Subproject A1.4

Three-Dimensional Photonic Crystals

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On average, this corresponds to 1.5 full-time-equivalent scientist positions funded by the CFN.

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Introduction and Summary

Broadly speaking, photonic crystals as well as photonic metamaterials can be viewed as artificial optical materials exhibiting properties that simply do not occur in any known natural material. Hence, these man-made materials allow for performing novel optical functions. Subproject A1.4 is concerned with dielectric periodic structures the lattice constant of which is comparable to the wavelength of light, i.e., it is concerned with "photonic crystals".

Regarding photonic crystals in subproject A1.4, a first prominent example for a novel optical property/function is the possibility of a complete three-dimensional photonic band gap, leading to the optical analogue of semiconductors for electrons – as independently theoretically suggested by Eli Yablonovitch and Sajeev John in 1987 [1,2]. Such structures can provide a "designer vacuum" for light. Incorporating intentional and controlled defect cavities or waveguides, spectrally located within the photonic band gap, potentially allows for high-quality nanocavities, hence for novel nanolasers. Optical chirality enabling "poor man's" optical isolators and frequency-selective polarization optics also inherently requires three-dimensional (3D) rather than planar photonic nanostructures.

Obviously, a versatile and inexpensive technique suitable for fabricating complex 3D dielectric nanostructures is required – "just" the analogue of 2D electron-beam lithography. The direct laser writing (DLW) technology developed in subproject A1.4 has reached such a level of sophistication that we started working on commercializing the instrument in collaboration with Carl Zeiss, which financed a first demonstrator. This collaboration emerged from the Carl Zeiss Research Award 2006, jointly for Kurt Busch and Martin Wegener, the two senior principal investigators of CFN project A1. As a result, the spin-off company Nanoscribe GmbH has officially been founded in December 2007. Around that time, Nanoscribe GmbH was partially financially supported by an incubation program of the Helmholtz Association. Today, Nanoscribe GmbH is selling stand-alone DLW instruments (see Fig.1), with annual sales in excess of one million Euro. The four founders of Nanoscribe GmbH (Georg von Freymann, Martin Hermatschweiler, Michael Thiel, and Martin Wegener) obtained the Otto-Haxel-Award of the "Freundeskreis des Forschungszentrums Kalsruhe" in 2008.

- In the timeframe 2006-2010, subproject A1.4 has led to 30 publications, among which are 1 article in *Nature Mater.*, 10 in *Adv. Mater.*, 5 in *Opt. Lett.*, 4 in *Opt. Express*, 3 in *Appl. Phys. Lett.*, and one 100-page review in *Phys. Rep.* [A1.4:7], coauthored by Kurt Busch and members of his group.
- Since 2006, subproject A1.4 has led to 25 invited talks at international conferences, including 2 plenary talks.
- In 2006, Martin Wegener was awarded with the Carl Zeiss Research Award (jointly with Kurt Busch) for work on photonic crystals and photonic metamaterials in CFN project A1.
- In 2008, Martin Wegener became Fellow of the Optical Society of America (OSA) for "… his seminal experimental contributions to the fields of three-dimensional photonic crystals and metamaterials and for his service for OSA" in CFN project A1.
- In 2010, Georg von Freymann accepted the offer for a professorial position at Universität Kaiserslautern.

Fig.1: The three-dimensional optical lithography system commercialized by the start-up company Nanoscribe GmbH, which emerged out of CFN subproject A1.4. Nanoscribe GmbH was officially founded in December 2007. In 2008, Carl Zeiss AG acquired nearly 40% of the shares of Nanoscribe GmbH.

1. Three-Dimensional Photonic-Band-Gap Materials

The technique of direct laser writing (DLW) is based on very tightly focused femtosecond laser pulses which expose a photoresist via two-photon absorption only in a small volume localized in all three dimensions. Scanning of the resist with respect to the focus allows for fabricating almost arbitrary 3D porous polymer/air structures. DLW, which had been introduced previously [3], has been perfected and largely automated within CFN subproject A1.4 throughout recent years. A nice overview on various structures can be found on the Nanoscribe GmbH website (www.nanoscribe.de). Today, we can routinely fabricate 3D structures with about 100-nm lateral feature sizes in several different photoresist systems.

