image of the bottom of the etched pores taken with helium ion microscope (HIM) at ultra high resolution of less than 1 nm. It reveals for the first time that scallop of the Bosch etching is also present at the very bottom of the etched structure and moreover shows the extreme smoothness of the walls of

Figure 4.2: SEM image of the cross section of the 2D array of pores with 250 nm radius etched with Bosch process. 2 micron scale bar is shown on the picture.

the pores above the scalloping region and impressively flat bottom. From this images we conclude that no further specific optimization of the sidewall erosion is needed for our structures at the current stage.

The deepest pores we achieved were etched with the Bosch process on the SPTS etching machine. The process flow that was used for etching is listed in the Table 4.2. The process flow is based on the etching method reported in the work by L.A. Woldering et al. [6, 7]. The difference between the process flow we are using and the process flow suggested in the Reference [7] is the CCP power. The optimum CCP power differs due to the differences in matching the CCP

Parameter	Value
SF_6 gas flow	62 sccm
C_4H_8 gas flow	200 sccm
Etching step duration	3 seconds
Deposition step duration	2 seconds
CCP power	Varied from 30 to 70 W
ICP power	1500 W

Table 4.2: The process flow for DRIE of HARS in Si with the SPTS machine.

source in the SPTS etcher used in this section and Adixen etcher used in the work of Reference [7]. The CCP power of 150 W suggested in the Reference [7] resulted in a strong overetching of the structure such that it is not feasible to define pore depths or diameters after etching. Thus we tuned the CCP power down and performed series of experiments with CCP power in the range between 20 and 70 W. As a figure of merit for the etching process we provide here the

maximum aspect ratio measured from the cleaved pores. The maximum aspect ratio obtained in the etched structures at different CCP is shown in Figure 4.3. SPTS etcher has a possibility to ramp the CCP power during etching cycle. Thus when we plot a value of 35 W, this implies that the power was set to be ramped up from 30 to 40 W. It is seen from Figure 4.3 that the larger CCP power leads

Figure 4.3: Aspect ratio dependence on the power of CCP plasma source. When the power is set to be ramped up from 30 to 40 W during etching cycle the data point is placed at the value of 35 on the plot. The straight line is a guide to the eye.

to the higher aspect ratio of etched structures. This is due to the increase in the ions energy when CCP power is increased. With the higher energy ions reach the bottom of the pores with higher kinetic therefore can reach deeper into the pores with sufficient energy for removing the protection layer. Tuning the CCP power even higher introduces a risk to reach the point when the physical sputtering of the hard mask occurs due to the extensive ion bombardment. Thus a CCP power ramp from 50 to 60 W was chosen as the optimum value for etching. Using an etching recipe listed in the Table 4.2 with the CCP power ramp from 50 to 60 allowed us to achieve the world record high aspect ratio nanopores in Si. We performed the series of experiments with different total etching time to determine the maximum aspect ratio that can be achieved with this parameters. Figure 4.4 shows the aspect ratio measured for different total etching times. Figure 4.5 shows the etching result with 21.4 μm deep pores etched in Si with total etching time of 20 minutes. The diameter of one pore is 509 nm employing the aspect ratio as high as 42. Up to our knowledge these are the highest aspect ratio pores etched in Si with DRIE. In 20 minutes there are 240 full cycles consisting of an one etching and one protection step. The large amount of particles visible on top

Figure 4.4: Aspect ratio dependence on the total etching time for the Bosch process described in Table 4.2. The straight line is guide to the eye.

of the pores is the result of the cleaving of a wafer.

4.5 Advanced two-sided etching for 3D nanofabrication

For fabrication of inverse woodpile structure (see Chapter 1, Figure 1.2) consisting of two perpendicular array of pores it is necessary to etch pores in two perpendicular directions. We chose to do so it two steps. After the etch mask is fabricated on two oblique faces of Si bar (see Chapter 2) one face of the Si bar is etched first then the sample is rotated by 90 deg and second side is etched. This approach brings complications in the etching process since, firstly, the mask on the second etch side is present in the etching chamber during the first etching step and thus being affected by all the plasma components present in the chamber. Secondly, the when etching the second set on pores the first set of pores is already etched and so the etching is happening in the non-bulk but structured material. The present of a complicated structure in the material affect ions angular distribution inside the structure and thus affects the etching result. Thirdly, it is a complicated task to evaluate the etching result of a 3D structure since a precise cross sectioning is required to view the inner structure or a non-destructive method such as X-ray tomography described in the Chapter 5 of this thesis. The etching of 3D photonic crystals described in this section was done with two different etching machines.

Figure 4.5: Ultra high aspect ratio pores etched with DRIE according to the process flow listed in Table 4.2 in Si. The depth of $21.4\ \mu\text{m}$ and diameter of $510\ \text{nm}$ yield the world record aspect ratio of 42. 10 microns scale bar is shown on the picture. The particles on the surface are residuals from the cleaving.

4.5.1 Choice of ICP power

The process flow that was used for two-step etching of 3D inverse woodpile photonic crystals with Adixen was initially adopted from the Reference [7] as listed in the Table 4.5 with ICP power set to $ICP_{high} = 1500\text{W}$ during both etching and protection step. The etching time was set to 10 minutes (120 etching and protection cycles) as suggested by Reference [7]. The etching was performed twice: on one side of the Si bar and on the perpendicular side. The etching resulted in the typical for micro masking and strong over etching effect of nanowires all over the surface of Si bar and complete destruction of the structure. We associate this with ions bombardment of the etch mask especially aggravated because there two etching steps in total. Due to the ions bombardment Cr mask was physically sputtered and Cr particles spread over the chamber landing on the Si bar randomly providing micro masking effect. In Figure 4.6 we show the SEM image of the Cr mask (a) after 6 minutes of etching and (b) after 12 minutes of etching. It is clear from the images that after 12 minutes of etching (144 etching cycles) Cr mask is already significantly damaged and the diameter of individual apertures expands so much that the apertures are connected to each other. Naturally this implies that the structure etched under the mask after 12 minutes is also destroyed. To observe the evolution of the Cr etch mask depending

Parameter	Value
SF_6 gas flow	62 sccm
C_4H_8 gas flow	200 sccm
Etching step duration	3 seconds
Deposition step duration	2 seconds
CCP power	160 W
Etching step ICP power	$ICP_{high} = 1500$ W
	$ICP_{low} = 500$ W
Deposition step ICP power	1500 W

Table 4.3: The process flow for the etching of deep pores in Si with Adixen etcher.

Figure 4.6: Evolution of the etch mask after 6 minutes (a) and 12 minutes (b) of etching with the Bosch process described in the Table 4.5 and a high ICP power $ICP_{high} = 1500W$.

on the total etching duration we performed a series of experiments where we measured the diameter of the apertures on the etch mask after each minute of etching. Figure 4.7(a) shows the result for the etching process with ICP power $ICP_{high} = 1500W$. It is seen from the plot that aperture size on the mask level starts to steadily increase already after 8 minutes of etching. The smallest pitch between the pores in the design used for this experiment is $c = 288$ nm thus it is clear that when the aperture diameter increases to values larger than 277 ± 15 nm such as at 12 minutes etch the apertures start to overlap. With the etching time more than 12 minutes the mask is destroyed thus it is not feasible to measure the aperture diameter anymore. From the plot in Figure 4.7(a) we conclude that the total etching duration with the set of parameters given in the Table 4.5 can not exceed 8 minutes. The depth of the pores d depends strongly on the etching duration and for 8 minutes is determined from the cross sections to be only $d = 3.2 \mu m$. Therefore we choose to modify the recipe such that we can reduce the ion bombardment and physical sputtering of the mask in order to increase etching time. In order to reduce the risk of physics sputtering one can change the CCP or ICP power that control energy of ions or density of ions respectively [12, 13]. The decrease of CCP power results in a poor directionality of ions and thus significant tapering of the pores [7]. Therefore we tune the ICP power down

Figure 4.7: The pore radius on the etch mask depending on the total etching time with the Bosch process described in the Table 4.5 and high ICP power $ICP_{high} = 1500W$ (a) and low ICP power $ICP_{low} = 500W$.

during the etching step. Changing the ICP power may change the etch rate as well therefore we measured the etch rate at high ICP power $ICP_{high} = 1500W$ and low ICP power $ICP_{low} = 500W$. The etch rate measured from the cross sections of the pores is shown in Figure 4.8. It is seen that the etch rate drops by a factor of 2 from $0.4 \mu m/min$ to $0.2 \mu m/min$ with decrease of ICP power from 1500 to 500 W. This change in the etch rate has to be taken into account when determining the total etching time required for the fabrication. Now let us consider the evolution of the etch mask for the Bosch process etching with parameters listen in Table 4.5 and low ICP power $ICP_{low} = 500W$. Figure 4.9 shows the view of the Cr etch mask (a) after 7 minutes of etching and (b) after 12 minutes of etching. It is clear from the comparison of two SEM images that after 12 minutes of etching with lower ICP power Cr mask is not damaged. We performed a series of experiments to determine the aperture size on the mask level depending on the total etching time. Figure 4.7(b) shows the aperture size measured on the Cr mask after the etching depending on the etching duration. It is seen from the plot that aperture diameter on the mask level changes insignificantly up to 10 minutes of etching then there is an increase in the aperture size up to 23% of its diameter and it stays nearly constant up to 25 minutes of etching. From the etch rate of $0.2 \mu m$ determined in the Figure 4.8 for the

Figure 4.8: The etch rate dependence on the ICP power. Error bars are within the symbol size. Straight line is a guide to the eye.

Figure 4.9: Evolution of the etch mask after 7 minutes (a) and 12 minutes (b) of etching with the Bosch process described in the Table 4.5 and low ICP power $ICP_{low} = 500W$.

etching with low ICP power $ICP_{low} = 500W$ the depth of the pores d after 25 minutes of etching is $d = 5 \mu m$.

4.5.2 Polymer residuals after the Bosch process

It was observed during the fabrication that after the first side of the photonic crystal is etched with the Bosch process described above there is a thick layer of polymer present on the perpendicular face of the Si bar that is to be etched second. This layer originates from the protection step of the Bosch process since the process is design to cover vertical surfaces with protective polymer layer. Figure 4.10(a) shows the corner of Si bar after the etching of the first side. In the bottom of the image there is a thick blurred layer of polymer covering the second etch side. Naturally this layer must be removed before the second etching can be

Figure 4.10: (a) The residuals of the polymer layer on the second etch side (bottom) after the Bosch process. The polymer layer is seen as thick blurred layer in the lower part of the image. (b) Second etch side after cleaning with oxygen plasma according to the process flow in Table 4.4. 2 microns scale bar is shown on the picture.

done. There are several possibilities to remove polymer residuals after the Bosch process. One of the standard approaches to remove polymer residuals from the surface is oxygen plasma stripping [14]. We developed a recipe for removal of the polymer layer from the second etch side using the same etcher as for the etching of the pores. The usage of the same equipment for several process steps decreases the amount of sample handling and transportation which is always preferable. The process flow for oxygen plasma cleaning in Adixen etching machine is listed in Table 4.4. The result of 5 minutes oxygen plasma cleaning according to the

Parameter	Value
O_2 gas flow	200 sccm
CCP power	0
ICP power	2000 W
Substrate temperature	-10 C
Time	5 min

Table 4.4: The process flow for oxygen plasma cleaning in Adixen etching machine.

flow listed in Table 4.4 is shown in Figure 4.10(b). From the SEM image shown in Figure 4.10 it is seen that polymer layer is removed from the second etch side sufficiently to open the second side etch mask for further etching. Thus after the

polymer layer is removed from the second etch side the sample is ready to be etched second time. We etch the second set of pores with the same recipe (see Table 4.5 with low ICP power) as the first set of pores. To evaluate the resulting structure we mill a cross section in the XY plane after two etching steps and view the inside of fabricated photonic crystal. The non-destructive inspection of 3D photonic crystals is presented in Chapter 5 of this thesis. The cross section view is shown in Figure 4.11. Two set of pores are clearly seen to be etched in perpendicular directions along X and Z axis. Due to the difficulty to precisely mill cross section parallel to XY plane there is a small tilt in the opened plane thus the pores running along X direction are viewed under an angle. The inset in the Figure 4.11 shows the zoom into two crossing pores. From the zoomed image it is clearly seen that the pores are well aligned with the pores in Z direction centered between pores in X direction. Notably the zoom image reveals that no significant scalloping has occurred during the etching and the walls of the pores are smooth. From the cross section in Figure 4.11 we conclude that we

Figure 4.11: Cross section milled in XY plane through the 3D inverse woodpile photonic crystal after two consecutive etching steps. The inset shows zoom image taken at the higher resolution into the pores where the alignment of pores in X and Z direction is clearly seen as well as the smooth sidewalls of the pores.

have successfully etched 3D inverse woodpile photonic crystal structures with two step DRIE process using Adixen etcher. 2D photonic crystal samples and Sample *E* that are studied by microscopic optical reflectivity in Chapter 6 and listed in the appendix B were fabricated using the process flow described in this

section.

4.5.3 Process flow transfer to SPTS Pegasus etcher

Due to the technical reasons the process flow for 3D photonic crystal fabrication had to be transferred to the more advanced etcher SPTS Pegasus (shortly SPTS). Due to the differences in the etching machines some changes in the process flow were made. In particular the CCP power was tuned down to be ramp from 50 to 60 W as was described earlier in the section 4.4 and ICP power was set to 1500 W during both etching and deposition steps. The resulting process flow is listed in Table 4.2. The oxygen plasma cleaning recipe for the polymer residuals removal

Parameter	Value
SF_6 gas flow	62 sccm
C_4H_8 gas flow	200 sccm
Etching step duration	3 seconds
Deposition step duration	2 seconds
CCP power etching step	ramp 50 to 60 W
CCP power deposition step	0 W
ICP power etching step	1500 W
ICP power deposition step	1500 W

Table 4.5: The process flow for the 3D photonic crystal fabrication with SPTS etcher.

on the second etch side was as well transferred to the SPTS etcher using the standard oxygen plasma chamber cleaning recipe as the basis. The process for cleaning of the second etch side before processing is listed in Table 4.6. Photonic

Parameter	Value
O_2 gas flow	200 sccm
CCP power	0
ICP power	1500 W
Substrate temperature	20 C
Time	5 min

Table 4.6: The process flow for oxygen plasma cleaning in SPTS etcher.

crystal samples **A**, **B**, **C**, **D** studied in Chapters 5 and 6 were fabricated using DRIE process on SPTS etcher.

4.6 Summary

In this Chapter we described the process flow for fabrication of ultra high aspect ratio 2D nanopores in Si with the aspect ratio up to 42. For fabrication of 3D photonic crystals we considered two process flows with high and low ICP powers and chose the one providing the deepest pores yet not destroying the etch

mask by physical sputtering. We addressed the issue of residual polymer layer deposition on the second etch face of the mask for 3D photonic crystal fabrication. We provide the oxygen plasma cleaning recipe for polymer layer removal. We successfully fabricate inverse woodpile 3D photonic crystal structures and provide the cross section view on the etched pores. From the cross section we observe that the structure geometry matches the design and show the little amount of roughness on the sidewalls of the pores.

Bibliography

- [1] Y.Nishi and R.Doering *Handbook of Semiconductor Manufacturing Technology* Marcel Dekker. New York, (2000) 59
- [2] B. Wu, A. Kumar, and S. Pamarthy *High aspect ratio silicon etch: A review* J. Appl. Phys. **108**, 051101 (2010) 59, 60
- [3]] K. R. Ryan and I. C. Plumb *A model for the etching of silicon in SF₆/O₂ plasmas*, Plasma Chemistry and Plasma Processing **10**, 207 (1990) 60
- [4] F. Karouta *A practical approach to reactive ion etching*, J. Phys. D: Appl. Phys., **47** 233501:1-14 (2014) 60, 62
- [5] R.J. Shul and S. J. Peatron *Handbook of Advanced Plasma Processing Techniques* Springer (2000) 62
- [6] L. A. Woldering, R. W. Tjerkstra, H. V. Jansen, I. D. Setija, and W. L. Vos *Periodic arrays of deep nanopores made in silicon with reactive ion etching and deep UV lithography* Nanotechnology **19** 145304: 1-11 (2008) 63
- [7] L. A. Woldering *Fabrication of Photonic Crystals and Nanocavities* PhD thesis, (2008) 61, 62, 63, 66, 67
- [8] F. Laermer and A. Schilp *Method of anisotropically etching silicon*, U.S. Patent 5501893 (1996) 60
- [9] K.Kitano, K. Suzuki, K. Ishizaki, and S. Noda *Three-dimensional photonic crystals fabricated by simultaneous multidirectional etching* Phys. Rev. B **91**,155308 (2015) 59
- [10] P. Latawiec, M. J. Burek, Y.-I. Sohn, and M. Loncar *Faraday cage angled-etching of nanostructures in bulk dielectrics* J. of Vac. Sci. and Tech. B **34** 041801 (2016) 59
- [11] J. M. van den Broek, L. A. Woldering, R. W. Tjerkstra, F. B. Segerink, I. D. Setija, and W. L. Vos *Inverse-woodpile photonic band gap crystals with a cubic diamond-like structure made from single-crystalline silicon* Adv. Func. Mater. **22**, 25-31 (2012) 60
- [12] Y. M. Im, Y. B. Hahn, and S. J. Pearton *Level set approach to simulation of feature profile evolution in a high-density plasma-etching system*, J. Vac. Sci. Technol. B **19**, 701 (2001) 67
- [13] M. Boufnichel, S. Aachboun, F. Grangeon, P. Lefauchaux, and P. Ranson, *Profile control of high aspect ratio trenches of silicon. I. Effect of process parameters on local bowing*, J. Vac. Sci. Technol. B **20**, 1508 (2002) 67
- [14] W.M. Moreau *Semiconductor Lithography: Principles, Practices, and Materials*, Plenum Press, New York and London (2008) 70

CHAPTER 5

Looking inside 3D photonic nanostructures with X-ray tomography

To critically assess the performance of three-dimensional (3D) photonic nanostructures, it is vital to view their internal structure. To this end, we have performed synchrotron X-ray tomography on diamond-like photonic band gap crystals made from silicon. In this chapter we describe the scientific background and experimental details of zoom X-ray nanotomography for 3D imaging of photonic nanostructures. As the result of data analysis we obtain the real space 3D density distribution of a number of complete photonic crystals with as low as 10 nanometer resolution. We also observe a number of hitherto buried deviations from the initial structure design that help to shed new light on optical performance.

5.1 Introduction

Three-dimensional (3D) photonic nanostructures are drawing a fast-growing attention for their advanced functionalities such as cloaking [1], metamaterials [2, 3], and photonic band gaps [4–6]. The optical properties of photonic nanostructures are in essence determined by their complex internal structure that typically consist of 3D arrays (periodic, aperiodic, random) of spheres, rods, pores, split-ring resonators, and other structural units [2–5]. Inevitably, a fabricated structure differs from the initial design, both systematically in case of structural deformations [7, 8], and statistically in case of size polydispersity and random positional disorder [9, 10]. Consequently, the observed performance differs from the designed one. It is therefore critical to assess the structure of a 3D material and verify how well it matches the design.

In case of one-dimensional or two-dimensional nanostructures, the dimensionality is sufficiently low to assess the detailed structure with 2D planar imaging techniques such as scanning electron microscopy (SEM) [11], or atomic force, or scanning tunneling microscopy[12]. In case of 3D materials, one supplements SEM with micromachining or ion beam milling [13] to slice away part of the nanostructure in order to view inside. Unfortunately, however, this approach is destructive and irreversible, moreover milling damage may modify the viewed structure compared to the true structure. Alternatively, transmission electron

microscopy (TEM) is used for 3D imaging with high resolution, however, since the required sample thickness is typically less than one micron [14], it is not suited for 3D photonic nanostructures.

For *in situ* and non-destructive structural characterization of 3D nanostructured materials, X-ray techniques are ideal in view of the high penetration of X-rays, and the short wavelength. Small-angle X-ray scattering (SAXS) is widely used to study 3D nanoparticle arrays [15]. Due to the statistical averaging, however, it is difficult to obtain information about local nano-sized features from SAXS [16, 17]. A powerful technique to study 3D structures with nanometer resolution is X-ray tomography that yields the real space 3D distribution of the material density [18, 19]. In traditional tomography, the contrast is provided by the sample absorption that is simply related to the brightness of the transmitted image or radiograph [20]. Nevertheless, silicon and similar materials that are prevalent in nanophotonics and in CMOS industry are so weakly absorbing that other tomographic methods are required. For such weakly absorbing samples the real space structural information can be obtained from the optical *phase change* of an X-ray beam that propagates through the sample. Since the phase change of the beam depends on the real part of the refractive index, this method is even suitable for weakly absorbing samples.

5.2 Zoom nanotomography

5.2.1 General scheme

In order to improve spatial resolution from the micron scale in previously existing tomography techniques [21] to the nanometer scale, a hard x-ray projection microscopy or zoom tomography is employed [22–24]. The schematic of a projection microscopy is shown in Figure 5.1. The main difference from the conventional tomography scheme is that a sample is set at a small distance z_s downstream of the focus and therefore *magnified* Fresnel diffraction patterns are recorded at the distance z_d from the sample. The experimental parameters are given in section 5.3.2. Changing the out of focus distance z_s allows to vary the magnification of the diffraction patterns, but at the same time will modify the pattern, as in Fresnel regime the diffraction pattern depends on the propagation distance, as is seen from our calculations in Appendix A. While focusing, the sample is illuminated with a spherical wave which relates to a plane wave illumination with an equivalent propagation distance D and a magnification M equal to [25]

$$D = \frac{z_s z_d}{z_s + z_d}, \quad M = \frac{z_s + z_d}{z_s}, \quad (5.1)$$

For each sample position z_s the projection radiographs are recorded for a number of angles in the order of 10^3 within 180° . Before a three-dimensional reconstruction can be applied, the collected radiographs must undergo three pre-processing steps to obtain projections of the sample.

Figure 5.1: A scheme of the zoomed-in tomography setup using focused beam [24]. The x-ray beam is focused using Kirkpatrick-Baez (KB) optics [26] into a $20 \times 30 \text{ nm}^2$ size focus. The sample is placed at multiple distances z_s from the focus point and z_d from the detector.

A first step is a correction related to the deviations with respect to a spherical wave of the sample illumination. The correction is implemented in a following way: two-dimensional phase grids are used as a calibration samples. The grids are imaged at the same position as the sample. Since real positions of maxima and minima of the grid image are known, the angular displacements of measured extrema to the calculated ones are determined. This information is used to undistort the radiographs [24].

The second preprocessing step is related to imperfections of Kirkpatrick-Baez (KB) optics. Due to the surface roughness of the KB mirrors, the incoming wave has non-flat phase profile. In order to correct for this fact, extra images besides an object image I^{object} are taken. One image is taken without an object and is called flat image I^{flat} and another image is taken without the beam and is called dark image I^{dark} . The dark image must be subtracted from all measured intensities including the flat one and then the intensity measured in presence of the object are normalized to the flat intensity:

$$I_{exp} = \frac{I^{object} - I^{dark}}{I^{flat} - I^{dark}}, \quad (5.2)$$

Another way to get rid of distortions introduced by KB optics is to randomly slightly change the sample position at every measured distance. In this way the position of the artifacts introduced by KB optics is also changed and therefore averages out in later reconstruction steps.

The third preprocessing step is to bring the raw images to the same magnification and origin using Equations 5.1. After all preprocessing corrections are done, the in-line holograms of the sample are obtained as in the parallel beam case. There the phase retrieval algorithm is applied [21], see section 5.2.2.

