Development of highly photosensitive low loss inorganic sol-gel films for direct ultraviolet-imprinting of planar waveguides

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Development of Highly Photosensitive Low Loss Inorganic Sol-Gel Films for Direct Ultraviolet- Imprinting of Planar Waveguides

Rajni

School of Electrical and Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

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To My Family

For affectionate support in all my endeavours.....

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Summary

Silica-on-silicon optical channel waveguide is a basic building block to fabricate photonic waveguide devices such as splitters, couplers and optical switches for the realization of photonic integrated circuits (PICs). Channel waveguides in the form of buried structure, rib waveguide and ridge waveguide configurations, require relatively large refractive index difference (i.e., $\sim 10^{-3}$) between core and cladding to obtain two-dimensional optical confinement. Conventional approach to fabricate channel-waveguides involves many steps like deposition, photolithography and etching processes. The fabrication of PICs, however, can be much simplified if channel waveguides can be formed by illuminating photosensitive films with ultraviolet (UV) irradiation to induce relatively large refractive index change (Δn) $\sim 10^{-3}$, termed here as a direct UV imprinting technique (DUI). Generally, the DUI technique is applied to planar slab-waveguides using polymers, organic or hybrid photosensitive materials. Nevertheless, these materials are not very stable and have poor optical performance at high operating temperature and show poor mechanical resistance. The alternative material is photosensitive inorganic SiO_2 based glasses which have low propagation loss, low cost, high reliability and good compatibility with optical fiber. Photosensitive germanium doped silica glasses (germanosilicate) have been widely used for Bragg gratings applications. However, the induced refractive index change reported is in the order of $10^{-5} \sim 10^{-4}$, which is too small

to form waveguiding channels. In this work, high quality sol-gel derived photosensitive inorganic germania (GeO_2) doped silica (SiO_2) films were developed and high values of UV induced refractive index change (Δn) $\sim 10^{-3}$ - 10^{-2} were obtained. These values of Δn are high enough to fabricate planar photonic waveguide devices by DUI technique. The simplicity of the DUI technique is shown in the fabrication of straight channel-waveguides of various widths, 1×2 Multimode-Interference (MMI) based 3 dB light splitter, and 2×2 directional coupler (DC) in one single processing step. These devices were fabricated by simply illuminating the highly photosensitive inorganic germania (GeO_2) doped silica (SiO_2) films by UV irradiations (KrF excimer laser) through pre-designed masks in contact with the films.

Sol-gel derived $x\text{GeO}_2:(1-x)\text{SiO}_2$ single layer thin films ~ 200 nm were firstly developed with different concentrations of germania, $x = 0.05, 0.1, 0.15, 0.2, 0.25$ and 0.3 . The fabrication process was developed to obtain dense, amorphous $x\text{GeO}_2:(1-x)\text{SiO}_2$ films and also highly photosensitive inorganic $x\text{GeO}_2:(1-x)\text{SiO}_2$ films with high GeO_2 concentration. This was achieved by varying the annealing temperature ($500 - 1000$ °C) and pH from 1 to 6. The films were comprehensively characterized using spectroscopic Ellipsometry, Fourier-transform infrared spectroscopy, UV-VIS spectroscopy, Atomic force microscopy, Scanning probe microscopy, X-ray diffraction and micro-Raman spectroscopy to study the optical and structural properties of samples. From the experimental data, the optimum molar composition of GeO_2 and SiO_2 was found to be 0.20 and 0.80 respectively ($0.2\text{GeO}_2:0.8\text{SiO}_2$). At this optimum composition, the films are highly photosensitive and yet there is no clustering and crystalline phase observed in the films. The clustering and crystalline phase may cause high optical propagation loss due to the scattering. High optical quality inorganic $0.2\text{GeO}_2:0.8\text{SiO}_2$ (germanosilicate) amorphous and dense thin films without the -OH content were obtained from the sol

prepared at pH~3 and the films were annealed at 900 °C and above, with fairly smooth surface and low absorption loss of about 0.42 dB/cm.

To study and develop large change of refractive index by UV irradiations, the germanosilicate films were illuminated by KrF excimer laser ($\lambda = 248$ nm) with 10 Hz repetition frequency. The UV induced refractive index change was studied by varying UV illumination time (1 minute to 20 minutes) and UV-irradiation energy (250 mJ/pulse to 450 mJ/pulse). The UV induced refractive index change (Δn) of dense germanosilicate thin film of ~ 200 nm thick was found to be 0.0094. This value of Δn is quite large as compared to the published values. The obtained value of Δn was found to be very stable and permanent. This UV induced Δn of sol-gel derived germanosilicate thin films is explained in term of the formation of GeE'/SiE' centers from the Ge²⁺ centers and to the creation of the oxygen deficiency related defects. The oxygen deficiency related defects were found to be associated with the absorption band at 620 – 740 cm⁻¹ in the FTIR spectra. Comprehensive study conducted in this work has demonstrated that the mechanism that responsible to the high value of Δn is mainly due to the creation of oxygen related defects by the UV radiation. To the author's knowledge, this has not been reported so far. The Rutherford backscattering analysis has also strongly indicated the creation of oxygen deficiency upon UV illumination. For porous germanosilicate samples, the author observed the formation of GeE'/SiE' centers from the Ge-Ge/Si-Si (neutral oxygen monovacancy; NOMV) and UV induced densification. This was not observed for the densified germanosilicate films (films annealed at 900 °C and above).

Hydrogen loading was normally used to enhance Δn . In this work, variation of Δn was also investigated for hydrogen loaded germanosilicate films annealed at various temperatures (700 °C, 800 °C and 900 °C). For the dense germanosilicate samples (the

samples annealed at 900 °C), the values of Δn of the non hydrogen-loaded and hydrogen loaded samples were found to be 0.0094 ± 0.0002 and 0.0096 ± 0.0002 , respectively. We notice that the values of Δn are quite similar. Therefore, for the sol-gel synthesized germanosilicate films the hydrogen loading is not necessary.

To obtain photonic waveguide devices, 3 μm thick layer of germanosilicate films were required to support a single mode at 1.55 μm . This was achieved by iterative deposition of dense thin films. The crack free 3 μm thick germanosilicate films were deposited on substrates of (10 μm) SiO_2/Si . The planar slab-waveguide (0.2 GeO_2 :0.8 SiO_2 /(10 μm) SiO_2/Si) was characterized using prism coupler technique and single mode propagation at 1.55 μm was obtained with the propagation loss of 0.26 dB/cm.

To study and develop large UV induced refractive index change in $\sim 3 \mu\text{m}$ thick germanosilicate films, the germanosilicate slab-waveguides were illuminated by the KrF excimer laser using 450 mJ/pulse energy and 10 Hz repetition frequency. The UV induced refractive index change (Δn) was studied by varying UV illumination time of 1 minute to 60 minutes. As expected, the value of Δn increases with the increase of the UV exposure time. The value of Δn was obtained to be ~ 0.0023 for 10 minutes of UV illumination time. The Δn value was found to almost saturate at ~ 0.005 after 30 minutes UV illumination. These values of refractive index change were found to be sufficient to form light guiding channel. Having obtained these values of Δn , the channel-waveguides were then developed by irradiating the 3 μm germanosilicate slab-waveguides with UV through a pre-designed mask in contact with the films. This technique is referred to as direct UV-imprinting (DUI). The photomask was designed for various channel widths using

OptiBPM software. Various channel-waveguides having widths of 5 - 12 μm were fabricated using different UV illumination time (10, 20 and 30 minutes). The outputs of various channel-waveguides were measured using near field optical microscopy. The experimental results of the output of the direct UV-imprinted channel-waveguides were found to be in good agreement with the theoretical (simulation) results. Some basic photonic waveguide devices such as 1×2 MMI based 3 dB light splitter and 2×2 directional coupler were also fabricated using the DUI technique. Again the experimental results were found to be in the good agreement with the theoretical (simulation) results.

Boron and germania co-doped silica is known to enhance the Δn value. Therefore, in addition to the above reported work, the author has also investigated the photosensitivity of sol-gel derived boron and germania co-doped silica films. For the boron and germania co-doped silica $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ films ($x = 0.05, 0.1$ & 0.2), it has been found that UV-induced Δn increases from 0.0089 to 0.014 corresponding to the increase of x -values from 0.05 to 0.20. However, the author has found some problems associated with the boron co-doping, as follows: (a) refractive indices of two polarizations (s - and p - polarizations) are different, and (b) the films appeared whitish after one month. Further development is required to produce better optical quality photosensitive boron and germania co-doped silica films.

In summary, the author has successfully developed highly UV photosensitive sol-gel derived inorganic germanosilicate films. Using single step direct UV-imprinting (DUI) technique, the author has also successfully fabricated inorganic germanosilicate films based photonic waveguide devices.

List of Abbreviations

1-D	one-dimensional
2-D	two-dimensional
AFM	atomic force microscope
BPM	beam propagation method
CATV	community antenna television
DC	directional coupler
DUI	direct ultraviolet -imprinting
<i>e</i> -beam	electron-beam
EIM	effective index method
EMA	effective medium approximation
FBGs	fiber Bragg gratings
FESEM	field emission scanning electron microscope
FD-BPM	finite difference beam propagation method
FHD	flame hydrolysis deposition
FTIR	fourier transform infrared spectroscopy
FWHM	full width half maximum
IOCs	integrated optical circuits
IR	infrared

LIST OF ABBREVIATIONS

LOM	Lorentz oscillator model
MFD	mode-field diameter
MMI	multimode interference
MRS	micro-Raman spectroscopy
NFOM	near field optical microscopy
NOMV	neutral oxygen mono-vacancy
PECVD	plasma enhanced chemical vapor deposition
PICs	photonic integrated circuits
RBS	Rutherford backscattering
RTP	rapid thermal processor
SE	spectroscopic ellipsometry
SEM	scanning electron microscope
TE	transverse electric
TEB	triethyl borate
TEOS	tetraethoxysilane
TIR	total internal reflection
TM	transverse magnetic
TMOS	tetramethoxysilane
TPOG	tetrapropyloxygermane
UV	ultraviolet
UVLI	UV light illumination
XRD	X-ray diffraction

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Chapter 1

Introduction

1.1 Motivation

Ever since the dawn of the computer age, the scientific world has been racing to build telecommunication components that are compact and that can transfer more information with higher speed. Development of optics and optical fiber based devices for optical communications began in the early 1960s and continues till today [1-1],[1-2]. In 1969, the concept of integrated optics was proposed by S. E. Miller to integrate the optical waveguide devices on one common substrate, known as photonic integrated circuits (PICs) [1-3]-[1-4]. The basic building block of PICs is photonic channel waveguides which can be formed by using various materials such as inorganic glasses, polymers, LiNbO_3 , and semiconductors. The silica based planar waveguide devices for PICs fabrications are extremely flexible and highly compatible with the existing optical fibers. The commercially available photonic devices are channel waveguides, array channel waveguides, optical switches, splitters/couplers, multiplexers/demultiplexers and interferometers [1-3]-[1-13]. In the development of efficient planar waveguide devices, the challenges involve bringing forward novel and easy methods of fabrications [1-6]-[1-11].

The conventional approach of fabricating waveguide based planar photonic devices involves deposition of waveguiding core and cladding materials, photolithography and etching processes [1-11]-[1-13]. This approach involves many complex processing steps. Direct ultraviolet (UV)-imprinting is an alternative way of fabricating planar optical waveguide devices. This is a relatively new technique used to form the channel waveguides by illuminating photosensitive films with UV irradiations [1-8],[1-9],[1-14]-[1-19]. The photosensitivity phenomenon refers to the permanent change in the refractive index of the material when exposed to UV irradiations. In case of direct UV-imprinting (DUI), the waveguiding core is formed by illuminating the photosensitive materials with UV irradiations to induce a refractive index change (Δn) in the materials. The use of this technique would eliminate complex processing steps such as photolithography and etching. The use of DUI would also allow much simplified creation of channel waveguides with novel shapes such as unique curves and bends in a single processing step. Furthermore, the DUI technique would form smooth interfaces in the channel-waveguides and reduce the bend losses. However, to fabricate planar photonic waveguide devices by this technique, relatively large values of UV induced refractive index change ($\Delta n \sim 10^{-3}$) is required and it obviously needs appropriate choice of photosensitive materials. Generally, the DUI technique is applied to planar slab-waveguides using polymers, organic or hybrid material compositions as the photosensitive materials [1-14]-[1-19]. Nevertheless, these materials are not very stable and have poor optical performance at high operating temperature and shows poor mechanical resistance [1-14]. The alternative material is photosensitive inorganic silica based glasses which have low propagation loss, low cost, high reliability and good compatibility with optical fiber [1-20]-[1-35]. The promising Germania (GeO_2) doped silica (SiO_2) glass material system commonly known as germanosilicate ($\text{GeO}_2\text{:SiO}_2$) exhibits photosensitivity [1-20]-[1-32] but the achievable value of Δn under

UV illumination is normally rather low i.e., 10^{-5} - 10^{-4} [1-9], [1-32]. This value of UV induced refractive index change is too small to form waveguiding core of planar photonic devices. Hence, the DUI technique is mostly used to realize Bragg gratings in inorganic waveguides [1-9],[1-26]-[1-31], which do not require large value of Δn . The low value of UV irradiation induced Δn (10^{-5} - 10^{-4}) is generally explained by photobleaching of neutral oxygen mono-vacancy (NOMV) defect center and formation of GeE' centers [1-23]-[1-25]. Details on various models of photosensitivity mechanism are covered in Chapter 2. Based on the above discussion, it is desirable to develop a technique to fabricate photosensitive germanosilicate films which can exhibit appreciably large UV induced refractive index change ($\Delta n > 10^{-3}$) with low propagation loss for the fabrication of channel-waveguide based optical devices. If this can be achieved, the fabrication of photonic waveguide devices will be done in one single processing step using a photomask to define the waveguiding cores.

The techniques such as Flame Hydrolysis Deposition (FHD), Plasma Enhanced Chemical Vapor Deposition (PECVD), Inductive Coupled Plasma Enhanced Chemical Vapor Deposition (ICP-CVD), Sputtering and Sol-Gel methods have been widely used to fabricate germanosilicate films [1-6]-[1-8], [1-11], [1-12], [1-21]-[1-25], [1-33]-[1-35]. Principles of these deposition techniques are covered in Chapter 2. Each method has its own advantages and disadvantages, but most of these techniques generally involve vacuum chambers, producing non-stoichiometric films and complex deposition conditions. Among them, sol-gel technique is found to be a promising route for the fabrication of homogenous and stoichiometric germanosilicate films. This technique also offers the flexibility to tailor the optical properties of the material by controlling the solution reaction at the molecular level [1-34]-[1-36]. Therefore in this work, the author has used the sol-gel

method combined with spin-coating technique to fabricate germanosilicate films. The details on choice of the deposition method are covered in Chapter 2.

With these considerations, the present Thesis work entitled “Development of Highly Photosensitive Low Loss Inorganic Sol-Gel Films for Direct Ultraviolet-Imprinting of Planar Waveguides”.

1.2 Objective

The objective of this work is, firstly, to develop highly photosensitive germanosilicate films using the sol-gel technique and secondly, to demonstrate photonic waveguide devices fabricated using the direct UV imprinting (DUI) technique by making use of the highly photosensitive germanosilicate films. Details are outlined below:

- i. To develop sol-gel derived inorganic photosensitive germanosilicate films having low propagation loss at the commonly used communication wavelength of 1.55 μm . This was achieved by optimizing several process parameters such as germania concentration, pH of solution and densification temperature. The details on the choice of material system and deposition method are discussed in Chapter 2 (Literature Review).
- ii. To fabricate crack free and low loss thick germanosilicate films (~ few micron thick films) to obtain single-mode (at 1.55 μm) planar slab-waveguide. This will serve as a basic platform for the development of photonic waveguide devices.
- iii. To obtain permanent, controllable and relatively large value of UV-induced refractive index change of about 10^{-3} and larger. This was achieved by optimizing

concentration of germania in silica, densification temperature of germanosilicate films, UV illumination time and power. Furthermore, the mechanism that is responsible for large values of UV-induced refractive index change ($\Delta n > 10^{-3}$) was also studied and investigated.

- iv. To demonstrate the photonic waveguide devices fabrication by using direct UV-imprinting technique.

1.3 Major contributions of the Thesis

The major contributions of this Thesis are summarized below:

- i. The author has successfully developed the fabrication of highly photosensitive dense inorganic germanosilicate (amorphous) films, using the sol-gel spin-coating technique, with optimum composition of $0.2\text{GeO}_2:0.8\text{SiO}_2$ and with low propagation loss of less than 0.5 dB/cm at 1.55 μm . In order to achieve this, several parameters such as pH level of the solution, temperature of densification and concentration of dopant germania in silica were optimized. The description will be presented in Chapter 5 [Paper-I], [Paper-II].
- ii. It was often observed by several researchers that few microns thick films fabricated by using sol-gel spin coating method had cracks problem. In this work, the author has fabricated crack free $\sim 3 \mu\text{m}$ thick germanosilicate films by iterative deposition technique for guiding layer of planar slab-waveguides. The guiding layer was found to be single-mode at 1.55 μm with low propagation loss of 0.26 ± 0.2 dB/cm and low polarization dependent loss of less than 0.005 dB/cm. The details description will be presented in Chapter 6 [Paper-I].

- iii. High value of UV-induced refractive index change of about 0.009 was achieved in germanosilicate thin films (~ 200 nm thick) when irradiated by the KrF (248 nm) excimer laser. This value of refractive index change in inorganic material was found to be quite large as compared to the published values [Paper-II].
- iv. The author has also investigated and studied the mechanism that is responsible for the high values of UV induced refractive index change (Δn) in the germanosilicate films obtained in this work. This is attributed to the creation of oxygen deficiency related defects under the UV illumination (the detail description will be presented in Chapter 5) [Paper-II]. Generally, the low values of UV induced refractive index change (about 10^{-5} - 10^{-4}) is explained in terms of conversion of NOMV to GeE' defect centers. The author has also investigated and studied the photosensitivity in hydrogen loaded germanosilicate thin films and not much difference was observed in Δn value in case of hydrogen loaded and non-hydrogen loaded germanosilicate films. The details will be presented in Chapter 5 [Paper-III].
- v. Having obtained high values of UV induced Δn (0.009) for ~ 200 nm germanosilicate films, the author further studied and developed the change of refractive index by UV irradiation in ~ 3 μm thick germanosilicate films (planar slab-waveguides). The UV induced refractive index change in germanosilicate slab-waveguides is about 0.005. The value was found to be quite appreciable to facilitate the fabrication of waveguide based optical functional devices by direct UV-imprinting technique in single processing step [Paper-IV].
- vi. Having obtained high values of UV induced refractive index change (~ 0.005) for thick films, the author developed and demonstrated photonic waveguide devices such as channel waveguides, multimode interference based 1×2 light splitter and direction coupler, fabricated by using the direct UV-imprinting technique. In order

to achieve this, the author has performed the theoretical simulation for photonic waveguide device design and for optical field propagation. The measurement results agree very well with the simulation results. The detail will be presented in Chapter 6 [Paper-IV], [Paper-V].

- vii. The author has also studied the photosensitivity of sol-gel derived boron co-doped germanosilicate films, which will be presented in Chapter 7. Based upon the obtained results, although the UV induced refractive index change (Δn) in boron co-doped germanosilicate are higher than those of germanosilicate films, the boron co-doped germanosilicate films developed so far are not desirable for the photonic device fabrication using the DUI technique due to some issues [Paper-VI].

In the broader view, the author would expect that these contributions will help photonic industry in the development of photonic integrated circuits using the direct UV-imprinting technique, which would enable us to fabricate photonic waveguide devices in a much simpler way, in a single processing step. The publications that have resulted from this work includes a patent [Patent], international journals papers [Paper-I]-[Paper-VI] and conference papers [Paper-VII]-[Paper-X] as listed below.

- [Patent] Kantisara Pita, Rajni, Tjin Swee Chuan, Kam Chan Hin, Yu Siu Fung, “Method of producing germanosilicate with a high refractive index change”, *PCT/SG2005/00414*, *International Publication Number* WO 2006/062486 (2006).

- [Paper-I] Rajni, Charles K. F. Ho, K. Pita, N. Q. Ngo, "Porosity control of 20GeO₂:80SiO₂ sol-gel derived thin films by varying the level of sol pH for low loss optical waveguide devices", *Journal of the Electrochemical Society*, 152 (2005) G456-G459.
- [Paper-II] Rajni, K. Pita, S. C. Tjin, S. F. Yu, C. H. Kam, "Enhanced photosensitivity in sol-gel derived 20GeO₂:80SiO₂ thin films", *Applied Physics-A: Materials Science & Processing*, 82 (2006) 535-541.
- [Paper-III] Rajni, K. Pita, Charles K. F. Ho, S. C. Tjin, C. H. Kam, "Photosensitivity of 20GeO₂:80SiO₂ hydrogen-loaded and non-hydrogen-loaded thin films", *Journal of Physics-D: Applied Physics*, 39 (2006) 2504-2508.
- [Paper-IV] Rajni, K. Pita, S. F. Yu, S. C. Tjin, C. H. Kam, "Fabrication of inorganic GeO₂:SiO₂ channel waveguides by ultraviolet imprinting", *Applied Physics Letters*, 89 (2006) 071105.
- [Paper-V] Charles K. F. Ho, Rajni, H. S. Djie, K. Pita, N. Q. Ngo, "Optical and physical properties of sol-gel-derived GeO₂:SiO₂ films in photonic applications", *Applied Optics* 46 (2007) 4397-4406.
- [Paper-VI] Rajni, K. Pita, "Photosensitivity of sol-gel derived inorganic xB₂O₃:20GeO₂:(80-x)SiO₂ system with various boron concentration", *Journal of Physics-D: Applied Physics*, 39 (2006) 1-5.
- [Paper-VII] Rajni, K. Pita, Charles K. F. Ho, S. C. Tjin, N. Q. Ngo, "Sol-gel derived GeO₂ doped SiO₂ films for photonics devices", *Proceedings of 2nd France-Singapore Workshop on Optoelectronics and RF Photonics Technology*, 27-28 October Singapore (2005).

- [Paper-VIII] Charles K. F. Ho, Rajni, H. S. Djie, K. Pita, N. Q. Ngo, “The application of sol-gel derived $\text{GeO}_2\text{:SiO}_2$ films in photonics”, *Proceedings of RIUPEEEC Hong Kong*, 14-15 July (2005).
- [Paper-IX] Charles K. F. Ho, D. C. L. Gwee, Rajni, K. Pita, N. Q. Ngo, C. H. Kam, “Planar optical waveguides fabricated by sol-gel derived inorganic silicate glass”, *Proceedings of 11th European Conference on Integrated Optics: Prague-Czech Republic*, 2-5 April (2003) 305-308.
- [Paper-X] Charles K. F. Ho, D. C. L. Gwee, Rajni, K. Pita, N. Q. Ngo, C. H. Kam, “Fabrication and characterization of optical waveguide material for integrated optics by the inorganic sol-gel process”, *Conference on the Optical Internet & Australian Conference on Optical Fiber Technology, Melbourne Australia*, 13-16 July (2003) 744-747.

1.4 Organization of the Thesis

The layout of the Thesis is as follows: Chapter 1 is titled as “**Introduction**” and categorized in four sections. These sections are Motivation, Objectives, Major contribution of the Thesis and the Organization of the Thesis. The rest of the Thesis is divided into eight chapters, which are outlined below:

Chapter 2 is “**Literature Review**”. In this chapter, the author will firstly give a review on the well known conventional waveguide fabrication technique, which involves photolithography followed by etching. The author then describes various waveguide fabrication techniques by direct writing such as ion-implantation, electron-beam writing, proton-beam writing, direct UV-writing and direct UV-imprinting. Suitable materials for

the direct UV-imprinting were explored and the mechanisms for photosensitivity are presented in detail. The author will also give a review on existing deposition techniques available for the fabrication of germanosilicate films which includes the description of sputtering process, chemical vapor deposition process, flame hydrolysis process and sol-gel process. Sol-gel technique is presented in detail as it is a choice of fabrication process in this work.

The theory of optical waveguides based on electromagnetic theory is introduced in Chapter 3 “**Theory of Optical Waveguides**”. In this chapter, the author will discuss the theory of guided modes in planar slab-waveguides and channel-waveguides. The fundamental equations to describe the behavior of light in these waveguides are introduced and discussed. Theoretical methods based on effective index method and beam propagation algorithm, known as beam propagation method are also given.

Chapter 4 is “**Characterization Techniques**”. In this chapter, the author will discuss thin films characterization tools such as Fourier Transform Infrared Spectra, Spectroscopic Ellipsometry and Micro-Raman Spectroscopy, Atomic Force and Scanning Electronic Microscopy, X-ray diffraction, UV-VIS absorption and Rutherford back scattering for the analysis of germanosilicate film properties. The description of experimental techniques such as prism coupler and near field optical microscopy for waveguide device characterization will also be presented.

Chapter 5 is “**Sol-gel Derived Photosensitive Germanosilicate Thin Films**”. In this chapter, the author presents the systematic study and development of the sol-gel derived high optical quality photosensitive germanosilicate thin films. The influence of UV radiation dose, time of UV-exposure and dopant (Germania) concentration on the photosensitivity of germanosilicate thin films are presented. Subsequently, the author

presents the mechanism that is responsible for UV induced refractive index change. The author will also present the systematic study on photosensitivity of hydrogen loaded germanosilicate thin films.

Fabrication of the sol-gel derived planar slab-waveguides and its photosensitivity are presented in Chapter 6 “**Development of Photonic Devices**”. In this chapter, the author firstly describes the fabrication, the characterisation and the photosensitivity of sol-gel derived planar germanosilicate slab-waveguides. It is then followed by the description of theoretical design and experimental optical field evaluation of various channel-waveguides and photonic devices such as 1×2 multimode-interference 3 dB power splitter and 2×2 directional coupler.

The study of UV photosensitivity was extended to sol-gel derived boron and germania co-doped silica films and will be discussed in Chapter 7 “**Photosensitivity of Sol-Gel Derived Boron and Germanium Co-doped Silica Films**”.

Finally in Chapter 8 “**Conclusions and Recommendations**”, the author concludes the Thesis and gives recommendations for future works, based on the findings in this work.

Chapter 2

Literature Review

2.1 Introduction

Optical fibers have been around for some time and frequently used as a light signal carrier in the telecommunication area. The optical fibers have successfully replaced the electronic wires and cables to a large extent. Similarly, planar photonic waveguide devices have been sought to replace electronics at the chip level in the form of photonic integrated circuits (PICs). This introductory chapter begins with a brief overview of PICs in Section 2.2 and followed by the description of various fabrication techniques of planar photonic waveguide devices using lithography and etching techniques, ion-implantation, direct writing techniques which includes electron-beam writing, proton-beam writing, laser self-writing, direct ultraviolet (UV)-writing and UV-imprinting in Section 2.3. Direct UV-imprinting technique is a choice of fabrication technique in this work, which is used to form the planar photonic waveguide devices by illuminating photosensitive films with UV irradiations. This simple fabrication technique has attracted considerable interest in photonics research because the complex photolithography and etching process may possible be replaced. Furthermore, the direct UV-imprinting technique would form smooth interfaces in the channel waveguides. To fabricate planar photonic waveguide devices by

this technique, the waveguiding layer of photosensitive germania doped silica (germanosilicate) is a choice of material system, so the author will review the doped silica materials in Section 2.4 and photosensitivity of germanosilicate material system in Section 2.5. Various deposition techniques for planar films such as sputtering, chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), flame hydrolysis deposition (FHD) and sol-gel will be presented in Section 2.6. The sol-gel method was found to be more suitable for this project because of its ability to produce highly stoichiometric and homogenous planar films. The details on theoretical aspects of sol-gel chemistry and sol-gel process steps will be described in Section 2.7.

2.2 Introduction to integrated photonic devices

The term “integrated photonics” refers to the integration of several photonic devices such as channel waveguides, splitters, couplers, gratings, and interferometers etc on a common planar substrate [2-1],[2-2]. These photonic devices are physical structures that guide electromagnetic waves at 1.55 μm (the wavelength that commonly used for communications) and can be used as building blocks to fabricate more complex planar photonic devices to perform a wide range of functions for applications in optical communication systems, community antenna television (CATV), instrumentation and sensors. Photonic waveguide devices are typically dielectric waveguides having high refractive index material (waveguiding core), surrounded by a material with lower refractive index (cladding). The first optical waveguide was fabricated at the end of the 1960s, on planar substrates [2-1]. In the mid-1970s, the successful operations of waveguides were demonstrated in a wide variety of materials, from glasses to crystals and semiconductors [2-2]-[2-4]. The photonic waveguide devices are based on a number of

materials platforms including dielectrics such as polymers, glasses or silica-on-silicon (SiO_2 -on-Si), and semiconductors such as indium phosphide (InP), gallium arsenide (GaAs) or even silicon (Si). The SiO_2 -on-Si is very common material system used for photonic waveguide devices. The silica has minimum attenuation loss at $1.55\ \mu\text{m}$ with respect to the other materials [2-1]-[2-4]. Typically, photonic waveguide devices have been fabricated by depositing few micron thick layers of doped amorphous SiO_2 on the SiO_2 -on-Si substrate. Various deposition techniques and waveguide fabrication technologies have been used for the fabrication of photonic waveguides and it has direct impact on waveguide device performances. The details of these topics will be dealt separately in this chapter (see Section 2.2 and Section 2.6).

Photonic waveguides devices can be classified according to their waveguide structures such as general channel, buried channel, ridge or cover ridge, rib and strip loaded and embedded strip. Some of the waveguide structures are illustrated in Figure 2.1 [2-4], where waveguiding core is represented by 'C'. Figure 2.1 also illustrates a picture of planar slab-waveguide, which usually provides a base for photonic waveguide device fabrication. In this work, the author has developed straight channel-waveguides and photonic functional devices such as light splitter and directional coupler (see Chapter 6).

Figure 2.1 Cross-section of various waveguide structures [2-4].

The optical waves propagate through photonic waveguide device by the phenomenon of total internal reflection. The basic understanding of light propagation in waveguides will be presented in Chapter 3. As the optical field propagates through a photonic waveguide, the intensity of the optical field may decrease and commonly known as propagation loss [2-3]. The propagation loss in the photonic waveguides is mainly due to the absorption and scattering, with the later being usually larger at 1.55 μm (the wavelengths of interest in optical communications). The scattering loss is mainly caused by volume scattering (due to local fluctuations in the refractive index resulting from compositional and density variations), surface scattering (due to the surface roughness), interfacial scattering and side wall scattering. The presence of crystalline phases also contributes to the scattering loss. The presence of hydroxyl groups (-OH) causes absorption losses, especially at the communication wavelengths.

2.3 Technologies for the photonic waveguide device fabrication

The conventional photolithography and etching techniques are generally used to form the channel-waveguides. Some alternative techniques such as ion-implantation technique, direct electron-beam writing, direct proton-beam writing, direct UV-writing and direct UV-imprinting can provide easy means of channel-waveguide fabrication. In this section, the author will provide the description and a comparison of different photonic channel-waveguides fabrication techniques.

2.3.1 Conventional waveguide fabrication method

The conventional waveguide device fabrication approach requires several steps [2-5]-[2-10], which is outlined in Figure 2.2. To start the fabrication, a planar SiO_2 -on-Si

substrate was used as shown in Figure 2.2 (a), and followed by the deposition of higher refractive index materials for the core layer (shown in Figure 2.2 (b)). The glass materials for the core layer are generally titania doped silica ($\text{TiO}_2\text{:SiO}_2$), germania doped silica ($\text{GeO}_2\text{:SiO}_2$) or phosphorous oxide doped silica ($\text{P}_2\text{O}_5\text{:SiO}_2$) [2-7],[2-9],[2-11]. In the photolithography process, a mask pattern of a pre-designed waveguide structure is transferred to a photoresist coated on the core layer (Figure 2.2 (c)). Next, the core layer which is not covered by the resist is etched away using the etching technique, thereby forming the waveguide structure, immediately below the photoresist mask (Figure 2.2 (d)). The remaining photoresist is then stripped away (Figure 2.2 (e)), and thereafter a cladding layer is deposited to provide the side-cladding and upper cladding (Figure 2.2 (f)). As an example, Figure 2.3 shows the micrographs of channel waveguide formed by the above described conventional method [2-7].

Figure 2.2 Deposition, lithography and etching steps for the fabrication of channel waveguide.

Figure 2.3 Scanning electron microscope photographs of typical ridge waveguides (a) before, (b) after cladding layer deposition [2-7].

It is clearly observed that the deposition of cladding is difficult because of the rough channel groove. Moreover, this technique requires expensive clean room processing at every fabrication stage, it is time consuming due to multisteps process and it is very demanding in terms of optimization of several process parameters. This method of fabrication has some serious issues such as sidewall roughness (because of etching process) that leads to the increase in waveguide propagation loss and increase in bend loss at $1.55\text{ }\mu\text{m}$ [2-7],[2-9].

The waveguiding core of channel-waveguides can be formed by changing the refractive index of the planar layer. This can be achieved by implanting ions into the materials, irradiating the materials with electron beam, proton beam or UV-irradiations. In the following sections, the author will review these techniques.

2.3.2 Waveguide development by ion-implantation

Ion-implantation is a process in which ions are implanted with sufficient high energy ($\sim$ MeV) to form the core of channel-waveguide devices [2-12],[2-13],[2-14]. Typically any element can be used for the implantation. Use of heavy ions are usually found to be more attractive than the light ions as it requires much lower dose [2-15]-[2-24]. Implantation of Si, Ge, P, Se, N, O, C, Er, He and H ions are generally used in silica based material system [2-15]-[2-24]. This technique is capable of forming waveguiding core in any type of substrates such as fused silica, thermally grown SiO_2 -on-Si, and even doped silica-on-silicon films. Several researchers have shown that the channel-waveguides can be formed in silica substrate by ion-implantation [2-15]-[2-17],[2-18].

Xue-Liu Wang et. al. reported the waveguide fabrication by the ion-implantation directly into fused silica as shown in Figure 2.4. In this technique, the thermal annealing step is always required after the implantation to form a waveguiding core (see Figure 2.4 (b)) [2-17].

(a)

(b)

Figure 2.4 The 633 nm light propagating from right to left through the fused quartz waveguide formed by 3.0 MeV O^+ ion implantation. (a) as implanted and (b) after annealing treatment at 500 °C in air, respectively [2-17].

This fabrication technique looks quite attractive but it requires sophisticated and expensive equipment for selection of particular species of ions. Moreover, this process is ballistic and causes damage to the material and results in high optical propagation loss. Substrates can be overheated if proper heat sink (thermal dissipation) is not used and adversely affect the overall material properties which lead to dimensional distortion. This technique is also limited by the low depth of ion implantation. Germanosilicate based channel-waveguides core can be formed by implanting light ions such as H^+ , but it would lead to the formation of Ge clusters and hydroxyl group [2-23]. As we know, clustering can lead to the scattering centers and hydroxyl group results in high absorption, which are undesirable for photonic waveguide devices.

2.3.3 Waveguide development by direct electron-beam writing

The electron-beam (*e*-beam) irradiation was originally suggested as a method of fabricating optical waveguides in bulk silica [2-25]. This technique is now being applied to silica based films fabricated by chemical vapor deposition, plasma enhanced chemical vapor deposition, flame hydrolysis deposition (FHD) etc. on Si substrates [2-26]-[2-30]. The waveguiding core of the channel-waveguide can be formed by changing the refractive index by *e*-beam irradiations [2-26],[2-29]. The refractive index change and the effective waveguide core depth depend upon the electron energy, and the dose. Figure 2.5 shows the optical micrograph of light transmitted through an *e*-beam written waveguide in glass deposited using the FHD technique [2-28].

Figure 2.5 Micrograph of light transmitted through an *e*-beam written waveguide in FHD glass [2-28].

As a consequence of the *e*-beam heating, the compaction of silica is usually observed in the *e*-beam exposed area [2-28]. The effect of *e*-beam has been found to be highly material dependent. The *e*-beam induced refractive index change shows poor thermal stability and it is difficult to obtain low propagation loss in waveguides [2-30].

2.3.4 Waveguide development by direct proton-beam writing

The proton-beam writing utilizes a highly focused beam of MeV protons to change the refractive index to form the waveguiding core [2-31]-[2-33]. This technique has already shown the unique ability to fabricate polymer waveguides [2-31],[2-34]-[2-40].

A glass based channel-waveguide device formed by proton-beam writing in Futuran glass is shown in Figure 2.6 (a) [2-41]. Figure 2.6 (b) illustrates the output image of mode profiles of the waveguides [2-41].

Figure 2.6 (a) Optical differential interference contrast image of the Foturan™ sample edge showing a waveguide and the end of range region, (b) optical images of the waveguide mode profiles for seven different proton-beam fluences (1.12×10^{14} , 2.06×10^{14} , 5.29×10^{14} , 1.07×10^{15} , 2.17×10^{15} , 5.12×10^{15} , 1.06×10^{16}). The laser used for these measurements was a 17 mW, 632.8 nm helium–neon laser [2-41].

It can be seen from Figure 2.6 (b) that a increase in proton-beam fluence results in better confinement of waveguide mode but simultaneously increases the loss of optical power in vertical direction i.e along the proton-beam writing path (see Figure 2.6 (a)). The loss of optical power along the proton-beam path was due to the change in refractive index along the path of the proton-beam writing. The average propagation loss reported for proton-beam written glass based waveguides is $\sim 8 - 12.9$ dB/cm which is very high [2-41]. Another drawback of proton-beam writing is the difficulties encountered in focusing MeV ions [2-36]. Heavy ions follow a large radius trajectory, and it is relatively difficult to focus MeV ions to few microns.

2.3.5 Waveguide development by direct laser writing

Irradiations from UV to red laser sources are known to change the refractive index of silica permanently [2-42],[2-43]. The change of refractive index of material under the light irradiations is known as photosensitivity. The waveguiding core of channel-waveguides can be formed by changing the refractive index of photosensitive films under the laser light irradiations. This process of UV induced waveguiding core formation can be

performed by several ways that include techniques such as self-writing waveguides, direct UV-writing and UV-imprinting technique.

2.3.5.1 Self-writing waveguide fabrication technique

The waveguide fabrication by a laser beam propagating in a photosensitive glass is known as self-writing [2-43],[2-44]. Self-writing is based upon a phenomenon of changing the refractive index along the propagation path of laser beam and simultaneously provides the optical field confinement [2-45]. Such effect has been observed in Kerr-type nonlinear materials [2-46],[2-47], as well as in photorefractive media [2-44],[2-48]-[2-51]. The first observation of self-writing in photosensitive glass at 488 nm was reported by Tanya M. Monro et. al in 1998 [2-43] using the experimental setup shown in Figure 2.7 (a). From the reported results (illustrated in Figure 2.7 (b) and Figure 2.8), it is clear that the beam width at the output decreases over time with the increase in peak intensity which indicates the confinement of optical power. This type of self-written channel-waveguides in germanosilicate material system has been demonstrated by Heike et. al. [2-52] and Robert J. Kruhlak [2-53].

Figure 2.7 (a) Setup used to observe the self-writing of a channel waveguide in a photosensitive material, (b) beam intensity profiles at the output edge at 0, 0.5, 3, and 8 hours, respectively, from the start of the exposure [2-43].

Figure 2.8 (a) FWHM of the intensity at the output as a function of time. The narrowing of the beam is an indicator that a channel is being self-written in the material. The solid line is the experimental result; the dashed line is the result of a numerical simulation, (b) the peak intensity at the output as a function of time. As time passes, the beam becomes more strongly guided down the self-written channel [2-43].

This technique is relatively new and seems to be very attractive. However, self-writing requires the material which allows the propagation of optical field and cause sufficient refractive index change for the optical confinement at the writing wavelength. Hence, the wavelengths of optical field used for self writing in germanosilicate materials are in visible and near-infrared region. Furthermore, the length of the photonic waveguides are restricted by the large attenuation of the optical guiding beam, and self-writing is a complex process where the induced refractive index distribution can only be determined indirectly by monitoring the evolution of the out-coming beam [2-43],[2-54]. It is desirable to develop a channel-waveguide device using photosensitive material which can operate at commonly used communication wavelength at 1.55 μm . This can be achieved by using direct UV-writing technique and UV-imprinting technique.

2.3.5.2 Direct UV-writing and UV-imprinting waveguide fabrication technique

The waveguide core of planar channel-waveguides can be formed by UV-irradiations in two ways, one is direct-UV writing technique and another is direct UV-imprinting technique. In case of direct UV-writing technique, a laser beam is focused on a photosensitive layer of planar slab-waveguide as shown in Figure 2.9 (a). A desired pattern can be written by moving either the UV-beam itself or the respective sample and requires precision control of micro-movements. The direct UV-writing technique can be much simplified by a direct UV-imprinting technique. In this technique, the refractive index change to form desired waveguiding core can be obtained simply by irradiating photosensitive layer with UV irradiation through a desired photomask (see Figure 2.9 (b)). The use of photomask is efficient and cost effective because one photomask can be used to reproduce similar patterns without the need of precision control of micro-movement.

Figure 2.9 Schematic view of (a) direct UV- writing by a focused beam, (b) direct UV-imprinting by UV exposure through a mask; for the fabrication of channel-waveguides.

The direct UV-imprinting technique is a comparatively simple fabrication technique with a single processing step and does not require the use of etching process and lithography. This single step waveguide fabrication technique provides an easy means of cost-effective device fabrication without the need of clean room processing. In addition, the waveguide layout is defined by a photomask that makes this technique very flexible and suited for rapid development of a simple straight channel waveguide or even complex waveguide circuits in a single step.

If we compare the direct UV-imprinting technique with other direct writing techniques such as ions-implantation, e -beam or proton-beam, we find that the UV-irradiations penetrations are more uniform. Figure 2.10 demonstrate various irradiation penetrations into the material and it is clear that UV-irradiations penetrate deep and straight into the material [2-31]. Due to the several advantages and the simplicity of direct UV-imprinting technique, the direct UV-imprinting technique has been finally adopted for waveguide device development for this project.