3D-2D-3D photonic crystal heterostructures [A1.4:3] (in collaboration with Sajeev John's group, Toronto) are an example for a particularly complex polymer structure. However, to obtain complete photonic band gaps in 3D, a high refractive-index contrast is necessary. Thus, the polymer templates need to be converted into, e.g., silicon structures. To this end, we have developed in subproject A1.4 the silicon double inversion procedure [A1.4:1] (in collaboration with Geoffrey Ozin's group and Sajeev John's group, Toronto). An example of a resulting silicon structure is depicted in Fig.2.

After intense further work and detail improvements over several years, this technology has also led to complete 3D photonic band gaps at telecom frequencies [A1.4:26] in 2010. Furthermore, waveguides within such 3D band gaps (see Fig.3) have also been fabricated and characterized. The comparison with theory from Kurt Busch's group in project A1 has led to very good agreement, evidencing high sample quality [A1.4:30].

A first alternative is the silicon single-inversion procedure [A1.4:9] by means of which we have fabricated the first silicon inverse woodpile photonic crystals. The technology is illustrated in Fig.4.

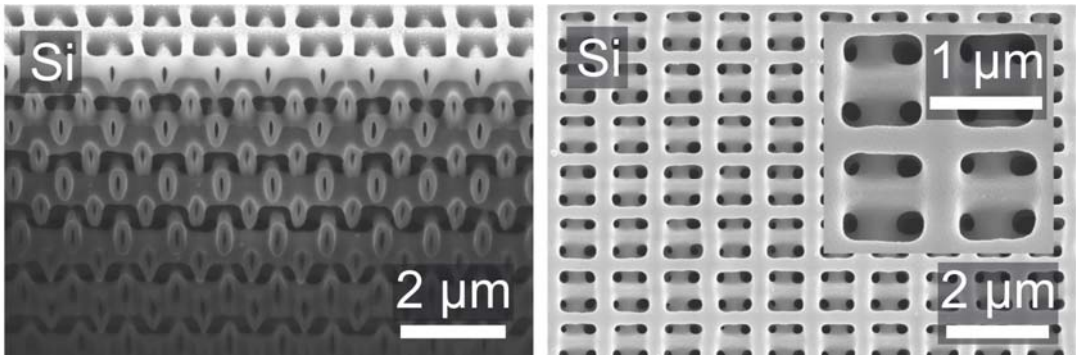

Fig.2: Electron micrographs of a 3D silicon woodpile photonic-band-gap material made via DLW and the silicon double-inversion procedure introduced within subproject A1.4. The left panel shows a focused-ion beam cut to reveal the 3D interior, the right panel a top view. Taken from Ref.[A1.4:1].

A second alternative is DLW into "photoresist" systems that lead to a sufficiently large refractive-index contrast right away. This approach has been followed in the DFG Emmy Noether group headed by Georg von Freymann within subproject A1.4. Along these lines, complete photonic band gap materials have been achieved as well [A1.4:2]. Special selective etchants have been developed [A1.4:10] and luminescent materials could be incorporated in a controlled fashion [A1.4:14]. This research has been performed and published jointly with the groups of Dieter Fenske and Manfred Kappes from CFN research area C. However, this approach will no longer be pursued because Georg von Freymann has left the CFN in 2010 to become professor of physics at Universität Kaiserslautern (see above).