5.2.2 Phase retrieval

A special phase retrieval algorithm is required to distinguish the phase and attenuation modulations introduced by the object. Let us consider an object with a transmission function

$$T(x, y) = \exp[-B(x, y)]e^{[j\phi(x, y)]} \quad (5.3)$$

that is illuminated with an incident monochromatic X-ray beam $u_{inc}(x, y)$ propagating along the Z axis, where

$$B(x, y) = \frac{2\pi}{\lambda} \int \beta(x, y, z) dz, \quad (5.4)$$

$$\phi(x, y) = \frac{2\pi}{\lambda} \int [1 - \delta(x, y, z)] dz = \phi_{air} - \frac{2\pi}{\lambda} \int \delta(x, y, z) dz, \quad (5.5)$$

and where δ is the real part and β is the imaginary part of the refractive index n described in Equation A.3. The field directly behind the object is equal to

$$u_0(x, y) = T(x, y) \cdot u_{inc}(x, y). \quad (5.6)$$

To obtain the field at a distance z behind the sample we use the same approach as in section A.7.2. In this approach the field at a distance z from the object is a convolution of the field at $z = 0$ and the Fresnel transfer function. The convolution in real space corresponds to a multiplication in Fourier space, therefore from now on we will consider field and intensity in the Fourier domain (f_X, f_Y)

$$u_z(f_X, f_Y) = H(f_X, f_Y) \cdot u_0(f_X^2 + f_Y^2), \quad (5.7)$$

with Fresnel transfer function H from equation A.45. The intensity of the field is equal to $I(x, y) = |u(x, y)|^2$, or, at the distance z in the Fourier domain $\tilde{I}_z(f_X, f_Y) = (u_z \star u_z^*)$. From now on symbols with a tilde indicate a Fourier transform. Here we limit the equation to a one-dimensional case as in References [27, 28].

$$\tilde{I}_z(f) = (u_z \star u_z^*)_f = \quad (5.8)$$

$$= e^{(-j\pi\tau f)} T(\tau) \star e^{(j\pi\tau f)} T^*(\tau) = \quad (5.9)$$

$$= \int_{-\infty}^{\infty} e^{(-j\pi\eta f)} T(\eta) e^{(j\pi(\tau-\eta)f)} T^*(\tau-\eta) d\eta = \quad (5.10)$$

$$= e^{-j\pi\lambda z f^2} \int_{-\infty}^{\infty} e^{j2\pi\eta f} T(\eta) T^*(\eta - \lambda z f) d\eta \quad (5.11)$$

In the derivation we change variable to $\lambda z f = \tau$ and use the definition of a convolution:

$$(g(t) \star f(f)) \equiv \int_{-\infty}^{\infty} g(\tau) f(t - \tau) d\tau, \quad (5.12)$$

To equation 5.8 we now apply the slowly varying phase (SVP) approximation [28]. Supposing

$$|\phi(\eta) - \phi(\eta - \lambda z f)| \ll 1, \quad (5.13)$$

we obtain under the integral in equation 5.11

$$T(\eta)T^*(\eta - \lambda z f) \approx 1 + j[\phi(\eta) - \phi(\eta - \lambda z f)]. \quad (5.14)$$

Neglecting the absorption ($B \ll \phi$) and substituting 5.14 into equation 5.11 we simplify 5.11 to

$$\check{I}_z(f) = e^{-j\pi\lambda z f^2} \int_{-\infty}^{\infty} e^{j2\pi\eta f} (1 + j[\phi(\eta) - \phi(\eta - \lambda z f)]) d\eta \quad (5.15)$$

$$= \int_{-\infty}^{\infty} e^{-j\pi\lambda z f^2} e^{j2\pi\eta f} d\eta + \int_{-\infty}^{\infty} e^{-j\pi\lambda z f^2} e^{j2\pi\eta f} j[\phi(\eta) - \phi(\eta - \lambda z f)] d\eta \quad (5.16)$$

$$= \delta(f) + \int_{-\infty}^{\infty} j e^{-j\pi\lambda z f^2} e^{j2\pi\eta f} \phi(\eta) d\eta - \int_{-\infty}^{\infty} j e^{-j\pi\lambda z f^2} e^{j2\pi\eta f} \phi(\eta - \lambda z f) d\eta \quad (5.17)$$

$$= \delta(f) + j e^{-j\pi\lambda z f^2} \check{\phi}(f) - j e^{j\pi\lambda z f^2} \check{\phi}(f) \quad (5.18)$$

$$= \delta(f) + 2\sin(\pi\lambda z f^2) \check{\phi}(f) \quad (5.19)$$

where $\check{\phi}$ is the Fourier transform of $\phi(\eta)$. Equation 5.19 shows a linear relationship in reciprocal space between the observed intensity $\check{I}_z(f)$ and the pursued phase $\check{\phi}(\eta)$, also found in Reference [29].

Taking into account the finite source size (therefore finite coherence γ_c), as well as the detector's point spread function R causes the real intensity measured in the experiment to differ from the theoretical one by multiplication in reciprocal space (convolution in real space) of above mentioned characteristics:

$$\check{I}_z^{exp}(f) = \check{I}_z^{theory}(f) \cdot \check{R}(f) \cdot \gamma_c(\lambda z f). \quad (5.20)$$

Since the result of equation 5.19 is obtained using the SVP approximation, the formula used to retrieve the phase information from the measured intensity is obtained by performing a least square minimization of the difference between the measured intensity and the approximated one. Let the cost function in reciprocal space be defined as

$$S_c \equiv \frac{1}{N} \sum_{m=1}^N \int df |\check{I}_{z_m}^{exp}(f) - \check{I}_{z_m}^{approx}|^2. \quad (5.21)$$

The summation here is applied over multiple propagation distances z_m where images are taken. Taking into account the result of derivation (5.19)

$$\check{I}_{z_m}^{approx}(f) = \delta(f) + 2\sin(\pi\lambda z_m f^2) \check{\phi}(f) \quad (5.22)$$

we find the minimum of equation 5.21 to occur when

$$\begin{aligned} \frac{\partial S_c}{\partial \check{\phi}} &= \frac{\partial [(\check{I}_{z_m}^{exp})^2 - 2\check{I}_{z_m}^{exp}\check{I}_{z_m}^{approx} + (\check{I}_{z_m}^{approx})^2]}{\partial \check{\phi}} = 0, \\ \check{\phi} &= \frac{\sum_m \check{I}_{z_m}^{exp} \sin(\pi\lambda z f^2)}{\sum_m 2\sin^2(\pi\lambda z f^2)} \end{aligned} \quad (5.23)$$

Now admitting the presence of weak absorption ($B(x) \ll 1$), described by the imaginary part of the sample's refractive index, we obtain an expression with an extra cosine term for the absorption [27]:

$$\check{I}_z(f) \approx \delta(f) + 2 \sin(\pi \lambda z f^2) \check{\phi}(f) - 2 \cos(\pi \lambda z f^2) \cdot \check{B}(f) \quad (5.24)$$

Applying the least square minimization approach in the same way as it is done above, the retrieval formulas for $\check{\phi}$ and $\check{B}$ are:

$$\check{B}(f) = \frac{1}{2\Delta} \left(A \cdot \sum_m \check{I}_{z_m}^{exp} \sin(\pi \lambda z_m f^2) - K \cdot \sum_m \check{I}_{z_m}^{exp} \cos(\pi \lambda z_m f^2) \right), \quad (5.25)$$

and

$$\check{\phi}(f) = \frac{1}{2\Delta} \left(C \cdot \sum_m \check{I}_{z_m}^{exp} \sin(\pi \lambda z_m f^2) - A \cdot \sum_m \check{I}_{z_m}^{exp} \cos(\pi \lambda z_m f^2) \right), \quad (5.26)$$

with the following coefficients:

$$\begin{aligned} A &= \sum_m \sin(\pi \lambda z_m f^2) \cos(\pi \lambda z_m f^2) \\ K &= \sum_m \sin(\pi \lambda z_m f^2)^2 \\ C &= \sum_m \cos(\pi \lambda z_m f^2)^2 \\ \Delta &= KC - A^2. \end{aligned} \quad (5.27)$$

Using equations (5.26) and (5.27) we obtain the object transmission function from the intensity distribution measured at several distances behind the sample. In practice there are few approaches to simplify the equations above that depend on prior knowledge about the sample.

Phase retrieval approach 1: phase-only object

Approach 1 is used in case the sample is purely a phase object. In this case the absorption term $\check{B}$ in equation (5.24) is neglected, therefore the relation between intensity and phase becomes

$$\check{I}_z(f) \approx \delta(f) + 2 \sin(\pi \lambda z f^2) \check{\phi}(f) \quad (5.28)$$

Following the same procedure as shown in equations 5.20-5.23, the phase is found by using only one equation 5.23. This simplified approach has a difficulty when the denominator vanishes at zero frequencies ($f = 0$). In order to overcome this problem the regularization of equation 5.21 is needed. The simplest regularization is the Tikhonov regularization [30] when the energy of the solution is added to the cost function 5.21 with a coefficient α to be determined:

$$S_c \equiv \frac{1}{N} \sum_{m=1}^N \int df |\check{I}_{z_m}^{exp}(f) - \check{I}_{z_m}^{approx}|^2 + \alpha \int df |\check{\phi}(f)|^2. \quad (5.29)$$

In this case the equation for the phase will be

$$\check{\phi} = \frac{\sum_m \check{I}_{z_m}^{exp} \sin(\pi \lambda z f^2)}{\sum_m 2(\sin^2(\pi \lambda z f^2) + \alpha)} \quad (5.30)$$

When a prior estimate of the phase of the object $\check{\phi}^{prior}$ is known, the regularization term is written as

$$S_c \equiv \frac{1}{N} \sum_{m=1}^N \int df |\check{I}_{z_m}^{exp}(f) - \check{I}_{z_m}^{approx}|^2 + \alpha \int df |\check{\phi}(f) - \check{\phi}^{prior}|^2. \quad (5.31)$$

In this case the equation for the phase is

$$\check{\phi} = \frac{\sum_m \check{I}_{z_m}^{exp} \sin(\pi \lambda z f^2) + \alpha \check{\phi}^{prior}}{\sum_m 2(\sin^2(\pi \lambda z f^2) + \alpha)} \quad (5.32)$$

The estimation of the $\check{\phi}^{prior}$ can be extracted from the prior knowledge about the sample.

Phase retrieval approach 1.a: homogeneously absorbing object

In case the absorption can not be neglected but the sample is homogeneous such that the ratio between real and imaginary parts of refractive index is constant over the sample

$$\frac{\delta}{\beta} = const., \quad (5.33)$$

one can use prior knowledge about the refractive index of the material to link the phase ϕ and attenuation $B(x, y)$ in equation 5.24. Phase and absorption terms can be written using β and δ as shown in equations 5.4 and 5.5:

$$\begin{aligned} B(x, y) &= \frac{2\pi}{\lambda} \int \beta(x, y, z) dz, \\ \phi(x, y) &= -\frac{2\pi}{\lambda} \int \delta(x, y, z) dz. \end{aligned} \quad (5.34)$$

Now we consider ϕ and B to be dependent and therefore we can express B in terms of ϕ as

$$B(x, y) = -\phi\left(\frac{\beta}{\delta}\right) \quad (5.35)$$

With this assumption the equation for the intensity (5.24) becomes

$$\check{I}_z(f) \approx \delta(f) + 2[\sin(\pi \lambda z f^2) + \cos(\pi \lambda z f^2) \cdot \frac{\beta}{\delta}] \check{\phi}(f) \quad (5.36)$$

This equation does not tend to zero in the low frequency limit, therefore there is no need for regularization. Nevertheless it is still necessary to measure the intensity for a number of distances z_m since the combined term $\sin(\pi \lambda z f^2) + \cos(\pi \lambda z f^2)$ can vanishes at certain frequencies f . In case of our 3D photonic crystal samples we neglect the spatial $\frac{\beta}{\delta}$ change inside the pores in order to use this approach.

Phase retrieval approach 2: non-homogeneous absorbing sample

Another approach to phase retrieval is based on additional absorption measurements of the sample $I_{z=0}^{abs}$. In this case an extra image of the sample is taken at a very close distance to the detector so that the influence of the phase contrast is minimal. After that the ratio between the intensity at every distance z_m to the absorption image in real space is calculated $\frac{I_{z_m}(x)}{I_{z=0}^{abs}}$. This approach can not be used in case of zoom tomography since at the very close distance to the detector the magnification is equal to 1 and the resolution is equal to the resolution of the detector, therefore the gain of resolution due to magnification is lost.

Phase retrieval approach 3: general dispersive and absorptive object

In this general approach the phase ϕ and attenuation B are considered to be totally independent and the full set of equations (5.25) -(5.27) is used for phase retrieval. This is the most complicated approach which is rarely used.

The group of above mentioned approaches are called contrast transfer function (CTF) methods. The contrast transfer function is a term $\sin(\pi\lambda z f^2)$ that appears in each of the approaches.

Paganin approach to phase retrieval using the transport of intensity equation

In addition to the CTF group of methods there are methods based on the transport of intensity equation (TIE) [31, 32]:

$$\frac{\partial I(r, z)}{\partial z} = -\frac{\lambda}{2\pi} \nabla(I(r, z) \nabla \phi(r, z)), \quad (5.37)$$

where $I(r, z)$ is the irradiance at the point (x, y, z) defined as

$$I_z(r) \equiv |u_z(r)|^2. \quad (5.38)$$

The wave amplitude can be expressed in terms of the irradiance I and the phase ϕ as follows:

$$u_z(r) = I_z(r)^{1/2} e^{i\phi_z(r)}. \quad (5.39)$$

To derive equation (5.37) let us consider light propagating in the z direction and time-dependent wave amplitude is written as $u_z(r)e^{(-i2\pi\omega t)}$, where r is a two-dimensional vector in the transverse direction. The amplitude then satisfies approximately the parabolic equation [32]

$$\left(i\frac{\partial}{\partial z} + \frac{\nabla^2}{2k} + k\right)u_z(r) = 0, \quad (5.40)$$

where $\nabla^2 = [(\partial^2/\partial x^2) + (\partial^2/\partial y^2)]$ and $k = 2\pi/\lambda$. This is shown in Reference [32] by direct substitution of Fresnel diffraction result (see equation A.19) in the appendix A.

Let equation (5.40) be multiplied on the left side by u_z^* and the complex conjugate of equation (5.40) be multiplied on the left side by u_z . The two resulting equations are subtracted, one gets

$$\frac{2\pi}{\lambda} \frac{\partial}{\partial z} I = -\nabla \cdot I \nabla \phi, \quad (5.41)$$

which is known as the transport-of-intensity equation. We first consider the case when the sample is illuminated with a collimated X-ray beam and therefore unit magnification. At the end of the derivation the modifications will be made for the non-collimated case. We also assume that the object under study is homogeneous. For normally incident plane-wave radiation of uniform intensity over the sample area, the intensity of the radiation right behind the sample ($z = 0$) is assumed to be approximated by Bouguer-Lambert-Beer's Law of absorption:

$$I(r, z = 0) = I^{in} e^{(-\mu T(r))}, \quad (5.42)$$

where $T(r)$ is the projected thickness of the homogeneous object onto a plane where the image is taken, μ is the linear attenuation coefficient, and I^{in} is the uniform intensity of the incident radiation. If the object is sufficiently thin, the phase $\phi(r, z = 0)$ of the illuminating beam right behind the sample is proportional to the projected thickness:

$$\phi(r, z = 0) = -\frac{2\pi}{\lambda} \delta T(r), \quad (5.43)$$

We substitute equations (5.42) and (5.43) in the transport of intensity equation (5.41) to we obtain:

$$\frac{2\pi}{\lambda} \frac{\partial}{\partial z} I(r, z = 0) = \nabla \cdot (I^{in} e^{(-\mu T(r))} \nabla \frac{2\pi}{\lambda} \delta T(r)), \quad (5.44)$$

where using the equality

$$\delta \nabla \cdot e^{(-\mu T(r))} \nabla T(r) = -\frac{\delta}{\mu} \nabla^2 e^{(-\mu T(r))} \quad (5.45)$$

equation (5.44) is written as

$$\frac{\partial}{\partial z} I(r, z = 0) = \frac{\delta}{\mu} I^{in} \nabla^2 e^{(-\mu T(r))}. \quad (5.46)$$

Let us estimate the left side of equation (5.46) using the intensity measurements in two sufficiently closely spaced planes separated by a distance R_2 :

$$\frac{\partial}{\partial z} I(r, z = 0) \approx \frac{I(r, z = R_2) - I(r, z = 0)}{R_2} = \frac{I(r, z = R_2) - e^{(-\mu T(r))} I^{in}}{R_2}. \quad (5.47)$$

Substituting equation 5.47 into equation 5.46 and re-arranging, gives

$$\left(-\frac{R_2 \delta}{\mu} \nabla^2 + 1 \right) e^{(-\mu T(r))} = \frac{I(r, z = R_2)}{I^{in}}. \quad (5.48)$$

To proceed we represent both images at the distance $z = 0$ and at the distance $z = R_2$ as Fourier integrals:

$$\begin{cases} I^{in} e^{(-\mu T(r))} = \frac{I^{in}}{2\pi} \iint F\{e^{(-\mu T(r))}\} e^{(ikr)} dk \\ I(r, z = R_2) = \frac{1}{2\pi} \iint F\{I(r, z = R_2)\} e^{(ikr)} dk \end{cases} \quad (5.49)$$

Substituting into equation (5.48) gives

$$F\{e^{(-\mu T(r))}\} = \mu \frac{F\{I(r, z = R_2)\}/I^{in}}{R_2 \delta |k|^2 + \mu} \quad (5.50)$$

Taking the inverse Fourier transform of equation (5.50) and solving for $T(r)$, we arrive at:

$$T(r) = -\frac{1}{\mu} \log_e \left(F^{-1} \left[\mu \frac{F\{I(r, z = R_2)\}/I^{in}}{R_2 \delta |k|^2 + \mu} \right] \right). \quad (5.51)$$

To conclude the derivation we need to remove the assumption of a collimated beam. To do so we take into account the magnification factor M given earlier in equation (5.1):

$$T(r) = -\frac{1}{\mu} \log_e \left(F^{-1} \left[\mu \frac{F\{M^2 I(Mr, z = R_2)\}/I^{in}}{R_2 \delta |k|^2/M + \mu} \right] \right). \quad (5.52)$$

Equation (5.52) shows how to solve the transport-of-intensity equation (5.37) for the projected thickness $T(r)$ of the sample. The phase of the radiation at the exit surface of the sample can be found by substituting the derived equation into equation (5.43).

The approach above is more exact in case of strong absorption, although in the limit of high frequencies the solution is not converging. This method can be used in order to find a good estimation of ϕ^{prior} for iterative phase retrieval approaches.

5.3 Experimental

5.3.1 Samples

As a first example of a 3D nanophotonic structure viewed by zoom tomography, we focus on 3D silicon photonic band gap crystals [33]. The density distribution $\rho_e(X, Y, Z)$ of the inverse woodpile structure is designed as two perpendicular two-dimensional (2D) arrays of pores, as discussed in Chapter 1.

Three 3D photonic crystal samples were chosen for tomography experiments. For the ease of reading samples are named **A**, **B** and **C** here. The corresponding names of the samples in the lab are given in Table B in Appendix B. Samples **A** and **B** are 3D photonic crystal samples that were fabricated with the two-step etch mask process. The detailed description of the fabrication process is given in Reference [36]. Typical SEM image of the crystal fabricated with two-step etch mask approach is shown in Figure 5.2. The fabrication of the 3D photonic crystal

with two-step mask approach starts with the complete Si wafer where deep pores are etched through the chromium mask filling the entire wafer. The wafer is then cleaved to open a perpendicular face for the second set of pores. The mask for the second array of pores is defined using focused ion beam lithography (FIB) and thus limited to be $10 \times 10 \mu\text{m}^2$ by the FIB field of view. Thus the extent of the 3D structure where both sets of pores are overlapping is at most $10 \times 10 \mu\text{m}^2$ and there is a large 2D array of pores surrounding the 3D structure as seen in the Figure 5.2. Sample **A** was additionally kept in a quantum dot suspension for spontaneous emission measurements [35].

Figure 5.2: Typical SEM image of the **external** surface of a sample fabricated in the same way as samples **A** and **B**. Two sets of pores are running in Z and X directions. The 3D crystal's estimated extent is delimited by the red dashed lines. The 3D crystal is surrounded by a large array of 2D pores running in Z direction due to the properties of a fabrication process. The scale bar is shown.

Sample **A** was studied in three different experiments. First, the sample was measured with 20 nm resolution. In a second measurement a small random displacement of the sample position was applied during the rotation. This is a step performed to average out beam artifacts with a fixed position on the detector as is described in section 5.2.1. The third measurement on this sample was performed with 10 nm resolution to compare to the experiment with 20 nm resolution.

Sample **B** was measured once with a resolution of 20 nm.

Sample **C** is an inverse woodpile 3D photonic crystal sample that was fabricated on a silicon bar using the novel single step etch mask approach described in chapter 2. A typical SEM image of the sample fabricated with a single step etch mask is shown in Figure 2.1 in chapter 2. The 3D structure is located on the edge of the silicon bar and surrounded by bulk silicon and air. The sample was measured with 10 nm resolution.

5.3.2 Experimental setup of beamline

X-ray tomography experiments were performed in collaboration with the team guided by P. Cloetens at the European Synchrotron Radiation Facility (ESRF), beamline ID16A [37]. The beamline has the possibility to focus x-ray beam using Kirkpatrick-Baez optics down to 20 by 30 nm^2 size and operate in a photon energy range between 17 and 33.6 keV. During all our experiments the photon energy of the beam was 17 keV that corresponds to the wavelength $\lambda = 0.07 nm$. Every sample was measured at 4 different sample to detector distances z_d , see Figure 5.1 and section 5.2.2. At each sample position between 1500 and 1800 images were recorded while rotating the sample from 0 to 180 degrees. For every image the exposure time was set to 0.3 seconds. The rotation axis was chosen to be approximately 12 micron deep inside the silicon.

The experimental data are collected as sets of transmission radiograms for every rotation angle θ and every distance z_d . A typical transmission radiogram from our sample is shown in Figure 5.3. There are three regions distinguished on the radiogram, firstly, at the top of the image there are black and white lines which are the result of Fresnel diffraction on the edge of the sample. Secondly, in the region indicated with the yellow rectangle the 3D structure is located. Thirdly, below the silicon to air interface the sample consist of a periodic array of pores in silicon that are oriented along the propagation of the x-ray beam, therefore in transmission such a structure results in the periodic pattern. The period of the pattern is 480 nm which corresponds to the period of 2D photonic array. The images taken at different sample to detector distances have different magnification and due to imperfections of mechanical translation are not always well aligned. Therefore the first step in data analysis is to bring all the images taken at one angle θ to the same magnification and align them with respect to each other. Typically translation shifts between images are calculated for every 100 images and then fitted with smooth curves to obtain shifts for remaining images. The lateral shift for every 100 images can be calculated automatically using image correlations, but in some cases such an automatic shift alignment does not lead to a good result and the manual alignment of the images needs to be applied. In most cases it is enough to apply manual alignment for all measured distances at rotation angle $\theta = 0$ and use the obtained shifts as a starting point for automatic alignment of all remaining angles. It appears that images taken from periodically ordered structures such as a photonic crystal are surprisingly difficult to align since the shifts by an integer number of lattice parameters can not be distinguished by automatic alignment algorithms. Since our samples are very well ordered and periodic, manual shift alignment needs to be applied. Shift of the images varies a lot from sample to sample and from distance to distance and typical values of the shift are within 50 - 150 nm in all directions. After all images at the different distances for every angle are aligned with respect to each other, the phase retrieval can be launched. After the phase retrieval is finished the data consist of a stack of phase maps for every rotation angle. In order to obtain a 3D structure from the phase maps we need to apply a standard tomographic 3D reconstruction based on filtered back projection.