Figure 2.10 Comparison of current irradiation penetration [2-31].

From the extensive literature survey, the author found that the UV illumination has been used to fabricate the photonic waveguide devices using polymers such as polymethyl-methacrylate or organic materials [2-55]-[2-58] and hybrid materials (hybrimers) [2-4],[2-59]-[2-63]. These reported works demonstrate various photonic devices such as channel waveguides [2-56],[2-58], power splitters [2-4],[2-58],[2-62],[2-63] and array waveguide gratings [2-60] at 1.55 μm fabricated by direct UV illumination. The refractive index change in polymer based materials is reported as high as ~ 0.25 at 1.55 μm [2-58]. The mechanism of achieving change in the refractive index under the UV illumination is through the sensitization of monomers that leads to the polymerization (cross-linking). However, these materials are not very stable, showing low performance due to poor mechanical resistance, and need low temperature environment [2-4].

The alternative is photosensitive inorganic doped silica glasses, which have high reliability and good compatibility with optical fiber, and have low loss at communication wavelength [2-64], [2-65]. However, the UV induced refractive index change reported is in the order of $10^{-5} \sim 10^{-4}$ [2-115],[2-117], which is too small to be able to form waveguiding channels in planar slab-waveguides. To facilitate high value of UV induced refractive index change $\sim 10^{-3} \sim 10^{-2}$ in inorganic material system for photonic device development, several enhancement techniques [2-66]-[2-68] are developed and the author will elaborate these in Section 2.5.4. With the aid of enhancement techniques in inorganic materials, various photonic devices have been fabricated using UV illumination such as channel waveguides [2-66], directional couplers [2-67],[2-68] and power splitters [2-68] at 1.55 μm . Some recent publications have shown the photonic devices using inorganic materials without the aid of enhancement techniques but their performances are shown at UV to visible propagation wavelength [2-43],[2-69].

It can be concluded from the above review that the direct UV-imprinting technique in inorganic doped silica based material system is desirable to fabricate photonic waveguide devices at 1.55 μm provided that highly UV-photosensitive inorganic material is synthesized. In order to present the suitable choice of photosensitive inorganic material for this project, the author will present a review on inorganic materials.

2.4 Inorganic materials for photonic waveguide devices

As we know, silica having refractive index of 1.46 (n at 632.8 nm) is well established for the cladding material [2-70]-[2-80] and the silica doped with the species of higher refractive index materials such as germania (GeO_2) of refractive index 1.61 (n at 632.8 nm) [2-79] or titania (TiO_2) of refractive index 2.2 (n at 632.8 nm) [2-80] is used to develop waveguiding layer. In this section, the author will present the understanding of silica, and present a review on various doped silica systems for waveguiding materials. Further, photosensitive germania doped silica material system will be described in details.

2.4.1 Silicate material

In silicate glasses, the basic unit is SiO_4 tetrahedron in which a Si atom is bonded to four oxygen atoms at the corners. Each tetrahedron is randomly connected to another tetrahedron at the apex oxygen, thus producing the 3-dimensional (3-D) framework of strong Si-O-Si glassy structure (see Figure 2.11) [2-77].

Figure 2.11 Silica glass structural unit and structural arrangement of silica [2-77].

Alternatively, if each tetrahedron is connected to another tetrahedron in a regular and orderly fashion, it forms a 3-D network that leads to crystalline form (quartz). When the composition of a silica glass deviates from the standard Si-O-Si formula, the resulted silica is said to be non-stoichiometric having commonly known defect as Si-Si wrong bond which is intrinsic to the glass [2-78].

2.4.2 Doped silicate materials

The silica can be doped with the species of higher refractive index materials to form waveguiding layer on SiO₂-on-Si substrate to form photonic waveguide devices. Some examples of doped silica systems for waveguiding layer are GeO₂:SiO₂ [2-65],[2-81],[2-82], B₂O₃:GeO₂:SiO₂ [2-83],[2-84], TiO₂:SiO₂ [2-6],[2-80],[2-85]-[2-87], GeO₂:P₂O₅:SiO₂ [2-88],[2-89], Al₂O₃:GeO₂:SiO₂ [2-89], B₂O₃:P₂O₅:SiO₂ [2-90],[2-91], PbO:SiO₂ [2-92],[2-93], and Er/Yb:GeO₂:SiO₂ [2-89],[2-94] and Er/Yb:TiO₂:SiO₂ [2-95]. The properties of doped silica materials depend upon the concentration of dopant. For example, Figure 2.12 illustrates the refractive index variation of GeO₂ doped SiO₂ (germanosilicate) as a function of GeO₂ concentration, reported by J. W. Fleming [2-81]. It can be observed that the refractive index increases linearly with the increase in GeO₂ concentration in SiO₂.

Figure 2.12 Refractive index (at $\lambda = 589.3$ nm) vs composition for $\text{GeO}_2\text{:SiO}_2$ glasses prepared and measured by various researchers. The line represents the computed values using the mixed sellmeier model [2-81].

The aforementioned doped silica system can form the waveguiding layer but only some of them are UV-photosensitive. For example, TiO_2 and P_2O_5 doped silica material systems are not photosensitive [2-11],[2-96]. The purpose of co-doping of rare earth materials like Er/Yb is generally carried out to achieve optical amplification. Lead (Pb) doping in silica are known to form very high photosensitive materials [2-92],[2-93], however no photonic device has been reported because this material system is generally crystalline and therefore give high optical propagation loss. The crystallization must be avoided since the crystallization would lead to scattering when light propagates in waveguides. The promising candidates are $\text{GeO}_2\text{:SiO}_2$ (germanosilicate) and $\text{B}_2\text{O}_3\text{:GeO}_2\text{:SiO}_2$ (boron and germania co-doped silica) material systems which are known

for their high photosensitivity and appropriate for the photonic waveguide devices. In particular, B_2O_3 doping in germanosilicate is used to enhance the photosensitivity, however boron incorporation reduces the overall refractive index [2-83] and deteriorates the thermal stability [2-83]. The details of reported work related to $B_2O_3:GeO_2:SiO_2$ photosensitive material system will be covered in Section 2.5.4.5.

The promising photosensitive germanosilicate is a widely accepted material system for waveguiding core and has been used to develop Bragg-gratings using UV-irradiations [2-97]. Due to its promising photosensitivity, various research groups have reported the work using germanosilicate material system [2-97],[2-98],[1-103]-[1-137]. The inherent advantages of germanosilicate material system for the planar waveguide device fabrication is its high compatibility with already existing optical fiber and its ability to achieve better planar devices in terms of low propagation loss [2-8],[2-64],[2-65]. With these considerations, the germanosilicate material system has been chosen for this project and will be discussed further in details. However, generally, the induced refractive index change reported to be in the order of $10^{-5} \sim 10^{-4}$, which is too small to form waveguiding channels in planar slab-waveguides [2-115],[2-117]. Hence, direct UV-imprinting or UV-writing technique is used to realize Bragg grating in SiO_2 based waveguides as Bragg grating does not require large value of Δn [2-84],[2-108]. It is desirable to have high value of UV induced refractive index change $10^{-3} \sim 10^{-2}$ in germanosilicate glass to fabricate photonic waveguide devices by direct UV-imprinting technique. As mentioned in Chapter 1 (Section 1.1 and Section 1.2), the objective of this project is to develop the sol-gel derived photosensitive inorganic germanosilicate material system and to demonstrate the waveguide based devices by direct UV-imprinting technique.

2.4.3 Germanosilicate material system

The GeO_2 is a chemical analogue of SiO_2 . Furthermore, it is also to some extent a structural analogue, as the low and high-pressure short-range order (tetrahedral and octahedral) is the same [2-72]. However, a number of differences exist. For example, the bond lengths, angles and the relative size of Ge versus Si are different [2-72]. The glassy structure of $\text{GeO}_2\text{:SiO}_2$ can be viewed as continuous random network of Ge-O-Si and Si-O-Si, as illustrated in Figure 2.13. Ge, unlike Si, has two moderately stable oxidation states, +2 and +4, thus germania can be expected to form both GeO_2 and GeO in glasses. It is well known that the suboxide GeO becomes more stable than GeO_2 at higher temperature [2-72]. Germania doped silica is prone to clustering and crystallization which are related to the concentration of dopant and the densification temperature [2-79],[2-98]-[2-102]. The higher germania concentration is desirable for higher photosensitivity.

Figure 2.13 Structural arrangement of amorphous germanosilicate [2-77].

Like SiO_2 , $\text{GeO}_2\text{:SiO}_2$ material system also exhibits non-stoichiometric defects [2-64],[2-103]-[2-105]. A commonly known defect in germanosilicate material system is Ge-Si wrong bond namely neutral oxygen mono-vacancy (NOMV) having absorption at ~ 240

nm. The NOMV defect responds to the UV-irradiations and attributed to UV induced refractive index change of germanosilicate material system. The detailed study of germanosilicate photosensitivity will be described in the next section (Section 2.5).

2.5 Review of germanosilicate photosensitivity

In this section, the author presents the details of the reported work on photosensitivity of germanosilicate materials.

2.5.1 Introduction of the photosensitivity of germanosilicate materials

As stated previously, the term photosensitivity refers to the light induced refractive index change of the material. The first observation of photosensitivity in germanosilicate was reported in 1978 by Hill *et. al.* in optical fibers when exposing a germanium doped silica core optical fiber with Ar-ion laser at 488 nm and forming a fiber Bragg gratings (FBGs) [2-97]. The changes in refractive index, were in the range 10^{-6} ~ 10^{-5} [2-97]. The use of UV irradiations at 244 nm was found to be much more effective as proposed by Meltz *et al.* in 1989 [2-106]. The experiment of Meltz and co-workers was a starting point for a dynamically grown research area of FBGs, for waveguide gratings and many more applications of germanosilicate photosensitivity [2-35],[2-106],[2-107]. Thus, with the evolution of FBG technology, the interest in germanosilicate photosensitivity increases. There exist a large number of different laser sources capable of exhibiting photosensitive changes in germanosilicate material system. Some examples are excimer ArF laser irradiation at 193 nm [2-103],[2-104],[2-107]-[2-116], excimer KrF laser at 248nm [2-64],[2-107],[2-112],[2-115],[2-117]-[2-130], and deep UV F₂ laser at 157 nm [2-131]-[2-133], cw frequency doubled Ar⁺ laser generating light at 244 nm [2-52],[2-68],[2-115],[2-

134],[2-135], Xenon lamp at 254 nm [2-127]-[2-129], Hg lamp ~200nm [2-126],[2-130], Hg/Xe lamp ~220-360 [2-129], Hg/Xg lamp ~220-260 [2-57] also 488 nm [2-43],[2-52], cw Kr⁺ laser at 647 nm and 676 nm [2-42]. In this work, the author has used KrF excimer laser at 248 nm which have relatively higher energy per pulse and large spot size (24 mm × 12 mm), which is available in our research laboratory.

The interest in photosensitivity has widened into the planar waveguides area, following the advances in FBGs. In channel waveguides, UV processing of the core region can be carried out to either tune optical components [2-10] or fabricate components such as Bragg gratings [2-108]. The fabrication of planar photonics devices can also be simplified by using photosensitive glass layer, and by directly writing a channel waveguide in a photosensitive film (as stated in Section 2.3.5.2). Directly writing the waveguide cores, without the use of photolithography or etching process, give a much simpler fabrication technique. The photo-induced refractive index changes must however be in the order of $\sim 10^{-3}$ - 10^{-2} to form a waveguide core at standard communication wavelength of 1.55 μm .

Over the last decade or so, numerous groups have conducted research in different aspects of photosensitivity such as investigation of different exposure wavelengths, fluences, various dopant species and their concentrations, mechanisms of photosensitivity, and exploration of different methods for increasing the photosensitive effects. The author will review in details the aforementioned points in the following sections (Section 2.5.2, Section 2.5.3 & Section 2.5.4).

2.5.2 Mechanism of photosensitivity in germanosilicate

This section is intended to review various models which have been used to explain the mechanisms of UV induced refractive index change in germanosilicate material system. These explanations will serve as background for the further discussion of the photosensitive phenomenon of prepared germanosilicate films developed by the author (described in Chapter 5).

2.5.2.1 Model-I: Color-center model

The color-centre model predicts small change in UV induced refractive index change, $\sim 10^{-5}$ to 10^{-4} , at infrared wavelengths due to the absorption change in the UV region [2-69],[2-125],[2-129],[2-130],[2-149]-[2-150]. Hand et. al. [2-148] and Dong et. al [2-125] linked the absorption changes in the UV region to the change in refractive index using the Kramers-Kronig relation. The explanations of the absorption change in UV region are given below:

The UV absorption at ~ 240 nm in germanosilicate is always associated with presence of NOMV defects [2-138],[2-139],[2-140],[2-123],[2-130],[2-141],[2-142]. Irradiating the germanosilicate with ~ 240 nm results in the bleaching of 240 nm absorption band and a simultaneous growth of absorption band near 200 nm which is associated with the GeE' defects [2-64],[2-98],[2-118],[2-121],[2-122],[2-126],[2-128],[2-141]-[2-148]. The color center mechanism of germanosilicate photosensitivity can be described by Equation (2.1):

Figure 2.14 (a) illustrates the variation of NOMV defects absorption around 240 nm as a function of germanium concentration and Figure 2.14 (b) shows the change in absorption of NOMV defects after UV illumination ~ 200 nm [2-64]. This shows that absorption around 240 nm increases with the increase in germanium concentration (see Figure 2.14 (a)) and the UV illuminations result in bleaching of 240 nm absorption band and the growth in absorption around 200 nm (Figure 2.14 (b)).

Figure 2.14 UV absorption spectra of (a) $\text{GeO}_2:\text{SiO}_2$ films with different inflow gas concentrations (to incorporate Ge), and (b) films under different treatment conditions. Inset in (a) shows a roughly linear relationship between the 240 nm absorption and the inflow TMOG (Tetramethoxygermane) concentrations. Inset in (b) shows relationships between the 240 nm absorption and annealing temperatures or UV laser exposure times [2-64].

2.5.2.2 Model-II: Stress relaxation model

The stress-relief or structural relaxation model was introduced in 1991 as an alternative to the color center model to explain the mechanism responsible for the UV induced refractive index change in germanosilicate optical fibers [2-151],[2-152]. The estimated UV induced refractive index change due to the stress relaxation in highly stressed optical fiber is in the order of 10^{-3} [2-155]. Due to UV-irradiations, the induced refractive index change is a consequence of the relaxation of the stressed glass network initiated by breakage of Ge-Si or Ge-Ge wrong bonds [2-154],[2-155]. The presence of stress was also found in germanosilicate planar films but UV induced refractive index changes was never reported to be associated with stress-relief model in planar films. The presence of stress in germanosilicate planar films is attributed by the mismatch of thermal expansion coefficients of germanosilicate to silicon substrate [2-153]. Figure 2.15 illustrates the stress variation with respect to SiO_2 concentration in planar germanosilicate films [2-153].

Figure 2.15 As-deposited intrinsic and extrinsic stress components in germanosilicate glasses (1 mm thick films on silicon substrate) [2-153].

2.5.2.3 Model-III: Densification (compaction) model

The UV irradiation induced densification in the amorphous silica was known even before the investigations of photosensitivity [2-154]-[2-156]. Poumellec et al. [2-157] proposed the densification model, which was developed from the experiment performed in optical fibers and preforms and that causes the change in refractive index. Direct evidence of densification or compaction has been demonstrated in germanosilicate glass by using the measurement techniques such as atomic force microscopy and transmission electron microscopy [2-107].

2.5.3 Complex nature of germanosilicate photosensitivity

Germanosilicate photosensitivity has generally been seen as a positive change in refractive index, where the index change increases with UV exposure fluence [2-107]. However, an increase in refractive index is not the only case that has been observed. The complex nature of refractive index change was reported by H. Fernando et. al [2-158] and M. V. Bazylenko et. al. [2-159] in germanosilicate planar films under the 193 nm excimer laser illumination as a function of energy fluence.

Figure 2.16 [2-158] illustrates the refractive index change as a function of UV laser energy fluence. It can be seen from Figure 2.16 that the overall refractive index change for Ge-doped silica layer is negative. The results of refractive index change were explained as follows [2-158]: Due to large compressive stress at the germanosilicate-silicon interface, UV-induced relaxation starts immediately after irradiations are applied and it decreases the refractive index. From a certain fluence level, bond breaking takes place in the glass matrix and generation of color centers become more and more efficient and contributes to the increase in refractive index. With further increase in fluence, the color center

generation process tends to saturate and further relaxation of the interfacial and intrinsic stress shifted the refractive index towards lower values.

Figure 2.16 193 nm excimer laser induced refractive index change (Δn) for Ge-doped silica sample as function of laser energy fluence [2-158].

2.5.4 Enhancement techniques for germanosilicate photosensitivity

This section is intended to present the reviews of germanosilicate UV photosensitivity enhancement techniques such as hydrogen loading, thermal treatment, mechanical treatment and boron co-doping. These enhancement techniques are used to increase the value of UV induced refractive index change.

2.5.4.1 Hydrogen loading treatment

In 1993, Lemaire et al. reported the photosensitivity enhancement in hydrogen-loaded germanosilicate optical fibers [2-160]. Since then hydrogen (H_2)-loading treatment

has been used to enhance the photosensitivity in germanosilicate optical fibers [2-161],[2-162] and in planar films [2-83],[2-115],[2-67],[2-142]. The UV induced refractive index change in optical germanosilicate glass can be enhanced to $\sim 10^{-3}$ by hydrogenation (H_2 -loading) prior to the UV exposure. From the reported work, the author found that the photobleachable absorption at 240 nm (previously described in 2.5.2.1) increases with the hydrogen exposure time during hydrogen loading treatment [2-98],[2-120],[2-142],[2-164]. An example of this study is shown in Figure 2.17 [2-142].

Figure 2.17 UV absorption spectra for sol-gel thin-film waveguide samples that treated at 550 °C under a flowing H_2/N_2 (1:20 volume ratio) atmosphere. Samples (a)-(d) represent data for 45 mol % germania films. The treatment schedules are as follows: (a) 2 Hr; (b) 1 Hr; (c) 30 minutes. (d) as-deposited sample, no heat treatment. Insert shows the integrated intensity of the absorption band located near 240 nm in the spectra [2-142].

In principle, H_2 -loading is a method in which hydrogen is incorporated in germanosilicate matrix by the simple process of diffusion. When the hydrogen is

incorporated in germanosilicate structure, hydroxyl and hydride bonds form [2-83] and this process is described below in Equation (2.2):

The exposure of H₂-loaded germanosilicate to the UV irradiation causes the photobleaching of hydride bonds (typically at Ge sites: germanium hydride bond) and results in the formation of GeE' centers. Using this technique, the obtained value of refractive index change is about 10⁻³ [2-121],[2-160],[2-165].

Hydrogen loading treatment can be carried out in different ways such as high and low temperature hydrogen loading, flame brushing and the -OH flooding. These methods are described below:

High temperature hydrogen treatment: Hydrogen loading treatment can be performed at higher temperature (~ 600 °C) in hydrogen atmosphere and leading to the formation of hydroxyl and hydride bonds that result in increase of absorption around 240 nm [2-163].

Low temperature hydrogen treatment: Hydrogen loading treatment can be performed at room temperature in a high-pressure hydrogen atmosphere where hydrogen molecules diffuses into the glass network and form the hydroxyl and hydride bonds that results in increase of absorption around 240 nm [2-166], [2-161].

Flame brushing: In this technique, localized heating of fibers or waveguide is performed by using hydrogen rich flame [2-167]. Heating under a hydrogen rich flame leads to the in-diffusion of hydrogen.

OH Flooding: An increase in photosensitivity can also be obtained by a significant increase of hydroxyl concentration in germanosilicates matrix [2-119],[2-168]. This can be achieved by rapid heat treatment of hydrogen loaded system at very high temperature such as 1000 °C [2-168].

From the above description, the hydrogen-loading treatment seems to be well established way to enhance the refractive index change to $\sim 10^{-3}$, but in general, the fragility of the glass is greatly increased after using any of these methods. Apart from being a time consuming extra step, the major disadvantage of hydrogen sensitisation is strong -OH absorption peaks formation from SiOH and GeOH centres. Such formation increases the propagation losses at 1.55 μm . Furthermore, this technique is found to be less applicable for planar germanosilicate films because of rapid out-diffusion of hydrogen and increase in propagation loss.

2.5.4.2 CO₂ laser exposure prior to UV-illumination

Exposure of germanosilicate films [2-169] and fibers [2-170] to the CO₂ laser irradiation prior to UV laser results in the increase in absorption at 240 nm. This means that the exposure of CO₂ laser irradiations increases the NOMV defects in germanosilicate and thus the refractive index change. The UV induced refractive index change increases only up to 10^{-4} [2-170].

2.5.4.3 Mechanical treatment

In 1997, Taunay et. al. [2-137] and Isabelle Riant et.al [2-136] investigated the effect of strain on the photosensitivity of single-mode optical fiber. In strained optical fiber, they found the decrease in refractive index change with less fluency of laser. On the

contrary, by applying larger strain on the optical fibers during UV illumination, a significant increase in refractive index change of 2×10^{-3} was reported by E. Salik et. al. [2-171]. The effect of strain was also studied in a long period fiber grating by twisting the fiber at elevated temperature [2-172] and by introducing residual tension stress [2-173]. This enhancement process for increasing the UV induced refractive index change is studied well in germanosilicate optical fiber and shows that under stress, UV induced refractive index change increases. This enhancement technique is promising but it is difficult to perform in planar films.

2.5.4.4 Annealing in reducing atmosphere

As described in the above sections, the refractive index change is usually found to be associated with NOMV, and several attempts were made to increase the NOMV defects for the purpose of increasing UV induced refractive index change. The NOMV defects can also be increased during the fabrication process [2-125],[2-126] and it has been done by using a reducing atmosphere (He + 1%D₂) [2-174].

2.5.4.5 Boron co-doping

Co-doping of B₂O₃ with germania in silica results in UV induced refractive index change of about 10^{-3} [2-175]. Addition of boron to germanosilicate does not alter the 240 nm UV absorption band (or NOMV defect centers) characteristics for germanosilicate glass [2-175]. For the boron doped silica glass, no absorption band is present at 240 nm but the UV absorption starts to increase at 190 nm. This shows that boron doping does not attribute to the NOMV related photosensitivity mechanism. The enhancement of photosensitivity of B₂O₃-codoping has been attributed to the densification enhancement due to stress effects [2-176].

B₂O₃ doping considerably increase the UV induced refractive index change (10^{-3}) but has significant drawbacks, such as high propagation loss, poor thermal stability, and high polarization mode dispersion [2-177]-[2-181]. Addition of boron decreases the overall refractive index of the germanosilicate material system and makes the glass system hygroscopic.

2.6 Silica-on-silicon deposition techniques

In this section, the author will describe various deposition techniques for the fabrication of germanosilicate planar films that include sputtering process, Chemical Vapour Deposition (CVD), Plasma Enhanced Chemical Vapor Deposition (PECVD), Flame Hydrolysis Deposition process (FHD), and the sol-gel process.

2.6.1 Sputtering process

Fabrication of planar waveguide layers by sputtering process involves creating argon plasma, by high voltage discharge in a vacuum chamber [2-12]. The substrate is placed inside vacuum chamber. The positive ions of the plasma, having the kinetic energies in the range 10 eV to 2 KeV, are accelerated towards the surface of the target [2-12], causing the break off of target atoms which then condense on the substrate. Several variations of the basic sputtering technique include magnetron sputtering, direct current (DC) or radio frequency (RF) sputtering. Sputtering is relatively a simple technique and can be used with any material [2-12]. Sputtering has been used to deposit germanosilicate films [2-103],[2-130],[2-182],[2-183]. However, sputtering deposition technique has some disadvantages. The deposition rate is slow and it is hard to preserve the stoichiometry of the deposited materials [2-183].

2.6.2 Chemical vapor deposition process

Chemical Vapor Deposition (CVD) is one of the methods of deposition of planar waveguide layers in which the substrate is placed inside a reactor to which number of gases are supplied. The fundamental principle of the process is that a chemical reaction takes place between the source gases. The product of that reaction is a solid material which condenses on all surfaces inside the reactor including substrate.

The two most important CVD technologies are Low Pressure Chemical Vapor Deposition (LPCVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD) [2-184],[2-8],[2-12],[2-65],[2-68],[2-108],[2-111]. PECVD is a modified version and industry proven technique, developed for the microelectronics industry. The main problems of LPCVD are the high deposition temperature (higher than 600 °C) and relatively slow deposition rate. The PECVD process operates at lower temperature (down to 300 °C). Germanosilicate films have been fabricated by using PECVD [2-64],[2-83]. To deposit germanosilicate films by PECVD, the SiH_4 and N_2O is the most usual mixture and Germane (GeH_4) is commonly used dopant material.

To achieve low loss planar waveguide layers, some modified version of PECVD are available that includes inductively coupled-PECVD [2-64],[2-83] and Hollow Cathode-PECVD [2-185],[2-113]. PECVD offers many advantages, for instance, a dopant may be introduced easily and the fabricated layers are of very high quality and low loss [2-64],[2-83]. However, the disadvantages associated with this technique are the difficulty to obtain uniform and stoichiometric films [2-64]. It also requires the handling of gases that are often toxic, explosive or corrosive (or a combination of all three).

2.6.3 Flame hydrolysis deposition process

Flame hydrolysis deposition (FHD) technology is mainly used for the fabrication of optical fiber preforms. It was adopted for the production of planar waveguide layers for optical communication in 1990 [2-154] and is now commonly used for the deposition of waveguide layer for PICs [2-9],[2-66],[2-114]. Germanosilicate films also been fabricated by FHD [2-66],[2-114].

In this technique, the reagents are oxidized in an oxy-hydrogen flame that is directed on the substrate. The reagents are liquid halide materials (typically, SiCl_2 and GeCl_2 are used to deposit germanosilicate films), which are vaporized in bubblers. The temperature of the halide container (bubbler), and the flow rate of the gas through the bubbler, controls the quality of the halide transported to the burner. A carrier gas, usually nitrogen or oxygen, is used to transport the vapour into flame. The oxidization of the particles by the flame produces low density soot that deposit on the substrate. The flame is moves across the substrate to deposit uniform layers of soot. The soot is then consolidated in a furnace to form fully dense glass layer. By varying the speed of the moving flame and the gas flow rate, the quantity of the deposited soot can be controlled, so that the different thickness can be obtained for the waveguide layer.

The FHD has been shown to produce low loss films [2-9]. As compared to the PECVD, the layer deposited using the FHD is highly uniform and higher in purity. However, this technique has disadvantages as it requires relatively high temperature (1200-1380 °C) and the FHD deposited films often observed to be non-stoichiometric [2-66].

2.6.4 Sol-gel process

Sol-gel is a process for making ceramic and glass materials with high purity and high homogeneity. The sol-gel process involves the transition of a system from liquid into a solid phase. A “sol” is a colloidal suspension of solid particles ($\sim 1\text{ nm} - 1\text{ }\mu\text{m}$) in a liquid and the “gel” is a porous network (pores of sub-micrometer dimensions) of interconnected particles.

From the extensive review, the author found that the sol-gel process is a suitable deposition process to fabricate planar films of wide range of materials including organic [2-55],[2-57],[2-187],[2-188] or hybrid [2-59]-[2-62] material system, and inorganic material system [2-80],[2-6],[2-86],[2-87],[2-135],[2-186]. In order to obtain thin and thick films of silica and doped silica, the so-called alkoxide precursor route has been widely accepted [2-186],[2-189]-[2-202]. The main fabrication steps of the sol-gel process are the hydrolysis in which alkoxide precursor reacts with water and polymerization occurs. Thereafter the solvent evaporates and becomes a viscous liquid which transformed into a glass after annealing at suitable high temperature far lower than the melting temperature of the corresponding oxides.

In the sol-gel process, the properties of films can be easily controlled by controlling the concentration of dopant at the molecular level and by varying the process parameter. Some advantages of sol-gel process are outlined below:

Flexibility: Sol-gel allows the tailorability of optical properties by incorporating different concentration of dopants or co-dopants, controlling the reaction kinetics and process parameters such as annealing temperature and time (details are covered in Section 2.7.5).

Homogeneity: Sol-gel is a solution-based chemical process in which the elements are well mixed at molecular level and formed homogenous material system.

Purity: Highly purified precursors such as metal alkoxides and mixed alkyl/alkoxide are commercially available for the use in sol-gel process.

Low cost: The available deposition methods for sol-gel scheme are often simple and inexpensive. The chemical used in the sol-gel process and equipment required are of low cost in comparison with the other methods.

High Optical quality: This process allows the synthesis of high optical quality stoichiometric and amorphous films with low waveguide propagation loss [2-189]-[2-192].

Based on these arguments, sol-gel process was chosen for this project. Without the detailed review and description of sol-gel process and sol-gel chemistry, this review is incomplete. So, the detail review of these topics will be given in next section.

2.7 Review of sol-gel process

In this section, the fundamentals of sol-gel processing steps and the sol-gel reaction chemistry will be described in more details. It will be further supplemented with the discussion of the limitations of sol-gel process.

2.7.1 Introduction of sol-gel method

The first, although incidental, observation of the sol-gel process dates back to 1846 [2-193] and the process has been extensively studied since 1930s. In 1939, reports were published [2-194],[2-195] and aimed specifically for the SiO₂ layers fabrication by the sol-

gel process. Sol-gel was used in the development of rearview mirrors for automobiles, which have been in production since 1953 [2-196],[2-197] and further followed by anti-reflective coating which have been in production since 1964, and solar reflecting coating, deposited on flat-glass which is in production since 1969 [2-193],[2-195],[2-197]. The chemistry involved in the reactions of several metal alkoxides was reported in 1971 [2-196] and it allows the production of multicomponent oxide glasses, glass-ceramic and crystalline layers [2-196],[2-197]. The sol-gel processing is suitable to produce thin films and dense materials as illustrated in Figure 2.18 [2-198].

Figure 2.18 Sol-gel processes to prepare thin film and dense glass [2-198].

2.7.2 Fundamentals of sol-gel process

The concept of “sol” is evolved from a colloid [2-198],[2-199]. Colloids are suspensions of particles of linear dimensions between 1 nm and 1 μm where gravitational forces are negligible and interactions are dominated by short-range forces, such as Vander Waals attraction and surface charges attraction. The sol-gel process, as the name implies,

involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). In the sol-gel process, the precursors (starting compounds) for preparation of a colloid consist of a metal or metalloid element surrounded by various ligands namely Metal-alkoxides [2-200]-[2-202]. Metal-alkoxides are members of the family of metalloorganic compounds, which have an organic ligand attached to a metal or metalloid atom like $\text{Si}(\text{OR})_4$ [2-202]-[2-204]. The R represents a proton or other ligand. In the synthesis of SiO_2 , for example, the most widely used metal-alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS: $\text{Si}(\text{OCH}_3)_4$) and tetraethoxysilane (TEOS: $\text{Si}(\text{OC}_2\text{H}_5)_4$). The most thoroughly studied metal-alkoxide is tetraethoxysilane or tetraethyl orthosilicate or TEOS. This metal-alkoxide is popular precursors because it reacts readily with water, which is an important criterion for hydrolysis to take place [2-198].

2.7.3 Formation of silica films by sol-gel

To illustrate the principle of sol-gel process, the author is going to firstly discuss the formation of SiO_2 film and thereafter, formation of germanosilicate films. The formation of SiO_2 can be expressed by two simple chemical reactions: Hydrolysis and Condensation. The hydrolysis reaction for TEOS replaces alkoxide group (OC_2H_5) with hydroxyl group (OH) as presented below by Equation (2.3a) [2-198]:

Depending on the amount of water and catalyst [204-212], hydrolysis may go to completion. The major variables in the reaction sequence include the type of precursor, the catalyst (acid or base) and its concentration (pH level), the ratio $[H_2O]/[Si]$, and the reaction temperature. The effect of all these parameters will be discussed separately in Section 2.7.5.

The silanols ($Si-(OH)_4$) (see Equation (2.3a)), i.e. hydrolyzed molecules can link together to form $\equiv Si-O-Si \equiv$ monomers in the alcohol and water condensation reactions as expressed by Equation (2.3b) and (2.3c) respectively [2-198]:

or

These tiny monomers can aggregate to form small particles or polymerizes to form linear, branched or three-dimensional structure [2-213]. The rate of hydrolysis and condensation depend upon the type of metal alkoxides too. In a multicomponent system, the appropriate choice of starting metal alkoxides is required otherwise it can lead to the chemical induced phase separation [2-214], [2-198],[2-200],[2-203].

2.7.4 Sol-gel processing steps

The sol-gel derived silica glass processing (using TEOS precursor) are briefly described below.

Step 1 - Mixing: In this step, the liquid TEOS precursors are initially diluted with alcohol and then water is added [2-205],[2-214]. A ternary system, TEOS-Ethanol-H₂O is therefore obtained which present a miscibility gap at room temperature, as illustrated in Figure 2.19 [2-198].

Figure 2.19 TEOS-H₂O-Ethanol ternary phase diagram [2-198]. For purer ethanol, the miscibility line is shifted slight to the right.

As stated previously, firstly the hydrolysis reaction occurs which are facilitated by water along with the catalyst, and then the polymerisation takes place to form Si-O-Si bonds. Under most conditions, condensation commences (Equation (2.3b) & Equation (2.3c)) before hydrolysis is complete (Equation (2.3a)) [2-198]. Because water and TEOS are immiscible (see Figure 2.19), a mutual solvent such as alcohol is normally used as

homogenizing agent [2-198]. However, gel can be prepared from TEOS and water mixtures without added solvent, since alcohol produced as the by-product of hydrolysis reaction is sufficient to homogenize the initially phase separated system. It should be noted that alcohol is not simply a solvent. As indicated by the reverse of Equation (2.3a) and Equation (2.3b), it can participate in esterification or alcoholysis reactions [2-198].

Step 2 - Aging: During this step, the sol is allowed to stand either at room temperature or at an elevated temperature for a period of time during which hydrolysis and condensation reactions cause aggregation and cross-linking. The aggregation and cross-linking of the sol increases with aging to achieve sufficient viscosity for coating and to tailor the porosity for a particular application, aging must be carried out [2-198],[2-216].

Step 3 - Gelation: With time, condensed silica species linked together to form a three-dimensional network having pores. The physical characteristics of the gel network depends greatly upon the pore size, the size of the particles and extend of cross-linking prior to gelation [2-198],[2-211],[2-215].

Step 4 - Deposition: The sol-gel process allows various means of films deposition such as dip coating, spin coating, electrophoresis or thermophoresis [2-80],[2-88]. In our case, for planar film synthesis, spin-coating has been used because of its ability to produce both the thin and thick films with controlled thickness. This process will be described in detail in Chapter 5 (Section 5.2).

Step 5 - Drying: Although the author has not used this step but presented its outlines because this is commonly used step after the gelation to produce monoliths and bulk silica.

During drying, the liquid is removed from the interconnected pores network [2-199]. Large capillary stresses can be developed during drying when the pores are small

(<20 nm). These stresses will cause the gels to crack catastrophically unless the drying process is controlled by decreasing the liquid surface energy [2-217].

Step 6 - Dehydration and densification: After the film deposition, this step involves the removal of silanol (Si-OH) bonds (see Figure 2.20) and the pores within the network by using heat treatment process [2-199],[2-218],[2-219].

Figure 2.20 The dehydroxylation of different Si-OH groups [2-199].

The densification temperature depends considerably on the dimensions of the pore network, the connectivity of the pores, and on the surface area. Thermal treatment leads to the collapse of the pores and hence the formation of a dense silica [2-217],[2-219],[2-220].

For the low absorption loss, which is an essential requirement for the application in optical devices, the densification temperature must be chosen properly. Thermal dehydroxylation (see Figure 2.20) generally involves heating of the gel to the temperature up to 1100°C [2-199]. In this work, the author has carried out rapid thermal annealing (RTP) at various temperatures in the range of 500 – 1000 °C to investigate the densification temperature of prepared germanosilicate films (see Section 5.3 of Chapter 5).

2.7.5 Various critical parameters of sol-gel reaction mechanism

There are many parameters that can affect the silicate network formation which includes the precursor type, water/precursor ratio, level of pH for hydrolysis, the catalyst type, the reaction temperature, aging and drying conditions.

Effect of precursor type: The most common precursors used in the fabrication of silicate network are tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS). It was found that TEOS produces films with a wider and more controllable range of porosities than the TMOS [2-198],[2-200]. This behavior is related to the slower hydrolysis rate of TEOS due to steric hindrance by the larger ethoxy group [2-214].

Effect of H₂O/TEOS (r) molar ratio: The most obvious effect with the increase in r value is to increase the rate of hydrolysis. The gelling time in sol-gel process is highly dependent on this factor (r) together with the type of precursor. The hydrolysis reaction can be performed with r-values ranging from 1 to 25 [2-198] depending on desired polysilicate which permits to hydrolyze -OR bonds. When TEOS is used as a precursor, r value of 4 is theoretically sufficient to complete the hydrolysis for the formation of stoichiometric silica glass [2-215],[2-224]. This means that 4 moles of water is required for each mole of alkoxide (ie. $r = 4$) in order to the completion of reactions.

Effect of pH level and type of catalyst: pH is defined as $\text{pH} = -\log(a\text{H}^+)$ where $a\text{H}^+$ is the hydrogen ion activity. The amount of catalyst can change the pH level and the rate of hydrolysis and condensation [2-216]-[2-224]. Therefore, catalyst markedly affects the microstructure and properties of the resulting gel and glass [2-221],[2-223]. Catalyst in the form of acids or bases are capable of accelerating the reactions of sol-gel process. Common sol-gel catalysts are Hydrochloric acid (HCl), Hydrofluoric acid and Nitric acids (HNO_3) [2-198],[2-205],[2-207]. Various catalysts affect the overall hydrolysis and condensation rate and judged by the time required for gelation as summarized in Table-2.1 [2-198].

Table-2.1: Gel time and sol pH for TEOS systems employing different catalyst [2-198].

Catalyst	Concentration (mol :TEOS)	Initial pH of solution	Gelation Time (h)
HF	0.05	1.90	12
HCl	0.05	0.05 ^a	92
HNO_3	0.05	0.05 ^a	100
H_2SO_4	0.05	0.05 ^a	106
HOAc	0.05	3.70	72
NH_4OH	0.05	9.95	107
No catalyst	-	5.00	1000

^a between 0.01 and 0.05

The acidity of the sol determines the mechanism by which hydrolysis and condensation occur. Under acidic-condition, it is likely that an alkoxide group is protonated rapidly, as shown in Equation (2.4a) [2-225]. Electron density is withdrawn from the silicon atom, making it more electrophilic and thus more susceptible to attack from water (see Equation (2.4a)). Chemical reaction under very acidic condition is shown in Equation (2.4b) [2-225].

(2.4b)

The base-catalyzed hydrolysis of silicon alkoxides proceed much more slowly than the acid-catalyzed hydrolysis at an equivalent catalyst concentration [2-225],[2-198]. The basic alkoxide oxygens tend to repel the nucleophile -OH. However, once an initial hydrolysis has occurred, subsequent reactions proceed rapidly, with each subsequent alkoxide group is more easily removed from the monomer than the previous one. Therefore, more highly hydrolyzed silicones are more prone to attack. Thus, under basic conditions, it is likely that water dissociates to produce hydroxyl anions rapidly (see Equation (2.5a)) [2-225]. The hydroxyl anion then attacks the silicon atom, as shown in Equation (2.5b) [2-225]:

(2.5b)

Acids protonate negative charged alkoxide groups, enhancing the reaction kinetics by producing a good leaving group. Therefore, acid-catalyzed condensation is directed preferentially towards the ends rather than the middles of chains, resulting in more extended and less highly branched polymers.

Structural evolution based on choice of catalyst: Sol-gel polymerization occurs in three stages: (1) Polymerization of monomers to form particles, (2) Growth of particles, (3) Linking of particles into chains and then forming the networks that extend throughout the liquid medium. The sol-gel derived silica networks, under acid-catalyzed conditions, yield primarily linear or randomly branched polymers which entangle and form additional branches resulting in gelation. On the other hand, silica networks derived under base-catalyzed conditions, yield more highly branched clusters, which do not interpenetrate prior to gelation and thus behave as discrete clusters (see Figure 2.21) [2-214]. Therefore, the author has used acid catalyst in sol-gel processing of film preparation (see Chapter 5).

Figure 2.21 Typical polymers under (a) acidic condition - yield primarily linear or randomly branched polymer, (b) basic condition - yield highly branched clusters [2-214].

Effect of the temperature: The hydrolysis and condensation reaction rate increases as the temperature increases. So, the gelling time decreases as the temperature increases [2-199]. In this work, the author has carried out sol preparation at room temperature (see Section 5.2 of Chapter 5).

Effect of the aging time: To produce a sol of sufficient viscosity for coating and to tailor the porosity for a particular application, aging or pre-polymerisation step can be carried out [2-216]. During this step, the sol is allowed to stand either at room temperature or at an elevated temperature for a period of time during which hydrolysis and condensation reactions cause aggregation and cross-linking. This process can enhance the stability as well control the porosity of the films. The author has used about 40 minutes of aging time in this work (see Section 5.2 of Chapter 5).

2.7.6 Formation of germanosilicate films by sol-gel

The mechanism of germania doped silica films synthesis by sol-gel process is quite similar to the silica film synthesis. As germanium and silicon both belong to the group IV in the periodic table, both form tetrahedron units in a similar way. When GeO_2 is mixed in SiO_2 at a molecular level as in sol-gel, the Ge atoms randomly substitute Si atoms in SiO_4 tetrahedra, so that the microstructure of the film would remain a continuous three-dimensional network consisting of interconnected SiO_4 and GeO_4 tetrahedra [2-100]. The reactions that take place [2-204], [2-226] are described by the Equations 2.6(a) - (c);

The suitable preparation scheme of germania doped silica film synthesis was developed by the author and the details will be presented in Chapter 5.

