Ionic Self-Assembled Multilayers Adsorbed on Long Period Fiber Gratings for Use as Biosensors

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ABSTRACT

Biosensors have widespread applications in many areas. Currently the Surface Plasmon Resonance (SPR) biosensor is one of the most prevalent types of biosensor. However, it has several disadvantages such as being delicate, expensive, and non-portable. Ionic Self-Assembled Multilayers (ISAMs) adsorbed on Long Period Fiber Gratings (LPGs) provides an attractive platform for building optical sensors, which could potentially overcome the disadvantages of SPR biosensors. The ISAM technique is a type of layer-by-layer deposition technique for building nanoscale thin films. An LPG is a type of fiber device that is sensitive to physical property changes of the ambient environment. LPGs have been extensively investigated for use as optical sensors. We have carried out a study on combining these two techniques to build efficient biosensors.

In this thesis, we demonstrate ultra-sensitive LPGs whose attenuation can be changed by 25 dB (~99.7%) over a 48-nm spectral band, with ambient-index changes of only $2.7 \times 10^{-4}$. The device schematic allows arbitrarily high index sensitivities to be achieved, which makes it an attractive platform for realizing sensors and modulators that respond to small index changes. For a thin-film coated LPG, we find theoretically that the resonant wavelength shift of the LPG can result from either the variation of the thickness of the film and/or the variation of its refractive index. Furthermore, results illustrate that the sensitivity of the sensor could be enhanced using a nm-thick thin-film (e.g. ISAM films) whose refractive index is greater than silica. Experimentally, we demonstrate the fabrication of nm-thick ISAM films deposited on LPGs, which induces dramatic shifts in the resonant wavelength. The refractive index and the thickness of the ISAM film was precisely controlled by altering the relative fraction of the anionic and cationic materials combined with layer-by-layer deposition. Finally, we demonstrate that ISAM-coated LPGs can function effectively as biosensors by using the biotin-streptavidin system. These demonstrations confirm that the ISAM-LPG scheme provides a thermally-stable, reusable, and robust platform for building efficient optical sensors.
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Chapter 1. Introduction

1.1. Background of the Proposed Research

1.1.1. Motivation

Biological sensors (biosensors) have the potential to revolutionize the way genomics, proteomics, diagnostics, and environmental monitoring is performed. Furthermore, recent global events have demonstrated the significant threat of weaponized pathogenic microorganisms. For example, the anthrax terrorism attacks occurring in U.S. in 2001 bring us a serious warning. Other than its significance in the biowarfare area, biosensors possess huge application markets. According to the study of Fuji-Keizai USA Inc. on April 2004,\(^1\) the market size for worldwide biosensors at the end of the year 2003 was about $7.3 billion. Even with a weak global economy, the market is projected to improve and grow to about $10.8 billion in 2007 with a growth rate of about 10.4%. The biosensor technology is mainly involved in five applications areas. Seemingly, medical applications are the most important one among all the applications areas. The increasing rate of obesity and the alarming rise in the rate of diabetes in the industrialized world is driving a need for more biosensors to monitor diabetic patients' glucose levels, for example. The pharmaceutical research industry is driving the need for new rapid assay biosensors to speed the progress of drug discovery. Biosensors also help monitor food

\(^1\) http://www.mindbranch.com/listing/product/R98-105.html
safety and detect environmental pollution. Finally, as mentioned before, the war on terrorism is driving the need for new, rapid detection biosensors against biowarfare agents for military and civil defense applications.

The motivation of this research is to address all these recent increasing needs for biosensors. For example, one of the most difficult problems facing people (e.g. military and law enforcement personnel) is to develop biosensors capable of rapid detection and confirmation of the release of biological agents in acts of bioterrorism. Simple conventional colorimetric assays yield rapid results, but they lack the sensitivity needed for detection of microbes and toxins that will be in environmental samples. Highly sensitive immunoassays, cellular response assays, and “lab on a chip” formats have been developed, but they generally require multiple or specialized reagents for detection, and some formats can be time-consuming.

1.1.2. History of biosensors

The history of biotechnology can be traced to ancient ages. Mankind has used genetic engineering of a sort for thousands of years in producing crops of a singular strain. It was not until 1953 that the method by which such engineered genetic qualities are passed on to successive generations was discovered. Then it took another two decades for this research to develop into successful genetic engineering: manipulating genetic codes to provide specialized organisms. Subsequent research has developed methods for designing and arranging the building blocks of DNA into a required structure. Whereas the early synthesis of human insulin required genetic material from human cells, it can now be entirely artificially constructed.

However, with the development of biotechnology, some individuals have taken advantage of it to build destructive biological agents to threaten “enemies”. But the prospects are not entirely dire. As the technology to design destructive agents increases, so also does the ability to manufacture vaccines and other protective measures. It is biotechnology that will provide protective vaccines. It will provide protection in other ways as well. The characteristic of an organism to feed on a given nutrient, and convert it to another substance, can be used to make very sensitive and selective sensors. These biosensors will be engineered to act as rapid and cheap chemical agent detectors. The protective measures against chemical and biological agents are of no use unless they are deployed in time. The biosensors will be able to detect such small concentrations in such rapid time that effective protective measures can be taken.

Up to now, various biosensors have already moved from the proof-of-concept stage to field testing and commercialization in the United States, Europe, and Japan. Several U.S. federal agencies are evaluating the technologies for studies of ecological and human exposure. Biosensors have potential for continuous and in situ applications, such as downhole or perimeter groundwater monitoring, and they are suitable for a variety of substances including soil extracts, groundwater, blood, and urine. Some biosensors can operate in high concentrations of organic solvents (e.g., methanol and acetonitrile) and can be used for in situ monitoring of contaminated organic media or process streams that contain mixed organic wastes. They can be constructed from a wide array of immunochemicals and even genetically engineered microorganisms, and they can be configured to be reversible.
The first biosensors were reported in the early 1960s and comprised enzymes immobilized to oxygen electrodes.\(^3\) Continued development of this kind of biosensor led to the commercialization of various devices for such applications as the measurement of glucose in blood and the detection of glutamate, aspartame, sulfite, lactose, and ethanol in food products. Reports of enzyme-electrode biosensors continue to dominate the literature. In the environmental area, pioneering work on an antibody-based biosensor for benzo-pyrene was done in the 1980s at the U.S. Department of Energy's Oak Ridge National Laboratory.\(^2\)

### 1.1.3. Principle of biosensors

A biosensor is an analytical device that consists of a physical element (signal transducer that signals a recognition event) and a biological element on a solid-state surface, enabling a reversible biological specific interaction with the analyte (i.e. creates a recognition event).\(^4\) The biological element is a layer of biological molecules responsible for biological recognition, such as receptors, enzymes, peptides, single-stranded DNA, and even living cells are applicable. Many biosensor devices are connected with a flow-through cell which enables a flow-injection analysis (FIA) operation mode. Biosensors combine high analytical specificity with the powerful processing techniques of modern electronics to achieve highly sensitive biological detection systems.

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Generally, biosensors can be mainly classified as two types: biocatalysis-based and bioaffinity-based biosensors. The biocatalysis-based biosensor mainly adopts enzymes as the biological element, catalyzing a signaling biochemical transformation. The bioaffinity-based biosensor adopts specific binding proteins, lectins, nucleic acids, dyes, cell membrane receptors, whole cells, antibodies, or antibody-related substances for biomolecular recognition. It is designed to detect the binding event itself. In addition, for some specific applications, there exist some other types of classifications. For instance, for environmental monitoring applications, there is another type of biosensors called Microorganism-based biosensors.\(^5\)

If antibodies or antibody-related substances are adopted as the biological element, the device is called an immunosensor. Immunosensors fall into bioaffinity-based biosensors. The antibodies are proteins, which are produced by the immune system of some animals in response to the entry of “foreign” materials (the antigen) into the body (for example, viruses and bacteria and implanted medical devices).\(^6\) Usually antibodies do not catalyze chemical transformations but rather undergo a physical transformation, in which they tightly bind to the antigen that prompted the response and mark it by other elements of the immune system. Additionally, antibodies are very specific which means they recognize and bind to the “foreign” materials only and they do not bind to materials native to the organism itself. This specificity is designed by biosensor researchers. Typically, antibodies specifically directed against the material of interest (i.e. the desired analyte) are immobilized on the transducer of the biosensor. Then, the sensor is exposed to the medium of interest (e.g. the blood or other biological fluid). If the specific antigen

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\(^6\) [http://www.fraserclan.com/biosens1.htm](http://www.fraserclan.com/biosens1.htm)
is present in that medium, it will be bound by the immobilized antibody to form an antigen-antibody complex. This binding event will change some physical properties of the monitored environment at the transducer surface of the sensor. As a result, the change of properties will be signaled by the transducer subsequently as shown in Fig. 1-1.

![Diagram of the principle of biosensors](image)

**Fig.1-1. Schematic of the principle of biosensors**

As the biological element in biocatalysis-based biosensors, the enzyme is adopted as the specific tool for creating the recognition event. In the organism, enzymes serve as the tools for digesting food substances. As tools, enzymes must be extremely specific in their actions. For example, any given enzyme will always turn substance A into B and never into C; likewise, the same enzyme will never accept substance D and turn it into B. This specificity is based on the fact that enzymes can recognize differences of a single atom in the substance’s chemical structure by virtue of their exquisite three-dimensional structure. Accordingly, it makes all the difference in whether the enzyme accepts a reactant or not. Unlike antibodies the enzyme does not undergo a physical transformation but rather catalyzes chemical transformations. The specificity of enzyme-based
biosensors is based on this specificity of enzymatic action. For instance, if an enzyme that is specific for a reaction with glucose is incorporated in a biosensor, the sensor has the basis only for glucose and glucose alone. The sensor will not detect a material that is related very closely chemically. The signal should result only from the change in the transducer prompted by the interaction of glucose and the glucose-reactive enzyme.

The main categories of transducers used in biosensors are:

(i) Electrical transducers — consisting of amperometric enzyme-coated electrodes. The enzyme decomposes the analyte to produce a redox active species, whose oxidation or reduction at the electrode results in a detectable current.

(ii) Thermal transducers — the heat released by the analyte molecules binding to receptors is detected by a thermocouple;

(iii) Mechanical (acoustic) transducers — the vibration frequency of a plate is decreased in proportion to the number of analyte molecules adsorbed on its surface;

(iv) Optical transducers — the optical properties of a biomolecule-modified surface are altered by the presence of bound analyte.

Nowadays, biosensors have been extensively used as diagnostic tools, predominately in point-of-care testing. The in vitro near patient measurement of capillary glucose by utilizing various hand-held systems with disposable reagent cartridges probably is the most successful commercialization of biosensors today.7

In all biosensor applications, the most important features are specificity, sensitivity, and the time required to attain the signal in response to the recognition event. Also, if a sensor platform is to be used in the field, it must be portable, simple to operate,

and rugged. Ideally, the recognition event in biosensors should be transduced to a measurable signal without requiring the use of a complex protocol or fluorescently- or radioactively-labeled reagents. A biosensor platform that combines the features of sensitivity, specificity, portability, and simplicity is needed to respond to the many applications in national security, environmental monitoring, life sciences research, pharmaceutical development and other areas.

1.2. Optical biosensors

Optical biosensors, especially optical immunosensors, are most popular for biological analysis and are today’s largest group of transducers. The reason for this is mainly because of the advantages of the optical transducer’s mechanism — applying visible radiation — in comparison to other transducer techniques. The resulting benefits from it are the nondestructive operation mode, and the rapid signal generation and reading. Especially, the introduction of fiber optics technologies (e.g. optical planar waveguides, optical fiber waveguides) and sophisticated optoelectronics provides applications of interest with increased versatility of these analytical devices.

Optical biosensors comprise optical-based transducers for detecting the presence of biological molecules of interest. Because surface transducers were found to be far more sensitive than bulk ones, the surface-sensing has been more extensively investigated and emphasized. The higher sensitivity of the surface-sensing originates from the fact that most of the biological recognition processes actually take place at surfaces, notably the solid/liquid interface (e.g. membrane/cytoplasm). Changes in absorption,

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fluorescence, luminescence, scattering or refractive index occur when light is reflected at sensing surfaces. Optical biosensor techniques are based on this transduced information. Usually, the detectors used for optical biosensors are photodiodes or photomultipliers.

Although all optical transducers depend on the optical property changes of light interacting with a solid/liquid interface, they can be divided into two classes: (1) direct — the intrinsic optical properties of the analyte are measured (e.g. its refractive index, absorption, or emission); (2) indirect — the color or fluorescence of an immobilized indicator, label or any other optically detectable bioprobe is monitored. The primary examples of the direct class include ellipsometry, Scanning Angle Reflectometry (SAR) and Optical Waveguide Lightmode Spectroscopy (OWLS). The primary examples of the indirect class include Total Internal Reflection Fluorescence (TIRF), Surface Plasmon Resonance (SPR), and Total Internal Reflection Spectroscopy (TIRS). Because all these techniques employ weak radiations for signal detections, they are totally non-destructive and only invasive insofar as TIRF has to use labeling.

In comparison to traditional methods for achieving molecular recognition, optical biosensors have four main advantages:
1. They can work in the nondestructive operation mode;
2. For most of them, there is no need to label the biological molecules being detected;
3. Because signal-to-noise ratios are better, their sensitivity and accuracy are higher;
4. They can be applied to monitor recognition events in real time in situ. The availability of kinetic information has revealed that the unbinding (dissociation) of a bound recognition pair is often very slow, which precludes equilibrium conditions being attained and hence invalidates a necessary condition for many affinity assays;
Currently the Surface Plasmon Resonance (SPR) biosensor is one of the most prevalent types of biosensor that is commercially available. It has several advantages. For instance, it is a non-destructive, labeling-free, and real-time technique. Most importantly, it has a very high sensitivity with the ability to measure the surface mass concentration as low as few pg/mm$^2$.\(^9\)

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**Fig.1-2. Schematic of the principle of SPR biosensors**

The basic principle of the SPR biosensor is shown in Fig. 1-2.\(^{10}\) To obtain SPR, it is necessary to generate an evanescent field, that is, an exponential-decaying wave, at the sensor surface. An evanescent field is generated when total internal reflection of incident light occurs at the interface of two different substances, one with a high-refractive index and another with a low-refractive index - for example a glass-air interface. The incident light is completely reflected even though an electromagnetic field component of the light penetrates the substance with the low-refractive index. Surface Plasmon Resonance occurs under certain conditions when a thin film of gold is placed at the position of the evanescent wave. When the incoming light is monochromatic and p-polarized (i.e. the

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\(^9\) http://www.ibs.fr/content/ibs_eng/presentation/platform/Facilities/biacore.htm

electric vector component is parallel to the plane of incidence), the free electrons of the metal will oscillate and absorb energy at a certain angle of incident light. The angle of incident light when SPR occurs is called the SPR angle. SPR is detected by measurement of the intensity of the reflected light. At the SPR angle a sharp decrease or 'dip' of intensity is measured. The position of the SPR angle depends on the refractive index in the substance with a low-refractive index close to the sensing surface. In an SPR biosensor, the refractive index near the sensor surface changes because of binding of macromolecules to the receptor molecules on the surface. As a result, the SPR angle will change according to the amount of bound macromolecules. There is a linear relationship between the amount of bound material and the shift of the SPR angle.

However, SPR biosensors still have several disadvantages: such as (1) measurement accuracy for the SPR angle needs to be very small (<0.001°) — making SPR sensors expensive and delicate; (2) its optical alignment is too sensitive to move, so it is non-portable; (3) the sensing film deposited on the SPR sensor is typically done by thiol-on-gold self-assembled monolayer (SAM) — which is quite slow, requiring several bars.

1.3. Fiber grating sensors
1.3.1. History of fiber gratings

Fiber photosensitivity was first observed by Hill et al. in 1978 at the Canadian Communications Research Centre (CRC), Ottawa, Ont., Canada, but “Hill gratings” can only function at light wavelengths in the visible close to the wavelength of the writing
light, so they have not achieved widespread use.\textsuperscript{11} This limitation on photosensitivity was overcome by Meltz et al. in 1989. They used 244 nm ultraviolet light as source to fabricate the first Bragg grating in germanium doped fibers whose resonant wavelength is within the communications window by side writing interferometry. This technique called the “transverse holographic technique” attracted a lot of attention. Since then, researchers have done extensive research on the optical characteristics, fabrication technologies, and applications of the fiber grating and made great progress.

UV-written fiber gratings have caused a revolutionary change in various areas including optical fiber communications, fiber sensors, optical computations, and optical information processing. In the area of optical communications, fiber gratings affect almost every aspect of optical communications from the optical transmitter, the optical amplification, and the dispersion compensation to the optical receiver. The fiber grating technology has played an important role in the design of fiber lasers and semiconductor lasers by enabling the fabrication of highly spectrally selective feedback elements directly into the fiber core leading to the single longitudinal mode output with linewidth 100 kHz. Fiber gratings can also be used in optical amplifiers to help achieve gain flattening through the whole bandwidth of optical amplifiers and suppress the Amplified Spontaneous Emission (ASE) noise effectively, which improves the efficiency of the pumps and achieves ideal low noise amplification. Fiber gratings can also be used to create WDM Demultiplexers and Add/Drop Multiplexers. Besides, the good linear characteristics between the resonant wavelength of gratings and temperature/stress also offers fiber gratings a good opportunity for use as sensors.

Although fiber photosensitivity was observed more than 20 years ago, its physical explanation and mechanism are not entirely clear yet due to the physical complication and shortage of enough and detailed experimental data. Further research on fiber gratings will be very meaningful and valuable.