Figure 5.3: A typical transmission radiogram from 3D photonic crystal sample **A** measured with 20 nm resolution. The sample consists of a 2D photonic crystal structure and a 3D structure. The area of the 3D photonic crystal structure is indicated with the yellow rectangle. The straight red line indicates the approximate position of silicon to air interface. Black and white lines at the top of the image are the result of Fresnel diffraction on the edge of the sample. The periodic pattern visible in the lower portion originates from the 2D array of pores.

5.4 Results and discussions

5.4.1 Choice of the phase retrieval algorithm

For comparison of phase retrieval algorithms we used two different phase retrieval approaches for sample **A**: approach 1.a for homogeneous absorbing object and Paganin phase retrieval approach based on the transport of intensity equation. In the approach 1.a for homogeneous absorbing object the ratio between δ/β is used as a prior knowledge. For silicon at 17 keV the ratio $\delta/\beta = 174$ was obtained from the look up table [38]. A typical phase map out of the stack is shown in the figure 5.4 and the gray value cross section taken along the yellow line is shown in the figure 5.5(a). The gray value is proportional to the relative phase delay in the transmission and exhibits a linear behavior. The linear behavior of the phase delay is explained by the linear increase in sample thickness along the X axis where the cross section was taken.

Sample **A** was also analyzed using the Paganin phase retrieval approach. The Paganin approach was used in the recursive way - the phase maps obtained after the first phase retrieval iteration are used as a preliminary information for the next iteration. The gray value cross section through the phase map is shown in Figure 5.5(b). The gray value that is proportional to the relative phase delay of the beam transmitted through the object exhibits a linear behavior which agrees

Figure 5.4: A typical phase map obtained for sample **A** at 0 degree rotation angle using phase retrieval approach 1.a. The gray scale represents relative phase delay of the transmitted beam with white color corresponding to zero relative phase fluctuation. The 3D structure is located inside the yellow rectangle. The straight yellow line indicates where the gray value cross section was taken in Figure 5.5(a).

with the linear increase in sample thickness along the X axis. It is noticed that there are less fluctuations in case of Paganin approach compared to approach 1.a. In order to make a quantitative comparison we obtain the maximum gray value contrast between air and silicon for both phase retrieval approaches. The gray value is proportional to the phase delay obtained after the x-ray the beam is propagated through the sample. The sample is a silicon slab of homogeneous thickness and thus the projected thickness of the sample is linear along the X axis resulting in the linear phase delay. The fluctuations of the phase especially at the silicon to air interface indicate the presence of artifacts and thus will result in the distorted image after the reconstruction. It is seen from Figure 5.5 that both phase retrieval approaches give smooth linear dependence of the phase delay but in case of Paganin phase retrieval approach there are less phase fluctuations of the phase near the Si to air interface. Therefore we conclude that the Paganin phase retrieval approach is more preferable for this kind of sample.

After obtaining the stacks of phase maps from the two approaches the tomographic reconstruction is applied to both of them. The output of the reconstruction process is a stack of 2D slices in plane with the beam propagation direction and with gray values proportional to the electron density of the material. A comparison of reconstructed result for two slices - from the middle of 3D structure (a) and from the area with only 2D structure (b) is shown in figure 5.6. The dark regions show high material density and the light regions show low material density. The 2D array of pores is indicated on the picture with the red rectan-

Figure 5.5: Gray value cross section taken from the retrieved phase maps of the sample **A**. The white color corresponds to the zero relative phase delay. Silicon to the air interface is located approximately at the distance 450 pixels. (a) The cross section from the phase map retrieved with approach 1.a for the homogeneous absorbing object. (b) The gray value cross section for the phase map retrieved using Paganin approach.

gle. The straight periodic lines in 2D region are the pores etched in the silicon, whereas the lines in air or in bulk silicon are measurement artifacts. The 3D structure is located within the yellow rectangle. The white area within the 3D structure gives an indication of the internal void inside the crystal. We associate the formation of a void in the structure to the capillary drying “stiction” after the infiltration of a quantum dot suspension for optical measurements and possible fabrication errors. Notably, the presence of the void inside the structure is invisible for the external inspections such as SEM imaging. There is a clear difference in the quality between images obtained with phase retrieval approach 1.a for the homogeneous absorbing object and Paganin approach based on the transport of intensity equation. Both in 3D and 2D areas the structure appears to be sharper in case of Paganin recursive phase retrieval. The air area contains no sample, therefore in the case of perfect reconstruction the material density should be constant and close to zero. Therefore we conclude that the distortions appearing in the air area are tomographic reconstruction artifacts. It is clear from the images that the number of artifacts is smaller in case of the Paganin

recursive phase retrieval approach than in the case of 1.a approach. From this comparison we conclude that for our structures the Paganin approach reveals the better image quality and with less artifacts. In combination with the phase behaviour we deduced to employ only Paganin approach from here on.

Figure 5.6: (a,b) Two slices of sample **A** reconstructed from the experiment using phase retrieval approach 1.a. (c,d) Two slices of sample **A** reconstructed with Paganin phase retrieval approach. Slices (a) and (c) are located in the middle of the 3D structure and slices (b) and (d) are located in the 2D region. Dark region is bulk silicon and light region is air. The 3D structure is indicated with yellow rectangle, the 2D array of pores is indicated with red rectangle. The straight periodic lines in the 2D region represent pores etched in the silicon. The lines outside 2D region in the bulk silicon are measurement artifacts. The white area within the 3D structure is an internal void inside the crystal due to stiction.

One of the common tomographic artifacts appears as circular rings centered around the rotation axis of the sample. Such rings are the results of beam imperfections that are independent on the sample rotation and thus do not move on the detector when the sample is rotating. There are two possible ways to overcome this distortion. A first one is a post processing of the image and computational correction for the rings. Another one is to adjust the experiment in such a way that a sample performs a small random move at every measured angle. Thus the relative position of distortions introduced by the beam shifts for each angle and therefore after tomographic reconstruction averages away. The comparison between the reconstructed image after the experiment with and without random

displacement of the sample and is shown in Figure 5.7 (a) and (b). Image in the Figure 5.7 (a) has clear ring distortion artifacts centered at the top of the image causing the blurriness of the structure. In comparison the image in the Figure 5.7 (b) is clear from the circular distortions and thus the structure of interest has better contrast.

Figure 5.7: Comparison between the reconstructed image (a) without use of random displacement of the sample between scans and (b) with random displacement of the sample. It is clearly seen that circular distortions of the image vanish when the sample is randomly displaced.

5.4.2 Choice of the resolution

To compare the tomography results at different resolutions samples were studied in experiments with 20 and 10 nm resolution. Sample **A** reported above in a study with 20 nm resolution was also studied with the experiment with the ultimate 10 nm resolution. Based on the results of previous subsection 5.4.1, the Paganin recursive algorithm was chosen for the phase retrieval.

Figure 5.8 shows the comparison between the reconstructed slices of sample **A** with 10 and 20 nm resolutions. The lateral shift of the images is caused by the shift in the sample position in the chamber in between the two experiments. From Figure 5.8 it is seen that the image obtained with 10 nm resolution is sharper than the image obtained with 20 nm resolution. To characterize the contrast on both images we take a gray value cross-section through the reconstructed slices. To compare the data taken in different experiments and to estimate the resolution, we propose a model consisting of a binary density function for silicon ρ_{Si} and vacuum ρ_{vac} , convoluted with a Gaussian resolution function [39]. This model serve two purposes, one is to obtain Gaussian width σ as an effective resolution of the image and second is to obtain the value of pore diameter and thickness of Si walls from the fit. Here we consider the Gaussian width σ since we are interested in the choice of resolution and in the section 5.4.3 we will discuss the pore diameter and Si walls thicknesses obtained from the model. The density function assumes two values, namely ρ_{Si} for silicon and ρ_{vac} for vacuum:

Figure 5.8: Comparison between the reconstructed slices from the data (a) obtained with 10 nm resolution and (b) with 20 nm resolution. Red lines indicate the positions where electron density profile was taken to model the data.

$$\rho(x) \equiv \begin{cases} \rho_{vac} & \text{if } x < -a/2 \\ \rho_{Si} & \text{if } -a/2 < x < a/2 \\ \rho_{vac} & \text{if } x > a/2. \end{cases}$$

The density $\rho(x)$ is convoluted with a normalized Gaussian resolution function with center b and width σ :

$$\begin{aligned} \rho_{mod}(x) &= \rho(x) * G(x) = \int_{-\infty}^{\infty} \rho(\tau) G(x - \tau) d\tau = \\ &= \frac{\rho_{Si}}{2} \left(\operatorname{erfc} \left(\frac{b - a/2 - x}{\sqrt{2}\sigma} \right) - \operatorname{erfc} \left(\frac{b + a/2 - x}{\sqrt{2}\sigma} \right) \right) + \rho_{vac}, \end{aligned} \quad (5.53)$$

with $\operatorname{erfc}(x)$ the complementary error function. The density model $\rho_{mod}(x)$ is fitted to the experimental data. The adjustable parameters of the model are the width a and center position b of a silicon wall, the Gaussian width σ , the silicon gray scale ρ_{Si} , and the vacuum gray scale density ρ_{vac} . Thus we can compare extracted σ for images taken at different resolutions. We take a cross section through the single pore at each slice as shown in Figure 5.8 with the red lines. The resulting cross section, convolution function and the model density are shown in Figure 5.9 (a) for the slice measured with 10 nm resolution and (b) for the slice measured with 20 nm resolution. The pore diameters and a Gaussian resolution widths for slices measured with different resolutions are the following: from the data obtained at 10 nm resolution the pore diameter is found to be $d_{10nm}^{model} = 392$ nm, the Gaussian resolution width $\sigma_{10nm} = 18$ nm. From data obtained with 20 nm resolution the pore diameter is $d_{20nm}^{model} = 380$ nm with a Gaussian resolution width $\sigma_{20nm} = 41$ nm. The Gaussian width is nearly twice smaller in case of data measured with 10 nm resolution than the Gaussian width for the data measured with 20 nm resolution which agrees with the experimental resolution setting. The amplitude of the gray value contrast between the silicon

Figure 5.9: Electron density profile through the single pore for the data (a) measured with 10 nm resolution and (b) with 20 nm resolution. The position where the electron density profiles were taken are shown in Figure 5.8 with red lines. The black dashed curve is the convolution of a square density function (blue hatched bars) and a Gaussian resolution function.

and air is clearly larger in case of data obtained 10 nm resolution (Figure 5.9 (a)) than in case of 20 nm resolution (Figure 5.9 (b)). With 10 nm resolution the amplitude contrast between the Si and air obtained from the fit model is $\Delta\rho_{10nm} = 45$ and with 20 nm resolution data the contrast is $\Delta\rho_{10nm} = 34$. We associate the larger contrast of the gray value in case smaller resolution with the smaller voxel size and thus the electron densities are averaged over a smaller volume. This results in a sharper image in case of 10 nm resolution experiment as is clearly seen in Figure 5.8 . On the other hand, a 10 nm resolution can sometimes not be employed when the field of view (equal to a number of pixels times the set resolution) is too small for a sample under study.

After comparing multiple phase retrieval approaches and different experimental procedures we conclude that for our structures the best way of performing x-ray tomography is with 10 nm resolution using the random sample displacement to remove artifacts and applying Paganin recursive phase retrieval approach to the obtained data.

5.4.3 Results and discussion on photonic crystals

Combining all 2D slices of the electron density distribution, we obtain a full 3D real space representation of the structure. The list of samples with their internal lab names and fabrication history is in the Appendix C. The full 3D representation of the sample **A** measured with 10 nm resolution and retrieved with Paganin phase retrieval approach is shown in Figure 5.10.

Figure 5.10: (a) Volume rendering of the sample **A**. The air is shown transparent for the clarity. The internal void is seen inside the structure in ZY plane. The void is attributed to the capillary forces while sample was drying after being kept in the quantum dots suspension. (b) Cross section in the YZ plane through the middle of the reconstructed volume. The internal void is clearly seen in the center of the slice. 2 microns scale bar is shown on the picture.

The internal void hidden from the outside observer is clearly seen inside the structure of the sample after tomographic reconstruction. The void formation is attributed (1) to the fabrication error resulting in the larger pore radius than designed and thus thinner silicon walls between pores and (2) capillary forces appearing after the sample was dried multiple times from a quantum dot suspension for spontaneous emission measurements. Since the 3D structure in this sample appeared to be broken the analysis was performed on the remaining surrounding 2D array of poress. The pore radius obtained from the tomography data is $r_A = 190 \pm 20 \text{ nm}$ and the pore depth is $d_A = 6080 \pm 20 \text{ nm}$. Comparing the pore radius to the design $r_{design} = 163 \text{ nm}$ it is clear that the errors were made during fabrication process resulting in wider pores than designed. The tapering of the pores was analyzed by measuring the pore radius at the different depths: at the

top, in the middle and at the bottom. The pore radius at the top was found to be $r_A^{top} = 190 \pm 20 \text{ nm}$, at the middle it increased to $r_A^{middle} = 200 \pm 20 \text{ nm}$ and at the bottom the radius decreased to $r_A^{bottom} = 160 \pm 20 \text{ nm}$. The summary of the characteristic values for each sample is given in table 5.4.3 below.

Sample **B** was measured with 20 nm resolution and reconstructed using the Paganin recursive phase retrieval approach. A bird's-eye view of the reconstructed 3D structure is shown in Figure 5.11(a). This sample reveals a 3D structure inside and is thus analyzed in more details. The reconstructed sample volume is a cube that includes the 3D photonic crystal structure that is surrounded by bulk silicon below, and by the 2D array of deep pores. To keep the rich set of tomographic data tractable, we choose for analysis three 2D slices in arbitrary planes in the reconstructed volume, as shown in Figure 5.11(b). The slices are chosen in the ZY , ZX and XY symmetry planes of the photonic crystal structure. For simplicity, we first discuss the simple 2D array of pores that is shown in the XY slice in Fig. 5.11(c). The array reveals the designed centered rectangular structure. Several pores the top of the image are connected by pores running in the X -direction that are made in a second etch-step to obtain the 3D structure.

Figure 5.11: 3D rendered images of a 3D photonic band gap crystal sample **B**. X , Y , Z axes are shown with each panel. a) Bird's-eye view of the reconstructed sample volume. The color scale is the normalized electron density interpolated between silicon ($\rho_n = 1$) and air ($\rho_n = 0$). For clarity, electron densities close to air are transparent. b) Locations of the 2D slices of the electron density chosen for detailed investigation. The reconstructed volume is shown as the outline and the view point is the same as in (a). c) Zoom-in of a 2D XY slice located at a depth $Z = 400 \text{ nm}$ below the crystal surface. Gray and black lines show trajectories where the gray value profiles were taken (Fig. 5.12). (d) 2D slice in the ZX plane. Black dashed line indicated a 2° misalignment of the pores. (e), (f) 2D slices of electron densities located in ZY and XY planes respectively. A 1 micron scale bar is shown on each slice.

Figure 5.12: (a) Density profile in the X -direction, and (b) in the Y -direction through pores shown in Figure 5.11(c) (red circles). The black dashed curves are the convolution of a square density function (blue hatched bars) and a Gaussian resolution function.

We now discuss one-dimensional cross-sections through the 2D pore array along lines shown in Fig. 5.11(c) for a detailed comparison between the tomographic data and the structural design. Fig. 5.12(a) shows a cross-section in the X -direction, starting from a pore via a Si wall to a second pore and a second Si-wall into a third pore. The distance between the centers of the Si walls is $\Delta X = 520 \pm 20$ nm. Fig. 5.12(b) shows a cross-section in the Y -direction, also from a pore via a Si-wall, a second pore and a second Si-wall to a third pore. The distance between the centers of the Si walls is $\Delta Y = 750 \pm 20$ nm. Importantly, the ratio $\frac{\Delta X}{\Delta Y} = 1.44 \pm 0.06$ agrees with the designed $\sqrt{2}$ ratio required for a cubic structure. Analyzing the nearest neighbor distance in the X -direction over 14 unit cells (see Figure 5.13) yields a statistical mean $\Delta X_m = 481 \pm 20$ nm with a standard deviation $\sigma_m = 30$ nm, which agrees excellently with the designed lattice parameter $c = 488$ nm. The obtained mean value is shown in the Figure 5.13 with black dashed line, standard deviation is shown with the gray bar and the design lattice parameter is shown with red solid line. In the Y -direction, we find

Figure 5.13: Nearest neighbor distance between pores in a 3D photonic crystal sample **B** measured from tomography data over 15 unit cells. The distance between pore in the 1st unit cell and it the 2nd unit cell is shown number 1.5. Mean value $\Delta X_m = 481 \pm 20$ nm is shown with black dashed line and standard deviation $\sigma_m = 30$ nm is shown with the gray bar. The mean value agrees well with the designed lattice parameter $c = 488$ nm shown with red solid line.

$\Delta Y_m = 700$ nm with $\sigma_m = 27$ nm standard deviation, in very good agreement with the designed lattice parameter $a = 686$ nm. The results confirm that the structure is periodic over many unit cells, with average lattice parameters that match the designed ones very well.

The data in Fig. 5.12(a) are modeled as described in a section 5.4.2 above with a binary model consisting of two Si walls and air in between them. From the fit model a width of one wall was found to be $w_1 = 140$ nm with a Gaussian resolution width $\sigma_1 = 32$ nm, and the second wall has $w_2 = 176$ nm width with $\sigma_2 = 37$ nm. Given the voxel size of 20 nm, the widths of the Si walls agree within the resolution with the designed width $w = 156$ nm, thus the structural design was faithfully realized. The corresponding pore diameter of 340 nm obtained from the cross section agrees well with the designed diameter of 328 nm. The model for Y-cross-sections shown in Fig. 5.12(b) consist of two Si walls with $w_1 = 441$ nm, with a Gaussian resolution width $\sigma_1 = 41$ nm and $w_2 = 484$ nm with $\sigma_2 = 52$ nm. The widths of the Si walls are somewhat wider than the designed width of 358 nm, possibly due to a slight deformation of the pore. The Gaussian resolution of 30 nm in the X-direction (45 nm in the Y-direction) agrees well with the focus size of 20 nm (30 nm in the Y-direction); it is reasonable that the modeled resolution is somewhat larger in view of the fact that it is the result of a tomographic reconstruction where several data analysis steps described above were taken.

Figure 5.11(d) shows a ZX slice that contains both arrays of pores and allows us to determine the maximum depths of both sets of pores. The Z -pores have a depth of 6280 ± 20 nm and a diameter of 366 ± 20 nm at the middle of the depth, and a correspondingly high aspect ratio of 17.20 ± 0.04 , as expected from the deep reactive-ion etching settings [40]. Previously, the aspect ratio of pores deeply etched in silicon could only be assessed *ex-situ* and destructively, by SEM inspection of ion-milled slices or of a cleaved structure [36, 40]. The Z -pore diameter at the surface is found to be 322 ± 20 nm and is reduced to 300 ± 20 nm at the bottom due to the tapering. The X -pores have an even greater depth of 8000 ± 20 nm, corresponding to a high aspect ratio of 24.3 ± 0.04 . This is the first unequivocal observation that a second set of deep-etched pores runs even deeper than a first set. This effect can be explained as follows: one limiting factor in the deep etching of pores is the diffusion of reaction products that cannot easily diffuse out of a deep and narrow pore. This limitation affects the first set of pores, but not the second set of pores: While the second set of pores is being etched, the reaction products diffuse outwards through the first set of pores. The X -pores pore diameter thus also differs from Z -pores diameter and is found to be 272 ± 20 nm at the top surface, 328 ± 20 nm in the middle of the pore depth and 200 ± 20 nm at the bottom.

A salient feature in Figure 5.11(d) is that the pores running in the X -direction are not exactly perpendicular to the pores in the Z -direction. It appears that the angle between the pore arrays systematically deviates from the 90° design by 2° ; from results on several crystals we find at most 6° . This means that the crystal structure is slightly monoclinic. Nevertheless, plane-wave band structure calculations reveal that the 3D photonic band gap is robust to a 6° shear of the cubic crystal structure [8]: the gap hardly changes from 24% relative bandwidth to more than 21%, plenty for strong spontaneous emission control and other metamaterial applications.

Figure 5.11(e) shows an ZX slice that crosses the first set of pores along their greatest depth. All pores in the slice have a similar etched depth of 6000 ± 20 nm confirming that the deep reactive etching process gives a homogeneous pore formation in bulk Si, including a substantial etch depth. Figure 5.11(f) shows an XY slice that contains the second array of pores. It is seen that the depth of the pores varies between 5000 ± 20 and 8500 ± 20 nm at different Y . We attribute this pore depth variation to changes in etching process due to penetration of the etchant and the etching products through the array of pores that was first etched. As a consequence, optical transport measurements will reveal smooth spectra, without Fabry-Perot fringes. The main characteristics of the sample measured from tomography data are listed in Table 5.4.3 at the end of the section.

The next 3D photonic crystal sample under investigation is sample **C** that was fabricated using a novel single step etch mask approach described in details in chapter 2. This approach improves the alignment of the etch mask during fabrication process and allows to achieve less structural deviations from the design. Figure 5.14(a) shows a volume rendering of the 3D photonic crystal sample. Electron densities close the air are shown transparent for clarity. Two sets of pores

Figure 5.14: (a) Volume rendering of the 3D photonic crystal sample **C**. Two sets of pores are running in X and Z direction. Black lines are the guides for the eye indicating the positions of the pores in the crystal. (b) Cross section in XZ plane through the reconstructed volume. Two sets of pores in X and Z direction are seen to be crossing each other under 89 degree angle.

are running in X and Z direction. Figure 5.14(b) shows the cross section in XZ plane. The pore diameter for the pores running in Z direction which is the first etch side is found to be 370 ± 10 nm at the top, 410 ± 10 nm at the middle depth and 350 ± 10 nm at the bottom. Pores exhibit common trend to get wider in the middle and reduce in diameter at the bottom known, as tapering effect. The depth of the pores in Z direction is 3770 ± 10 nm. Pores in X direction, the second etch direction differ from the first direction and have 300 ± 10 nm diameter at the top, 310 ± 10 nm diameter at the middle and 155 ± 10 nm at the bottom. Thus pores etched on the second side exhibit larger tapering and overall smaller radius than pores that were etched first. This is explained with residuals of the protective layer left from the Bosch etching process on the mask for the second etch side. The depth of the pores in X direction is 4630 ± 10 nm. In this sample two sets of pores are seen to be crossing each other under 89 ± 1 degree angle. All the characteristics of the sample measured from tomography data are listed in Table 5.4.3 at the end of the section. The angular alignment of pores is thus significantly improved to be within the error bar compared to observed above misalignment of 2 degrees in the sample **B**. Thus tomography data shows improvement in the fabrication process of the photonic crystal. Additionally one more sample **D** was studied in tomography experiments. On the sample **D** two photonic crystal structures were investigated - Structure D_1 and Structure D_2 that are 3D inverse woodpile photonic crystals without embedded defects intended for reflectivity study described in Chapter 6. From tomography pores in the structure D_1 have the depth $l_Z = 4580 \pm 10$ nm in Z direction and $l_X = 2940 \pm 10$ nm in X direction. As listed in Table 5.4.3 diameter of the pores in Z direction on the top surface is found to be $d_z^{top} = 304 \pm 10$ nm, in the

middle of the pore $d_z^{mid} = 318 \pm 10$ nm and at the bottom $d_z^{bot} = 300 \pm 10$ nm. For pores in X direction the diameters are found to be $d_x^{top} = 270 \pm 10$ nm, $d_x^{mid} = 246 \pm 10$ nm and $d_x^{bot} = 160 \pm 10$ nm. For the Structure D_2 in Z direction the depth of the pores is $l_Z = 3440$ nm and in X direction $l_X = 2800 \pm 10$ nm. The Z -pores diameter at the top is found to be $d_z^{top} = 301 \pm 10$ nm, at the middle depth $d_z^{mid} = 280 \pm 10$ nm and at the bottom $d_z^{bot} = 280 \pm 10$ nm. For the pores running in X direction $d_x^{top} = 300 \pm 10$ nm, $d_x^{mid} = 266 \pm 10$ nm and $d_x^{bot} = 222 \pm 10$ nm. Tomography data are obtained for the Structures D_1 and D_2 are used in order to extract an important for optical properties averaged over structure ratio of R/a where R is the pore radius and a is the lattice spacing. To do so we obtain the electron density of the air ρ_{air} by averaging the gray value in the region outside the crystal and silicon bar, the density of silicon ρ_{Si} by averaging the gray value in the bulk silicon regions and the average density of 3D structure ρ_{3D} by averaging the gray value over the entire volume of 3D structure. Considering the following relations:

$$\begin{aligned}\rho_{Si} \cdot v_{Si} + \rho_{air} \cdot v_{air} &= \rho_{3D} \\ v_{Si} + v_{air} &= 1\end{aligned}\tag{5.54}$$

where v_{Si} is the volume fraction of Si in the structure and v_{air} is the volume fraction of air in the structure, we can find the volume fraction of air in the structure that is directly related to the R/a ratio as is shown in Figure 1.3 in the Chapter 1. The obtained from tomography data ratio of R/a we call R/a_{tomo} and in the later chapter compare to the R/a ratio extracted from reflectivity measurements. For the Structure D_1 the R/a ratio obtained from tomography data is $R/a_{tomo} = 0.197 \pm 0.010$ and for the Structure D_2 $R/a_{tomo} = 0.21 \pm 0.015$. The good correspondence of the obtained ratios to the optical reflectivity measurements is discussed in Chapter 6.