2.7.7 Sol-gel process limitations

Despite all these advantages, sol-gel process has limitations too. The author would like to address some important issues which were finally resolved in this project. The precursors are often sensitive to moisture, although not insuperable but do require careful attention. The complete removal of residual hydroxyl bond requires proper attention of heat treatment temperature. Incorporation of higher concentration of germania in silica is known to produce crystalline phases at higher temperature, so optimization of temperature is required for every composition of germania in silica for the hydroxyl free non-crystallized films. The problems of stress induced cracking upon drying or heat treatment limit the formation of thick films. The formation of few micron thick films is indeed required for the photonic waveguide devices. These limitations require the need to develop and optimize the sol-gel preparation scheme and parameters, to be able to exploit the advantages of the sol-gel process which are not attainable by other deposition methods. In this work, the author has successfully synthesized the crack free photosensitive, dense inorganic germanosilicate (amorphous) thin and thick films, using the optimized sol-gel spin-coating scheme. The description of the fabrication process will be presented in Chapter 5 and Chapter 6.

2.8 Summary

The author has reviewed the brief history of integrated photonics and described the key technologies that have been developed for the fabrication of optical channel waveguide devices. Each of the fabrication technologies presented has advantages and disadvantages, with no clear winner across the board. The direct UV-imprinting technique

is a promising way to fabricate photonic waveguide devices because it is relatively a simple and easy fabrication technique and does not require complex processing steps like etching technique and lithography. The author has also reviewed various doped silica material systems for the optical waveguide device. The promising photosensitive inorganic germanosilicate material system has been discussed in great detail because it is a choice of material in this project. The author reviewed the detailed description of photosensitivity mechanism in inorganic germanosilicate material system that includes the description of various models. The author has also presented the description of various deposition methods. The selection of deposition method was dictated by the specific requirements of waveguiding material such as homogeneity, stoichiometry and low propagation loss of planar films. The author has selected the sol-gel method with spin-coating technique to synthesize germania doped silica films for this project. Lastly, the detailed reaction mechanism and theory of the sol-gel processing has been presented.

Chapter 3

Theory of Optical Waveguides

3.1 Introduction

This chapter is intended to present the basics of waveguide theory. The theory of planar waveguides is presented here to give the understanding of the photonic waveguide devices fabricated by the author, which will be described in Chapter 6. For more detailed account, the reader is directed to the literatures [3-1]-[3-9]. In Section 3.2, the author will present the theoretical aspects of slab-waveguides. The electromagnetic theory of the allowed optical modes of propagation in slab-waveguides will be covered in Section 3.3. The wave equation and the wave guidance conditions are examined for both transverse electric and magnetic modes in Section 3.4. In Section 3.5, the beam propagation method (BPM) is introduced for a solution of propagation phenomenon in channel waveguides.

3.2 Introduction to the planar slab-waveguide

The basic concept of planar photonic waveguides is the confinement of light, same as in optical fibers. The planar slab-waveguide structure is shown schematically in Figure

3.1 (a) which consists of substrate, buffer, cover and a waveguiding layer which is also called waveguide core. The buffer and the cover are both usually semi-infinite and have refractive index n_2 and n_3 respectively. The waveguiding core layer of thickness h , and refractive index n_1 is where most of the optical energy is concentrated. The author will assume without any loss of generality that $n_1 > n_2 > n_3$. Light guidance in such planar guides can be easily understood on the basis of total internal reflection (TIR). As shown in Figure 3.1 (b), in a planar slab-waveguide, light is trapped by TIR in a waveguiding core (non-dashed region) when incident with an angle (θ_i). The maximum acceptance angle (θ_i) is limited by the critical angle (θ_c) of incidence at the core-cladding boundary. This angle corresponds to waveguide modes in wave optics.

Figure 3.1 (a) Schematic illustration of planar slab-waveguide structure, (b) light guidance by the total internal reflection.

In the description above, the author has briefly described the guiding or “trapping” of the light in the optical waveguides using the ray optics theory. Next, the author will analyze the planar slab-waveguide problem by solving the Maxwell’s equations and obtain the mathematical solutions of modal field distributions by using the boundary conditions.

3.3 The wave equations for planar slab-waveguide

The spatial distribution of the optical field within a waveguide can be determined using Maxwell equation as a starting point [3-6]. For a linear isotropic dielectric and non-magnetic medium, the electric ($\vec{E}$) and magnetic ($\vec{H}$) field vectors are linked by the following forms of Maxwell’s equations [3-6],[3.8]:

$$\vec{\nabla} \times \vec{E} = -\mu_o \frac{\partial \vec{H}}{\partial t}, \quad (3.1)$$

$$\vec{\nabla} \times \vec{H} = \varepsilon \frac{\partial \vec{E}}{\partial t} + \vec{J}, \quad (3.2)$$

$$\vec{\nabla} \cdot \vec{E} = 0, \quad (3.3)$$

$$\vec{\nabla} \cdot \vec{H} = 0, \quad (3.4)$$

where μ_o and ε are the permeability and permittivity of the medium, $\vec{J}$ is the displacement current and in here in this analysis of dielectric material it is consider to be zero, $\partial/\partial t$ is the partial derivative with respect to time t and $\vec{\nabla}$ is the spatial vector operator:

$$\vec{\nabla} = \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z} \quad (3.5)$$

Taking the curl of Equation (3.1) leads to

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{E}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{E}) - \nabla^2 \vec{E} = -\mu_o \frac{\partial}{\partial t} \vec{\nabla} \times \vec{H} \quad (3.6)$$

Using Equation (3.2) and (3.3) allows us to derive the homogeneous wave equation to be calculated in terms of the $\vec{E}$ field. This equation relates the spatial and temporal components of the $\vec{E}$ field:

$$\nabla^2 \vec{E} - \mu_o \epsilon \frac{\partial^2}{\partial t^2} \vec{E} = 0 \quad (3.7)$$

The wave equation can also be expressed in the terms of the $\vec{H}$ field by applying the same reasoning to Equation (3.2). The same equation is obtained in terms of $\vec{H}$ instead of $\vec{E}$:

$$\nabla^2 \vec{H} - \mu_o \epsilon \frac{\partial^2}{\partial t^2} \vec{H} = 0 \quad (3.8)$$

Solving the wave equation is simplified by allowing the wave to propagate along the z -axis as this eliminates the spatial variation of the field along this axis. For wave propagating along the z -axis, the following general form of the solution can be assumed:

$$\vec{E} = (E_x(x, y)\hat{x} + E_y(x, y)\hat{y} + E_z(x, y)\hat{z})e^{i(\alpha x - \beta z)} \quad (3.9)$$

$$\vec{H} = (H_x(x, y)\hat{x} + H_y(x, y)\hat{y} + H_z(x, y)\hat{z})e^{i(\alpha x - \beta z)} \quad (3.10)$$

where $i = \sqrt{-1}$, β is the optical field propagation constant and ω the angular frequency.

The unit vectors in each direction $\hat{x}$, $\hat{y}$ and $\hat{z}$ while E_x , E_y and E_z are the relative magnitude coefficients of the electric field in the x , y and z direction respectively and H_x , H_y and H_z

are the relative magnitude coefficients of the magnetic field. The solutions can be calculated by using the continuity condition at the interfaces.

3.4 Solution for a planar slab-waveguide

To analyse the wave propagation in a planar slab-waveguide, the cross section of waveguiding structure shown in Figure 3.1 is re-illustrated schematically in Figure 3.2 (a). In this analysis, for the structure shown in Figure 3.2 (a), corresponding refractive index profile is illustrated in Figure 3.2 (b). The core (refractive index of n_1) has step index with respect to the buffer layer (refractive index n_2) and the cover layer (refractive index of n_3). As mentioned before $n_1 > n_2 > n_3$ and extends indefinitely in the x and z direction.

Figure 3.2 (a) Cross-section of slab-waveguide, (b) refractive index profile of slab-waveguide, $n_1 > n_2 > n_3$.

Using Equation (3.7), the two mutually orthogonal polarization states: transverse electric and transverse magnetic (TM) supported by this structure can be calculated separately. For the wave propagating along the $\hat{z}$ direction and having electric field $\vec{E}$

polarized along the $\hat{x}$ axis, $E_x \neq 0$, $E_y = E_z = 0$ & $H_z \neq 0$ and similarly, for the TM mode having magnetic field $\vec{H}$ polarized along the $\hat{x}$ axis, $H_x \neq 0$, $H_y = H_z = 0$ & $E_z \neq 0$. These non-zero field components are listed in Table-3.1 [3-8].

Table-3.1: TE and TM optical field components.

TE field components	TM field components
E_x	H_x
$H_y = -\frac{\beta}{\omega\mu_o} E_x$	$E_y = \frac{\beta}{\omega\epsilon_o n^2} H_x$
$H_z = -\frac{1}{i\omega\mu_o} \frac{\partial}{\partial y} E_x$	$E_z = \frac{\beta}{i\omega\epsilon_o n^2} \frac{\partial}{\partial y} H_x$

The TE and TM optical field components will be used in the following (Equation (3.7) and Equation (3.8)) derivations to obtain solutions for the TE and TM field distribution. For the TE optical field component, the y and z components of the $\vec{E}$ field are zero see the above, hence the expression of the field can be written as

$$E = E_x(y) e^{i(\alpha x - \beta z)} \quad (3.11)$$

plugging this Equation (3.11) into Equation (3.7) will gives:

$$\nabla^2 \vec{E}_x - (k_0^2 n^2 - \beta^2) \vec{E}_x = 0 \quad (3.12)$$

where $k_0 = \omega\sqrt{\mu_o\epsilon_o} = \omega/c$ is a free space wave number and $c (=1/\sqrt{\mu_o\epsilon_o})$ is the speed of light in free space. Where $n = n_1, n_2$, or n_3 , depending on the position y, as described in Figure 3.2 (b). For $y > h$, we would use n_3 , while for $h \geq y \geq 0$, we would use n_1 and for $y < 0$ we would use n_2 . The general solution to Equation (3.12) will depend on relative magnitude of β with respect to $k_0 n$. If $\beta < k_0 n_2$ or $k_0 n_3$ the optical field would vary

sinusoidally in cladding regions. For $\beta > k_0 n_1$, the solution to the wave equation would give optical field to be exponential in all regions. For guiding field propagation constant, β , is bounded by the condition [3-12].

$$k_0 n_3, k_0 n_2 < \beta < k_0 n_1 \quad (3.13)$$

In case where $\beta < k_0 n_2$ or $k_0 n_3$, we define attenuation coefficient, α_1 and α_2 as:

$$\begin{aligned} \alpha_1^2 &= \beta^2 - k_0^2 n_3^2 \\ \alpha_2^2 &= \beta^2 - k_0^2 n_2^2 \end{aligned} \quad (3.14)$$

In case $\beta > k_0 n_1$, we define transverse wavevector, κ as:

$$\kappa^2 = k_0^2 n_1^2 - \beta^2 \quad (3.15)$$

Thus, the wave guiding condition can be derived from Equation (3.14) and (3.15) and expressed in the form:

$$\kappa^2 + \beta^2 = k^2 \quad (3.16)$$

Total wavevector, $k = k_0 n_1$, in the guiding film.

The TE solutions to the wave equations in the three regions are

$$E_x(y) = E_{x0} \begin{cases} Ae^{-\alpha_1 y} : & y > h, \\ B \cos(\kappa y) + C \sin(\kappa y) : & 0 < y < h \\ De^{-\alpha_2 y} : & y < 0 \end{cases} \quad (3.17)$$

where A, B, C and D are amplitude coefficient to be determined by boundary conditions and in writing the solutions in region $y > h$ and $y < 0$, the author have neglected the exponentially amplifying solution. α_1 and α_2 refer to the attenuation coefficients in cover

and buffer, respectively. κ is the transverse wavevector within the core and E_{x0} is the maximum amplitude of the electric field in the x -direction.

Since there is no E_y component to the field, we get explicit equation for the tangential component of magnetic field, H_z , and using the expression from Table-3.1 for H_z gives:

$$H_z = -\frac{1}{i\omega\mu_0} \frac{\partial}{\partial y} E_x \quad (3.18)$$

Using solution from Equation (3.17), Equation (3.18) yields

$$H_z(y, z) = \begin{cases} \frac{i\alpha_1}{\omega\mu_0} A e^{-\alpha_1 y} E_{x0} : & y > h, \\ \frac{i\kappa}{\omega\mu_0} B \sin(\kappa y) E_{x0} - \frac{i\kappa}{\omega\mu_0} C \cos(\kappa y) E_{x0} : & 0 \leq y \leq h \\ \frac{i\alpha_2}{\omega\mu_0} D E_{x0} e^{-\alpha_2 y} : & y < 0 \end{cases} \quad (3.18)$$

Using boundary conditions, namely the continuity of E_x and $\partial E_x / \partial y$ at $y = 0$ and $y = h$ to obtain eigen value equations:

For TE, eigen value equation for β is [3-9]:

$$\tan(h\kappa) = \frac{\alpha_1 + \alpha_2}{\kappa \left[1 - \frac{\alpha_1 \alpha_2}{\kappa^2} \right]} \quad (3.19)$$

For TM, eigen value equation for β is [3-9]:

$$\tan(h\kappa) = \frac{\kappa \left[\frac{n_1^2}{n_3^2} \alpha_1 + \frac{n_1^2}{n_2^2} \alpha_2 \right]}{\kappa^2 - \frac{n_1^4}{n_2^2 n_3^2} \alpha_1 \alpha_2} \quad (3.20)$$

The transcendental equation can be solved numerically or graphically. Each solution of the light guidance conditions gives allowed guided field propagation or modes. The tangent function in above two equations is periodic for a sufficient thickness of h . Multiple solutions for $m = 0, 1, 2, \dots$ are denoted by **TE_m modes**. Effective index of each TE mode is $n_{eff} = \beta/k_o$. Figure 3.3 shows the schematic plots of the field variation of TE modes with $m = 0, 1$ and 2 across the cross-section of the slab waveguide. The mode number m corresponds to the number of times the field cross the axis. It can be seen that higher order modes penetrate deeper into the substrate and cover than lower order modes. Same procedure is used to obtain TM modes for the multiple solutions for different values of $m = 0, 1, 2, \dots$. These are known as **TM_m modes**.

Figure 3.3 Schematic of field distribution of the TE mode corresponding to (a) $m = 0$, (b) $m = 1$, and (c) $m = 2$ in planar waveguides. Observe that higher modes corresponding to higher value of m penetrate deeper into the substrate and cover. Also the number of intersections of the field with the axis is just m .

3.5 Planar channel-waveguide

The study of light propagation in planar slab-waveguide provides an understanding of the physical phenomenon of light guiding and the parameter influencing it. In this work,

the photonic devices, namely channel waveguides, 1×2 multimode interference (MMI) 3 dB power splitter and 2×2 directional coupler (DC), was fabricated by using direct UV-imprinting technique and will be described in Chapter 6 (see Section 6.5 of Chapter 6). The structure shown in Figure 3.4 is a cross-section of planar channel-waveguide which consists of buffer, cover, side-cladding and a waveguiding channel. Again the buffer and the cover are both semi-infinite and have refractive index n_2 and n_3 respectively. The waveguiding channel of thickness h , width w and refractive index $n_1 + \Delta n$ have cladding of refractive index n_1 at its both sides. In this case, the optical energy will be confined in waveguiding channel with refractive index $n_1 + \Delta n > n_1 > n_2 > n_3$. The light guiding in this case is a result of confinement in both x (lateral) and y (transverse) direction.

Figure 3.4 Cross-section of a rectangular channel-waveguide that can confine optical field in two directions, namely x (lateral) and y (transverse).

The 2-dimensional (2-D) wave equation can be expressed in the terms of the $\vec{E}$ field by Equations (3.21) [3-6],[3-8].

$$\frac{\partial^2 E_x}{\partial x^2} + \frac{\partial^2 E_x}{\partial y^2} + (k_0^2 n^2 - \beta^2) E_x = 0 \quad (3.21)$$

Similarly, the 2-D wave equation can be expressed in the terms of the $\vec{H}$ field by Equations (3.22) [3-6],[3-8]:

$$\frac{\partial^2 H_x}{\partial x^2} + \frac{\partial^2 H_x}{\partial y^2} + (k_0^2 n^2 - \beta^2) H_x = 0 \quad (3.22)$$

The above two equations generally cannot be solved analytically but requires numerical treatment. Several techniques for the numerical and semi-analytical solution have been studied [3-10],[3-11]. There are a few approximate analytical approaches to solve the problem (e.g. [Marcatilli, Bell Syst. Tech. J. 48, 2071 (1969)] [3-12]-[3-19]). While being quite economical with computational resources, their applicability is limited by the approximations they rely on. More versatile methods are usually based on finite element or finite difference approximations of Maxwells equations [3-20]-[3-31], or beam propagation techniques [3-32]-[3-36]. Others expand the electromagnetic fields into sets of orthogonal functions [3-37]-[3-40], [3-41]. One of the most popular modelling method is the Beam Propagation Method (BPM) [3-43]-[3-44]. Two classes of the beam propagation method (BPM) exist. The original method uses fast Fourier transform-BPM (FFT-BPM) whereas the more recent one uses finite difference BPM (FD-BPM) method and it is found to be more efficient and stable when compared to the FFT-BPM [3-45]. The author has used the FD-BPM provided by Optiwave Systems Inc and the basic theory can be found in user reference of BPM [3-46] and more information on BPM are available in [3-47]-[3-52]. Using OptiBPM, the simulations can be carried out in two ways. One way is 3 - dimensional (D) version of BPM and another way is combination of the effective index method (EIM) with 2-D BPM [3-5]. For straight channel waveguide designs, the author

will use 3-D mode solver and 3-D isotropic simulation of OptiBPM whereas for photonics functional devices designs like MMI 3dB light splitter and DC, the author will use EIM with 2-D isotropic simulation. In order to solve the system for channel waveguide devices, OptiBPM will apply a mesh to the region where the simulations are performed [3-46]. From the device geometry, each point in the mesh is associated with a refractive index, and has an electromagnetic field. In Chapter 6, the author will present the results of the simulations of the designed channel waveguides and 1×2 MMI 3dB light splitter and 2×2 DC and will also compare with the experimental results. It has been found that they were in good agreement (see Chapter 6 Section 6.5).

3.6 Summary

The three layer planar slab-waveguide, which consists of buffer, cover and waveguiding core layers, was introduced in first section of this chapter as it illustrates the principle of light confinement and propagation in the core layer. For this structure the modal field profiles can be analyzed analytically. The wave equation was established from Maxwell equations and the solutions were analysed for both TE and TM modes. The theoretical aspects of channel-waveguide were introduced and due to the complexity of solving wave equations for channel-waveguides and other photonic devices such as MMI 3dB light splitter and DC in 3-D, the author reviewed some numerical methods to obtain the behaviour of optical field propagation having confinement in two directions and to design photonic devices. Beam propagation method (BPM) was found to be suitable and introduced in this chapter. BPM will be used for the design and analysis of optical field propagation of various photonic channel-waveguide devices in Chapter 6.

Chapter 4

Characterization Techniques

4.1 Introduction

This chapter is devoted to give the understanding of various characterization techniques that were used to comprehensively study sol-gel derived photosensitive germanosilicate films and photonic waveguide devices. The fabrication of the sol-gel derived photosensitive germanosilicate films and photonic waveguide devices will be presented in Chapter 5 and Chapter 6, respectively. In Section 4.2, the author will present the description of thin film characterization techniques to study the optical and physical properties of germanosilicate thin films. In Section 4.3, various imaging techniques are described. Characterization of waveguide devices were carried out by using prism coupler technique and near field optical microscopy and will be described in Section 4.4.

4.2 Thin film characterization techniques

It is very important to have characterization techniques which can provide the in-depth knowledge of optical, structural and physical properties of germanosilicate thin

films. The types of information obtained from these techniques ranges from small-scale information to large-scale. The various parameters to be obtained are optical constants (refractive index (n), absorption coefficient (k), porosity), physical parameters (like thickness, surface roughness) and the knowledge of stoichiometry of the films.

4.2.1 Thin film characterization: Spectroscopy techniques

The author has used many spectroscopy techniques such as Fourier transform infrared (FTIR) spectroscopy, ultraviolet (UV)-Vis spectroscopy, and spectroscopic Ellipsometry (SE) which will be described below.

4.2.1.1 FTIR spectroscopy

It is well known that Infrared (IR) spectroscopy is a powerful tool to study the functional group of materials, irrespective of crystalline or amorphous nature [4-1]-[4-11]. This technique is also widely used to study the structural sites occupied by water molecules and hydroxyl (-OH) groups in oxide glasses [4-8]-[4-11]. The use of IR spectroscopic analysis in this work is to determine different chemical functional groups and -OH groups in the germanosilicate samples.

FTIR refers to the Fourier transform infrared spectroscopy. Unlike a dispersive instrument, FTIR spectrometer collects all wavelengths simultaneously [4-12]. FTIR is advantageous due to its high speed and better sensitivity. FTIR is typically based on a Michelson Interferometer [4-13]; this is shown in Figure 4.1. The interferometer consists of a beam splitter, a fixed mirror, and a mirror that can move back and forth very precisely. IR radiation from the source strikes the beam splitter and separates into two beams. One beam is transmitted through the beam splitter to the moving mirror and the second is reflected off the beam splitter to the fixed mirror. The fixed and moving mirrors

reflect the radiation back to the beamsplitter. Again, half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam directed to the sample and detector. The resulting signal at the detector is called an interferogram (plot of intensity versus moving mirror position). To make identification of the molecular vibrations, an absorption spectrum (plot of intensities versus wavenumbers) is required. The transformation is accomplished by the mathematical process of Fourier transformation which is performed by the means of high speed electronic computer.

Figure 4.1 Schematic diagram of Fourier Transform Infrared spectrometer.

FTIR spectra reported in this thesis were carried out between $2.5\ \mu\text{m}$ to $25\ \mu\text{m}$ ($4000\ \text{cm}^{-1}$ to $400\ \text{cm}^{-1}$) with $1\ \text{cm}^{-1}$ resolution by using Perkin-Elmer Spectrum 2000 spectrometer in transmission mode. Prior to the FTIR measurement of the prepared germanosilicate samples, background spectrum was obtained by using the substrate. The substrate used to obtain the background spectrum was the same as that used for the

samples. The range of wavenumbers from 4000 to 400 cm^{-1} encompasses absorptions by the majority of common functional groups and -OH groups of germanosilicate material system. Some of the expected vibrations bands of germanosilicate system are summarized in Table-4.1.

Table-4.1: Assignment of infrared frequencies related to $\text{GeO}_2\text{:SiO}_2$ [4-6]-[4-11].

Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
425	Si-Si stretching in	300-350 700-800	GeO_4^{2-}
430	Si-O-Si 6membered rings of SiO_4 tetrahedra, symmetric stretching	900-1000	Ge-O
460	Si-O-Si bending mode	1620	O-H bend of water
550	Ge-O-Si /Ge-O-Ge, deformation mode	2100-2250	Si-H
670	Si-O-Ge, deformation mode	1990-2160	Ge-H
776	Ge-(OH) stretching mode	2050-2250, 667,2350	CO_2
800	Si-O-Si, deformation mode	2200-2500	CO
800-850	Si-O-C, symmetric stretching mode	2600-2950	Higher-frequency stretching modes of -OH in the H bonding of Si-O-H
880	Ge-O-Ge ² , antisymmetric stretching mode	2969-2952 2884-2860	- CH_3^1
961	Ge-O-Ge ³ , antisymmetric stretching mode	2912-2949 2843-2861	- CH_2^1
960-1020	Si-O-Ge, antisymmetric stretching ¹	2800-3550	Stretching modes of H_2O
1090	Si-O-Si ² , antisymmetric stretching mode	3350	O-H stretch of water and H--Si-OH
1000-1110	Si-O-C, asymmetric stretching mode	3330-3700	Stretching mode of the free Si-O-H group
1180	Si-O-Si ³ , antisymmetric stretching mode	3000-3800	O-H stretching

¹vs: very strong, ²TO: Transverse Optical, LO³: Longitudinal Optical

4.2.1.2 UV-Vis spectroscopy

Absorbance spectroscopy is a widely used analytical technique. This method involves comparing the light transmitted through air to the light transmitted through germanosilicate samples. UV-Vis absorption spectroscopy was used to obtain information of the absorption spectrum of germanosilicate films at various wavelengths from UV to near infrared (190 - 1100 nm). The purpose of this measurement is to detect neutral oxygen mono-vacancy (NOMV) defect centers (~ 240 nm) and GeE' centers (~ 200 nm) [4-14] in germanosilicate samples.

Schematic representation of UV-Vis spectrometer is shown in Figure 4.2 [4-15]. It consists of a deuterium discharge lamp to generate for UV light and a tungsten-halogen lamp to produce visible and near infrared (NIR) spectra. The instruments automatically swap lamps when scanning between the UV and visible regions. Spectrometer design and optical components are optimized to reject stray light, which is one of the limiting factors in absorbance measurements.

Figure 4.2 Block diagram of UV-Vis spectrometer [4-15].

The absorption spectra of various samples reported in this thesis was measured in a wavelength range from 190 - 1100 nm by Hewlett Packard model HP8453 UV-Vis spectrometer. The maximum resolution of the instrument is 1 nm [4-15].

4.2.1.3 Spectroscopic Ellipsometry

Spectroscopic Ellipsometry (SE) is a non-invasive optical technique for determining the optical constants n and k (refractive index and extinction coefficient respectively), as well as film thickness. The author independently checked film thickness using other measurement technique such as surface profiler, and the two methods agree well within 5 %. This method measures the change in the state of polarization of light upon reflection from the sample surface and determines the ellipsometric parameters Δ & ψ [4-16], [4-17]. These values are related to the ratio of Fresnel reflection coefficients, R_p and R_s for p - and s -polarized light, respectively given by Equation (4.1).

$$\tan(\psi)e^{i\Delta} = \frac{R_p}{R_s} \quad (4.1)$$

Experimental arrangement of SE is shown in Figure 4.3 (a). The light from the light source is polarized by a polarizer and incident to a sample. The reflected light is then transmitted through an analyzer and detected using a detector. The rotation angles of the polarizer and analyzer enable the determination of the phase difference (Δ) and amplitude ratio ($\tan \psi$) of the two components (s and p) of the reflected light. The interaction of polarized light with the sample is shown in Figure 4.3 (b) where a linearly polarized input beam is converted to an elliptically polarized reflected beam.

Figure 4.3 (a) Experimental set-up for spectroscopic Ellipsometry, (b) interaction of light with the sample [4-17].

In this work, Ellipsometric parameters (ψ and Δ) were obtained by J. A. Woollam Company VASE, Inc. spectroscopic ellipsometer using the rotating analyzer. The

measurements were performed at the room temperature with the angle of incidence at 75° and in the wavelength range from 270 to 1700 nm. The ellipsometric parameters are fitted using the Levenberg-Marquardt regression method and the fitting was carried out by using the WVASE32 software package (by J. A. Woollam Inc) to determine the n , k , and thickness (h) of the sample. The fitting procedure involves several steps and is illustrated in Figure 4.4. In this work, the author has used two models namely Lorentz model and Effective Medium Approximation (EMA) for dense germanosilicate thin films and porous germanosilicate thin films respectively as discussed below.

Figure 4.4 Spectroscopic Ellipsometry data analysis [4-17].

The Lorentz model has been selected and one oscillator case was found to work well for the dense germanosilicate thin films developed in this work. The general Equation (4.2) used to describe the Lorentz Oscillator model is [4-17]:

$$\varepsilon = \varepsilon_{\infty} \left(1 + \sum_{j=1}^m \frac{A_j^2}{(E_{center})_j^2 - E^2 + iE\nu_j} \right) \quad (4.2)$$

where ε is Lorentz Oscillator dielectric function, ε_{∞} is an offset term known as high-frequency lattice dielectric constant, for j^{th} oscillator, $(E_{center})_j$ is center energy or bandgap, A_j is the amplitude (strength) of each oscillator. ν_j is vibration frequency (broadening) of the j oscillator. In our case $j = 1$ since only one oscillator was used. E is the photon energy ($= h\nu$), h is plank's constant and ν is frequency of photons.

For the porous films, effective medium approximation (EMA) was used to determine the porosity of the films. A general Equation that describes the EMA model is Equation (4.3) [4-17]:

$$\frac{\varepsilon - \varepsilon_h}{\varepsilon + Y\varepsilon_h} = \sum_{j=1}^m f_j \frac{\varepsilon_j - \varepsilon_h}{\varepsilon_j + Y\varepsilon_h} \quad (4.3)$$

where ε_j is dielectric constant of material j , f_j is volume fraction of material j , ε is dielectric constant of total system, ε_h is dielectric constant of the host material, Y is screening/depolarisation factor (The screening factor equals to $1/3$, which best models a spherical microstructure). The value ε_h assigned to the host dielectric constant depends on which EMA model is being used. The Bruggeman EMA has been selected for our optimization since it is typically used to model random or aggregated structure which can well describe a sol-gel synthesized germanosilicate thin films having pores too [4-18],[4-19]. In this case, two materials of the composite porous films are the germanosilicate (film material) and the air (void).

Finally, the experimental data (ψ and Δ) was compared with the generated values using a comparator function “mean square error (MSE)” which is equivalent to the reduced chi-square (χ^2). The lowest MSE suggests the best agreement between fitting and experimental values. The MSE as described by Equation (4.4), is the difference between experimental data and fitting data [4-17].

$$MSE = \frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{\text{mod}} - \psi_i^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}} \right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}} \right)^2 \right] = \frac{1}{2N - M} \chi^2 \quad (4.4)$$

where σ is the standard deviation, N is the total number of (ψ , Δ) pairs, M is the number of “fit parameters”, “*exp*” and “*mod*” signifies experimental and fitting values respectively.

4.2.2 Thin film characterization: Structural techniques

In this section, the author will describe the characterization techniques such as X-ray Diffraction (XRD), micro-Raman Spectroscopy (MRS), and Surface Profiler for the investigation of structural properties of prepared germanosilicate thin film samples.

4.2.2.1 X-ray Diffraction (XRD)

X-rays are electromagnetic radiation having wavelength of about 1 Å (10^{-10} m). This is non-destructive technique and does not require any sample preparation for the measurement. The amorphous nature of the prepared germanosilicate samples was confirmed by using X-ray diffraction (XRD).

When a beam of X-ray impinges on a crystalline material, diffraction pattern is obtained when the reflection from successive planes interfere constructively. Conversely,

there will be no diffraction pattern if the scattered X-rays interfere destructively. In principle, the well known Bragg's Law is the condition for diffraction from atomic planes with spacing d , and is given by: $m\lambda = 2d \sin\theta$ (shown in Figure 4.5), where θ is the angle between the atomic planes and the incident X-ray beam and m is the order of diffraction. A schematic diagram of the XRD experimental setup is shown in Figure 4.6 [4-20]. The main components of the XRD are X-ray source, sample holder, and detector. The incident angle θ is defined as the angle between the incident beam and the sample, and 2θ defined as the angle between the incident and diffracted beams. Resultant diffraction pattern (the intensity of the diffracted beams as a function of 2θ) can be used to identify any crystalline phases.

Figure 4.5 Reflection of X-rays from two planes of atoms.

Figure 4.6 Experimental setup of XRD [4-20]

Siemens D5005 X-ray Diffractometer system [4-20] with Copper- $K\alpha$ source was used to determine the presence of any type of crystalline phase arise in germanosilicate films as a result of high temperature annealing. Samples were scanned at 40 kV, 40 mA for 10 to 80° having 2θ with the steps of 0.05.

4.2.2.2 Micro-Raman spectroscopy

Raman spectroscopy is used to determine vibrational energies of the molecular due to change in the polarizability [4-21]. The Micro-Raman spectroscopy (MRS) was used to determine the crystalline phase associated with the signature of Si-O-Si or Ge-O-Ge in germanosilicate.

This is basically the measurement of wavelengths and intensities of inelastically scattered light from molecules. The Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations (phonons). There are two types of the scattered light. The first one is having energy less than the incident light called Stokes scattering and the second one is having energy more than the incident light called anti-Stokes scattering. The wavenumber of the Stokes and anti-Stokes scattering are a direct measure of the vibrational energies of the molecule. Micro-Raman spectroscopy (MRS) was used to confirm the amorphous nature of the dense germanosilicate thin film together with the XRD measurement as there is no crystalline signature peak of Si-O-Si or Ge-O-Ge.

The MRS by Renishaw Ramanscope [4-21] using argon ion laser at 514 nm was used for the Raman measurement within the range of 100 - 1200 cm^{-1} .

4.2.2.3 Profilometer: Surface profiler

To determine the film thickness, the author has used the surface profiler. The surface profiler operates by lightly dragging a sharp stylus across a sample surface and records the topological profile. Stylus is a small feeler-needle that comes in contact with the surface and moves up and down. The signal generated by the motion of the stylus tip is used to create profile of the surface. Figure 4.7 (a) shows surface profiler and Figure 4.7

(b) shows the scan trace measurement across deep etched trench acquired with stylus profiler.

Figure 4.7 (a) Scanning hardware of the surface profiler machine, (b) Scan trace measurement by surface profiler.

In this work, DekTak profilometer was used to get the accurate film thickness. A step pattern was obtained in the horizontal span of 500 μm .

4.2.3 Rutherford backscattering

Rutherford backscattering (RBS) technique provides depth profile of the concentration of different atoms within sample. Normally high energy Helium ions, in the order of MeV, are used as a primary beam in RBS. The resulting scattering due to columbic repulsion between the Helium ion and the target nucleus is called Rutherford backscattering. The number of scattered ions and their energy is measured. This data provides information on the composition of the sample, the distribution of those components and the thickness of the sample without the need of any standard sample for

comparison. In this work, RBS technique was used to establish creation of oxygen deficiencies in prepared germanosilicate films when illuminated by UV irradiations (this is discussed in Section 5.5 of Chapter 5).

Figure 4.8 illustrates an ion with mass M_1 and energy E_0 impinging a solid consisting of an atom with mass M_2 . If θ_s is the scattering angle, then the energy E_1 of the back scattered ion is given by the following Equation: $E_1 = K.E_0$, where K is the kinematic factor given by the relation in Equation (4.5) [4-22];

$$K = \frac{\left\{ M_1 \cos \theta_s + (M_2^2 - M_1^2 \sin^2 \theta_s)^{1/2} \right\}^2}{(M_1 + M_2)^2} \quad (4.5)$$

Figure 4.8 Atomic model [4-22].

Once the incident ion and the angular position of the ion detector are selected, K depends on the atomic weight of the target atom. The RBS experiments in this work were performed by the instrument which used 2 MeV He+ beam with a 2.5 mm diameter spot size [4-23]. Spectra were acquired at backscattering angles of 160° with samples mounted

in an optimally ion channeled orientation. For an example, a graph is shown in Figure 4.9 which illustrates the RBS spectrum of our germanosilicate ($0.2\text{GeO}_2:0.8\text{SiO}_2$) thin film samples.

Figure 4.9 Experimental (black) and simulated (red) RBS energy vs backscattered yield spectra of $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin film on Si.

Using RUMP computer simulation program [4-24], the composition and depth distribution of elements are determined from the energy distribution of these ions. In Figure 4.9, the area under the spectral peak represents the total number of atoms of a given element and the peak height (H) represents the atomic concentration. RBS technique was used in this work to determine the film thickness and the content of silicon, germanium and oxygen in the prepared thin films. The RBS results were analyzed and will be

presented in Chapter 5. The sensitivity of this instrument for light masses is poor and this technique was found to be unsuitable to detect hydrogen and boron.

4.3 Imaging techniques

The imaging techniques such as atomic force microscopy, optical microscopy, and the scanning electron microscopy were used to characterize the prepared films and described below in the subsequent sections.

4.3.1 Atomic force microscope

Atomic Force Microscope (AFM) was used to measure the surface roughness of the prepared germanosilicate films. Surface roughness will cause scattering of the light propagating in the films which leads to additional propagation loss in the waveguide device.

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the sample surface. In principle, a probe or “tip” is placed very close to the sample as shown in Figure 4.10. Tip is deflected by atomic forces exerted by sample. This force can be attractive or repulsive. The tip radius of curvature is typically $< 400 \text{ \AA}$. Variation of the surface height will cause variation in the deflection of the cantilever. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes and provide roughness value in nm range.

In this work, Scanning Probe Microscope by digital instruments (Dimension 3000) with a Nanoscope IIIa control module was used in tapping mode to measure the surface roughness of the prepared samples. The focusing of laser beam on the cantilever was

performed before taking the measurement. The accuracy in root mean square (rms) value of the surface roughness was 0.1 nm [4-20].

Figure 4.10 Measurements by atomic force microscope.

4.3.2 Optical microscopy

NIKON optical microscope was used to observe the surface quality of prepared films. The optical microscopy was used specifically during the multilayered germanosilicate slab-waveguide fabrication. The optical microscope was found to be useful to detect if particles were landed during deposition which could spoil the quality of the prepared films.

4.3.3 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to observe the surface topography of the germanosilicate films and to inspect the presence of cracks in lateral and cross sectional view of the germanosilicate slab-waveguides.

A schematic diagram of scanning electron microscope is shown in Figure 4.11. Electrons thermionically emitted from a tungsten source are drawn to an anode and focused by successive condenser lenses into a very fine spot size. Scanning coils located at the objective lens deflect the beam either linearly or raster over a rectangular area of the specimen surface. The energetic electrons strike the sample and various reactions can occur as illustrated in Figure 4.12 [4-25]. Secondary electrons were detected by the semiconductor detector and the variation in the intensity of these secondary electrons gives a contrast on the screen and shows the surface topography of the sample.

Figure 4.11 Scanning electron microscope [4-25]. Figure 4.12 Sample interaction [4-25]

In this work, the author has used JEOL JSM-5600LV SEM to investigate the morphology of the surface and cross-section edge of the prepared slab waveguides. To detect small features like porosity in the films, field emission scanning electron microscope (LEO 982 Digital FESEM) was used. The image contrast was obtained using

secondary electron mode with an accelerating voltage ~ 3 KV. The scanning electron microscopy requires a conducting sample to avoid a build-up of charges by the electrons impinging the samples. So in order to study non-conducting germanosilicate samples, the author had coated a thin layer of platinum on the surface of the samples.

4.4 Waveguide device characterization techniques

In this section, the author will describe the experimental techniques used to characterize germanosilicate slab-waveguides and direct UV-imprinted photonic waveguide devices. The prism coupler technique was used to measure the properties of the planar germanosilicate slab-waveguides such as refractive index, thickness and propagation loss. Near field optical microscopy (NFOM) was used to investigate the modal-field distribution at the output of prepared photonic waveguide devices.

4.4.1 Prism coupler technique

The prism coupler technique [4-26]-[4-34] is the most commonly used technique to characterize planar slab-waveguide properties such as refractive index, thickness and propagation loss [4-27],[4-29],[4-32]. This technique was employed because of its inherent advantage of high coupling efficiency (up to 80% for a Gaussian beam), applicability to the planar waveguides and selective excitation of any of the guided modes. Figure 4.13 (a) shows a schematic diagram of the prism coupling measurement set-up. The laser beam is incident onto the base of the prism at an angle θ_1 . If θ_1 is large enough this beam is total-internally-reflected at the prism base onto a detector. This wave has propagation constant $\beta_1 = k_1 \sin \theta_1$ [4-33]. At certain discrete values of the incident angle

θ_1 , called mode angles (θ_p), the evanescent wave extends beyond the base of the prism into the space (d_p) separating the waveguide sample and the prism [4-32],[4-33]. The field will then be coupled to the waveguide sample and therefore causing a sharp drop in the intensity of light reaching the detector, as illustrated in Figure 4.13 (b).

Figure 4.13 (a) Prism coupler arrangement, (b) measure of intensity pattern by the detector [4-32].

The effective index (n_{eff}) of the waveguide propagation mode can be obtained by Equation (4.6) [4-34]:

$$n_{eff} = n_p \sin (\alpha + \sin^{-1} (\sin(\theta_p)/n_p)) \quad (4.6)$$

where θ_p is coupling angle, n_p is refractive index of prism, and α is the angle of prism. The actual value of refractive index and thickness of waveguiding layer can be further obtained from the measured effective index (n_{eff}) value through dispersion equation [4-34].

The measurement was performed by using Metricon 2010 prism coupler as illustrated in Figure 4.14 (a). This setup has two different wavelength sources which are HeNe laser at $0.6328\ \mu\text{m}$ and Laser Diode at $1.55\ \mu\text{m}$. A prism of refractive index 2.4 was used in the measurements. Figure 4.14 (b) shows the sample is mounted for the prism coupling arrangement to determine the refractive index and thickness. The pressure of the waveguide against the base of the prism was adjusted in order to adjust the air gap to improve the coupling efficiency. A precision rotation stage was used which allows the variation in angle of incident beam with respect to the waveguide. The accuracy in refractive index measurements was obtained to be 0.0005 when the films supported two or more modes [4-32].

Figure 4.14 (a) Metricon 2010 prism coupler apparatus [4-32], (b) germanosilicate slab-waveguide placed for the mode detection in prism-coupler configuration.

Loss measurement by the prism coupler technique: The propagation loss of optical slab-waveguides was measured by using the moving fiber arrangement of Metricon. In this method, the exponential decay of light is measured by a fiber probe moving along the

length of propagating beam. The equation which describes the decay of light in waveguide is given by Equation (4.7):

$$I(x) = I_0 \exp(-\alpha x) \quad (4.7)$$

where α is the attenuation coefficient per unit length, I_0 is the initial power, x is the distance, $I(x)$ is the transmitted power through a waveguide at distance x . The assumption in this measurement is that the intensity at any point in waveguide sample is proportional to the scattered intensity. The intensity profile as a function of scanning distance was recorded by a computer. The part of the scanned distance was selected for the calculation of propagation loss by avoiding obvious peaks caused due to scratches, particles, or other surface imperfections. Loss in dB/cm is then calculated by a least squares fit to the intensity data and the resulting exponential fit is superimposed over the intensity profile. Figure 4.15 shows the prism coupler arrangement for the waveguide loss measurement using HeNe laser.