1.3.2. Advantages of fiber grating sensors

Optical fiber-based sensor technologies have been extensively studied because they possess many advantages over other conventional sensors for environmental sensing applications, which have promoted a worldwide research activity in optical fiber sensing. These advantages include:

1. Sensed signal is immune to electromagnetic interference (EMI) and radio frequency interference (RFI);
2. Intrinsically safe in explosive environments;
3. Highly reliable and secure with no risk of fire/sparks;
4. High voltage insulation and absence of ground loops and hence obviate any necessity of isolation devices like optocouplers;
5. Low volume and weight, e.g., one kilometer of 200 µm silica fiber weighs only 70 gm and occupies a volume of about 30 cm³;
6. As a point sensor, they can be used to sense normally inaccessible regions without perturbation of the transmitted signals;
7. Potentially resistant to nuclear or ionizing radiation;
8. Can be easily interfaced with low-loss optical fiber telemetry and hence affords remote sensing by locating the control electronics for LEDs/lasers and detectors far away from the sensor head;

9. Large bandwidth and hence offers possibility of multiplexing a large number of individually addressed point sensors in a fiber network or distributed sensing i.e. continuous sensing along the fiber length;

10. Chemically inert and they can be readily employed in chemical, process, and biomedical instrumentation due to their small size and mechanical flexibility;

11. High sensitivity, high accuracy, and cost-effectiveness.

Besides the general advantages of optical fiber-based sensors, fiber grating sensors possess many other attractive features over competing technologies, including ultrahigh sensitivity, high resolution, self-referenced capabilities, and multiplexing capabilities. The resonant wavelength of the grating is intrinsically independent of the input optical power, which offers grating-based sensors self-referenced capabilities against the worry about the input optical power random variation caused by the thermal fluctuation of the optical source or the physical distortion of the fiber (e.g. macrobend). Grating-based sensors appear to be useful for a variety of applications. For example, the area of distributed embedded sensing in materials for creating “smart structures” is one of the primary interests, in which fibers with sensor arrays can be embedded into the materials to allow measurement of parameters such as load, strain, temperature, and vibration. As a result, the health of the structure can be assessed and tracked on a real-time basis. To date fiber grating sensors have been buried in bridges and tunnels to

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monitor their structure parameters. Fiber gratings are also proving to be useful as the optical sensing element in a broad range of other optical sensing areas: grating-based chemical sensors, pressure sensors, accelerometers and biosensors are additional examples.

1.4. Ionic self-assembled multilayers (ISAMs)

Ionic self-assembled multilayers (ISAMs) are fabricated by a layer-by-layer deposition technique and exhibit excellent reliability, stability and film quality in comparison to other types of thin-films.\(^{13,14}\) Through alternately immersing a charged substrate into anionic and cationic polyelectrolytic aqueous solutions, a nanoscale multilayer thin film is built by consecutive adsorption of polyanions and polycations onto a solid substrate driven by electrostatic forces. The ISAM fabrication method provides a highly controllable means to build precise, nm-thick films on the surfaces of fibers (indeed, they can be incorporated on any surface of different sizes and topologies with a minimum charge density, such as metals, glass, silica or mica, for instance). Moreover, they can be tailored to incorporate a diverse array of materials, such as clay platelets, proteins, virus particles etc. In addition, films with various architectures could be designed and are fully dependent on the dipping sequences of various polyion solutions, such as ABAB, ABCBAB and etc. Hence, the ISAM technique shows more flexibility on choices of substrate or template and thin-film overlay materials for devices. Furthermore, ISAMs on gratings provide several advantages: (a) ability to fine tune grating resonances

in a simple manner, (b) construction of efficient index sensors or index-modulating fiber devices, and (c) application to biosensors.

1.5. Thin films adsorbed on LPGs

Normally, the index sensitivity is attributed to the index of the bulk medium surrounding the fiber, and features with sub-wavelength sizes are not expected to modulate the resonance of LPGs. However, Ashwell and coworkers\textsuperscript{15} have recently reported resonant shifts in LPGs with films of sub-wavelength thickness, using Langmuir-Blodgett (LB) films. It suggests that thin-film coated LPGs can be used as chemical or biological sensors, because the sensing element of a practical LPG-based chemical/biological sensor would often be a nm-thick thin-film coated on the surface of the LPG where the thin-film is synthesized by incorporating sensing chemical/biological molecules into it. However, in the report of Ashwell et. al, the observed optical response was relatively small with maximal shifts of 10 nm in wavelength with 400 nm of deposited film. Moreover, LB films are not amenable to practical device construction. This is because the LB technique has demanding requirements of expensive special equipment to precisely control the pressure on the liquid surface and is relatively slow. More significantly, films deposited by the LB technique show poor mechanical and thermal stability because the van Der Waals interaction is the primary binding mechanism.

1.6. Scope of the Proposed Research

The major objective is to investigate and develop a feasible biosensor technology by using ISAMs adsorbed on Long Period Fiber Gratings (LPGs) for military or medical sensing applications (e.g. rapid detection against biowarfare agents and monitoring diabetic patients’ glucose levels). The research work described in this dissertation is focused on three primary issues: (1) Improve the sensitivity of LPGs to the adsorption of the nm-thick thin film. (2) Fundamental study of ISAM technique and develop procedures to attach probe biological molecules (affinity ligands) to nm-thick ISAMs adsorbed onto the LPGs and optimize sensitivity/specificity to target species. (3) Theoretically and experimentally investigate and develop an ISAM-coated LPG biosensor technology for practical use.

1.7. Outline

This thesis is organized as follows. Chapter 2 provides an introduction to LPGs in optical fibers and chapter 3 provides background on ISAMs. Chapter 4 describes the theoretical approach for simulating LPG spectra. It is shown that LPGs can be highly sensitive to the presence of nm-thick thin films on the cladding surface and that Turn-Around-Point (TAP) LPGs are even more sensitive than conventional LPGs. Chapter 5 describes the experimental results of studies of the index sensitivity of TAP LPGs, studies of the index sensitivity of ISAMs coated LPGs, and ISAMs adsorbed on LPGs for use as biosensors. It is shown that: (i) the sensitivity of TAP LPGs is ultra-high, which makes it an attractive platform for realizing sensors and modulators that respond to small index changes; (ii) Nm-thick ISAM films deposited on LPGs can induce dramatic shifts
in the resonant wavelength. The refractive index and the thickness of the ISAM film can be precisely controlled by altering the relative fraction of the anionic and cationic materials combined with layer-by-layer deposition; (iii) ISAM-coated LPGs function effectively as biosensors using the biotin-streptavidin system, which confirms that the ISAM-LPG scheme provides a thermally-stable, reusable, and robust platform for building efficient optical sensors.
Chapter 2. Principle of long period fiber grating

2.1. Theory of optical fiber

2.1.1. Scalar mode $LP_{lm}$

In this dissertation, we adopt the weakly-guiding scalar mode theory developed by Snyder, Marcatili, and Gloge to analyze the fiber modes in an optical fiber whose core and cladding have very nearly the same refractive index.\textsuperscript{16,17} The cross-section of an optical fiber is shown in Fig.2-1. Region 1 with refractive index $n_1$ is the fiber core, region 2 with index $n_2$ is the cladding. Initially, we assume that the cladding is infinitely extended, in spite of the fact that it has finite radius for practical fibers. The reason for assuming an infinitely extended cladding region comes from the fact that the guided modes have exponentially decaying fields outside the core. If the cladding radius is large enough, the guided mode fields have decayed to insignificant values at the outer boundary of the cladding.

Based on Maxwell’s equations, we can obtain the homogeneous wave equation,\textsuperscript{18}

$$\nabla^2 \vec{E} - \mu \varepsilon \frac{\partial^2 \vec{E}}{\partial t^2} = 0, \quad (2-1)$$

where $\mu$ is the magnetic permeability of the medium and $\varepsilon$ is the electric permittivity of the medium. If we assume a time-harmonic field with the factor of $e^{j\omega t}$, and use $k = \sqrt{\mu_0 \varepsilon_0 \omega}$ (assuming $\mu = \mu_0$), the wave equation becomes,

$$
\nabla^2 \tilde{E} + k_0^2 n^2 \tilde{E} = 0,
$$

(2-2)

The electric field is a vector, and there are three components, each of which is a function of $r$, $\phi$, and $z$:

$$
\tilde{E}(r, \phi, z) = iE_z(r, \phi, z) + \hat{\phi}E_\phi(r, \phi, z) + \hat{z}E_z(r, \phi, z),
$$

(2-3)

Since $E_z$ couples only to itself, it is possible to write the scalar wave equation for $E_z$ directly in cylindrical coordinates by using the vector Laplacian identity,

$$
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial E_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 E_z}{\partial \phi^2} + \frac{\partial^2 E_z}{\partial z^2} + k_0^2 n^2 E_z = 0,
$$

(2-4)

and to solve this equation for $E_z$.

By taking the weakly-guiding condition of $n_1 \approx n_2$ and the $z$-dependent phase term of $e^{j\beta z}$, where $\beta$ is the $z$ component of the wavevector $k$ in the waveguide, we obtain the

![Cross-section of a round optical fiber](image-url)
solutions for the transverse component of the electric field of the scalar mode $LP_{lm}$ by following Marcuse’s derivations:\(^1\)\(^8\)

\[
\psi = \begin{cases} 
A \cdot J_l \left( \frac{Ur}{a} \right) \cos(l\psi) + B \cdot K_l \left( \frac{Wr}{a} \right) \cos(l\psi), & r < a \\
A \cdot J_l \left( \frac{Ur}{a} \right) \sin(l\psi) + B \cdot K_l \left( \frac{Wr}{a} \right) \sin(l\psi), & r > a
\end{cases}
\]

(2-5)

where $\psi$ represents either $E_x$ or $E_y$, $U = k_0 a \sqrt{n_0^2 - n_{\text{eff}}^2}$ and $W = k_0 a \sqrt{n_0^2 - n_{\text{eff}}^2}$, $n_{\text{eff}}$ is the effective index of the mode $LP_{lm}$, $A$ and $B$ are constants, $l$ is the azimuthal order of the scalar mode, $J_l$ is the first kind Bessel functions respectively, $K_l$ is the second kind modified Bessel function, $a$ is the radius of the fiber core, $k_0 = 2\pi/\lambda$.

Based on the boundary conditions that $\psi$ and $d\psi/dt$ are continuous at boundary $(r=a)$, we obtain the eigenvalue equation for the mode $LP_{lm}$,

\[
\frac{J_l(U)}{U \cdot J_{l-1}(U)} + \frac{K_l(W)}{W \cdot K_{l-1}(W)} = 0,
\]

(2-6)

The relationship of the index $l$ and the index $\nu$ for the azimuthal order of the vector mode is given by,

\[
l = \begin{cases} 
1, TE_{0m}, TM_{0m}, HE_{2m} \\
\nu - 1, HE_{\nu m}, \nu \geq 1 \\
\nu + 1, EH_{\nu m}, \nu \geq 0
\end{cases}
\]

(2-7)

The linear $x$-polarized or $y$-polarized scalar mode $LP_{lm}$ is a superposition of two vector modes of $HE_{\nu + 1, m}$ mode and $EH_{\nu - 1, m}$ mode. The longitudinal component $E_z$ of the electrical field is much smaller than the transverse component. The field is thus almost transverse.
2.1.2. Dispersion in single-mode fiber

Dispersion describes the spreading of an optical pulse in time.\textsuperscript{19} There are two types of dispersion in single-mode fiber (SMF): material dispersion and waveguide dispersion, a combination of which is referred to as the chromatic dispersion. In material dispersion, different wavelengths of light travel at different velocities within a given medium. Waveguide dispersion is a more subtle effect. The propagation constant $\beta$ is determined by the structure of the optical fiber and is dependent on the wavelength, even within a single mode different wavelengths will propagate at slightly different speeds. It can be used to cancel material dispersion, allowing the design of special dispersion-shifted fibers.

If a signal or pulse contains more than one wavelength (e.g. in practical SMF), the individual components of this signal will travel at different group velocities. These components will reach the receiver at different times. This effect is called group velocity dispersion (GVD). Because the material dispersion and the waveguide dispersion usually coexist in the SMF, we can derive them together from deriving GVD.

Consider an optical pulse with a finite special bandwidth, $\Delta \lambda$, traveling through a dispersive SMF. The time required to travel a distance $L$ is referred to as the latency $\tau$,

$$\tau = \frac{L}{v_g} = \frac{d\beta}{d\omega} L, \quad (2-8)$$

where $v_g = d\omega / d\beta$ is the group velocity. The pulse spread in the time domain is given by,

$$\Delta \tau = L \cdot \Delta \lambda \cdot D, \quad (2-9)$$

where $D$ is the dispersion parameter. After manipulations of Eq. (2-8) and Eq. (2-9), we obtain the expression for $D$,

\[ D = -\frac{\lambda}{c} \frac{d^2 n_{\text{eff}}}{d\lambda^2}, \]  
\[ (2-10) \]

where \( c \) is the light speed in vacuum. Eq. (2-10) includes both the material dispersion and the waveguide dispersion in SMF. If we continue to do some manipulations by using parameters \( V = k_o a \sqrt{n_i^2 - n_2^2} \) and \( b = (n_{\text{eff}}^2 - n_2^2)/(n_i^2 - n_2^2) \), \( D \) can be derived to be two separate terms to describe the material dispersion and the waveguide dispersion respectively. In this dissertation, we utilize Eq. (2-10) to calculate the dispersion of our fibers.

2.1.3. Single-mode condition

SMF supports only one guided fiber mode — the \( LP_{01} \) mode, also known as the fundamental mode of the fiber. The fiber is designed such that all higher-order modes are cut off at the operating wavelength, which means they can’t be guided in the fiber for a long distance propagation. When a mode is just cut off at a given wavelength, its propagation constant \( \beta \) will satisfy the relationship that \( \beta = n_2 k_0 \). In this dissertation, the single-mode condition is met by numerically calculating the cut-off solution (let \( \beta = n_2 k_0 \)) for the \( LP_{11} \) mode based on Eq.(2-6).

2.2. Coupled-mode theory

Fiber gratings are essentially mode converters, which couple one fiber mode (core modes, cladding modes, or radiation modes) into another or other fiber modes. Therefore, mode couplings need to be addressed in this dissertation. Coupled-mode theory is a good tool for obtaining quantitative information of mode couplings in fiber gratings. In this
section, coupled-mode theory is introduced based on the class notes of “Optical Waveguide” instructed by Dr. Safaai-Jazi of the Electrical Engineering Department.

Let us consider a cylindrical waveguide with refractive index \( n(x,y,z) \) and with a particular solution of \( \vec{E} ( \vec{E} = \vec{e}(x,y)e^{j(\alpha x - \beta z)}) \) and \( \vec{H} ( \vec{H} = \vec{h}(x,y)e^{j(\alpha x - \beta z)}) \) fields in an unperturbed waveguide. In addition, a perturbed waveguide is described by \( n'(x,y,z), \vec{E}' \) and \( \vec{H}' \). Both sets of fields satisfy Maxwell’s equations,

\[
\begin{align*}
-\nabla \times \vec{E} &= j\omega \mu_0 \vec{H} \\
-\nabla \times \vec{H} &= -j\omega \varepsilon_0 n^2 \vec{E}^* \\
\end{align*}
\]

(2-11)

After applying vector identities, the divergence theorem and other manipulations, we finally have

\[
\int_s \frac{d}{dz} \left[ (\vec{E}_s^s \times \vec{H}_s^s + \vec{E}_s^s \times \vec{H}_s^s) \hat{a}_z \right] ds = -j\omega \varepsilon_0 \int_s \left[ (n^2 - n'^2) \vec{E}^s \vec{E}^s \right] ds, \\
\]

(2-12)

where \( s \) is the infinite cross section of the cylindrical waveguide. This is the expression of the reciprocity theorem in cylindrical waveguide. If we take \( (\vec{E}, \vec{H}) \) and \( (\vec{E}', \vec{H}') \) to be two different modes of one waveguide \( (n' = n) \), and let the first set of fields represent mode M and the second set mode N, we will obtain

\[
\int_s \left( [\hat{e}_{\vec{h}_{\vec{h}}} \times \vec{h}_{\vec{h}}^*] \hat{a}_z \right) ds = 0, \\
\]

(2-13)

Eq. (2-13) is the mode orthogonality relationship. It indicates that different modes are orthogonal to each other. The total power in a waveguide supporting several modes is the sum of the power of individual modes. Therefore, the fields of the perturbed waveguide can expanded in terms of the fields of the unperturbed waveguides, because the modes of the latter guide are orthogonal.
where the subscript $t$ means the transverse component, and $a_m$ is the $z$-dependent amplitude coefficient of different modes. We assume the fields of the unperturbed waveguide to be those of a $k$th mode.

We now substitute for the two sets of fields $(\vec{E}, \vec{H})$ and $(\vec{E}', \vec{H}')$ in (2-12). After applying the orthogonality relation Eq. (2-13) to the integral in the L.H.S. of (2-12), we obtain the coupled-mode equation,

$$\frac{da_k}{dz} = -j \sum_m a_m e^{i(\beta_k - \beta_m)z} c_{km},$$  \hspace{1cm} (2-15)

where

$$c_{km} = \frac{1}{4P \omega \varepsilon_0} \text{sgn}(\beta_k) \int (n^2 - n_0^2) \vec{E}_k \cdot \vec{E}_m ds,$$  \hspace{1cm} (2-16)

$P$ is the power of the $k$th mode and may be set equal to unity if normalized fields are used, sgn($\beta_k$) is plus if the $k$th mode travels in the $+z$ direction and is a minus if it travels in the $-z$ direction, $c_{km}$ is the coupling coefficient between the $k$th mode and the $m$th mode.

2.3. Long period fiber grating theory

A fiber grating is an optical fiber with ultraviolet (UV)-induced modulations of the refractive index of fiber core as shown in Fig. 3-2. $A$ is the grating period of the fiber grating. According to the magnitude of the grating period, fiber gratings can be broadly classified into two types: Bragg gratings (FBG, also called reflection and short-period gratings), in which coupling occurs between modes traveling in opposite directions; and transmission gratings (also called long-period gratings — LPG), in which the coupling is
between modes traveling in the same direction. Generally, $\Lambda$ is less than 1 $\mu$m for FBG and greater than 100 $\mu$m for LPG.

![Fig.2-2. Schematic of a fiber grating structure](image)

We follow Erdogan’s analysis to introduce the LPG theory. For simplicity we assume that there is a UV-induced perturbation to the core refractive index of the guided mode(s) of interest, described by

$$\delta n_{\text{core}}(z) = \overline{\delta n_{\text{core}}}(z) \left\{ 1 + v \cdot \cos \left[ \frac{2\pi}{\Lambda} z + \phi(z) \right] \right\}, \quad (2-17)$$

where $\overline{\delta n_{\text{core}}}$ is the “dc” index change spatially averaged over a grating period, $v$ is the fringe visibility of the index change, and $\phi(z)$ describes grating chirp.