Below we provide a table summarizing the characteristic values of pore diameter, depth and angular misalignment for all samples discussed above.

5.5 Summary

In this chapter we describe recently developed technique zoom in nanotomography which allows to perform 3D imaging of the material with nm resolution. We are the first to apply zoom in nanotomography with ultimate 10 and 20 nm resolution to the fabricated 3D photonic nanostructures. We provide experimental scheme as well as detailed theoretical description of the required phase retrieval algorithms for zoom in tomography. We use our experimental data of tomographic scans measured on 3D silicon photonic crystal samples to compare different phase retrieval algorithms and different experimental approaches for X-ray nanotomography. After comparing multiple phase retrieval approaches and different experimental procedures we conclude that for our structures the optimal way of performing X-ray tomography is with 10 nm resolution using additional the random displacement of the sample in order to remove artifacts. In the process of data analysis due to periodic geometry of our structures it appeared to

Sample	Pore diameter d in Z and X directions	Pore depth l in Z and X direction	Angle between sets of pores
A	$d_z^{top} = 380 \pm 20$ nm $d_z^{mid} = 400 \pm 20$ nm $d_z^{bot} = 160 \pm 20$ nm	$l_z = 6080 \pm 20$ nm	Not possible to determine since the structure is destroyed
B	$d_z^{top} = 322 \pm 20$ nm $d_z^{mid} = 366 \pm 20$ nm $d_z^{bot} = 300 \pm 20$ nm	$l_z = 6280 \pm 20$ nm	$88 \pm 1^\circ$
	$d_x^{top} = 272 \pm 20$ nm $d_x^{mid} = 328 \pm 20$ nm $d_x^{bot} = 200 \pm 20$ nm	$l_x = 8000 \pm 20$ nm	
C	$d_z^{top} = 370 \pm 10$ nm $d_z^{mid} = 410 \pm 10$ nm $d_z^{bot} = 350 \pm 10$ nm	$l_z = 3770 \pm 10$ nm	$89 \pm 1^\circ$
	$d_x^{top} = 300 \pm 10$ nm $d_x^{mid} = 310 \pm 10$ nm $d_x^{bot} = 155 \pm 10$ nm	$l_x = 4630 \pm 20$ nm	
D_1	$d_z^{top} = 304 \pm 10$ nm $d_z^{mid} = 318 \pm 10$ nm $d_z^{bot} = 300 \pm 10$ nm	$l_z = 4580 \pm 10$ nm	$89 \pm 1^\circ$
	$d_x^{top} = 270 \pm 10$ nm $d_x^{mid} = 246 \pm 10$ nm $d_x^{bot} = 160 \pm 10$ nm	$l_x = 2940 \pm 10$ nm	$89 \pm 1^\circ$
D_2	$d_z^{top} = 301 \pm 10$ nm $d_z^{mid} = 280 \pm 10$ nm $d_z^{bot} = 280 \pm 10$ nm	$l_z = 3440 \pm 10$ nm	$89 \pm 1^\circ$
	$d_x^{top} = 300 \pm 10$ nm $d_x^{mid} = 266 \pm 10$ nm $d_x^{bot} = 222 \pm 10$ nm	$l_x = 2800 \pm 10$ nm	$89 \pm 1^\circ$

Table 5.1: Main characteristics of the samples measured in X-ray tomography experiments. The pore diameters are listed separately for pores in Z direction d_z and X direction d_x . Z direction is the first etch direction and Y direction is the second etch direction. Diameters are measured for each direction at the top of the pore close to the surface d^{top} , at the middle d^{mid} and at the bottom d^{bot} .

be necessary to perform manual shift alignment of projections taken at different distances. The best phase retrieval results are achieved using recursive Paganin approach.

We have studied a number of 3D photonic band gap crystals made from silicon by CMOS-compatible methods. We have managed to obtain the 3D material density throughout the fabricated crystals. We observed that the structural design is in most aspects faithfully realized by the fabricated nanostructure, apart from a shear of the cubic crystal structure for the sample fabricated with the two-step etch mask. We observed an improvement in structure alignment after applying a single step etch mask fabrication approach. We suggested a binary model that describe tomography data and allows to use them as an input for *ab initio* numerical models in order to compute optical properties *free from assumptions*. We conclude that 3D X-ray tomography is a powerful tool for the structural characterization of any complex photonic nanostructure with arbitrary short- or long-range order with no need for irreversible sample preparation. Therefore, X-ray tomography has great potential to solve a wide variety of outstanding questions in metamaterial research and applications.

Bibliography

- [1] T. Ergin, N. Stenger, P. Brenner, J.B. Pendry, and M. Wegener, *Three-dimensional invisibility cloak at optical wavelengths*, Science **328**, 337-339 (2010) 77
- [2] C.M. Soukoulis and M. Wegener, *Past achievements and future challenges in the development of three-dimensional photonic metamaterials*, Nature Photon, **5**, 523 (2011) 77
- [3] J.K. Gansel, M. Thiel, M.S. Rill, M. Decker, K. Bade, V. Saile, G. von Freymann, S. Linden, and M. Wegener, *Gold helix Photonic metamaterial as broadband circular polarizer*, Science **18**, 1513-1515 (2009) 77
- [4] J.E.G.J. Wijnhoven and W.L. Vos, *Preparation of photonic crystals made of air spheres in titania*, Science **281**, 802-804 (1998) 77
- [5] S. Noda, K. Tomoda, N. Yamamoto, and A. Chutinan, *Full three-dimensional photonic bandgap crystals at near-infrared wavelengths*, Science **289**, 604-606 (2000) 77
- [6] J.D. Joannopoulos, S.G. Johnson, J.N. Winn, and R.D. Meade, *Photonic crystals, Molding the flow of light* (Princeton University Press, Princeton NJ, 2008) 2nd Ed. 77
- [7] A. Chutinan and S. Noda, *Effects of structural fluctuations on the photonic bandgap during fabrication of a photonic crystal*, J. Opt. Soc. Am. B **16**, 240-244 (1999). 77
- [8] L.A. Woldering, A.P. Mosk, R.W. Tjerkstra, and W.L. Vos, *The influence of fabrication deviations on the photonic band gap of three-dimensional inverse woodpile nanostructures*, J. Appl. Phys. **105**, 093108: 1-10 (2009). 77, 100
- [9] S. Hughes, L. Ramunno, J. F. Young, and J. E. Sipe, *Extrinsic Optical Scattering Loss in Photonic Crystal Waveguides: Role of Fabrication Disorder and Photon Group Velocity*, Phys. Rev. Lett. **94**, 033903: 1-4 (2005) 77
- [10] A.F. Koenderink, A. Lagendijk, and W.L. Vos, *Optical extinction due to intrinsic structural variations of photonic crystals*, Phys. Rev. B **72**, 53102: 1-4 (2005). 77
- [11] D. McMullan *Scanning electron microscopy* Science **17**, 175-185 (1995) 77
- [12] G. Binnig and H. Rohrer *Scanning tunneling microscopy from birth to adolescence* Rev. Mod. Phys. **59**, 615-625 (1987) 77
- [13] J. Goldstein, D.E. Newbury, D.C. Joy, C.E. Lyman, P. Echlin, E. Lifshim, L. Sawyer, and J.R. Michael, *Scanning electron microscopy and X-ray microanalysis*, (Springer, New York, 2003) 3rd Ed. 77
- [14] R. Xu, C.-C. Chen, L. Wu, M. C. Scott, W. Theis, C. Ophus, M. Bartels, Y. Yang, H. Ramezani-Dakhel, M. R. Sawaya, H. Heinz, L. D. Marks, P. Ercius,

- and J. Miao *Three-dimensional coordinates of individual atoms in materials revealed by electron tomography* Nat. Mater. **14** 1099-1103 (2015) 78
- [15] B. Chu and B.S. Hsiao, *Small-angle X-ray scattering of polymers*, Chem. Rev. **101** 1727-1761 (2001) 78
- [16] M. Megens, C.M. van Kats, P. Bösecke, and W.L. Vos, *In situ characterization of colloidal spheres by synchrotron small-angle X-ray scattering*, Langmuir **13**, 6120-6129 (1997) 78
- [17] A.G. Shabalin, J.-M. Meijer, R. Dronyak, O. M. Yefanov, A. Singer, R.P. Kurta, U. Lorenz, O.Y. Gorobtsov, D. Dzhigaev, S. Kalbfleisch, J. Gulden, A. V. Zozulya, M. Sprung, A. V. Petukhov, and I. A. Vartanyants, *Revealing three-dimensional structure of an individual colloidal crystal grain by coherent X-ray diffractive imaging*, Phys. Rev. Lett. **117**, 138002: 1-6 (2016) 78
- [18] P.C.J. Donoghue, S. Bengtson, X.-p. Dong, N.J. Gostling, T. Hultgren, J.A. Cunningham, C. Yin, Z. Yue, F. Peng, and M. Stampanoni, *Synchrotron X-ray tomographic microscopy of fossil embryos*, Nature (London) **442**, 680-683 (2006) 78
- [19] A. Sakdinawat and D. Attwood, *Nanoscale X-ray imaging*, Nature Photon. **4**, 840-848 (2010) 78
- [20] B. Pollak, *Experiences with planography* Dis. Chest. **24**, 663-669 (1953) 78
- [21] P. Cloetens, W. Ludwig, J. Baruchel, D. van Dyck, J. van Landuyt, J.P. Guigay, and M. Schlenker, *Holotomography: Quantitative phase tomography with micrometer resolution using hard synchrotron radiation x rays*, Appl. Phys. Lett. **75**, 2912 (1999) 78, 79
- [22] C. S. Schroer, J. Meyer, M. Kuhlmann, B. Benner, T. F. Gunler, B. Lengeler, C. Rau, T. Weitkamp, A. Snigirev, and I. Snigireva, *Nanotomography based on hard x-ray microscopy with refractive lenses* Appl. Phys. Lett. **81**, 1527-1529 (2002) 78
- [23] C. A. Larabell and M. A. L. Gros, *X-ray Tomography Generates 3-D Reconstructions of the Yeast, Saccharomyces cerevisiae, at 60-nm Resolution* Mol. Biol. Cell **15**, 957-962 (2003) 78
- [24] R. Mokso, P. Cloetens, E. Maire, W. Ludwig, and J.-Y. Buffire, *Nanoscale zoom tomography with hard x rays using Kirkpatrick-Baez optics* Appl. Phys. Lett. **90**, 144104 (2007) 78, 79
- [25] A. Pogany, D. Gao, and S. W. Wilkins, *Contrast and resolution in imaging with a microfocus x-ray source* Rev. Sci. Instrum. **68**, 2774-2782 (1997) 78
- [26] P. Kirkpatrick and A.V. Baez, *Formation of optical images by X-rays*, J. Opt. Soc. Am. **38**, 766-774 (1948) 79
- [27] S. Zabler, P. Cloetens, J.-P. Guigay, J. Baruchel, and M. Schlenker, *Optimization of phase contrast imaging using hard x rays* Rev. Sci. Instrum. **76**, 073705:1-7 (2005) 80, 82
- [28] J.-P. Guigay, *Fourier transform analysis of Fresnel diffraction patterns and in-line holograms* Optik (Shtuttgart), **49**, 121-125 (1977) 80
- [29] A. V. Bronnikov *Theory of quantitative phase-contrast computed tomography* J. Opt. Soc. Am. A., **19**, 472-480 (2002) 81
- [30] A.N. Tikhonov, *On the stability of inverse problem*, Dokl. Acad. Nauk SSSR, **39**, 195-198 (1943) 82

- [31] D. Paganin, S. C. Mayo, T. E. Gureyev, P. R. Miller, S. W. Wilkins *Simultaneous phase and amplitude extraction from a single defocused image of a homogeneous object*, J. Microsc., **206**, 33-40 (2002) 84
- [32] M. R. Teague *Deterministic phase retrieval: a Green's function solution* J. Opt. Soc. Am. **73**, 1434-1441 (1983) 84
- [33] K. M. Ho, C. T. Chan, C. M. Soukoulis, R. Biswas, and M. Sigalas *Photonic band gaps in three dimensions: New layer-by-layer periodic structures*, Solid State Comm. **89** 413-416 (1994) 86
- [34] M. Maldovan and E. L. Thomas, *Diamond-structured photonic crystals* Nature Mater. **3**, 593-59 (2004).
- [35] M.D. Leistikow, A.P. Mosk, E. Yeganegi, S.R. Huisman, A. Lagendijk, and W.L. Vos, *Inhibited spontaneous emission of quantum dots observed in a 3D photonic band gap*, Phys. Rev. Lett. **107**, 193903 (2011). 87
- [36] J. M. van den Broek, L. A. Woldering, R. W. Tjerkstra, F. B. Segerink, I. D. Setija, and W. L. Vos, *Inverse-woodpile photonic band gap crystals with a cubic diamond-like structure made from single-crystalline silicon*, Adv. Func. Mater. **22**, 25-31 (2012) 86, 100
- [37] <http://www.esrf.eu/UsersAndScience/Experiments/XNP/ID16A> (on 160310) 88
- [38] <http://henke.lbl.gov> (on 170510) 89
- [39] M.S. Nixon and A.S. Aguado *Feature Extraction and Image Processing* (Newnes, Oxford, 2002) 93
- [40] L. A. Woldering, R. W. Tjerkstra, H. V. Jansen, I. D. Setija, and W. L. Vos, *Periodic arrays of deep nanopores made in silicon with reactive ion etching and deep UV lithography* Nanotechnology **19**, 145304:1-11 (2008) 100
- [41] A.F. Koenderink, A. Alú, and A. Polman *Nanophotonics: Shrinking light-based technology* Science **348**, 516-521 (2015)
- [42] J. E. G. J. Wijnhoven, L. Bechger, and W. L. Vos *Fabrication and characterization of large macroporous photonic crystals in titania* Chem. Mater. **13** 4486-4499 (2001)
- [43] W. L. Vos, M. Megens, C. M. van Kats, and P. B'osecke *X-ray diffraction of photonic colloidal single crystals* Langmuir **13**, 6004-6008 (1997)

X-ray tomography

CHAPTER 6

Reflectivity of silicon photonic crystals with and without embedded point defects

To probe and evaluate optical properties of photonic crystals we discuss broadband microscopic reflectivity measurements on two-dimensional (2D) and three-dimensional (3D) photonic crystals. We present the broadband optical microscopy setup that is used. We study reflectivity spectra of 3D inverse woodpile diamond-like photonic band gap crystals. We identify the spectral features that match with stop gaps obtained from theory. We investigate the effect of embedding controlled defects in a 3D photonic band gap crystals. We also study in detail the polarization behavior of light in 2D photonic crystals that are the parent structures of the 3D crystals. We investigate the angular dependence of both the incident and the reflected polarization while these polarizations are mutually parallel or perpendicular. We find evidence for strong birefringence in the 2D stop gap.

6.1 Introduction

To achieve desired control over light propagation beyond designing and fabricating photonic crystal structures it is necessary to evaluate their optical performance and understand their optical properties. Depending on the functionality of the structure different experiments serve to evaluate its performance [1–3]. Nevertheless it remains a challenging task to experimentally demonstrate the presence of a complete photonic band gap in a sample. One possibility is to place light emitters inside the crystal and study the spontaneous emission spectra [2, 3]. The great advantage of such approach is that it is free from theory assumptions and directly probes the local density of states (LDOS) inside the structure. The difficulties with spontaneous emission measurements are that it is hard to control the spatial position of the emitters inside the crystal and filter the signal from the emitters located outside the crystal. Another possibility to verify the presence of stop gaps and band gaps is to measure light reflected from or transmitted through the photonic crystal. In the presence of the stop gap, light with a certain incident wave vectors k will be reflected since it can not propagate inside the crystal. When light is tuned to the frequency range of the 3D photonic band gap, light will be reflected for any incidence k vector. The

disadvantage of such approach is the difficulty of the interpretation of reflectivity and transmission spectra. One needs a complicated theory to compare and interpret experimental results and differences occur from the fact that calculated geometries inevitably differ from the real structures. Moreover stop bands may occur in the reflectivity or transmission due to so-called silent modes. These modes appear when the incident plane waves can not couple to the modes inside the crystal and thus being reflected.

One of the properties of the stop gaps is that the wave vector $\mathbf{k}$ has a complex value inside the stop gap $\mathbf{k}=\mathbf{k}'+j\mathbf{k}''$ where the imaginary part is caused by Bragg interference [4]. Thus light in the stop gap is attenuated and there is less intensity in the transmission (trough) and conversely there is more intensity in the reflection (peak). To prove the presence of 3D band gap one needs to study all possible incident $\mathbf{k}_{in}$ from 0 to 2π . This requirement means that one needs to have the NA of the incident objective $NA_{in} = 1.0$. Practically the consideration arises how large NA can be achieved for reflectivity measurements and how large NA is enough to be representative.

In this Chapter we concentrate on 3D inverse woodpile structures due to their large predicted relative band gap $\frac{\Delta\omega}{\omega_c} = 25\%$ [5]. Previous reflectivity and transmission studies performed on the similar structures are reported in the references [6] on the TiO_2 infiltrated woodpile structures with nearly perfect reflectance, [7] on the direct Si woodpile structure, [8] on the transmission measurements of 3D photonic crystals based on macroporous silicon and [16] on the reflectivity measurements of Si inverse woodpile photonic crystals with similar structure to the samples under investigation in this chapter but surrounded by the large array of 2D photonic crystal.

In the present work we study 3D inverse woodpile photonic crystal with lateral extend $\Delta X \Delta Y \approx 10 \times 10 \mu m$ surrounded by quasi-infinite high refractive index medium (Si) from 4 sides and low refractive index medium (air) from 2 other sides. The extend in ΔZ direction (thickness) is less significant as is reported in the Reference [9] and has negligible affect on the crystal reflectivity. Due to the finite size in $\Delta X \Delta Y$ directions we need to precisely focus laser light on the surface of 3D photonic crystal and thus employ microscopy setup to perform reflectivity measurements. To study large range of $\mathbf{k}$ vectors we focus light with high NA objective. Due to the broad width of stop gaps under study we need to carefully select optics used in the experiments and perform spectroscopic measurements for frequency resolution.

The parent 2D structure of 3D inverse woodpile is centered rectangular 2D array of deep pores. Since the array of pores is highly anisotropic, it is relevant to wonder about polarization behavior of light reflected from 2D photonic crystal. Previously a large birefringence of 0.366 below the first photonic band edge at the wavelength of $6.52 \mu m$ was reported by F. Genereux *et al* [10] in the triangular lattice crystal of air cylinders in silicon. Birefringence in their study is defined as a difference in the effective refractive indices of the electric fields polarized parallel and perpendicular to the cylinder axis. Here we propose a polarization-resolved study of our 2D photonic crystals where we rotate polarization and keep analyzer parallel or perpendicular to polarizer.

6.2 Optical setup for broadband reflectivity

For measurements of the reflectivity spectra from our nanophotonic structures an optical reflectivity setup was built based on previous versions[11]. Since we are interested in the optical properties of fabricated structures both inside and outside of the predicted band gaps and stop gaps, the reflectivity needs to be measured in large range of optical frequencies thus a broad band light source is required. For our samples the expected stop gaps are located in the near infrared (NIR) part of the spectrum ($4000 - 10000 \text{ cm}^{-1}$). This imposes the requirements on the optical components of the setup to be dispersionless throughout the whole range of interest. In order to avoid chromatic aberration the entire optical setup should be built without use of lenses but with reflecting optics. For focusing and expanding of the beam curved mirrors are used.

Figure 6.1: Schematic of the microscopic optical reflectivity setup. The beam of the broadband supercontinuum white light source is expanded with reflective beam expander BE and focused onto the sample using a dispersionless reflective microscope objective with $\text{NA}=0.65$. The signal is reflected from the sample and analyzed using an FTIR spectrometer and InGaAs detector. For imaging of the sample surface the light from the LED illuminates the sample and then focused onto a CCD camera. Incidence and reflected beams are separated with beam splitter BS. P1 polarizes the incident beam and P2 analyzes the polarization of the reflected beam.

The scheme of the setup is shown in the Figure 6.1. It consists of a supercontinuum source, a beam expander (BE), a high numerical aperture (NA) reflecting objective and a Fourier-Transform infrared (FTIR)spectrometer equipped with an external detector. The supercontinuum source covers the spectral range from 4000 cm^{-1} to $22\,000 \text{ cm}^{-1}$. The beam from the supercontinuum white laser source is collimated at the fiber output of the source and spatially filtered with an adjustable iris to select the central part with the most uniform spectral distribution. 96% of the laser power is dumped and the beam is expanded with the reflective beam expander BE (Thorlabs BE06R) to cover fully the pupil of

the reflective objective (Ealing 74x) with a numerical aperture $NA=0.65$. The full width at half maximum (FWHM) of the focus was measured by scanning along the sharp edge of wafer and was found to be around $4\mu\text{m}$. The sample was mounted on an (x, y, z) stage with piezomotors (Autotocube ECC100) for precise positioning. In between the measurements we observed the position of the beam on the sample with the white LED illumination and the CCD camera. A polarizer and analyzer Thorlabs LPNIRA050 are used to investigate the polarization effects. The reflected signal is analyzed using the FTIR spectrometer Biorad FTS6000 with a resolution of 8 cm^{-1} and detected with an external In-GaAs detector Teledyne Judson J23. The electric output of the detector was fed to the spectrometer electronics via a preamplifier and filter Stanford Research Systems SR560. All reflectivity spectra were calibrated by taking the ratio of the measured spectra to a reference spectrum that was measured on a gold mirror before and after the measurements using the same experimental conditions as the photonic structure under investigation. We also took reflectivity spectra of bulk silicon near the photonic crystal structure that were sometimes used as reference spectra in case there was no time to take gold reference spectra.