Figure 4.15 Prism coupler set-up for waveguide propagation loss measurement of a germanosilicate slab-waveguide.

4.4.2 Near-field optical microscopy technique

Near-Field Optical Microscopy (NFOM) technique was used to investigate the modal field distribution at the output of the prepared waveguide devices. In NFOM, the near-field is the region away from the waveguide which is typically in the order of a nanometer or less than the wavelength of incident light [4-35]-[4-38]. Figure 4.16 shows the schematic of the measurement of near field optical images using NFOM technique. The experimental setup was done by the author and shown in Figure 4.17.

Figure 4.16 Block diagram of optical mode imaging by near field optical microscopy.

Referring to Figure 4.17, the power was launched from tunable laser source (TLS) into the fiber and an inline polarization controller (P) was used to maintain the correct polarization of light. In the experimental setup shown in Figure 4.17, the author has used 2.5 mW of optical power at 1.55 μm from the ANDO TLS with Newport F-POL-IL fiber polarization controller. The polarized light was launched into the direct UV-imprinted

waveguide device samples (channel waveguides, power splitter and directional coupler which will be presented in Chapter 6) from single-mode optical fiber in a butt-coupling configuration. The near field output profiles and the images were obtained by focusing CCD camera on to waveguide devices using 10X objective lens. A Beamstar infrared-camera attached with the computer was used with a beam profiler to capture the modal-field distributions.

Figure 4.17 Measurement setup of the near field optical microscopy.

Since the optical fiber was used to launch laser light, the output profile of the optical fiber was characterized. In order to do this, the polymer coating of optical fiber was stripped off and the end of optical fiber was cleaved properly. Figure 4.18 (a) shows the schematic of the geometry of optical fiber. The optical mode-field diameter (MFD) (illustrated in Figure 4.18 (b)) of the optical fiber was characterized by the NFOM set-up. Mode-field diameter

is a measure of the spot size or beam width of light propagating in a single-mode fiber. Mode-field diameter is a function of source wavelength, fiber core diameter, and core and cladding refractive difference. The author has used optical fiber which is single-mode at $1.55\ \mu\text{m}$, core diameter $\sim 8.2\ \mu\text{m}$ and cladding diameter $\sim 125\ \mu\text{m}$ having refractive index difference of 0.36 % [4-39]. A 10X objective lens was used to focus the end of the cleaved optical fiber. An image was captured using a CCD infrared-camera (IR Beam star camera) and recorded in a computer. Figure 4.19 shows the optical image and corresponding intensity distribution profile at the output of the optical fiber. The author found that the lateral optical intensity distribution is single mode at $1.55\ \mu\text{m}$ having MFD of $10.8\ \mu\text{m}$. This value of MFD is similar to the given value of the fiber in use. This measurement also ensures that no higher order modes will affect the measurement.

Figure 4.18 (a) Geometry of optical fiber, (b) light distribution in a single-mode optical fiber.

Figure 4.19 (a) Near field image from the cleaved single-mode optical fiber, (b) Near field profile of the corresponding image.

4.4 Summary

This chapter presents the description of various characterization techniques used to analyze and characterize the properties of the planar germanosilicate films and germanosilicate photonic waveguide devices (slab waveguides, channel waveguides, power splitter and directional coupler which will be presented in Chapter 6). The techniques described in this chapter are Fourier transform infrared spectroscopy, spectroscopic Ellipsometry and UV-Vis spectroscopy, X-ray diffraction, Micro-Raman spectroscopy, Surface profiler, Rutherford back scattering, Optical microscopy, Atomic force microscopy, Scanning electron microscopy, Prism coupler and Near field optical microscopy.

Chapter 5

Sol-Gel Derived Photosensitive Germanosilicate Thin Films

5.1 Introduction

Fabrication of densified and optically high quality inorganic oxide films is required for the development of low loss waveguide devices. This Chapter is devoted to present the preparation of ultraviolet (UV) photosensitive $\text{GeO}_2\text{:SiO}_2$ thin films by the sol-gel method. Firstly in Section 5.2 of this chapter, the detailed preparation schemes of solutions starting from the alkoxide precursors are described. The details of the film synthesis via spin-coating method and the heat treatment (annealing) processes are also given in the same section. In the sol-gel process when GeO_2 (germania) is mixed with SiO_2 (silica) at a molecular level, Ge atoms randomly substitute Si atoms in SiO_4 tetrahedral and the microstructure of the film is continuous three-dimensional network consisting of interconnected SiO_4 and GeO_4 tetrahedral [5-1],[5-2]. The fabrication process was developed to obtain dense, amorphous $x\text{GeO}_2\text{:}(1-x)\text{SiO}_2$ films and also high germania concentration to obtain highly photosensitive inorganic $x\text{GeO}_2\text{:}(1-x)\text{SiO}_2$ films without the problem of clustering and crystalline phases. As described in Chapter 2, the characteristics

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and the properties of sol-gel synthesized material systems are influenced by a number of factors. The author has investigated the densification temperature of the sol-gel derived thin films and optimized the dopant concentration (x -value) for the dense amorphous thin films of $x\text{GeO}_2:(1-x)\text{SiO}_2$ for $0.05 \leq x \leq 0.3$, and will be described in Section 5.3. The level of the solution pH is the factor that directly controls the polymerization growth and aggregations of the species throughout the transition from sol to gel. Therefore, the properties of the germania doped silica (germanosilicate) thin films were investigated and optimized as a function of various pH levels and will be presented in the same Section 5.3.

The UV KrF laser at 248 nm has been used as a source to introduce changes of refractive indices in our sol-gel synthesized thin film samples. In Section 5.4, the refractive index change of prepared germanosilicate thin films under various UV illumination times and laser energies pulses will be presented. Further, the investigation of UV photosensitive mechanism in germanosilicate system will be described in Section 5.5.

5.2 Preparation of germanosilicate thin films by sol-gel process

Germanosilicate thin films were prepared by using the sol-gel process as shown schematically in Figure 5.1. A homogeneous, transparent and stable solution was prepared by using alkoxide precursors such as Tetraethoxysilane (TEOS, molecular formula: $\text{Si}(\text{OC}_2\text{H}_5)_4$, 99.99% purity from Aldrich) for silica (SiO_2) and Tetrapropoxygermane (TPOG, molecular formula: $\text{Ge}(\text{OC}_3\text{H}_7)_4$, 99.99% purity from Chemat Technology Inc.) for germania (GeO_2).

To prepare a silica solution, the TEOS and ethanol (EtOH) were mixed in 1:1 by volume ratio and continuously stirred using a magnetic stirrer for about 15 minutes.

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Various catalyzed solutions were prepared by varying the acid (HNO_3) quantity in water (H_2O) to investigate the optimum level of pH. These catalyzed solutions were added to the TEOS and EtOH mixture to obtain different pH levels from 1 to 6, and named as sol-S. The level of pH in the sol-S was measured by using a Cyberscan pH2000 pH meter supplied by Eurotech with the combination of glass electrodes from Orion Research Inc. The catalyzed solution to alkoxides molar ratio (R value) was maintained at 2. The sol-S was continuously stirred for 30 minutes under room temperature.

To prepare the germania solution, the TPOG and isopropanol (IPA) were mixed in 1:1 volume ratio and continuously stirred for about 10 minutes. This solution is named as sol-G. No catalysts were used here because TPOG is very reactive. Furthermore, all the reactions were performed in a dry glove box maintained at relative humidity (RH) of 13-15 %, which was achieved by continuously flushing the dry box with dry nitrogen gas.

Sol-G and sol-S were mixed to get $x\text{GeO}_2:(1-x)\text{SiO}_2$ composition (sol-SG) and vigorously stirred. Before the mixing of sol-S and sol-G another portion of ethanol (50 % - 80 % by volume) was added to sol-S. The dilution would make the final sol (sol-SG) transparent to last a few hours without turning milky. The final sol-SG was aged for about 40 minutes and would remain suitable for deposition on a solid substrate within span of few hours. After about 8 hours to 10 hours span of aging the transparent solution turned into a milky gel and cannot be used for spin-coating.

Figure 5.1 Flow-chart of the sol-gel process for germanosilicate thin film preparation.

In this work, $x\text{GeO}_2:(1-x)\text{SiO}_2$ thin films were prepared with different molar concentrations of germania dopant ($x = 0, 0.05, 0.1, 0.15, 0.20, 0.25$ and 0.30). Variation in the concentration of germania was necessary to determine the composition at which problem of clustering and crystallinity starts.

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The prepared sol-SG was dispensed using a syringe fitted with a $0.1\ \mu\text{m}$ filter onto substrates. The substrates used were [100] oriented, highly resistive ($12\text{-}16\ \Omega\text{-cm}$) p-doped (Boron) Si wafer of $5000\ \mu\text{m}$ in thickness and silica plates of $1\ \text{mm}$ thickness. The silica plate substrates were normally used for UV-Visible transmission measurement study. The author performed the spin-coating process at room temperature in the dry glove box (RH $\sim 13\text{-}15\%$) by using Laurell WS-400-LITE spin-coater as shown in Figure 5.2 (a). A typical spin coating consists of four stages. After delivering the liquid to the substrate, centrifugal forces drive the liquid across the substrate (spin-up). The excess liquid leaves the substrate during spin off. When flow in the thin coating is no longer possible, evaporation takes over to further reduce the film thickness [5-3]. Various stages of spin-coating are summarized below as shown in Figure 5.2 (b). The wafer was spun on a spin-coater at a constant speed of $\sim 2500\text{ - }3000\ \text{rpm}$ for ~ 30 seconds in a dry glove box maintained at RH of $\sim 15\%$ under room temperature.

(a)

(b)

Figure 5.2 (a) Spin-coater equipment, (b) various stages of spin-coating process.

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Subsequent heat treatment processing is required to achieve full densification for the evaporation of solvent, removal of water, removal of residual hydroxyls and organics and collapse of pores [5-4],[5-5]. The spin-coated films were heat treated in JIPELEC rapid thermal processor (RTP). The heat treatment program in the JETFIRST processor is shown in Figure 5.3. The heat treatment was performed in the presence of O_2 . During heat treatment, the $-OR$ or $-OH$ react with the O_2 to form CO_2 (gas) or H_2O (gas). Lastly, viscous sintering driven by energy gained by reduction in surface area of a porous body leads to dense films [5-5]-[5-7]. In this work, the annealing temperature was varied from 500 to 1000 °C in steps of 100 °C.

Figure 5.3 RTP program for the heat treatment process.

5.3 Development of densified germanosilicate thin films

In this section, the author will present the optimization results of the densification temperature, the dopant composition of germania and also the sol pH level. To optimize the annealing temperature of densification, the films of $0.2GeO_2:0.8SiO_2$ composition has

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been prepared with the sol of pH level ~ 3 . Such films have optimum germania contents ($x = 0.2$) with no clustering and crystallinity. The details investigations on optimum composition and optimum pH level will be presented in Section 5.3.1 and Section 5.3.2 respectively.

To investigate the trend of effective elimination of hydroxyl bond, the author varied the annealing temperature in the range of 500 to 1000 °C. Figure 5.4 shows the Fourier transform infrared (FTIR) spectra between 4000 - 400 cm^{-1} of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films annealed at various temperatures from 500 to 1000 °C. The relevant peaks are labeled in the Figure 5.4 [5-7]-[5-11]. The Si-OH stretching band around 900 cm^{-1} is visible only in case of films annealed at 500 °C. The -OH stretching band around 3400 cm^{-1} , magnified in the inset, decreases in intensity with increasing annealing temperature.

Figure 5.4 FTIR spectra of $0.2\text{GeO}_2:0.8\text{SiO}_2$ films annealed at various temperatures, inset showing variation in the band of -OH stretching vibration.

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The -OH stretching band disappeared at 900 °C and 1000 °C. This shows that at 900 °C and 1000 °C annealing temperature the films are -OH free. The shoulder around the 980 cm^{-1} is the assignment of Si-O-Ge bonds [5-9],[5-10]. No absorption peak corresponding to organic radicals are visible. From the FTIR results it can be concluded that the inorganic 0.2GeO₂:0.8SiO₂ thin film become -OH free at 900 °C and above.

The refractive indices of 0.2GeO₂:0.8SiO₂ thin films were investigated using the Spectroscopic Ellipsometry (SE). The porosity value was derived from the refractive index (n) of the films. The refractive index and the porosity were used to evaluate the complete densification of the 0.2GeO₂:0.8SiO₂ films [5-12]-[5-14]. Figure 5.5 shows the structure of a 0.2GeO₂:0.8SiO₂ thin film on a Si substrate. This structure was used for the modelling by using the WVASE32 package. As shown in the Figure 5.5, SiO₂ layer was also incorporated in between the layer of Si substrate and 0.2GeO₂:0.8SiO₂ layer because annealing the films at higher temperature may result in the growth of SiO₂ to about 20 to 40 Angstrom.

Figure 5.5 Physical layer model for Spectroscopic Ellipsometry.

The optical constants (n and k) of the densified films were obtained by using a Lorentz oscillator (single) model (LOM) and the porosity of the porous films was obtained

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using the Bruggeman effective medium approximation (EMA) (see Section 4.2.1.3 of Chapter 4). As an example, fitting results of experimental and the theoretical values of the film annealed at 1000 °C is shown in Figure 5.6. Various parameters of the Lorentz oscillator used in the modelling are tabulated in Table-5.1.

Figure 5.6 Spectroscopic Ellipsometry fitting results.

Table-5.1: SE fitting parameters for sample annealed at 1000 °C

Parameters	ϵ_{∞}	$(E_{\text{center}})_j$ (eV)	A_j	ν_j	MSE
Single oscillator model ($j = 1$)	1.699 ± 0.279	8.3516 ± 0.3	33.972 ± 6	0.01 ± 0.003	3.9

Figure 5.7 shows the plot of the refractive index (n) of the films annealed from 500 °C to 1000 °C as a function of various wavelength (270 – 1600 nm). The variation of the n at 0.630 μm and 1.55 μm and the variation of porosity with the annealing temperature are shown in the inset of Figure 5.7. It is observed that the n increases with increasing annealing temperature from 500 to 900 °C. From 900 to 1000 °C, the index is relatively

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constant at about 1.4894 ± 0.0004 at $0.630 \mu\text{m}$. The n value at $0.630 \mu\text{m}$ is similar to the bulk value of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ germanosilicate system estimated using the linear approximation ($n = 1.49$) [5-1]. Following the behaviour of the n value with the increasing annealing temperature, porosity decreases with the increase in annealing temperature and reaching lowest porosity at 900°C and above. This result shows that the films are densified when annealed at 900°C and above, which is consistent with the previous FTIR results. Furthermore, the absorption loss (α) was estimated to be 0.432 dB/cm by using $\alpha = 4\pi k/\lambda$ (at $\lambda = 1550 \text{ nm}$), from the extinction coefficient ($k = 0.533 \times 10^{-5}$) derived from the LOM.

Figure 5.7 Refractive indices of $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films at various annealing temperatures, inset showing the refractive index value and film porosity at various annealing temperatures.

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The film thickness obtained by the SE was confirmed by using the step profiler technique. For the step profiler measurements, the sample having steps was used (see Section 4.2.2.3 of Chapter 4). These steps were visible under the SEM image (see Section 4.3.3 of Chapter 4) as shown in the Figure 5.8. Variation in the film thicknesses of $0.2\text{GeO}_2:0.8\text{SiO}_2$ as a function of annealing temperature is shown in Figure 5.9 and the obtained thickness was $0.232\text{ }\mu\text{m}$ at $500\text{ }^\circ\text{C}$. The shrinkage of the films was resulted due to the increase in annealing temperature. The thickness of the film annealed at $900\text{ }^\circ\text{C}$ and above was about 30 % less than the thickness of the films annealed at $500\text{ }^\circ\text{C}$.

Figure 5.8 SEM image showing the contrast due to steps.

Figure 5.9 Thickness variation of $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films as a function of annealing temperatures.

Field emission scanning electron microscope (FESEM) technique (see Section 4.3.3 of Chapter 4) was used for the structural investigations of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films annealed at various annealing temperatures and shown in the Figure 5.10. As shown in Figure 5.10 (a), some structures were observed on the surface of the film annealed at

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500 °C, probably due to the presence of organic components because 500 °C is a relatively low temperature to burn off the organic components. It seems hard to determine the pores even at low annealing temperature of 700 °C and 800 °C. Although some striation marks are visible in case of film annealed at 800 °C. Film annealed at 900 °C shows pores free fairly smooth surface.

Figure 5.10 FESEM images of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films annealed at various temperatures (a) 500 °C, (b) 700 °C, (c) 800 °C (d) 900 °C.

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Surface morphology of the films were studied by the Atomic Force Microscopy (AFM) (see Section 4.3.1 of Chapter 4) and the images are shown in Figure 5.11 (a) and (b) for the film annealed at 900 °C and the film annealed at 500 °C respectively. AFM measurements reveal sub-nanometer roughness for all the films annealed at various temperatures, the root mean square (rms) surface roughness values are summarized in Table 5.2. The roughness value was found to be quite small ~ 0.390 nm for the films annealed at 900 °C and above, this shows that the surface is very smooth.

Figure 5.11 3-D surface images ($1 \times 1 \mu\text{m}$) of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films (a) annealed at 900 °C, (b) annealed at 500 °C.

Table-5.2: Roughness of $0.2\text{GeO}_2:0.8\text{SiO}_2$ films annealed at various temperatures.

Annealing temperatures (°C)	RMS roughness (nm)
500	2.757
700	2.179
800	0.987
900	0.390
1000	0.387

This concludes the optimum annealing temperature 900 °C and above, leads to a densified inorganic 0.2GeO₂:0.8SiO₂ films having low absorption loss and having fairly smooth surface. Thus, from the above results the author has successfully established the sol-gel process to produce high optical quality films which is suitable for photonic waveguide devices.

5.3.1 Determination of optimum dopant concentration (x -value) in $x\text{GeO}_2:(1-x)\text{SiO}_2$

In this section, the author will describe the results for establishing the optimum dopant concentration (x -value) for the dense amorphous thin films of $x\text{GeO}_2:(1-x)\text{SiO}_2$, for $0.05 \leq x \leq 0.3$.

As shown in previous section, -OH band (4000 - 2800 cm⁻¹) in FTIR spectra was used to obtain the densification temperature for 0.2GeO₂:0.8SiO₂. Similarly, the author has optimized the annealing temperature for the fabrication of dense films having different compositions of $x\text{GeO}_2:(1-x)\text{SiO}_2$, for $0.05 \leq x \leq 0.3$. The densification temperature was found to be different with the different concentration of GeO₂ and shown in Figure 5.12 (a). It can be seen that increase in GeO₂ concentration (x value) results in noticeable decrease in annealing temperature. This behaviour is obvious because germania has lower melting point than silica and so, the higher the concentration of germania, the lower the densification temperature will be.

Figure 5.12 (b) shows the FTIR spectra in the range of 1600 - 400 cm⁻¹ of the densified $x\text{GeO}_2:(1-x)\text{SiO}_2$ films, for $0.05 \leq x \leq 0.3$ and all the prominent peaks are assigned as Si-O-Si (1080 – 1200 cm⁻¹ and ~ 460 cm⁻¹), Si-O-Ge (960 – 1020 cm⁻¹) and Ge-O-Ge (900 – 980 cm⁻¹) [5-8]-[5-11]. It can be seen from the Figure 5.12 (b) that in the case of $x = 0.25$ and $x = 0.30$, a noticeable increase in peak intensity of FTIR vibrations

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around $900 - 980 \text{ cm}^{-1}$ and it overlaps with the FTIR vibrations $960 - 1020 \text{ cm}^{-1}$. This suggests that for the germania concentration of $x = 0.25$ and $x = 0.30$, there is a difficulty in conversion to Ge-O-Si linkages due to the formation of Ge-O-Ge clusters and therefore such compositions must be avoided.

Figure 5.12 (a) Annealing temperature for the removal of -OH in $(x)\text{GeO}_2:(1-x)\text{SiO}_2$ thin films (b) FTIR spectra of $(x)\text{GeO}_2:(1-x)\text{SiO}_2$; for $0.05 \leq x \leq 0.30$.

Formation of crystalline phase is always found to be associated with the higher germania concentration in silica [5-1][5-2]. In order to fabricate dense amorphous $x\text{GeO}_2:(1-x)\text{SiO}_2$ system for the purpose of photonic waveguide device application, the film should be free from any crystalline phase because crystallinity leads to the scattering of light propagation. X-ray diffraction (XRD) and micro-Raman measurements (see Section 4.2.2.1 and 4.2.2.2 of Chapter 4) were used to reveal the presence of signature peaks of crystalline GeO₂ of various $x\text{GeO}_2:(1-x)\text{SiO}_2$ thin films for $0.05 \leq x \leq 0.30$.

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Figure 5.13 (a) shows the XRD spectra of the dense films of $x\text{GeO}_2:(1-x)\text{SiO}_2$ at $x = 0.30, 0.25$ and 0.20 . As shown in the figure, for $x = 0.30$ and 0.25 , the author has observed the peaks around 2θ of 24° which indicate the signature of GeO crystalline phase [5-15]. At $x = 0.20$, no peak was observed corresponding to any crystalline phase of GeO, hence this composition can be used to form the amorphous dense films at 900°C and 1000°C . Micro-Raman spectra of the dense films of $x\text{GeO}_2:(1-x)\text{SiO}_2$ at $x = 0.30, 0.25$ and 0.20 are shown in Figure 5.13 (b). The two peaks $\sim 520\text{ cm}^{-1}$ and $\sim 950\text{ cm}^{-1}$ are clearly visible in all the cases, which correspond to the crystalline Si substrate but a peak $\sim 300\text{ cm}^{-1}$ is visible only in the case of $x = 0.30$ and 0.25 which corresponds to the signature of GeO [5-16]. Similar to the XRD results, the micro-Raman study also revealed that the prepared densified films are indeed amorphous for $x = 0.20$. It is obvious that for the value of x below 0.20 , the dense films are indeed amorphous.

Figure 5.13 (a) XRD spectra of $(x)\text{GeO}_2:(1-x)\text{SiO}_2$ thin films, (b) micro-Raman spectra of $(x)\text{GeO}_2:(1-x)\text{SiO}_2$, $0.02 \leq x \leq 0.3$: (i) $x = 0.30$, (ii) $x = 0.25$, (iii) $x = 0.20$ (annealed at 900°C), (iv) $x = 0.2$ (annealed at 1000°C).

From the above results, the densified films of germanosilicate ($x\text{GeO}_2:(1-x)\text{SiO}_2$, $0.05 \leq x \leq 0.3$) having germania in excess to $x = 0.20$ found to be associated with the clustering and crystallinity. Certainly such films cannot be used for photonic device fabrication because it will produce high scattering loss at propagation wavelength. Thus, the most promising binary system of germania and silica is $0.2\text{GeO}_2:0.8\text{SiO}_2$ which can produce amorphous thin films even at annealing temperature 900°C and 1000°C .

5.3.2 Influence of sol pH level on the properties of $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films

It is known that the pH of the sol influence the growth of particles [5-7],[5-17]. Therefore, the author has investigated the variation of the sol pH level to obtain the $0.2\text{GeO}_2:0.8\text{SiO}_2$ densified films. The $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films were prepared by the same scheme as shown in Figure 5.1, by using the sol-S of different pH level ranging from 1 to 6. The densification and the properties of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films were studied at two different temperatures of 700°C and 900°C . The -OH contents in the thin films were estimated from the intensity of the -OH absorption band of the FTIR spectra ($4000 - 2800\text{ cm}^{-1}$). FTIR spectra of the thin films prepared with different pH values (ranging from 1 to 6) and annealed at 700°C are shown in Figure 5.14 (a). The peak intensities of -OH stretching band around 3400 cm^{-1} of the films annealed at 700°C and 900°C are plotted as a function of the sol pH levels in Figure 5.14 (b). It can be seen from the Figure 5.14 (b) that the samples annealed at 700°C have higher -OH content than the samples annealed at 900°C . In the case of 700°C , the intensity of -OH stretching band first decreases from pH ~ 1 to pH ~ 3 and then increases rather sharply till pH ~ 5 , after that there is a slight increase till pH 6. For the films annealed at 900°C , the intensity of the -OH stretching band also decreases from pH ~ 1 till pH ~ 3 and then increases sharply till pH ~ 4 , after that there is a slight increase in intensity till pH ~ 6 . The data in Figure 5.14

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(b) shows that the minimum -OH stretching band occurs at pH ~ 3 for both the films annealed at 700 °C and 900 °C. For the film annealed at 900 °C, the -OH stretching band at pH ~ 3 has disappeared and saturates at the pH level of 4 and above.

These results demonstrate that the dehydroxylation of germanosilicate films can be facilitated by varying the pH values. In this work, a dense and high quality film is obtained at annealing temperature of 900 °C with pH ~ 3.

Figure 5.14 (a) FTIR spectra showing the -OH stretching vibration band of samples prepared at different pH level ranging from 1 to 6, and annealed in RTP at temperature = 700 °C, (b) change in the intensity of the IR absorption due to -OH variation in germanosilicate thin films at different pH levels, and annealed at two different temperatures of 700 °C and 900 °C.

The change in optical properties such as refractive index and porosity were also analyzed as a function of pH level. The refractive indices at 0.630 μm and at 1.55 μm of the thin films prepared at various pH levels were obtained for both 700 °C and 900 °C

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annealing temperatures and are shown in Figure 5.15 (a). It is observed that the refractive indices of the films annealed at 900 °C are clearly shown to be higher than those annealed at 700 °C. We noticed that for the films annealed at 700 °C, there is a gradual rise in the refractive index value of ~ 0.0038 from pH ~ 1 to pH ~ 3 . After this pH level of 3, there is a sharp decrease of the index value of 0.0112 till pH ~ 5 and a slight decrease of the index value thereafter till pH ~ 6 . For the films annealed at 900 °C, there is also an increase in the index value of ~ 0.0029 from pH ~ 1 to pH ~ 3 , but this rise is not as sharp as that compared to the films annealed at 700 °C. Thereafter, till pH ~ 6 there is a decrease in the index value of ~ 0.0151 with a decrease till pH ~ 5 being relatively sharper. The index rise from pH ~ 1 to pH ~ 3 suggests that there is an increase in the film densification from pH ~ 1 to pH ~ 3 . The refractive index of the germanosilicate thin films prepared at pH ~ 3 and heat treated at 900 °C ($n = 1.4887 \pm 0.0004$) have nearly the same refractive index values as the films annealed at 1000 °C ($n = 1.4894 \pm 0.0004$). This saturation in the index value with an increase in the annealing temperature from 900 °C and above has a similar index value to the bulk value of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ germanosilicate system estimated using a linear approximation ($n = 1.49$) [5-1]. Thus, we can say that a highly densified film can be obtained at pH ~ 3 at an annealing temperature of 900 °C. The porosity values of the films annealed at 700 °C and 900 °C for various pH levels were obtained using the EMA (see Section 4.2.1.3 of Chapter 4) and are shown in Figure 5.15 (b). The trend of the porosity as a function pH is identical to the results obtained by FTIR spectroscopy (See Figure 5.14 (b)). The behavior can be explained in terms of the accelerated growth of particles with an increase in pH [5-17]. The increase of the sol pH results in an increase in particle sizes and the formation of larger particles leads to the larger pore sizes [5-7],[5-17]. From pH ~ 1 to pH ~ 3 , the particles grow reaching an optimum size at pH ~ 3 , where all the particles are nicely packed and fitted together resulting in -OH-free and zero

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porosity films. From our experiments, we observe that the refractive index of the –OH-free film annealed at 900 °C is highest and the porosity is lowest at pH ~ 3. Thus, at pH~3, a packed structure of germanosilicate with –OH free and zero porosity is obtained. Beyond pH ~ 3, the particles continue to grow with increasing pH values. The particle size is now larger than the optimum value and may not fit together resulting in the porosity. Consequently, the refractive index becomes smaller and the –OH bonds would exists. This is exactly what we observe in Figure 5.15 (a) and Figure 5.14 (b). Beyond pH ~ 3, the refractive index decreases with increasing pH values (see Figure 5.15 (a)) and the –OH content increases with increasing pH values (see Figure 5.14 (b)). Furthermore in Figure 5.15 (b), we observe that the film porosity increases beyond pH ~ 3 and saturates at pH ≥ 5, and this may indicate that the growth of the particle size will saturate at pH ≥ 5.

Figure 5.15 (a) Variation of refractive index at 0.630 μm and 1.55 μm of samples prepared at different pH level and annealed at 700 °C and 900 °C, (b) porosity behavior as function pH level different pH levels and annealed at 700 °C and 900 °C (porosity data error $\leq \pm 0.01\%$).

The above experiments show the fabrication of –OH-free and fully densified 0.2GeO₂:0.8SiO₂ thin films (prepared at pH level ~ 3 and annealed at 900 °C) with no porosity. In addition, it has been noticed that the surface roughness of thin films prepared with pH ~ 3 has lower value than the other thin films at different pH levels. The dense films prepared with pH ~ 3 and annealed at 900 °C have the lowest surface roughness ~ 0.390 nm.

5.4 Photosensitivity of 0.2GeO₂:0.8SiO₂ thin films

To investigate the photosensitivity (change of n) of the 0.2GeO₂:0.8SiO₂ films, the prepared thin films was illuminated directly by UV irradiations by using a KrF excimer laser source at $\lambda = 248$ nm. The experimental set-up is shown in Figure 5.16. The detail of the KrF laser source is described in Appendix [I] [5-18]. The beam-splitter indicated in the figure was not used in our work. A sample holder was used to mount the samples and placed in front of the laser for the direct UV illumination. The area of exposure was the spot of the laser which was rectangular shaped with dimensions approximately 25 mm by 11 mm for the major and minor axes, respectively (see Appendix [I]). The laser has the maximum output energy up to 450 mJ per pulse, therefore in our work we have used laser energy of 450 per pulse or lower. There are other variables of laser setting such as frequency and exposure time. In this work, the frequency was kept constant at 10 Hz, and the exposure time was varied. To stabilize the samples after UV exposure, heat treatment of ~ 140 °C were performed under vacuum which is termed here as post-bake [5-19]-[5-21].

Figure 5.16 Experimental setup for the direct UV- illumination.

After UV treatment, the refractive indices of the films have been observed to increase by an amount of Δn . The variation of Δn at 1.55 μm with UV exposure time (from 1 to 20 minutes) when irradiated by 450 mJ per pulse energy for various samples annealed at different temperature is shown in Figure 5.17 (a). It is observed that Δn increases significantly after 1 minute UV-exposure. Beyond 1 minute, the increase is very small and roughly linear with exposure time. Furthermore, we observe that Δn is higher for the films annealed at higher temperature. We can observe that there is very small difference between the value of Δn for the sample treated at 900 $^{\circ}\text{C}$ and with that for sample treated at 1000 $^{\circ}\text{C}$. For the dense films, Δn is 0.0094 and 0.0098 for the samples annealed at 900 $^{\circ}\text{C}$ and 1000 $^{\circ}\text{C}$ respectively. We see that the value of Δn does not change significantly for the dense samples. To our knowledge, such a large change in n in inorganic germanosilicate thin film prepared by sol-gel has not been reported yet.

The author has also investigated the variation in Δn of dense samples (sample treated at 1000 $^{\circ}\text{C}$) at 1.55 μm with UV exposure time (from 1 to 20 minutes) for different

UV irradiation energies (250, 350 and 450 mJ per pulse), and shown in Figure 5.17 (b). It is observed that Δn increases significantly with the increase in UV irradiation energy.

Figure 5.17 (a) Comparison of Δn at 1.55 μm for the 0.2GeO₂:0.8SiO₂ samples prepared at various annealing temperatures when irradiated by 450 mJ per pulse energy for different illumination time, (b) Comparison of Δn at 1.55 μm for the dense 0.2GeO₂:0.8SiO₂ films (sample treated at 1000 °C) when illuminated at different laser energy and time.

From the above results, the author conclude that the highly photosensitive sol-gel derived 0.2GeO₂:0.8SiO₂ films developed here can give UV induced refractive index changes (Δn) in the range of 10^{-3} to about 10^{-2} which is large enough for the development of photonic waveguide device fabrication by direct UV-imprinting.

5.5 Mechanisms of photosensitivity of 0.2GeO₂:0.8SiO₂ thin films

In the section above, the author has shown the large UV induced Δn in 0.2GeO₂:0.8SiO₂ film fabricated by the sol-gel technique as developed in this work. Here, the author will discuss the mechanism of UV induced refractive index change.

We firstly consider the optical absorption spectra of the films annealed at various annealing temperatures as shown in Figure 5.18. For the as-deposited film annealed at 500 °C, there is an absorption peak at ~ 240 nm (see Figure 5.18-(i)), due to the Ge-Ge/Ge-Si bonds, which are known as neutral oxygen monovacancy (NOMV) [5-22],[5-23]. As-deposited film annealed at 900 °C and 1000 °C, the NOMV absorption at ~ 240 nm is significantly lower, which indicates that the NOMV has been much reduced (see the Figure 5.18-(iv) and (v)). Our results show that the NOMV absorptions decrease with increasing annealing temperature, which means the films become more stoichiometric. This is not surprising since the annealing was performed in O₂ environment. This behavior is also observed by Zhang et. al. [5-22].

Figure 5.18 UV absorbance spectra of the films annealed at different temperatures.

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For the porous films (i.e. the films annealed below 900 °C), after UV illumination, the NOMV absorption band at ~ 240 nm is bleached and followed by the increase in the absorption at ~ 200 nm. Figure 5.19 (a) - (i) to (v) shows the change in optical absorption spectra for various illumination time for the films annealed at 500 °C to represent our porous films.

Figure 5.19 (a) UV absorbance spectra of the sample annealed at 500 °C showing the bleaching of band around 240 nm and simultaneously increase in intensity towards shorter wavelength region at various UV light illumination (UVLI), and (b) the UV absorption spectra of the sample annealed at 1000 °C showing the increase in intensity towards shorter wavelength at various UVLI.

This process is well known, which is due to the conversion of Ge-Ge/Ge-Si bonds (NOMV) to GeE' or SiE' centers (~ 200 nm) by the UV illumination. This process is expressed by Equation (5.1) [5-22],[5-24]-[5-26].

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The increase of the refractive index (Δn) associated with the reduction of NOMV and formation of GeE' or SiE' centers is small, roughly about 10^{-4} [5-24],[5-27],[5-28]. Figure 5.19 (b) - (i) to (v) show the optical absorption spectra for the films annealed at 1000 °C (to represent dense sample) after UV illumination. We observe there is significant change in the absorption intensity $\sim 200\text{nm}$ after the UV illuminations even in the absence of NOMV for the dense sample. This might be attributed to two photon absorption demonstrated by Masahide Takahashi et.al. in their sol-gel prepared germanosilicate system irradiated by UV [5-24]. Briefly, in the two photon absorption, the photo-ionized Ge^{2+} (Germanium lone pair center; GLPC) forms Ge-O bond with the nearby non-bridging oxygen (NBO) to neutralize the positive charge under UV illumination [5-25]. The final product of this process will also be the GeE' centers as described by Equation (5.2) [5-24],[5-25].

Again, the reported increase in Δn in the two photon absorption is also in the order of $\sim 10^{-5}$ - 10^{-4} [5-25]. Overall, the two mechanisms discussed above only gives small contribution, in the order of 10^{-4} , to the large Δn (in the order of 10^{-3}) observed in our experiment. For the porous samples (films annealed below 900 °C), we observe that the -

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OH stretching band around 3400 cm^{-1} decreases with increasing UV illumination time. This is illustrated in Figure 5.20 for the sample annealed at $500\text{ }^{\circ}\text{C}$ to represent our results. The results suggest that the porous germanosilicate system have been densified in some extent by the UV illumination which is also demonstrated by Jae Hyeok Jang et.al. [5-29].

Figure 5.20 FTIR spectra of porous film annealed at $500\text{ }^{\circ}\text{C}$ at different UVLI.

For the densified films (films annealed at $900\text{ }^{\circ}\text{C}$ and above), we could not observe further densification by the UV illumination. The UV illumination, however, has induced an absorption band around 620 cm^{-1} to 740 cm^{-1} , shown in Figure 5.21. We notice that the absorption band increases significantly after 1 minute UV exposure time and then increases slowly from 1 to 20 minutes. This behavior is consistent with the change of the refractive index with the UV exposure time as shown in Figure 5.17 (a).

Figure 5.21 FTIR spectra of dense $0.2\text{GeO}_2:0.8\text{SiO}_2$ samples, UV illuminated for different time, inset shows the change occurs in structural band due to different UV exposure time.

5.5.1 Formation of oxygen deficiency defects

To investigate the mechanism that is responsible for the large refractive index change (Δn), the following experiments were carried out by the author. As shown in Figure 5.21, the UV irradiation has induced an absorption band around $620 - 740\text{ cm}^{-1}$ in FTIR spectra. To examine the UV induced absorption band around $620 - 740\text{ cm}^{-1}$, the 20 minutes UV illuminated dense samples were separately heat treated at $900\text{ }^\circ\text{C}$ for 1 hour in two different atmospheres, namely oxygen and inert argon atmospheres. The FTIR spectra in Figure 5.22 (a) shows that the induced absorption band around $620 - 740\text{ cm}^{-1}$ of the samples heat treated in the oxygen atmosphere has disappeared (see Figure 5.22 (a) - (iv)), whereas the absorption band of the samples heat treated in the inert argon atmosphere still remains (see Figure 5.22 (a) - (iii)). Figure 5.22 (b) shows the refractive indices of the samples corresponding to those in the FTIR spectra in Figure 5.22 (a).

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Figure 5.22 (a) Change in the structural band of 20 minutes of UV illuminated dense sample after different post annealing treatment, (b) refractive index (n) of dense samples at $1.55 \mu\text{m}$ with UV treatment and post annealing treatment in oxygen and argon environment.

The reduction of the UV induced absorption band at $\sim 620 - 740 \text{ cm}^{-1}$ of the samples heat treated in oxygen atmosphere shown in Figure 5.22 (a) - (iv) is accompanied with the decrease of the refractive index from 1.4841 ± 0.0004 to 1.4765 ± 0.0005 shown in Figure 5.22 (b) - (ii) and (iv). For the sample annealed in inert atmosphere, however, the refractive index remains unchanged; it is still the same as that after UV irradiation (see Figure 5.22 (b) - (ii) and (iii)). From our data in Figure 5.22 (b), we also note that although the refractive index of the 20 minutes UV illuminated dense sample has been lowered by 1 hour annealing in oxygen at $900 \text{ }^{\circ}\text{C}$, it could not be completely reversed to its original value. This is not due to the annealing effect, since it is still higher than the refractive index of the non-UV illuminated dense sample annealed in oxygen atmosphere at $900 \text{ }^{\circ}\text{C}$ for 1 hour (see Figure 5.22 (b) - (iv) and (v)). This is possibly due to the structural changes

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caused by the UV illumination which could not be completely reversed by the annealing. These results suggest that the UV illumination has induced oxygen deficiency in the sol-gel derived dense germanosilicate sample causing large refractive index change of about 0.009.

To confirm the formation of oxygen deficiency the Rutherford Backscattering (RBS) measurements were performed. RBS is an analysis technique that produces a depth profile of the concentration of different atoms within a sample. Here, this technique was used to determine the oxygen content in the films. Figure 5.23 shows the variation in the oxygen contents of the dense sample by the UV treatment and the heat treatment at 900 °C in two environment conditions namely Argon and Oxygen. These values are obtained from the RBS analysis as described in Section 4.2.3 of Chapter 4.

Figure 5.23 Oxygen content variations with UV treatment and post annealing heat treatment in oxygen environment and argon environment.

It is observed that after the 20 minutes of UV illumination the oxygen contents of dense germanosilicate film are reduced from 0.67 to 0.648. The oxygen contents in our stoichiometric films are quite similar to the published value [5-30]. The heat treatment in oxygen rich environment at high temperature of 900 °C reverts back the oxygen contents to 0.663 whereas the heat treatment in Argon environment at 900 °C does not alter the oxygen contents and keep it as 0.649. The RBS analysis together with the refractive index analysis as presented above (see Figure 5.23) strongly suggests the creation of oxygen deficiency upon UV illumination. We also have the data to indicate that the high refractive index change due to this oxygen deficiency is stable, as there is no sign of the degradation of the refractive index change for long period of time (more than a year).

5.5.2 Effect of annealing temperatures on photosensitivity of $0.2\text{GeO}_2:0.8\text{SiO}_2$ films

From the above results, the high refractive index change in sol-gel derived germanosilicate material films is due to the creation of oxygen related deficiency. This phenomenon is likely related to the low bond strength (strain bonds) of sol-gel derived germanosilicate materials densified at 900 °C to 1000 °C. In order to investigate whether this oxygen deficiency is related with the strength of the bonds within the material system the following experiment was performed and described below.

In order to relax the bonds linkage within the sol-gel derived germanosilicate material system annealed at 900 °C to 1000 °C, the prepared films were further annealed at 1100 °C, 1200 °C and 1300 °C for 1 hour. These films were then illuminated by the UV light for 20 minutes with the laser energy of 450 mJ per pulse. Figure 5.24 shows the refractive index n of films annealed at various annealing temperature and their corresponding UV induced refractive index values. It is observed that the Δn for the films

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annealed at 1100 °C, 1200 °C and 1300 °C does not change but, for the films annealed at 1000 °C, the change in UV induced refractive index is appreciable. Similarly, from the FTIR spectra the author do not observe any change in the region of $620\text{ cm}^{-1} - 740\text{ cm}^{-1}$ of the films after the UV exposure of the films annealed at 1100 °C, 1200 °C and 1300 °C that is why not shown here. These results suggest that the photosensitive changes are related to the bond strength of material and highly dependent upon the annealing temperature.

Figure 5.24 Refractive index variations as a function of annealing temperature.

