1. Introduction and aim of this work

Future generations of high-performance chips will contain as many as a half billion transistors on a single chip [1]. As the wiring dimensions and pitch decrease, the resistance of the metal and the capacitance of the insulator increase significantly. It results in cross-talk and capacitative coupling between the metal interconnect lines which leads to increased signal delays. To overcome these problems higher-conductivity Cu has now successfully replaced Al interconnects, but there is still a need for new dielectric insulators with very low dielectric constants, as an interlayer dielectric [2]. Potential candidates must fulfill the current integration requirements, such as thermal stability in excess of 400°C, good mechanical properties, low ion content, low water uptake, lithographic processability, low thermal film stresses, good adhesion to a variety of substrates, and low reactivity with conductor metals at elevated temperatures. The semiconductor industry is currently targeting new intermetal dielectric films with dielectric constants $k < 2.5$, and it is anticipated that, as the packing density of metal lines on the semiconductors continues to increase, interlevel dielectric films with ultra-low k ($k < 2.0$) will soon be required [3].

One important distinguishing factor for the candidates is the deposition methodology. Solution spin-on technology is a cheaper alternative to the current insulator deposition by plasma processes or the chemical vapor deposition. One candidate with $k < 2.2$, polytetrafluoroethylene (Teflon), can be spun from surfactant-stabilized aqueous microemulsions, but Teflon films are very soft with questionable thermal stability above 400°C [1].

Signal propagation and switching speeds in the electronic integrated circuits are inherently limited. Therefore, a new computing and communication revolution based on photonics has to be entered. Photonics applications are immune to electromagnetic crosstalk and interference, and are lightweight and possibly smaller in size compared to electronics. The optical integrated circuits and devices are recently getting very popular on the frontier line in research [4].

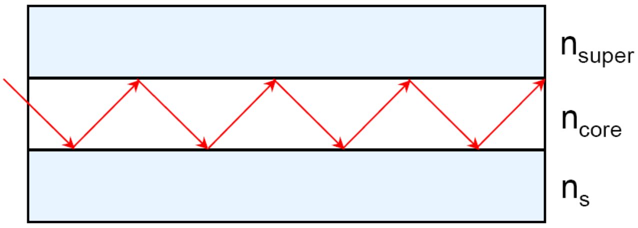

Figure 1.1: *The principle of an optical waveguide.*

Two dimensional photonic crystals (2D PhCs) are promising systems in the integrated optics, because planar slab structures can be structured using current fabrication technology [5]. In general, a waveguide consists of combination of a superstrate with refractive index n_{super}, a waveguide core with refractive index n_{core} and a substrate with refractive index n_s (Figure 1.1). Vertical confinement of light is facilitated by total internal reflection. Only a discrete and finite set of possible total reflection angles are capable of producing the constructive interference patterns which allows light to travel along the waveguide with minimum radiation loss [6]. These interference patterns are called guided modes. The light cannot be guided unless $n_{core} > n_s, n_{super}$. Since air can be considered as a superstrate with $n_{super} = 1$, a low-n substrate with a refractive index n_s close to that of air is needed to achieve the high vertical refractive index contrast Δn.

The photonic crystal waveguides consist of 2D lattice of air-holes etched through the slab. The light propagates through the slab waveguide and interacts with a 2D lattice of air-holes. Due to air inclusions, the effective refractive index n_{eff} of the PhC is lower than n_{core} of the core material. Therefore, a substrate with a very low n_s is needed to still achieve a high refractive index contrast. For stability reasons and ease of fabrication, planar photonic crystal waveguides should have solid substrates. Due to the lack of available low-n materials, air-bridge structures have been fabricated [7], which are potentially fragile.

The refractive index contrast is also a key figure of merit for dielectric multilayer structures and optical resonators. For distributed Bragg reflectors, the reflectivity, the spectral width of the high-reflectivity stop band, the optical penetration depth, and the maximum angle for high reflectivity directly depend on the refractive index contrast [8]. In optical micro-resonators, the effective cavity length, and thus the spontaneous emission enhancement also directly depends on the index contrast. Also here, a high refractive index contrast is limited by the availability of materials with a low refractive index. This creates a substantial demand [8] for a new class of optical materials that have refractive indices much lower than those of conventional materials.