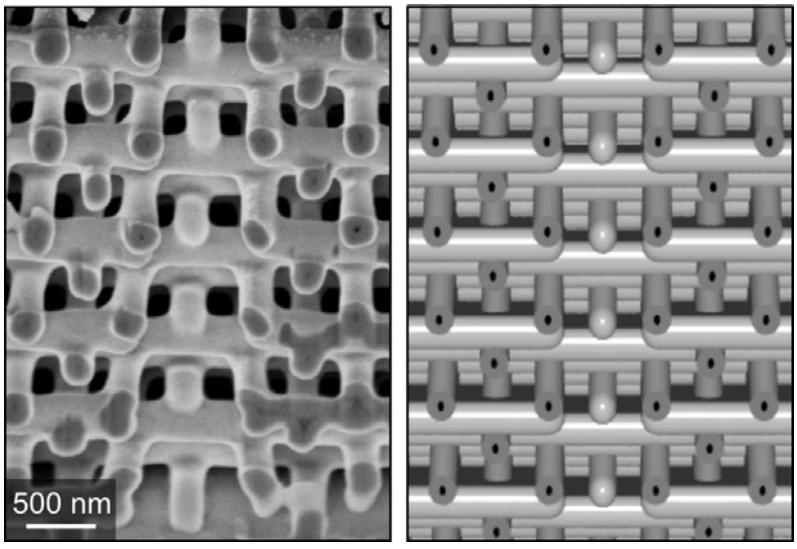

Fig.3: Electron micrograph of a vertical waveguide within a three-dimensional silicon photonic-band-gap structure after focused-ion-beam milling to reveal the interior (left) and corresponding scheme (right).

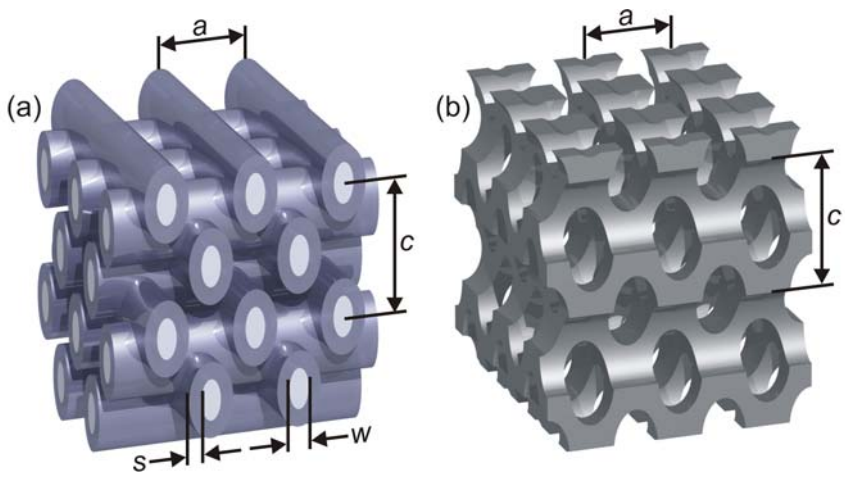

Fig.4: Illustration of the silicon single-inversion procedure introduced by subproject A1.4 (patent pending). Taken from Ref.[A1.4:9].

2. Three-Dimensional Chiral Photonic Crystals

A distinct class of 3D photonic crystals are chiral structures that can exhibit a so-called polarization stop band. This means that no photonic states exist within a certain energy and momentum range for one circular polarization of light, whereas states do exist for the other circular polarization. As a result, for a certain wavelength regime, e.g., right-circular polarized incident light is transmitted by the structure, while left-circular polarized light is not. Following and modifying a theoretical proposal [4], we have fabricated corresponding 3D spiral photonic crystals and observed such polarization stop bands for the first time [A1.4:8]. Later, we have proposed, designed, and realized a simpler structure, namely a twisted version of a 3D woodpile photonic crystal [A1.4:13] that is also amenable to alternative layer-by-layer fabrication approaches.