5.5.3 Effect of GeO₂ concentration on the photosensitivity of $x\text{GeO}_2:(1-x)\text{SiO}_2$

In order to ascertain that the presence of germanium is necessary to induce photosensitivity in the sol-gel derived germanosilicate films, a film without the dopant GeO₂ (i.e. pure SiO₂) was also prepared. To investigate the refractive index change behaviour under the UV illumination as a function of GeO₂ concentration, the author considered the amorphous and dense films having different concentration of GeO₂ in $x\text{GeO}_2:(1-x)\text{SiO}_2$, for $0 \leq x \leq 0.2$. The refractive index of $x\text{GeO}_2:(1-x)\text{SiO}_2$ is a function of GeO₂ concentration (x), which is well approximated as a linear function, as seen in Figure 5.25 (a). When the refractive index is extrapolated to pure GeO₂, the refractive index is 1.61, which agrees well with the refractive indices of thin films of GeO₂ as reported in the literature [5-1]. The refractive index of the GeO₂ doped SiO₂ films can be controlled by the amount of GeO₂ doping, i.e. the higher the GeO₂ concentration, the higher the refractive index. Figure 5.25 (a) also shows the bandgap variation of $x\text{GeO}_2:(1-x)\text{SiO}_2$ as a function of GeO₂ concentration (x) and shows good agreement with the published values.

The $x\text{GeO}_2:(1-x)\text{SiO}_2$ films, for $0 \leq x \leq 0.2$, were exposed to KrF laser with an energy of 450 mJ per pulse for 20 minutes. Figure 5.25 (b) shows the variation in Δn with different GeO₂ concentration in SiO₂. It can be observed clearly that, firstly, no change in Δn was observed in the case of pure silica which corresponds to $x = 0$ in $x\text{GeO}_2:(1-x)\text{SiO}_2$ and, secondly, Δn increases with increasing germania concentration for $0.05 \leq x \leq 0.2$. From the above results, it can be concluded that UV induced refractive index changes in germanosilicate occur due to the presence of GeO₂.

Figure 5.25 (a) Refractive index variations as a function of germania concentration, (b) UVLI of 450 mJ energy for 20 minutes induced Δn variation as a function of germania concentration.

In conclusion, the results reported here enable us to fabricate low loss PIC by single step direct UV-imprinting technique, potentially replacing the conventional photolithography and etching technique.

5.5.4 Effect of hydrogen loading to the photosensitivity of 0.2GeO₂:0.8SiO₂ films

From the literature review in Section 2.5.4.1 of Chapter 2, the author understands that hydrogen loading enhances the UV induced refractive index change $\sim 10^{-3}$ in germanosilicate material system [5-31],[5-32]. In this section, the author will describe the results of photosensitivity of hydrogen loaded sol-gel derived films.

The samples used in the experiments were prepared at an optimum composition of 0.2GeO₂:0.8SiO₂ by using the same preparation scheme as demonstrated in Figure 5.1. To investigate the effects of the hydrogen-loading, the films annealed at 700 °C, 800 °C and

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900 °C were soaked in a hydrogen (H₂) atmosphere at 1600 psi for 15 days at room temperature. To study the photosensitivity, the hydrogen loaded films were irradiated by 248 nm KrF laser with repetition rate of 10 Hz and energy of 450 mJ per pulse for 20 minutes. To stabilize the refractive index change, the UV exposed samples were post annealed under vacuum for an hour at 140 °C.

The author has investigated the effect of hydrogen loading on –OH contents of the different films. Figure 5.26 shows the FTIR spectra in the range of 2800 – 4000 cm⁻¹ for the films annealed at various annealing temperatures of 700 °C, 800 °C and 900 °C. The effect of hydrogen-loading and UV-treatment on the film can be seen from the –OH stretching band centered around 3400 cm⁻¹ in the case of porous samples (films annealed at 700 °C and 800 °C), as shown in Figure 5.26 (a) and Figure 5.26 (b). Obviously this band is absent for the film annealed at 900 °C as shown in Figure 5.26 (c).

In Figure 5.26 (a) and (b), the author observed the increase in –OH absorption band after the hydrogen loading. This is expected because the diffused hydrogen in the germanosilicate system will result in more hydroxyl bonds. During hydrogen loading, hydrogen is incorporated in germanosilicate structure to form the hydroxyl and hydride bonds [5-33] as described below:

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Figure 5.26 FTIR spectra related to -OH band ($2800 - 4000 \text{ cm}^{-1}$) of UV light illuminated (UVLI) and non-UV illuminated, with and without hydrogen-loaded samples at different annealing temperatures; (a) annealing temperature at 700 °C, (b) annealing temperature at 800 °C, (c) annealing temperature at 900 °C.

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Upon UV exposure, there is a clear reduction of -OH intensity for the porous samples (see Figure 5.26 (a)–(iv) and Figure 5.26 (b)–(iv)). This is not observed for the sample annealed at 900 °C since the sample is dense.

Another band of interest is between 400 and 1400 cm^{-1} , where the network structural bonds are found. Figure 5.27 shows the FTIR spectra in the range of 400 – 1400 cm^{-1} of the films annealed at various annealing temperatures of 700 °C, 800 °C and 900 °C. Figure 5.27 also shows the effect of hydrogen-loading and UV-treatment on FTIR spectra of the films annealed at various annealing temperatures of 700 °C, 800 °C and 900 °C. The relevant peaks are labelled in the figures (see Figures 5.27 (a) to Figures 5.27 (c)). The signature peak of Si-H bond is around 500 - 600 cm^{-1} [5-34]. For all samples, the author observed that the absorption around 500 - 600 cm^{-1} increases after the hydrogen loading, which indicates the formation of Si-H bonds after the hydrogen treatment as given in Equation (5.3) (see Figures 5.27). After UV illumination, the Si-H peaks for all the samples are no longer observable.

The formation of Si-H and Ge-H bonds after the hydrogen-loading, and subsequent elimination of these bonds after UV exposure, is thought to be responsible for the enhancement of UV induced refractive index change (as compared with the samples without the hydrogen-loading). This is very likely since the change in refractive index (Δn) after UV exposure is generally explained in terms of the bleaching of the Si-Si/Ge-Ge bonds (defects) followed by the formation of GeE' or SiE' centres as described by Equation 5.2.

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Figure 5.27 FTIR spectra in the range of $400 - 1400 \text{ cm}^{-1}$ of UV light illuminated (UVLI) and non-UV illuminated, with and without hydrogen loaded samples at different annealing temperatures; (a) annealing temperature at 700°C , (b) annealing temperature at 800°C , (c) annealing temperature at 900°C .

The UV induced Δn for the as-deposited samples annealed at various temperatures and the hydrogen-loaded samples are shown in Figure 5.28. The values of Δn of the hydrogen-loaded samples are slightly higher as compared to those of the as-deposited samples annealed at different temperatures. For the dense samples (the samples annealed at 900 °C), the values of Δn of the as-deposited and hydrogen loaded samples are 0.0094 ± 0.0002 and 0.0096 ± 0.0002 , respectively.

Figure 5.28 Refractive index change (Δn) after the UV light illumination (UVLI) of as-deposited samples annealed at various temperatures and the hydrogen loaded samples.

Therefore, from the above results, we can see that the hydrogen loading does not enhance the Δn significantly, since we have obtained relatively high values of Δn , about 0.0094, for the as-deposited dense films. This high Δn for the as-deposited films is explained in terms of the UV-induced oxygen related deficiency as described in Section 5.5.1. For this reason, hydrogen loading in sol-gel derived dense films does not necessarily contribute to the photosensitivity. Furthermore, the hydrogen detected in the films will cause absorption loss at $\sim 1.55 \mu\text{m}$ which is undesirable for the waveguide devices.

5.6 Summary

High optical quality photosensitive thin film were prepared and studied to develop the optical devices by direct UV-imprinting. The sol-gel process has been developed to obtain the optimum concentration of dopant GeO_2 in SiO_2 without clustering and crystallization. The optimized concentration of GeO_2 in SiO_2 is 0.2 and used for further developments. Detail investigations of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ thin films annealed at various temperatures, in the range of 500 °C to 1000 °C, were performed to optimize the densification temperature. The increase in annealing temperature results in the decrease of -OH band in the Fourier transform infrared (FTIR) spectra. At 900 °C and above, no -OH was observed. From the Spectroscopic Ellipsometry (SE) results, the refractive index saturation was achieved for the films annealed at 900 °C and above. Therefore, this indicates that the films annealed 900 °C and above are fully densified. The pH level of the sol in the range of 1 to 6 was varied and the optimum pH level ~ 3 was found to give minimum porosity at annealing temperature of 900 °C. For the densified films, the X-ray diffraction and micro-Raman measurement shows no crystallization. For densified films; the surface roughness was also found to be very small ~ 0.390 nm and indicates that the films have fairly smooth surface.

The photosensitivity in sol-gel derived samples of GeO_2 doped SiO_2 was investigated extensively. The UV KrF laser at 248 nm has been used to induce the change in the refractive index of the samples. The UV irradiation on the $0.2\text{GeO}_2:0.8\text{SiO}_2$ film samples show the increase in n . The author has achieved a large refractive index change (Δn) of 0.009 after UV illumination in excess of one minute for our dense germanosilicate films. The increase in Δn with the increasing illumination time shows that Δn can be controlled simply by varying the time of UV exposure. The Δn increases with the increase

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in energy of UV laser source and the highest change in Δn was measured to be 0.009 for 450 mJ/pulse. To our knowledge, this was the largest UV-induced refractive index change reported at the time and resulted in a patent application and international journal papers.

A number of mechanisms have been proposed to explain the photosensitivity, including the already known color-center model and densification model. Neutral oxygen monovacancy (NOMV) having the absorption around 240 nm was observed only in the case of porous samples as shown in the UV-Vis absorption spectra. The conversion of NOMV (absorption around 240 nm) defects to GeE' and SiE' centers (absorption around 200 nm) after UV exposure was also observed for the porous samples. For the stoichiometric dense samples, UV radiation has also increased the absorption at 200 nm, this is possibly due to the conversion of Ge²⁺ defects to GeE' centers by the two photon absorption mechanisms. However, the conversion of Ge²⁺ defects to GeE' centers alone cannot account for the high value of $\Delta n \sim 10^{-2}$ as obtained in our case. So it is clear that other processes must occur. FTIR spectra revealed that UV illumination has induced absorption band $\sim 620 - 740 \text{ cm}^{-1}$ in the case of densified samples. The UV induced band $\sim 620 - 740 \text{ cm}^{-1}$ were investigated and attributed to the creation of oxygen deficiency. The Rutherford backscattering analysis has also indicated the creation of oxygen deficiency upon UV illumination.

UV exposure on the sol-gel derived dense pure silica film suggests that the Δn is due to the presence of GeO₂ dopant in SiO₂. The Δn value increases with the increase in germania concentration from $x = 0.05$ to $x = 0.2$. Furthermore, the sol-gel derived 0.2GeO₂:0.8SiO₂ did not require hydrogen-loading in order to exhibit photosensitivity. Post baking process after UV treatment reveals that the obtained Δn is stable over time.

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From the optical constant measurement, the absorption coefficient of the UV treated and non-treated densified films were estimated to be 0.445 & 0.432 dB/cm respectively.

In conclusion, the author has successfully developed sol-gel derived photosensitive $0.2\text{GeO}_2:0.8\text{SiO}_2$ films. It has been shown in this chapter that germanium doped silica films deposited by sol-gel exhibit large photosensitivity when exposed to UV irradiation, without the need for any type of enhancement technique. The results presented here have shown the sol-gel deposition of doped silica films is a promising technology to fabricate optical waveguide at $1.55\text{ }\mu\text{m}$ with the low propagation loss. Furthermore, the photosensitivity of $0.2\text{GeO}_2:0.8\text{SiO}_2$ thick films are presented in the next Chapter 6 that were used for the development of several photonic waveguide devices by the direct UV-imprinting technique.

Chapter 6

Development of Photonic Devices

6.1 Introduction

In the previous chapter (Chapter 5), the author has successfully developed good optical quality and highly photosensitive germanosilicate thin films. For a single layer film of about 200 nm thick, the ultraviolet (UV) irradiation induced refractive index change was obtained to be about 0.009. This result opens the possibility to fabricate photonic devices by single-step direct UV-imprinting technique.

Optical propagation in integrated photonic devices is conveyed through optical channels with dimensions of a few micrometres, both in depth and in width. Planar slab-waveguides are the base for the development of photonic devices. In Section 6.2 and Section 6.3, the author will present the development and characterization of efficient planar slab-waveguides respectively. In Chapter 5, high UV induced refractive index change was obtained for the germanosilicate thin films and here the investigation on photosensitivity will be extended for the thick germanosilicate films. In order to fabricate the channel waveguides by the single-step direct UV-imprinting technique, the photosensitivity of thick germanosilicate films (approximately $\sim 3 \mu\text{m}$) in the form of slab-

waveguide were evaluated and will be presented in Section 6.4. The photosensitivity in germanosilicate planar slab-waveguides was further developed for channel waveguides, power splitter and optical power switch which will be presented in Section 6.5. In order to fabricate the photonic devices, the author has designed the aforementioned photonic devices using Optiwave software. The optical field distributions were also evaluated by using the beam propagation method. A comparison between the theoretically and experimentally obtained results of modal field distributions will also be provided.

6.2 Fabrication of germanosilicate planar slab-waveguides

As described in the Chapter 5, the spin-coated sol-gel derived amorphous $0.2\text{GeO}_2:0.8\text{SiO}_2$ (germanosilicate) thin films with relatively low material absorption losses of about 0.432 dB/cm and high UV induce refractive index change opens the path for development of channel waveguide devices. In this section, the author will firstly describe the schematic fabrication scheme for optically high quality planar slab-waveguides with low propagation loss. This development of planar slab-waveguides was aimed to achieve single-mode guiding at 1.55 μm . Si wafers having $\sim 10\text{ }\mu\text{m}$ thick silica layer were used as substrates ($10\text{ }\mu\text{m SiO}_2/\text{Si}$). The thick layer of silica has double purposes: to provide a low refractive index region to allow light confinement and also to prevent the penetration of optical field in the highly absorbing silicon substrate. Therefore, this layer is called a buffer layer.

The waveguide core is formed by deposition of few-micron thick layer of a germanosilicate film which of course has higher refractive index than silica. The author fabricated few-micron thick germanosilicate layer by iterative deposition of the several

thin layers of germanosilicate [6-1]-[6-3]. The detailed fabrication process is shown in Figure 6.1. The solution preparation scheme and the sol pH are the same as those described in Section 5.2 (of Chapter 5). In the iterative spin-coating deposition, each layer was annealed at 900 °C on a 10 μm SiO_2/Si substrate. The multilayer germanosilicate was heat treated at 1000 °C for one hour in electric furnace to consolidate the thick film. The purpose of this thermal treatment is to homogenize or equalize the properties of the multilayer film. This multilayer waveguide preparation scheme leads to good quality thick films by eliminating the residual organic solvents, -OH and water content in each layer during the depositions. Removal of such undesirable matters was found to be necessary to make a low absorption loss guiding layer. The author performed 16 layers of spin-coating to build $\sim 3 \mu\text{m}$ thickness to achieve the single-mode guiding at 1.55 μm .

Schematic diagram of planar slab-waveguide is shown in Figure 6.2. The waveguide has a $\sim 3 \mu\text{m}$ thick germanosilicate waveguiding core layer (refractive index n_1) deposited on a buffered Si substrate with a $\sim 10 \mu\text{m}$ thick Silica (SiO_2) layer (refractive index n_2).

Figure 6.1 Flow-chart of the entire sol-gel process for the fabrication of germanosilicate planar slab-waveguides.

Figure 6.2 Schematic diagram of germanosilicate planar slab-waveguide.

The author has used scanning electron microscopy (SEM) technique to examine the cross-section and surface of the planar germanosilicate slab-waveguide. Figure 6.3 (a) shows the SEM image of cross-section of planar germanosilicate slab-waveguide and Figure 6.3 (b) shows the SEM image of a part of the planar germanosilicate slab-waveguide top surface. It is observed that 3 μm germanosilicate layer is free from the micro-cracks having fairly smooth surface.

Figure 6.3 SEM images of germanosilicate planar slab-waveguide (a) cross-sectional image of the multilayer film showing no cracks and sharp edge, (b) surface image of the multilayer film showing no cracks and smooth surface.

This fabrication of thick layer of germanosilicate involved considerable challenge for the author. During the multilayer depositions, the author noticed that the quality of the spin-coated films depends on the cleanliness of the spin-coater. This is mainly due to the high reactivity of germania which can form solid particles very easily, thereby can easily contaminate the successive layer. This problem was overcome by spraying the ethanol. Spraying of ethanol successfully reduced the particles from the inside surfaces of the spin-coater and avoid wafer contamination. For example, Figure 6.4 (a) represents a coated thin film with many particles. This film is obviously unusable for the spin-coating of subsequent layer. Spraying of ethanol has also helped to reduce the striation [6-4]. If thick planar waveguide is prepared by repetitive cycles of deposition, striations are formed on each single layer, leading to cumulative surface roughness. Such striation produces non-uniform films which causes significant surface scattering in the multilayer films [6-4].

Next challenge involved the formation of crack free multilayer films. The author noticed that cracks can appear above a critical thickness due to the generated stress. Figure 6.4 (b) represents a case where six layered film showing cracks on its surface. This happened when the author has not used the step of dilution before the addition of germania dopant. Without the dilution, mixing of Sol-G in sol-S causes gelation faster and make final solution highly viscous. Viscous solution produces thicker film of about 400 nm which was probably more than the critical thickness and result in the evolution of cracks. The cracks shown in Figure 6.4 (b) on to the surface of multilayer film are obviously unusable for waveguide device fabrication.

(a)

(b)

Figure 6.4 Microscopic view of germanosilicate films; (a) particle on the surface of thin film (b) cracks on the surface of multilayer film.

6.3 Characterization of germanosilicate planar slab-waveguides

The optical properties of the smooth and crack free planar germanosilicate slab-waveguides were characterized by prism coupler (Metricon). Figure 6.5 (a) and (b) shows

the measured intensity profile of the planar germanosilicate slab-waveguides at $0.6328\ \mu\text{m}$ in transverse electric polarization (*s*-polarization) and transverse magnetic polarization (*p*-polarization) condition, respectively. From the resonance intensity curve it is clear that the three dip into the curves is a representation of three optical modes at $0.6328\ \mu\text{m}$ propagation wavelength with both the polarization state of propagation wavelength. A similar measurement was performed for the *s*-polarization and *p*-polarization conditions at $1.55\ \mu\text{m}$ as shown in Figure 6.5 (c) and (d). It is observed that the resonance intensity curve showing a single dip which is a representation of single optical mode at $1.55\ \mu\text{m}$ propagation wavelength with both polarization state of propagation. We can see each dip corresponds to an angle value and these values were used to calculate the refractive index and thickness (as described in Section 4.4.1 of Chapter 4). The detailed results are summarized in Table 6.1. The refractive index of the germanosilicate core layer, n_1 , of the planar slab-waveguides at *s*-polarization is $n_{\text{TE}} = 1.4687 \pm 0.0002$ and that of *p*-polarizations is $n_{\text{TM}} = 1.4704 \pm 0.0005$ at $1.55\ \mu\text{m}$. The propagation loss measurement was also carried out using Metricon equipment by employing the moving-fiber method. The intensity profile as a function of scanning distance is shown in Figure 6.6. By using the least square fitting to the intensity data (shown by the dotted line) in Figure 6.6 (a), the author estimated the propagation loss of *s*- polarization at $0.6328\ \mu\text{m}$ was about 1.07 ± 0.2 dB/cm. Similarly, by using the least square fitting to the intensity data (shown by the dotted line) in Figure 6.6 (b), the author estimated the propagation loss of *s*-polarization at $1.55\ \mu\text{m}$ was about 0.26 ± 0.2 dB/cm. Furthermore, the polarization dependent loss (PDL) was also calculated and was found to be less than 0.05 dB/cm. This shows efficient performances of the sol-gel derived germanosilicate planar slab-waveguide which is single-mode at $1.55\ \mu\text{m}$ and has low propagation loss.

Figure 6.5 (a) Resonance intensity curve of germanosilicate slab-waveguide for *s*-polarized and (b) *p*-polarized at $0.6328 \mu\text{m}$, (c) Resonance curve of germanosilicate slab-waveguide for *s*-polarized, and (d) *p*-polarized at $1.55 \mu\text{m}$.

Figure 6.6 Intensity profiles of germanosilicate slab-waveguide for *s*-polarized at (a) $0.6328 \mu\text{m}$, (b) at $1.55 \mu\text{m}$.

Table-6.1: Properties of germanosilicate slab-waveguide measured by prism-coupler.

Number of Layers	16	
Operating Wavelength	0.6328 μm	1.55 μm
Thickness (μm)	3.01 ± 0.04	
Number of modes	3	1
Refractive Indices		
(n_{TE})	1.4838 ± 0.0002	1.4687 ± 0.0002
(n_{TM})	1.4841 ± 0.0004	1.4704 ± 0.0005
Propagation loss (dB/cm)	1.07 ± 0.2	0.26 ± 0.2

6.4 Photosensitive study of germanosilicate planar slab-waveguides

Having obtained good optical quality planar slab-waveguides, the UV induced refractive index change (Δn) of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ core layer of the planar slab-waveguides were investigated. The KrF laser ($\lambda = 248 \text{ nm}$) with energy of 450 mJ/pulse and 10 Hz repetition rate was used to illuminate the slab-waveguides. The experimental setup shown in Figure 5.16 and described in Section 5.4 of Chapter 5 was used to illuminate the samples. The slab-waveguides were illuminated for different time and the UV-induced Δn was measured by the prism coupler method. Figure 6.7 shows the variation of Δn versus UV exposure time for the planar slab-waveguide. As expected, the value of Δn increases with the increase of the exposure time. This shows that we can control the value of Δn by varying the exposure time. It is observed that Δn saturates at the UV exposure time longer than 20 minutes. The tailorability of Δn as a function of UV illumination time will be very helpful for the fabrication of various photonic waveguide devices with different optical field confinement controlled by the values of Δn . Furthermore, the propagation loss values were also measured and were found to be less than 0.5 dB/cm in all cases.

Figure 6.7 Planar slab-waveguide directly exposed to KrF laser ($\lambda = 248$ nm) and refractive index were measured by the prism coupler and the Δn was calculated for various time of UV exposure.

6.5 Development of photonic devices by direct UV-imprinting

Relatively high values of UV induced Δn (larger than 0.002 for 10 minutes illumination) has been obtained for ~ 3 μm thick germanosilicate films and described in Section 6.4 above. These results would allow the author to develop photonic waveguide devices by direct UV-imprinting (DUI) technique. The author will demonstrate the performances of channel waveguides, multimode interference (MMI) based light splitters and directional coupler (DC) fabricated by using the DUI technique. In order to do this, the author will firstly present the theoretical study and design of these devices using OptiBPM software using the Δn values obtained in Section 6.4 (see Figure 6.7). The design parameters have been calculated at commonly used communication wavelength at 1.55 μm . In the next sections, the author will demonstrate the fabrication and

performances of aforementioned photonic devices by using DUI technique and its comparison with the theoretical results.

6.5.1 Theoretical evaluation and design of channel-waveguides

The straight channel-waveguides is a simplest photonic structure to show the applicability of direct UV-imprinting (DUI) to guide the light with 2-dimensional (2-D) optical confinement. This section will provide different characteristics of various channel waveguides. In the design, the author emphasized that the waveguides should remain mono-mode at 1.55 μm in order to easily control of the modal-field distribution and to avoid mode dispersion. If the waveguides were multi-mode, the control of modal fields would be much more complicated, because of the different propagation characteristics of each modal-field.

The author has performed theoretical investigations using 3-dimensional (3-D) isotropic BPM simulation to investigate the dynamic behaviour of optical power along the propagation direction and at the output of channel waveguides. The simulations or studies were performed for various channel widths and values of Δn obtained in Figure 6.7.

6.5.1.1 Design of channel-waveguides

The theoretical design of straight channel waveguides was performed by using the OptiBPM software. The channel waveguides were designed according to the schematic diagram shown in Figure 6.8. As shown in Figure 6.8, the channel waveguides consist of rectangular waveguiding channel of refractive index $n_1 + \Delta n$, side cladding of refractive index n_1 and buffer layer SiO_2 of refractive index n_2 . The refractive index n_1 and thickness of the side cladding was $n_{\text{TE}} = 1.4687$ and 3 μm , respectively, taken from Table-6.1 in

Section 6.3. The author has used s -polarization in the simulations as there is no large difference between n_{TE} and n_{TM} (see Table-6.1). The refractive index $n_2 = 1.456$ and thickness of $10\ \mu\text{m}$ was used for the SiO_2 buffer layer. Using the OptiBPM software, the author designed and evaluated various channel waveguides with different values of Δn (0.0003 to 0.0061 which corresponds to UV illumination from 1 minute to 60 minutes) and different values of channel widths ($4 - 12\ \mu\text{m}$). The axes and coordinate system used in the simulation are also shown in Figure 6.8, where the light propagates along the z -direction. The x and y -axes are taken to be lateral and transverse directions, respectively.

Figure 6.8 Schematic illustration of straight channel-waveguide.

Here, in the simulation the standard length of the waveguide devices was taken to be 2.5 cm in accordance with the maximum length of the spot size of KrF laser. In actual

cases, all the devices were fabricated for the maximum length of ~ 2 cm in order to avoid any non-uniformity of laser beam near to the edges. The geometrical position of the input field is defined at the centre of the waveguide by coordinates $x = 0$, $y = 1.5$, $z = 0$. In the simulation, the Gaussian beam of $10.8 \mu\text{m}$ MFD was used as the input field. MFD of $10.8 \mu\text{m}$ was in accordance to the fiber obtained in Section 4.4.2 of Chapter 4. Figure 6.9 shows the image of the normalized input field which was used for the simulation. The colour code in Figure 6.9 is given to describe the intensity distribution scheme. The input field image does not seem to be circular in Figure 6.9 due to the difference in the scale used for X and Y axes. The polarization of the input field is also taken into account in the simulation.

Figure 6.9 Input field distribution (at $z = 0$) used to start propagation in the designed waveguide.

6.5.1.2 Simulation results of channel-waveguides

For the single-mode optical field propagation at $1.55 \mu\text{m}$, the author has firstly investigated the modal-index of channel waveguides (detailed waveguide parameters are given in Section 6.5.1.1) having channel width in the range of $4 - 12 \mu\text{m}$ for various values of Δn obtained in Figure 6.7. The 3-D mode solver of OptiBPM software was used to determine the modal-index value of all the channel waveguides at $1.55 \mu\text{m}$ for s -polarization. Figure 6.10 illustrates the fundamental modal-index of different channel

waveguides having different channel widths and having different Δn values corresponding to different illumination time.

Figure 6.10 Variation in modal index as function of various channel widths having different Δn values corresponding to different UV light illumination (UVLI) time.

As expected, we observe the increase in modal-index value with increase of channel widths and with the increasing UV illumination time corresponding to higher Δn . The value of modal-index seems to saturate after the 8 μm of channel width. For Δn value = 0.0003 corresponding to the 1 minute of UV illumination, the single-mode propagation was found to start from 6 μm and remains single-mode for 12 μm channel width. No mode was found for 4 μm and 5 μm of channel width. For Δn value = 0.0006 and 0.0009 corresponding to the 2 and 5 minutes of UV illumination respectively, the single mode propagation was found to start from 5 μm and remains single mode for 12 μm channel width. For Δn of 0.0023, 0.0048 and 0.0055 corresponding to 10, 20 and 30 minutes of

UV illumination respectively, the single mode propagation were obtained for all channel waveguides having channel widths from 4 μm to 12 μm . Whereas, for $\Delta n = 0.0058$ and 0.0061 corresponding to 40 minutes and 60 minutes of UV illumination, respectively, the single-mode propagations were found for the channel widths in the range of 4 - 10 μm , and for larger channel width of 11 μm and 12 μm , dual-mode propagations was obtained. This behaviour is obvious because high Δn leads to the propagation of more number of modes. Using the OptiBPM software, the author evaluated the single-mode optical field propagation at 1.55 μm along the z -direction in various channel waveguides (detailed waveguide parameters are given in Section 6.5.1.1) of 4 - 12 μm channel width using various values of Δn obtained in Figure 6.7. As an example, Figure 6.11 (a) and Figure 6.11 (b) shows the simulated optical field propagating in channel waveguides having channel width of 8 μm and refractive index ($n_1 + \Delta n$) for $\Delta n = 0.0003$ (corresponds to 1 minute of UV illumination) and $\Delta n = 0.0048$ (corresponds to 20 minutes of UV illumination), in both XZ and YZ planes respectively. The colour code in the figures (Figure 6.11 (a) & Figure 6.11 (b)) represents intensity distribution scheme. The field distribution in x -direction as shown in Figure 6.11 (a) is less confined and much reduced than shown in Figure 6.11 (b) which is obvious as Δn along lateral direction is higher in later case than in former case. The author has compared the relative intensity within the various channel waveguides of different channel widths. As an example, Figure 6.12 (a) and Figure 6.12 (b) shows the relative intensity of optical field propagating along the z -direction in channel waveguides for various channel widths and for two different values of Δn , namely $\Delta n = 0.0003$ (corresponds to 1 minute of UV illumination) and $\Delta n = 0.0048$ (corresponds to 20 minutes of UV illumination) respectively.

Figure 6.11 Optical field propagations in both XZ and YZ planes (a) Δn corresponding to the 1 minute of UV illumination, (b) Δn corresponding to the 20 minutes of UV illumination.

Figure 6.12 Relative power in channel waveguides having various channel widths and having (a) Δn corresponds to 1 minute of UV illumination, (b) Δn corresponds to 20 minutes of UV illumination.

As shown in Figure 6.12 (a), it is observed that the increase of the relative power within the various channel waveguides with the increase of channel width is not uniform along the direction of propagation. This behaviour is expected because of the small value of $\Delta n = 0.0003$ is not sufficient to confine the mode along the lateral direction. It can also be seen from the Figure 6.12 (a), the power which is propagating along z direction still decreases even at a distance of $25000 \mu\text{m}$ (2.5 cm). This is mainly because such small Δn between core and the side cladding in lateral direction requires longer length of channel waveguides to stabilize the power (or to have constant propagating power). Hence, $\Delta n = 0.0003$ is not suitable to fabricate waveguide devices. Similar behaviour was observed in case of $\Delta n = 0.0006$ and $\Delta n = 0.0009$, corresponding to the 2 and 5 minutes of UV illumination time. On the other hand, Figure 6.12 (b) illustrates the relative power along the propagation direction for various channel widths, from 4 to $12 \mu\text{m}$ having $\Delta n = 0.0048$ which corresponds to the 20 minutes of UV illumination. It is observed that the power propagating in the z -direction is constant and so this value of Δn is sufficient to confine the mode in the lateral direction for channel widths from 4 to $12 \mu\text{m}$. Similar behaviour of single-mode optical field propagation (at $1.55 \mu\text{m}$) was observed for the various channel waveguides having $\Delta n = 0.0023$, 0.0055 , 0.0058 and 0.0061 corresponding to the 10 minutes, 30 minutes, 40 minutes and 60 minutes of the UV illumination, respectively.

3-D BPM simulation allows the evaluation of the optical-field distribution at the output of the waveguides in XY plane. Figure 6.13 shows the intensity distribution at the output of the various channel waveguides having channel width of $8 \mu\text{m}$ for different values of Δn which corresponds to 1 minute, 2 minutes, 5 minutes, 10 minutes, 20 minutes, 30 minutes, 40 minutes and 60 minutes of UV illumination. Again, the colour code in the figure (Figure 6.13) represents the intensity distribution scheme.

Figure 6.13 Optical field in XY plane, Δn corresponds to (a) 1 minute, (b) 2 minutes, (c) 5 minutes, (d) 10 minutes, (e) 20 minutes, (f) 40 minutes, (g) 60 minutes of UV illumination .

Figure 6.14 (a) and Figure 6.14 (b), respectively, shows the normalized optical fields along lateral and transverse direction of channel waveguides which correspond to the intensity profiles illustrated in Figures 6.13 (a) to Figures 6.13 (g). Figure 6.13 (a) to Figures 6.13 (g) and Figure 6.14 (a) shows that the lateral optical-mode confinement is getting better with the increasing Δn , which corresponds to the increasing UV illumination time. Figure 6.14 (b) shows that the transverse optical mode confinement does not change much with the values of Δn . From the image plot shown in Figure 6.13 (a), (b), and (c) corresponding modal field intensity shown in Figure 6.14, the mode is less confined within the core of the waveguides. This is obvious because the refractive index of the core is not large enough to confined guided power. From the intensity image as shown in Figure 6.13 (d), (e), (f) and (g) and corresponding modal-field intensity shown in Figure 6.14, the mode is well confined within the channel along the lateral direction.

Figure 6.14 Variation in modal field of 8 μm channel widths as function of different Δn values as correspond to different UV light illumination (UVLI) time (a) along lateral direction (X), (b) along transverse direction (Y).

From the above simulation results, the refractive index difference (Δn) = 0.0023 or more (corresponding to the 10 minutes UV-illumination time or more) were found to be sufficient for the confinement of modal-field along the lateral direction.

The knowledge of modal-field distributions in XY plane at the output of channel waveguides, allows the calculation of confinement factor (CF). Confinement factor is the portion of guided energy within waveguide boundaries. Figure 6.15 shows the variation in CF as function of channel widths for different Δn values, which corresponds to different UV illumination time. It is clearly observed that the confinement of modal field increases with the increasing channel width and with the increasing UV illumination time.

Figure 6.15 Variation in confinement factor as function of various channel widths for different Δn value which corresponds to different UV light illumination (UVLI) time.

In order to test the practicability of direct UV-imprinted (DUI) channel waveguides, the author has selected the range of channel waveguides channel width which can confine

modal power of about 50 % and remain single-mode at 1.55 μm . In the next section, the author will present the experimental performances of some DUI channel waveguides having channel width in the range of 5 -12 μm , with $\Delta n = 0.0023, 0.0048, 0.0055$ corresponding to the UV illumination time of 10, 20, 30 minutes.

6.5.2 Fabrication and evaluation of channel-waveguides

The author has fabricated and characterized the various channel-waveguides of different channel widths ranging from 5 - 12 μm by direct UV-imprinting (DUI) , for 10, 20 and 30 minutes of illumination time, which correspond to the Δn values of 0.0023, 0.0048, and 0.0055, respectively.

6.5.2.1 Fabrication of channel-waveguides

A photomask with a series of different aperture widths (5, 6, 7, 8, 9, 10, 11 and 12 μm) was designed and fabricated on a quartz substrate. Figure 6.16 shows the microscopic images at 2X and 10X magnifications of the photomask having different aperture of different widths through which UV irradiations can pass and allows the fabrication of different channel widths in planar germanosilicate slab-waveguide described in Section 6.2 by direct UV-imprinting technique.

The realization of waveguiding channel of the channel waveguides by the direct UV-imprinting (DUI) technique using the photomask is shown schematically in Figure 6.17. For illustration, the germanosilicate slab-waveguide is placed under the photomask but in actual case the author has used photomask in contact with the slab-waveguides in order to avoid diffraction.

Figure 6.16 Microscopic images of the photomask (a) under 2X magnification, (b) under 10X magnification.

Figure 6.17 Fabrication procedures of the channel waveguides by DUV: single-step fabrication process of the stripe refractive index pattern in the planar slab-waveguide realized by exposing the waveguide through a line patterned photomask under UV illumination.

Figure 6.18 shows the experimental setup for the fabrication of channel waveguides. As shown in Figure 6.18, the KrF laser ($\lambda = 248$ nm) source (see Section 6.4) of an open shutter was used for the UV illumination. The beam-splitter indicated in the figure was not used in our work. A sample holder was used to mount the samples and a photomask was placed in front of samples facing the KrF laser. The planar slab-waveguide samples were illuminated through the photomask for 10 minutes, 20 minutes and 30 minutes by UV-irradiations.

Figure 6.18 Setup for the DUI of channel waveguide device fabrication.

6.5.2.2 Characterization and theoretical comparison of channel-waveguides

The DUI channel-waveguides were characterized by measuring the intensity distribution of the guided modes at the output of the waveguide by the near field optical microscopy (NFOM) technique. This measurement technique was described in Chapter 4, Section 4.4.2. To characterize the channel waveguides the input and output facets of the

UV-imprinted waveguides were cleaved. The output images and modal-field distribution in the form of intensity profiles of channel waveguides was captured with 10X microscope objectives onto the aligned infrared Beam-star camera. The author has investigated the guided mode for all channel waveguides, with varying lateral channel width from 5 - 12 μm fabricated using different UV illumination durations (10 , 20 and 30 minutes). The near field image at the output of channel waveguides shows 2-dimensional (2-D) well confined modal-field distribution. For example, Figure 6.19 shows the optical image and the corresponding intensity distribution profile of channel waveguides having channel width of 8 μm for different UV illumination of 10 , 20 and 30 minutes. The outputs from channel waveguides are obviously different from that of the optical fiber shown in Figure 4.19 in Chapter 4. The author also noticed some side peaks during the measurements and found that under better coupling condition these peaks could be avoided. In Figure.6.19, the experimental and simulation profiles show excellent agreement. Figure 6.20 shows the plots of the measured and theoretical full-width at half-maximum (FWHM) of the lateral intensity distribution of the guided modes versus the width of the waveguide cores for $\Delta n = 0.0023$ (corresponding to the 10 minutes of UV illumination), 0.0048 (corresponding to the 20 minutes UV illumination) and 0.0055 (corresponding to the 30 minutes UV illumination). As expected, the FWHM increases almost linearly with the increase of the width of the core for all the exposure times (i.e., all values of Δn), and, in addition, the FWHM becomes smaller with higher Δn (i.e. longer exposure time). It is observed that the theoretical values show good agreement with the experimental values in case of Δn corresponds to the 20 minutes and 30 minutes of UV illumination. In case of smaller width of waveguide cores having Δn which corresponds to the 10 minutes of UV illumination, the agreement between the measured and simulation results is not very good, this is due to smaller modal-field confinement as observed in Figure 6.15.

Figure 6.19 CCD image at the output shows the 2-D modal confinement of the field after propagating into waveguides having $8\ \mu\text{m}$ wide channel, imprinted by (a) 10 minutes (b) 20 minutes and (c) 30 minutes of UV illumination.

Figure 6.20 Lateral FWHM as a function of channel waveguide width, fabricated under the various time of UV illumination.

The results above show that the direct UV-imprinting technique has the simplicity and flexibility to form and control waveguide cores of different widths and refractive indices, i.e to control the mode confinement, by simply varying the channel width in the photomask and/or varying the UV illumination time. This technique would lead to much simplified fabrication of integrated optical circuits (IOCs).

6.5.3 Development of optical functional devices

The optical components of IOCs can be constructed with basic functional devices such as straight channel-waveguides, power splitters and the optical power switch. In earlier section, the author has presented the propagation of light in straight channel waveguides fabricated by the DUI technique. In this section, the author would like to present the power splitters and an optical power switch fabricated using the DUI technique. There are basically three different geometries of power splitters such as Y-branch configuration, multimode interference (MMI) splitter and directional coupler (DC).

Figure 6.21 shows different geometries: Y-branch (see Figure 6.21 (a)), multi-mode interference splitter (see Figure 6.21 (b)) and directional coupler (see Figure 6.21 (c)).

Figure 6.21 Various type of optical splitters geometries (a) Y-branch configuration, (b) multi-mode interference (MMI) splitter and (c) directional coupler (DC).

The simplest version of a power splitter is the Y-branch (Figure 6.21 (a)), which is easy to design but relatively quite sensitive to fabrication tolerances. The curvature radii of the two branches, as well as the junction, must be carefully designed in order to avoid power losses. Such problem can be overcome by using the MMI light splitter geometry. Compared to Y-branch, devices based on multimode interference are shorter and more compact, preserve the balanced output characteristics and have good fabrication tolerance. Therefore, the author has selected the MMI splitter and directional coupler to demonstrate the fabrication of splitter and optical power switch, respectively, by the DUI technique. The design of these devices was performed using the BPM, and the author has used Optiwave software for this purpose. In this section, the author will experimentally demonstrate the performance of DUI aforementioned functional photonic devices.

6.5.3.1 Fabrication of 1×2 MMI light splitter

The Multi-mode interference (MMI) device splitters are based on the self-imaging effect [6-5]-[6-15]. The self-imaging property of a multimode waveguide is due to the constructive interference of the waveguide modes. In order to launch light into or recover light from a multimode waveguide, a number of access waveguides can be placed at its beginning and at its end. The input and output optical waveguides are usually narrower and single-mode. Figure 6.22 shows diagram of a typical 1×2 MMI splitter. As shown in Figure 6.22, the 1×2 MMI splitter consists of a input waveguide, multimode region of width W_{MMI} and length L_c , and two output waveguides separated with distance w_p . The MMI splitter, here, was designed at communication wavelength of $1.55 \mu\text{m}$. The dimensions of the 1×2 MMI light splitter were selected to 1) allow easy coupling with the optical fibers, 2) avoid power overlapping at the output ports, and 3) enable effective splitting of optical power. With these requirements, the author has designed the 1×2 MMI power splitter shown schematically in Figure 6.22.

Figure 6.22 Schematic diagram of 1×2 MMI power splitter.

The widths of the input and output ports of the MMI light splitter was chosen to be $8\ \mu\text{m}$ wide in order to match with the modal characteristics of the cleaved single-mode fiber used to excite the optical modes inside the MMI light splitter. The central structure (MMI region) of the MMI light splitter is designed to support a large number of modes. As for the case of channel waveguides described above, the refractive indices of the waveguiding core region, side cladding, substrate and upper cladding were taken to be $n_{\text{core}} = n_1 + \Delta n$ ($\Delta n = 0.0048$ from Figure 6.7), n_1 , n_2 and 1, respectively. The thickness (height) of the core region and side cladding was $3\ \mu\text{m}$. Due to the complex structure of MMI based splitter (as it includes bends and curves), the 3-D structure of 1×2 MMI splitter was simplified to 2-D structure by using the effective index method (EIM). The EIM is a well known accurate method to solve the 3-D problem to 2-D [6-16],[6-17]. The effective index was solved by the MATLAB code in Appendix [II]. Simulation of MMI device geometry was performed using the Optiwave software to obtain the most appropriate width (W_{MMI}) and length (L_c) of the MMI region in order to divide equal powers in two output ports. Several values of W_{MMI} were evaluated and the corresponding values of L_c were obtained at which the power was found to be equally distributed in two output portions separated by w_p . These values are tabulated in Table 6.2.