6.3 Reflectivity of 2D silicon photonic crystals

We have studied one 2D photonic crystal sample with internal sample name in Ad3a-14112008. The crystal consists of an array of deep pores etched in silicon using the Bosch reactive ion etching process [12]. The SEM image of the 2D photonic crystal is shown in Figure 6.2. The pores are etched in the X direction. The pore depth is $6\mu\text{m}$ and the pore radius at half depth is $r = 130 \pm 5\text{ nm}$. Thus the reduced pore radius equals $r/a = 0.19$, which determines the photonic band structure[12]. The pores are ordered in a centered rectangular lattice in ZY plane with lattice parameters $a = 690\text{ nm}$ and $c = 480\text{ nm}$ and ratio $c/a = \sqrt{2}$. The high-symmetry ΓK direction of light propagation coincides with the Z axis. In Reference [13] the reflectance of similar 2D photonic crystals is studied for TE- and TM-polarized light. 2D photonic crystals exhibit different reflectance for TE- and TM-polarized light but the detailed study of the polarization dependent reflectivity was not yet reported.

Here we address the polarization behavior of 2D photonic crystals in the following way. Two sets of experiments are performed. In the first set the analyzer is set parallel to the polarizer that sets the incidence polarization. The incident polarization θ of the $\mathbf{E}$ field is set with respect to the X axis as shown in the Figure 6.2. Both polarizer and analyzer are rotated by the same angle θ and the reflectivity is measured for each polarizer angle θ . Thus if the incident polarization is set to $\theta_P = 45^\circ$ the analyzer is also set $\theta_A = 45^\circ$. We refer to this case as “parallel polarizer” case. In the second set of experiments, called “crossed polarizer”, the analyzer is set perpendicularly to the incidence polarization angle θ . Thus if the polarizer is set to $\theta_P = 45^\circ$, the analyzer is set to $\theta_A = 125^\circ$. The reflectivity spectra are recorded for incidence polarization angles between 0 and 90° with 5 degrees step for both cases.

Figure 6.2: SEM image of the 2D photonic crystal under investigation. Deep pores in silicon are running along the X axis and are arranged in the centered rectangular lattice in the ZY plane with the lattice parameters $a = 690$ nm, $c = 480$ nm and pore diameter $d = 260$ nm. The angle of incident polarization of the electric field θ is measured starting from the Y axis as shown in the picture. The propagation direction of the axis of the incoming beam is parallel to the ΓK high symmetry direction.

Figure 6.3 shows reflectivity measured in the parallel polarizer case. The $\theta = 0$ polarization case (6.3(a)) corresponds to the TM polarization for which stop gap frequencies were calculated earlier in Reference [13]. The first observed reflectivity peak is centered at 5027 cm^{-1} and agrees well with the calculated stop gap in ΓK direction centered at 4997 cm^{-1} and extending from 4882 to 5112 cm^{-1} . The second observed reflectivity peak centered at 6268 cm^{-1} may correspond to the stop gap in the ΓB direction that extends outside the Brillouin zone and was not a part of the band structure calculation. The third observed reflectivity peak is centered at 9028 cm^{-1} and agrees well with the calculated stop gap centered at 8771 cm^{-1} and extending from 7812 to 9731 cm^{-1} . Figure 6.3(c) shows the TE polarized reflectivity spectra. The first observed reflectivity peak is centered at 4722 cm^{-1} and does not correspond to any known stop gap in the band diagram. The second wide reflectivity peak observed with the center at 5899 cm^{-1} agrees reasonably well with the calculated stop gap centered at 6187 cm^{-1} and extending from 5110 to 7265 cm^{-1} . This stop gap is the sub-Bragg gap that was first identified in Reference [13]. The third and the fourth reflectivity peaks centered at 8289 and 9828 cm^{-1} respectively do not match known stop gaps in the band diagram for ΓK direction, although they might be explained with calculations of the band structure beyond ΓK direction. The fifth reflectivity peak centered at 10610 cm^{-1} matches well with the calculated stop gap centered at 10755 cm^{-1} and extending from 10010 cm^{-1} to 11500 cm^{-1} . Figure 6.3(b) shows the reflectivity

Figure 6.3: Reflectivity measured from a 2D photonic crystal Ad3a-14112008 in case of parallel polarizer for incidence polarization angles $\theta = 0^\circ$ (TM mode) (a), $\theta = 45^\circ$ (b) and $\theta = 90^\circ$ (TE mode) (c). Gray bars indicate the extent of the calculated stop gaps.

tivity spectrum collected with polarizer set to $\theta = 45^\circ$, intermediate between the TE and the TM incident polarizations. The spectrum exhibits features common for both TE and TM reflectivity spectra such as peaks centered at 4910, 6185, 8458, 9786 and 10583 cm^{-1} , yet shifted in frequency.

Figure 6.4 shows a reflectivity map in parallel polarizer case measured for incident angles between 0 and 90 °. It is clear from the plot that high reflectivity peaks decrease in frequency when the incidence polarization angle θ increases. Two most pronounces reflectivity peaks centered around 6000 and 7000 cm^{-1} are present for every measured incident polarization angle and are changing in the bandwidth. Narrower reflectivity peaks centered around 5000 and 11000 cm^{-1} are only present for a range of incident polarization angles from 0 to 45 degrees

Figure 6.4: Reflectivity of 2D photonic crystal at the different angles of polarizer θ in the parallel polarizer case. The color scale represents the reflectivity value. On the horizontal axis is the wavenumber in cm^{-1} and on the vertical axis is the incidence polarization angle. The incident direction of the beam propagation is ΓK . Dashed lines indicate frequencies where reflectivity cross sections were taken for the plots in Figures 6.8 and 6.7.

and from 45 to 90 degrees respectively.

The next set of reflectivity measurements is done for the crossed polarizer case. Figure 6.5 shows reflectivity spectra collected in the crossed polarizer case. It is clear from the plot that for purely TE and TM incident polarizations (0 and 90 degrees polarizer angles) the reflectivity detected after the perpendicular analyzer is zero, which is expected for 2D photonic crystals since TE and TM are strictly separated [4]. However with polarizer set to $\theta = 45$ degree a reasonable reflectivity peak of 34% is observed at 5289 cm^{-1} . This frequency nearly corresponds to the center of the stop gap observed with parallel polarizer described above and confirmed with the band structure calculations. With crossed polarizers it is expected from the Fresnel laws of reflection and refraction [17] that the reflectivity vanishes for isotropic media at normal incidence. Non-zero reflectivity is observed only when the medium is anisotropic and the refractive index tensor has at least two different components $n_1 \neq n_2$. From observed in our experiment reflectivity peak of more than 35% in crossed polarizers case we conclude that our 2D photonic crystal exhibits large birefringent behavior.

Figure 6.6(a) shows the reflectivity map measured versus incidence polarization angle for the case of crossed polarizer. It is seen that a reflectivity peak of up to 35% appears in the range between 5125 and 5746 cm^{-1} at θ between 20 and 70° .

Figure 6.5: Reflectivity measured from 2D photonic crystal in case of crossed polarizer for the $\theta = 0^\circ$ (TM mode) (red), $\theta = 45^\circ$ (blue) and $\theta = 90^\circ$ (TE mode) (green) incidence polarization angle.

Less intense reflectivity peaks are also observed at higher frequencies 6584, 7338, 9155, 10938 and 11417 cm^{-1} in the same range of incidence polarization angles. The presence of a strong reflectivity peak in the frequency range of the stop gap in crossed polarizer configuration reveals that 2D photonic crystal behaves as a birefringent media inside the stop gaps.

To interpret the results that 2D photonic crystal exhibits birefringent behavior a model was designed. In our model we describe the crystal as a semi infinite slab of effective medium with the interface perpendicular to the Z axis with a

refractive index tensor equal to $n = \begin{bmatrix} n_1 & 0 & 0 \\ 0 & n_2 & 0 \\ 0 & 0 & n_3 \end{bmatrix}$. Thus there are two inde-

pendent components of the refractive index tensor n_1 and n_2 . We calculate the reflectance from the effective medium using the Fresnel coefficients derived in the Appendix C. We distinguish the two cases of parallel and crossed polarizers by considering separately TE- and TM-polarized components of the incidence wave and projecting the reflected wave on the axis of the analyzer. Thus we obtain the reflectivity of the semi infinite birefringent medium depending on the incident polarization angle for parallel and crossed polarizer cases. Then we apply a least square minimization of our model to the experimental data at each frequency and each incidence polarization angle. The resulting parameters are the effective refractive indices, whose dispersion is obtained n_1 and n_2 . In this first attempt to interpret the data we prefer to keep the model analytical and to minimize

Figure 6.6: (a) Reflectivity map measured fan a 2D photonic crystal versus angle of incident polarization of the E field and frequency. Incident and detection polarizers are *crossed*. High reflectivity is observed for a range of frequencies indicating the birefringent nature of the media. (b) Components (n_1 , n_2) of the effective refractive index tensor extracted from the model. Green dashed line shows n_1 and blue solid line shows n_2 . Purple dotted line is the absolute normalized difference between n_1 and n_2 . Dashed lines indicate frequencies at which reflectivity dependence on the angle of incidence polarization is plotted in Figures 6.8 and 6.7.

the number of adjustable parameters, therefore we restrict the refractive index components to be real.

Effective refractive index components n_1 and n_2 are plotted in Figure 6.6(b).

In addition we show the absolute normalized difference between n_1 and n_2 defined as $\Delta n \equiv 2 \times \left| \frac{n_1 - n_2}{n_1 + n_2} \right|$ to characterize the degree of anisotropy. At low frequencies below the calculated stop gap ($\nu/c < 4645 \text{ cm}^{-1}$) both components of refractive index n_1 and n_2 are equal which means that photonic crystal behaves as an isotropic media. The reflectivity at 4645 cm^{-1} and the corresponding model curve are shown in Figure 6.7. It is clearly seen from the plot that at this frequency reflectivity does not depend on the incidence polarization angle θ which agrees with obtained equality of refractive index components.

Figure 6.7: Reflectivity of 2D photonic crystal measured in the parallel polarizer case at different incidence polarization angles θ . Purple symbols shows reflectivity at 4645 cm^{-1} and green symbols shows reflectivity at 5293 cm^{-1} as indicated with red dashed lines in Figures 6.4 and 6.6. These frequencies correspond to the smallest anisotropy extracted from the effective media model. Dashed lines show corresponding fit curves from the proposed effective media model.

Above 4800 cm^{-1} in Figure 6.6(b) a large anisotropy of the refractive index is obtained from the model. Between 4800 and 5293 cm^{-1} the n_x element (n_1) of the refractive index tensor is higher than the n_y element (n_2). This can be rationalized with the hypothesis from Bragg stack [4] that waves concentrate their energy mostly in the high refractive index media on the low frequency side of the stop gap, which is in our case Si around the pores. The intuitive picture for the wave energy concentrated in the Si around the pore suggests that in X direction the vector of the electric field will oscillate along the long side of the Si wall and in Y direction the electric field vector will oscillate along the short side of the Si wall between two pores, thus the wave will “feel” the presence of air in the pore with lower refractive index. The reflectivity dependence on the incident

polarization angle at 5092 cm^{-1} is shown in Figure 6.8. The high reflectivity when incident polarization is along the X axis (0° angle of incidence polarization) agrees with the hypothesis above that the wave energy is concentrated in the high refractive index media and thus x component of the refractive index is higher than y component.

At 5293 cm^{-1} the two components of the refractive index in Figure 6.6(b) are becoming equal $n_1 = n_2$. The reflectivity at 5293 cm^{-1} and the corresponding model curve are shown in Figure 6.7. While the modeled refractive index components are equal as in the case of isotropic media, the experimental reflectivity as a function of incident polarization differs from the isotropic case. Reflectivity has maximum of 40% at 0 and 90° incidence polarization and a minimum of 19% at 45° . The unusual reflectivity dependence on the incidence polarization indicates that at this frequency an effective medium with two different components of refractive index $[n_1, n_2, n_2]$ cannot explain the behavior of the photonic crystal.

At frequencies larger than 5293 cm^{-1} the first component $n_1 = n_x$ of the refractive index has become larger than $n_2 = n_y = n_z$ component as shown in Figure 6.6(b). This can be explained with the change of the wave energy distribution to a low refractive index media [4]. If in the high frequency side of the stop gap the wave energy is concentrated more in the low refractive index material (pores), then the x component of the refractive index aligned along the pore depth is lower than y component of the refractive index which is aligned along the short side of the pore and thus “feels” the presence of surrounding Si. This hypothesis is supported with the experimentally observed reflectivity dependence on the incidence polarization angle shown in Figure 6.8. The high reflectivity of 60% is observed for 90° incidence polarization angle which means the polarization along the Y direction.

At frequencies larger than 6125 cm^{-1} Figure 6.6(b) shows that the difference between the components of the effective refractive index becomes close to zero meaning that the medium behaves like in isotropic medium. Above 7329 cm^{-1} anisotropy of refractive index appears and notably refractive index components alternate which one is larger n_1 or n_2 at frequencies 8363 , 9860 and 10276 cm^{-1} . The variations of the effective refractive index components is most likely associated with the first order Bragg condition and the second order stop gap in 2D photonic crystal.

Thus we observed for the first time large birefringence of 2D photonic crystals inside the stop gaps. The value of anisotropy Δn reaches up to $\Delta n = 0.9$ and is up to our knowledge the largest birefringence reported on 2D photonic crystals exceeding more than twice the birefringence below the stop gap reported by F. Genereux *et al* [10]. The effective refractive indices within the stop gap reaches values up to 8 due to the high reflectivity of 2D photonic crystal within the stop gap due to the Bragg diffraction. In order to void such unphysical values of the effective refractive indices the model needs to be extended to the complex values of the effective refractive indices to describe the behavior of the photonic crystal within the stop gap more physically. Moreover, in order to describe the situation when the components n_1 and n_2 of the effective refractive index are

Figure 6.8: Reflectivity of 2D photonic crystal measured in the crossed polarizer case versus incident polarization angle θ . Green symbols shows reflectivity at 5092 cm^{-1} and red symbols shows reflectivity at 5725 cm^{-1} as indicated with black dashed lines in Figures 6.4 and 6.6(b). These frequencies correspond to the largest anisotropy extracted from the effective medium model. Dashed lines show corresponding fit curves from the proposed effective medium model.

found from the model to be the same but the reflectivity nevertheless has strong angular dependence we suggest that effective refractive index tensor might not be diagonal.

6.4 Reflectivity study of 3D silicon photonic band gap crystals

6.4.1 Inverse woodpile photonic crystal

In this section we consider reflectivity measured on four different 3D inverse woodpile photonic crystal. The geometry of the inverse woodpile consists of two arrays of cylindrical pores where each array is arranged in a centered rectangular lattice as shown in Figure 1.2 in Chapter 1. The pore radius R and the lattice parameters a and c are chosen to be $a/c = \sqrt{2}$ such that the 3D crystal structure is face centered cubic with a diamond-like basis [14]. The ratio R/a determines the position and width of the expected band gap according to plane-wave band structure calculations [13] and was varied from sample to sample. We study here reflectivity from two different samples. All samples are listed in Appendix B with

their lab names, fabrication and measurements history.

First sample under investigation is listed in the Appendix B as Sample **D**. On the Sample **D** we study three structures: **D₁**, **D₂** and **D₃**. Structure **D₁** is a 3D photonic inverse woodpile crystal without intended defects thus we refer to such structure design as a quasi-perfect photonic crystal accounting for inevitable fabrication imperfections and finite size. The SEM image of the Structure **D₁** as an example of a typical quasi-perfect photonic crystal is shown in Figure 6.9 (a). The design R/a_{design} ratio for the structure **D₁** is 0.23 that is close to the optimum to form the widest band gap according to calculations in reference [12]. Structure **D₂** by design is equivalent to the Structure **D₁** thus we choose this two structures for comparison. Structure **D₃** contains the array of the cavities as shown in the Figure 6.9 (b). For the regular pores design parameter $R/a_{design}=0.23$. Each cavity is formed by the intersection of two pores with twice smaller radius $R' = 1/2R$. Every pore with smaller radius is indicated with the red circle on the picture. Thus there are 80 cavities inside the crystal arranged in a cubic lattice. The third sample studied in this chapter is sample **E** (see B for the name in the lab) where we consider on this sample a single 3D photonic crystal Structure **E₁** with 4 embedded cavities arranged diagonal along the crystal as is shown in figure 6.9(c). Each cavity is formed at the intersection of the smaller pore with radius $R' = 1/2R$.

Figure 6.9: SEM image of (a) Structure **D₁** as an example of a typical quasi-perfect 3D photonic crystal without embedded defects, (b) Structure **D₃** with 3D array of cavities based on smaller pores that are indicated with red circles and (c) Structure **E₁** consisting of 4 cavities diagonally deeper inside the crystal. The dashed red line indicates the 90 degree edge of silicon wafer. Scale bars are shown on the picture.

6.4.2 Reflectivity of 3D inverse woodpile photonic crystal without embedded defects

In this section we study reflectivity from Structures **D₁** and **D₂** that are by design equivalent quasi-perfect 3D photonic crystals without intended defects with $R/a_{design} = 0.23$. For the broadband reflectivity measurements we use the setup described in a section 6.2 above. Reflectivity of Structure **D₁** is shown

in the Figure 6.10. There are three distinguishable peaks of reflectivity seen in the spectrum. First observed stop band is centered at 5463 cm^{-1} and extends from 5310 cm^{-1} to 5617 cm^{-1} . Second stop band is a wide peak from 5876 cm^{-1} to 7414 cm^{-1} with the center at 6645 cm^{-1} . Third observed stop band is centered at 8556 cm^{-1} and extends from 8080 cm^{-1} to 9032 cm^{-1} . The gap in the spectrum around 9348 cm^{-1} is a result of filtering out the master source of the supercontinuum white light laser. The maximum reflectivity normalized to the

Figure 6.10: Reflectivity of the quasi-perfect photonic crystal Structure $\mathbf{D}_1$ with design $R/a = 0.23$ and without embedded defects. The observed stop bands are indicated with the gray bars. The gap in the spectrum around 9339 cm^{-1} is filtered out to remove artifacts from the pump source of the supercontinuum source.

gold mirror reaches up to 10%. We associate such low reflectivity from the crystal with few aspects. Firstly, the $4 \mu\text{m}$ focus size of a laser beam is comparable to the extent of the 3D photonic crystal determined from tomography measurement $\Delta X = 4.6 \mu\text{m}$ and $\Delta Y = 3.6 \mu\text{m}$ and since the crystal is located at the edge of Si bar some of the beam intensity leaks above the edge into the air during measurements close to the edge. Secondly, the crystal under investigation is a finite size structure in $\Delta X \Delta Y$ directions surrounded by the quasi-infinite high refractive index medium (Si) from 4 sides and low refractive index medium (air) from 2 sides. Previously reported high reflectivity such as 67% in the Reference [16] were measured for the 3D photonic crystal surrounded from 3 sides with a quasi-infinite array of 2D photonic crystal. Thirdly, we can expect a surface roughness to scatter light out of the collecting objective thus decreasing the reflectivity. The band diagram of inverse woodpile photonic crystal depends crucially on the (R/a) ratio of the structure (see Chapter 1 and Reference [16]).

Figure 6.11 shows the lower and higher band edges calculated in reference [16] and the central frequency ω_c . It is clear that the width of the band gap $\Delta\omega$ strongly depends on the R/a ratio. We overlap the observed stop bands from the reflectivity spectrum of the Structure **D₁** with the calculated positions of the band edges. From the overlap we can see that observed wide stop band between 5876 cm^{-1} and 7414 cm^{-1} is in perfect agreement with calculated band gap width $\Delta\omega$ and central frequency ω_c for the inverse woodpile structure with $R/a_{refl} = 0.196 \pm 0.001$. The R/a ratio extracted from tomography data discussed in the Chapter 5 $R/a_{tomo} = 0.197 \pm 0.01$ is in an excellent agreement with the R/a ratio obtained from reflectivity measurements $R/a_{refl} = 0.196 \pm 0.001$.

Figure 6.11: Observed stop bands (pink bars) of the Structure **D₁** overlapped with the calculated from the band structure positions of the lower (blue) and higher (black) band edges and central frequency ω_c of the inverse woodpile photonic crystal. The band edges are plotted for different R/a ratios.

Figure 6.12 shows the reflectivity measured from the Structure **D₂**. The structure is an equivalent to Structure **D₁** of a quasi-perfect 3D photonic crystal with the design $R/a_{design} = 0.23$. The reflectivity spectrum exhibits three distinguishable stop bands. The first one is a broad peak centered at 5557 cm^{-1} and extends from 4848 cm^{-1} to 6266 cm^{-1} . This stop band appears as a triplet of peaks and is located below the band gap. The second stop band extends from 6678 cm^{-1} to 8084 cm^{-1} with the center at 7381 cm^{-1} . The third stop band is centered at 8773 cm^{-1} and is located in frequency range between 8578 and 8969 cm^{-1} . In Figure 6.13 we overlap the observed stop bands with the band gap edges and central frequency calculated for different R/a . It is seen from the Figure 6.13 that the central frequency of the second stop band (6678 to 8084 cm^{-1}) is matching the

Figure 6.12: Reflectivity of the quasi-perfect photonic crystal Structure **D**₂ with design design $R/a = 0.23$ and without embedded defects on the sample D. The observed stop bands are indicated with the gray bars. The gap in the spectrum around 9339 cm^{-1} is filtered out to remove artifacts from the pump source of the supercontinuum source.

central frequency $\omega_c = 7381 \text{ cm}^{-1}$ of the band gap for $R/a_{refl} = 0.22 \pm 0.007$. From X-ray tomography data we obtained $R/a_{tomo} = 0.21 \pm 0.015$ which is in very good agreement with R/a estimated from stop band position. Thus we found two independent ways to determine the R/a ratio of 3D photonic crystal that are in excellent agreement with each other and therefore strongly supports the interpretation of optical reflectivity spectra. As was discussed in the Chapter 1 one of the characteristics of photonic crystal is photonic strength $S = \frac{\Delta\omega}{\omega_c}$. Photonic strength S calculated from the band diagram of inverse woodpile photonic crystal for different R/a is shown with the dashed line in Figure 6.14. From our reflectivity measurements we obtained experimentally the width of the stop band and the central frequency similarly as described above for the range of structures with different R/a . Thus we can plot experimental results of the photonic strength $S = \frac{\Delta\omega}{\omega}$ versus R/a (Figure 6.14). It is seen from the Figure 6.14 that one data point is matching excellently within the error bar the predicted photonic strength. This data point is obtained for the Structure **D**₁. The remaining data points are lying below the predicted photonic strength curve which can be associated with fabrication imperfections such as tapering of the pores resulting in the stop band narrower than the calculated one.

Figure 6.13: Observed stop bands (pink bars) of the Structure D_2 overlapped with the calculated from the band structure positions of the lower (blue) and higher (black) band edges of the inverse woodpile photonic crystal. The band edges are plotted for different R/a ratios.