Because the coupled-mode theory is straightforward, intuitive, and it can accurately model the optical properties of the LPG, we utilize it to analyze the LPG. In order to follow most closely the analysis of Erdogan, we make some modifications to the coupled-mode theory in preceding section. First, unlike previous conventions, the forward waves and backward waves are expressed by the factor of $e^{j\beta z}$ and $e^{-j\beta z}$, respectively. Second, we assume that the transverse component of the electric field can be expressed as a superposition of the ideal modes labeled $j$ (i.e., the modes in an ideal waveguide without perturbations). Unlike Eq.(2-14) it includes both forward waves and backward waves at this time. The electric field therefore is given by,

---

\[
\vec{E}_i(x, y, z, t) = \sum_j \left[ A_j(z) \exp(j \beta_j z) + B_j(z) \exp(-j \beta_j z) \right] \cdot \vec{e}_{\mu}(x, y) \exp(-i \omega t),
\] (2-18)

where \(A_j(z)\) and \(B_j(z)\) are amplitude coefficients of the \(j\)th mode traveling in the \(+z\) and \(-z\) directions, respectively. The ideal modes \(\vec{e}_{\mu}\) might depict the core modes, cladding modes or radiation LP modes. While the ideal modes are orthogonal in an ideal waveguide without exchanging energy, the modes will be coupled induced by a dielectric perturbation. The amplitude coefficients \(A_j(z)\) and \(B_j(z)\) of the \(j\)th mode evolve along the axis according to the coupled-mode equations,

\[
\frac{dA_j}{dz} = i \sum_k A_k \left( K'_{kj} + K''_{kj} \right) \exp \left[ i \left( \beta_k - \beta_j \right) z \right] + i \sum_k B_k \left( K'_{kj} - K''_{kj} \right) \exp \left[ -i \left( \beta_k + \beta_j \right) z \right],
\] (2-19a)

\[
\frac{dB_j}{dz} = -i \sum_k A_k \left( K'_{kj} - K''_{kj} \right) \exp \left[ i \left( \beta_k + \beta_j \right) z \right] - i \sum_k B_k \left( K'_{kj} + K''_{kj} \right) \exp \left[ -i \left( \beta_k - \beta_j \right) z \right],
\] (2-19b)

where \(K'_{kj}(z)\) is the transverse coupling coefficient between modes \(j\) and \(k\),

\[
K'_{kj}(z) = \frac{\alpha}{4} \int \int \Delta\varepsilon(x, y, z) \overrightarrow{e}_{\mu}(x, y) \cdot \overrightarrow{e}_{\mu}^*(x, y) dxdy,
\] (2-20)

where \(\Delta\varepsilon\) is the perturbation to the permittivity. Approximately \(\Delta\varepsilon \approx 2n_1 \delta n_{\text{core}}\) when \(\delta n_{\text{core}} \ll n_1\), according to the fact that the induced index change is approximately uniform across the core and nonexistent outside the core in most fiber gratings. \(K''_{kj}(z)\) is the longitudinal coupling coefficient, and it is usually neglected because generally \(K''_{kj}(z) \ll K'_{kj}(z)\) for fiber modes. Then we define two new coefficients,

\[
\sigma_{kj}(z) = \frac{\alpha m_{\text{core}}}{2} \delta n_{\text{core}}(z) \int \int \overrightarrow{e}_{\mu}(x, y) \cdot \overrightarrow{e}_{\mu}^*(x, y) dxdy,
\] (2-21a)

\[
\kappa_{kj}(z) = \frac{\nu}{2} \sigma_{kj}(z),
\] (2-21b)
where \( \sigma \) is a “dc” coupling coefficient and \( \kappa \) is an “AC” coupling coefficient, then the transverse coupling coefficient can be written as,

\[
K'_{ij}(z) = \sigma_{ij}(z) + 2\kappa_{ij}(z) \cdot \cos \left( \frac{2\pi}{\Lambda} z + \phi(z) \right),
\]

(2-22)

In an SMF-based LPG, mode interactions should be treated by computing the coupling among the fundamental mode and multiple cladding modes simultaneously at a particular wavelength, using coupled-mode theory. In most cases, the individual resonances are sufficiently narrow and spectrally separated, which results in coupling between the fundamental mode and a single cladding mode that well describes the transmission. In such cases, simple two-mode coupled-mode theory with slowly varying amplitudes can be employed, which method we use in the following LPG analysis.

We assume a mode “1” with the amplitude \( A_{1}(z) \) is strongly coupled to a co-propagating mode “2” with the amplitude \( A_{2}(z) \) near a particular wavelength. Eq. (2-19) can be simplified by retaining only terms that involve the amplitudes of these two modes.

Based on the synchronous approximation, the following equations are obtained,

\[
\frac{dR}{dz} = i\tilde{\sigma}R(z) + i\kappa S(z), \quad \text{(2-23a)}
\]

\[
\frac{dS}{dz} = -i\tilde{\sigma}S(z) + i\kappa^* R(z), \quad \text{(2-23b)}
\]

where \( R(z) = A_{1}\exp[-i(\sigma_{11} + \sigma_{22})z/2]\exp(i\tilde{\sigma}z - \phi/2) \), \( S(z) = A_{2}\exp[-i(\sigma_{11} + \sigma_{22})z/2]\exp(-i\tilde{\sigma}z + \phi/2) \), and where \( \sigma_{11} \) and \( \sigma_{22} \) are “dc” coupling coefficients defined in (2-21a). \( \kappa = \kappa_{21} = \kappa_{12}^* \) is the “ac” cross-coupling coefficient defined in (2-21b). \( \tilde{\sigma} \) is a general “dc” self-coupling coefficient and is defined as,
\[ \tilde{\sigma} = \delta + \frac{\sigma_{11} - \sigma_{22}}{2} - \frac{1}{2} \frac{d\phi}{dz}, \]  

(2-24)

where \( \delta \) is the detuning parameter and we assume it to be constant along \( z \),

\[ \delta = \frac{1}{2} \left( \beta_{1} - \beta_{2} - \frac{2\pi}{\Lambda} \right) = \pi (n_{eff1} - n_{eff2}) \left( \frac{1}{\lambda} - \frac{1}{\lambda_{D}} \right), \]  

(2-25a)

Where \( \lambda_{D} = (n_{eff1} - n_{eff2}) \Lambda \),

(2-25b)

Eq. (2-25) is the phase-matching condition we usually used for calculating LPG mode coupling. Normally, \( (\sigma_{11}, \sigma_{22}) \) is very small compared with \( \delta \) and can be ignored. Therefore, when \( \delta = 0 \), the strongest mode coupling between the mode “1” and the mode “2” occurs.

In our case the LPG is a uniform grating, in which \( \sigma \) and \( \kappa \) are constants and they can be evaluated numerically. Eq. (2-23) are coupled first-order ordinary differential equations with constant coefficients. Through applying appropriate initial conditions with \( R(0) = 1 \) and \( S(0) = 0 \) by assuming only one mode is incident from \( z = 0 \), solutions can be found. The power \textit{bar} transmission \( t_{\bar{z}} = |R(z)|^2 / |R(0)|^2 \) and \textit{cross} transmission \( t_{c} = |S(z)|^2 / |R(0)|^2 \) can be obtained,

\[ t_{\bar{z}} = \cos^2 \left( \sqrt{\kappa^2 + \sigma^2} \cdot z \right) + \frac{\sigma^2}{\kappa^2 + \sigma^2} \sin^2 \left( \sqrt{\kappa^2 + \sigma^2} \cdot z \right), \]  

(2-26a)

\[ t_{c} = \frac{\kappa^2}{\kappa^2 + \sigma^2} \sin^2 \left( \sqrt{\kappa^2 + \sigma^2} \cdot z \right), \]  

(2-26b)

Based on Eq. (2-26b), we can obtain the maximum power cross transmission when \( \sigma = 0 \),

\[ t_{c,\text{max}} = \sin^2 (\kappa \cdot L), \]  

(2-27)
and it occurs at the wavelength approximately,

$$\lambda_{\text{max}} = \left( 1 + \frac{\delta n_{\text{core}}}{n_{\text{eff 1}} - n_{\text{eff 2}}} \right) \lambda_D,$$

(2-28)

Eq. (2-25) and (2-26) are the equations that we use for most of our LPG simulations.

### 2.4. Simulations

Based on the scalar mode theory of the optical fiber and the LPG theory, we did simulations to investigate the optical properties of the LPG. Because the LPGs used in our experiments are uniform gratings without chirp, we set $\phi(z) = 0$ and $\delta n_{\text{core}}$ as a constant in Eq. (2-17). For simplicity, we set the fringe visibility $v = 0$.

#### 2.4.1. Phase matching curves

According to Eq. (2-25), we compute the Phase Matching Curves (PMC) of the LPG, which represents the grating period $\Lambda$ as a function of the resonant wavelength $\lambda_{\text{res}}$ when $\delta = 0$. Here we only consider the mode coupling between the fundamental mode and other fiber modes. The fiber parameters we chose are: the radius of the fiber core $a = 3.2$ $\mu$m, the radius of the fiber cladding $b = 59.2$ $\mu$m, the surrounding medium is air with the index $n_{\text{air}} = 1$, the core index $n_1$ and the cladding index $n_2$ are computed based on the Sellmeier’s equation as shown in Appendix A. The reason for the selection of these parameters is for simulating the experimental grating, which will be described in detail in chapter 4. The calculated results of the PMCs of this type of SMF are shown in Fig.2-3.
Fig. 2-3. Phase matching curves of the LPG — the grating period $\Lambda$ as a function of the resonant wavelength $\lambda_{\text{res}}$ when $\delta=0$. The curves from top to bottom represent for fiber modes from LP$_{0,2}$ to LP$_{0,12}$ in sequence, respectively.

From Fig. 2-3, we find out that (i) For a given grating period, the LPG can couple the energy of the fundamental mode into many other modes simultaneously at different resonant wavelengths; (ii) For a given particular resonant wavelength, we can select a specific grating period to make the LPG to couple the fundamental mode into a specific fiber mode; (iii) The higher the order of the coupled fiber mode, the shorter the grating period needed to obtain the occurrence of the mode coupling; (iv) The slope $d\Lambda/d\lambda_{\text{res}}$ gradually decreases from the lower-order mode to the higher order mode, which equivalently means $d\lambda_{\text{res}}/d\Lambda$ gradually increases from the lower-order mode to the higher order mode. It illustrates that the change of $\lambda_{\text{res}}$ in response to the change of $\Lambda$ becomes larger with the increased order of the coupled fiber mode for the same LPG. Because the change of $\Lambda$ can be caused by the change of the ambient temperature or the strain applied...
on the grating, hence, the sensitivity of the LPG to the temperature or the strain becomes larger with the increased order of the coupled fiber mode for the same LPG.

2.4.2. LPG spectra

In this section we study the optical transmission spectra of the LPG according to the Eq. (2-26). For the purpose of illustration, the fiber parameters we chose are: the radius of the fiber core $a=5 \ \mu m$, the radius of the fiber cladding $b=62.5 \ \mu m$, the surrounding medium is air with the index $n_{air}=1$, the core index $n_1$ and the cladding index $n_2$ are 1.455 and 1.45 respectively. The length $L$ of the grating is 10 mm and the period $\Lambda$ of the grating is 240 $\mu m$. The coupled fiber mode is the Mode $LP_{0,12}$ and the resonant wavelength $\lambda_{res}$ is about 1410 nm.

![LPG spectra evolution](image)

Fig.2-4. LPG spectra evolution with $\delta n_{core}$. (a) $\delta n_{core} = 0.0004$; (b) $\delta n_{core} = 0.0007$; (c) $\delta n_{core} = 0.001$; (d) $\delta n_{core} = 0.0015$. 
Fig.2-4 shows the simulated results, which depict the LPG power bar transmission \( t_\tau \) [defined in Eq. (2-26a)] spectrum variations as a function of the “dc” index change \( \delta n_{\text{core}} \) defined in Eq. (2-17). We find out that (i) According to Fig.2-4a and Fig.2-4b, as \( \delta n_{\text{core}} \) increases, first the main peak at \( \lambda_{\text{res}} \approx 1410 \text{ nm} \) becomes larger downwards which means the more and more energy is coupled from the fundamental mode to the mode \( LP_{0,12} \); (ii) After the main peak (at \( \lambda_{\text{res}} \approx 1410 \text{ nm} \)) reaches its biggest amplitude \( (t_\tau = 0) \) at \( \delta n_{\text{core}} \approx 0.0007 \) in Fig.2-4b, it becomes smaller and smaller while the sidelobes at nearby wavelength still becomes larger and larger as shown in Fig.2-4c, this phenomenon is called as “overcoupled” — the energy of the mode \( LP_{0,12} \) at the main peak (at \( \lambda_{\text{res}} \approx 1410 \text{ nm} \)) couples back to the fundamental mode while the energy of the fundamental mode still continues coupling to the mode \( LP_{0,12} \) at other wavelengths. (iii) At a specific \( \delta n_{\text{core}} \) (here \( \delta n_{\text{core}} \approx 0.0015 \)), the main peak (at \( \lambda_{\text{res}} \approx 1410 \text{ nm} \)) disappears \( (t_\tau = 1) \) which means the energy of the mode \( LP_{0,12} \) at the main peak (at \( \lambda_{\text{res}} \approx 1410 \text{ nm} \)) completely couples back to the fundamental mode; (iv) If we continue increasing \( \delta n_{\text{core}} \), the coupling between the fundamental mode and the mode \( LP_{0,12} \) repeats continuously. Basically the sidelobes have the same behaviours as the main peak.

Fig.2-5 depicts the LPG power bar transmission \( t_\tau \) [defined in Eq. (2-26a)] spectrum variations as a function of the length \( L \) of the LPG and \( \delta n_{\text{core}} \). We notice that with the increased \( L \), the bandwidth of the LPG becomes narrower. At the same time, \( \delta n_{\text{core}} \) needed to maintain the strength of the grating (e.g. \( t_\tau = 0 \)) at the resonant
wavelength) becomes proportionally smaller. For example, $\delta n_{core}$ needs to be 0.0014 for the grating of $L = 5\ \text{mm}$ in order to make $t = 0$ at the main peak (at the resonant wavelength $\lambda_{res} \approx 1410\ \text{nm}$) as shown in Fig.2-5a; while $\delta n_{core}$ needs to be only 0.0007 for the grating of $L = 10\ \text{mm}$ in order to make $t = 0$ at the main peak (at the resonant wavelength $\lambda_{res} \approx 1410\ \text{nm}$) as shown in Fig.2-5b.

**Fig.2-5.** LPG spectra evolution with the length $L$ of grating and $\delta n_{core}$. (a) $L=5\text{mm}$ and $\delta n_{core}=0.0014$; (b) $L=10\text{mm}$ and $\delta n_{core}=0.0007$; (c) $L=20\text{mm}$ and $\delta n_{core}=0.00035$.

### 2.5. Turn Around Point (TAP) LPGs

If we carefully inspect the PMCs in Fig.2-3, we will note that the PMCs of some high-order modes (e.g. $LP_{0,9}$, $LP_{0,10}$, $LP_{0,11}$, and $LP_{0,12}$) do not monotonically vary with the resonant wavelength; that is, the grating period $\Lambda$ does not monotonically increase with the increased resonant wavelength $\lambda_{res}$ when $\delta = 0$. The magnified Fig.2-3 for the high-order mode $LP_{0,9}$, $LP_{0,10}$, $LP_{0,11}$, and $LP_{0,12}$ clearly describes this behavior as seen in Fig. 2-6. It shows that in their PMCs first $\Lambda$ increases with increased $\lambda_{res}$ ($d\Lambda/d\lambda_{res} > 0$) but the slope $d\Lambda/d\lambda_{res}$ gradually decreases. Then at a specific $\lambda_{res}$, the slope $d\Lambda/d\lambda_{res}$ becomes
zero. After that point, $\Lambda$ decreases with increased $\lambda_{\text{res}}$ ($d\Lambda/d\lambda_{\text{res}}<0$) and the slope $d\Lambda/d\lambda_{\text{res}}$ continue to decrease. We call the point in the PMC where $d\Lambda/d\lambda_{\text{res}}=0$ as the Turn Around Point (TAP) of the grating — the solid black point as shown in Fig.2-6, and we call the LPG with a written period near the TAP as a TAP LPG.

Fig.2-6. Magnified Fig.2-3. Phase matching curves of the LPG — the grating period $\Lambda$ as a function of the resonant wavelength $\lambda_{\text{res}}$ when $\delta=0$. The curves from top to bottom represent for fiber modes from LP$_{0,2}$ to LP$_{0,12}$ in sequence, respectively.

As shown in Fig.2-6, our calculations suggest that, for each cladding mode of a fiber, there is a TAP at which the slope $d\Lambda/d\lambda_{\text{res}}$ switches from positive to negative. With increasing order of the cladding mode, the TAP of that cladding mode shifts to a shorter wavelength. Theoretically, each PMC must have another TAP in the middle or far IR at which the slope $d\Lambda/d\lambda_{\text{res}}$ from negative back to positive.$^{21}$ However, this second TAP should be too far in the IR ($\lambda > 10$ $\mu$m) to be observed; the absorption in this region is too high for the light to propagate in silicate fibers.

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2.5.1. Principle of TAP LPGs

For the convenience of studying the principle of TAP LPGs, Eq. (2-25) for the phase-matching condition for the LPG mode coupling is transformed to the form:

\[ \Phi(\lambda) = 2\pi\left(n_{\text{eff}1} - n_{\text{eff}2}\right)/\lambda_{\text{res}} = 2\pi / \Lambda, \]  

(2-29)

where \( n_{\text{eff}1} \) and \( n_{\text{eff}2} \) are the effective index of the fundamental mode and the coupled cladding mode in SMF, respectively.

![Diagram showing LPG resonances for fundamental–cladding mode coupling](image)

**wavelength** \( \lambda \)

Fig. 2-7. LPG resonances for fundamental–cladding mode coupling are found graphically by the intersection of the intermodal dispersion function \( \Phi(\lambda) \) and the horizontal dashed line representing the grating period. For cladding mode 1 the resonance shifts from \( \lambda_1 \) to \( \lambda_1' \) as the grating period shifts from \( \Lambda \) to \( \Lambda' \). However, for cladding mode 2 the resonant wavelength remains fixed at \( \lambda_2 \) as the grating period is changed, although the strength of the resonance varies. This coupling between the fundamental mode and cladding mode 2 has a quadratic-dispersion resonance.

