1. Introduction

Investigations of electromagnetic surface waves already date back to the beginning of the 20th century. In 1907, Zenneck [Zen07] and in 1909, Sommerfeld [Som09] demonstrated theoretically that radio-frequency electromagnetic surface waves occur at the boundary of two media if one medium is either a 'lossy' dielectric or a metal, and the other is a loss-free dielectric medium. More than 50 years later, in 1960, Powell and Swan [PS57] found the first experimental evidence that SPPs contribute to the energy loss of fast electrons in thin-film transmission following the theoretical prediction by Ritchie [Rit57] in 1957. Ritchie investigated the impact of the film boundaries on the production of collective excitations, and found that the boundary effect causes the appearance of a new lowered loss, due to the excitation of surface collective oscillations. In 1958, Ferrell extended this work and showed theoretically the coupling of electromagnetic radiation to surface plasmon polaritons (SPPs), presenting the first published SPP dispersion relation [Fer58]. The SPP excitation by light was demonstrated by Otto [Ott68] using an attenuated-total-reflection (ATR) setup, and by Kretschmann and Raether [KR68] independently in 1968. Since this time, a significant advance in theoretical and experimental investigations of SPPs has taken place. This progress has played a key role in many research fields, such as condensed matter and surface physics, for the interpretation of many experiments, and the understanding of various fundamental properties of solids. Some examples of this are the understanding of the nature of Van der Waals forces [IW75] [ZK76] [Ser05], the classical image potential acting between a point classical charge and a metal surface [Fei71] [Rit72] [RM72] [MSL72], the energy transfer in gas-surface interactions [GM80], surface energies [SL72] [WI77] [LP77], the damping of surface vibrational modes [CS80] [PR85], the energy loss of charged particles moving outside a metal surface [EP75] [EPMJ81] and the de-excitation of adsorbed molecules [Ueb92]. SPPs are also used in many studies ranging from electrochemistry [Kno98], wetting [SHP97] and biosensing [Mal93] [Bra98] [CC03] to scanning tunnelling microscopy [RBJ91], the ejection of ions from surfaces [SC93], nanoparticle growth [RJZ01] [RJM03], surface plasmon microscopy [RK88] [GFE95] and surface plasmon resonance technology [GE80] [BLL83] [SSCI93] [Sch97] [JHG99] [RR99] [RGT00].

The interest in SPPs has been renewed by investigations of the electromagnetic properties of nanostructured materials [Pen99] [EPN03], and especially concerning the feasibility of sub-wavelength optics. An example for this is the enhanced transmission of light through a periodic array of sub-wavelength holes in metallic films [TEW98] [HLE02]. The advantage of SPPs compared to classical optics is the tight bonding of light to a metal-dielectric interface with a penetration depth of about

10 nm into the metal, and more than 100 nm into the dielectric, depending on the wavelength. SPPs concentrate light in a region that is smaller than their wavelength, opening up the possibility of using them for the fabrication of nanoscale photonic circuits at optical frequencies [Ozb06] [WBE03], and giving the possibility of merging optical and electronic circuits on the same length scale. Using this the problems related to the size mismatch between the micrometer optical circuits and the nanometer electronic chips can be overcome. SPPs, as they are investigated in this work, can provide a basis for the construction of nano-circuits able to work for optical signals and electric currents. These optoelectronic circuits could consist of various components such as couplers, waveguides, switches, and modulators.

The main topic of this thesis is the fabrication and analysis of dielectric loaded surface plasmon polariton waveguides (DLSPPWs). The investigation on these structures and their application are realized theoretically by computational simulations, and also experimentally by leakage radiation microscopy. For the fabrication of the DLSPPWs, 2-Photon-Polymerization (2PP) is applied, and the fabrication process is optimized, from which the second task for this work arises. 2PP processing is investigated, and the fabrication speed is increased drastically to bring 2PP from a purely scientific rapid prototyping tool to a reliable, high speed rapid prototyping nanotechnology. To achieve this, a novel, 3-dimensional structuring system has been set up, allowing writing speeds up to 30 mm/s, more than 100 times faster than 2PP writing speeds reported so far.

The thesis is structured as follows:

- At the beginning of chapter 2, the state-of-the-art for different nanostructuring technologies is compared and 2-Photon-Polymerization is introduced in detail. A novel system for real, 3-dimensional structuring using 2PP developed during this work is described. Different laser systems are tested and compared in respect to their applicability to 2PP, and the two-photon absorption cross sections achievable with the laser systems in commercial ORMOCER material are determined. High speed 2PP structuring is demonstrated, with writing speeds of 30 mm/s, about 100 times higher than reported before. At the end, different examples of 2PP fabricated structures are given in the fields of micro-mechanics, micro-fluidics, micro-optics, and bio-medicine.