6.4.3 Signature of the cavity resonance in the 3D band gap

In this section we consider reflectivity from photonic crystal structures with embedded defects. The defects are designed as an intersection of two defect pores with radii twice smaller than the regular pore radius $R' = R/2$. According to the supercell band structure calculations in the Reference [15] for the infinitely repeated $5 \times 5 \times 5$ unit cells crystal with two crossing defect pores there are 5 isolated resonances appearing in the band gap the crystal. Considering the finite size of our structures under investigation we may expect a different optical behaviour than an infinite structure. We consider the presence of a trough within the stop band as a signature of a cavity resonance meaning that light propagation occurs inside the stop band. Figure 6.15 shows reflectivity spectra taken at different X positions on the Structure E_1 centered around the position of the cavity defect. Every spectrum in Figure 6.15 is plotted with the bias of 10% from the spectrum taken exactly at the position of crossed defect pores (blue) for clarity. We can see that at the distance $\Delta X = 2\mu\text{m}$ away from the crossing pores the spectrum (green in Figure 6.15) is flat in the range of calculated band gap frequencies (gray bar in the Figure). When approaching closer to the crossing pores at the distance $\Delta X = 1\mu\text{m}$ from the cavity position a trough centered at 5955 cm^{-1} starts to appear in the range of the expected band gap. The trough reaches the maximum depth of 22% of amplitude of the reflectivity peak exactly

Figure 6.14: Photonic strength ($\Delta\omega/\omega_c$) calculated from band diagram (dashed line) and experimentally observed from reflectivity spectra (red scatterers) as a function of reduced pore radii of the inverse woodpile photonic crystal structure.

at the position where two defect pores crosses (blue spectrum in Figure 6.15). At the distance $\Delta X = -1 \mu\text{m}$ from the crossing point the trough amplitude slightly decreases to 19.2% of the stop band peak amplitude. Reflectivity scan at the distance $\Delta X = -2 \mu\text{m}$ from the cavity position exhibits flat spectrum in the range of the calculated band gap alike to the spectrum at $\Delta X = +2 \mu\text{m}$ from the cavity position but with lower amplitude. The decrease in the reflectivity amplitude is associated with the end of photonic crystal. As is clear from the Figure 6.15 the central position of the laser beam during the scan at $\Delta X = -2 \mu\text{m}$ from the cavity is close to the edge of photonic crystal structure and thus considering $4\mu\text{m}$ size of the laser beam we probe bulk silicon as well as few last unit cells of photonic crystal. Figure 6.16 shows reflectivity spectra measured at different ΔY distances around the crossing of two defect pores positions which is indicated with yellow circle centered at the distance $\Delta Y = 2.3 \mu\text{m}$ from the edge of the Si bar. The $Y = 0$ is located at the edge of the Si bar since it is easier to determine the edge position from knife-edge measurements than any other position on the bar. The amount of reflected light below the edge of the bar is low since most of the laser beam energy is going into the air but due to the $4\mu\text{m}$ focus size there is still some intensity on the Si bar as is seen from the spectra centered at $-0.4\mu\text{m}$ from the edge of the crystal. Reflectivity spectra at $\Delta Y = 0.7 \mu\text{m}$ and $\Delta Y = 1.3 \mu\text{m}$ distances from the edge are already close to the cavity located at $\Delta Y = 2.3 \mu\text{m}$ from the edge and thus a through appears centered at 5955 cm^{-1} in the range of calculated band gap. The depth of the through is changing

Figure 6.15: Reflectivity spectra taken on the Structure $\mathbf{E}_1$ along the X axis. The X distance is measured from the position of the cavity where two defect pores cross. The through in the reflectivity spectra in the area of the predicted band gap appears when the laser beam approaches the cavity and disappears after the beam is receding from the cavity. The spectra are separated in amplitude by applying a 10% bias.

from 45% of the peak amplitude at the distance $0.7\mu\text{m}$ from the edge to 39% at the distance $1.3\mu\text{m}$ from the edge. At the $\Delta Y = 2.1\mu\text{m}$ from the edge the spectrum changes its shape drastically with the significant asymmetry of the stop band peak which makes it difficult to estimate the depth of the trough. Moving further away from the cavity position to $\Delta Y = 2.8\mu\text{m}$ and $\Delta Y = 3.5\mu\text{m}$ from the edge (blue and black spectra in Figure 6.16) makes spectrum flatten in the range of the calculated stop band as is expected. The presence of the trough in the range of calculated band gap frequencies at the spatial positions close to the crossing of two defect pores is an indication of the cavity resonances present in the band gap. The differences between experimental observation of the single trough within the stop band and predicted in the References [15] 5 isolated dispersionless resonances in the band gap can be explained due to first of all differences in the structure design since in the calculations the supercell model was used thus the band structure was calculated for the infinite crystal with two defect pores crossing every $5 \times 5 \times 5$ unit cells. Secondly the crystal under investigation is a finite size structure surrounded by the high refractive index medium (Si) and low refractive index medium (air)

Next we study Structure $\mathbf{D}_3$ (see Appendix B) that consists of the array of 80 cavities arranged in a cubic lattice as shown in Figure 6.9 (b). We choose this design of the array in order to compensate for the finite size of the laser beam and in future investigate light “hopping” from one cavity to another as depicted

Figure 6.16: Reflectivity spectra taken on the Structure $\mathbf{E}_1$ along the Y axis. The Y distance is measured from the crystal to air interface. The crossing of two defect pores is located at the $2.1 \mu\text{m}$ distance from the crystal to air interface. The through in the reflectivity spectra in the area of the predicted band gap appears when the laser beam reached the crystal surface and disappears after the beam passes the cavity position. The amplitude of each spectrum is unbiased.

in the Chapter 1 Figure 1.1. Moreover the ongoing work of S.A. Hack et al. is concerned about band structure calculations for such 3D crystal of cavities inside a 3D photonic band gap crystal [18]. Since the laser beam focus is not infinitely small during the measurements we are probing all the area that is illuminated with the beam size as well as regions that are illuminated with the light scattered from the defect. In our case for the broad band white light laser source from the knife-edge measurements we found 90 to 10 % of the intensity to be within $4 \mu\text{m}$ spot. Thus we arranged cavity defects periodically with the period of 3 unit cells in each direction covering the entire crystal volume. Moreover such design is closer to the model used for the $5 \times 5 \times 5$ and $3 \times 3 \times 3$ supercell calculations in the Reference [15] of an infinite photonic crystal with the cavity defect repeated every 5 or 3 unit cells respectively. The reflectivity measured on a Structure $\mathbf{D}_3$ in comparison to the quasi-perfect photonic crystal Structure $\mathbf{D}_1$ is shown in Figure 6.17. It is seen from the figure that in the reflectivity measured from the Structure $\mathbf{D}_3$ that contains cavity array two troughs appear within the range of the stop band (indicated with the gray bar). The troughs are centered at 6365 and 6750 cm^{-1} with the depth of 39% and 70% of the peak value respectively. Ongoing band structure calculations of S.A. Hack et al. [18] report bands in this range of frequencies hence sensible that reflectivity is lower. The experimental Q factor of the resonances can be estimated from

Figure 6.17: Comparison of the reflectivity spectra taken on the quasi-perfect photonic crystal D_1 with no intended defects (red) and photonic crystal Structure D_3 with the array of cavities (black). The stop gap is indicated with the gray bar. The band gap in the spectrum around 9339 cm^{-1} is filter out to remove artifacts from the pump source of the supercontinuum source.

the ratio $Q_{exp} = \frac{\lambda}{\Delta\lambda}$ and for the first trough centered at 6365 cm^{-1} is found to be $Q_1 = 44.8$ and for the second trough centered at 6750 cm^{-1} is found to be $Q_2 = 40$. The small value of the experimental Q factors for the resonances in the stop band can be associated with the presence of multiple resonances close to each other in the band gap that can not be resolved in the experiment due to the limited resolution of the spectrometer 8 cm^{-1} and as well due to the light leaking through the defect pores and scattering.

6.5 Summary

We studied optical properties of 2D and 2D photonic crystals by means of broadband microscope reflectivity measurements. We described the setup that was build for reflectivity measurements of photonic structures. We investigated in details polarization behavior of light reflected from the 2D photonic crystals with different configuration of polarizer and analyser. We observed for the first time a large birefringence within the stop bands of 2D photonic crystals. We interpret polarization behavior of 2D photonic crystals with the model of semi-infinite birefringent slab with the effective refractive index tensor and obtained the components of the effective refractive index by fitting the model to the experimental

data. We obtained from the fit model anisotropy of the effective refractive index for frequency range between 4000 and 12000 cm^{-1} . We studied reflectivity measurements of 3D photonic crystal structures with and without embedded defects. From the observed stop bands for quasi-perfect photonic crystal structures we obtained R/a ratio and found an excellent match to the R/a ratios obtained from tomography data. In the reflectivity spectra taken on the structures with embedded defects we observed a trough within the calculated band gap. We found good correspondence of the trough in the reflectivity peak with the spatial position of the cavity defect in X and Y directions. We observed decreased reflectivity in range of predicted extra bands as well as two resonances within the stop band of the crystal containing an array of 80 cavities arranged in a cubic lattice.

Bibliography

- [1] S. Takayama, H. Kitagawa, Y. Tanaka, T. Asano, and S. Noda, *Experimental demonstration of complete photonic band gap in two-dimensional photonic crystal slabs* Appl. Phys. Lett. **87**, 061107 (2005) 109
- [2] A. F. Koenderink, L. Bechger, A. Lagendijk, and W. L. Vos, *An experimental study of strongly modified emission in inverse opal photonic crystals* Phys. Stat. Sol. (A) **197**, (2003) 648-661 109
- [3] P. Lodahl, A. F. van Driel, I. S. Nikolaev, A. Irman, K. Overgaag, D. Vanmaekelbergh, and W. L. Vos, *Controlling the dynamics of spontaneous emission from quantum dots by photonic crystals* Nature **430**, (2004) 654-657 109
- [4] J.D. Joannopoulos, S.G. Johnson, J.N. Winn, and R. D. Meade, *Photonic crystals: molding the flow of light* Princeton university press (2008) 110, 115, 118, 119
- [5] K. M. Ho, C. T. Chan, C. M. Soukoulis, R. Biswas, and M. Sigalas, *Photonic band gaps in three dimensions: new layer-by-layer periodic structures* Solid State Commun. **89**, 413 (1994) 110
- [6] C. Marichy, N. Muller, L.S. Froufe-Pe'rez, and F. Scheffold, *High-quality photonic crystals with a nearly complete band gap obtained by direct inversion of woodpile templates with titanium dioxide* Sci. Rep. **6**, 21818: 1-8 (2015) 110
- [7] M. J. A. de Dood, B. Gralak, A. Polman, and J.G. Fleming, *Superstructure and finite-size effects in a Si photonic woodpile crystal* Phys. Rev. B **67**, 035322:1-8 (2003) 110
- [8] J. Schilling, F. Mller, S. Matthias, R. B. Wehrspohn, and U. Gsele, *Three-dimensional photonic crystals based on macroporous silicon with modulated pore diameter* Appl. Phys. Lett. **78**, 1180-1182 (2001) 110
- [9] D. Devashish, S.B. Hasan, J.J.W. van der Vegt, and W.L. Vos, *Reflectivity calculated for a three-dimensional silicon photonic band gap crystal with finite support* Phys. Rev. B **95** (2017) 110
- [10] F. Genereux, S.W. Leonard, A. Briner, U. Gösele, and H. M. van Driel, *Large birefringence in two-dimensional silicon photonic crystals* Phys. Rev. B **63** 161101:1-4 (2001) 110, 119
- [11] A. Hartsuiker, P. J. Harding, Y. Nowicki-Bringuier, J. M. Grard, and W. L. Vos, *Kerr and free carrier ultrafast all-optical switching of GaAs/AlAs nanostructures near the three photon edge of GaAs* J. Appl. Phys. **104**, 083105: 1-7 (2008) 111
- [12] L. A. Woldering, A. P. Mosk, R. W. Tjerkstra, and W. L. Vos, *The influence of fabrication deviations on the photonic band gap of three-dimensional inverse woodpile nanostructures* J. Appl. Phys. **105**, 09310: 1-10 (2009) 112, 121

- [13] S. R. Huisman, R. V. Nair, A. Hartsuiker, L. A. Woldering, A. P. Mosk, and W. L. Vos, *Observation of sub-Bragg diffraction of waves in crystals* Phys. Rev. Lett. **108**, 083901: 1-5 (2012) 112, 113, 120
 - [14] K.M. Ho, C.T. Chan, and C.M. Soukoulis, *Existence of a photonic gap in periodic dielectric structures* Phys. Rev. Lett. **25**, 3152-3155 (1990) 120
 - [15] L. A. Woldering, A. P. Mosk, and W. L. Vos, *Design of a 3D photonic band gap cavity in a diamond-like inverse woodpile photonic crystal* Phys. Rev. B **90**, 115140: 1-9 (2014) 125, 127, 128
 - [16] S. R. Huisman, R. V. Nair, L. A. Woldering, M. D. Leistikow, A. P. Mosk, and W. L. Vos, *Signature of a three-dimensional photonic band gap observed on silicon inverse woodpile photonic crystals* Phys. Rev. B **83**, 205313: 1-7 (2011) 110, 122, 123
 - [17] M. Born and E. Wolf, *Principles of Optics* Pergamon Press, Oxford, (1970) 115
 - [18] S.A. Hack, J.J.W. van der Vegt, and W.L.Vos *3D photonic crystal of cavities in a 3D photonic band gap crystal* unpublished (2017) 128
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CHAPTER 7

Outlook

This thesis presents a proposal and proof-of-concept experiments for a CMOS-compatible platform for the realization of 3D silicon nanophotonics. In addition an original x-ray tomography analysis is presented and the optical properties of fabricated structures are studied. In this Chapter we give an outlook for future research in this direction.

To build up a platform for 3D silicon nanophotonics it is important to consider fabrication issues. One of the most common issues with 3D nanofabrication is so-called overlay - the alignment of features located in different planes or layers. In Chapter 2 of this thesis we already presented a novel method to pattern the etch mask in one step on two oblique surfaces thus with ensured alignment of the features located in different planes. The method that we present allows to fabricate apertures of any arbitrary shape. Hence in future it is interesting to expand the method to more complex mask designs with possible interconnections between oblique surfaces or integrate on-chip devices with different functionalities: for example an optical data detection device on one surface and data processing electronic device in close vicinity on the adjacent surface, or an optical sensing device on one surface and a magneto-electronic memory device on the adjacent surface. The inspiration for the mask designs can be found in opto-electronics, integrated photonics and sensing.

Another direction for development of the single-step etch mask approach for 3D is to expand it to different types of lithography than reported in Chapter 2. The most promising type of lithography that is widely used nowadays in CMOS industry is deep UV (DUV) lithography. DUV lithography allows to fabricate samples on a wafer scale with high throughput and at low cost per device. The proof-of-principle experiment for exposures of apertures in different depths on the slope of Si wafer is presented in Chapter 3 of this thesis. The aim of the proof-of-principle experiments was to show that it is possible to achieve exposures of the apertures at different depths on the slope within a single DUV exposure. For our test experiments the apertures were located randomly along the slope of a Si wafer to investigate the positions where the exposures will be successful. The future development of the experiment suggests to design the reticle for the exposure and choose the width and the position of the V-trenches on a wafer based on the previous results to maximize the chance of successful exposure on the slope. Multiple exposures can be used to increase the depth of focus of DUV lithography and hence increase the range of the depths on the slope where apertures can be exposed. The next step in realization of 3D structures with

DUV lithography is to transfer pattern from the photoresist either to the hard mask material or directly to silicon. This can be done by means of reactive ion etching (RIE).

Etching of pores in silicon is one of the main processes in current nanofabrication. Developments in the etching equipment allow to constantly improve the process flows to achieve deeper and smoother structures, as for example reported in Chapter 4. To optimize the Bosch process durations of etching and deposition steps, capacitively coupled plasma source and inductively coupled plasma source powers and the gas flows can be tuned. We suggest that further improvements of the etching process can be achieved by investigating in more detail the effect of etching parameters on the resulting structure. For 3D nanofabrication we observe the need in finding an appropriate procedure to clean the polymer residuals from the sample surface that accumulates during the protection steps of Bosch process. Since the etching during the two-step etching process described in this thesis for 3D nanofabrication is not equivalent on the first etch side and second etch side, we also suggest that further investigations are needed to create separate etching process flows for the first and second etch sides. For example CCP and ICP powers can be adjusted for the second etching step taking into account that the hard mask has already undergone one full etching step.

Imaging of 3D nanostructures with X-ray tomography at 10 nm resolution allows to evaluate fabricated samples and obtain 3D material density distribution. One of the main difficulties during tomography reconstruction that leads to the lower quality of the reconstructed image is the alignment of radiograms taken at different sample-to-detector distances (see Chapter 5). To improve the alignment we propose to design markers of a sharp known shape in both perpendicular surfaces of silicon wafer such that they are visible in transmission radiograms. After the volume of the sample is reconstructed we suggest to expand the analysis of the obtained data to taking cross sections in multiple parallel planes and performing a cross correlation of the images to investigate how much deviations are occurring in the sample with depth. The material density that describes the structure can be used as an input into *ab initio* numerical models (*e.g.*, FEM or FDTD) to compute optical properties of the structure *free from modeling assumptions*. Other possible analysis may include the detailed comparison of the material densities inside the pores and outside the sample to obtain if there are residuals of polymer layer in the pores that may hamper subsequent surface chemistry as proposed by A. Schulz.

From the perspective of optical study of the structures described in this thesis we foresee the following interesting future directions. The suggested model to describe large birefringence observed in 2D photonic crystal structures (Chapter 6) can be expanded to include complex refractive indices and non diagonal elements of refractive index tensor. A similar polarization study as was performed on 2D photonic crystals are performed on 3D photonic crystal structures and need to be analyzed. As a part of “Stirring of light!” program 3D photonic crystals studied in this thesis are suggested to be considered as a back reflector for Si solar cells. Due to the high reflectivity within the band gap for all incident angles and all polarizations it is expected that photonic crystal back reflector will efficiently

increase absorption of light in Si. A numerical study of the increase in efficiency of solar cells with 3D silicon photonic crystal as a back reflector is currently being carried out by Devashish. Another direction of investigations is to use wavefront to avoid possible disorder and efficiently couple light to a cavity in 3D photonic band gap crystal as studied by R. Uppu. Coupling light to a selected cavity out of an array of cavities will allow to study light “hopping” from one cavity to another and compare to ongoing calculation, as being done by S. Hack.

APPENDIX A

Background on X-ray wave propagation

A.1 Basic equations.

Based on Reference [2], in a linear, isotropic, homogeneous and non-dispersive dielectric medium, all components of the electric and the magnetic field behave identically and their behavior is fully described by the following scalar wave equation

$$\nabla^2 u(\mathbf{P}, t) - \frac{n^2}{c^2} \frac{d^2 u(\mathbf{P}, t)}{dt^2} = 0, \quad (\text{A.1})$$

where $u(\mathbf{P}, t)$ depends on position $\mathbf{P}$ and time t , and represents any of the scalar components. The refractive index n of the medium is defined by

$$n = \left(\frac{\epsilon}{\epsilon_0}\right)^{1/2}, c = \frac{1}{\sqrt{\mu_0 \epsilon_0}}, \quad (\text{A.2})$$

where ϵ_0 is the permittivity of vacuum. In the case of x-rays we describe the refractive index of the media as

$$n = 1 - \delta + j\beta, \quad (\text{A.3})$$

where $\delta = r_c \lambda^2 \rho_e / (2\pi)$ and r_c is the classical electron radius and ρ_e is an electron density. It is convenient to use a Green function approach to solve the inhomogeneous differential equation:

$$a_2(x) \frac{d^2 U}{dx^2} + a_1(x) \frac{dU}{dx} + a_0(x) U = V(x). \quad (\text{A.4})$$

We choose here a one-dimensional variable x but equation A.4 can be generalized to a multidimensional position vector $\vec{r}$. When $V(x)$ is replaced by a delta function $\delta(x - x')$ and with the same boundary conditions the solution of the differential equation is called a Green function $G(x)$. The general solution $U(x)$ can then be found from

$$U(x) = \int_{-\infty}^{\infty} G(x - x') V(x') dx'. \quad (\text{A.5})$$

Let us consider the point of observation P_0 and a closed surface S around it. The problem is to express the optical disturbance at the point P_0 . To solve

this question we apply the Green function approach and choose as an auxiliary function a unit-amplitude spherical wave expanding from the point P_0 . Thus, the value of G at an arbitrary point P_1 with vector $\vec{r}$ is given by

$$G(\vec{r}) = \frac{e^{(jkr_{01})}}{r_{01}}. \quad (\text{A.6})$$

To exclude the discontinuity at P_0 , a small spherical surface S of radius ϵ is inserted around the point P_0 . Green's theorem is then applied, the volume of the integration V being the volume lying between S and S_ϵ and the surface of integration $S' = S + S_\epsilon$ ((See Reference [2] 3.18-3.21). From here the integral theorem of Helmholtz and Kirchhoff can be derived, that is used in order to find a field at any point P_0 (See Reference [2] 3-21):

$$U(P_0) = \frac{1}{4\pi} \oint_s \left\{ \frac{\partial U}{\partial n} \left[\frac{e^{(jkr_{01})}}{r_{01}} \right] - U \frac{\partial}{\partial n} \left[\frac{e^{(jkr_{01})}}{r_{01}} \right] \right\} ds \quad (\text{A.7})$$

This result is known as the integral theorem of Helmholtz and Kirchhoff and it allows the field at any point $\mathbf{P}_0$ to be expressed in terms of the boundary values of the wave on any closed surface surrounding the point.

Figure A.1: Kirchhoff diffraction by a plane screen. A wave disturbance impinges from the left on a screen with an aperture and the field is to be calculated at the point $\mathbf{P}_0$.

A.2 Kirchhoff diffraction

Let us consider the problem of diffraction of light by an aperture in an infinite opaque screen (A.1) [2]. The wave disturbance impinges on a screen with an aperture from the left and a field at the point $\mathbf{P}_0$ is to be calculated. Having disposed of the integration over the surface S_2 by taking the limit to infinite radius:

$$\lim_{R \rightarrow \infty} R \left(\frac{\partial U}{\partial n} - jkU \right) = 0, \quad (\text{A.8})$$

(Goodman 3.4 p42), the disturbance at P_0 is expressed as

$$U(P_0) = \frac{1}{4\pi} \iint_s \left\{ \frac{\partial U}{\partial n} G - U \frac{\partial G}{\partial n} \right\} ds. \quad (\text{A.9})$$

Kirchhoff diffraction is considered under the following assumptions: 1. Across the surface Σ , the field distribution U and its derivative $\partial U / \partial n$ are exactly the same as they would be in absence of the screen, 2. Over the portion of S_1 that lies in the geometrical shadow of the screen, the field distribution U and its derivative $\partial U / \partial n$ are zero.

These conditions are known as Kirchhoff boundary conditions. These assumptions hold in case the dimensions of the aperture Σ are large compared to the wavelength ($\Sigma \gg \lambda^2$). Suppose the aperture to be illuminated by a single spherical wave, $U(P_1) = \frac{A \exp(jkr_{21})}{r_{21}}$ we obtain the Fresnel-Kirchhoff diffraction formula for a field at the point P_0 : (Goodman 3-25 - 2-27)

$$U(P_0) = \frac{A}{j\lambda} \iint_{\Sigma} \frac{\exp[jk(r_{21} + r_{01})]}{r_{21}r_{01}} \left[\frac{\cos(\vec{n}, \vec{r}_{01}) - \cos(\vec{n}, \vec{r}_{21})}{2} \right] ds \quad (\text{A.10})$$

This equation can be interpreted to imply that the field at the point P_0 arises from an infinity of fictitious “secondary” point sources located within the aperture, that are related to the illuminating wave front and the angles of illumination and observation.

