

1. Introduction

Photonic crystals (PCs) are periodic, dielectric materials. Light, propagating through a PC experiences a periodic dielectric constant $\varepsilon(\mathbf{r})$. This has the same effect as the periodically varying potential that electrons experience when propagating through a semiconductor. An optical bandstructure arises and analogously to the bandgap between the valence and the conduction band in a semiconductor there can be a photonic bandgap (PBG) within a certain frequency band. Within the PBG light can not propagate through the PC. If a PBG exists for any wave vector in the reciprocal lattice, the bandgap is called a complete, three-dimensional PBG. There is a common belief that in future PCs will perform many functions in optical data processing that semiconductor devices do with electrons today.

So far, the research field of photonic crystals is mainly driven by the theoretical description of light propagating through periodic structures and by development of more efficient numerical methods for describing photonic crystals. The experimental realization of PCs with a complete, 3D bandgap in the visible or near infrared remains a major challenge and has not been realized yet. PBG materials must have a three dimensional periodicity with a period in the range of the PBG wavelength. Furthermore, the two distinct materials that form the periodic structure (generally a solid material and air) must have a contrast in refractive index of more than two.

It has recently been demonstrated by several groups that non-linear optical lithography based on two-photon polymerization (2PP) of photosensitive resins allows the fabrication of true 3D nanostructures and therefore of 3D photonic crystals. When tightly focused into the volume of a photosensitive resin, the polymerization process can be initiated by non-linear absorption of femtosecond laser pulses within the focal volume. By moving

the laser focus three-dimensionally through the resin, any 3D structure with a resolution down to 100 nm can be fabricated.

The main topic of this thesis will be the realization of photonic crystals by means of 2PP and their optical characterization. Nevertheless, there is also a great demand on 3D microstructures in many other disciplines such as bio-technology, micro-mechanics, medicine, and micro-optics. The most common technique for the fabrication of such structures is the micro-stereolithography having a resolution limit of several micro-meters. The 2PP process can be used for the fabrication of sub-micrometer structures, but by adapting the focusing optics, bigger structures can be produced as well. The potential of 2PP to serve these applications will be demonstrated.

In order to realize complicated 3D structures with a sub-micrometer resolution having optical quality, several questions have to be answered within this thesis: How far beyond the diffraction limit can the resolution of 2PP be pushed, which physical and technical parameters limit the resolution, and how reliable is the 2PP process?

The polymeric *woodpile structures* realized within this work possess a photonic bandgap for certain directions of incidence, but for the fabrication of PCs having a complete photonic bandgap a contrast in refractive index of more than two is necessary. Therefore, the polymeric PCs have to serve as templates for highly refractive replicas. First results on the infiltration of TiO_2 into the woodpile structures with subsequent calcination of the polymer templates will be shown.

This thesis is organized as follows.

- Chapter 2 lays down the theoretical framework to describe the principal of the 2PP process as well as the optical properties of photonic crystals. The resolution limit and other significant properties of the 2PP technique will be discussed theoretically. Furthermore, this chapter will provide an overview of established fabrication methods for photonic crystals including a discussion on the advantages and disadvantages of those methods.
- Chapter 3 describes the experimental techniques and the equipment that were used within this work. The main topics will be the experimental setup used for 2PP,

a description of the applied femtosecond laser system, the properties of the used polymers, and the methods used for the analysis of the produced structures.

- In chapter 4 we present the experimental results on the fabrication of 3D microstructures by means of 2PP. These results will be discussed with respect to the theoretical predictions. Besides photonic crystals and their optical properties, arbitrary 3D structures will be presented showing the potential of the 2PP process to serve applications within a variety of disciplines.

2. Basics and Theory

2.1 Two-photon absorption

Two-photon absorption (2PA) is a radiation-matter interaction that consists in the excitation of an atom or molecule from a lower quantum state $|1\rangle$ to an excited state $|2\rangle$ of the same parity as $|1\rangle$ in a single step [PAdVR03]. In contrast to single-photon absorption, this transition thus cannot be described as a dipole transition. The theory of 2PA was first developed by Maria Göppert-Mayer in 1931 in her PhD-thesis [GM31]. As a two-photon process, 2PA is closely related to Raman scattering, where one photon is absorbed while another is simultaneously emitted. Here, the energy difference of the two photons is retained by the molecule. While spontaneous Raman scattering was first observed in 1928 [Ram28], 2PA could not be observed until 1961 [KG61], when the laser was invented. The reason for that is the fact that Raman scattering is proportional to the intensity of the incident light while 2PA is proportional to the square of the light intensity. Thus to observe 2PA, a laser is needed to provide the high intensity.

2PA is an important tool in laser spectroscopy since transitions between two states can be observed that cannot be connected by dipole transitions. One of the most common applications of 2PA is the two-photon confocal microscopy ([BH02]) where the fluorescence of a dye molecule is observed after being excited by means of 2PA. The latter application also benefits from the fact that 2PA can be initialized anywhere in the volume of a transparent medium (see Fig. 2.1) and from the high resolution that can be achieved when working with two-photon excited spots. Using standard immersion oil objective lenses with a numerical aperture of $NA = 1.4$, as done in this work, a lateral resolution of about $100nm$ and a axial resolution of about $500nm$ can be achieved [Rez02]. 2PA is the