We can graphically study the coupling between the fundamental mode to the cladding mode phenomenon in the SMF-based LPG according to the intermodal dispersion function \( \Phi(\lambda) \). Fig.2-7 shows a plot of \( \Phi(\lambda) \) for a typical SMF. We can
graphically determine the resonances between the fundamental mode and a given cladding mode as the intersection(s) of $\Phi(\lambda)$ with the grating spatial frequency $2\pi/\Lambda$. For example, for the coupling between the fundamental mode and the cladding mode 1, the $\Phi(\lambda)$ is a monotonically decreasing function of $2\pi/\Lambda$ as well as $\lambda_{res}$ as shown in Fig.2-7. This is the conventional LPG case. Therefore, if the grating period is changed by the strain applied on the fiber, the resonant wavelength shifts to a new value. This is the basic principle of most fiber strain sensors — by measuring the change in resonant wavelength in response to the change of strain. However, for some coupling between the fundamental and cladding modes, Eq. (2-29) shows a parabola (similarly as we saw this in Fig.2-6), as depicted for cladding mode 2 in Fig. 2-7. When the LPG is operating near the base of this parabola, any change in the strain or the temperature applied on the grating alters only the coupling strength between the fundamental and cladding modes with a fixed resonant wavelength.

We can utilize the Taylor expansion of the mode dispersion function $\Phi(\lambda)$ in the vicinity of $\lambda_{res}$ to find out the change in the resonant wavelength $\lambda_{res}$, which is caused by a small change in the grating period $\Lambda$:

$$\Phi(\lambda) - \Phi(\lambda_{res}) = a_1(\lambda - \lambda_{res}) + a_2(\lambda - \lambda_{res})^2 + \ldots, \quad (2-30)$$

In Eq. (2-30), the first term for linear-dispersion gratings gives us monotonic curves like that of mode 1 in Fig. 2-7 and is usually the largest. All conventional LPGs belong to this category. The resonant wavelength changes linearly with a change of the grating period:

$$\delta\lambda = -\frac{2\pi}{a_1\Lambda^2} \cdot \delta\Lambda, \quad (2-31)$$
However, it is possible to find modes whose linear coefficient $a_1$ of Eq. (2-30) vanishes ($a_1=0$) at a specific resonant wavelength. At this point, the quadratic term $a_2$ dominates in Eq. (2-30), and the resonant wavelength change in response to a change of the grating period is given by:

$$
\delta \lambda = \pm \left( -\frac{2\pi}{a_2 \Lambda^2} \delta \Lambda \right) \frac{1}{2},
$$

(2-32)

In Fig. 2-7, we notice that $a_2>0$ for mode 2 because the curvature of the intermodal dispersion function $\Phi(\lambda)$ for mode 2 is positive. Therefore for $\delta \Lambda<0$ we can obtain two values of $\delta \lambda$ (i.e., there are two separate attenuation peaks in TAP LPGs), but for $\delta \Lambda>0$ we can not obtain any solution for $\delta \lambda$ (i.e. there will be no resonance in TAP LPGs). The latter case is the case for TAP LPGs — a quadratic dispersion resonance. As shown in Fig.2-7, when the grating period increases from $\Lambda$ to $\Lambda'$, there is no intersection of $\Phi(\lambda)$ with the grating spatial frequency $2\pi/\Lambda$ (i.e., the resonance is lost) for mode 2. However, for a TAP grating with only a little off resonance, there can still be a significant coupling between the fundamental mode and the cladding modes because the cross coupling coefficient is still nonzero for the grating period. There still exists a mode coupling between the fundamental mode and the cladding modes although with a smaller efficiency. As the grating period is changed due to the ambient perturbation, the strength of the TAP LPG (i.e., the amount of coupled energy) varies but the “resonant wavelength” at the maximum coupling remains fixed. These points are illustrated further in Fig. 2-8.

The TAP LPG phenomenon can be intuitively understood as follows: as shown in Eq. (2-29), the intermodal dispersion function $\Phi(\lambda)$ is wavelength dependent due to the
\(\lambda\)-dependent denominator and the \(\lambda\)-dependent effective indices in the numerator. At shorter wavelengths, the fundamental mode resides primarily in the core and its effective index \(n_{\text{eff}1}\) is close to that of the core \((n_1)\), while at longer wavelengths the fundamental mode tends to spread out into the cladding and its effective index approaches that of the cladding \((n_2)\). Hence the effective index of the fundamental mode is in the range of \(n_2 < n_{\text{eff}1} < n_1\). On the other hand, similarly the effective index of the cladding mode \(n_{\text{eff}2}\) decreases with increased wavelengths, and it is within the range between the refractive indices of the cladding and the ambient (e.g. air), that is \(n_3 < n_{\text{eff}2} < n_2\). We know that typical values of the refractive indices in the operation range of the fiber (i.e., around the infrared region) are \(n_1 \approx 1.45\), \(n_2 \approx 1.44\), and \(n_3 \approx 1.00\) (the ambient is air). As a result, the effective index of the fundamental mode \(n_{\text{eff}1}\) has almost no room to change from 1.44 to 1.45, while the effective index of the cladding mode \(n_{\text{eff}2}\) can change widely from 1.00 to 1.44. Therefore, as the operating wavelength increases, the numerator of intermodal dispersion function \(\Phi(\lambda)\) will be increased by the strong decrease of the cladding mode’s effective index (especially obviously for high-order cladding modes), which eventually overcomes the increase of its denominator due to the increased wavelength. This changes the sign of the slope of this function from negative to positive. The TAP LPG phenomenon (i.e., quadratic dispersion case) happens near the region where the sign of the slope switches.
2.5.2. Bandwidth of TAP LPGs

Because TAP LPGs can offer us strong LPGs with a broad bandwidth with 20-dB bandwidth up to 110 nm\textsuperscript{22} (20-dB bandwidth of conventional LPGs is less than 2 or 3 nm generally) and they are very sensitive to the ambient environment,\textsuperscript{23} they are very useful as optical sensors. Therefore, we will introduce them in detail here.

The resonance condition for LPGs can be characterized by a phase-matching relationship given by Eq. (2-25). Therefore, the slope $d\Lambda/d\lambda_{res}$ relies on the dispersive properties of the fiber modes:\textsuperscript{24}

$$\frac{d\Lambda}{d\lambda_{res}} = \frac{\Delta n_g}{\Delta n_{eff}^2},$$

(2-33)

where $\Delta n_{eff} = n_{eff1} - n_{eff2}$ is the difference in the effective refractive indices between the two modes and $\Delta n_g = n_{g1} - n_{g2}$ is the corresponding difference in their group indices.

Except for the fundamental modes, the other modes are cladding modes that we are concerned only in SMF. For two well-guided modes (far from cutoff) of a fiber with a operating wavelength of less than 2000 nm, the slope of the PMC does not change sign, and the resonance wavelength varies monotonically with grating period like the low order modes (e.g. $LP_{0,2}$, $LP_{0,3}$, $LP_{0,4}$, etc.) as shown in Fig.2-23. In such cases the 20-dB bandwidth of a uniform grating of length $L$ that offers 30-dB maximal coupling can easily be shown to be,

\[ \Delta \lambda = \frac{0.0955 \lambda^2_{\text{res}}}{L \Delta n_g}, \] 

Hence, for a conventional LPG of 1-cm-long the 20-dB bandwidth is typically \( \Delta \lambda \sim 1 \text{ nm} \). The operating range of the LPG with strong resonant mode coupling is limited to a few nanometers.

However, in SMF for high order modes (e.g. \( LP_{0,9}, LP_{0,10}, LP_{0,11}, \) and \( LP_{0,12} \)), for example \( LP_{0,12} \), when the \( LP_{0,12} \) mode is well guided at shorter wavelengths and reside predominantly in the cladding of the fiber, the group velocity of the \( LP_{0,12} \) mode approaches that of the cladding (which is higher than that of the core since it has a lower refractive index than the core). Hence, \( v_g(LP_{0,12}) > v_g(LP_{0,1}) \) and \( n_g(LP_{0,1}) > n_g(LP_{0,12}) \). The slope \( d\Delta/\Delta\lambda_{\text{res}} \) obtains a positive sign due to \( \Delta n_g > 0 \).

At longer wavelengths, the ray picture for waveguides accurately predicts that group velocity \( v_g(LP_{0,1}) > v_g(LP_{0,12}) \). Since the \( LP_{0,12} \) mode travels at much more steeper bounce angles than the \( LP_{0,1} \) mode with respect to its bounce angels at shorter wavelength, it is expected to travel more slowly through the waveguide than the \( LP_{0,1} \) mode. Correspondingly, \( v_g(LP_{0,12}) < v_g(LP_{0,1}) \) and \( n_g(LP_{0,1}) < n_g(LP_{0,12}) \). Now the slope \( d\Delta/\Delta\lambda_{\text{res}} \) obtains a negative sign instead of a positive sign due to \( \Delta n_g < 0 \). Thus, there exists a TAP in the PMC of the \( LP_{0,12} \) mode.

Above is another rough intuitive explanation of the occurrence of the TAP in PMCs. If we write a LPG with the period crossing the TAP, the bandwidth of the grating can no longer be determined from Eq. (2-33) as \( \Delta n_g = 0 \) at TAP. Expanding \( \Delta \beta = \beta_1 - \beta_2 \) as a Taylor expansion [in Eq. (2-25)] and retaining the next higher-order term (the next
higher-order term is the modal dispersion, \( D \sim d\beta^2/d\lambda^2 \), the 20-dB bandwidth of TAP gratings that offer 30-dB maximal coupling can be obtained\(^{24} \):

\[
\Delta \lambda = \frac{0.63 \lambda_{\text{res}}}{\sqrt{L \cdot \Delta D \cdot c}},
\]

(2-35)

where \( \Delta D \) is the difference in dispersion between the two modes and \( c \) is the velocity of the light in vacuum.

### 2.5.3. Optical properties of TAP LPGs

In order to clearly illustrate the optical properties of TAP LPGs, we simulate the PMC and the spectrum evolution of a TAP LPG. The fiber parameters chosen are same as those in section 2.4.1: the radius of the fiber core \( a=3.2 \ \mu m \), the radius of the fiber cladding \( b=59.2 \ \mu m \), the surrounding medium is air with the index \( n_{\text{air}}=1 \), the core index \( n_1 \) and the cladding index \( n_2 \) are computed based on the Sellmeier’s equation as shown in Appendix A. We select the typical high-order mode \( LP_{0,12} \) to illustrate the TAP LPG properties, whose TAP is located at \( \Lambda=147.3 \ \mu m \) with \( \lambda_{\text{res}} \approx 1550 \text{ nm} \). We set the length of the LPG as 50 mm and \( \overline{dn_{\text{core}}} = 0.000148 \).

The simulated results are shown in Fig.2-8. In Fig.2-8a, the solid curve represents the PMC of the mode \( LP_{0,12} \) and dash horizontal lines represents different grating periods (from bottom to top are 145.3\( \mu m \), 146.3\( \mu m \), 147.3\( \mu m \), 147.4\( \mu m \), 147.5\( \mu m \) and 147.8\( \mu m \), respectively); Fig.2-7b shows the corresponding LPG transmission spectra at different grating periods (145.3\( \mu m \), 146.3\( \mu m \), 147.3\( \mu m \), 147.4\( \mu m \), 147.5\( \mu m \) and 147.8\( \mu m \), respectively). We notice that (i) In Fig.2-8a, the grating period of either 145.3\( \mu m \) or 146.3\( \mu m \) intersects the PMC at two separate resonant wavelengths. Correspondingly, the
Grating spectrum caused by that period obtains two separate attenuation peaks at those two resonant wavelengths as shown in Fig.2-8b. Each peak has the narrowband characteristic of conventional LPGs. When the period approaches (increases but is still smaller than) the period $\lambda=147.3\mu$m for TAP, the two attenuation peaks move closer to each other. (ii) When the period equals 147.3$\mu$m at TAP, the two attenuation peaks merge to become one single broadband strong attenuation peak. The 3-dB or 20-dB bandwidth is much larger than the conventional LPG (e.g. either one peak of two separate attenuation peaks at $\lambda=145.3\mu$m). (iii) When the period moves away from (becomes larger than) the period $\lambda=147.3\mu$m for TAP, the grating period (e.g. 147.4$\mu$m, 147.5$\mu$m and 147.8$\mu$m) does not intersect the PMC at any wavelengths. The broad single attenuation peak becomes gradually smaller. The grating strength or the amplitude of the peak decreases in proportion to the separation between the grating period and the PMC, since the detuning $\delta$ becomes progressively larger. Ultimately, the PMC shifts far enough so that no resonance occurs such as in the LPG spectrum at $\lambda=147.8\mu$m.
2.5.4. Measurement techniques of TAP LPG-based sensors

Because of the unique characteristic of TAP LPGs, there are two novel measurement techniques appearing for sensing applications (or operating methods) with the use of TAP LPGs. One measurement technique can be called as the optical intensity-based measurement technique — that is the grating is operated as an optical intensity-based sensor, which is measuring the change of the strength of the grating instead of the resonant wavelength of the grating as conventional LPGs. The other measurement technique can be called as the dual peaks measurement technique — that is to measure the spectral separation between the two separate attenuation peaks.
2.5.4.1. Optical intensity-based measurement technique

Usually, conventional LPG-based optical sensors measure changes in temperature, strain, or refractive index, by measuring a shift in the LPG’s resonant wavelength because the strength of the grating usually remains approximately constant. However, due to the unique optical property of the TAP LPG — its strength varies with the change of the strain or the temperature at a fixed resonant wavelength. The primary advantages of this type of sensors are that (1) it does not need optical spectrometer or other dispersive device, (2) it can be used for real-time measurements, and (3) it is highly sensitive near the TAP region.

Conventional LPG-based sensor systems rely on a change of the resonant wavelength with the change of the temperature, the strain, or the ambient index. Accordingly, such systems need an optical spectrum analyzer to measure the wavelength. Because it takes a relatively long time to do the scanning and to analyze the spectrum for each measurement, these systems can not operate in real time mode and it can only measure the parameter of interest at discrete points of time. Therefore conventional LPG-based sensor systems are not well suited for high-speed or real-time applications because they are based on the measurement of the resonant wavelength.

In comparison, a TAP-LPG-based sensor system can operate at a fixed wavelength, which means no need for an optical spectrum analyzer. Like other optical intensity-based sensors, the TAP-LPG-based sensor system can carry out measurements in real time by using a light source at the resonant wavelength of the grating and a photodiode. Because the bandwidth of the resonance of a TAP LPG is typically very broad and flat near its
center, the light source does not need to stabilize the wavelength. An inexpensive LED can be used as the source for this system.

Feinberg et al.\textsuperscript{21} demonstrated a strain sensor using a TAP LPG. They fabricated an SMF-based TAP LPG with a period of 50.1 $\mu$m and a length of 1 cm. Fig.2-9 shows the experimental results of a TAP LPG operating as a strain sensor. Fig.2-9a illustrates that the strength (optical intensity) of the grating varies with the change of the strain applied on the grating while the resonant wavelength remained fixed. The strength of the grating decreases as the strain increases and the wavelength of the maximum coupling is fixed at 1415 nm. Fig.2-9b illustrates the strain sensor was operating in real time. The strain applied on the grating was increased by small steps (e.g. three different level of steps) and the strength of the grating was monitored in real time. The primary advantages of this real-time sensor includes: (i) its simplicity and low cost; (ii) there is no need for a spectrometer or time-consuming spectral processing. (iii) because the bandwidth of the grating resonance is broad, this sensor system is relatively insensitive to fluctuations of the operating wavelength of the optical source.
Fig. 2-9. TAP LPGs for use as strains sensors (a) the transmission spectrum variations of the grating as a function of the change of the strain applied on the grating while the resonant wavelength remained fixed at 1415 nm; (b) Change of transmission of the grating under increasing strain. The strain is increasing linearly with time in discrete steps. The three traces have different strain steps. (From V. Grubsky and J. Feinberg, “Long-period fiber gratings with variable coupling for real-time sensing applications,” *Optical Letters* 25, pp. 203–205, 2000)

### 2.5.4.2. Dual peaks measurement technique

According to the optical properties of the TAP LPG, we know that when the TAP LPG is working in the region with dual peaks (i.e., two separate peaks), each peak of the dual peaks has an opposite dispersive property to each other — the peak at a shorter wavelength has a positive slope $dA/d\lambda_{\text{res}}$ while the peak at a longer wavelength has a negative slope $dA/d\lambda_{\text{res}}$ as shown in Fig. 2-6. As a consequence, the two peaks have opposite characteristics in response to the ambient perturbation (e.g. temperature, strain, or refractive index), which means the resonant wavelengths of their peaks move to opposite directions with the change in temperature, strain, or refractive index. Therefore,
we can measure the change of the spectral separation between the two separate attenuation peaks as the temperature, strain, or refractive index varies. Accordingly, the sensitivity will be doubled if we measure the separation between the peaks.

Generally, conventional LPGs can only perform the measurement of the spectral separation between the two separate attenuation peaks with two different order modes. Because the two different order modes in conventional LPGs have the same dispersive property that induces their attenuation peaks move to same directions with the change in temperature, strain, or refractive index, the sensitivity or resolution of the dual peaks measurement with conventional LPGs is much lower than that with TAP LPGs.

Han et al. demonstrated a bending sensor with a TAP LPG by using the dual peaks measurement technique. They fabricated an SMF-based TAP LPG with a period of 150 µm and a length of 2 cm. Fig. 2-10 shows their experimental results of a TAP LPG for use as a bend or transverse load sensing by measuring the spectral separation of the dual peaks.

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2.5.5. SMF-based TAP LPG sensors

In this section, we will introduce the SMF-based TAP LPGs for use as sensors through summarizing the beautiful work done by Shu. The experimental results of highly sensitive TAP LPG-based sensors for temperature, strain, or refractive index will be presented in the following subsections. All of the TAP LPGs that Shu fabricated were based on B–Ge co-doped photosensitive single-mode fibers.