- In chapter 3, the theoretical framework to describe surface plasmon polaritons (SPPs) is introduced, and guiding in dielectric loaded surface plasmon polariton waveguides (DLSPPWs) is investigated using numerical simulations which use the Finite-Difference-Time-Domain method (FDTD) and Finite-Element-Method (FEM). After giving a brief overview of possible materials for DLSPPWs, two programs for the simulation of SPPs and their propagation are described. First basic investigations on DLSPPWs are performed and the properties of SPPs inside these waveguides are analysed.

- In chapter 4, the simulations of DLSPPWs are continued with more complex SPP structures. An SPP Y-splitter suggested by [KZ07] is analysed in detail. For the first time, inaccuracies induced by fabrication limitations of DLSPPW structures are taken into account, and a real-Y-splitter model is simulated. From this starting point, different possibilities for an improved Y-splitter design are suggested and simulated. At the end, a novel Y-splitter design, the so called cut-splitter, is introduced. The efficiency and tolerance to the fabrication defects of the cut-splitter is compared to the Y-splitter design, and a high efficiency and better defect tolerance is demonstrated.

- In chapter 5, the experimental investigations on DLSPPWs fabricated by 2PP are presented. Starting from the modes propagating in waveguides of different size and for different wavelengths, the measured efficiency of simple SPP components such as curved waveguides, bends and splitters are compared with results obtained from simulations. Also, the efficiency of the novel cut-splitter design, suggested in this work, is compared with theoretical predictions. Furthermore, Mach-Zehnder-interferometers are fabricated, analysed and simulated as first wavelength dependent component. As an outlook, some 3-dimensional structures for SPPs are suggested, as these can only be fabricated using 2PP.

2. Two-Photon Polymerization and experimental realization

In this chapter, different techniques for micro- and nanostructuring are reviewed and compared. The state of the art for Two-Photon Polymerization (2PP) is summarized, and a brief introduction to the theory of 2PP is given. After that, the 2PP system developed and commercialized during this work is introduced. The progress in 2PP with this system is pointed out, and different laser systems are tested in respect to their usability in 2PP. The two-photon absorption cross sections (2PCSs) for different wavelengths are compared, and the writing speed for 2PP is increased by a factor of about 500 with respect to previously published results. At the end of this chapter, various application examples of 2PP fabricated structures are presented briefly.

2.1. Overview of nanostructuring techniques

Micro- and nanotechnology are fast growing fields in research and industry. Many different technologies have been developed to structure materials with micrometer and nanometer resolution. The main goal of these developments is an improvement in resolution, and at the same time an increase in the fabrication speed and reduction of the fabrication costs. Also, the trend from pure 2-dimensional structures to 2.5-dimensional and 3-dimensional structures can be observed. The techniques mainly used for the generation of micro- and nano-structures can be divided into parallel and serial processing methods. The most important techniques for micro- and nanostructuring are shortly presented in this chapter.

Optical lithography is the most commonly used technique for nanostructuring, belonging to the parallel processing technologies [Mor88] [Ell89] [LFTB83]. It is mostly used on the scale of wafer size illumination, especially for the fabrication of computer chips. Since the late 1960s, when integrated circuits had line widths of $5\,\mu m$, to 1997, when minimum line widths reached $0.35\,\mu m$ in 64Mb DRAM circuits, optical lithography has been used for manufacturing. In 2006 a resolution of $32\,nm$ has been demonstrated by using a high index lens [Han06] as the next step of enhancement. This dominance of optical lithography in production is the result of a worldwide effort to improve optical exposure tools and resists. Although lithography system costs, which are typically more than one third the costs of processing a wafer to completion, increase as minimum feature size on a semiconductor chip decreases, optical lithography remains attractive because of its high wafer throughput. The drawback of this technology is the lack of flexibility. The illumination in optical lithography takes place through a mask which must first be manufactured. These masks are commonly produced using electron-beam technology, as discussed later [TRGB93]. Optical lithography is a 2-dimensional technique which is extended to 2.5-dimensions using layer by layer fabrication techniques. This layer by layer structuring slows down the fabrication process, but the throughput remains high, due to the large areas which can be processed. Optical lithography is performed with different wavelengths, ranging from 355 nm down to 193 nm and 157 nm in the deep-UV. The feature size recently demonstrated with 193 nm illumination was less than 40 nm [MTK07] [JdKH07]. Optical lithography has the drawback of a low flexibility and 2-dimensionality. Nevertheless, it is the best technique for the fabrication of computer chips today. In research the high costs and the leak of flexibility are very important drawbacks resulting in only little use.