Table-6.2: The optimal values of gaps between the adjacent output waveguides for designing the 1×2 multimode interference optical power splitter.

$W_{\text{MMI}}\ (\mu\text{m})$	$L_c\ (\text{mm})$	$w_p\ (\mu\text{m})$
40	0.96	20
60	1.97	30
80	3.5	40

Figure 6.23 shows the relative intensities of the light in the device (input intensity, interference intensity in the body of the MMI splitter and output intensity) for various values of W_{MMI} , L_c and w_p tabulated in Table 6.2. The colour used in the figure represents the relative intensity in the device. From Figure 6.23 (a), (b) and (c), respectively, it is observed that the outputs of MMI for $W_{MMI} = 40 \mu\text{m}$ and $W_{MMI} = 60 \mu\text{m}$ are overlapped, whereas the output of the MMI for $W_{MMI} = 80 \mu\text{m}$ is well separated. Therefore, the author has fabricated an MMI device using the DUI technique based on the design in Figure 6.23 (c).

The final design of 1×2 MMI splitter is shown in Figure 6.24 with all dimensions described in the figure. The s-bend was introduced to the two output waveguides to further separate the output power. The two ends of the output waveguides are made to be $68 \mu\text{m}$ apart to (a) effectively avoid output power overlapping, (b) ensure effective splitting of the optical power and (c) make the measurement easier. Figure 6.25 shows the schematic diagram of a 1×2 MMI light splitter fabricated using the DUI technique with $\Delta n = 0.0048$ which corresponds to 20 minutes UV exposure time.

Figure 6.23 Simulation for the 1×2 MMI splitter with evaluation of the modal field in multi-mode section having different MMI region of (a) $W_{MMI} = 40 \mu\text{m}$ (b) $W_{MMI} = 60 \mu\text{m}$ and (c) $W_{MMI} = 80 \mu\text{m}$.

Figure 6.24 Simulation designed of 3dB MMI 1×2 splitter. The output waveguides are joined to S-bends for larger separation.

Figure 6.25 Schematic diagram of direct UV-imprinted 1×2 MMI 3dB-light splitter. The splitter was fabricated by UV illuminating a planar germanosilicate slab-waveguide for 20 minutes through a photomask.

Figure 6.26 shows the output intensity profile from the 3dB MMI light splitter measured by the NFOM technique. It is observed that the input power is split into two outputs and the intensity profiles of both output power are almost identical. Again the experimental values agree well with the simulation results. The near field output image from the CCD camera is also given in Figure 6.26.

Figure 6.26 Lateral field profiles and near field images from the output of the imprinted 1×2 MMI 3dB-light splitter. Output modal-field profile of the splitter shows good agreement with the simulation.

6.5.3.2 Fabrication of 2×2 directional coupler

In addition to the 3dB MMI 1×2 power splitter describe above, the author has also designed an 2×2 directional coupler (DC) geometry to demonstrate the use of direct UV-

Figure 6.28 shows the relative intensity of the light propagating in a DC obtained from the simulation. The length of coupling region (L) used in the simulation was $3250\text{ }\mu\text{m}$. The refractive index values of the waveguiding channel, the buffer and the side cladding were the same as those used for MMI design. Two values of the separations of the two parallel waveguides in the central coupling region ($L_g = 20.1\text{ }\mu\text{m}$ and $13.4\text{ }\mu\text{m}$) were considered in the simulation.

Figure 6.28 Simulation design of directional coupler showing (a) no power exchange between the two waveguides, (b) complete power transfer from one waveguide to another.

The input power was launched from port-2. As shown in Figure 6.28 (a), for $L_g = 20.1 \mu\text{m}$ the power was not transferred to another waveguide. Therefore, no power was found at the output port-3. On the other hand, for $L_g = 13.4 \mu\text{m}$ (see Figure 6.28 (b)) the input power in port-2 was completely transferred to the port-3. Therefore, to further demonstrate the applicability of the direct UV-imprinting technique to fabricate waveguide based devices, the author has fabricated a DC based on the design shown in Figure 6.28 (b). Figure 6.29 shows the schematic diagram of a DC fabricated using the DUI technique with $\Delta n = 0.0048$ which corresponds to 20 minutes UV illumination.

Figure 6.29 Schematic diagram of direct UV-imprinted directional coupler. The directional coupler was fabricated by UV illuminating a planar germanosilicate slab-waveguide for 20 minutes through a photomask.

Figure 6.30 shows the output intensity profile from the DC coupler measured using the NFOM technique. The power was launched from the right side to the left side (see Figure 6.29). As expected, the input power from the right side of the device (port-2 in Figure 6.29) was completely transferred to another waveguide (port-3 in Figure 6.29). The intensity profiles at the outputs were compared with the theoretical curves. Again the experimental values agree well with the simulation results.

Figure 6.30 Lateral field profiles and near field images from the output of the direct UV-imprinted directional coupler. Output modal profile of the directional coupler shows good agreement with the simulation.

From the above results, the author has shown that the direct UV-imprinting technique developed in this project is able to realize optical functional devices in a planar configuration in a single processing step. The performance of the optical devices fabricated by the direct UV imprinting technique is only dependent on the preparation of the contact-photo-mask. Using the direct UV-imprinting technique, complicated optical devices can be fabricated with ease in a single processing step. Furthermore, it is obvious that the direct imprinting technique will reduce the fabrication cost of high reliability inorganic SiO₂ based planar waveguides.

6.6 Summary

The author has demonstrated that high quality planar slab-waveguides can be fabricated by the iterative deposition of sol-gel derived thin films of 0.2GeO₂:0.8SiO₂ on the 10 μm SiO₂ buffered Si substrate. The 3 μm thick waveguiding layer was achieved by iteratively depositing 16 layers of thin films. This guiding layer is able to support a single mode at 1.55 μm with low propagation loss of 0.26 dB/cm. The UV induced refractive index change, Δn , increases with the increase of the UV illumination time from 1 minute to 60 minutes. The value of Δn obtained to be ~ 0.005 for 20 minutes of UV illumination and start to saturate. Such a high value of Δn (for example, Δn of ~ 0.005 obtained after 20 minutes of UV illumination) is sufficient to fabricate channel waveguide devices. Single-mode channel waveguides operating at 1.55 μm with various waveguiding core widths and refractive index profiles have been studied and designed using OptiBPM software. Based on the design, the author fabricated single-mode channel waveguides using the direct UV-imprinting technique in a single processing step. The measured modal profiles of the

channel waveguides are in good agreement with the simulation results. A 1×2 MMI 3dB light splitter and DC have also been fabricated, again, using the direct UV-imprinting technique in single processing step, which shows the simplicity of the direct UV-imprinting technique. The measured profile and simulation results agree well. In conclusion, the author has demonstrated the effective fabrication of channel waveguides and photonic functional devices by the direct UV-imprinting technique using the sol-gel derived photosensitive inorganic germanosilicate material system. This is made possible because relatively high value of the UV induced refractive index change has been obtained in this project.

Chapter 7

Photosensitivity of Sol-Gel Derived Boron and Germania Co-doped Silica Films

7.1 Introduction

In the previous chapters, the author has presented the detailed development of highly photosensitive sol-gel derived inorganic germanosilicate material system and successfully demonstrated the fabrication of photonic devices by direct UV-imprinting technique. From the literature review in Section 2.5.4.5 of Chapter 2, the author understands that boron and germania co-doped silica will produce higher UV induced refractive index changes compared to the germanosilicate materials. Therefore, as additional work, the author has also studied the photosensitivity of sol-gel derived boron and germania co-doped silica films, which will be presented in this chapter.

In Section 7.2, the author will present the fabrication scheme of sol-gel derived boron and germania co-doped silica $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ thin and thick films for $x = 0.05, 0.1, 0.2$. In Section 7.3, the author will describe the characterization results of the sol-gel derived $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ single-layer thin films carried out by various characterization techniques such as Fourier transform infra-red spectroscopy (FTIR),

spectroscopic Ellipsometry (SE), X-ray diffraction (XRD) and Atomic force microscope (AFM). In the same Section 7.3, the densification temperature of each composition $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$, for $x = 0.05, 0.1$ and 0.2 were also described. In Section 7.4, the characterization results of few micron thick $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ planar slab-waveguides will be presented which was carried out by prism-coupler technique. Finally in Section 7.5, the UV induced refractive index change (Δn) of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ slab-waveguides will be discussed.

7.2 Development of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ films

Boron and germania co-doped silica films were prepared by using the sol-gel spin-coating technique as shown schematically in Figure 7.1. The precursors Tetraethoxysilane (TEOS, 99.99% purity from Aldrich) for silica (SiO_2), Tetrapropyloxygermane (TPOG, 99.99% purity from Chemat Technology Inc.) for germanium oxide (GeO_2) and Triethyl Borate (TEB, 99.99% purity from Chemat Technology Inc.) for boron oxide (B_2O_3) were used to prepare the solutions. From the previous work (as presented in Section 5.3 of Chapter 5), the composition $0.2\text{GeO}_2:0.8\text{SiO}_2$ having 0.20 molar GeO_2 content in SiO_2 is the optimum and were able to produce good optical properties without the problem of clustering. Therefore in this work 0.20 (molar) Germania was incorporated and the concentration of B_2O_3 was varied for $x = 0.05, 0.10$ and 0.20 in $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$.

TEOS and EtOH (ethanol) were mixed in 1:1 ratio by volume. For hydrolysis, acid catalyst HNO_3 was added to maintain pH level ~ 3 and water to alkoxide molar ratio (R) of 2. This sol was named as sol-S. The pH level of 3 was found to be an optimum pH level

CHAPTER 7 PHOTSENSITIVITY OF SOL-GEL DERIVED $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$

to prepare good optical quality germanosilicate thin films (see Section 5.3 of Chapter 5). The solution was stirred continuously for 30 minutes. Solution called sol-B was prepared by mixing TEB with EtOH in 1:1 volume ratio and was then mixed with sol-S. This sol was named as sol-SB and stirred vigorously for a day in a dry glove box having relative humidity (RH) ~15%. The RH was maintained by continuous flushing of dry nitrogen. Solution called sol-G was also prepared by mixing TPOG with isopropanol (IPA) in 1:1 volume ratio in a dry glove box maintained at RH ~ 15%. Sol-G was then mixed to sol-SB, and this final solution was vigorously stirred for 30 to 40 minutes. The amount of the sols mixed were calculated to obtain $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ composition. The films were prepared by spin coating sol-SBG onto 500 μm thick [100] p-doped (boron) Si wafers, with resistivity of 12-16 $\Omega\text{-cm}$. The spin coated films were heat treated at 100 $^\circ\text{C}$ inside the dry glove box for few minutes and after that the films were annealed at higher temperature in JIPELEC rapid thermal processor (RTP) for 15 s in the presence of O_2 . The annealing temperature was varied from 500 $^\circ\text{C}$ to 1000 $^\circ\text{C}$ in steps of 100 $^\circ\text{C}$.

Iterative deposition of 14 thin layers with each layer annealed at 900 $^\circ\text{C}$ was carried out to build a crack free guiding-layer (core), to fabricate single-mode planar slab-waveguide at 1.55 μm wavelength. This multilayer deposition was performed on a Si wafer having 10 μm thick SiO_2 , which acts as a cladding. Lastly, an electric furnace at 1000 $^\circ\text{C}$ in air was used for one hour to consolidate the guiding structure.

Figure 7.1 Flow chart of the entire sol-gel process and film preparation scheme of boron and germania co-doped silica.

7.3 Characterization results of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ thin films

In this section, various characterization results of Fourier transform infra-red spectroscopy (FTIR), spectroscopic Ellipsometry (SE), X-ray diffraction (XRD) and Atomic force microscope (AFM) will be described.

The FTIR measurements were carried out by Perkin-Elmer Spectrum 2000 spectrometer and the spectra were measured in the transmission mode between 4000 cm^{-1} to 400 cm^{-1} ($2.5\text{ }\mu\text{m}$ to $25\text{ }\mu\text{m}$). Figure 7.2 (a), Figure 7.2 (b) and Figure 7.2 (c) show the FTIR spectra of the $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ thin films annealed at various temperatures from $500\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$ for different concentration of B_2O_3 , $x = 0.05, 0.10$ and 0.20 respectively. The relevant peaks are labeled in the Figures 7.2 [7-1], [7-2], [7-3]. As shown in Figure 7.2 the shoulder around the 980 cm^{-1} is the assignment of Si-O-Ge bonds [7-2], [7-3]. No absorption peak corresponding to organic radicals are visible. The absorption band at around 645 cm^{-1} , attributed to Si-O-B deformation vibration [7-2]. The band attributed to stretching vibration of Si-O-B at around 935 cm^{-1} . B-O (boron-oxygen) band at around 1450 cm^{-1} , increases with increasing boron concentration. It is obvious that the intensity of the B-O bands increase with B_2O_3 concentration. Absorption band at 1645 cm^{-1} due to -BH (boron-hydrogen bonds) is visible only in case of film annealed at $500\text{ }^\circ\text{C}$ and significantly reduced with the increase of temperature and with the boron concentration. The -OH stretching bands around 3400 cm^{-1} decrease in intensity with increasing annealing temperature. The -OH stretching vibration band disappeared at $900\text{ }^\circ\text{C}$ and above in all the cases. However this band is significantly smaller at $800\text{ }^\circ\text{C}$ and above in case of $x = 0.20$.

(a)

(b)

(c)

Figure 7.2 FTIR spectra of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ thin film samples annealed at various temperature, for (a) $x = 0.05$, (b) $x = 0.10$, (c) $x = 0.20$.

Figure 7.3 (a) shows the refractive index n at $1.55\ \mu\text{m}$ of the films annealed from $500\ ^\circ\text{C}$ to $1000\ ^\circ\text{C}$ for different x values in $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$. The refractive indices were obtained using SE. For each value of x , it is observed that the index n increases with increasing annealing temperature from $500\ ^\circ\text{C}$ to $900\ ^\circ\text{C}$. The value of refractive indices saturates at $900\ ^\circ\text{C}$ and above for $x = 0.05$ and 0.10 and above $800\ ^\circ\text{C}$ for $x = 0.20$. The refractive index n decreases with the increase of B_2O_3 concentration.

The variation of the thickness and the porosity with the annealing temperature is shown in Figure 7.3 (b) & Figure 7.3 (c) respectively. As expected, for each values of x in $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$, the film thickness decreases with increasing annealing temperature due to the densification of the films. The thickness increases with the increase of B_2O_3 concentration. The porosity calculated using the Bruggeman effective medium approximation (see Section 4.2.1.3 of Chapter 4) decreases with the increasing temperature for each value of x in $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$. The porosity reached zero porosity at $900\ ^\circ\text{C}$ and above. This result shows that the films are densified when annealed at $900\ ^\circ\text{C}$ and above at various concentration of boron, which is consistent with the previous FTIR results (as shown in Figure 7.2). Furthermore, porosity decreases with increase of B_2O_3 concentration.

Figure 7.3 Spectroscopic Ellipsometry results: (a) Refractive index at 1.55 μm as a function of x -values in $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ thin films annealed at various temperatures, (b) thickness as a function of x -values in $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ thin films annealed at various temperatures, (c) porosity as a function of x -values in $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ thin films annealed at various temperatures.

No crystalline peak was observed by XRD measurement for all the densified films of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ as depicted by XRD spectra in Figure 7.4. Figure 7.5 shows the AFM images of densified thin films $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$, for $x = 0.05, 0.1$ and 0.2 . The root mean square surface roughness value of the films were observed to increase from 0.375 nm , 0.394 nm , 0.430 nm with the increasing B_2O_3 concentration for $x = 0.05, 0.10$ and 0.20 respectively. The reason of this increasing roughness is likely to be due to the increasing concentration of boron co-doping, since it is hygroscopic.

Figure 7.4 XRD spectra showing no crystalline peak in thin film samples of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ for $x = 0.05, 0.10$ and 0.20 when annealed at 900°C annealing temperature.

(a)

(b)

(c)

Figure 7.5 AFM $10 \times 10 \mu\text{m}^2$ image of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ thin films sample annealed at 900°C for (a) $x = 0.05$, (b) $x = 0.10$ and, (c) $x = 0.20$.

7.4 Characterization results of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ slab-waveguide

The refractive index, thickness and propagation loss of the planar slab-waveguide (multi-layered structure) was characterized by using prism-coupler equipment (Metricon 2010) at 1.55 μm . Slab-waveguide parameters measured by the prism-coupler technique are tabulated in Table-7.1. As observed in Table-7.1, the transverse magnetic (TM) refractive index (n_{TM}) grow slightly higher than the transverse electric (TE) refractive index (n_{TE}), and so the difference between n_{TE} and n_{TM} becomes larger with the increasing boron concentration. The increase in the waveguides thicknesses were observed with increasing B_2O_3 concentration. The propagation loss values were also found to increase with the increase in B_2O_3 concentration, which can be attributed to the increase in surface roughness. It is observed that the average propagation loss after boron co-doping is higher than that of propagation loss value of germanosilicate slab-waveguide as reported in Section 6.3 of Chapter 6.

Table-7.1: Properties of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ planar slab-waveguides, for $x = 0.05, 0.1$ and 0.2 , measured by using prism-coupler method.

Waveguide description	Thickness ($\pm 0.04 \mu\text{m}$)	n_{TE} (± 0.0004)	$\Delta(n_{\text{TM}} - n_{\text{TE}})$ (± 0.0002)	Propagation Loss ($\pm 0.2 \text{ dB/cm}$)
$0.05\text{B}_2\text{O}_3:0.2\text{GeO}_2:0.75\text{SiO}_2$	2.64	1.4679	0.0017	0.32
$0.1\text{B}_2\text{O}_3:0.2\text{GeO}_2:0.7\text{SiO}_2$	2.67	1.4677	0.0019	0.46
$0.2\text{B}_2\text{O}_3:0.2\text{GeO}_2:0.6\text{SiO}_2$	2.86	1.4625	0.0026	0.54

7.5 Photosensitivity of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ slab-waveguide

The induced refractive index change (Δn) of the slab-waveguides by the UV-irradiation were studied by illuminating the samples for 20 minutes with a KrF excimer laser ($\lambda = 248$ nm) operated at 10Hz repetition rate and energy of 450 mJ per pulse. To stabilize the samples after the UV illumination, annealing at 140 °C for 24 hours under vacuum was carried out.

After the UV exposure, the refractive indices (n_{UVLI}) of the films change by an amount Δn . The variation of Δn at 1.55 μm with the 20 minutes UV exposure for various samples is shown in Figure 7.6. The value of Δn for x equals to zero (i.e with zero B_2O_3 concentration) is also included. It is observed that Δn increases significantly after the incorporation of B_2O_3 into the network.

Figure 7.6 UV-induced Δn as a function of x -values in $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$.

The values of Δn for TE (Δn_{TE}) are ~ 0.0089 , ~ 0.011 and ~ 0.014 , for $x = 0.05$, 0.1 and 0.2 respectively. The values of Δn for TM (Δn_{TM}) are ~ 0.0092 , ~ 0.0115 and ~ 0.015 , for $x = 0.05$, 0.1 and 0.2 respectively. The increase in the difference between Δn_{TE} and Δn_{TM} ($\Delta n_{\text{TE}} - \Delta n_{\text{TM}}$) with increasing B_2O_3 concentration may be due to the increase of stress with increasing B_2O_3 concentration, which is possibly caused by the increasing mismatch of the thermal expansion coefficient of $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ and silica [7-4]. The refractive index changes by UV-irradiations have been shown to increase under the stress [7-5]-[7-8]. So, in our case, the enhancement of Δn with increasing B_2O_3 concentration could possibly due to the enhancement of the creation of oxygen related defects (as shown in Section 5.5 of Chapter 5) by the UV irradiation, which is caused by larger stress present in the boron doped films [7-5]. Furthermore, the author monitored the prepared slab-waveguide samples for one month and found that their performances degraded and films appeared cloudy, since it is hygroscopic.

7.6 Summary

Sol-gel derived $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ (for $x = 0.05$, 0.1 and 0.2) thin films were spin-coated and annealed at various temperatures ranging from 500°C to 1000°C in O_2 atmosphere. Films annealed at 900°C and above are fully densified, and the films annealed below 900°C are porous. This is evident from the FTIR study and the behavior of the refractive index as function of temperatures. The surface roughness of the films is low and there is no crystalline phase observed even for the films annealed at high temperature. Iterative deposition of thin films annealed at 900°C produces a slab-waveguide with monomodal behavior at $1.55\ \mu\text{m}$. The values of the UV-induced Δn were

CHAPTER 7 PHOTSENSITIVITY OF SOL-GEL DERIVED $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$

found to be increasing with increasing boron concentrations from 0.0081 to 0.0014. This could possibly be due to the enhancement of the creation of oxygen related defects caused by the larger stress present in the boron doped films. However, some issues were identified in the case of boron and germania co-doped silica films such as difference between refractive index of two polarizations (n_{TE} and n_{TM}) and the boron and germania co-doped silica films appeared to be cloudy, since it is hygroscopic. Based upon the results presented above, although the UV induced refractive index changes in boron and germania co-doped silica films are higher than those of germanosilicate films, the boron and germania co-doped silica films developed so far are not desirable for the photonic device fabrication using the direct UV-imprinting technique. Therefore, at this stage, the author would like to recommend germanosilicate material system without boron co-doping for the photonic device fabrication by the direct UV-imprinting technique.

Chapter 8

Conclusions and Recommendations

8.1 Conclusions

This chapter summarizes the results and achievements of this thesis and discusses some suggestions for future work. The results presented in this thesis open the possibility to fabricate photonic waveguide devices by direct UV-imprinting (DUI) technique in highly photosensitive inorganic germanosilicate films deposited using the sol-gel technique. The main conclusions drawn from the previous chapters of this thesis are summarized below:

- Literature review establishes the comparative evaluation of various fabrication techniques of channel-waveguides devices and introduces the DUI technique and principles. The demand for suitable photosensitive material system for DUI brings in inorganic germanosilicate as a choice of material system. In the literature review, the author presented various deposition methods and their advantages and disadvantages. Sol-gel process was found to be attractive to produce non-stoichiometric films and a detailed description on sol-gel was also provided.

- Sol-gel technique together with the spin-coating deposition process was used to synthesize germanosilicate $x\text{GeO}_2:(1-x)\text{SiO}_2$ films, for $x = 0.05, 0.1, 0.2, 0.25$ and 0.3 . The optimum concentration of germania was found to be $x = 0.2$ (20 %) without the problem of clustering and was used throughout this work.
- The properties of the $0.2\text{GeO}_2:0.8\text{SiO}_2$ (germanosilicate) was investigated by varying the annealing temperature in the range of 500 to 1000 °C. These investigations show the densification temperature to be 900 °C and above. Here, densification refers to the optical films with no -OH contents and porosity. The -OH content in the thin films were estimated by Fourier Transform Infra-Red (FTIR) spectroscopy. The porosity values were derived from the refractive index (n) of the films as determined by Spectroscopic Ellipsometry (SE).
- Level of sol pH in the range of 1 to 6 was also optimized to obtain dense germanosilicate films. The optimized value was obtained to be pH ~ 3.
- Dense, crack free optically good quality germanosilicate thin films having smooth surfaces and low absorption loss ~ 0.42 dB/cm was obtained when prepared with a solution of pH level ~3 and annealed at 900 °C and above.
- KrF excimer laser at 248 nm was used to induce the change in the refractive index of the germanosilicate thin films. Effect of UV exposure on the refractive index change of sol-gel derived inorganic germanosilicate thin films were studied as function of UV illumination time. The values of refractive index change of dense germanosilicate thin film increases to 0.0094 after UV illumination in excess of 1 minute. The UV induced refractive index changes (Δn) were found to saturate around 20 minutes of UV exposure time. The high value of $\Delta n \sim 0.0094$ was achieved in germanosilicate thin films (~200 nm) which opens the possibility to fabricate photonic waveguide devices by the single step DUI fabrication technique.

- The obtained high value of UV induced Δn is relatively large as compared to other published values using inorganic dense germanosilicate material system. The mechanism of UV induced Δn change in dense germanosilicate films was investigated and explained in terms of the formation of GeE' center by the UV induce bleaching of Germanium lone pair center (GLPC) Ge²⁺ and to the creation of the oxygen deficiency related defects. From our experiments, the oxygen deficiency related defects correspond to the absorption band at 620 – 740 cm⁻¹ in the FTIR spectra. To confirm the formation of UV induced oxygen deficiency the Rutherford backscattering (RBS) measurements were performed. The RBS analysis strongly suggests the creation of oxygen deficiency upon UV illumination. For porous germanosilicate samples, the formation of GeE' centers from the Ge-Ge/Si-Si (neutral oxygen monovacancy; NOMV) and UV induced densification have been observed. This was not observed for the densified germanosilicate films (films annealed at 900 °C and above).
- Hydrogen loading was normally used to enhance the values of Δn . In this work, variation of Δn was also investigated for hydrogen loaded germanosilicate films annealed at various temperatures (700 °C, 800 °C and 900 °C). For the dense germanosilicate samples (the samples annealed at 900 °C), the values of Δn of the non hydrogen-loaded and hydrogen loaded samples were found to be 0.0094 ± 0.0002 and 0.0096 ± 0.0002 , respectively. We notice that the values of Δn are quite similar. Therefore, for the sol-gel synthesized germanosilicate films the hydrogen loading is not necessary.
- In order to fabricate photonic waveguide devices by DUI, ~ 3 μm thick films are required. Iterative deposition of dense germanosilicate thin films was used to fabricate a 3 μm single-mode (at 1.55 μm wavelength) planar optical waveguide with a low propagation loss of 0.26 dB/cm. The UV induced Δn values were evaluated for various

UV exposure time, ranging from 1 minute to 60 minutes, in $\sim 3 \mu\text{m}$ thick germanosilicate planar slab-waveguides. The variation of UV induced Δn in planar slab-waveguides as a function of UV illumination time was found to increase with increase in UV illumination time. The Δn value was obtained to be ~ 0.0023 for UV illumination of 10 minutes. The Δn value was found to almost saturate at ~ 0.005 after 30 minutes UV illumination. These values of refractive index change were found to be sufficient to form light guiding channel.

- The technique of DUI allows the fabrication of photonic waveguide devices in a single processing by using the appropriately designed photomask. The photomask was designed for various photonic devices using OptiBPM software and the propagation of light at $1.55 \mu\text{m}$ wavelength was examined theoretically by the beam propagation method. Various channel waveguides having widths of $5 - 12 \mu\text{m}$ were fabricated by using different UV illumination time of 10, 20 and 30 minutes. The outputs of various channel waveguides were measured using near field optical microscopy. The experimental performances of the output of the direct UV-imprinted channel waveguides found in the good agreement with the theoretical (simulation) results.
- Photonic waveguide devices such as 1×2 Multimode-Interference - 3dB-light splitter and 2×2 directional coupler were developed by irradiating the $3 \mu\text{m}$ germanosilicate slab-waveguides with UV light through a pre-designed mask in contact with the films. Again the experimental performances were found to be in good agreement with the theoretical (simulation) results.
- Boron and germania co-doped silica is known to enhance the UV induced Δn value. In this work, boron and germania co-doped silica $x\text{B}_2\text{O}_3:0.2\text{GeO}_2:(0.8-x)\text{SiO}_2$ (for $x = 0.05, 0.1$ and 0.2) shows that the UV-induced Δn increases with increasing boron concentration from 0.0081 to 0.0014. However, the author has found some problems

associated with the boron co-doping, as follows: (a) refractive indices of two polarizations (*s* and *p*- polarization) are different, (b) the films became non transparent and appeared whitish after one month, which implies that the films are not stable. At the present moment, these results suggest that boron and germania co-doped silica are not suitable for photonic device fabrications. Further development is required to produce better optical quality photosensitive boron and germania co-doped silica films. Therefore, the author would like to recommend germanosilicate without boron co-doping for the photonic device fabrication.

- In conclusion, the author has successfully developed the single step DUI technique to fabricate photonic devices in inorganic highly photosensitive sol-gel derived germanosilicate films. This is made due to the relatively large values of UV induced refractive index change (Δn) developed in this project. The use of DUI technique will simplify and lower the cost of the fabrication of photonic waveguide device for photonic integrated circuits.

8.2 Recommendations for future works

The work presented here can be seen as a ground work of a more ambitious project. Some of these proposals are outlined below:

- To establish the potential of DUI technique for grating based devices such as optical filters. The channel-waveguides developed in this thesis by employing the DUI is suitable for the future imprinting of Bragg gratings. Waveguide Bragg grating inscription can follow the same technique as that of waveguide imprinting by using the suitable mask of desired grating period (Λ). This is also possible in a single step by the

use of grey scale photomask. If one can have the UV induced refractive index change (Δn) values as a function of UV illumination for each grey scale, then guiding channel and grating can be formed in a single UV exposure.

- To fabricate graded index waveguides for beam expander. The graded index can be formed by exposing the photosensitive slab-waveguides to UV irradiation through a grey scale mask. It is difficult and costly to fabricate graded index waveguides by other techniques.
- It has been established that the photonic waveguide devices produced during the course of this work exhibit 2-dimensional optical field confinement. As seen from the result of confinement factor (Section 6.5 Chapter 6) that an increase in UV induced refractive index change (Δn) has resulted in better confinement of the modal field. Therefore, future work can evolve towards further increase in Δn using the germanosilicate material system itself or may be by incorporating some feasible co-dopants.
- To increase the values of UV induced refractive index change, UV-exposure processing may be performed simultaneously during the heat treatment to densify the films. This could possibly increase the UV induced oxygen deficiency and therefore increase the Δn value. Such advancement will require a development of rapid thermal processing equipment with built-in UV-laser system.

Author's Publications

Patent

Kantisara Pita, Rajni, Tjin Swee Chuan, Kam Chan Hin, Yu Siu Fung, "Method of producing germanosilicate with a high refractive index change", *PCT/SG2005/00414*, *International Publication Number-WO 2006/062486* (2006).

Journal Papers

- [1] Rajni, K. Pita, S. F. Yu, S. C. Tjin, C. H. Kam, "Fabrication of inorganic GeO₂:SiO₂ channel waveguides by ultraviolet imprinting", *Applied Physics Letters*, 89 (2006) 071105.
- [2] Rajni, K. Pita, S. C. Tjin, S. F. Yu, C. H. Kam, "Enhanced photosensitivity in sol-gel derived 20GeO₂:80SiO₂ thin films", *Applied Physics-A: Materials Science & Processing*, 82 (2006) 535-541.
- [3] Rajni, K. Pita, Charles K. F. Ho, S. C. Tjin, C. H. Kam, "Photosensitivity of 20GeO₂:80SiO₂ hydrogen-loaded and non-hydrogen-loaded thin films", *Journal of Physics-D: Applied Physics*, 39 (2006) 2504-2508.
- [4] Rajni, K. Pita, "Photosensitivity of sol-gel derived inorganic xB₂O₃:20GeO₂:(80-x)SiO₂ system with various boron concentration", *Journal of Physics-D: Applied Physics*, 39 (2006) 1-5.

- [5] Rajni, Charles K. F. Ho, K. Pita, N. Q. Ngo, "Porosity control of 20GeO₂:80SiO₂ sol-gel derived thin films by varying the level of sol pH for low loss optical waveguide devices", *Journal of the Electrochemical Society*, 152 (2005) G456-459.
- [6] Charles K. F. Ho, Rajni, H. S. Djie, K. Pita, N. Q. Ngo, "Optical and physical properties of sol-gel-derived GeO₂:SiO₂ films in photonic applications", *Applied Optics*, 46 (2007) 4397-4406.

Conference Papers

- [1] Rajni, K. Pita, Charles K. F. Ho, S. C. Tjin, N. Q. Ngo, "Sol-gel derived GeO₂ doped SiO₂ films for photonics devices", *Proceedings of 2nd France-Singapore Workshop on Optoelectronics and RF Photonics Technology*, 27-28 October Singapore (2005).
- [2] Charles K. F. Ho, Rajni, H. S. Djie, K. Pita, N. Q. Ngo, "The application of sol-gel derived GeO₂:SiO₂ films in photonics", *RIUPEEEEC Hong Kong* (2005) 14-15 July.
- [3] Charles K. F. Ho, D. C. L. Gwee, Rajni, K. Pita, N. Q. Ngo, C. H. Kam, "Planar optical waveguides fabricated by sol-gel derived inorganic silicate glass", *Proceedings of 11th European Conference on Integrated Optics: Prague-Czech Republic*, 2-5 April (2003) 305-308.
- [4] Charles K. F. Ho, D. C. L. Gwee, Rajni, K. Pita, N. Q. Ngo, C. H. Kam, "Fabrication and characterization of optical waveguide material for integrated optics by the inorganic sol-gel process", *Conference on the Optical Internet & Australian Conference on Optical Fiber Technology, Melbourne Australia*, 13-16 July (2003) 744-747.

Bibliography

- [1-1] Ajoy Ghatak, K. Thyagrajan, “Optical Electronics”, *Cambridge University Press* (1998).
- [1-2] Ajoy Ghatak, K. Thyagrajan, “Introduction to Fiber Optics”, *Cambridge University Press* (1998).
- [1-3] Clifford Pollock, Michal Lipson, “Integrated Photonics”, *Kluwer Academic Publishers* (2003).
- [1-4] S. E. Miller, “Integrated Optics: An Introduction”, *The Bell System Technical Journal*, 48 (1969) 2059-2068.
- [1-5] L. Gasman, “New materials renew life for integrated optics”, *WDM Solutions*, November (2001) 17-20.
- [1-6] A. S. Holmes, R. R. A. Syms, Ming Li, Mino Green, “Fabrication of buried channel waveguides on silicon substrates using spin on glass”, *Applied Optics*, 32 (1993) 4916-4921.
- [1-7] E. M. Yeatman, K. Pita, M. M. Ahmad, “Strip-loaded High-Confinement waveguide for photonic application”, *Journal of Sol-Gel Science and Technology*, 13 (1998) 517-521.
- [1-8] G. D. Maxwell, B. J. Ainslie, “Demonstration of a directly written directional coupler using UV-induced photosensitivity in a planar silica waveguide”, *Electronics Letters*, 31 (1995) 95-96.

- [1-9] P. Niay, M. Douay, P. Bernage, W.X. Xie, B. Leconte, D. Ramecourt, E. Deleuaque, J. F. Bayon, H. Poignant, B. Poumellec, "Does Photosensitivity pave the way towards the fabrication of miniature coherent light sources in inorganic glass waveguides ?", *Optical Materials*, 11 (1999) 115-129.
- [1-10] F. Fransoo, D. Van Thourhout, L. Van Landschoot, A. Verbiest, W. Van. Parys, P. Vandaele, R. Baets, "Using a multimodal waveguide for enhanced resolution in optical data storage", *National Conference Proceedings* (2002).
- [1-11] Liping Zuo, Hisanori Suzuki, Kenneth Kong, Junjie Si, Minyt Minyt Aye, Atsushi Watabe, Shiro Takahashi, "Athermal silica-based interferometer type planar lightwave circuits realized by a multicore fabrication method", *Optics Letters*, 28 (2003) 1046-1048.
- [1-12] T. Kominato, Y. Ohmori, H. Okazaki, M. Yasu, "Very low loss GeO₂-doped silica waveguides fabricated by flame hydrolysis deposition method", *Electronics Letters*, 26, (1990) 327-328.
- [1-13] R. R. A. Syms, A. S. Homles, W. Huang, V. M. Schneider, M. Green, "Development of the SC-RTA process for fabrication of sol-gel based silica-on-silicon integrated optic components", *Journal of Sol-Gel Science and Technology*, 13 (1998) 509-516.
- [1-14] P. Coudray, P. Etienne, Y. Moreau, "Integrated optics based on organo-mineral materials", *European Materials Conference-Strasbourg*, 3 (2000) 331-337.
- [1-15] M. A. Fardad, M. Fallahi, "Sol-gel multimode interference power splitters", *IEEE Photonics Technology Letters*, 11 (1999) 697-699.
- [1-16] Soon-Ryong Park, Jaewan Jeong, Beom-Hoan, Seung-Gol Lee, El-Hang Lee, "Design and fabrication of polarization-insensitive hybrid sol-gel arrayed waveguide grating", *Optics Letters*, 28 (2003) 381-383.

BIBLIOGRAPHY

-
- [1-17] Byeong-Soo Bae, Oun-Ho park, "Direct laser writing of self-developed waveguides in benzyldimethylketal-doped sol-gel hybrid glass", *Journal of Material Research*, 16 (2001) 3184-3187.
 - [1-18] P. Coudray, J. Chisham, "Ultraviolet light imprinted sol-gel silica glass waveguide devices on silicon", *Optics Communications*, 128 (1996) 19-22.
 - [1-19] T. Touam, G. Milova, Z. Saddiki, M. P. Andrews, M. A. Fardad, S. Juma, J. Chrostowski, S. I. Najafi, "Organoaluminophosphate sol-gel silica glass thin films for integrated optics", *Proceedings of SPIE*, 2997 (1997) 79-84.
 - [1-20] B. Malo, F. Bilodea, J. Albert, D. C. Johnson, K. O. Hill, "Photosensitivity in optical fiber and silica-on-substrate waveguides", *SPIE*, 2044 (1993) 42-54.
 - [1-21] Akifumi Sakoh, Masahide Takahashi, Toshinobu Yoko, "Photochemical process of divalent germanium responsible for photorefractive index change in $\text{GeO}_2\text{-SiO}_2$ ", *Optics Express*, 11 (2003) 2679-2688.
 - [1-22] Mourad Essid, Jacques Albert, John L. Brebner, Koichi Awazu, "Correlation between oxygen-deficient center concentration and KrF excimer laser induced defects in thermally annealed Ge-doped optical fiber preforms", *Journal of Non-Crystalline Solids*, 246 (1999) 39-45.
 - [1-23] Q. Y. Zhang , K. Pita , Charles K. F. Ho, N. Q. Ngo, L. P. Zuo, S. Takahashi, "Low optical loss germanosilicate planar waveguides by low-pressure inductively coupled plasma-enhanced chemical vapor deposition", *Chemical Physics Letters*, 368 (2003) 183-188.
 - [1-24] Q. Y. Zhang, K. Pita, S. C. Tjin, C. H. Kam, L. P. Zuo, S. Takahashi, "Laser-induced ultraviolet absorption and refractive index changes in Ge-B-SiO₂ planar waveguides by inductively coupled plasma-enhanced chemical vapor deposition", *Chemical Physics Letters*, 379 (2003) 534-538.
-

BIBLIOGRAPHY

- [1-25] Junji Nishii, Nayouki Kitamura, Hiroshi Yamanaka, "Ultraviolet-radiation-induced chemical reactions through one-and two-photon absorption process in $\text{GeO}_2\text{-SiO}_2$ glasses", *Optics Letters*, 20 (1995) 1184-1186.
- [1-26] Bai-Ou Guan, Hwa-Yaw, Xioa-ming Tao, Xio-Yi Dong, "Highly stable fiber Bragg gratings written in hydrogen-loaded fiber", *IEEE Photonics Technology Letters*, 12 (2000) 1349-1351.
- [1-27] Kevin P. Chen, Peter R. Herman, "Trimming phase and Birefringence errors in photosensitivity-locked planar optical circuits", *IEEE Photonics Technology Letters*, 14 (2002) 71-73.
- [1-28] L. Dong, J. Pinkstone, P. St. J. Russell, D. N. Payne, "Ultraviolet absorption in modified chemical vapor deposition performs", *Journal Optical Society America B*, 11 (1994) 2106-2111.
- [1-29] I. Camlibel, D. A. Pinnow, F. W. Dabby, "Optical aging characteristics of borosilicate clad fused silica core fiber optical waveguide", *Applied Physics Letters*, 26 (1975) 185-187.
- [1-30] Kenji Kintaka, Junji Nishii, "Temperature sensitivity of Ge-B-SiO_2 waveguide Bragg grating on a crystallized glass substrate", *Optics Letters*, 27 (2002) 1394-1396.
- [1-31] C. S. Kim, Y. G. Han, B. H. Lee, W. T. Han, U. C. Paek, Y. Chung, "Induction of refractive index change B-doped optical fibers through relaxation of the mechanical stress", *Optics Communications*, 185 (2000) 337-342.
- [1-32] Masahide Takahashi, Hikari Shigemura, Yoji Kawamoto, Junji Nishii, Toshinobu Yoko, "Photochemical reaction of Ge-related defects in $10\text{GeO}_2:90\text{SiO}_2$ glass prepared by sol-gel process", *Journal of Non-Crystalline Solids*, 259 (1999) 149-155.

BIBLIOGRAPHY

- [1-33] Feridun Ay, Atilla Aydinli, Sedat Agan, “Low-loss as-grown germanosilicate layers for optical waveguides”, *Applied Physics Letters*, 83 (2003) 4743-4745.
- [1-34] Lidia Armelo, Monica Fabrizio, Silvia Gross, “Molecular interconnected SiO₂-GeO₂ thin films: sol-gel synthesis and characterization”, *Journal of Materials Chemistry*, 10 (2000) 1147-1150.
- [1-35] Makoto Fujimaki, Shigeyuki Shimoto, Nahoko Miyazaki, Yoshimichi Ohki, “Effect of annealing on Ge-doped SiO₂ thin films”, *Journal of Applied Physics*, 86 (1999) 5270-5273.
- [1-36] C. Jeffrey Brinker, George W. Scherer, “Sol-gel science: The physics and Chemistry of sol-gel processing”, *Boston: Academics Press*, (1990).