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2.5.5.1. Temperature sensors

Fig.2-11. TAP LPG temperature sensors. (a) Transmission spectrum of the grating at different temperatures. (b) Resonant wavelength shifts over the temperature range 0 °C –80 °C. The curve 1, 2 and 3 represent the cladding mode \( LP_{0,11} \), \( LP_{0,12} \) and \( LP_{0,13} \), respectively. (From Xuewen Shu, et. al., “Sensitivity Characteristics of Long-Period Fiber Gratings”, J. Lightwave Technol. 20, pp. 255–266, 2002)
Fig.2-11 illustrates how the TAP LPG serves as a temperature sensor. Fig.2-11b shows the evolution of the transmission spectra as a function of the temperature. It clearly illustrates that as the ambient temperature varies from 80 °C to 0 °C, the shape of the transmission spectrum of TAP LPG will vary from two separate peaks to a single peak, and then the single peak becomes smaller and smaller in amplitude due to the diminished coupling efficiency. Fig. 2-11b shows the resonant wavelength shifts over the temperature range of 0 °C –80 °C. Shu investigated three high order cladding modes $LP_{0,11}$, $LP_{0,12}$ and $LP_{0,13}$, which are represented by the curve 1, 2 and 3 respectively. For all of the three modes, we notice that (i) Within the temperature range of 0 °C – 10 °C for curve 1 and 0 °C – 20 °C for curve 2 and 3, the single resonance is temperature independent and fixed; (ii) Starting from 20 °C for curve 1 and 30 °C for curve 2 and 3, the single resonance splits and becomes two separate resonances. Then, as the temperature increases, the two resonances continue to move in opposite direction and separate to each other further; (iii) The magnitudes of shifts of the blue-shifted (shift to shorter wavelength) resonances are slightly larger than those of shifts of the red-shifted (shift to longer wavelength) resonances.
2.5.2.2. Strain sensors

Fig.2-12. TAP LPG strain sensors. (a) Transmission spectrum of the grating at different strains. (b) Spectral separation of the two resonant wavelength as a function of the strain. (From Xuewen Shu, et. al., “Sensitivity Characteristics of Long-Period Fiber Gratings”, J. Lightwave Technol. 20, pp. 255–266, 2002)

Fig.2-12 illustrates how the TAP LPG serves as a strain sensor. Fig.2-12a shows the evolution of the transmission spectra as a function of the strain. As the strain increases from 0 με to 3000 με, the two separate attenuation peaks move closer to each
Fig.2-12b shows the spectral separation of the two resonant wavelength as a function of the strain.

2.5.5.3. Refractive index sensors

![Graph showing transmission spectrum and spectral separation as a function of refractive index.](image)

Fig.2-13 illustrates how the TAP LPG serves as a refractive index sensor. Fig.2-13a shows the evolution of the transmission spectra as a function of the surrounding refractive index. The graph indicates that the transmission spectra change significantly with different refractive indexes, demonstrating the sensitivity of the TAP LPG to refractive index variations.


Fig.2-13a shows the evolution of the transmission spectra as a function of the surrounding refractive index. The solid lines represent the transmission spectra for different refractive indexes, while the dotted lines with open circles and crosses indicate the spectral separation of the two resonant wavelengths. The graph clearly demonstrates the high sensitivity of the TAP LPG to refractive index changes.
refractive index. As the surrounding refractive index increases, the single resonance splits and becomes two separate resonances. Then, as the surrounding refractive index increases, the two resonances continue to move in opposite directions and separate from each other further. Fig. 2-13b shows the resonant wavelength shifts over the surrounding refractive index range of 1 — 1.44. Shu investigated two high order cladding modes $LP_{0.12}$ and $LP_{0.13}$, which are represented by the curves 1 and 2 respectively. The behaviors of these two modes in response to the surrounding refractive index are similar with only a difference in resonant wavelengths.
Chapter 3. Principle of Ionic Self-Assembled Multilayers

3.1. Introduction

Organic thin films have been playing an important role in many applications, including sensors\textsuperscript{28}, surface coatings\textsuperscript{29}, optoelectronics\textsuperscript{30} and nonlinear optics\textsuperscript{14}. In general, these applications require well-ordered films consisting of molecules with specific properties, carefully aligned to each other and the substrate. Therefore, it is highly desirable to develop methods for building organic thin films at the nanometer scale, and for that reason the self-assembly of polymers has been increasingly explored for the preparation of well-defined thin films for many years.\textsuperscript{31} By repetitive Layer-By-Layer (LBL) depositions, self-assembly techniques provide a precise control over the total thickness of the thin-film of multi-molecular layers, in the range from a few angstroms up to a micron. Additionally, the LBL procedures allow for a well-controlled structuring in at least the vertical dimension. Self-assembled organic thin films combine the advantages of versatile organic synthesis with spontaneous molecular self-assembly, which produces stable structures in thermodynamic equilibrium. The fabrication of such

self-assembled organic thin films requires a multidisciplinary approach, including such fields as organic synthesis, physical chemistry, physics, materials science, and electrical engineering for film preparation, modification, and characterization.

In the early 1990s, the group of Decher developed a practical method referred to as Ionic Self-Assembled Multilayers (ISAMs) technique for building nano-architectured thin films with good positioning of individual layers, and whose fabrication is largely independent on the nature, size, and topology of the substrate.\textsuperscript{13,32} the process involves immersing a substrate alternately into solutions containing positively- and negatively-charged molecules. Due to its striking simplicity, the ISAM technique has developed a rapidly increasing interest in the thin-film area. The ISAM is extremely versatile because not only polyelectrolytes are applicable, but also any charged nano-objects (e.g. molecule aggregates, clusters, or colloids) can be used as film materials. Unlike traditional self-assembled monolayers (SAMs), it can be tailored to allow multimaterial assembly of several compounds without special chemical modifications. The fabrication of multicomposite films by the ISAM technique literally means the possible assembly of hundreds of different materials (though, most commonly, several materials) in a single device by using an environmentally friendly, inexpensive technique. The materials can be small organic molecules or inorganic compounds\textsuperscript{33, 34, 35}, macromolecules\textsuperscript{36, 37}

biomacromolecules such as proteins or DNA or even colloids (metallic or oxide colloids or latex particles). The technique can be applied to almost any kind of solvent-accessible surfaces and any shape, even including microcapsules, colloids, or biological cells, in addition to the more commonly-used solid substrates.

### 3.2. ISAM technique

The ISAM deposition process involves the immersion of a charged substrate into oppositely charged aqueous poly-electrolytic solutions of polyanions and polycations in alternating sequence at room temperature and ambient conditions. This results in a multilayered thin-film to grow on the substrate with molecular-level control. The resulting macroscopic properties of the thin-film are determined by the properties of individual molecules as well as the dipping sequence or the architecture of the composite thin-film.

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The process is schematically shown in Fig. 3-1. First, a clean, charged substrate (a negatively charged one shown in the figure) is dipped into the polycation solution. Due to the strong Coulombic attraction between the negatively charged substrate and the positively charged polycation, a monolayer of polycation molecules is deposited on the substrate. As a result an effective sign reversal of the surface charge is realized and now the surface is charged positively, which limits further polycation adsorption. Then the polycation-coated substrate is removed from the solution and rinsed with deionized water to remove excess polycation molecules that are not ionically bonded. Next, the substrate is immersed into the polyanion solution. Coulombic attraction as described above, now causes a monolayer of polyanion molecules to be adsorbed onto the substrate. Finally, these two steps are repeated to obtain a multilayered thin-film with an \((AB)_n\) architecture until the desired film thickness is reached. The combination of one monolayer of polycation and polyanion together are denoted a bilayer. Since the ISAM process requires only that successive layers have opposite ion charge (anion/cation), it is possible to construct films whose structure is more complicated than \((AB)_n\) architecture. Films with
(ABAC)ₙ architecture, for example, have been fabricated and other structures are also possible. This allows polymers layers with different functionality to be easily incorporated into a single film with precise structural control.

Given the large set of materials which are easily incorporated into ISAM films, the ISAM technique is a rather general approach for the fabrication of complex surface coatings. It is possible to coat nearly any solvent-accessible surface form sub-micron objects up to the inside of tubings or even objects with a surface of several square meters. Similar to a chemical reaction, the precise structure of each layer depends on a set of control parameters such as solvent, concentration of adsorbing species, adsorption times, ionic strength, pH, temperature, nature and concentration of added salt, rinsing time, humidity of the surrounding air, drying, agitation during adsorption or rinsing, dipping speed and so forth, but in general the processing window is very broad.

Polyelectrolyte multilayer films are dependent of the underlying substrate to some extent. However, since polyanion and polycation adsorption is repeated consecutively, each polyanion adsorbs onto a polycation-covered surface and vice versa. This means that after a few layers, the structure and properties of each layer are governed by the

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choice of polyanion/polycation pair and by the deposition conditions and that the influence of the substrate is typically lost after a few deposition cycles.  

The ISAM technique possesses many advantages over other traditional thin film techniques such as:

1. ISAM procedure is simple, rapid, environmentally friendly, and inexpensive.
2. Diversity of ISAM film materials (e.g. various polyelectrolytes incorporated with clay platelets, proteins, virus particles, etc.)
3. Diversity of substrate materials with various nature, sizes, topology (e.g. metals, glass, silica, mica, etc.)
4. Thickness of ISAM films can be precisely controlled at the nm level.
5. Refractive index of ISAM films can be controlled by using different film materials or altering pH of polycation and/or polyanion solutions.
6. Flexibility of film structure, which depends on dipping sequences (e.g. ABAB, ABCBAB).
7. Good reliability, thermal stability, and film quality.

3.3. Characterization of ISAM films

The methods for characterizing ISAM films can be classified into ex situ characterization methods and in situ characterization methods. Reported ex situ methods include UV/Vis spectroscopy, X-ray/neutron-ray reflectometry, nuclear magnetic resonance (NMR), while reported in situ methods include zeta potential, quartz crystal

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microbalance, surface plasmon spectroscopy, optical waveguide lightmode spectroscopy (OWLS), optical reflectometry in stagnation point flow cells, scanning angle reflectometry (SAR), ellipsometry, in situ atomic force microscopy (AFM), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), surface forces measurements, and second harmonic generation (SHG). In the following two sub-sections, two typical characterization methods used in our group are introduced.

3.3.1. UV/Vis spectroscopy

UV/Vis spectroscopy is probably the easiest way to follow multilayer buildup which works for all colored materials. By measuring the optical absorbance of the ISAM film samples, we can qualitatively track the buildup procedure of ISAM films adsorbed on substrates. We utilized glass microscope slides purchased from Fisher Scientific Inc. as substrates. Poly(allylamine hydrochloride) (PAH) and Poly[1-[4-(3-carboxy-4-}
hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt (PCBS) solutions at 10 mM concentration were used as the polycation and polyanion, respectively. Molecular structures of PAH and PCBS are shown in Fig. 3-2. pH values of PAH and PCBS are 7.5 and 7 respectively. The slides were prepared by using RCA cleaning process\textsuperscript{63}. We deposited 10, 20, 30, 40 bilayers of PAH/PCBS-based ISAM films on the glass slide and measured them by UV/Visible spectroscopy, respectively. The experimental results are shown in Fig.3-3.

Fig.3-2. Molecular structure of Poly(allylamine hydrochloride) (PAH) and Poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt (PCBS).

Fig. 3-3. UV/Visible spectroscopy results (a) absorbance spectra (b) absorbance at the peak wavelength ($\lambda=370\text{nm}$) versus number of bilayers of PAH/PCBS-based ISAM films

3.3.2. Ellipsometry

Ellipsometry can be used to characterize the optical constants (refractive index and extinction coefficient) and thickness of thin films. The instrument we used is a Variable Angle Spectroscopic Ellipsometer (VASE©) ellipsometer made by J.A. Woollam Co.
Ellipsometry measures the change in polarization state of light reflected from the surface of a sample. The measured values are expressed as $\Psi$ and $\Delta$. These values are related to the ratio of Fresnel reflection coefficients, $R_p$ and $R_s$ for $p$ and $s$-polarized light, respectively.

$$\tan(\Psi)e^{i\Delta} = \frac{R_p}{R_s}, \quad (3-1)$$

The optical constants define how light interacts with a material. The complex refractive index is a representation of the optical constants of a material, it is represented by

$$\tilde{n} = n + ik, \quad (3-2)$$

The real part or index of refraction, $n = \nu/c$, defines the phase velocity of light in the material where $\nu$ is the speed of light in the material and $c$ is the speed of light in vacuum. The imaginary part or extinction coefficient, $k$, determines how fast the amplitude of the wave decreases. The extinction coefficient determines the absorption of a material and is related to the absorption coefficient by:

$$\alpha = \frac{4\pi k}{\lambda}, \quad (3-3)$$

where $\alpha$ is the absorption coefficient and $\lambda$ is the wavelength of light in vacuum.

For example, we deposited 10, 15, 20 bilayers of PAH/PCBS-based ISAM films on the glass slide and measured them by ellipsometry. The pH values of PAH and PCBS are 9 and 8, respectively. The results are shown in Fig. 3-4.

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$^{64}$ Handbook of Variable Angle Spectroscopic Ellipsometer (VASE®) ellipsometer by J.A. Woollam Co.
PAH/PCBS-based ISAM films measured by ellipsometry (PAH at pH=9, PCBS at pH=8)

(c)

Fig.3-4. Ellipsometry results (a) modeling of $\Delta$, (b) modeling of $\Psi$, (c) thickness and refractive index of PAH/PCBS-based ISAM films versus number of bilayers.
Chapter 4. Simulations of ISAM-coated LPGs

4.1. Introduction to simulations

The schematic of a nm-thick thin-film (e.g. ISAM films) coated LPG and its corresponding refractive index profile is shown in Fig.4-1.

Fig.4-1. (a) Illustrative schematic of LPG with nm-thick thin-film coating (b) Index profile of nm-thick thin-film coated LPG, \( n_1 \) is index of fiber core, \( n_2 \) is index of fiber cladding, \( n_3 \) is index of nm-thick thin-film, \( n_{\text{air}} \) is index of air. Ambient consists of \( n_3 \) and \( n_{\text{air}} \), and \( n_3 > n_1 > n_2 > n_{\text{air}} \).

where \( r \) is the radius of the fiber, \( n_1 \) is the refractive index of the fiber core, \( n_2 \) is the refractive index of the fiber cladding, \( n_3 \) is the refractive index of the thin-film (e.g. ISAM films), \( n_{\text{air}} \) is the refractive index of the air. Media outside the cladding are together referred to as the ambient of the fiber. In our case, the ambient consists of the ISAM film and the air. To simulate the material dispersion of the glass fiber, in our modeling we calculated \( n_1 \) and \( n_2 \) from the Sellmeier’s equation given in the Appendix A.
For illustrative purpose, the size of the fiber core and the ISAM film relative to the fiber cladding have been greatly exaggerated in the figure. In our simulation, we programmed the modeling in Matlab environment.

Scalar modes analysis method was employed in this modeling. Considering in practice the LPGs were UV-induced on OFS TrueWave RS™ fiber which is standard Single-Mode Fiber (SMF), we simplified the fiber profile of the ISAM-coated LPG by using a three-layer fiber structure when we calculated the properties of cladding modes. For the fundamental core mode LP\(_{01}\), we simplified the fiber profile by using a two-layer fiber structure.

### 4.2. Fundamental core mode LP\(_{01}\)

#### 4.2.1. Calculating \(n_{\text{core}}\)

![Fiber profile of single mode fiber](image)

Because the mode field of the fundamental core mode LP\(_{0,1}\) is nearly isolated from the ambient for SMF, the fiber profile is simplified to be the two-layer structure for solving the effective index \(n_{\text{core}} (n_1 > n_{\text{core}} > n_2)\) of the mode LP\(_{0,1}\) as shown in Fig.4-2.

Based on Marcuse’s analysis, for LP\(_{l,m}\) modes, \(b\) is a solution to the dispersion relation,
\[ V \sqrt{1-b} \frac{J_{l-1}(V \sqrt{1-b})}{J_{l}(V \sqrt{1-b})} = -V \sqrt{b} \frac{K_{l-1}(V \sqrt{b})}{K_{l}(V \sqrt{b})}, \]  

(4-1)

where \( l \) is the azimuthal order of the mode and \( V = (2\pi / \lambda) r_{\text{core}} \sqrt{n_1^2 - n_2^2} \) is the normalized frequency, with \( r_{\text{core}} \) the core radius. \( n_{\text{core}} \) is related to \( b \) through \( b = \left( n_{\text{core}}^2 - n_2^2 \right) / \left( n_1^2 - n_2^2 \right) \). By setting \( l=0 \), we could obtain \( n_{\text{core}} \) of the mode LP\(_{0,1} \) through computer numerical calculations.

### 4.2.2. Calculating dispersion parameter \( D \)

After obtaining \( n_{\text{core}} \), we could calculate the dispersion parameter \( D \) according to the definition as following.\(^{65}\)

\[ D = -\frac{\lambda}{c} \frac{d^2 n_{\text{core}}}{d\lambda^2}, \]  

(4-2)

### 4.2.3. Calculating single mode operating condition

To make our approximate modeling approach reality as closely as possible and to obtain accuracy of the modeling as high as possible, we need to examine the single mode operating condition of our modeling as well, which is to calculate the cutoff wavelength \( \lambda_{\text{cut}} \) of the fiber mode LP\(_{1,1} \).

By means of the same analysis as that for the fundamental mode LP\(_{0,1} \) and setting \( l=0 \) in Eq.(4-1), we could obtain the effective index \( n_{11} \) of the mode LP\(_{1,1} \) through numerical calculations. According to the plot of \( n_{11} \) with respect to \( \lambda \), we will obtain \( \lambda_{\text{cut}} \).

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\(^{65}\) Lecture notes of the class “Optical Waveguides” instructed by Dr. A. Safaai-Jazi of Electrical Engineering Department at Virginia Tech.
for the single mode operating condition of our modeling. Through adjusting the $r_{core}$ and the index difference used for the step-index approximation, we will try to match the calculated $\lambda_{cut}$ with the measured $\lambda_{cut}$ of the fiber we used.

In practice, we chose the combination of the two parameters which matched the measured 1275 nm $\lambda_{cut}$ of the fiber correctly, and also resulted in the best match of the resonant wavelength $\lambda_{res}$ versus the grating period $\Lambda$ in air to experimentally determined values when combined with the values of $n_2$ for $n_3= n_{air}=1$ as shown in Fig.4-3a. The condition was met for $r_{core} =3.2$ µm and core-cladding index difference of 0.0078 at $\lambda=1300$ nm.