Such chiral photonic crystals can already serve as “poor man’s” optical isolators: Suppose that right-circular polarized light is transmitted by a left-handed spiral structure, whereas left-circular polarized light is reflected. Upon transmission through the photonic crystal and reflection by a mirror, the circular polarization of light switches from right to left. The handedness of the chiral crystal does not depend on from which side one looks at it. As left-circularly polarized light is not transmitted by the photonic crystal, it does not propagate back into the monochromatic laser source – which is the purpose of the isolator. Yet, incident circular polarization of light is required. If linear incident polarization shall be used, a 1D periodic lamella structure on top of the spiral crystal, fabricated monolithically through DLW, can serve as a quarter-wave plate (patent pending). Such 1D-3D photonic crystal heterostructures as well as corresponding 1D-3D-1D heterostructures have also successfully been demonstrated by us [A1.4:11] for the first time.

However, all of the chiral structures presented so far are uniaxial. For some applications, more isotropic chiral structures may be desirable. To this end, subproject A1.4 has invented so-called bi-chiral photonic crystals [A1.4:19] that have been inspired by “blue-phase” cholesteric liquid crystals. Here, two different types of chirality come into play: the chirality of the motif, i.e., of the helices, and the chirality of the fictitious backbone (the “corner”) onto which these helices are arranged. Thus, left/left, left/right, right/left, and right/right-handed structures exist. Interestingly, the versions left/left and right/right show the most pronounced chiral optical effects in our experiments. Both of these do *not* occur in nature. A corresponding example is illustrated in Fig.5.

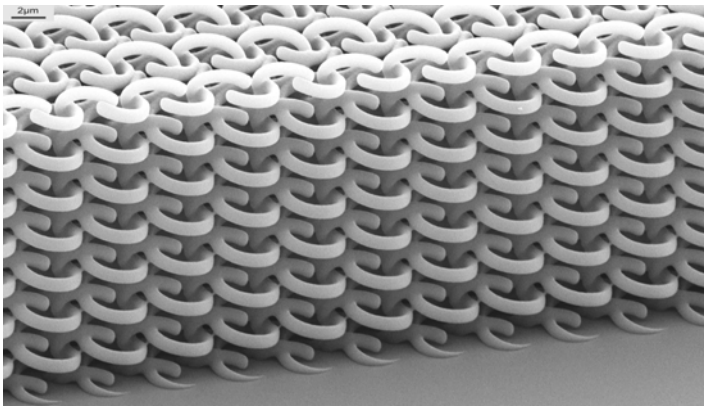

Fig.5: Electron micrograph of a fabricated bi-chiral photonic crystal. Taken from Ref.[A1.4:19].

Notably, the work on chiral photonic crystals in subproject A1.4 has stimulated the work on gold-helix metamaterials in A1.5. The metal structures there are much (!) broader in terms of operation frequency and more compact compared to the vacuum wavelength of light. Furthermore, metal structures show much (!) more pronounced chiral effects.

3. Three-Dimensional Photonic Quasicrystals

Possibly the most complex structures that we have realized so far are 3D photonic quasicrystals [A1.4:5] – again in collaboration with international partners, in this case with Geoffrey Ozins's (Toronto) and Diederik Wiersma's group (Firenze).

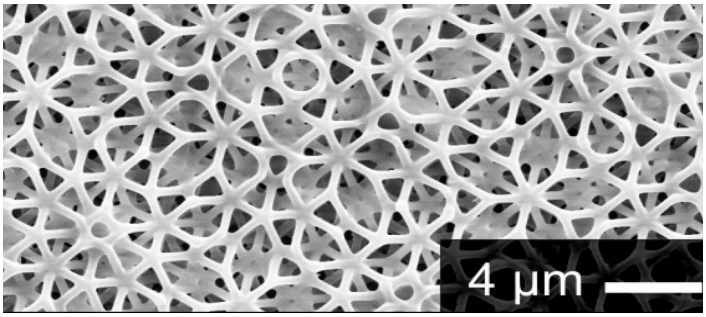

Fig.6: Top-view electron micrograph of a 3D icosahedral photonic quasicrystal. Note the local five-fold symmetry axis. Taken from Ref.[A1.4:7].