Another technology representing a parallel processing approach is nanoimprint lithography. For this, a master stamp is used to imprint structures into a polymer [MBK02] [Cho06]. Three different approaches are used for polymerization. The first possibility is to heat the polymer above its glass transition temperature during imprinting, making it flexible. The polymer cools down after the stamp is pressed into the polymer and solidifies, taking over the structures from the stamp. Another possibility for imprinting techniques is stamping into a liquid photosensitive polymer and illuminating it with UV-light through a transparent stamp. For these two techniques, the stamp is separated from the surface after the polymer hardened. In the next processing step the polymer is etched down to remove the residual layer resulting from the stamping process, and achieving polymer structures on a clean substrate. The third possibility for imprinting is the electro-chemical approach. For this, a stamp made from a fast ion (superionic) conductor such as silver sulfide is used. The stamp is brought into contact with a metal. In this configuration, electrochemical etching can be carried out by applying voltage, structuring the metal with the inverse pattern of the stamp.

With imprinting technologies a minimal resolution of about 20 nm is achievable and used for mass fabrication [SC96] [XL07]. The drawback is the stamp, which has to be fabricated using other nano-writing techniques, like e-beam direct writing.

The other group of technologies are the serial techniques mainly represented by electron and ion-beam, and direct UV writing. Also 2PP belongs to this group.

The primary advantage of electron beam lithography is the resolution in the nanometer regime. Beam widths can be in the order of nanometers [Man98] [HHT95] [dJK95]. This form of lithography has found wide usage in mask-making for optical and nanoimprint lithography, low-volume production of semiconductor components, and research and development. E-beam lithography is not suitable for high-volume manufacturing because of its limited throughput. It is a serial process because the beam must be scanned across the surface. This makes pattern generation very slow compared with a parallel technique like optical lithography, in which the entire surface is patterned at once. Typical writing speeds of e-beam system nowadays are in the range of $\mu m/s$, making it impossible to compete with optical lithography for mass production.

Ion-beam lithography works in the same way as E-beam lithography, but uses accelerated ions instead of electrons. It has more or less the same advantages of high resolution and flexibility, and the drawbacks of high costs and slow production

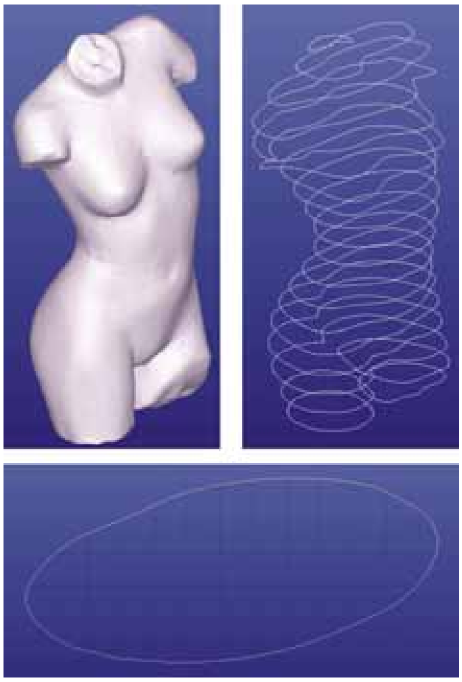

Figure 2.1.: The principle of slicing. Starting from a 3-dimensional file (left top) it is sliced into layers (right top) and each layer is filled with a hatching to give the structure more stability (bottom).

speed as E-beam lithography, but it is a much younger technique and not so wide spread.

An example of the direct write UV technique is the micro-stereolithography (MSL). Stereolithography (STL) is the best known laser based rapid prototyping (RP) technology, and was first reported in 1981, independently by [Hul84], [JAdW84], [Kod81]. It is a 2.5 dimensional production process based on polymerization of a photosensitive monomer by a laser beam scanning the surface of the photocurable resin. MSL is the extension of stereolithography to a better resolution of a few micrometers. Stereolithography starts from a 3-dimensional CAD (computer assisted design) model (a STL-file) which is sliced into a series of horizontal planes representing the 2-dimensional cross sections of the object (see figure 2.1) at different z-coordinates. The 2-dimensional models are translated into a machine control code and send to the writing system. In each slice the contour obtained from the STL-file can be filled with different styles of hatching (mostly lines). By filling the contour, the structure becomes more stable or can be provided with a sub-structure. The structure is built from a UV-curable resin in a layer-by-layer technique. The advantage of this technique is a quite fast and highly flexible production of 2.5-dimensional structures. Also, the relatively low costs compared to E-beam and ion-beam lithography are an advantage, while the drawback is the resolution of only about $5 \mu m$.

For micro-stereo-lithography, it should be mentioned that the writing speed is not the only limiting factor to production speed. Because the polymerized material is moved relative to the liquid polymer, there must be a waiting time between the structuring of two layers, reducing the effective fabrication time and leading to a very strong dependence of fabrication time on the structural design.