In addition, we also examined the dispersion property of our modeling. The fiber used in our experiments was OFS TrueWave RS™ dispersion shifted fiber (DSF) whose zero-dispersion wavelength is located at 1550 nm. The combination of the two parameters results in a predicted value for the zero-dispersion wavelength of 1380 nm as shown in Fig.4-3b. This illustrates the difficulty in matching a dispersion-shifted fiber to a step-index equivalent. However, because changes in the ambient index only affect the effective index of the cladding modes, the difficulty in making a good approximation to the core mode does not affect the utility of the model for predicting the relative resonant wavelength shifts of the grating, as long as a reasonable match to the experimental $\lambda_{res}$ versus $\Lambda$ can be made. Once the set of values for $n_{core}$ was determined by matching theory and experiment at $n_3= n_{air}=1$, the same $n_{core}$ was used in all calculations of $\lambda_{res}$ versus $\Lambda$, with the effective index $n_{clad}$ of the cladding modes recalculated for each different ambient index of interest.
Fig. 4-3. Properties of fiber modes when $r_{\text{core}} = 3.2 \, \mu\text{m}$ and core-cladding index difference of 0.0078 at $\lambda = 1300 \, \text{nm}$. (a) effective index $n_{11}$ of mode LP$_{1,1}$ (b) dispersion of mode LP$_{0,1}$

4.3. Cladding mode LP$_{0,m}$

For convenience of calculating the properties of the cladding modes, the fiber profile of the thin-film-coated LPG could be approximated by using the three-layer profile as shown in Fig. 4-4.

Fig. 4-4. Simplified fiber profile of thin-film-coated LPG
According to the scalar mode analysis method, considering that the effective index $n_{clad}$ of the cladding modes satisfies the condition of $n_2 > n_{clad} > n_{air}$, the mode field $\Psi(r)$ of cladding mode LP$_{0,m}$ is given by,\(^6\)

$$
\Psi(r) = \begin{cases} 
A_1J_0(\mu_2 r), r < a \\
A_2J_0(\mu_3 r) + A_3Y_0(\mu_3 r), a < r < b \\
A_4K_0(\mu_4 r), r > b 
\end{cases}
$$

(4-3)

where

$$
\begin{align*}
\mu_2 &= k_0 \sqrt{n_2^2 - n_{clad}^2}, \\
\mu_3 &= k_0 \sqrt{n_3^2 - n_{clad}^2}, \\
\mu_4 &= k_0 \sqrt{n_{clad}^2 - n_{air}^2}, \\
k_0 &= \frac{2\pi}{\lambda}
\end{align*}
$$

$J_0$ and $Y_0$ are the first kind and second kind Bessel functions respectively, $K_0$ is the second kind modified Bessel function, and $A_i$ (i=1,2,3,4) are constant coefficients.

Applying boundary conditions to Eq.(4-3), that is $\Psi(r)$ and $d\Psi(r)/dr$ are continuous at $r=a$ and $r=b$, respectively, following equations are obtained,

$$
\begin{align*}
A_1J_0(\mu_2 a) &= A_2J_0(\mu_3 a) + A_3Y_0(\mu_3 a), \\
A_1J_0'(\mu_2 a) &= A_2J_0'(\mu_3 a) + A_3Y_0'(\mu_3 a), \\
A_4K_0(\mu_4 b) &= A_2J_0(\mu_3 b) + A_3Y_0(\mu_3 b), \\
A_4K_0'(\mu_4 b) &= A_2J_0'(\mu_3 b) + A_3Y_0'(\mu_3 b),
\end{align*}
$$

(4-4)\text{---}(4-7)

\subsection*{4.3.1. Calculating $n_{clad}$}

Converting Eq.(4-4) — Eq.(4-7) into matrix form, we obtain,\(^6\)
\[
\begin{pmatrix}
J_0(\mu_2a) & -J_0(\mu_3a) & -Y_0(\mu_3a) & 0 \\
\mu_2J_0'(\mu_2a) & -\mu_3J_0'(\mu_3a) & -\mu_3Y_0'(\mu_3a) & 0 \\
0 & J_0(\mu_3b) & Y_0(\mu_3b) & -K_0(\mu_3b) \\
0 & \mu_3J_0'(\mu_3b) & \mu_3Y_0'(\mu_3b) & -\mu_4K_0(\mu_4b)
\end{pmatrix}
\begin{pmatrix}
A_1 \\
A_2 \\
A_3 \\
A_4
\end{pmatrix} = 0,
\] (4-8)

For this system of equations to have a nontrivial solution, the determinant of the coefficients must vanish, then we obtain,

\[
\det = \begin{pmatrix}
J_0(\mu_2a) & -J_0(\mu_3a) & -Y_0(\mu_3a) & 0 \\
\mu_2J_0'(\mu_2a) & -\mu_3J_0'(\mu_3a) & -\mu_3Y_0'(\mu_3a) & 0 \\
0 & J_0(\mu_3b) & Y_0(\mu_3b) & -K_0(\mu_3b) \\
0 & \mu_3J_0'(\mu_3b) & \mu_3Y_0'(\mu_3b) & -\mu_4K_0(\mu_4b)
\end{pmatrix} = 0,
\] (4-9)

Eq.(4-9) is the characteristic equation for solving \( n_{\text{clad}} \) of the cladding modes.

**4.3.2. Calculating \( \Psi(r) \)**

To obtain the mode field \( \Psi(r) \), \( A_i(i=1,2,3,4) \) are required to be determined after we obtain \( n_{\text{clad}} \). First, based on Eq.(4-4) we obtain,

\[
A_2 = \frac{A_1J_0(\mu_2a) - A_3Y_0(\mu_3a)}{J_0(\mu_3a)},
\] (4-10)

By means of replacing \( A_2 \) in Eq.(4-5) with Eq.(4-10), we obtain,

\[
A_3 = A_4 \frac{\mu_2J_0'(\mu_2a)J_0(\mu_3a) - \mu_3J_0'(\mu_3a)J_0(\mu_2a)}{\mu_3Y_0'(\mu_3a)J_0(\mu_3a) - \mu_3J_0'(\mu_3a)Y_0(\mu_3a)},
\] (4-11)

Similarly, based on Eq.(4-6) we obtain,
\[ A_i = \frac{A_i J_0(\mu_i b) + A_i Y_0(\mu_i b)}{K_0(\mu_i b)}, \quad (4-12) \]

Therefore, according to Eq.(4-10) — Eq.(4-12) we have the relations of \( A_i (i=2,3,4) \) as a function of \( A_1 \) which is determined by the initial condition of the incident power from the optical source. In our modeling, for simplification we set \( A_1 = 1 \). Based on Eq.(4-3) we could obtain \( \Psi(r) \).

**4.3.3. Calculating effective area \( A_{\text{eff}} \)**

After obtaining \( \Psi(r) \), we could calculate the effective area \( A_{\text{eff}} \) according to the definition as following,

\[
A_{\text{eff}} = 2\pi \frac{\int_0^\infty \int_0^\infty \psi^2(r) r dr \right)^2}{\int_0^\infty \int_0^\infty \psi^4(r) r dr}, \quad (4-13)
\]

where in our case

\[
\left[ \int_0^\infty \psi^2(r) r dr \right]^2 = \left\{ \int_a^b \left| A_1 J_0(\mu_1 r) \right|^2 r dr + \int_a^b \left| A_2 J_0(\mu_2 r) + A_2 Y_0(\mu_2 r) \right|^2 r dr + \int_a^b \left| A_3 K_0(\mu_3 r) \right|^2 r dr \right\}^2
\]

and

\[
\int_0^\infty \psi^4(r) r dr = \int_a^b \left| A_4 J_0(\mu_4 r) \right|^4 r dr + \int_a^b \left| A_4 Y_0(\mu_4 r) \right|^4 r dr + \int_a^b \left| A_5 K_0(\mu_5 r) \right|^4 r dr.
\]

**4.3.4. Calculating dispersion parameter \( D \)**

After obtaining \( n_{\text{clad}} \), we could calculate the dispersion parameter \( D \) according to the definition as following,
\[ D = -\frac{\lambda}{c} \frac{d^2 n_{\text{clad}}}{d\lambda^2}, \]  

(4-14)

4.4. Long period fiber gratings

Long Period Fiber Gratings (LPG) are fabricated by exposing an optical fiber to a spatially varying pattern of ultraviolet intensity. In most fiber gratings, the UV-induced refractive index perturbation is approximately uniform across the core and nonexistent outside the core. For simplicity, we assume that the perturbation \( \delta n_{\text{core}} \) to the refractive index \( n_{\text{core}} \) of the fiber core is described by, \(^{20}\)

\[
\delta n_{\text{core}}(z) = \overline{\delta n_{\text{core}}}(z) \left\{ 1 + \nu \cdot \cos \left[ \frac{2\pi}{\Lambda} z + \phi(z) \right] \right\}
\]

(4-15)

where \( \overline{\delta n_{\text{core}}} \) is the “dc” index change spatially-averaged over a grating period, \( \nu \) is the fringe visibility of the index change, \( \Lambda \) is the nominal period, and \( \phi(z) \) represents grating chirp. If the fiber has a step-index profile and the induced index change \( \delta n_{\text{core}}(z) \) is uniform across the core, then we will find the perturbation \( \delta n_{\text{eff}} \) to the effective refractive index \( n_{\text{eff}} \) of the guided mode of interest is proportional to \( \delta n_{\text{core}} \) by the core power confinement factor, which is assumed as a constant for simplicity in our modeling.
4.4.1. Coupled mode theory

We utilized the coupled mode theory to analyze LPGs. Based on the ideal-mode approximation, we made an assumption that the transverse component of the electric field could be given by a superposition of the unperturbed ideal modes labeled $j$, which is shown in Eq. (4-16),

$$
\vec{E}_t(x, y, z, t) = \sum_j [A_j(z) \exp(j \beta_j z) + B_j(z) \exp(-j \beta_j z)] \cdot \vec{e}_{jt}(x, y) \exp(-i\omega t)
$$

(4-16)

where $A_j(z)$ and $B_j(z)$ are modal amplitudes of the $j$th fiber mode traveling in the $+z$ and $-z$ directions with slow variations, respectively. The transverse mode field $\vec{e}_{jt}(x, y)$ might be the guided core modes, guided cladding modes, or radiation modes. Although the modes are orthogonal to each other in the unperturbed ideal waveguide, the dielectric perturbation (e.g. the refractive index perturbation in LPGs) causes the modes to be coupled. Hence, the modal amplitudes $A_j(z)$ and $B_j(z)$ of the $j$th fiber mode would vary along the $z$ axis by the following equations,

$$
\frac{dA_j}{dz} = i \sum_k A_k \left(K_{kj}^t + K_{kj}^z\right) \exp\left[i\left(\beta_k - \beta_j\right)z\right] + i \sum_k B_k \left(K_{kj}^t - K_{kj}^z\right) \exp\left[-i\left(\beta_k + \beta_j\right)z\right] \tag{4-17}
$$

$$
\frac{dB_j}{dz} = -i \sum_k A_k \left(K_{kj}^t - K_{kj}^z\right) \exp\left[i\left(\beta_k + \beta_j\right)z\right] - i \sum_k B_k \left(K_{kj}^t + K_{kj}^z\right) \exp\left[-i\left(\beta_k - \beta_j\right)z\right] \tag{4-18}
$$

where $K_{kj}^t(z)$ is the transverse coupling coefficient between modes $j$ and $k$ described by,

$$
K_{kj}^t(z) = \frac{\omega}{4} \int dxdy \left(\Delta\varepsilon(x, y, z)\vec{e}_{jt}(x, y)\cdot\vec{e}_{jt}^*(x, y)\right)
$$

(4-19)

where $\Delta\varepsilon$ is the perturbation to the permittivity, approximately $\Delta\varepsilon \approx 2n\delta n$ when $\delta n << n$. The longitudinal coupling coefficient $K_{kj}^z(z)$ is similar to $K_{kj}^t(z)$, but for fiber modes.
normally \( K_{kj}^x(z) \ll K_{kj}^t(z) \), and hence \( K_{kj}^y(z) \) is often ignored. Furthermore, we define two new coefficients,

\[
\sigma_{kj}(z) = \frac{\alpha n_{\text{core}}}{2} \delta n_{\text{core}}(z) \int_{\text{core}} dx dy \left( \overline{e}_{kj}(x,y) \cdot \overline{e}_{kj}^*(x,y) \right)
\]  \hspace{1cm} (4-20)

\[
\kappa_{kj}(z) = \frac{\nu}{2} \sigma_{kj}(z)
\]  \hspace{1cm} (4-21)

where \( \sigma \) is a “dc” (period-average) coupling coefficient, and \( \kappa \) is an “ac” coupling coefficient. Therefore the transverse coupling coefficient \( K_{kj}^t(z) \) can be described by,

\[
K_{kj}^t(z) = \sigma_{kj}(z) + 2\kappa_{kj}(z) \cdot \cos \left[ \frac{2\pi}{\Lambda} z + \phi(z) \right]
\]  \hspace{1cm} (22)

The Eqs.(4-17)-(4-22) are the coupled mode equations which we take advantage of to depict LPGs spectra in the following section.

### 4.4.2. Long period grating spectra

Although the mode coupling could occur between the incident fiber mode and any other modes, near a specific wavelength there is only one fiber mode that has the strongest coupling from the incident fiber mode. For simplicity of calculations, we assume a mode “1” of modal amplitude \( A_1(z) \) is strongly coupled to a copropagating mode “2” with modal amplitude \( A_2(z) \). Hence, we could simplify Eq.(4-17) and Eq.(4-18) by retaining only terms that involve the amplitudes of these two modes. By considering the usual synchronous approximation, the equations result in,\(^{20}\)

\[
\frac{dR}{dz} = i\sigma R(z) + i\kappa S(z)
\]  \hspace{1cm} (4-23)

\[
\frac{dS}{dz} = -i\sigma S(z) + i\kappa^* R(z)
\]  \hspace{1cm} (4-24)
where \( R(z) = A_1 \exp[-i(\sigma_{11} + \sigma_{22})z/2] \exp(i\delta z - \phi/2) \) and \( S(z) = A_2 \exp[-i(\sigma_{11} + \sigma_{22})z/2] \exp(-i\delta z + \phi/2) \), and \( \sigma_{11} \) and \( \sigma_{22} \) are “dc” coupling coefficients defined in Eqn.(4-20). \( \kappa = \kappa_{21} = \kappa_{12}^* \) is the “ac” cross-coupling coefficient from Eqn.(4-21). \( \tilde{\sigma} \) is a general “dc” self-coupling coefficient defined as

\[
\tilde{\sigma} = \delta + \frac{\sigma_{11} - \sigma_{22}}{2} - \frac{1}{2} \frac{d\phi}{dz}
\]  

(4-25)

The detuning parameter \( \delta \), which is assumed to be constant along \( z \), is given by,

\[
\delta = \pi (n_{\text{eff}1} - n_{\text{eff}2}) \left( \frac{1}{\lambda} - \frac{1}{\lambda_D} \right)
\]  

(4-26)

where \( n_{\text{eff}1} \) and \( n_{\text{eff}2} \) represent the effective index of mode “1” and mode “2”, respectively. \( \lambda_D = (n_{\text{eff}1} - n_{\text{eff}2}) \Lambda \) is the Design wavelength for a weak grating.

For an LPG with a uniform refractive index variation inside the core, \( \tilde{\sigma} \) and \( \kappa \) are constants. By applying the appropriate initial conditions (e.g. assuming only one mode is incident from \( z = -\infty \)), the solution to the transmission \( t \) of the power is given by,

\[
t = \cos^2 \left( \sqrt{\kappa^2 + \tilde{\sigma}^2} \cdot L \right) + \frac{1}{1 + \frac{\kappa^2}{\tilde{\sigma}^2}} \sin^2 \left( \sqrt{\kappa^2 + \tilde{\sigma}^2} \cdot L \right)
\]  

(4-27)

The Eq.(4-27) is the formula we used for simulating the LPG transmission spectra.

4.4.3. Calculating Turn Around Point of LPGs

To make our approximate modeling match the experimental LPG as closely as possible, we examined the Turn Around Point (TAP) of the LPG, which determines in
part the dispersion property of the grating. The LPGs we used were UV-induced on TrueWave RS™ fibers with a grating period of 116 µm and a length of 5 cm. This yielded gratings that couple the fundamental mode to the LP$_{0,12}$ cladding mode at a resonant wavelength, $\lambda_{\text{res}}$ of 1420 nm. We found out that the TAP of the experimental LPG is around 1550 nm. By adjusting the radius $a$ of the fiber cladding, we found out that the condition was met for $a = 59.2$ µm, with which the simulated PMC of LP$_{0,12}$ is shown in Fig.4-5.

![Simulated phase matching curve of cladding mode LP$_{0,12}$](image)

**Fig.4-5.** Simulated phase matching curve of cladding mode LP$_{0,12}$

### 4.5. Modeling refractive index of ISAM films

According to the ellipsometry results we obtained, $n_3$ of the ISAM thin-films could be modeled by exponential fitting the ellipsometry experimental data, which will be used in following simulations. Both the experimental data and the fitted results of $n_3$ are shown in Fig.4-6. Fig.4-6 illustrates that different pH combinations of PAH and PCBS result in different $d$ and $n_3$ of the thin-film.
Fig.4-6. Modeling refractive index $n_3$ of ISAM film with different experimental results of pH combinations [(7.5,6), (7.5,8), (9,6), (9,8)] of PAH solution and PCBS solution by exponential fitting, [fit (7.5,6), fit (7.5,8), fit (9,6), fit (9,8)] represent fitting results correspondingly.

4.6. Simulation results

4.6.1. Thin-film effect on LPGs

In this section, simulation results of the LPG modeling are illustrated and compared with the experimental results. To investigate the effects of the thickness $d$ ($d=b-a$) and the refractive index $n_3$ of the nm-thick thin-film on LPGs, first we simulated PMC variations of the grating by altering $d$ and $n_3$ separately and together. For $n_3$, we ignored its material dispersion for the simplified demonstration and selected four typical values ($n_3$=1.5, 1.6, 1.7, 1.8) which are within the refractive index range of commercial polymers. For $d$, we set it as $d$=0, 20, 40, 60, 80, 100 nm, respectively, to distinguish its effect clearly in simulations. We chose two typical cladding modes LP$_{0,4}$ and LP$_{0,12}$ to illustrate the lower-order and the higher-order cladding modes’ PMC behaviors. Our simulations were all run under Matlab software environment.
Fig. 4-7. Phase Matching Curves (PMC) shifts as functions of $n_3$ and thickness $d$ of nm-thick thin film. (a) PMC of mode LP$_{0,4}$ shifts with $d$ ($d=0, 20, 40, 60, 80, 100$ nm) at $n_3=1.8$, (b) PMC of mode LP$_{0,12}$ shifts with $d$ ($d=0, 20, 40, 60, 80, 100$ nm) at $n_3=1.8$, (c) PMC of mode LP$_{0,4}$ shifts with $n_3$ ($n_3=1.5, 1.6, 1.7, 1.8$) at $d=40$ nm and $d=100$ nm, (d) PMC of mode LP$_{0,12}$ shifts with $n_3$ ($n_3=1.5, 1.6, 1.7, 1.8$) at $d=40$ nm and $d=100$ nm.