- [2-1] S. E. Miller, “Integrated Optics: An Introduction”, *The Bell System Technical Journal*, 48 (1969) 2059-2068.
- [2-2] M. A. Powell, A. O. Donnell, “What integrated optics is really used for”, *Optics and Photonics News*, September (1997) 23-29.
- [2-3] H. Nishihara, M. Haruna, T. Suhara, Optical integrated circuits, *McGraw-Hill, New York* (1985).
- [2-4] P. Coudray, P. Etienne, Y. Moreau, “Integrated optics based on organo-mineral materials”, *European Materials Conference-Strasbourg* (1999).
- [2-5] N. Hairston, “Lithography aids integration of optics”, *Laser Focus World*, 37 November (2001) 93-98.
- [2-6] R. R. A. Syms, A. S. Homles, W. Huang, V. M. Schneider, M. Green, “Development of the SC-RTA process for fabrication of sol-gel based silica-on-silicon integrated optic components”, *Journal of Sol-Gel Science and Technology*, 13 (1998) 509-516.

BIBLIOGRAPHY

- [2-7] A. S. Holmes, R. R. A. Syms, Ming Li, Mino Green, "Fabrication of buried channel waveguides on silicon substrates using spin on glass", *Applied Optics*, 32 (1993) 4916-4921.
- [2-8] R. A. Bellman, G. Bourdon, G. Alibert, A. Beguin, E. Guiot, L. B. Simpson, P. Lehuède, L. Guizieu, "Ultralow loss high delta silica Germanium planar waveguides" *Journal of the Electrochemical Society*, 151 (2004) G541-G547.
- [2-9] T. Kominato, Y. Ohmori, H. Okazaki, M. Yasu, "Very low loss GeO₂-doped silica waveguides fabricated by flame hydrolysis deposition method", *Electronics Letters*, 26 (1990) 327-328.
- [2-10] Liping Zuo, Hisanori Suzuki, Kenneth Kong, Junjie Si, Minyt Minyt Aye, Atsushi Watabe, Shiro Takahashi, "Athermal silica-based interferometer type planar lightwave circuits realized by a multicore fabrication method", *Optics Letters*, 28 (2003) 1046-1048.
- [2-11] Zhai Jiwei, Zhang Liangying, Yao Xi, S. N. B. Hodgson, "Characteristics of laser-densified and conventionally heat treated sol-gel derived silica-titania films", *Surface and Coating Technology*, 138 (2001) 135-140.
- [2-12] Richard Syms, John Cozens, "Optical guided waves and devices", *London; New York: McGraw-Hill* (1992).
- [2-13] S. Iraj Najafi, "Introduction to glass integrated optics", *Boston: Artech House* (1992).
- [2-14] Edmond J. Murphy, "Integrated optical circuits and components: design and applications", *New York: Marcel Dekker* (1999).
- [2-15] J. Gazecki, J. M. Kubica, M. Zamora, G. K. Reeves, C. M. Johnson, M. C. Ridgway, "Refractive indices and thickness of optical waveguides fabricated by ion implantation into silica glass", *Thin Solid Films*, 340 (1999) 233-236.

- [2-16] P. W. Leech, M. Ridgway, M. Faith, "Channel waveguides formed in fused silica and silica-on-silicon S, P and Ge ion implantation", *IEE Proc. Optoelectronics*, 143 (1996) 281-286.
- [2-17] Xue-Lin Wang, Ke-Ming Wang, Gang Fu, Shi-Ling Li, "Low propagation loss of the waveguides in fused quartz by oxygen ion implantation", *Optics Express*, 12 (2004) 4675-4680.
- [2-18] M. Verhaegen , L. B. Allard , J. L. Brebner , M. Essid, S. Roorda, J. Albert, "Photorefractive waveguides produced by ion-implantation of fused silica", *Nuclear Instruments and Methods in Physics Research-B*, 106 (1995) 438-441.
- [2-19] Shi-Ling Li, Ke-Ming Wang, Feng Chen Xue-Lin Wang, Gang Fu, Qing-Ming Lu, Li-Li Hu, Ding-Yu Shen, Hong-Ji Ma, "Property studies of optical waveguide formed by 6.0 MeV carbon ion implantation into Nd:silicate glass" *Journal of Physics D: Applied Physics*, 38 (2005) 2899-2903.
- [2-20] P. W. Leech, M. Faith, P. C. Kemeny , M. C. Ridgway , R. G. Elliman ,G. K. Reeves, W. Zhou, "Channel waveguides formed by germanium implantation in fused silica" *Nuclear Instruments and Methods in Physics Research-B*, 106 (1995) 442-446.
- [2-21] P. J. Hughes, A. P. Knoghts, B. L. Weiss, "High temperature proton implantation induced photosensitivity of Ge-doped SiO₂ planar waveguide", *Applied Physics Letters*, 74 (1999) 3311-3313.
- [2-22] R. H. Magruder III, R. A Weeks, R. A. Weller, R. A. Zuhr, D. K. Hensley, "Formation and photosensitivity of defects in Se implanted silica", *Journal of Non-Crystalline Solids*, 239 (1998) 78-83.

- [2-23] Ken-ichi Kawamura, Yoshikazu Kameshima, Hideo Hosono, Hiroshi Kawazoe, "Proton implantation-induced optical phenomenon in $\text{SiO}_2\text{:GeO}_2$ glasses formation of photosensitive defects and nanometer sized Ge crystal", *Materials Science and Engineering*, B54 (1998) 18-23.
- [2-24] D. M. Ruck, S. Brunner, K. Tinschert, W. F. X. Frank, "Production of buried waveguides in PMMA by high energy ion implantation", *Nuclear Instruments and Methods in Physics Research-B*, 106 (1995) 447-451.
- [2-25] A. J. Houghton, P. D. Townsend, "Optical waveguides formed by low-energy electron irradiation of silica", *Applied Physics Letters*, 29 (1976) 565-566.
- [2-26] S. J. Madden, Mino Green, D. Barbier, "Optical channel waveguide fabrication based on electron beam irradiation of silica", *Applied Physics Letters*, 57 (1990) 2902-2903.
- [2-27] R. R. A. Syms, T. J. Tate, J. J. Lewandowski, "Near-Infrared channel waveguides formed by electron-beam irradiation of silica layers on silicon substrates", *Journal of Lightwave Technology*, 12 (1994) 2085-2090.
- [2-28] S. Garcia, A. Glidle, J. H. Davies, J. S. Aitchison, J. M. Cooper, "Electron-beam-induced densification of Ge-doped flame hydrolysis silica for waveguide fabrication", *Applied Physics Letters*, 79 (2001) 2889-2891.
- [2-29] Susan M. R. Spaargaren, "Characterization of defects in waveguides formed by electron irradiation of silica-on-silicon", *Journal of Lightwave Technology*, 18 (2000) 555-561.
- [2-30] R. R. A. Syms, T. J. Tate, Richard Bellerby, "Low-loss near-infrared passive optical waveguide components formed by electron beam irradiation of silica-on-silicon", *Journal of Lightwave Technology*, 13 (1995) 1745-1749.
- [2-31] <http://www.tokyo.afosr.af.mil/ASL/asl44.htm#Information>.

- [2-32] K. Liu, E. Y. B. Pun, T. C. Sum, A. A. Bettiol, J. A. van Kan, F. Watt, "Erbium-doped waveguide amplifiers fabricated using focused proton beam writing", *Applied Physics Letters*, 84 (2004) 684-686.
- [2-33] E. J. Teo, M. B. H. Breese, E. P. Tavernier, A. A. Bettiol, F. Watt, "Three-dimensional microfabrication in bulk silicon using high-energy protons", *Applied Physics Letters*, 84 (2004) 3202-3204.
- [2-34] J. A. van Kan, A. A. Bettiol, F. Watt, "Three-dimensional nanolithography using proton beam writing", *Applied Physics Letters*, 83 (2003) 1629-1631.
- [2-35] J. L. Archambault, L. Reekie, P. St. J. Russell, "100% reflectivity Bragg reflectors produced in optical fibers by single excimer laser pulses," *Electronics Letters*, 29 (1993) 453-455.
- [2-36] A. A. Bettiol, T. C. Sum, F. C. Cheong, C. H. Sow, S. Venugopal Rao, J. A. van Kan, E. J. Teo, K. Ansari, F. Watt, "A progress review of proton beam writing applications in microphotonics", *Nuclear Instruments and Methods in Physics Research-B*, 231 (2005) 364-371.
- [2-37] A. A. Bettiol, S. Venugopal Rao, T. C. Sum, J. A. van Kan, F. Watt, "Fabrication of optical waveguides using proton beam writing", *Journal of Crystal Growth*, 288 (2006) 209-212.
- [2-38] T. C. Sum, A. A. Bettiol, J. A. van Kan, F. Watt, "Proton beam writing of low-loss polymer waveguides", *Applied Physics Letters*, 83 (2003) 1707-1709.
- [2-39] T. C. Sum, A. A. Bettiol, S. Venugopal Rao, J. A. Van Kan, A. Ramam, F. Watt, "Proton beam writing of passive polymer optical waveguides", *Proc. of SPIE*, 5347 (2004) 160-169.

- [2-40] T. C. Sum, A. A. Bettiol, H. L. Seng, J. A. van Kan, F. Watt, "Direct measurement of proton-beam-written polymer optical waveguide sidewall morphology using an atomic force microscope", *Applied Physics Letters*, 85 (2004) 1398-1400.
- [2-41] A. A. Bettiol, S. Venugopal Rao, E. J. Teo, J. A. van Kan, Frank Watt, "Fabrication of buried channel waveguides in photosensitive glass using proton beam writing", *Applied Physics Letters*, 88 (2006) 171106.
- [2-42] K. O. Hill, B. S. Kawasaki, D. C. Johnson, Y. Fujii, "Optical fiber reflective filter", *US Canadian Patents and Development Limited*, (1984) 4474427.
- [2-43] Tanya M. Monro, D. Moss, M. Bazylenko, MartijndeSterke, L. Poladian, "Observation of self-trapping of light in a self-written channel in a photosensitive glass", *Physical Review Letters*, 80 (1998) 4072-4075.
- [2-44] M. Segev, B. Crosignani, A. Yariv, "Spatial solitons in photorefractive media", *Physical Review Letters*, 68 (1992) 923-926.
- [2-45] Tanya M. Monro, Peter D. Miller, L. Poladian, C. Martjin de Sterke, "Self – similar evolution of self-written waveguides", *Optics Letters*, 23 (1998) 268-270.
- [2-46] W. Torruellas, Z. Wang, C. R. Menyuk, "Observation of two-dimensional spatial solitary waves in a quadratic medium", *Physical Review Letters*, 74 (1995) 5036-5040.
- [2-47] J. S. Aitchison, A. M. Weiner, Y. Silberberg, D. E. Leaird, M. K. Oliver, J. L. Jackel, P. W. E. Smith, "Experimental observation of spatial soliton interactions", *Optics Letters*, 16 (1991) 15-17.
- [2-48] A. S. Kewitsch, A. Yariv, "Self-focusing and self-trapping of optical beams upon photopolymerization", *Optics Letters*, 21 (1996) 24-26.

- [2-49] Xiao Sheng Wang, Wei Long She, "Circularly polarized optical spatial solitons", *Optics Letters*, 30 (2005) 863-865.
- [2-50] Kalaichelvi Saravanamuttu, Mark P. Andrews, "Visible laser self-focusing in hybrid glass planar waveguides", *Optics Letters*, 27 (2002) 1342-1344.
- [2-51] S. J. Frisken, "Light-induced optical waveguide uptapers", *Optics Letters*, 18 (1993) 1035-1037.
- [2-52] Heike Ebendorff-Heidepriem, "Laser writing of waveguides in photosensitive glasses", *Optical Materials*, 25 (2004) 109-115.
- [2-53] Robert J. Kruhlak, Joseph S. C. Wong, David A. Wardle, John Harvey, "Permanent refractive-index modification in germanium-doped optical fibers by use of red light", *Optics Letters*, 30 (2005) 462-464.
- [2-54] Ami M. Ljungström, Tanya M. Monroe, "Light-induced self-writing effects in bulk Chalcogenide glass", *Journal of Lightwave Technology*, 20 (2002) 78-85.
- [2-55] Y. Moreau, P. Arguel, P. Coudray, J. Porque, "Index modulation Bragg gratings directly imprinted on sol-gel layers", *SPIE Proc.* 3278 (1998) 179-186.
- [2-56] Byeong-Soo Bae, Oun-Ho park, "Direct laser writing of self-developed waveguides in benzyldimethylketal-doped sol-gel hybrid glass", *Journal of Material Research*, 16 (2001) 3184-3187.
- [2-57] Jae Hyeok Jang, Dong Jun Kang, Byeong-Soo Bae, "Large photoinduced densification in organic modified germanosilicate glasses", *Journal American Ceramic Society*, 87 (2004) 155-158.
- [2-58] Dominique Bosc, Philippe Grosso, Isabelle Hardy, Imane Assaid, Thomas Batte, Severine Haesaert, Bruno Vioze, "High refractive index contrast in a photosensitive polymer and waveguide photo-printing demonstration", *Optics Communications*, 235 (2004) 281-284.

- [2-59] Dong Jun Kang, Woo Kim, Byeong-Soo Bae, "Direct photofabrication of refractive index modulation multimode optical waveguide using photosensitive sol-gel hybrid materials", *Applied Physics Letters*, 87 (2005) 221106 (1-3).
- [2-60] Soon-Ryong Park, Jaewan Jeong, Beom-Hoan, Seung-Gol Lee, El-Hang Lee, "Design and fabrication of polarization-insensitive hybrid sol-gel arrayed waveguide grating", *Optics Letters*, 28 (2003) 381-383.
- [2-61] T. Touam, G. Milova, Z. Saddiki, M. P. Andrews, M. A. Fardad, S. Juma, J. Chrostowski, S. I. Najafi, "Organoaluminophosphate sol-gel silica glass thin films for integrated optics", *Proc. of SPIE*, 2997 (1997) 79-84.
- [2-62] P. Coudray, J. Chisham, "Ultraviolet light imprinted sol-gel silica glass waveguide devices on silicon", *Optics Communications*, 128 (1996) 19-22.
- [2-63] M. A. Fardad, M. Fallahi, "Sol-gel multimode interference power splitters", *IEEE Photonics Technology Letters*, 11 (1999) 687-699.
- [2-64] Q. Y. Zhang , K. Pita , Charles K. F. Ho , N. Q. Ngo , L. P. Zuo, S. Takahashi, "Low optical loss germanosilicate planar waveguides by low-pressure inductively coupled plasma-enhanced chemical vapor deposition", *Chemical Physics Letters*, 368 (2003) 183-188.
- [2-65] Feridun Ay, Atilla Aydinli, Sedat Agan, "Low-loss as-grown germanosilicate layers for optical waveguides", *Applied Physics Letters*, 83 (2003) 4743-4745.
- [2-66] Wu Yuan-Da, Xing Hua, Zhang Le-Tian, Li Ai-Wu, "Preparation of a waveguide array in flame hydrolysis deposition $\text{GeO}_2\text{:SiO}_2$ glasses by excimer laser irradiation", *Chinese Physics Letters*, 19 (2002) 1877-1879.
- [2-67] G. D. Maxwell, B. J. Ainslie, "Demonstration of a directly written directional coupler using UV-induced photosensitivity in a planar silica waveguide", *Electronics Letters*, 31 (1995) 95-96.

BIBLIOGRAPHY

- [2-68] M. Svalgaard, "Direct writing of planar waveguide power splitters and directional coupler using a focused ultraviolet laser beam", *Electronics Letters*, 33 (1997) 1694-1695.
- [2-69] Masahide Takahashi, Akifumi Sakoh, Kentaro Ichii, Yomei Tokuda, Toshinobu Yako, Junji Nishii, "Photosensitive GeO₂-SiO₂ films for ultraviolet laser writing of channel waveguides and Bragg-gratings with Cr-loaded waveguide structure", *Applied Optics*, 42 (2003) 4594-4597.
- [2-70] <http://scholar.lib.vt.edu/theses/available/etd-08102002-151200/unrestricted/Thesis.pdf>
- [2-71] Ajoy Ghatak, K. Thyagrajan, "Introduction to Fiber Optics", *Cambridge University Press* (1998).
- [2-72] M. Micoulaut, L. Cormier, G.S. Henderson, "The structure of amorphous, crystalline and liquid GeO₂", *arXiv:cond-mat/0609730v128 Sep (2006)*.
- [2-73] Clifford R. Pollock, Michal Lipson, "Integrated photonics", *Boston: Kluwer Academic* (2003).
- [2-74] S. Iraj Najafi, "Introduction to glass integrated optics", *Boston: Artech House* (1992).
- [2-75] Hiroaki Yanagida, Kunihiro Koumoto, Masaru Miyayama, "The chemistry of ceramics", *John Wiley and Sons* (1996).
- [2-76] Andrei M. Efimov, "Optical constant of inorganic glasses", *CRC Press, Florida* (1995).
- [2-77] <http://www.ptc.tugraz.at/specmag/struct/s.htm>.
- [2-78] Raman Kashyap, "Fiber Bragg Grating", *Academic press; New York* (1999).
- [2-79] Giovanna Brusatin, Massimo Guglielmi, Alessandro Martucci, "GeO₂ based sol-gel films", *Journal of American Ceramics Society*, 80 (1997) 3139-3144.

- [2-80] X. Orignac, R. M. Almeida, "Silica sol-gel optical waveguides on silicon", *IEE Proc. Optoelectronics*, 143 (1996) 287-292.
- [2-81] James W. Fleming, "Dispersion in GeO₂-SiO₂ glasses", *Applied Optics*, 23 (1984) 4486-4493.
- [2-82] K. Susa, I. Matsuyama, S. Satoh, T. Suganuma, "Sol-gel derived Ge-doped silica glass for optical fiber application", *Journal of Non-Crystalline Solids*, 119 (1990) 21-28.
- [2-83] Q. Y. Zhang, K. Pita, S. C. Tjin, C. H. Kam, L. P. Zuo, S. Takahashi, "Laser-induced ultraviolet absorption and refractive index changes in Ge-B-SiO₂ planar waveguides by inductively coupled plasma-enhanced chemical vapor deposition", *Chemical Physics Letters*, 379 (2003) 534-538.
- [2-84] Kenji Kintaka, Junji Nishii, "Temperature sensitivity of Ge-B-SiO₂ waveguide Bragg grating on a crystallized glass substrate", *Optics Letters*, 27 (2002) 1394-1396.
- [2-85] E. M. Yeatman, K. Pita, M. M. Ahmad, "Strip-loaded High-Confinement waveguide for photonic application" *Journal of Sol-Gel Science and Technology*, 13 (1998) 517-521.
- [2-86] R. R. A. Syms, A. S. Homles, "Deposition of thick silica-titania sol-gel films on Si substrates", *Journal of Non-Crystalline Solids*, 170 (1994) 223-233.
- [2-87] E. M. Yeatman, E. J. C. Dawney, "Doped Sol-Gel films for silica-on silicon photonics components", *Journal of Sol-Gel Science and Technology*, 8 (1997) 1007-1011.
- [2-88] R. R. A. Syms, V. M. Schneider, W. Huang, M. M. Ahman, "High- Δn silica-on-silicon channel waveguides based on sol-gel germanophosphate glass", *Electronics Letters*, 33 (1997) 1216-1217.

- [2-89] A. Martucci, G. Brusatin, M. Guglielmi, "Fabrication and characterization of sol-gel $\text{GeO}_2\text{-SiO}_2$ Erbium-doped planar waveguide", *Journal of Sol-Gel Science and Technology*, 13 (1998) 535-539.
- [2-90] R. R. A. Syms, W. Huang, V. M. Schneider, "Optimization of borophosphosilicate glass composition for silica-on-silicon integrated optical circuits fabrication by the sol-gel process", *Electronics Letters*, 32 (1996) 1233-1234.
- [2-91] R. R. A Syms, V. Scheinder, W. Huang, A. S. Holmes, "Low loss achieve in sol-gel based silica-on-silicon integrated optics using borophosphosilicate glass", *Electronics Letters*, 31 (1995)1833-1834.
- [2-92] X. C. Long, S. R. J. Brueck, "Composition dependence of the photoinduced refractive-index change in lead silicate glasses". *Optics Letters*, 24 (1999) 1136-1138.
- [2-93] X. C. Long, S. R. J. Brueck, "Large photosensitivity in lead-silicate glasses", *Applied Physics Letters*, 74 (1999) 2110-2112.
- [2-94] C. Strohhofer, S. Capecchi, J. Fick, A. Martucci, G. Brusatin, M. Gulielmi, "Active optical properties of erbium-doped GeO_2 -based sol-gel planar waveguides", *Thin Solid Films*, 326 (1998) 99-105.
- [2-95] Xavier Orignac, Denis Barbier, Xin Min Du, Rui M. Almieida, Orla MacCarthy, Eric Yeatman, "Sol-gel silica/titania-on-silicon Er/Yb-doped waveguides for optical amplification at $1.5\ \mu\text{m}$ ", *Optical Materials*, 12 (1998) 1-18.
- [2-96] V. Yordanova, K. Starbova, W. Hintz, J. Tomas, U. Wendt, "Excimer laser induced photo-thermal changes of sol-gel TiO_2 thin films", *Journal of Optoelectronics and Advanced Materials*, 7 (1995) 2601-2606.

- [2-97] K. O. Hill, Y. Fujii, D. C. Johnson, B. S. Kawasaki, "Photosensitivity in optical fiber waveguides: Application to reflection filter fabrication", *Applied Physics Letters*, 32 (1978) 647-649.
- [2-98] Jae Hyeok Jang, Junmo Koo, Byeong-Soo Bae, "Fabrication and ultraviolet absorption of sol-gel derived germanium oxide glass thin films", *Journal of American Ceramic Society*, 83 (2000) 1356-1360.
- [2-99] Y. Kanno, J. Nishino, "Effect of hydrolysis water on the crystallization of sol-gel derived GeO_2 ", *Journal of Materials Science Letters*, 12 (1993) 110-112.
- [2-100] Lidia Armelo, Monica Fabrizio, Silvia Gross, "Molecular interconnected SiO_2 - GeO_2 thin films: sol-gel synthesis and characterization", *Journal of Materials Chemistry*, 10 (2000) 1147-1150.
- [2-101] Nobuhiro Nagano, Mitsunori Saito, Mitsunobu Miyagi, Nobuyoshi Baba, "Refractive Indices of SiO_2 - and GeO_2 -based glasses near the infrared absorption peaks", *Journal of Non-Crystalline Solids*, 135 (1991) 114-121.
- [2-102] Da-Ming Zhu, T. Kosugi, "Thermal conductivity of GeO_2 - SiO_2 and TiO_2 mixed glasses", *Journal of Non-Crystalline Solids*, 202 (1996) 88-92.
- [2-103] J. Khaled, T. Fujiwara, M. Ohama, A. J. Ikushima, "Generation of second harmonics in Ge-doped SiO_2 thin films by ultraviolet irradiation under poling electric field", *Journal of Applied Physics*, 87 (2000) 2137-2141.
- [2-104] Syuji Matsumoto, Takumi Fujiwara, "Crystallization and optical non-linearity in GeO_2 - SiO_2 glass poled with ArF excimer-laser irradiation", *Journal of Applied Physics*, 82 (2000) 6993-6996.
- [2-105] O. Sugihara, M. Nakanishi, H. Fujimura, C. Egami, N. Okamoto, "Thermally poled silicate thin films with large second-harmonic generation" *Journal of the Optical Society of America B*, 15 (1998) 421-425.

- [2-106] G. Meltz, W. W. Morey, W. H. Glenn, "Formation of Bragg gratings in optical fibers by a transverse holographic method", *Optics Letters*, 14 (1989) 823-825.
- [2-107] M. Douay, W.X. Xie, T. Taunay, P. Bernage, P. Niay, P. Cordier, B. Pommellec, L. Dong, J. F. Bayon, H. Poignant, E. Delevague, "Densification involved in the UV-based photosensitivity of silica glasses and optical fibers", *IEEE- Journal of Lightwave Technology*, 15 (1997) 1329-1342.
- [2-108] J. Canning, D. J. Moss, M. Faith, P. Leech, P. Kemeny, C. V. Poulsen, O. Leistiko, "Ultra strong UV written gratings in PECVD grown germanosilicate rib waveguides", *Electronic Letters*, 32 (1996) 1479-1480.
- [2-109] Bertrand Pommellec, Pierre Niay, "Direct measurement of 248-and 193-nm excimer-induced densification in silica-germania waveguide blanks: comment", *Journal of Optical Society of America*, 19 (2002) 2039-2041.
- [2-110] J. Albert, B. M. Aalo, K. O. Hill, F. Bilodeau, D. C. Johnson, "Comparison of one-photon and two-photon effects in the photosensitivity of germanium-doped silica optical fibers exposed to intense ArF excimer laser pulses", *Applied Physics Letters*, 67 (1995) 3529-3531.
- [2-111] H. N. J. Fernando¹, J. Canning, L. Wosinski, B. Jaskorzynska, "Engineering UV-photosensitivity in planar lightwave circuits by plasma enhanced chemical vapour deposition", *Journal of Physics D: Applied Physics*, 37 (2004) 2804.
- [2-112] M. Essid, J. L. Brebner, "Difference in the behaviour of oxygen deficient defects in Ge-doped silica optical fiber performs under ArF and KrF excimer laser irradiation", *Journal of Applied Physics*, 84 (1998) 4193-4197.
- [2-113] M. V. Bazylenko, M. Gross, "Mechanisms of photosensitivity in germanosilica films", *Journal of Applied Physics*, 81 (1997) 7497-7505.

BIBLIOGRAPHY

- [2-114] M. Aslund, J. Canning, G. Yoffe, "Locking in photosensitivity within optical fiber and planar waveguides by ultraviolet pre-exposure", *Optics Letters*, 24 (1999) 1826-1828.
- [2-115] P. Niay, M. Douay, P. Bernage, W. X. Xie, B. Leconte, D. Ramecourt, E. Delevaque, J. F. Bayon, H. Poignant, B. Poumellec, "Does Photosensitivity pave the way towards the fabrication of miniature coherent light sources in inorganic glass waveguides?", *Optical Materials*, 11 (1999) 115-129.
- [2-116] A. I. Gusarov, D. B. Doyle, "Contribution of photoinduced densification to refractive-index modulation in Bragg-gratings written in Ge-doped silica fiber", *Optics Letters*, 25 (2000) 872-874.
- [2-117] Masahide Takashashi, Hikari Shigemura, Yoji Kawamoto, Junji Nishii, Toshinobu Yoko, "Photochemical reactions of Ge-related defects in 10GeO₂:90SiO₂ glass prepared by sol-gel process", *Journal of Non-Crystalline Solids*, 259 (1999) 149-155.
- [2-118] Mourad Essid, Jacques Albert, John L Brebner, Koichi Awazu, "Correlation between oxygen-deficient center concentration and KrF excimer laser induced defects in thermally annealed Ge-doped optical fiber performs", *Journal of Non-Crystalline Solids*, 246 (1999) 39-45.
- [2-119] Akifumi Sakoh, Masahide Takahashi, Toshinobu Yoko, "Photochemical process of divalent germanium responsible for photorefractive index change in GeO₂-SiO₂", *Optics Express*, 11 (2003) 2679-2688.
- [2-120] Jae Hyeok Jang, Junmo Koo, Byeong-Soo Bae, "Photosensitivity of Germanium Oxide and Germanosilicate glass sol-gel films", *Journal of Non-Crystalline Solids*, 259 (1999) 144-148.

- [2-121] Yasuhiro Miyake, Hiroyuki Nishikawa, Eiki Watanabe, "Change in the optical properties of Ge doped silica glass during exposure to KrF excimer laser", *Journal of Non-Crystalline Solids*, 222 (1997) 266-271.
- [2-122] B. Malo, F. Bilodea, J. Albert, D. C. Johnson, K. O. Hill, "Photosensitivity in optical fiber and silica-on-substrate waveguides", *SPIE* -44, 2044 (2001) 2-14.
- [2-123] Junji Nishii, Nayouki Kitamura, Hiroshi Yamanaka, "Ultraviolet-radiation-induced chemical reactions through one-and two-photon absorption process in GeO₂-SiO₂ glasses", *Optics Letters*, 20 (1995) 1184-1186.
- [2-124] Junji Nishii, Kohei Fukumi, Hiroshi Yamanaka, "Photochemical reaction in GeO₂-SiO₂ glasses induced by ultraviolet irradiation: comparison between Hg lamp and excimer", *Physical Review B*, 53 (1995) 1661-1665.
- [2-125] L. Dong, J. L. Archambault, L. Reekie, P. St. J. Russell, D. N. Payne, "Photoinduced absorption change in germanosilicate performs: evidence for color-center model of photo sensitivity", *Applied Optics*, 34 (1995) 3436-3440.
- [2-126] Hikari Shigemura, Yoji Kawamoto, Juji Nishi, Masahide Takahashi, "Ultraviolet photosensitive effect of sol-gel derived GeO₂:SiO₂ glasses", *Journal of Applied Physics*, 85 (1999) 3413-3416.
- [2-127] Jiannrong Qiu, N Wada, F. Ogura, K. Kojima, K. Hirao, "Structural relaxation and long-lasting phosphorescence in sol-gel-derived GeO₂ glass after UV irradiation", *Journal of Physics: Condensed Matter*, 14 (2002) 2561-2567.
- [2-128] Jae Hyeok Jang, Junmo Koo, Byeong-Soo Bae, "Photo bleaching of sol-gel derived germanium oxide glass thin films", *Journal of Material Research*, 15 (2000) 282-284.
- [2-129] Hideo Hosono, Yoshihiro Abe, "Nature and origin of the 5eV band in SiO₂:GeO₂ glasses", *Physical Review B*, 46 (1992) 445-451.

- [2-130] Junji Nishii, Hiroshi Yamanaka, "Characteristics of 5-eV absorption band in sputter deposited $\text{GeO}_2\text{-SiO}_2$ thin glass films", *Applied Physics Letters*, 64 (1994) 282-284.
- [2-131] Kevin P. Chen, Peter R. Herman Dragan Corie, Jianzhao Li, Midori Wei, "F₂-Laser photosensitivity applications in germanosilicate fiber and planar waveguides", *Proc. of SPIE*, 4540 (2002)158-169.
- [2-132] Kevin P. Chen, Peter R. Herman, Jie Zhang, "Large Photosensitivity in Germanosilicate planar waveguides induced by 157nm F₂-Laser radiation", *Optical Fiber Comm. Conf. Tech. Digest OSA; Wash. Dc*, (2001) WDD81-13.
- [2-133] Peter R. Herman, Kevin P. Chen, Sandy Ng, Dragan Coric, "Photosensitivity in glasses: comparing ultrafast lasers with vacuum-ultraviolet laser", *OSA Conference on Laser and Electro-Optics*, (2001) 490-491.
- [2-134] B. Poumellec, P. Niay, M. Douay, "The UV-induced refractive index grating in Ge:SiO₂ Preform;additional CW experiments and the macroscopic origin of the change in index", *Journal Physics D*, 29 (1996) 1842-1856.
- [2-135] A. D. Razafimahatratra, M. Bentsou, M. Bouazaoui, W. X. Xie, C. Mathieu, A. Dacosta, M. Douray, "UV-induced permanent gratings in sol-gel germanosilicate thin films", *Optical Materials*, 13 (2000) 439-448.
- [2-136] Isabelle Riant, Fabrice Haller, "Study of the Photosensitivity at 193 nm and comparison with photosensitivity at 240 nm influence of fiber tension: type IIa aging", *Journal of Lightwave Technology*, 15 (1997) 1464-1469.
- [2-137] T. Taunay, P. Niay, P. Bernage, M. Douay, W. X. Xie, D. Pureur, P. Cordier, J. F. Bayon, H. Poignant, E. Delevaque, B. Poumellec, "Bragg grating inscriptions within strained monomode high NA germania-doped fibers: part I. Experimentation", *Journal Physics D: Applied Physics* 30 (1997) 40-52.

- [2-138] G. Feher, "Observation of nuclear magnetic resonances via the electron spin resonance line", *Physics Review*, 103 (1956) 834-835.
- [2-139] G. Kordas, "EPR spectroscopy on sol-gel glasses", *Journal of Non-Crystalline Solids*, 147 & 148 (1992) 106-114.
- [2-140] Y. Bar-Yam, J. D. Joannopoulos, "Theories of defects in amorphous semiconductors", *Journal of Non-Crystalline Solids*, 97 & 98 (1987) 267-474.
- [2-141] Maureen K. Schurman, Minoru Tomozawa, "Equilibrium oxygen vacancy concentrations and oxidant diffusion in germania, silica and germania-silica glasses", *Journal of Non-Crystalline Solids*, 202 (1996) 93-106.
- [2-142] K. D. Simmons, B. G. Potter, G. I. Stegeman, "Red photoluminescence and Optical absorption in hydrogen-treated $\text{GeO}_2\text{-SiO}_2$ sol-gel-derived planar waveguides", *Applied Physics Letters*, 64 (1994) 2537-2539.
- [2-143] D. L. Williams, B. J. Ainslie, R. Kashyap, G. D. Maxwell, J. R. Campbell, R. Wyatt, "photosensitivity index changes in germania doped silica glass fibers and waveguides, *SPIE-55*, 2044 (2001)15-28.
- [2-144] Junji Nishii, Kenji Kintaka, Hiroaki Nishiyama, Masahide Takahashi, "Photosensitivity and athermal glasses for optical channel waveguide", *Journal of Non-Crystalline Solids*, 326 & 327 (2003) 467-471.
- [2-145] Masahide Takahashi, Takumi Fujiwara, Taji Kawachi, Akira J. Ikuhima, "Thermal equilibrium of Ge-related defects in a $\text{GeO}_2\text{-SiO}_2$ glass", *Applied Physics Letters*, 72 (1998) 1287-1289.
- [2-146] Masahide Takahashi, Hikari Shigemura, Yoji Kawamoto, Junji Nishii, Toshinobu Yoko, "Photochemical reactions of Ge-related defects in $10\text{GeO}_2.90\text{SiO}_2$ glass prepared by sol-gel process", *Journal of Non-Crystalline Solids*, 259 (1999) 149-155.

- [2-147] Motoshi Ohama, Takumi Fujiwara, Akira J. Ilkushima, "Decay of Ultraviolet-induced optical absorption in Ge:SiO₂ glass", *Applied Physics Letters*, 73 (1998) 1481-1483.
- [2-148] D. P. Hand, P. St. J. Russell, "Photoinduced refractive-index changes in germanosilicate fibers" *Optics Letters*, 15 (1990) 102-104.
- [2-149] J. Garapon, B. Poumellec, S. Vacher, A. N. Trukhin, "Observation of a new photoluminescence band at 320nm under 270nm excitation in Ge-doped silica glass", *Journal of Non-Crystalline Solids*, 311 (2002) 83-88.
- [2-150] A. Anedda, C. M. Carbonaro, F. Clemente, R. Corpino, A. Serpi, "Excitation pattern of the blue emission in Ge-doped silica", *Journal of Non-Crystalline Solids*, 315 (2003) 161-165.
- [2-151] M. D. Sceats, S. B. Poole, "Stress-relief-The mechanism of photorefractive index control in fiber cores", *Proc. 16th Australian Conference on Optical Fiber Technology*, (1991) 302-305.
- [2-152] M. D. Sceats, G. R. Atkins, S. B. Poole, "Photolytic index changes in optical fibers", *Annual Review of Materials Science*, 23 (1993) 381-410.
- [2-153] R. T. Croswell, A. Reisman, D. L. Simpson, D. Temple, C. K. Williams, "Planarization processes and applications III. As-deposited and annealed film properties", *Journal of the Electrochemical Society*, 147 (2000) 1513-1524.
- [2-154] C. Fiori, R. A. B. Devine, "Ultraviolet irradiation induced compaction and photoetching in amorphous, thermal SiO₂", *Material Research Society*, 61 (1986) 187-195.
- [2-155] H. G. Limberger, P. Y. Fonjallaz, R. P. Salathe, F. Cochet, "Compaction- and photoelastic-induced changes in fiber Bragg gratings", *Applied Physics Letters*, 66 (1996) 3069-3071.

- [2-156] A. Othonos, K. kalli, "Fiber Bragg gratings, Fundamentals and applications in telecommunication and sensing", *Artech House* (1999).
- [2-157] B. Poumellec, P. Guenot, I. Riant, P. Sansonetti, P. Niay, P. Bernage, J. F. Bayon, "UV induced densification during Bragg grating inscription in Ge:SiO₂ preform", *Optical Materials*, 4 (1995) 441-449.
- [2-158] H. Fernando, J. Canning, L. Wosinski, B. Jaskorzynska and M. Dainese, "Characterization of UV-induced changes in planar waveguides", *Journal of optics A: Pure and Applied Optics*, 5 (2003) 335-340.
- [2-159] M. V. Bazylenko, D. Moss, J. Canning, "Complex photosensitivity observed in germanosilica planar waveguides", *Optics Letters*, 23 (1998) 697-699.
- [2-160] P. J. Lemaire, R. M. Atkins, V. Mizrahi, "High pressure H₂ loading as a technique for achieving ultrahigh UV photosensitivity and thermal sensitivity in GeO₂ doped optical fibers", *Electronics Letters*, 29 (1993) 1191-1193.
- [2-161] Bai-Ou Guan, Hwa-Yaw, Xioa-ming Tao, Xio-Yi Dong, "Highly stable fiber Bragg gratings written in hydrogen-loaded fiber", *IEEE Photonics Technology Letters*, 12 (2000) 1349-1351.
- [2-162] Tiziana Tambosso, "Indication of re-circulating catalyst in photosensitive reactions with H₂-saturated silica fiber", *Optical Fiber Communication Conference*, (2002) 105-107.
- [2-163] G. Meltz, W. W. Morey, "Bragg-grating formation and germanosilicate fiber photosensitivity", *International Workshop On Photoinduced Self Organized Effects In Fiber*, SPIE Proc. 1516 (1991) 185-199.
- [2-164] Kelly D. Simmons, George I. Stegeman, Barrett G. Potter Jr., Joseph H. Simmons, "Photosensitivity in germano-silicate sol-gel thin films", *Journal of Non-Crystalline Solids*, 179 (1994) 254-259.

- [2-165] Mikael Svalgaard, Anders Harpoth, Mare Andersen, "The role of local heating in formation of UV written optical waveguides", *Optics Express*, 13 (2005) 7823-7831.
- [2-166] V. Grubsky, D. S. Starodubov, J. Feinberg, "Photochemical reaction of hydrogen with germanosilicate glass initiated by 3.4 - 5.4 eV ultraviolet light", *Optics Letters*, 24 (1999) 729-731.
- [2-167] F. Bilodeau, B. Malo, J. Albert, D. C. Johnson, K. O. Hill, Y. Hibino, M. Abe, M. Kawachi, "Photosensitization of optical fiber and silica-on-silicon/silica waveguides", *Optics Letters*, 18 (1993) 953-955.
- [2-168] Micheal Fokine, Walter Margulis, "Large increase in photosensitivity through massive hydroxyl formation" *Optics Letters*, 25 (2000) 302-304.
- [2-169] E. M. Starr, N. Nourshargh, J. S. McCormack, "Effect of laser heating on optical properties of germania doped silica optical waveguides", *Material Research Society Symp. Proc.*, 88 (1987).
- [2-170] G. Brambilla, V. Pruneri, L. Reekie, D. N. Payne, "Enhanced photosensitivity in germanosilicate fibers exposed to CO₂ laser irradiation", *Optics Letters*, 24 (1999) 1023-1025.
- [2-171] E. Salik, D. S. Starodubov, V. Grubsky, "Increase of photosensitivity in Ge-doped fibers under strain", *Optics Letters*, 25 (2000) 1147-1149.
- [2-172] Oleg V. Ivanov, "Fabrication of long-period fiber gratings by twisting a standard single-mode fiber", *Optics Letters*, 30 (2005) 3290-3292.
- [2-173] Young-Guen Han, "Temperature sensitivity control and mechanical stress effect of Boron-doped Long period gratings", *Fiber and Integrated Optics*, 20 (2001) 591-600.

BIBLIOGRAPHY

- [2-174] L. Dong, J. Pinkstone, P. St. J. Russell, D. N. Payne, "Ultraviolet absorption in modified chemical vapor deposition preforms", *Journal Optical Society America-B*, 11 (1994) 2106-2111.
- [2-175] D. L. Williams, B. J. Ainslie, J. R. Armitage, R. Kashyap, R. Campbell, "Enhanced UV photosensitivity in boron codoped germanosilicate fibers", *Electronics Letters*, 29 (1993) 45-47.
- [2-176] I. Camlibel, D. A. Pinnow, F. W. Dabby, "Optical aging characteristics of borosilicate clad fused silica core fiber optical waveguide", *Applied Physics Letters*, 26 (1975) 185-187.
- [2-177] Kevin P. Chen, Peter R. Herman, "Trimming phase and birefringence errors in photosensitivity-locked planar optical circuits", *IEEE Photonics Technology Letters*, 14 (2002) 71-73.
- [2-178] D. L. Williams, R. P. Smith, "Accelerated lifetime test on UV written intra core gratings in boron codoped silica fiber", *Electronics Letters*, 31 (1995) 2120-2121.
- [2-179] S. R. Baker, H. N. Rourke, V. Baker, D. Goodchild, "Thermal decay of fiber Bragg grating written in boron and germanium co-doped silica fiber", *Journal of Lightwave Technology*, 15 (1997) 1470-1477.
- [2-180] K. E. Chisholm, K. Sugden, I. Bennion, "Effect of thermal annealing on fiber Bragg grating in boron/germania co-doped fiber", *Journal of Physics-D: Applied Physics*, 31 (1998) 61-64.
- [2-181] C. S. Kim, Y. G. Han, B. H. Lee, W. T. Han, U. C. Paek, Y. Chung, "Induction of refractive index change B-doped optical fibers through relaxation of the mechanical stress", *Optics Communications*, 185 (2000) 337-342.