For example, the icosahedral photonic quasicrystals in Fig.6 show a ten-fold symmetry of the Laue diffraction pattern for incident green light – in close analogy to Shechtman's original discovery using X-ray diffraction [5]. Later, dielectric 3D quasicrystals have also been realized at microwave frequencies [6]. Yet, a detailed analysis of the optical spectra and data was inhibited by the fact that no corresponding quantitative theory was available. In the meantime, we have developed an approach based on periodic approximants for the 3D quasicrystals and subsequent calculation of all relevant diffracted orders using the scattering-matrix approach [A1.4:17]. The response of these 3D photonic quasicrystals turns out to be rather complex as multiple photon scattering in the quasicrystals tends to mimic multiple light scattering in disordered ("glassy") systems. For example, we find trailing exponential tails of femtosecond light pulses transmitted by the structures.

Furthermore, the sum of transmittance and reflectance is much smaller than unity even for a perfect structure. The remaining energy is channeled into numerous diffraction orders in both forward and backward direction.

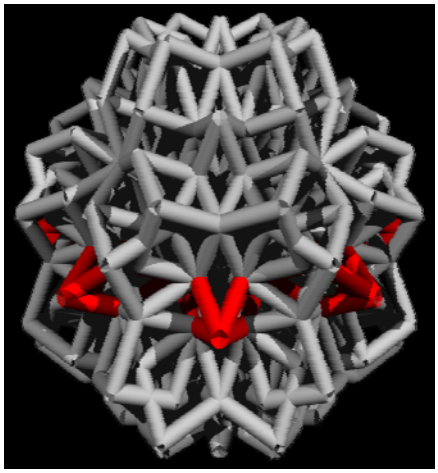

Fig.7: Scheme of part of a three-dimensional rhombicuboctahedral quasicrystal. The local eight-fold rotational symmetry is highlighted in red. Taken from Ref.[A1.4:25], where our fabricated structures have also been presented.

Notably, all three-dimensional quasicrystals known to mankind – be it "normal" quasicrystals, photonic quasicrystals, or phononic quasicrystals – have been icosahedral. This is surprising in view of the fact that numerous different types of quasicrystals are known in one and in two dimensions. Given the fact that DLW allows for fabricating essentially any structure, we have tackled the challenge to find something different from icosahedral in subproject A1.4. In a complex but rational approach, we have successfully constructed, fabricated, and characterized three-dimensional rhombicuboctahedral quasicrystals [A1.4:25].

4. Service for CFN Nano-Biology Projects

Following several meetings with biologists within the CFN aiming at identifying possible new areas of collaborative research, Martin Bastmeyer from Zoologisches Institut suggested to us fabricating tailored 3D templates (rather than 2D nanotemplates they had been working on already) for biological cell growth studies via direct laser writing. In two correspondingly initiated Diplom theses, supervised and supported by CFN A1 scientists, a very large variety of different topologies and resist materials has been explored. SU-8 structures turned out to be inadequate because of very strong auto-fluorescence in the following confocal imaging step. However, first usable structures were accomplished by thin silica coating of the SU-8 templates and subsequent removal of the SU-8 via calcination. Another successful approach is based on using PDMS as photoresist. Mechanically flexible structures, which are especially attractive for these applications, have also been realized using ORMOCER photoresists.

The corresponding scientific results will be reported under subproject E2.3, headed by CFN member Martin Bastmeyer. A first joint publication has appeared in 2010 [A1.4:22].