Fig. 4-7. shows PMC shifts as functions of $d$ and $n_3$ of the nm-thick thin film. Compared to the larger wavelength range for the mode LP$_{0,12}$, the PMCs of the mode LP$_{0,4}$ are focused on a smaller wavelength range for the purpose of showing the variations.
clearly. Additionally, we purposely select the wavelength range covering the experimental LPG (LP\(_{0,12}\))’s TAP wavelength of 1500nm in order to illustrate the variation of TAP. Fig.4-7a illustrates PMC of the mode LP\(_{0,4}\) shifts with \(d\) at \(n_3=1.8\), and Fig.4-7b illustrates PMC of the mode LP\(_{0,12}\) shifts with \(d\) at \(n_3=1.8\). We note that when \(n_3\) is fixed, PMCs of both LP\(_{0,4}\) and LP\(_{0,12}\) shifts upwards as \(d\) increases and the magnitude of the PMC shift is not uniform despite a 20 nm uniform increment of \(d\). The pace of the PMC shift grows faster gradually as \(d\) increases from 0 nm to 100 nm, which means the sensitivity to \(d\) grows higher gradually. Obviously, PMC of LP\(_{0,12}\) shifts much faster than that of LP\(_{0,4}\) which means the sensitivity of LP\(_{0,12}\) to \(d\) is much higher than that of LP\(_{0,4}\). For example, the PMC of LP\(_{0,4}\) shifts upwards, on average, about 0.5 µm with 100 nm increment of \(d\) in terms of the grating period while PMC of LP\(_{0,12}\) shifts upwards about 1.5 µm with the same increment of \(d\).
Fig. 4-8. LPG transmission spectra shifts as functions of $n_3$ and thickness $d$ of nm-thick thin film (a) spectra of mode LP$_{0,4}$ shifts with $d$ ($d=0$, 20, 40, 60, 80, 100 nm) at $n_3=1.8$, (b) spectra of mode LP$_{0,12}$ shifts with $d$ ($d=0$, 20, 40, 60, 80, 100 nm) at $n_3=1.8$, (c) spectra of mode LP$_{0,4}$ shifts with $n_3$ ($n_3=1.5$, 1.6, 1.7, 1.8) at $d=40$ nm and $d=100$ nm, (d) spectra of mode LP$_{0,12}$ shifts with $n_3$ ($n_3=1.5$, 1.6, 1.7, 1.8) at $d=40$ nm and $d=100$ nm.

Fig. 4-8 shows LPG transmission spectra shifts as functions of $d$ and $n_3$ of the nm-thick thin film, respectively. To be comparable, the criterion for choosing periods for LP$_{0,4}$ and LP$_{0,12}$ is to set such that the resonant wavelengths of LP$_{0,4}$ and LP$_{0,12}$ are $\lambda_{0,4}=\lambda_{0,12}=1420$ nm, which is the resonant wavelength of our experimental LPG. To meet this condition, we found out that the periods for LP$_{0,4}$ and LP$_{0,12}$ are 324.82 $\mu$m and 146.28 $\mu$m, respectively. Fig. 4-8a to Fig. 4-8d describe the LPG transmission spectra variations corresponding to the same conditions of Fig.4-7a to Fig.4-7d, respectively, which means the variation conditions of $d$ and $n_3$ of each graph in Fig.4-8 are the same as that of its counterpart in Fig.4-7. In order to be comparable with experimental LPG spectra, Fig.4-8 focuses on different wavelength ranges than that of Fig.4-7, and spectra.
of LP\textsubscript{0,12} are focused on a smaller wavelength range this time in order to show the variations clearly.

According to the simulations as shown in Fig. 4-8, we note that: (i) when \( n_3 \) is fixed, the spectra of LP\textsubscript{0,4} and LP\textsubscript{0,12} shift towards shorter wavelengths as \( d \) increases. The spectral shift gradually increases as \( d \) is increased from 0 nm to 100 nm (e.g. for \( n_3 \)=1.8 as shown in Fig. 4-8b, a resonant-wavelength shift of \( \sim 9 \) nm is obtained for a change in \( d \) from 20 nm to 40 nm, but the corresponding resonant-wavelength-shift is \( \sim 20 \) nm when \( d \) is increased by the same amount from 80 nm to 100 nm). This means that the sensitivity to \( d \) increases with \( d \); (ii) For fixed \( d \), the LP\textsubscript{0,4} and LP\textsubscript{0,12} resonances shift to shorter wavelengths as \( n_3 \) increases, and the rate of change increases with the magnitude of \( n_3 \) (e.g. for \( d = 100 \) nm as shown in Fig. 4-8d, a resonant-wavelength shift of \( \sim 9 \) nm is obtained when \( n_3 \) is increased from 1.5 to 1.6, but a wavelength shift of \( \sim 20 \) nm is obtained when \( n_3 \) is increased from 1.7 to 1.8) which means the sensitivity to \( n_3 \) increases as \( n_3 \) increases; (iii) When \( d \) is fixed, the spectra shift leftwards as \( n_3 \) increases. The magnitude of the spectral shift upon each 0.1 increment of \( n_3 \) is obviously larger at larger \( d \) (e.g. as shown in Fig. 4-8d, a wavelength shift of \( \sim 3 \) nm is obtained at \( d = 40 \) nm when \( n_3 \) is increased from 1.7 to 1.8, but a wavelength shift of \( \sim 20 \) nm is obtained at \( d = 100 \) nm under the same condition), which means the sensitivity to \( n_3 \) increases as \( d \) increases; (iv) For either fixed \( d \) or \( n_3 \), the spectrum of LP\textsubscript{0,12} shifts much more than that of LP\textsubscript{0,4}, which means the sensitivity of LP\textsubscript{0,12} to \( d \) and \( n_3 \) is much higher than that of LP\textsubscript{0,4}. The enhanced sensitivity of higher order cladding modes is due to two factors: the PMC of the higher order mode has a smaller gradient (operates closer to the TAP), which implies that small changes in any parameter lead to large resonant-wavelength shifts. Secondly, a
higher order mode interrogates material further from the core of the fiber, and hence changes in film thicknesses and refractive indices far from the core have a larger effect. Furthermore, although the thickness of the thin-film is at only the nanometer level, the resonant wavelength of the LPG can be shifted by more than 60 nm for LP_{0,12} with 100 nm film thickness as shown in Fig. 4-8b. Additionally, as shown in Fig. 4-7, we note that the PMCs exhibit the same behaviors as that of the corresponding grating’s spectra.

In practice, in applications of LPG-based optical devices it is desirable to control \(d\) and \(n_3\) to high accuracy for precise designs, while in applications of LPG-based optical sensors, the effects of \(d\) and \(n_3\) usually mix with each other which reflects the real ambient variations. Our simulations potentially provide us an opportunity of simultaneously sensing the thickness variation and the refractive index variation of the ambient thin-film through theoretically calculating both effects on the LPG spectra and discriminating their difference. Furthermore, our analysis of simulated results offers us an approach to designing efficient ultra-sensitive index-sensing or thickness-sensing LPG-based fiber sensors and index-modulating or thickness-modulating LPG-based fiber devices.

### 4.6.2. Comparison of experimental and simulation results

We did the simulations based on the experimental data of \(d\) and \(n_3\) obtained by ellipsometry, and the method for simulations follows the theoretical analysis described in the beginning of this chapter. The details of the experimental procedure and results are described in the following Chapter 5. Fig.4-9a shows the comparison between the experimental LPG transmission spectrum and the simulated LPG transmission spectrum.
without the ISAM thin-film coating. They are in good agreement. The experimental LPG is an Turn-Around-Point (TAP) LPG with the mode LP_{0,12}, which has two peaks as described in Chapter 2. Fig.4-9b shows the experimental LPG spectra with different bilayers (that is different thicknesses) of PAH/PCBS ISAM film for PAH solution pH of 9.0 and PCBS solution pH of 8.0. One bilayer represents about 2.6 nm in thickness. Fig.4-9c shows the simulated LPG spectra with different bilayers of PAH/PCBS ISAM film for PAH solution pH of 9.0 and PCBS solution pH of 8.0. The simulated results resemble the experimental results except for the smaller resonant wavelength shifts of LP_{0,12}. 

(a)
Fig. 4-9. Comparison between experimental LPG transmission spectra and simulated LPG transmission spectra (a) LPG without ISAM coating (b) experimental LPG spectra with 0, 5, 10, 15 and 20 bilayers of PAH/PCBS ISAM film for PAH solution pH of 9.0 and PCBS solution pH of 8.0. (c) simulated LPG spectra with 0, 5, 10, 15 and 20 bilayers of PAH/PCBS ISAM film for PAH solution pH of 9.0 and PCBS solution pH of 8.0. Note: 1 bilayers ≈ 2.6 nm in thickness with PAH/PCBS (9.0,8.0).

4.6.3. Surrounding refractive index effect on thin-film coated LPGs

Fig. 4-10. Index profile of nm-thick thin-film coated LPG, $n_1$ is index of fiber core, $n_2$ is index of fiber cladding, $n_3$ is index of nm-thick thin-film, $n_{sur}$ is index of surrounding medium. Ambient consists of $n_3$ and $n_{sur}$, and $n_3 > n_1 > n_2 > n_{sur}$.

In section 4.6.1, we systematically analyzed the effects of the thickness $d$ and the refractive index $n_3$ of the nm-thick thin-film on LPGs at the fixed surrounding refractive index $n_{sur}$ ($n_{sur} = n_{air}$=1) as shown in Fig.4-10. In this section, we will analyze the
surrounding refractive index effect on the nm-thick thin-film coated LPGs. Because we already know that the index sensitivity of LPGs will be increased with increased $d$ and $n_3$ as shown in the section 4.6.1, we will simulate the spectral variations of the LPG at a fixed $d$ and $n_3$ with different $n_{\text{sur}}$ to only study the surrounding index effect. We selected $d=80\text{nm}$ and $n_3=1.8$ to show the typical spectral variations in response to the changes of the surrounding refractive index. For $n_{\text{sur}}$, we ignored its material dispersion for the simplified demonstration and selected four typical values ($n_{\text{sur}}=1.0, 1.1, 1.2, 1.3$). We choose the mode LP$_{0,12}$ to do the simulation. To be comparable, the criterion for choosing periods for LP$_{0,12}$ at different $n_{\text{sur}}$ is to set the resonant wavelengths of LP$_{0,12}$ to be $\lambda_{012}=1420\text{nm}$ when $d=0\text{nm}$ at different $n_{\text{sur}}$.

Fig.4-11 shows LPG transmission spectra shifts as functions of $n_{\text{sur}}$. We note that (i) the spectra of LP$_{0,12}$ shift towards shorter wavelengths as $n_{\text{sur}}$ increases from 1.0 to 1.3. This means that the LPG sensitivity to the thin-film coating increases with $n_{\text{sur}}$; (ii) the rate of the spectral shift increases with the magnitude of $n_{\text{sur}}$. Hence, this means that if we increase the surrounding refractive index of the surrounding medium, we could increase the LPG index sensitivity, which is important for LPG-based optical sensors.
4.6.4. Simulated results of thin-film-coated TAP LPGs

Due to the unique optical properties and the high sensitivity of TAP LPGs, the thin-film-coated TAP LPGs are very promising for use as ultra-sensitive optical sensors. In order to theoretically investigate the index sensitivity of TAP LPGs, we simulated the transmission spectra variations of thin-film-coated TAP LPGs in response to changes of the thickness $d$ and the refractive index $n_3$ of the film. Because we’ve done the systematic analyses of the index sensitivity of conventional LPGs in section 4.6.1 and the trend of spectra variations of TAP LPGs is the same as that of conventional LPGs (i.e. the sensitivity to $d$ increases with $d$, and the sensitivity to $n_3$ increases with $n_3$), we only show here that the index sensitivity of LPGs would be dramatically improved by utilizing TAP LPGs instead of conventional LPGs by comparing to the results in the section 4.6.1.

Fig. 4-11. LPG transmission spectra with the mode LP$_{0,12}$ shifts as functions of $n_{\text{sur}}$ and $n_3=1.8$. 

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Fig. 4-12. Simulated thin-film coated TAP LPG transmission spectra with mode LP$_{0,12}$ at $n_3 = 1.8$ (a) $d = 95, 98, 100$ or $120$ nm; (b) optical intensity-based sensor scheme at $d = 98$, or $100$ nm; (c) dual peak-based sensor scheme at $d = 100$ or $120$ nm.

All the parameters of the fiber and the LPG used in the simulations are the same as those used in the section 4.6.1 except that the period of the grating is selected to be 148.61 µm which sets the TAP of the grating at $d = 100$ nm. Fig. 4-12 shows the simulated thin-film-coated TAP LPG transmission spectra with the mode LP$_{0,12}$ with $n_3 = 1.8$. We notice that if the operating point of the grating is set to be closer to the TAP, the sensitivity of the grating will be much higher. For instance, about 22 dB optical intensity variation is obtained and the sensitivity is about 11 dB/nm when $d$ is increased.
from 98 nm to 100 nm by 2 nm, while only about 8 dB optical intensity variation is obtained and the sensitivity is about 2.7 dB/nm when \( d \) is increased from 95 nm to 98 nm by 3 nm. The reason for this difference is because the operating point of the grating at \( d=98 \) nm is closer to the TAP than that at \( d=98 \) nm. Similarly, about 120 nm resonant wavelength shift of the left peak is obtained when \( d \) is increased from 100 nm to 120 nm by 20 nm, which is about six times larger than that of the conventional grating in Fig.4-8b under the same condition. Additionally, we notice that Fig.4-12b demonstrates an optical intensity-based optical sensor scheme and Fig.4-12c demonstrates a dual peak-based optical sensor scheme, which are described in Chapter 2. Both of these measurement schemes have the potential to dramatically improve the sensitivity of LPGs, which is very important for implementation of LPGs as optical sensors.
Chapter 5. Experimental Studies of ISAM-coated LPG

5.1. Ultrasensitive SMF-based TAP-LPG

5.1.1. Introduction to LPG index sensitivity

Long-period fiber gratings (LPG) couple light between copropagating modes of an optical fiber, and have been used as spectral shapers, mode converters and ambient index sensors. Ambient index sensing with LPGs has attracted a lot of attention, since the LPG is a resonant device that couples between the fundamental and cladding-guided modes of a fiber, where the cladding mode’s propagation constant is modulated by the ambient conditions.

Hence, several studies have concentrated in improving the ambient index sensitivity of LPGs, where the sensitivity is defined in this section as the index change required for a 20-dB or larger change in transmitted intensity in the spectral range of interest. Patrick et al. have shown that the sensitivity monotonically increases as the ambient index value approaches that of the glass cladding. Yin et al. have demonstrated that index sensitivities of 0.001 are achievable in fibers whose cladding is etched down to 30 μm in outer diameter. Shu et al. have studied the sensitivity of LPGs,

for a variety of cladding modes, and have identified specific cladding modes that have index sensitivities of 0.01. A major drawback of narrowband LPGs as index sensors is that the modulation of the resonant condition causes a spectral shift in a resonance.

It is possible to realize LPGs where a shift in the resonant condition leads to true-amplitude modulation — Poole et al.\textsuperscript{69} demonstrated that a few-mode fiber can be designed to possess two modes with identical group velocities, and that LPG coupling in that condition leads to broadband mode-conversion. This condition is called the turn-around-point (TAP) condition, where LPG coupling occurs between the fundamental mode and a specific higher order cladding mode. Shu et al.\textsuperscript{27} have demonstrated true-amplitude modulation with index sensitivities of 0.01, by inducing coupling at the TAP. The unique spectral characteristics of TAP gratings are a strong function of the dispersive conditions for the two modes that are being coupled, and recently we demonstrated that the bandwidth, sensitivity, and spectral shape of such a resonance can be accurately tailored by dispersion engineering two core guided modes by standard fiber design and manufacturing tools.\textsuperscript{24} Cladding modes are primarily guided by the glass cladding of a fiber, and such precise dispersion tailoring of these modes is obviously harder than in the case of core-guided modes. Likewise, sensitive TAP resonances demonstrated to date have been significantly less susceptible to waveguide design and engineering — they occur at predetermined wavelengths, and the mode order defines the sensitivity achievable. The possibility of dispersion engineering in the cladding has recently been

theoretically postulated by Jeong and Oh\textsuperscript{70}, and may enable complex dispersion engineering to tailor the bandwidth and coupling wavelengths of TAP resonances.

5.1.2. Theoretical study of TAP LPG index sensitivity

For convenience, the resonant condition for LPG coupling is often described through,

\[ \delta = \frac{1}{2} \left( \beta_{01} - \beta_{0m} - \frac{2\pi}{\Lambda} \right), \tag{5-1} \]

where \( \delta \) is the detuning parameter, \( \Lambda \) is the grating period, and \( \beta_{01} \) and \( \beta_{0m} \) are the propagation constants of the fundamental mode and the \( m \)th-order cladding mode, respectively. The condition \( \delta = 0 \) is called the phase matching condition, and represents the wavelength at which strong resonant coupling results. This condition may be plotted as a function of wavelength to yield a phase-matching-curve (PMC). While strong coupling occurs at resonance (when \( \delta = 0 \)), the coupling magnitude decreases monotonically as \( \delta \) departs from zero.

The PMC for the fiber used in our device is shown in Fig. 5-1a. A unique feature is the existence of a turn-around-point (TAP). A grating with a period that induces coupling at the TAP will yield broadband spectra as shown in Fig. 5-1b. Also shown in Fig. 5-1 are the PMCs and grating spectra for the same fiber with different ambient indices. A decrease in the ambient index shifts the PMC such that the dashed horizontal line representing the grating period does not intersect the curve at any wavelength. The grating strength or amplitude decreases in proportion to the separation between the dashed line and the PMC, since the detuning $\delta$ becomes progressively larger. Ultimately,
the PMC shifts far enough such that no resonance occurs. This yields an ambient index sensor whose *strength* rather than resonant *wavelength* changes over a broad bandwidth.