- [2-182] N. Imoto, N. Shimizu, H. Mori, M. Ikeda, "Sputtered silica waveguides with an embedded three-dimensional structure", *IEEE Journal of Lightwave Technology*, LT-1 (1983) 289-293.
- [2-183] Zhong-Yi Yin, B. K. Garside, "Low-loss GeO₂ optical waveguide fabrication using low deposition rate rf sputtering", *Applied Optics*, 21 (1982) 4324-4328.
- [2-184] L. L. Atl, S. W. Ing, Jr., K. W. Laendle, "Low-temperature deposition of silicon oxide films," *Journal of Electrochemical Society*, 110 (1963) 465.
- [2-185] M. V. Bazylenko, M. Gross, P. L. Chu, D. Moss, "Photosensitivity of Ge-doped silica deposited by hollow cathode PECVD", *Electronics Letters*, 32 (1996) 1198-1199.
- [2-186] Kelly D. Simmons, George I. Stegeman, Barrett G. Potter, Jr., Joseph H. Simmons, "Photosensitivity of sol-gel derived germanosilicate planar waveguides", *Optics Letters*, 18 (1993) 25-27.
- [2-187] Amir Fradad, Mark Andrews, Galina Milova, Ali Malek-Tabrizi, Najafi, "Fabrication of ridge waveguide: a new sol-gel route", *Applied Optics*, 37 (1998) 2429-2434.
- [2-188] Kar Pong Lor, Qing Liu, Kin Seug Ching, "UV-written long period grating on polymer waveguides", *IEEE Photonics Technology Letters*, 17 (2003) 594-596.
- [2-189] Rajni, K. Pita, Tjin Swee Chuan, S. F. Yu, Kam Chan Hin, "Enhanced photosensitivity in sol-gel derived 20GeO₂:80SiO₂ thin films" *Applied Physics-A-Materials Science & Processing*, 82 (2006) 535-541.
- [2-190] Rajni, Charles Ho Kin Fai, Kantisara Pita, N. Q. Ngo, "Porosity control of 20GeO₂:80SiO₂ sol-gel derived thin films by varying the level of sol pH for low loss optical waveguide devices" *Journal of the Electrochemical Society*, 152 (2005) G456-G459.

- [2-191] Charles K. F. Ho, D. C. L. Gwee, Rajni, K. Pita, Q. N. Ngo, C. H. Kam, "Planar optical waveguides fabricated by sol-gel derived inorganic silicate glass", *Proceedings of 11th European Conference on Integrated Optics: Prague-Czech Republic*, 2-5 Apr (2003) 305-308.
- [2-192] Charles K. F. Ho, D. C. L. Gwee, Rajni, K. Pita, N. Q. Ngo, C. H. Kam, "Fabrication and characterization of optical waveguide material for integrated optics by the inorganic sol-gel process," *Conference on the Optical Internet & Australian Conference on Optical Fiber Technology, Melbourne Australia*, 13-16 July (2003) 744-747.
- [2-193] <http://smtp2.thewwwstore.com/chemat/solgelinfo/newsitem2.tpl?cart=llllll>.
- [2-194] W. Geffcken, E. Berger, Ger. Patent 736,411 (1939).
- [2-195] www.byegm.gov.tr/yayinlarimiz/NEWSPOT/1997/1/N9.htm
- [2-196] Helmut Dislich, "New routes to multicomponent oxide glasses", *Angewandte Chemie International Edition*, 10 (1971) 363-370.
- [2-197] Angus Macleod, "The early days of optical coatings", *Journal of Optics A: Pure and Applied Optics*, 1 (1999) 779-783.
- [2-198] C. Jeffrey Brinker, George W. Scherer, "Sol-gel science: The physics and Chemistry of sol-gel processing", *Boston: Academic Press*, (1990).
- [2-199] John D. Wright, Nico A. J. M. Sommerdijk. "Sol-gel materials: chemistry and applications", *Amsterdam: Gordon & Breach Science* (2001).
- [2-200] Ram C. Mehrotra, "Chemistry of alkoxide precursors", *Journal of Non-Crystalline Solids*, 121 (1990) 1-6.
- [2-201] D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, A. Singh, "Alkoxo and aryloxo derivatives of metals", *San Diego, California: Academic Press* (2001).

BIBLIOGRAPHY

- [2-202] Nataliya Ya. Turova, Evgenia P. Turevskaya, "The chemistry of metal alkoxides", *Boston, Massachusetts: Kluwer Academic Publishers* (2002).
- [2-203] M. Klotz, A. Ayrat, C. Guizard, L. Cot, "Tailoring of the porosity in sol-gel derived silica thin layers", *Bull. Korean Chemical Society*, 20 (1999) 879-882.
- [2-204] T. N. M. Bernards, E. W. J. L. Oomen, M. J. van Bommel, A. H. Boonstra, "The effect of TEOG on the hydrolysis-condensation mechanism of a two step Sol-Gel process of TEOS", *Journal of Non-Crystalline Solids*, 142 (1992) 215-224.
- [2-205] Ahmed, M. Gadalla, Su-Jin Yun, "Characterization of gels prepared from silicon ethoxide in presence of HCl and HF", *Journal of Non-Crystalline Solids*, 143 (1992) 121-132.
- [2-206] I. Matsuyama, S. Satoh, M. Katsumoto, K. Susa, "Raman and GC-MS Study of the initial stage of hydrolysis of tetraethoxysilane in acid and base catalyzed sol-gel process", *Journal of Non-Crystalline Solids*, 135 (1991) 22-28.
- [2-207] Wen Lai Huang, "Effect of HCl in a two-step sol-gel process using TEOS", *Journal of Non-Crystalline Solids*, 258 (1999) 234-238.
- [2-208] Jackie Y. Ying, Jay B. Benziger, "Structural tailoring of alkoxide silica", *Journal of Non-Crystalline Solids*, 147 & 148 (1992) 222-231.
- [2-209] William G. Fahrenholtz, Douglas M. Smith, Duen Wu Hua, "Formation of microporous silica gels from a modified silicon alkoxide. I. Base-catalyzed gel", *Journal of Non-Crystalline Solids*, 144 (1992) 45-52.
- [2-210] Daniela C. L. Vasconcelos, Wagner R. Campos, Vanderley Vasconcelos, Wander L. Vasconcelos, "Influence of process parameters on the morphological evolution and fractal dimension of sol-gel colloidal silica particles", *Material Science and Engineering*, A334 (2002) 53-58.

- [2-211] Jae Chul, In Jae Chul, "Rheology of silica sols during the gelation process" *Journal of Non-Crystalline Solids*, 126 (1990) 259-266.
- [2-212] Jackie Y. Ying, Jay B. Benziger, "Structure tailoring of alkoxide silica", *Journal of Non-Crystalline Solids*, 147-148 (1992) 222-231.
- [2-213] W. G. Klemperer, K. D. Ramamurthi, "A flory-stockmayer analysis of silica sol-gel polymerization", *Journal of Non-Crystalline Solids*, 121 (1990) 16-20.
- [2-214] S. Y. Chang, T. A. Ring, "Map of gel times for three phase region tetraethoxysilane, ethanol and water", *Journal of Non-Crystalline Solids*, 147-148 (1992) 56-61.
- [2-215] H. Kozuka, H. Kuroki, S. Sakka, "The change of flow characteristics of $\text{Si}(\text{OC}_2\text{H}_5)_5$ solutions in the course of sol-gel conversion", *Journal of Non-Crystalline Solids*, 101 (1998) 120-122.
- [2-216] H. Hdach, T. Woignier, J. Phalippou, "Effect of aging and pH on the modulus of arogels", *Journal of Non-Crystalline Solids*, 121 (1990) 202-205.
- [2-217] Ravindra Deshpande, Duen-Wu Hua, Douglas M. Smith, C. Jeffery Brinker, "Pore structure evolution in silica gel during aging/drying III. Effects of surface tension", *Journal of Non-Crystalline Solids*, 144 (1992) 32-44.
- [2-218] Yin Ming-Zhi, Yao Xi, Zhang Liang-Ying, "Novel fabrication of meso-porous silica film by sol-gel of TEOS", *Journal of Zhejiang University Science*, 5 (2004) 422-427.
- [2-219] Atsunori Matsuda, Yoshihiro Matsuno, "Change in porosity and amount of adsorbed water in sol-gel derived porous silica films with heat treatment", *Journal of Sol-Gel Science Technology*, 20 (2001) 129-134.

- [2-220] L. C. Klein, T. A. Gallo, "Densification of sol-gel silica: constant rate heating, isothermal and step heat treatment", *Journal of Non-Crystalline Solids* 121(1990) 119-123.
- [2-221] Wolfram Vogelsberger, Andreas Seidel, Tilo Breyer, "Kinetics of sol particles formation as a function of pH studied by viscosity measurements in silica solution", *Langmuir*, 18 (2002) 3027-3033.
- [2-222] M. Misheva, N. Djourellov, F. M. A. Margaca, I. M. Miranda Salvado, "Positronium study of porous structure of sol-gel prepared SiO₂: influence of pH", *Journal of Non-Crystalline Solids*, 279 (2001) 196-203.
- [2-223] N. V. Gaponenko, H. Gnaser, P. Becker, "Carbon depth distribution in spin-on-silicon dioxide films", *Thin Solid Films*, 261 (1995) 186-191.
- [2-224] F. M. A. Margaca, I. M. Miranda Salvado, J. Teixeira, "Small Angle Neutron Scattering study of silica gels: influence of pH", *Journal of Non-Crystalline Solids*, 258 (1999) 70-77.
- [2-225] <http://www.psrc.usm.edu/mauritz/solgel.html>.
- [2-226] T. N. M. Bernards, M. J van Bommel, E. W. J. L Oomen, "Hydrolysis-condensation mechanism of a two-step sol-gel process of mixtures of TEOS and TEOG", *Journal of Non-Crystalline Solids*, 147 & 148 (1992) 13-17.
- [3-1] J. Clerk Maxwell, "A dynamical theory of the electromagnetic field", *Philosophical Transactions of the Royal Society of London* 155 (1865) 459–512; Abstract: *Proceedings of the Royal Society of London*, 13 (1864) 531-536.
- [3-2] R. A. Soref, J. Schnidtchen, K. Petermann, "Large single-mode rib waveguide in GeSi-Si and Si-on-SiO₂", *IEEE Journal of Quantum Electronics*, 27 (1991) 1971-1974.

- [3-3] D. Yevick, "A guide to electric field propagation techniques for guided wave optics", *Optical and Quantum Electronics*, 26 (1994) S185-S197.
- [3-4] D. Yevick, B. Hermansson, "Efficient beam propagation techniques", *IEEE Journal of Quantum Electronics*, 26 (1990) 109-112.
- [3-5] Young-Tak Han, Jang-UK Shin, Duk-Jun Kim, Sang-Ho Park, Yoon-Jung Park, Hee-Kyung Sung, "A rigorous 2D approximation technique for 3D waveguide structures for BPM calculations", *ETRI Journal*, 25 (2003) 535-537.
- [3-6] A. K. Ghatak, K. Thyagarajan, "Optical Electronics", *Cambridge University Press* (1998).
- [3-7] Richard Syms, John Cozens, "Optical guided waves and devices", *McGraw-Hill Book Company* (1992).
- [3-8] John H. Marsh, Richard M. De La Rue, "Waveguide optoelectronics", *Kluwer Academic Publishers* (1992).
- [3-9] Clifford R. Pollock, "Fundamentals of Optoelectronics", *Irwin Publishers* (1995).
- [3-10] K. S. Chiang, "Review of numerical and approximate methods for the modal analysis of general optical dielectric waveguides", *Optical and Quantum Electronics*, 26 (1994) S113-S134.
- [3-11] C. Vassallo "Optical mode solvers", *Optical and Quantum Electronics*, 29 (1997) 95-114.
- [3-12] E. A. J. Marcatilli, "Dielectric rectangular waveguide and directional coupler for integrated optics", *Bell System Technical Journal*, 48 (1969) 2071-2102.
- [3-13] R. K. Varshney, A. Kumar, "A simple and accurate modal analysis of strip-loaded optical waveguides with various index profiles", *Journal of Lightwave Technology*, 6 (1988) 601-606.

- [3-14] A. Sharma, P. K. Mishra, A. K. Ghatak, "Single-mode optical waveguides and directional couplers with rectangular cross section: a simple and accurate method of analysis", *Journal of Lightwave Technology*, 6 (1988) 1119-1125.
- [3-15] P. N. Robson, P. C. Kendall, "Rib Waveguide theory by the spectral index method", *New York Wiley* (1990).
- [3-16] T. Rozzi, G. Cerri, M. N. Husain, L. Zappelli, "Variational analysis of the dielectric rib waveguide using the concept of transition function. and including edge singularities", *IEEE Transactions on Microwave Theory and Techniques*, 39 (1991) 247-257.
- [3-17] W. Huang, H. A. Haus, "A simple variational approach to optical rib waveguides", *Journal of Lightwave Technology*, 9 (1991) 56-61.
- [3-18] G. M. Berry, S. V. Burke, "Analysis of optical rib self-imaging multimode interference (MMI) waveguide devices using the discrete spectral index method", *Optical and Quantum Electronics*, 27 (1995) 921-934.
- [3-19] K. S. Chiang, "Analysis of the effective-index method for the vector modes of rectangular-core dielectric waveguides", *IEEE Transactions on Microwave Theory and Technology*, 44 (1996) 692-700.
- [3-20] B. M. A. Rahman, J. B. Davies, "Finite-element solution of integrated optical waveguides", *Journal of Lightwave Technology*, 2 (1984) 682-687.
- [3-21] B. M. A. Rahman, J. B. Davies, "Vector-H finite-element solution of gaas/gaas rib waveguides", *IEE Proceedings*, 132 (1985) 349-353.
- [3-22] M. S. Stern, "Semivectorial polarized finite difference method for optical waveguides with arbitrary index profiles", *IEE Proceedings*, 135 (1988) 56-63.
- [3-23] M. S. Stern, "Semivectorial polarized H-field solutions dielectric waveguides with arbitrary index profiles", *IEE Proceedings*, 135 (1988) 333-338.

- [3-24] K. Bierwirth, N. Schulz, F. Arndt, "Finite-difference analysis of rectangular dielectric waveguide structures", *IEEE Transactions on Microwave Theory and Techniques*, MTT-34 (1986) 1104-1113.
- [3-25] U. Rogge, R. Pregla, "Vectorial method of lines for the analysis of strip-loaded optical waveguides", *Journal of the Optical Society of America B*, 8 (1991) 459-463.
- [3-26] Z. E. Abid, K. L. Johnson, A. Gopinath, "Analysis of dielectric guides by vector transverse magnetic field finite elements", *Journal of Lightwave Technology*, 11 (1993) 1545-1549.
- [3-27] M. Koshiha, S. Maruyama, K. Hirayama, "A vector finite element method with the high-order mixed-interpolation-type triangular elements for optical waveguiding problems", *Journal of Lightwave Technology*, 12 (1994) 495-502.
- [3-28] J. Y. Su, P. K. Wei, W. S. Wang, "A new iterative method for the analysis of longitudinally invariant waveguide couplers", *Journal of Lightwave Technology*, 12 (1994) 2056-2065.
- [3-29] P. Lusse, P. Stuwe, J. Schule, H.-G. Unger, "Analysis of vectorial mode fields in optical waveguides by a new finite difference method", *Journal of Lightwave Technology*, 12 (1994) 487-493.
- [3-30] G. R. Hadley, R. E. Smith, "Full-vector waveguide modeling using an iterative finite-difference method with transparent boundary conditions", *Journal of Lightwave Technology*, 13 (1995) 465-469.
- [3-31] H. Noro, T. Nakayama, "A new approach to scalar and semivector mode analysis of optical waveguides", *Journal of Lightwave Technology*, 14 (1996) 1546-1556.

- [3-32] P. L. Liu, B. J. Li, "Semivectorial helmholtz beam propagation by lanczos reduction", *IEEE Journal of Quantum Electronics*, 29 (1993) 2385-2389.
- [3-33] P. L. Liu, S. L. Yang, D. M. Yuan, "The semivectorial beam propagation method", *IEEE Journal of Quantum Electronics*, 29 (1993) 1205-1211.
- [3-34] P. C. Lee, E. Voges, "Three dimensional semi-vectorial wide-angle beam propagation method", *Journal of Lightwave Technology*, 12 (1994) 215-224.
- [3-35] F. Wijnands, H. J. W. M. Hoekstra, G. J. M. Krijnen, R. M. de Ridder, "Modal fields calculation using the finite difference beam propagation method", *Journal of Lightwave Technology*, 12 (1994) 2066-2072.
- [3-36] F. Wijnands, T. Rasmussen, H. J. W. M. Hoekstra, J. H. Povlsen, R. M. de Ridder, "Efficient semivectorial mode solvers", *IEEE Journal of Quantum Electronics*, 33 (1997) 367-374.
- [3-37] C. H. Henry, B. H. Verbeek, "Solution of the scalar wave equation for arbitrarily shaped dielectric waveguides by two-dimensional fourier analysis", *Journal of Lightwave Technology*, 7 (1989) 308-313.
- [3-38] A. S. Sudbo, "Film mode matching: a versatile numerical method for vector mode fields calculations in dielectric waveguides", *Pure and Applied Optics*, 2 (1993) 211-233.
- [3-39] S. J. Hewlett, F. Ladouceur, "Fourier decomposition method applied to mapped infinite domains: scalar analysis of dielectric waveguides down to modal cutoff", *Journal of Lightwave Technology*, 13 (1995) 375-383.
- [3-40] M. Shamonin, P. Hertel, "Analysis of nonreciprocal phase shifters for integrated optics by the Galerkin method", *Optical Engineering*, 34 (1995) 849-852.

- [3-41] H. J. W. M. Hoekstra, "An economic method for the solution of the scalar wave equation for arbitrarily shaped optical waveguides", *Journal of Lightwave Technology*, 8 (1990) 789-793.
- [3-42] G. Lifante, "Effective index method for modelling sub-wavelength two-dimensional periodic structures", *Physica Scripta*, T118 (2005) 72-77.
- [3-43] H. P. Uranus, H. J. W. M. Hoekstra, E. van Groesen, "Analysis of integrated optical waveguides", *Journal of Indonesian Mathematical Society (MIHMI)*, 8 (2002) 49-63.
- [3-44] K. Kawano, T. Kitoh, "Introduction to optical waveguide analysis", *John Wiley & Sons Inc.*, (2001).
- [3-45] Y. Chung, N. Dagli, "An assessment of finite difference beam propagation method", *IEEE Journal of Quantum Electronics*, 26 (1990) 1335-1339.
- [3-46] User Reference OptiBPM.
- [3-47] H. J. W. M. Hoekstra, G. J. M. Krijnen, P. V. Lambeck, "New formulations of the beam propagation based on the slowly varying envelope approximation", *Optics Communication*, 97 (1993) 301-303.
- [3-48] R. Accornero, M. Artiglia, G. Coppa, P. Di Vita, G. Lapenza, M. Potenza, P. Ravetto, "Finite difference methods for the analysis of integrated optical waveguide", *Electronics Letters*, 26 (1990) 1959-1960.
- [3-49] G. R. Hadley, "Transparent boundary condition for the beam propagation method", *IEEE Journal of Quantum Electronics*, 28 (1992) 363-370.
- [3-50] F. Fogli, G. Bellanca, P. Bassi, "TBC and PML conditions for 2D and 3D BPM a comparison", *Optical and Quantum Electronics*, 30 (1998) 443-456.

- [3-51] G. R. Hadley, "Full-vector waveguide modelling using an interactive finite-difference method with transparent boundary conditions", *Journal of Lightwave Technology*, 13 (1995) 465-469.
- [3-52] T. Tamir, H. Kogelnik, W. K. Burns, A. F. Milton, R. C. Alfarness, I. P. Kaminow, R. S. Tucker, F. J. Leonberger, J. F. Donnelly, "Guided wave optoelectronics", *Springer-Verlag Berlin Heidelberg New York* (1988).
- [4-1] Andrei M. Efimov, "Optical constant of inorganic glasses", *CRC Press, Boca Raton; Florida* (1995).
- [4-2] M. Ocana, V. Fornes, C. J. Serna, "The variability of the infrared power spectrum of amorphous SiO₂", *Journal of Non-Crystalline Solids*, 107 (1989) 187-192.
- [4-3] Krystyna E. Lipinska-Kalita, "FT Infrared and laser Raman spectroscopy of amorphous and crystalline germanates", *Journal of Non-Crystalline Solids*, 119 (1990) 41-48.
- [4-4] Hiroyuki Yoshino, Kanichi Kamiya, Hiroyuki Nasu, "IR study on the structural evolution of sol-gel derived SiO₂ gels in the early stage of conversion to glass", *Journal of Non-Crystalline Solids*, 126 (1990) 68-78.
- [4-5] R. M. Almeida, "Characterization of silica gels by infrared reflection spectroscopy", *Journal of Non-Crystalline Solids*, 121 (1990) 193-197.
- [4-6] Plinio Innocenzi, "Infrared spectroscopy of sol-gel derived silica based films: a spectra-microstructure overview", *Journal of Non-Crystalline Solids*, 316 (2003) 309-319.

BIBLIOGRAPHY

- [4-7] Shyama P. Mukherjee, Shiv K. Sharma, “Structural studies of gels and gel-glasses in $\text{SiO}_2\text{-GeO}_2$ system using vibrational spectroscopy”, *Journal of American Ceramic Society*, 11 (1986) 806-810.
- [4-8] Andrei M. Efimov, Vera G. Pogareva, “Water-related IR absorption spectra for some phosphate and silicate glasses”, *Journal of Non-Crystalline Solids*, 275 (2000) 189-198.
- [4-9] V.G. Plotnichenko, V. O. Sokolov, V. M. Mashinskii, V. A. Sidorov, “Hydroxyl groups in GeO_2 glass”, *Inorganic Material*, 32 (2002) 738-745.
- [4-10] Gan Fuxi, “Optical and spectroscopic properties of glasses”, *Shanghai: Shanghai Scientific and Technical Publishers* (1992).
- [4-11] Kazu Nakamoto, “Infrared and Raman spectra of inorganic and coordination compounds”, *A Wiley-Interscience Publication* (1986).
- [4-12] <http://elchem.kaist.ac.kr/vt/chem-ed/spec/vib/ir-instr.htm>.
- [4-13] PerkinElmer FTIR manual.
- [4-14] Q. Y. Zhang , K. Pita , Charles K. F. Ho , N. Q. Ngo , L. P. Zuo , S. Takahashi, “Low optical loss germanosilicate planar waveguides by low-pressure inductively coupled plasma-enhanced chemical vapor deposition”, *Chemical Physics Letters*, 368 (2003) 183-188.
- [4-15] Agilent 8453 UV-Vis spectroscopy system manual.
- [4-16] L. Ward, “The optical constants of bulk materials and films”, *Bristol; Philadelphia: Institute of Physics Publication* (1994).
- [4-17] Manual J. A. Woollam.
- [4-18] H. Xie, J. Wei, “Characterization of sol-gel thin films by spectroscopic Ellipsometry”, *Journal of Physics: Conference Series*, 28 (2006) 95-99.

BIBLIOGRAPHY

- [4-19] C. Wongmanerod, S. Zangoie, H. Arwin, "Determination of pore size distribution and surface area of thin porous silicon layers by ellipsometric ellisometry", *Applied Surface Science*, 172 (2001) 117-125.
- [4-20] <http://www.ntu.edu.sg/eee/eee6/DLC/facilities.asp>.
- [4-21] <http://carbon.cudenver.edu/public/chemistry/classes/chem4538/raman.htm>.
- [4-22] http://www.kobelco.co.jp/technobook/p238/Principle/Principle_e.htm.
- [4-23] <http://www.ciba.nus.edu.sg/facilities.html>.
- [4-24] <http://www.genplot.com/doc/RUMP/intro.htm>.
- [4-25] <http://www.unl.edu/CMRAcfem/semoptic.htm>.
- [4-26] S. Martellucci, A. N. Chester, M. Bertolotti, "Advances in integrated optics", *Plenum Press. New York and London* (1994).
- [4-27] H. P. Weber, F. A. Dunn, W. N. Leibolt, "Loss measurements in thin-film optical waveguides", *Applied Optics*, 12 (1973) 755-757.
- [4-28] P. K. Tien, R. Ulrich, "Theory of prism-film coupler and thin-film light guides", *Journal of the Optical Society of America*, 60 (1970) 1325-1337.
- [4-29] R. Ulrich, "Theory of the prism-film coupler by plane wave analysis", *Journal of the Optical Society of America*, 60 (1970) 1337-1350.
- [4-30] A. C. Adams, D. P. Schinke, C. D. Capio, "An evaluation of the prism coupler for measuring the thickness and refractive index of dielectric films on silicon substrates", *Journal of Electrochemical Society*, 126 (1979) 1539-1543.
- [4-31] R. Ulrich, R. Torge, "Measurement of the thin film parameters with a prism coupler", *Applied Optics*, 12 (1973) 2901-2908.
- [4-32] www.metricon.com.
- [4-33] Optical waveguiding educator kit *Optosci*.

BIBLIOGRAPHY

- [4-34] Mohd Haniff Ibrahim, Norazan Mohd Kassim, Abu Bakar Mohammad, Mee-Koy Chin, "Prism coupling measurement of benzocyclobutene (BCB 4024-40) polymer for optical devices application", *ELEKTRIKA* , 8 (2006) 13-16.
- [4-35] Ajoy Ghatak, K. Thyagrajan, "Introduction to Fiber Optics", *Cambridge University Press* (1998).
- [4-36] R. G. Hunsperger, "Integrated optics: theory and technology", *Springer Verlag, New York*, 3rd Ed. (1991).
- [4-37] R. Regener, W. Sohler, "Loss in low-finesse Ti:LiNbO₃ optical waveguide resonators", *Applied Physics B*, 36 (1985) 143-147.
- [4-38] D. L. Lee, "Electromagnetic principles of optics", *John Wiley and Sons, New York*, (1986) 86-89.
- [4-39] Optical fiber product information sheet.

- [5-1] Giovanna Brusatin, Massimo Guglielmi, Alessandro Martucci, "GeO₂ based sol-gel films", *Journal of American Ceramics Society*, 80 (1997) 3139-3144.
- [5-2] Y. Kanno, J. Nishino, "Effect of hydrolysis water on the crystallization of sol-gel derived GeO₂", *Journal of Materials Science Letters*, 12 (1993) 110-112.
- [5-3] Dunbar P. Birnie, Manuel Manley, "Combined flow and evaporation of fluid on a spinning disk", *Physics of Fluids*, 9 (1997) 870-875.
- [5-4] Xin Min Du, Xavier Organic, Rui M. Almeida, "Striation-free, spin-coated sol-gel optical films", *Journal of American Ceramic Society*, 78 (1995) 2254-2256.
- [5-5] Atsunori Matsuda, Yoshihiro Matsuno, "Change in porosity and amount of adsorbed water in sol-gel derived porous silica films with heat treatment", *Journal of Sol-Gel Science Technology*, 20 (2001) 129-134.

BIBLIOGRAPHY

- [5-6] Yin Ming-Zhi, Yao Xi, Zhang Liang-Ying, "Novel fabrication of meso-porous silica film by sol-gel of TEOS", *Journal of Zhejiang University Science*, 5 (2004) 422-427.
- [5-7] C. Jeffrey Brinker, George W. Scherer, "Sol-Gel Science: The physics and chemistry of sol-gel processing", *Boston: Academic Press*, (1990)
- [5-8] Plinio Innocenzi, "Infrared spectroscopy of sol-gel derived silica-based films: a spectra-microstructure overview", *Journal of Non-Crystalline Solids*, 316 (2003) 309-319.
- [5-9] S. P. Mukherjee, S. K. Sharma, "Structural studies of gels and gel-glasses in the SiO₂-GeO₂ system using vibrational spectroscopy", *Journal of American Ceramics Society*, 11 (1988) 806-810.
- [5-10] Gan Fuxi, "Optical and spectroscopic properties of glass", *Shanghai: Shanghai Scientific and Technical Publishers*, (1992).
- [5-11] Andrei M. Efimov, "Optical constant of inorganic glasses", *CRC Press, Boca Raton; Florida* (1995).
- [5-12] F. N. Dultsev, M. R. Baklanov, "Nondestructive determination of pore size distribution in thin films deposited on solid substrates", *Electrochemical and Solid-State Letters*, 2 (1992) 192-194.
- [5-13] D. J. Taylor, P. F. Fleig, S. L. Hietala, "Technique for characterization of thin film porosity", *Thin Solid Films*, 332 (1998) 257-261.
- [5-14] C. McDonagh, P. Bowe, K. Mongey, B. D. MacCraith, "Characterization of porosity and sensor response times of sol-gel-derived thin films for oxygen sensor applications", *Journal of Non-Crystalline Solids*, 306 (2002) 138-148.

BIBLIOGRAPHY

- [5-15] Krystyna E. Lipinska-Kalita, "FT Infrared and laser Raman spectroscopy of amorphous and crystalline germinates", *Journal of Non-Crystalline Solids*, 119 (1990) 41-48.
- [5-16] O. Pilla, A. Fontana, S. Caponi, F. Rossi, G. Vilianni, M. A. Gonzalez, E. Fabiani, C.P.E. Varsamis, "Vibrational dynamic of 'strong' glasses: the case of v-SiO₂ and v-GeO₂", *Journal of Non-Crystalline Solids*, 322 (2003) 53-57.
- [5-17] F. M. A. Margaca, I. M. Miranda Salvado, J. Teixeira, "Small angle neutron scattering study of silica gels: influence of pH", *Journal of Non-Crystalline Solids*, 258 (1999) 70-77.
- [5-18] www.lambdaphysik.com/pdf/pdf_325.pdf.
- [5-19] S. R. Baker, H. N. Rourke, V. Baker, D. Goodchild, "Thermal decay of fiber Bragg grating written in boron and germanium codoped silica fiber", *Journal of Lightwave Technology*, 15 (1997) 1470-1477.
- [5-20] K. E. Chisholm, K. Sugden, I. Bennion, "Effect of thermal annealing on fiber Bragg grating in Boron/Germania co-doped fiber", *Journal of Physics-D: Applied Physics*, 31 (1998) 61-64.
- [5-21] Jacob Rathje, Martin Kristensen, "Continuous anneal method for characterizing the thermal stability of ultraviolet Bragg gratings", *Journal of Applied Physics*, 88 (2000) 1050-1055.
- [5-22] Q. Y. Zhang , K. Pita , Charles K. F. Ho , N. Q. Ngo , L. P. Zuo, S. Takahashi, "Low optical loss germanosilicate planar waveguides by low-pressure inductively coupled plasma-enhanced chemical vapor deposition", *Chemical Physics Letters*, 368 (2003) 183-188.

BIBLIOGRAPHY

- [5-23] Yasuhiro Miyake, Hiroyuki Nishikawa, Eiki Watanabe, Daisuke Ito, "Change in the optical properties of Ge-doped silica glass during exposure to KrF excimer laser", *Journal of Non-Crystalline Solids*, 222 (1997) 266-271.
- [5-24] Masahide Takahashi, Hikari Shigemura, Yoji Kawamoto, Junji Nishii, Toshinobu Yoko, "Photochemical reaction of Ge-related defects in 10GeO₂:90SiO₂ glass prepared by sol-gel process", *Journal of Non-Crystalline Solids*, 259 (1999) 149-155.
- [5-25] Mourad Essid, Jacques Albert, John L Brebner, Koichi Awazu, "Correlation between oxygen-deficient center concentration and KrF laser induced defects in thermally annealed Ge-doped optical fiber preforms", *Journal of Non-Crystalline Solids*, 246 (1999) 39-45.
- [5-26] Kelly D. Simmons, George I. Stegeman, Barrett G. Potter Jr, Joseph H. Simmons, "Photosensitivity in germanosilicate sol-gel thin films", *Journal of non crystalline solids*, 179 (1994) 254-259.
- [5-27] P. Niay, M. Douay, P. Bernage, W. X. Xie, B. Leconte, D. Ramecourt, E. Delevaque, J. F. Bayon, H. Poignant, B. Poumellec, "Does photosensitivity pave the way towards the fabrication of miniature coherent light sources in inorganic glass waveguides?", *Optical Materials*, 11 (1999) 115-129.
- [5-28] Yasuhiro Miyake, Hiroyuki Nishikawa, Eiki Watanabe, Daisuke Ito, "Change in the optical properties of Ge-doped silica glass during exposure to KrF excimer laser", *Journal of Non-Crystalline Solids*, 222 (1997) 266-271.
- [5-29] Jae Hyeok Jang, Dong Jun Kang, Byeong-Soo Bae, "Large photoinduced densification in organically modified germanosilicate glass", *Journal of America Ceramics Society*, 87 (2004) 155-158.

BIBLIOGRAPHY

- [5-30] S. K. Tan, K. L. Yeo, A. Wee, "In situ XPS and SIMS analysis of O_2^+ beam-induced silicon oxidation", *Surface And Interface Analysis*, 36 (2004) 640-644.
- [5-31] P. J. Lemaire, R. M. Atkins, V. Mizrahi, "High pressure H_2 loading as a technique for achieving ultra high UV photosensitivity and thermal sensitivity in GeO_2 doped optical fibres", *Electronics Letters*, 29 (1993) 1191-1193.
- [5-32] G. D. Maxwell, B. J. Ainslie, D. L. Williams, R. Kashyap, "UV written 13 dB reflection filters in hydrogenated low loss planar silica waveguides", *Electronics Letters*, 29 (1993) 425-426.
- [5-33] Q. Y. Zhang, K. Pita, S. C. Tjin, C. H. Kam, L. P. Zuo, S. Takahashi, "Laser-induced ultraviolet absorption and refractive index changes in Ge-B- SiO_2 planar waveguides by inductively coupled plasma-enhanced chemical vapor deposition", *Chemical Physics Letters*, 379 (2003) 534-538.
- [5-34] Andrei M. Efimov, "Optical constant of inorganic glasses", *CRC Press, Boca Raton; Florida* (1995).
-
- [6-1] R. R. A Syms, "Stress in thick sol-gel phosphosilicate glass films formed on Si substrates", *Journal of Non-Crystalline Solids*, 167 (1994) 16-20.
- [6-2] R. R. A Syms, A. S. Holmes, "Deposition of thick silica- titania sol-gel films on Si substrates", *Journal of Non-Crystalline Solids*, 170 (1994) 223-233.
- [6-3] R. R. A Syms, A. S. Holmes, W. Huang, V. M. Schneider, M. Green, "Development of the SC-RTA process for fabrication sol-gel based on silica-on-silicon integrated optic components", *Journal of Sol-Gel Science and Technology*, 13 (1998) 509-516.

- [6-4] Xin-Min Du, Xavier Orignac, Rul M. Almeida, “Striation-free, spin coated sol-gel optical films”, *Communication of the American Ceramic Society*, 78 (1995) 2254-2256.
- [6-5] L. B. Soldano, Erik C. M. Pennings, “Optical multi-mode interference devices based on self-imaging: principles and applications,” *Journal of Lightwave Technology*, 13 (1995) 615-627.
- [6-6] A. Ferreras, F. Rodríguez, E. Gómez-Salas, J. L. de Miguel, F. Hernández-Gil, “Useful formulas for multimode interference power splitter/combiner design,” *IEEE Photonics Technology Letters*, 5 (1993) 1224-1227.
- [6-7] B. M. A. Rahman, M. Rajarajan, T. Wongcharoen, K. T. V. Grattan, “Accurate analysis of multimode interference devices”, *IEEE Photonics Technology Letters*, 8 (1996) 809-811.
- [6-8] M. Bachmann, P. A. Besse, H. Melchior, “Overlapping-image multimode interference couplers with a reduced number of self-images for uniform and nonuniform power splitting”, *Applied Physics*, 34 (1995) 6898-6910.
- [6-9] P. A. Besse, M. Bachmann, H. Melchoir, L. B. Soldano, M. K. Smit, “Optical bandwidth and fabrication tolerances of multimode interference couplers”, *Journal of Lightwave Technology*, 12 (1994) 1004-1009.
- [6-10] R. Ulrich, G. Ankele, “Self-imaging in homogeneous planar optical waveguides”, *Applied Physics Letters*, 27 (1975) 337-339.
- [6-11] H. H. El-Reffaey, D. A. M. Khalil, “Rigorous modal analysis of multi-mode interference (MMI) structures by radiation spectrum method with multiple reflection”, *Optics Communications*, 144 (1997) 306-314.
- [6-12] C. Themistos, B. M. A. Rahman, “Design issues of a multimode interference based 3-dB splitter”, *Applied Optics*, 41 (2002) 7037-7044.

- [6-13] M. Bachmann, P. A. Besse, H. Melchior, "General self-imaging properties in $N \times N$ multimode interference couplers including phase relations", *Applied Optics*, 33 (1994) 3905-3911.
- [6-14] L. B. Soldano, F. B. Veerman, M. K. Smit, B. H. Verbeek, A. H. Dubost, E. C. M. Pennings, "Planar monomode optical couplers based on multimode interference effects", *Journal of Lightwave Technology*, 10 (1992) 1843-1850.
- [6-15] M. Rajarajan, B. M. A. Rahman, T. Wongcharoen, K. T. V. Grattan, "Accurate analysis of MMI devices with two-dimensional confinement", *Journal of Lightwave Technology*, 14 (1996) 2078-2084.
- [6-16] Young-Tak Han, Jang-UK Shin, Duk-Jun Kim, Sang-Ho Park, Yoon-Jung Park, Hee-Kyung Sung, "A rigorous 2D approximation technique for 3D waveguide structures for BPM calculations", *ETRI Journal*, 25 (2003) 535-537.
- [6-17] C. R. Pollock, "Fundamentals of Optoelectronics", *Irwin publisher* (1995).
- [6-18] A. K. Ghatak, K. Thyagarajan, "Optical Electronics", *Cambridge University Press* (1998).
- [6-19] T. Tamir, H. Kogelnik, W. K. Burns, A. F. Milton, R. C. Alfarness, I. P. Kaminow, R. S. Tucker, F. J. Leonberger, J. F. Donnelly, "Guided wave optoelectronics", *Springer-Verlag Berlin Heidelberg New York* (1988).
- [7-1] Plinio Innocenzi, "Infrared spectroscopy of sol-gel derived silica based films: a spectra-microstructure overview", *Journal of Non-Crystalline Solids*, 316 (2003) 309-319.
- [7-2] Ahmet Kasgoz, Takahisa Misono, Yoshimoto Abe, "Sol-gel preparation of borosilicates", *Journal of Non-Crystalline Solids*, 242 (1999) 168-174.

BIBLIOGRAPHY

- [7-3] Gan Fuxi, "Optical and spectroscopic properties of glasses", Shanghai, *Shanghai Scientific and Technical Publishers* (1992).
- [7-4] R. T. Croswell, A. Reisman, D. L. Simpson, D. Temple, C. K. Williams, "Planarization processes and applications III. As-deposited and annealed film properties", *Journal of the Electrochemical Society*, 147 (2000) 1513-1524.
- [7-5] L. Dong, J. Pinkstone, P. St. J. Russell, D. N. Payne, "Ultraviolet absorption in modified chemical vapor deposition performs", *Journal of the Optical Society of America B*, 11 (1994) 2106-2111.
- [7-6] I. Camlibel, D. A. Pinnow, F. W. Dabby, "Optical aging characteristics of borosilicate clad fused silica core fiber optical waveguides", *Applied Physics Letters*, 26 (1975) 185-187.
- [7-7] E. Salik, D. S. Starodubov, V. Grubsky, "Increase of photosensitivity in Ge-doped fibers under strain", *Optics Letters*, 25 (2000) 1147-1149.
- [7-8] Young-Guen Han, Woo-Taek Han, Byeong Ha Lee, Un-Chul Paek, Youngjoo Chung, Chang-Seok Kim, "Temperature sensitivity control and mechanical stress effect of boron-doped long-period fiber gratings", *Fiber and Integrated Optics*, 20 (2001) 591-600.

Appendix [I]

KrF Laser Source

The purpose of this Appendix is to provide information about the Lambda Physik LPX 120i pulse KrF excimer UV laser source. The spectral output of KrF excimer laser is a property of the emission band of the KrF excimer molecule having the main peak at 248 nm with the pulse width of 25 ns durations. This laser can deliver maximum 500 mJ energy per pulse but the pulse energy reduces as time progresses due to static discharge of the laser gas as shown in Figure I.1. Therefore, the pulse energy of 450 mJ and lower was found to be more feasible for the experiments.

Figure I.1 Variation in the pulse energy status due to the variation in static gas life time of excimer laser.

The spot size of the KrF laser is shown in Figure I.2 and the dimension of measured beam is 24 mm $\times$ 12 mm. To monitor the actual beam intensity distribution, a burn mark was made on a photosensitive paper and the author obtained the uniform burn spot of 25 mm (length) $\times$ 11 mm (width) after the 30s to 40s of exposure time. Hence, 1 minute of minimum exposure time was chosen to attain uniformity in the exposed area at a given energy.

Figure I.2 Burn mark from Lambda Physik KrF (248nm) laser.

Appendix [II]

MatLab code for the calculation of effective index

```
% Dimensions of the waveguide
h = 3 % [micron]
w = 8 % [micron]
% Indexes of the waveguide
nchannel = 1.4733
nside = 1.4685
nSiO2 = 1.45
% Wavelength
lambda0 = 1.55 % [micron]
k0 = (2 .* pi) ./ lambda0

% Calculation of neff

% neffsides (Both the side regions are same)

kappamax = sqrt( k0.^2 .* nside.^2 - k0.^2 .* nSiO2.^2 )
nair = 1
nmiddle = nside
ndown = nSiO2
kappasides0 = pi ./ (2.*h)
beta = sqrt( k0.^2 .* nside.^2 - kappasides0.^2 )
neffsides = beta ./ k0

% neffguide (Channel region)

kappamax = sqrt( k0.^2 .* nchannel.^2 - k0.^2 .* nSiO2.^2 )
nair = 1
nmiddle = nchannel
ndown = nSiO2
kappaguide0 = pi ./ (2.*h)
beta = sqrt( k0.^2 .* nchannel.^2 - kappaguide0.^2 )
neffguide = beta ./ k0
```