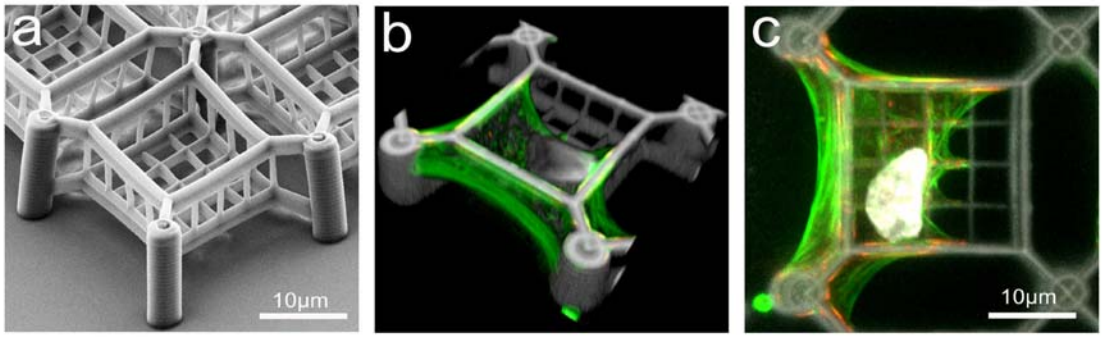

Fig.7: Example of a 3D *ORMOCER* template structure fabricated via DLW in A1.4 for biological cell growth studies in CFN subproject E2.3. Taken from Ref.[A1.4:22].

A second publication employing a two-step DLW lithography procedure to allow for spatially selective functionalization in 3D has recently been submitted.

We note that additional financial support for these service activities has neither been requested nor granted by either the CFN or any other funding source. We would like to keep it that way for the future, however, we do also emphasize that this service activity does require considerable manpower and consumables out of subproject A1.4.

5. Diffraction-Unlimited Optical Lithography in Three Dimensions

Since its beginning, the ultimate dream of the field of nanoscience has been to tailor matter in three dimensions from the nanometer to the macroscopic scale. “Normal” direct laser writing (DLW) allows for obtaining lateral feature sizes slightly below 100 nm at exposure wavelength around 800 nm. However, DLW is strictly diffraction limited. This means that DLW has been stuck at this level of resolution without the perspective to ever achieve substantially smaller feature sizes. In particular, the resolution of DLW is much worse than that of electron-beam lithography, which continues to be one of the work horses of nanotechnology. However, electron-beam lithography is planar.

Thus, it would be highly desirable to develop a lithography approach that is truly three-dimensional and that – at the same time – allows for obtaining 10-30 nm spatial resolution in all three dimensions. On this basis, subproject A1.4 started a high-risk effort on STED-DLW *lithography* inspired by a recent revolution in diffraction-unlimited far-field stimulated emission depletion (STED) optical *microscopy* [7]. Today, lateral resolutions in optical *microscopy* of 20-30 nm have almost become routine, spectacular world record values of down to just 8 nm have also been reported by Stefan W. Hell’s group.

The main challenge lies in developing suitable photoresist systems. A first step in this direction has been taken in our recent publication [A1.4:27]. The Jablonski diagram of a photoinitiator molecule is illustrated in Fig.8.

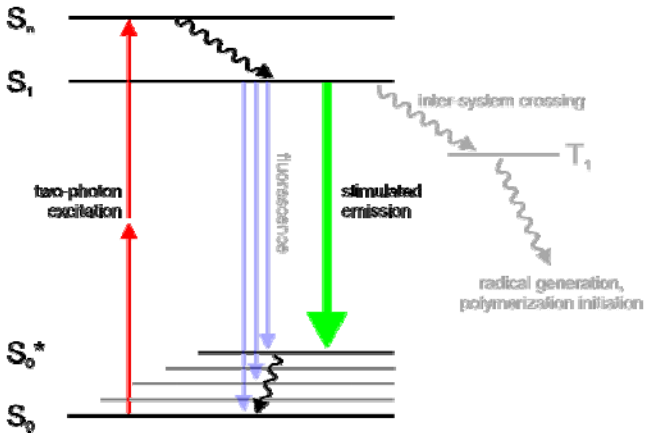

Fig.8: Jablonski diagram of a photoinitiator molecule. Taken from Ref.[A1.4:27].