A.3 Rayleigh-Sommerfeld diffraction

Kirchhoff theory has an inconsistency since both the normal derivative and the field strength vanish on the boundaries, which mathematically means that function must vanish on the entire plane. Sommerfeld removed this inconsistency by eliminating the necessity for **both** field strength and its normal derivative to vanish at boundaries. Instead, either field strength **or** its normal derivative must vanish at the boundaries. Suppose G is generated not only by a point source at P_0 but also by a source placed at the mirror imaged point $\bar{P}_0$ which in case when this two sources oscillate with a 180° phase difference gives a Green function as

$$G_-(P_1) = \frac{e^{(jkr_{01})}}{r_{01}} - \frac{e^{(jkr_{01})}}{\bar{r}_{01}}, \quad (\text{A.11})$$

and in case when this two sources are in phase:

$$G_+(P_1) = \frac{e^{(jkr_{01})}}{r_{01}} + \frac{e^{(jk\overline{r_{01}})}}{\overline{r_{01}}}, \quad (\text{A.12})$$

which lead to the following Rayleigh-Sommerfeld diffraction formula (Goodman 3-30 - 3-44):

$$U_I(P_0) = \frac{1}{j\lambda} \iint_{\Sigma} U(P_1) \frac{e^{(jkr_{01})}}{r_{01}} \cos(\vec{n}, \vec{r_{01}}) ds. \quad (\text{A.13})$$

In case of $U(P_1) = A \frac{e^{(jkr_{21})}}{r_{21}}$ this gives us

$$U_I(P_0) = \frac{A}{j\lambda} \iint_{\Sigma} \frac{e^{[jk(r_{21}+r_{01})]}}{r_{21}r_{01}} \cos(\vec{n}, \vec{r_{01}}) ds \quad (\text{A.14})$$

and

$$U_{II}(P_0) = -\frac{A}{j\lambda} \iint_{\Sigma} \frac{e^{[jk(r_{21}+r_{01})]}}{r_{21}r_{01}} \cos(\vec{n}, \vec{r_{01}}) ds \quad (\text{A.15})$$

The first Rayleigh-Sommerfeld solution gives a prediction to a well known Huygens-Fresnel principle: the observed field $U(P_0)$ is a superposition of diverging spherical waves $\exp(jkr_{01})/r_{01}$ originating from every point P_1 withing the aperture Σ .

From the equation (A.13), the intensity observed on the screen at the distance r_{01} from the aperture is

$$I_Q(x_1, y_1) = |u_Q|^2 = \left| \frac{1}{i\lambda} \iint_{\Sigma} u_p(x, y) \frac{e^{(jkr_{01})}}{r_{01}} \cos(\vec{n}, \vec{r_{01}}) ds \right|^2 \quad (\text{A.16})$$

In rectangular coordinates the Huygens-Fresnel principle (that comes from the first Rayleigh-Sommerfeld solution) can be expressed as (GM 3-15 and 4-9)

$$U(x, y) = \frac{z}{j\lambda} \iint_{\Sigma} U(\xi, \eta) \frac{e^{(jk(r_{01}))}}{r_{01}} d\xi d\eta \quad (\text{A.17})$$

Where $r_{01} = \sqrt{z^2 + (z - \xi)^2 + (y - \eta)^2}$.

A.4 Fresnel diffraction

To reduce Huygens-Fresnel principle, we introduce the following approximation for r_{01} :

$$r_{01} = z \sqrt{1 + \frac{(x - \xi)^2}{z^2} + \frac{(y - \eta)^2}{z^2}} \approx z \left[1 + \frac{1}{2} \frac{(x - \xi)^2}{z^2} + \frac{1}{2} \frac{(y - \eta)^2}{z^2} \right] \quad (\text{A.18})$$

The error introduced by dropping all the terms but z in the denominator of equation A.17 is small, however, for r_{01} in the exponent errors are more critical, therefore, equation A.17 turns into

$$U(x, y) = \frac{e^{(jkz)}}{zj\lambda} \iint_{\Sigma} U(\xi, \eta) e^{\left[j \frac{k}{2z} [(x-\xi)^2 + (y-\eta)^2]\right]} d\xi d\eta \quad (\text{A.19})$$

and, in another form (see Reference [2], eq. 4-17):

$$U(x, y) = \frac{e^{(jkz)}}{zj\lambda} e^{(j \frac{k}{2z} (x^2 + y^2))} \iint_{\Sigma} U(\xi, \eta) e^{\left[j \frac{k}{2z} [\xi^2 + \eta^2]\right]} e^{(-j \frac{2\pi}{z\lambda} (x\xi + y\eta))} d\xi d\eta \quad (\text{A.20})$$

In order to distinguish the Fresnel and the Fraunhofer regimes the Fresnel number approach is useful: let us define the Fresnel number to be

$$F \equiv \frac{a^2}{L\lambda}, \quad (\text{A.21})$$

where a is a characteristic size of the aperture, L is the distance between the screen and the aperture. Physically Fresnel number describes the number of zones in which wavefront phase changes by π counted from the center to the edge of the aperture as seen from the observational point. If the Fresnel number is less than 1, then the curvature of the wavefront is small and diffraction follows more simple Fraunhofer description.

A.5 Fraunhofer diffraction

In the Fraunhofer approximation ($z \gg \frac{k(\xi^2 + \eta^2)_{max}}{2}$), corresponding to a Fresnel number $F \ll 1$, the field is described as (Reference [2] equation 4-25)

$$U(x, y) = \frac{\exp(jkz)}{zj\lambda} \exp(j \frac{k}{2z} (x^2 + y^2)) \iint_{-\infty}^{\infty} U(\xi, \eta) \exp(-j \frac{2\pi}{z\lambda} (x\xi + y\eta)) d\xi d\eta \quad (\text{A.22})$$

Equation A.22 is a Fourier transform of the aperture distribution $U(\xi, \eta)$ multiplied by a phase factor. In the experiment the observable quantity is the intensity which is defined as $I(x, y) \equiv |U(x, y)|^2$. This means that in Fraunhofer regime all phase information is lost. Since in x-ray tomography we are interested in phase information, the Fraunhofer regime is not suitable for this purpose.

A.6 Talbot effect for amplitude grating

Talbot effect is important to consider as a background for x-ray tomography since the presence of a Talbot effect imposes a requirement to record diffraction patterns at multiple sample to detector distances in a tomography experiment. Let

us first consider a sinusoidal amplitude grating that is modeled as a transmitting structure with an amplitude transmittance equal to

$$t_A(\xi, \eta) = \frac{1}{2}[1 + m \cos(2\pi\xi/L)] \quad (\text{A.23})$$

In the Fresnel regime, the transfer function is (GM 4-21)

$$H(\xi, \eta) = \frac{e^{jkz}}{j\lambda z} e^{[j\frac{\pi}{\lambda}(\xi^2 + \eta^2)]} \quad (\text{A.24})$$

Therefore, Fourier transform is

$$F\{H(x, y)\} = e^{[-j\pi\lambda z(f_X^2 + f_Y^2)]} \quad (\text{A.25})$$

The frequency spectrum of the field transmitted by the structure is the Fourier transform of the amplitude transmittance:

$$F\{t_A(\xi, \eta)\} = \frac{1}{2}\delta(f_X, f_Y) + \frac{m}{4}\delta(f_X - \frac{1}{L}, f_Y) + \frac{m}{4}\delta(f_X + \frac{1}{L}, f_Y) \quad (\text{A.26})$$

The transfer function in equation (A.25) is equal to 1 at the origin and at $(f_X, f_Y) = (\pm\frac{1}{L}, 0)$

$$H(\pm\frac{1}{L}, 0) = e^{[-j\frac{\pi\lambda z}{L^2}]} \quad (\text{A.27})$$

Thus after propagation over distance z behind the grating, the Fourier transform of the field becomes

$$F\{U(x, y)\} = \frac{1}{2}\delta(f_X, f_Y) + \frac{m}{4}e^{-j\frac{\pi\lambda z}{L^2}}\delta(f_X - \frac{1}{L}, f_Y) + \frac{m}{4}e^{-j\frac{\pi\lambda z}{L^2}}\delta(f_X + \frac{1}{L}, f_Y) \quad (\text{A.28})$$

Applying inverse Fourier transform to this spectrum, we find the field in real space at the distance z from the grating to be

$$U(x, y) = \frac{1}{2} + \frac{m}{4}e^{-j\frac{\pi\lambda z}{L^2}}e^{j\frac{2\pi x}{L}} + \frac{m}{4}e^{-j\frac{\pi\lambda z}{L^2}}e^{j\frac{2\pi x}{L}} = \frac{1}{2}\left[1 + me^{-j\frac{\pi\lambda z}{L^2}}\cos\left(\frac{2\pi x}{L}\right)\right] \quad (\text{A.29})$$

Then the intensity distribution ($I(x, y) = |U(x, y)|^2$) is given by

$$I(x, y) = \frac{1}{4}\left[1 + 2m\cos\left(\frac{\pi\lambda z}{L^2}\right)\cos\left(\frac{2\pi x}{L}\right) + m^2\cos^2\left(\frac{2\pi x}{L}\right)\right] \quad (\text{A.30})$$

If we consider the intensity distributions at the so-called Talbot distances ($z = \frac{2nL^2}{\lambda}$, or $\frac{\pi\lambda z}{L^2} = 2n\pi$), it is seen that the intensity distributions in such cases are either exact images of the grating, or phase-reversed images (Figure A.2):

1. If $\frac{\pi\lambda z}{L^2} = 2\pi n$, then the intensity is equal to

$$I(x, y) = \frac{1}{4}\left[1 + m\cos\left(\frac{2\pi x}{L}\right)\right]^2 \quad (\text{A.31})$$

which can be interpreted as a perfect image of the grating.

2.If $\frac{\pi\lambda z}{L^2} = (2n+1)\pi$, then the intensity is equal to

$$I(x, y) = \frac{1}{4} \left[1 - m \cos\left(\frac{2\pi x}{L}\right) \right]^2 \quad (\text{A.32})$$

which corresponds to a perfect image of the grating but with a 180° spatial phase shift, in other words, a phase-reversed Talbot image.

3.If $\frac{\pi\lambda z}{L^2} = (2n-1)\pi/2$, then the intensity is equal to

$$I(x, y) = \frac{1}{4} \left[1 - m^2 \cos^2\left(\frac{2\pi x}{L}\right) \right]. \quad (\text{A.33})$$

In in this case the image has a doubled frequency compared to the original one and a reduced contrast. This situation is a so-called subimage.

Figure A.2: Spatial location of Talbot images when a sinusoidal amplitude grating is illuminated with a plane wave.

A.7 Talbot effect for a phase grating

In a holotomography experiment that we performed the contrast is provided by the phase delay of the beam propagated through the sample rather than amplitude change, therefore it is important to consider a Fresnel diffraction on a phase periodic sample. Due to Talbot effect it appears to be necessary to perform tomography scans for several distances in order to avoid blindness of Fresnel diffraction to a certain spatial frequencies at every distance.

A.7.1 Numerical calculation in the Fresnel regime.

In Reference[4] the deep Fresnel diffraction ($r \gg \lambda/2\pi$) of a sinusoidal phase grating is considered. The “deep Fresnel regime” is defined as a regime in between

near-field diffraction, when the propagation distance is confined to a few wavelengths from the grating and far-field Fraunhofer regime. Let the transmission function of the grating $t(x_0)$ be

$$t(x_0) = \exp[jnka_0 \sin(2\pi x_0/d) + j\varphi_0], \quad (\text{A.34})$$

where k is the wavenumber, a_0 and d thickness and period of the grating respectively, φ_0 is an additional constant phase and n is the refractive index of grating.

The transmission function can be rewritten in terms of Bessel functions of the first kind using the equality

$$\exp\left[j\frac{m}{2}\sin(2\pi f_0\xi)\right] = \sum_{q=-\infty}^{\infty} J_q\frac{m}{2}\exp(j2\pi qf_0\xi), \quad (\text{A.35})$$

which gives

$$t(x_0) = \sum_{m=-\infty}^{\infty} J_m(nka_0)e^{[j\frac{2\pi mx_0}{d}]}, \quad (\text{A.36})$$

The diffraction field $u(x, z)$ in the observation plane satisfies the Helmholtz equation[3] $(\nabla + k^2)u(x, z) = 0$, and, using the Green's theorem, the field in the observation plane $u(x, z)$ can be written as

$$u(x, z) = \frac{1}{4\pi} \int \left\{ u_0(x_0) \frac{\partial G(x_0, x, z)}{\partial n_0} - G(x_0, x, z) \frac{\partial u_0(x_0)}{\partial n_0} \right\} dx_0, \quad (\text{A.37})$$

where $G(x_0, x, z)$ is the Green function, $u_0(x_0) = At(x_0)$ is the field immediately after the grating and $\partial/\partial n_0$ is the normal derivative. In the one-dimensional case the Green function is $G(x_0, x, z) = j\pi H_0^{(1)}(kr)$, where $H_0^{(1)}$ is the zero-order Hankel function of the first kind

$$H_n^{(1)}(z) = \frac{1}{j\pi} \int_0^\infty \frac{e^{(z/2)(t-1/t)}}{t^{n+1}} dt, \quad (\text{A.38})$$

and $r = [(x - x_0)^2 + (z - h)^2]^{1/2}$ is the distance from the object point x_0 to the observational point x . Using the recurrence relation for the Hankel function[7] $\left(\left(\frac{1}{z} \frac{d}{dz}\right)^m (z^{-n} f_n(z)) = (-1)^m z^{-n-m} f_{n+m}(z)\right)$, the derivative of the Green function can be written as

$$\frac{\partial G(x_0, x, z)}{\partial n_0} = \frac{-j\pi k(z - h)H_1^{(1)}(kr)}{r}. \quad (\text{A.39})$$

When the propagation distance z is larger than several wavelength and the thickness a_0 is much smaller than the period of the grating, the derivative of the height function $h(x_0) = a_0 \sin(2\pi x_0/d)$ is so small compared to the derivative of the Green function that it can be neglected. Therefore the term $\partial u_0(x_0)/\partial n_0$ in equation A.37 can be neglected as well. Therefore, the diffraction field can be written

$$u(r) = \frac{-jkr}{4} \int [t(x_0)(z - h)H_1^{(1)}(kr)/r] dx_0. \quad (\text{A.40})$$

In the deep Fresnel regime $kr \gg 1$, so that the Hankel function can be replaced by its asymptotic expression $H_1^{(1)}(kr) \sim \sqrt{2/\pi kr} \exp(jkr - j2\pi/4)$. From the equations above, the diffraction intensity of the one-dimensional sinusoidal grating is

$$I(x, y) = \frac{kA^2}{8\pi} \left| \int \sum_{m=-\infty}^{\infty} J_m(nka_0) e^{jm2\pi \frac{x_0}{d}} \times (z-h) e^{(ikr)} / r^{3/2} dx_0 \right|^2 \quad (\text{A.41})$$

A numerical calculation of this integral was made with the following parameters: grating size $s = 3 \text{ cm}$, wavelength $\lambda = 0.8 \text{ }\mu\text{m}$, $n = 1.532$, grating period $d = 20 \text{ }\mu\text{m}$, grating thickness $a_0 = 1 \text{ }\mu\text{m}$. Figure A.3 shows a cross section at $y = 0$ of the intensity distribution behind the sinusoidal phase grating illuminated with a plane wave. The wave is incident from the left side of the picture on a grating (at $z = 0$) and propagates to the right side. The interference pattern has a strong dependence on the distance from the grating.

Figure A.3: Diffraction pattern of the sine phase grating in the deep Fresnel region, calculated in Reference[4]. Waves are propagating from left to right. The diffraction pattern shown in the figure is a cross section at the fixed value of $y = 0$.

A.7.2 Diffraction using transfer function approach

Let us now consider a sinusoidal phase grating similar to the 2D photonic crystal structures that surround our 3D crystal which is defined by a transmittance function

$$t_A(\xi, \eta) = \exp\left[j\frac{m}{2} \sin(2\pi f_0 \xi)\right] \text{rect}\left(\frac{\xi}{2w}\right) \text{rect}\left(\frac{\eta}{2w}\right), \quad (\text{A.42})$$

Where $f_0 = 1/L$ spatial frequency of the grating, w is a half width of the grating and rect is a rectangular function which has a value of unit when the argument is within $\pm 1/2$ interval. To simplify the analysis let us use the identity A.35, where J_q is a Bessel function of the first kind, and order q . Given

$$F\left\{\exp\left[j\frac{m}{2} \sin(2\pi f_0 \xi)\right]\right\} = \sum_{q=-\infty}^{\infty} J_q \frac{m}{2} \delta(f_X - qf_0, f_Y), \quad (\text{A.43})$$

A Fourier transform of a transmittance function in that case will be

$$\begin{aligned} F\{t_A(\xi, \eta)\} &= [A \text{sinc}(2wf_X) \text{sinc}(2wf_Y)] \otimes \left[\sum_{q=-\infty}^{\infty} J_q \frac{m}{2} \delta(f_X - qf_0, f_Y) \right] \\ &= \sum_{q=-\infty}^{\infty} AJ_q \frac{m}{2} \text{sinc}[2w(f_X - qf_0)] \text{sinc}(2wf_Y) \end{aligned} \quad (\text{A.44})$$

The transfer function in case of Fresnel diffraction is (GM 4-21)

$$H(f_X, f_Y) = \exp[-j\pi\lambda z(f_X^2 + f_Y^2)] \quad (\text{A.45})$$

Therefore, using a transfer function approach (3-74 GM), we multiply equations A.44 and A.45 and find the Fourier transform of a field at the position z to be

$$F\{U(x, y)\} = \sum_{q=-\infty}^{\infty} AJ_q \frac{m}{2} \exp[-j\pi\lambda z(f_X^2 - f_Y^2)] \text{sinc}[2w(f_X - qf_0)] \text{sinc}(2wf_Y) \quad (\text{A.46})$$

Analytical form of the expression A.46 involves convolution integrals that are difficult to interpret therefore it is more revealing to use numerical methods.

Applying numerically inverse Fourier transform to a in Equation A.46, we can obtain field distribution $U(x, y)$ for different distances from the grating. The intensity behind the grating will be then $I(x, y) = |U(x, y)|^2$. We plot intensity distribution behind the grating in the Figure A.4. For comparison with the reference[4] we applied the same parameters as described in section A.7.1. In order to simulate the case of x-ray diffraction on photonic crystal sample,

Figure A.4: Diffraction pattern of the sine phase grating with parameters taken from Reference[4] numerically calculated by us using transfer function approach.

the following parameters were chosen: $\lambda = 0.072 \text{ nm}$, that corresponds to the beam energy of 17 keV; grating period [6] of 690 nm, real part of the refractive index[5] $\delta = 1.5$. The diffraction pattern calculated for this case is shown in

Figure A.5. It is seen that at the number of distances z such as from the grating there is no contrast. This is a result of Talbot effect for a phase periodic object. The intensity cross sections in Figure A.6 have been taken for com-

Figure A.5: Diffraction pattern of the sinusoidal phase grating with a period $d = 690 \text{ nm}$ illuminated with an x-ray beam with photon energy of 17 keV corresponding to $\lambda = 0.07 \text{ nm}$.

parison at the Talbot distances ($z_{Tb} = N2d^2/\lambda = 130 \text{ } \mu\text{m}$) and at non-Talbot distances $z_1 = z_{Tb} + 200 \text{ } \mu\text{m}$ and $z_2 = z_{Tb} + 0.1 \text{ m}$. It is clearly seen that the contrast at Talbot distance is close to zero, unlike the contrast at the distance $z_1 = z_{Tb} + 200 \text{ } \mu\text{m}$. Zero contrast at the Talbot distance for the phase periodic sample means that in order to reconstruct all the spatial frequencies of a periodic sample one need to record diffraction patterns at multiple distances z .

Figure A.6: Cross section of intensity pattern shown in Figure A.5 at the Talbot distance z_{Tb} (blue) and for a distances $z_1 = z_{Tb} + 200 \text{ } \mu\text{m}$ (purple) and $z_2 = z_{Tb} + 0.1 \text{ m}$ (red).

A.8 Diffraction pattern from a 2D centered rectangular grating

Using the same transfer function approach as in the section above we have calculated the intensity distribution for a two-dimensional rectangular centered grating. The grating is chosen to represent the geometry of our 2D photonic crystal. The 2D rectangular centered array of pores is the first step in the fabrication process of our 3D inverse woodpile photonic crystals[6]. The grating consist of $10\text{ }\mu\text{m}$ thick material with real part of the refractive index equal to $\delta = 1.5$, which corresponds to refractive index of silicon for $\lambda = 0.072\text{ nm}$. The field distribution U_0 at the distance $z = 0$ just behind grating is shown in the figure A.7. This distribution defines the transmittance of the grating. For calculations we used following grating parameters: $a = 2\mu\text{m}$, $\frac{a}{c} = \sqrt{2}$ and the pore size $d = 200\text{ nm}$. The calculated diffraction intensity distribution over the range of

Figure A.7: The field distribution at the distance $z = 0$ behind the 2D centered rectangular grating.

distances for a fixed y value of $y = 0.01\mu\text{m}$ from the center of the grating is shown on the figure A.8. The cross section of intensity distribution for Talbot distance $z_{Tb} = 5.5\text{ m}$ and non-Talbot distance $z_1 = z_{Tb} + 1\text{ m}$ is shown in Figure A.9. Notably, that since 2D rectangular centered grating has different periodicity in x and y directions (namely a and c), the Talbot distances z_{Tb} differ for different spacial frequencies of the grating, therefore even at Talbot distances the intensity contrast is non-zero.

In this appendix we described basic theory required for understanding of x-ray interaction with the dielectric media and propagation on the output side. We give the background on such important for x-ray tomography phenomena as Fresnel and Fraunhofer diffraction, Talbot effect. Besides calculations of Talbot effect for an amplitude grating which is widely described in a literature, we provide calculations of Talbot effect for a different types of 2D phase gratings - sinusoidal and centered rectangular grating.

Figure A.8: The diffraction intensity at distance z from the centered rectangular phase grating. The y value is fixed to the $y = 0.01\mu\text{m}$ from the center of the grating.

Figure A.9: The cross section of diffraction intensity shown in Figure A.8 at the Talbot distance $z_{Tb} = 5.5\text{ m}$ (blue) and at non-Talbot distance $z_1 = z_{Tb} + 1\text{ m}$ (purple). Intensity is normalized to the intensity of incoming wave.

Bibliography

- [1] C. A. Larabell and M. A. L. Gros, *X-ray Tomography Generates 3-D Reconstructions of the Yeast, *Saccharomyces cerevisiae*, at 60-nm Resolution* Mol. Biol. Cell **15**, 957-962 (2003)
- [2] J.W. Goodman, *Introduction to Fourier optics* (Roberts and Company, Englewood CO, 2005) 3rd Edition. 139, 140, 141, 143
- [3] M. Born, and E. Wolf *Principles of Optics*, (Cambridge U. Press, 2001) 7th Edition. 146
- [4] S. Teng, N. Zhang, Q. Dong, and C. Cheng, *Diffraction of a one-dimensional phase grating in the deep Fresnel field* J. Opt. Soc. Am. A **24**, 3636-3643 (2007) 145, 147, 148
- [5] M. Deutsch, and M. Hart, *X-ray refractive-index measurement in silicon and lithium fluoride*, Phys. Rev. B **30**, 640-642 (1984) 148
- [6] J. M. van den Broek, L. A. Woldering, R. W. Tjerkstra, F. B. Segerink, I. D. Setija, and W. L. Vos *Inverse-woodpile photonic band gap crystals with a cubic diamond-like structure made from single-crystalline silicon* Adv. Func. Mater. **22**, 25-31 (2012) 148, 150
- [7] M. Abramowitz and I.A. Stegun *Handbook of mathematical functions* United States Department of Commerce (1964) 146

APPENDIX B

Sample list

Sample and Structure name in the text	Sample name in the lab	History
A	AD2A24082008	3D photonic crystal sample fabricated with the two-step etch mask process [1] in September 2008. The 3D structure is surrounded with a large 2D array of pores. This sample was kept in a quantum dot suspension for optical emission measurements reported in [2] subsequently rinsed, dried and re-infiltrated several times.
B	AD2A2909	3D photonic crystal sample fabricated with the two-steps etch mask process [1] in August 2008. The 3D structure is surrounded with a large 2D array of pores.
C Structure 1	PG-10062016-EBAR-CH02, Structure 10	3D photonic crystal sample fabricated with the single-step etch mask process described in the 2 in June 2016. Structure contains a line defect at the row 3. The design $R = 150$ and $a = 750$. 3D structure is surrounded by bulk silicon. Tomography is performed in June 2016, experiment HC(2520). Optical reflectivity measurements reported in chapter 6 were performed in March 2017
D Structure 1	PG-EBAR-16032017-CH4B, Structure 5	3D photonic crystal sample fabricated with the single-step etch mask process described in the 2 in March 2017. Structure is a quasi-perfect without embedded defects. The design $R = 160$ and $a = 686$. 3D structure is surrounded by bulk silicon. Tomography is performed in April 2017, experiment CH(5092). Optical reflectivity measurements reported in chapter 6 were performed in March 2017.