One promising way of reducing both the dielectric constant k and the refractive index n is to introduce the porosity. Porosity is defined as the fraction p of the total volume of the film comprised by pores, i.e. air inclusions: $p=V_p/V$, where V_p is pore volume and V is total volume of the film [9]. Air has the lowest dielectric constant of 1, and the dielectric constant of a composite is determined by mixture rules. In the simplest approximation the mixing rule for dielectric constants, and therefore the squares of the refractive indices, is linear. To achieve highly defined porous materials, sol-gel processes [10] modified by surfactants can be applied.

The use of mesoporous materials as low-k and low-n materials has attracted a high interest [11]. Both material types can exploit the high porosity for the low material density as well as the well-defined mesoscopic structure resulting in low optical scattering or low leakage currents, respectively. They differ in the regarded frequency range leading to the decisive role of OH groups and water for the low-k materials. Both applications require perfect films of these materials.

Despite of the measured or claimed interesting dielectric properties of the mesoporous materials, real examples for applications are rare. There have been some recent studies on the application of porous xerogel [12] or mesoporous silica films [3] as low-k materials. Optically applicable xerogel films for waveguide cladding layers were prepared using an ethylene glycol co-solvent procedure and the core layer was prepared using plasma-enhanced chemical vapor-deposited silicon dioxide or a siloxane epoxy polymer. These polymer-xerogel waveguides had a maximum refractive index contrast Δn of 0.34, whereas the PECVD oxide-xerogel planar waveguides were fabricated with a maximum refractive index contrast of only

0.28, i.e. that the refractive index of the xerogel substrate was n_s = 1.17. A low dielectric constant of 1.8 to 2.5 was measured for the spin-coated mesoporous silica films [3], but no realization of the waveguides with this system has been reported so far.

The first application of mesoporous silica films in the field of photonic crystals has been recently published [13]. A mesoporous film was used for the confinement of the light in a 2D polymeric waveguide PhC. With other supports, the fields can also be guided, but the penetration depth into these substrates is decisively higher, resulting in high waveguide losses. Another advantage of the mesoporous support for the waveguides is the approximate symmetry of the guided waves resulting in a low mixing of transversal magnetic and transversal electric modes. For the fabrication of a 2D PhC sample as used in that study [13], a reliable support fabrication is needed delivering structure type, low refractive index, and high film thickness reproducibly. These requirements were achieved with the mesoporous system described in the present work.

The goals of this work are:

- to find out the existence region of optically perfect films in the compiled synthesis field,
- to determine the nanostructure and the most important properties of the films,
- to examine their applicability as a low-n support for diverse waveguides, like polymeric or ferroelectric.

First, the historical development of the porous materials will be briefly reviewed with a particular emphasis on the sol-gel theory and the mechanism of self-assembly. Furthermore, basic aspects of photonic crystals and thin films of lead zirconate titanate (PZT) will be described. The details for the fabrication of the mesoporous silica films, as well as the PMMA and PZT films will be given afterwards. The used experimental methods like white light and angle-dependent interferometry, special methods of atomic force microscopy (AFM), small angle X-ray scattering (SAXS), transmission and scanning electron microscopy (TEM, SEM), and UV-Vis diffuse reflectance spectroscopy will be described in detail.

Subsequently, the results of the characterisation of the mesoporous silica films will be presented and discussed. The MSFs will be classified according their visual appereance, and the most important processing parameters will be figured out. A theory which predicts the film thickness will be discussed on examples of the samples with a homogeneous thickness and the samples with the thickness gradient. A detailed investigation of the structure of the MSFs will be presented, and their formation mechanism will be discussed. The determination of the refractive index with an interferometric method will be presented in detail. Based on the refractive index the porosity of the films will be estimated. Further, the results of investigations of other important properties, like optical scattering, electrical and mechanical properties will be discussed. Finally, the attempts for the realization of the polymeric or inorganic waveguides with the use of the mesoporous silica films as an ultra low-*n* support will be presented. After the first own experiments with a PMMA waveguide on the MSF, the results of the waveguiding experiments realized with the collaboration partner will be presented as well. PZT films deposited onto MSFs will be characterized and, finally, first attempts for the structuring of PZT will be presented.

Additionally, it will be shown that small angle X-ray scattering by use of the general area detector diffraction system (GADDS) is a powerful technique for the structure determination of related materials. The structure of the spun-on mesoporous silica films and of the mesoporous silica particles will be discussed as an example.

Conclusions from the whole work will be drawn, and an outlook for the possibilities to answer remaining open questions will be given at the end.