Upon two-photon excitation and vibrational relaxation, the electronic excitation is supposed to exhibit intersystem crossing to, e.g., initiate polymerization. For example, this step can be inhibited by stimulated emission depletion as illustrated by the green arrow in Fig.8. Alternatively, the electron could also be excited to some higher level and eventually return to the ground state. For simplicity, we will call all of these possibilities STED – as is common in the STED microscopy community as well.

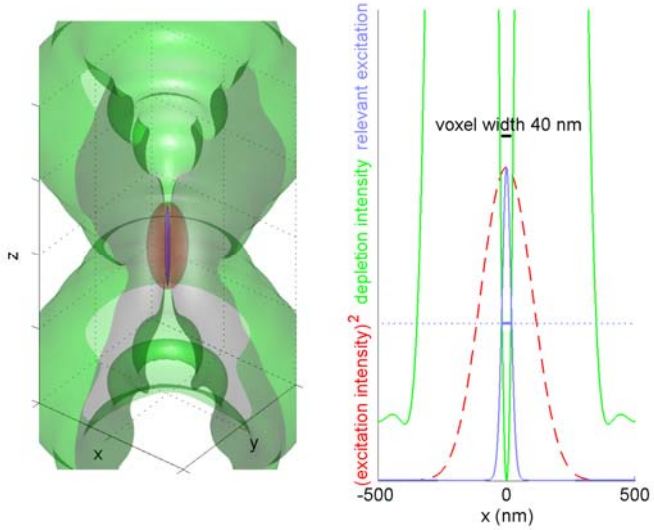

Fig.9: Illustration of the foci of light used in lateral STED-DLW in 3D (left panel). The red profile excites, the green profile depletes, leading to the effective dose profile shown in blue. The right panel shows a cut through the focal plane. Parameters are 810 nm wavelength of light (red) for the excitation, 532 nm (green) for the depletion, and a microscope lens numerical aperture of NA=1.4. Taken from Ref.[A1.4:27].

Usual photoresist are optimized for large intersystem crossing rates. Thus, spontaneous emission is weak and stimulated emission is expected to be ineffective as well. Indeed, all usual photoinitator molecules have not worked in our corresponding STED-DLW experiments. Thus, we have searched for photoinitiators with reasonably large fluorescence quantum efficiencies. This search has led to isopropylthioxanthone (ITX) and to 7-diethylamino-3-thenoylcoumarin. Both have been mixed into the monomer pentaerythritol triacrylate with the quencher monomethyl ether hydroquinone. ITX has been used in our first corresponding 2010 publication [A1.4:27]; the ketocoumarin is better as it

avoids undesired two-photon absorption of the depletion beam. It has been used in our more recent unpublished work.

The second crucial ingredient to STED-DLW is the specially shaped focus of light for the depletion beam. This aspect is illustrated in Fig.9. Along these lines, we have achieved an encouraging 55 nm lateral resolution [A1.4:27] (65 nm minus twice 5 nm for the gold sputtering) on the basis of ITX.

More importantly, STED-DLW also allows for reducing the axial resolution. As can be seen from the red profile on the left-hand side of Fig.9, the excitation profile is strongly elongated along the optical axis. Using home-made phase masks, we have accomplished foci reducing the axial resolution such that even woodpile photonic crystals with rod spacings of 300 nm have become possible. In a bcc structure, this value corresponds to a layer-to-layer separation along the axial direction of less than 100 nm. This progress opens completely new horizons. For example, three-dimensional visible photonic metamaterials via STED-DLW come into reach.

To strengthen this promising new direction in the future, subproject A1.4 will be redirected towards a focus on diffraction-unlimited optical lithography. Subproject A1.4 will continue to provide samples for subproject A1.5 as well as for the CFN nano-biology project E2.

References

- own work with complete titles -

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We also refer to the large number of references to the vast literature given in our own reviews published in 2007 in *Physics Reports* [A1.4:7] and in 2010 in *Advanced Functional Materials* [A1.4:23].