D Structure 2	PG-EBAR-16032017-CH4B, Structure 12	3D photonic crystal sample fabricated with the single-step etch mask process described in the 2 in March 2017. Structure is a quasi-perfect without embedded defects. The design $R = 160$ and $a = 686$. 3D structure is surrounded by bulk silicon. Tomography is performed in April 2017, experiment CH(5092). Optical reflectivity measurements reported in chapter 6 were performed in March 2017.
D Structure 3	PG-EBAR-16032017-CH4B, Structure 4	3D photonic crystal sample fabricated with the single-step etch mask process described in the 2 in March 2017. 3D photonic crystal contains array of cavities. The design $R = 160$ and $a = 686$, defect pore $R' = 80$. 3D structure is surrounded by bulk silicon. Tomography is performed in April 2017, experiment CH(5092). Optical reflectivity measurements reported in chapter 6 were performed in March 2017.
E Structure 1	3D-Si-bar, Structure 4	3D photonic crystal sample fabricated with the single-step etch mask process described in the 2 in October 2014. 3D photonic crystal contains array of cavities. The design $R = 160$ and $a = 686$, defect pore $R' = 80$. 3D structure is surrounded by bulk silicon. Optical reflectivity measurements reported in chapter 6 were performed in October 2014

Bibliography

- [1] J. M. van den Broek, L. A. Woldering, R. W. Tjerkstra, F. B. Segerink, I. D. Setija, and W. L. Vos, *Inverse-woodpile photonic band gap crystals with a cubic diamond-like structure made from single-crystalline silicon*, Adv. Func. Mater. **22**, 25-31 (2012) 155
- [2] M.D. Leistikow, A.P. Mosk, E. Yeganegi, S.R. Huisman, A. Lagendijk, and W.L. Vos, *Inhibited spontaneous emission of quantum dots observed in a 3D photonic band gap*, Phys. Rev. Lett. **107**, 193903 (2011).

APPENDIX C

Wave propagation in the birefringent media

C.1 Wave propagation in the birefringent media

Let us first consider a uniform plane wave propagating in a lossless isotropic dielectric media [1] in the direction of a wave vector $\mathbf{k}$ given by:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}e^{-j\mathbf{k}\cdot\mathbf{r}}, \mathbf{H}(\mathbf{r}) = \mathbf{H}e^{-j\mathbf{k}\cdot\mathbf{r}}, \text{ with } \hat{\mathbf{k}} \cdot \mathbf{E} = 0, \mathbf{H} = \frac{n}{\eta_0} \hat{\mathbf{k}} \times \mathbf{E} \quad (\text{C.1})$$

where n is the refractive index of the medium $n = \sqrt{\epsilon/\epsilon_0}$, $\eta_0 = 1/c_0\epsilon_0$ the free-space impedance. and $\hat{\mathbf{k}}$ the unit-vector in the direction of $\mathbf{k}$, such that

$$\mathbf{k} = k\hat{\mathbf{k}}, k = |\mathbf{k}| = \omega\sqrt{\mu_0\epsilon} = nk_0, k_0 = \frac{\omega}{c_0} = \omega\sqrt{\mu_0\epsilon_0} \quad (\text{C.2})$$

and k_0 is the free-space wavenumber. Thus, $E, H, \hat{\mathbf{k}}$ form a right-handed system. For the k lying in the xz plane at the angle θ from z -axis, $\hat{\mathbf{k}} = \hat{x} \sin \theta - \hat{z} \cos \theta$, then there are two independent polarization solutions: TM, parallel (p=polarization) and TE, perpendicular (s-polarization) with fields given by

$$\begin{aligned} \text{TM, p - polarization : } \mathbf{E} &= E_0(\hat{x} \cos \theta - \hat{z} \sin \theta), \mathbf{H} = \frac{n}{\eta_0} E_0 \hat{y} \\ \text{TE, s - polarization : } \mathbf{E} &= E_0 \hat{y}, \mathbf{H} = \frac{n}{\eta_0} E_0(-\hat{x} \cos \theta + \hat{z} \sin \theta) \end{aligned} \quad (\text{C.3})$$

In both cases for TE and TM polarizations the propagation phase factor is

$$e^{-j\mathbf{k}\cdot\mathbf{r}} = e^{-j(k_z z + k_x x)} = e^{-jk_0 n(z \cos \theta + x \sin \theta)} \quad (\text{C.4})$$

From now on the dielectric interface is taken to be xy plane and the xz plane is a plane of incidence.

Let us now consider a birefringent medium. We choose xyz coordinate axes to coincide with the principal dielectric axes (so that permittivity tensor is diagonal). The wave vector $\mathbf{k}$ lies in the xz plane and the angle θ from the z -axis as shown in Figure C.1. The relation between $\mathbf{B}$ and $\mathbf{H}$ is assumed to be $\mathbf{B} = \mu_0 \mathbf{H}$. Let $\epsilon_1, \epsilon_2, \epsilon_3$ be the permittivity values along the principal axes with corresponding refractive indexes $n_i = \sqrt{\epsilon_i/\epsilon_0}$, where $i=1,2,3$. Then the relationship between D and E is:

Figure C.1: The geometry of the TE and TM wave. The coordinate system xyz is aligned with principal axis of the dielectric media and the coordinate system $x'y'z'$ is aligned with the wave vector $\mathbf{k}$. The dielectric interface is taken to be xy plane. values along the principal axes with corresponding refractive indices

$$\begin{bmatrix} D_x \\ D_y \\ D_z \end{bmatrix} = \begin{bmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_2 & 0 \\ 0 & 0 & \epsilon_3 \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \epsilon_0 \begin{bmatrix} n_1^2 & 0 & 0 \\ 0 & n_2^2 & 0 \\ 0 & 0 & n_3^2 \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

The wave vector $\mathbf{k}$ can be written as follows:

$$\mathbf{k} = k\hat{\mathbf{k}} = k(\hat{\mathbf{x}} \sin \theta + \hat{\mathbf{z}} \cos \theta) = \hat{\mathbf{x}}k_x + \hat{\mathbf{z}}k_z \quad (\text{C.5})$$

We now may define the effective refractive index N such that:

$$k = Nk_0 = N \frac{\omega}{c_0} \quad (\text{C.6})$$

In order to derive N let us find propagating solutions for Maxwell equations. Taking into account that gradient of the fields is equal to $-j\mathbf{k}$, Maxwell equations can be written as

$$\begin{aligned} \nabla \times \mathbf{E} &= -j\omega\mu_0\mathbf{H} & \mathbf{k} \times \mathbf{E} &= \omega\mu_0\mathbf{H} \\ \nabla \times \mathbf{H} &= -j\omega\mathbf{D} & \mathbf{k} \times \mathbf{H} &= -\omega\mathbf{D} \\ \nabla \cdot \mathbf{D} &= 0 & \mathbf{k} \cdot \mathbf{D} &= 0 \\ \nabla \cdot \mathbf{H} &= 0 & \mathbf{k} \cdot \mathbf{H} &= 0 \end{aligned} \quad (\text{C.7})$$

Replacing $\mathbf{k} = k\hat{\mathbf{k}} = Nk_0\hat{\mathbf{k}}$, where N is the effective refractive index to be determined.

$$\begin{aligned} N \frac{\omega}{c_0} \hat{\mathbf{k}} \times \mathbf{E} &= \omega\mu_0\mathbf{H}, \\ \mathbf{H} &= \frac{N}{\eta_0} \hat{\mathbf{k}} \times \mathbf{E} \end{aligned} \quad (\text{C.8})$$

Where $\eta_0 = c_0\mu_0$. Then we write from equations C.7:

$$\begin{aligned}\mathbf{D} &= -\frac{1}{\omega}\mathbf{k} \times \mathbf{H} = -\frac{1}{\omega}N\frac{\omega}{c_0}\hat{k} \times \mathbf{H} = \frac{N^2}{\eta_0 c_0}\hat{k} \times (\mathbf{E} \times \hat{k}) \\ \hat{k} \times (\mathbf{E} \times \hat{k}) &= \frac{1}{\epsilon_0 N^2}\mathbf{D}\end{aligned}\quad (\text{C.9})$$

Using the vectorial multiplication rules we can transform $\hat{k} \times (\mathbf{E} \times \hat{k}) = \mathbf{E} - \hat{k}(\hat{k} \cdot \mathbf{E})$. Thus we obtain

$$\mathbf{E} = \frac{1}{\epsilon_0 N^2}\mathbf{D} = \hat{k}(\hat{k} \cdot \mathbf{E}) \quad (\text{C.10})$$

This is a linear equation thus in order to have a non trivial solution its determinant must be zero. This provides a condition to find N . Let us write the equation C.10 separately for each component of $\mathbf{E}$. Here we use the expression for $\mathbf{D}$ and that $\hat{k} \cdot \mathbf{E} = E_x \sin \theta + E_z \cos \theta$:

$$\begin{aligned}\left(1 - \frac{n_1^2}{N^2}\right)E_x &= (E_x \sin \theta + E_z \cos \theta) \sin \theta \\ \left(1 - \frac{n_2^2}{N^2}\right)E_y &= 0 \\ \left(1 - \frac{n_3^2}{N^2}\right)E_z &= (E_x \sin \theta + E_z \cos \theta) \cos \theta\end{aligned}\quad (\text{C.11})$$

Here we consider two cases separately: TE and TM polarizations.

C.1.1 TE polarization

In case of TE polarization $E_y \neq 0$ and $E_x = E_z = 0$. Thus second from the set of equations C.11 immediately implies that $N = n_2$. Then we obtain solution for TE case:

$$\begin{aligned}\mathbf{E}(\mathbf{r}) &= E_0 \hat{y} e^{(-j\mathbf{k} \cdot \mathbf{r})} \\ \mathbf{H}(\mathbf{r}) &= \frac{n_2}{\eta_0} E_0 (-\hat{x} \cos \theta + \hat{z} \sin \theta) e^{(-j\mathbf{k} \cdot \mathbf{r})}\end{aligned}\quad (\text{C.12})$$

and the TE propagation factor is

$$e^{(-j\mathbf{k} \cdot \mathbf{r})} = e^{(-jk_0 n_2 (z \cos \theta + x \sin \theta))} \quad (\text{C.13})$$

C.1.2 TM polarization

For TM polarization $E_x \neq 0, E_z \neq 0$ and $E_y = 0$. Then linear system C.11 becomes

$$\begin{aligned}\left(1 - \frac{n_1^2}{N^2}\right)E_x &= (E_x \sin \theta + E_z \cos \theta) \sin \theta \\ \left(1 - \frac{n_3^2}{N^2}\right)E_z &= (E_x \sin \theta + E_z \cos \theta) \cos \theta\end{aligned}\quad (\text{C.14})$$

Using $\sin^2 \theta + \cos^2 \theta = 1$ we can rewrite above equations in a matrix form:

$$\begin{bmatrix} \cos^2 \theta - \frac{n_1^2}{N^2} & -\sin \theta \cos \theta \\ -\sin \theta \cos \theta & \sin^2 \theta - \frac{n_3^2}{N^2} \end{bmatrix} \begin{bmatrix} E_x \\ E_z \end{bmatrix} = 0$$

To have non trivial solutions the matrix has to have zero determinant, thus

$$(\cos^2 \theta - \frac{n_1^2}{N^2})(\sin^2 \theta - \frac{n_3^2}{N^2}) - \sin^2 \theta \cos^2 \theta = 0 \quad (\text{C.15})$$

Solving the above equation we get

$$\begin{aligned} \frac{1}{N^2} &= \frac{\cos^2 \theta}{n_1^2} + \frac{\sin^2 \theta}{n_3^2} \\ N &= \frac{n_1 n_3}{\sqrt{n_1^2 \sin^2 \theta + n_3^2 \cos^2 \theta}} \end{aligned} \quad (\text{C.16})$$

Solving the linear system we find for TM polarization

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= E_0 \frac{N}{\sqrt{n_1^2 + n_3^2 - N^2}} (\hat{x} \frac{n_3}{n_1} \cos \theta - \hat{z} \frac{n_1}{n_3} \sin \theta e^{-j\mathbf{k}\cdot\mathbf{r}}) \\ \mathbf{H}(\mathbf{r}) &= \frac{E_0}{\eta_0} \frac{n_1 n_3}{\sqrt{n_1^2 + n_3^2 - N^2}} \hat{y} e^{-j\mathbf{k}\cdot\mathbf{r}} \end{aligned} \quad (\text{C.17})$$

with TM propagation factor

$$e^{-j\mathbf{k}\cdot\mathbf{r}} = e^{-jk_0 N(z \cos \theta + x \sin \theta)} \quad (\text{C.18})$$

C.1.3 Reflection and refraction from birefringent medium

Here we now consider reflection and refraction of waves from the birefringent media. Figure C.2 shows the geometry of TE and TM cases.

The plane wave is incident from both sides on a planar interface separating two media ϵ and ϵ' . In case of TM polarization the electric fields lie on the plane of incidence and magnetic fields are perpendicular to that plane when in TE case it is other way around - electric fields are perpendicular to the plane of incidence and magnetic fields lie in that plane. In case of birefringent media left and right media are described with triplets of principal indices $\mathbf{n} = [n_1, n_2, n_3]$ and $\mathbf{n}' = [n'_1, n'_2, n'_3]$. The principal indices are aligned along xyz axes, the xy -plane is the interface plane, and the xz -plane is the plane of incidence. The boundary conditions require that tangential components of electric field are matched, which means E_x components in the TM case and E_y in the TE case. Thus we can express equations C.12 in terms of E_y and equation C.17 in terms of E_x . Taking into account that for the TM case $\mathbf{E} = \hat{x}E_x + \hat{z}E_z = E_x(\hat{x} - \hat{z} \tan \hat{\theta})$ we obtain

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= E_x (\hat{x} - \hat{z} \frac{n_1^2}{n_3^2} \tan \hat{\theta}) e^{-j\mathbf{k}\cdot\mathbf{r}} \\ \mathbf{H}(\mathbf{r}) &= \frac{E_x n_1^2}{\eta_0 N \cos \theta} \hat{y} e^{-j\mathbf{k}\cdot\mathbf{r}} \end{aligned} \quad (\text{C.19})$$

Figure C.2: The geometry of the reflection and refraction for TE and TM wave. The coordinate system xyz is aligned with principal axis of the dielectric media and the coordinate system $x'y'z'$ is aligned with the wave vector $\mathbf{k}$. values along the principal axes with corresponding refractive indices

Similarly we write for the TE case:

$$\begin{aligned}\mathbf{E}(\mathbf{r}) &= E_y \hat{y} e^{-j\mathbf{k} \cdot \mathbf{r}} \\ \mathbf{H}(\mathbf{r}) &= \frac{E_y n_2 \cos \theta}{\theta_0} (-\hat{x} + \hat{z} \tan \theta) e^{-j\mathbf{k} \cdot \mathbf{r}}\end{aligned}\quad (\text{C.20})$$

Where the propagation factors are:

$$e^{-j\mathbf{k} \cdot \mathbf{r}} = e^{-jk_0 x N \sin \theta - jk_0 z N \cos \theta} \quad (\text{C.21})$$

with the corresponding effective refractive indices N . Assuming the interface is at $z = 0$, the equality of the total tangential electric fields implies the propagation phase factors to match at all values of x :

$$e^{-jk_{x+}x} = e^{-jk_{x-}x} = e^{-jk'_{x+}x} = e^{-jk'_{x-}x} \quad (\text{C.22})$$

which means that $k_{x+} = k_{x-} = k'_{x+} = k'_{x-}$ and since $k_x = k \sin \theta = N k_0 \sin \theta$:

$$N \sin \theta_+ = N \sin \theta_- = N' \sin \theta'_+ = N' \sin \theta'_- \quad (\text{C.23})$$

This equation provides us Snel's law for the birefringent media:

$$N \sin \theta = N' \sin \theta \quad (\text{C.24})$$

Due to the dependence of N on polarization, there will be two different refraction angles for the same angle of incidence. The Snel's law can be thus written

separately for two polarizations:

$$\text{TM, p - polarization : } \frac{n_1 n_3 \sin \theta}{\sqrt{n_1^2 \sin^2 \theta + n_3^2 \cos^2 \theta}} = \frac{n_1 n_3 \sin \theta}{\sqrt{n_1^2 \sin^2 \theta + n_3^2 \cos^2 \theta}} \quad (\text{C.25})$$

$$\text{TE, s - polarization : } n_2 \sin \theta = n'_2 \sin \theta$$

The Fresnel coefficients for the TE and TM case are the following:

$$\begin{aligned} \rho_{TM} &= \frac{n_{TM} - n'_{TM}}{n_{TM} + n'_{TM}} = \frac{\frac{n_1^2}{N \cos \theta} - \frac{n_1^2}{N' \cos' \theta}}{\frac{n_1^2}{N \cos \theta} + \frac{n_1^2}{N' \cos' \theta}} \\ \rho_{TE} &= \frac{n_{TE} - n'_{TE}}{n_{TE} + n'_{TE}} = \frac{n_2 \cos \theta - n'_2 \cos' \theta}{n_2 \cos \theta + n'_2 \cos' \theta} \end{aligned} \quad (\text{C.26})$$

Where we used transverse refractive indices

$$\begin{aligned} n_{TM} &= \frac{n_1 n_3}{\sqrt{n_3^2 - N^2 \sin^2 \theta}} \\ n_{TE} &= n_2 \cos \theta \end{aligned} \quad (\text{C.27})$$

We can also write analytical expressions for reflection coefficients in terms of the angle θ only:

$$\begin{aligned} \rho_{TM} &= \frac{n_1 n_3 \sqrt{n_3'^2 - N^2 \sin^2 \theta} - n'_1 n'_3 \sqrt{n_3^2 - N^2 \sin^2 \theta}}{n_1 n_3 \sqrt{n_3'^2 - N^2 \sin^2 \theta} + n'_1 n'_3 \sqrt{n_3^2 - N^2 \sin^2 \theta}} \\ \rho_{TE} &= \frac{n_2 \cos \theta - \sqrt{n_2'^2 - n_2^2 \sin^2 \theta}}{n_2 \cos \theta + \sqrt{n_2'^2 - n_2^2 \sin^2 \theta}} \end{aligned} \quad (\text{C.28})$$

In Chapter 5 we use the absolute square of the equations C.28 to determine the intensities of TE and TM reflected light.

Bibliography

- [1] S.J. Orfanidis *Electromagnetic Waves and Antennas* Available online
<http://eceweb1.rutgers.edu/orfanidi/ewa/> (on 170511) 159

Nederlandse samenvatting

In deze dissertatie bestuderen en ontwikkelen wij een platform voor het realiseren van driedimensionale (3D) silicium nanofotonica. Het veld van de silicium fotonica heeft zich in al afgelopen 20 jaar gestaag ontwikkeld. Alle benodigde structuren worden tot nu toe gemaakt op planaire wijze in een tweedimensionale vlak. Er wordt moeite gedaan om zulke 2D structuren te stapelen om zo 3D structuren te vormen waarbij het een grote uitdaging is om 3D structuren monolithisch te maken. In hoofdstuk 2 van deze dissertatie doen we een voorstel voor en demonstreren een enkelstaps etsmasker om 3D nanostructuren te fabriceren door op twee loodrecht op elkaar staande vlakken in een stap een patroon te genereren. Het gewenste patroon is op twee aanliggende vlakken geprojecteerd als een foto zodat de uitlijning van de structuren op de verschillende vlakken is vastgelegd in het ontwerp. Op deze manier ontwijken wij het probleem van uitlijning dat zo centraal is in de huidige halfgeleiderindustrie. We tonen verschillende voorbeelden van etsmaskers gemaakt met de enkelvoudige fotografische methode. De maskers die worden getoond in dit hoofdstuk zijn ontworpen om 3D fotonische kristallen te produceren. We tonen aan dat de uitlijning van openingen in verschillende vlakken binnen 3-5 nm is, wat hoofdzakelijk bepaald wordt door de nauwkeurigheid van de elektronen microscoop. In hoofdstuk 3 doen we het voorstel en tonen we aan hoe we de voorgenoemde enkelvoudige methode kunnen uitbreiden naar diep Ultraviolet (DUV) lithografie en belichten van openingen op het hellende vlak op een silicium wafel. Het hebben van masker openingen op loodrecht op elkaar staande vlakken is de sleutel tot het bereiken van 3D structuren na het etsen. We presenteren de eerste experimenten op het homogeen bedekken van de hellende vlakken met een laag fotogevoelige lak. We laten zien dat het met een enkelvoudige ultraviolet belichting mogelijk is om openingen te fabriceren op 1.18 micrometer diep op de helling. In hoofdstuk 4 bediscussiëren we het etsen van diepe poriën in silicium. We beschouwen de diep reactieve etsprocesparameters voor het etsen van poriën met extreem grote aspect verhoudingen in silicium. Het proces dat we hebben ontworpen staat ons toe om nanoporiën te etsen met een aspect verhouding van 42. Hierna beschouwen we het etsen van twee loodrechte sets van poriën in silicium voor het vormen van drie dimensionale structuur en het noodzakelijke bijstellen van de ets parameters. We stellen voor om een extra zuurstofplasma schoonmaak stap toe te voegen tussen het etsen van de twee sets poriën om de achtergebleven polymeer resten van de voorgaande stappen te verwijderen. We fabriceren en presenteren 3D fotonische bandkloof kristallen met en zonder ingebouwde defecten. In hoofdstuk 5 presenteren we de toepassing van zoom tomografie met röntgestraling als niet invasieve beeld vormende techniek

van 3D fotonische nanostructuren. We beschrijven het experimentele schema en we geven de volledige afleiding van de theoretische beschrijving van het faseherleidingalgoritme dat noodzakelijk is voor de reconstructie van de beelden. We passen zoom tomografie toe op onze 3D fotonische bandkloof kristallen en nemen 3D materiaal dichtheid verdeling in de gefabriceerde kristallen waar met een ultieme resolutie van 20 en 10 nm. Ook presenteren we een binair model dat tomografie data beschrijft en het toestaat om deze te gebruiken als invoer voor *ab initio* numerieke modellen met als doel om de optische eigenschappen vrije vorm aannames te berekenen. In hoofdstuk 6 bestuderen we de optische eigenschappen van 2D en 3D fotonische kristallen door middel van breedband microscopische reflectiviteit metingen. We onderzoeken het polarisatie gedrag van licht dat gereflecteerd wordt door 2D fotonische kristallen met verschillende configuraties van de polarisator en analysator en nemen voor het eerst een grote mate van dubbelbreking binnen de stop band waar. We interpreteren het polarisatie gedrag van het 2D kristal met een model van een half oneindige dubbelbrekende plaat met de effectieve brekingsindextensor door het model te passen op de experimentele data en daardoor verkregen de anisotropie van de effectieve brekingsindex. We bestuderen de reflectiviteit van 3D fotonische kristal structuren met en zonder ingebouwde defecten. Van de waarneming van stopbanden in reflectiviteit verkrijgen we structurele eigenschappen van fotonische kristallen welke we vergelijken met de verkregen waarden uit het tomografie experiment en vinden een overeenkomst. In de reflectiviteit spectra die genomen zijn van de 3D kristallen met ingebouwde defecten nemen we zoals verwacht een trog waar binnen de berekende bandkloof. We vinden goede overeenkomst van de trog in de reflectiviteit piek met de ruimtelijke positie van het trillholte defect in het kristal. The results presented in this thesis allow to kick off fabrication and metrology for 3D silicon nanophotonics. De resultaten welke in deze dissertatie gepresenteerd worden geven aanleiding tot de start van fabricatie en metingen van 3D nanofotonica.

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