Since the core mode is highly isolated from the ambient by the glass cladding of the fiber, $\beta_{01}$ is insensitive to the surrounding material’s index and slight changes of the cladding radius, while $\beta_{0m}$ (of the cladding mode) is sensitive to small fluctuations in either parameter.

The sensitivity can be further increased by engineering the fiber waveguide to possess a TAP feature for any ambient index value. This is achieved by etching the outer glass slightly, to engineer a waveguide whose cladding mode always has a group velocity similar to that of the core mode. The relationship of the sensitivity of the LPG to changes in ambient index can be analysed using waveguide theory. The sensitivity of the propagation constant $\beta_{0m}$ to $n_{\text{sur}}$ can be calculated from the asymptotic expression

$$\frac{d \beta_{0m}}{dn_{\text{sur}}} = \frac{u_m^2 \lambda_{\text{res}}^2}{n_{cl} 4 \pi^2 r_{cl}^3} \left( n_{cl}^2 - n_{\text{sur}}^2 \right)^{3/2},$$

where $\lambda_{\text{res}}$ is the resonant wavelength, $u_m$ is the $m^{\text{th}}$ root of the Bessel’s function of the first kind, $J_0$ ($m$ is the mode order), $r_{cl}$ is the cladding radius, and $n_{cl}$ and $n_{\text{sur}}$ are the refractive indices of the cladding and ambient, respectively. Equation 5-2 indicates that the index change required for modulation of TAP-LPGs decreases monotonically, with increasing ambient index, $n_{\text{sur}}$, up to the limit at which $n_{\text{sur}} = n_{cl}$.

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Fig. 5-2. Spectra of TAP-LPG with different ambient indices. (a) ambient index = 1.4325 => sensitivity ~ 0.0050, (b) ambient index = 1.4440 => sensitivity ~ 0.0015, (c) ambient index = 1.4486 => sensitivity ~ 0.0004. Sensitivity increases as ambient index approaches cladding index.
5.1.3. Experimental study of TAP LPG index sensitivity

The fiber used for our experimental investigations is TrueWave RSTM, which is an SMF with \( r_{cl} = 62.5 \, \mu m \) and \( n_{cl} = 1.4573 \). The TAP-LPG was fabricated by exposing the fiber to 248 nm UV radiation from an excimer laser through a chrome-plated amplitude mask. The TAP LPG is 5 cm long with a period \( \Lambda \) of 114 \( \mu m \) and a resonant wavelength \( \lambda_{res} \) of 1350 nm. Coupling is induced between the core mode and the \( \text{LP}_{0,14} \) cladding mode.

The TAP LPG is immersed in oils with different refractive indices to study its response to various ambient index conditions. As mentioned earlier, index changes serve to change the strength of the LPG. The index difference that changes the LPG strength from 0 to 25 dB, is recorded for a variety of base index values of the oils. From Eq. (5-2), we note that the index sensitivity increases as the base index value approaches that of the cladding silica. Etching the fiber slightly ensures that the TAP feature of the PMC can be maintained for a variety of ambient indices. We etched the fiber from 62.5 \( \mu m \) to 60 \( \mu m \) to maintain the TAP feature for oils ranging in ambient index values between 1.42 and 1.45. Figure 5-2 shows the spectra for 3 fibers that were etched to yield TAP-LPGs at the corresponding ambient index values. An index change of \(~5 \times 10^{-3}\) is required (for 25-dB modulation) when the ambient index is \(~1.4325\), but an index change of only \(~4 \times 10^{-4}\) is required when the ambient index is 1.4486.

Figure 5-3 shows both the theoretical simulation based on Eq. (5-2) and the experimental results of index sensitivities for 25-dB modulation, at various ambient index values. The experimental results agree well with the theoretical simulation. The main
reason for the difference between them results from the temperature-sensitive nature of the oil index. In the experiments, the highest sensitivity measured was $2.7 \times 10^{-4}$ for 25-dB modulation over a 48-nm spectral band, obtained with an ambient index of 1.449. Note that further engineering the cladding could have resulted in even higher index sensitivities, as is apparent from the theoretical curve.

Fig.5-3. Index sensitivity vs. ambient index. Decreases monotonically. Record sensitivity $\sim 2.7 \times 10^{-4}$ observed. Theory matches well with experiment.

In summary, in this section, we describe the demonstration of dispersion engineering in cladding modes to obtain TAP gratings with arbitrary bandwidth and ambient index sensitivity, which can be induced in any desired spectral range. This is achieved by increasing the surrounding material’s index while maintaining the distinct TAP feature that yields the sensitive broadband attenuation. We demonstrate that this dispersive condition can be engineered in SMFs coupling the fundamental mode to a
cladding mode, regardless of the ambient condition of the LPG. This is used to
demonstrate an LPG that exhibits 25-dB attenuation changes in response to an ambient
index change of only $2.7 \times 10^{-4}$. This novel LPG-device overcomes the weakness of
conventional LPGs – the ambient index change results in modulation of the amplitude of
the grating rather than a shift in its resonant wavelength, thus affording true amplitude
modulation. At the same time, it offers an extinction ratio of more than 25 dB over a 48-
nm spectral band, which can cover the entire C or L-band. These two distinct properties,
made possible by dispersion engineering of cladding modes, enable an LPG-device
whose amplitude can be changed by large amounts for arbitrarily small ambient index
changes. The fiber used for this device is similar to standard SMF, and hence it maintains
its compatibility with fiber-optic transmission lines. Since the required index change is
small enough to be similar to those afforded by electro-optic materials, this enables the
prospect of electro-optic modulation using in-fiber TAP-LPG devices, as well as ultra-
sensitive sensors.

5.2. LPGs in solutions

From the perspective of practical optical sensor device construction, we should
measure the LPG while immersed in a constant temperature, buffered aqueous solution.
Thus, it is important to study the optical response of LPGs in the aqueous environment.

The LPGs were UV-induced on TrueWave™ RS single-mode fibers with a
grating period of 116 µm and a length of 5 cm. This yielded gratings that couple the
fundamental mode to the $LP_{0,12}$ cladding mode at a resonant wavelength of 1420 nm. The
LPG transmission spectra were measured by an Ando optical spectrum analyzer after the
LPG was immersed in a solution. The Fig.5-4 shows the resulting transmission spectra when the LPG was immersed in deionized water (n=1.33) and Acetone (n=1.36) versus in air. We notice that (i) the resonant wavelength of the LPG shifts to shorter wavelengths versus that in air after immersing in the aqueous environment; (ii) aqueous environments with different refractive indices cause the resonant wavelength of the grating to shift to shorter wavelengths by different magnitudes, and the resonant wavelength shift is larger in a liquid environment with a larger refractive index than a liquid environment with a smaller refractive index as the deionized water and Acetone illustrate; (iii) the strength (amplitude) of the grating is still strong without little diminishment after immersion in the deionized water and Acetone, which provides the possibility for us to detect the LPG spectrum variation when the LPG serves as a sensor.

Fig.5-4. LPG transmission spectra when LPG was immersed in deionized water and Acetone versus in air, respectively.
5.3. PAH/PCBS-based ISAM-coated LPG

LPGs that couple the fundamental mode of a single-mode fiber (SMF) to one of its cladding modes are ultra-sensitive to the refractive index of the material surrounding the fiber. Normally, the index sensitivity is attributed to the index of the bulk medium surrounding the fiber, and features with sub-wavelength sizes are not expected to modulate the resonance of LPGs. However, Rees and coworkers\textsuperscript{15} have recently reported resonant shifts in LPGs with films of sub-wavelength thickness, using Langmuir-Blodgett (LB) films. The observed optical response was relatively small with maximal shifts of 10 nm in wavelength with 400 nm of deposited film. Moreover, LB films are not amenable to practical device construction. This is because the LB technique has demanding requirements of expensive special equipment to precisely control the pressure on the liquid surface and is relatively slow. More significantly, films deposited by the LB technique show poor mechanical and thermal stability because the weak van Der Waals interaction is the primary binding mechanism.

ISAMs, on the other hand, are formed by a layer-by-layer deposition technique and exhibit enhanced reliability, stability, and film quality in comparison to LB films.\textsuperscript{13,14} The ISAM fabrication method provides a highly controllable means to build precise, nm-thick films on the surfaces of fibers (indeed, they can be incorporated on any surface with a minimum charge density, such as metals, glass, or silica). Moreover, they can be tailored to incorporate a diverse array of particles, such as clay platelets, proteins, virus particles etc. Thus, compared with the LB technique, ISAM technique shows more flexibility on choices of substrate or template and thin-film overlay materials for devices. Hence, ISAMs on LPGs provide several advantages: (a) ability to fine tune grating
resonances in a simple manner, (b) construction of efficient index sensors or index-modulating fiber devices, and (c) application to biosensing.

5.3.1. Experimental procedures

In our study, we first investigated the feasibility of depositing ISAM films on the LPG because to our knowledge no one had reported an LPG coated by an ISAM thin-film. The ISAM procedure was described in detail in Chapter 3. In our experiments, an LPG was used as the substrate. Poly (allylamine hydrochloride) (PAH) at 10 mM concentration was used as the polycation, and poly[1-[4-(3-carboxy-4-hydroxy-phenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt (PCBS) at 10 mM concentration was used as the polyanion. The LPG was cleaned by Acetone.

The setup for the grating characterization is shown in Fig. 5-5. In the grating characterization experiments, the Ando AQ6317 Optical Spectrum Analyzer (OSA) was used. The white-light source we used is the LS-1 Tungsten Halogen Light Source of Ocean Optics Inc., which is a versatile white-light source optimized for the VIS-NIR (360-2500 nm). The fiber optic cleaver we used is Fujikura CT-07. The buffered fiber adapters we used are FC buffered fiber adapters of Fiber Instrument Sales Inc.

Fig. 5-5. The setup for the grating characterization
5.3.2. Removable feature of ISAMs

In LPG fabrications, it is often necessary to tune the resonant wavelength of the LPG to high accuracy for many applications due to rigorous wavelength requirements. It has been demonstrated that the resonant wavelength could be shifted by etching the fiber cladding of LPG with hydrofluoric acid through postfabrication. However, this technique for tuning the resonance is not only irreversible but also lacks the precise controllability of etching to an exactly desired thickness. In addition, for fiber grating sensor applications, it is attractive to be able to completely remove the probe-element coating from the surface of the grating without physically modifying the properties of the grating, which makes the same grating reusable multiple times. The ISAM technique offers the possibility to address these two concerns, which will enhance the flexibility and the cost-efficiency of fiber grating-based sensors or devices. In order to demonstrate the removable feature of an ISAM film deposited on a fiber grating, we compared the LPG spectrum taken before depositing the ISAM on it with the spectrum taken after immersing an ISAM-coated LPG in a prepared acid mixture. PAH at pH=7.5 was used as the polycation, and PCBS at pH=8 was used as the polyanion. The acid mixture consists of 95% sulfuric acid and 5% nitric acid. This is sufficient to remove the organic ISAM film without affecting the silica fiber. In the ISAM removal experiment, first the acid mixture was put into a beaker, and it was heated up to about 80 °C. Then the ISAM-coated LPG was immersed into the hot acid mixture with only the ISAM-coated section for approximately 20 minutes. Fig.5-6 shows the comparison of the LPG spectra of two LPGs we tested — one with the coupled cladding mode $LP_{0,12}$ and the other with $LP_{0,14}$. It demonstrates that the LPG spectrum was completely restored with a negligible
variation by immersing the ISAM-coated LPG in the acid mixture, which means the ISAM film was completely removed from the surface of the LPG. In our experiments, we utilized this method to reuse the same LPG to do ISAM-coating related experiments for dozens of times. On one hand, it guarantees the repeatability and the comparability of the experimental results, while on the other hand it enhances the flexibility, the cost-efficiency, and the time-efficiency of the experiments.

![ISAM removal tests](image)

Fig.5-6. Comparison of the LPG spectrum taken before depositing ISAM on it with the spectrum taken after immersing an ISAM-coated LPG in the acid mixture (95% sulfuric acid and 5% nitric acid). Two LPGs — LP$_{0,12}$ (top) and LP$_{0,14}$ (bottom) were tested.

5.3.3. Annealing effect of ISAMs

For either fiber optic sensor applications or other fiber optic device applications, it is attractive for the LPG-based fiber optic devices to possess good thermal stability because the operating environment may continuously fluctuate in temperature. We have
studied the thermal stability of the ISAM-coated LPG. We compared the ISAM-coated LPG spectrum taken before annealing it with the spectrum taken after annealing it in an oven at 140 °C for fourteen hours. We deposited 10-bilayer, 20-bilayer, and 25-bilayer PAH/PCBS-based ISAM films on the same grating and investigated the annealing effect on each of them, respectively. PAH at pH=7.5 was used as the polycation, and PCBS at pH=8 was used as the polyanion. According to the results shown in Fig.5-7, we noted that the grating spectra before and after annealing in all three cases are almost identical, which proves ISAM-coated LPGs have an excellent thermal stability. This illustrates that after depositing the ISAM film on the grating, there is no need to anneal the grating to stabilize it as the usual grating fabrication procedure does. Therefore, it saves time and cost for grating fabrications. Furthermore, it proves ISAM-coated LPGs are thermally reliable.

![Graph showing comparison of ISAM-coated LPG spectrum before and after annealing](https://example.com/fig5-7.png)

Fig.5-7. Comparison of the ISAM-coated LPG spectrum taken before annealing with the spectrum taken after annealing in an oven at 140 °C for fourteen hours. One bilayer of PAH/PCBS ISAM is ~1.5 nm in thickness.
5.4. LPG spectra versus layer-by-layer PAH/PCBS

As mentioned before, from the perspective of practical device construction, we should measure the LPG while immersed in a constant temperature, buffered aqueous solution. For example, when evaluating the sensitivity of the LPG sensor, the LPG will be exposed to the target solution for a given time, rinsed to remove non-specifically adsorbed material, and immersed in the buffered reference solution for measurements. Thus, it is important to study the sensitivity of LPGs in the aqueous environment. For this purpose, we first studied the sensitivity of an ISAM-coated LPG in the aqueous environment before investigating the deposition of ISAM films incorporated with biological elements onto the LPG. The LPG we used was UV-induced on TrueWave RS™ fibers with a grating period of 116 µm and a length of 5 cm. This yielded gratings that couple the fundamental mode to the LP\textsubscript{0,12} cladding mode. In this experiment, PAH and PCBS serve as the probe element and the target element, respectively.

First, we deposited the probe element (PAH) onto the surface of LPG, and then we immersed the probe-coated LPG into the target (PCBS) solution to measure the LPG spectrum variation. The LPG was alternately immersed in the PAH solution at pH=7.5 and the PCBS solution at pH=8.0 to deposit a total of four PAH/PCBS bilayers. The LPG spectrum was measured during each immersion in the PCBS solution. Meanwhile, in comparison, we also measured the LPG spectrum while the LPG was exposed to the air after each immersion in the PCBS solution. Fig.5-8a depicts the resonant wavelength shift $\Delta \lambda_{\text{res}}$ of the LPG (measured in the PCBS solution) as a function of the number of PAH monolayers, and the inset describes the corresponding LPG spectrum variation after
immersing the probe-coated LPG into the PCBS (target) solution. It shows that the adsorption of each successive PAH/PCBS bilayer was readily observed in the PCBS aqueous solution as a systematic $\Delta \lambda_{res}$ of more than 1 nm, which confirmed good sensitivity to adsorbed monolayers in an aqueous solution. Fig.5-8b depicts the corresponding $\Delta \lambda_{res}$ of the LPG (measured in air) as a function of the number of PAH monolayers, and the inset describes the corresponding LPG spectrum variation. We noticed that the sensitivity of the LPG in the PCBS solution (total $\Delta \lambda_{res}$ of 5.6 nm) was at the same level as that in the air (total $\Delta \lambda_{res}$ of 5.8 nm), which means the sensitivity of LPG was not degraded in the PCBS solution. Finally, Fig.5-8c depicts $\Delta \lambda_{res}$ of the LPG (measured in air) as a function of the dipping sequence number of the ISAM procedure, which means we measured the LPG spectrum in air immediately after each deposition in either the PAH solution or the PCBS solution.
Fig. 5-8. (a) The resonant wavelength shift $\Delta \lambda_{\text{res}}$ of the LPG (measured in the PCBS solution) as a function of the number of PAH monolayer. (b) $\Delta \lambda_{\text{res}}$ of the LPG (measured in air) as a function of the number of PAH monolayer. (c) $\Delta \lambda_{\text{res}}$ of the LPG (measured in air) as a function of the dipping sequence number of the ISAM procedure. One bilayer of PAH/PCBS ISAM is $\sim 1.5$ nm in thickness.
5.5. pH dependent PAH/PCBS-based ISAMs properties

5.5.1. Ellipsometry results

In our study, we first investigated the dependence of the properties of ISAM films on the variation of the pH of the polyanion and polycation solutions by using variable angle spectral ellipsometry. Standard microscope glass slides were used as substrates. Poly (allylamine hydrochloride) (PAH) at 10 mM concentration was used as the polycation, and poly[1-[4-(3-carboxy-4-hydroxy-phenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt (PCBS) at 10 mM concentration was used as the polyanion. The slides were prepared by the RCA cleaning process. Several samples were fabricated with PAH and PCBS solutions of different pH levels. The pH of the PAH solutions ranged from 6 to 9 and that of the PCBS solutions ranged from 6 to 8, respectively. All samples were prepared by depositing 20 bilayers of PAH/PCBS on the slides.

Fig. 5-9 shows the values of total thickness $d_{tot}$ and refractive index $n$ as a function of pH of the polyanion/cation solutions measured by ellipsometry. When the pH of the PCBS solution is fixed, $d_{tot}$ increases while $n$ decreases as the pH of the PAH solution increases. In contrast, when the pH of the PAH solution is fixed, both $d_{tot}$ and $n$ decrease as the pH of the PCBS solution increases. The reason for this is that both PAH and PCBS are weak electrolytes such that variations of pH will change the charge density of the adsorbing polymer. This behavior is understood as follows – both solutions are fully charged at neutral pH. As the pH is lowered from neutral, the charge density of PCBS decreases since its acid groups become protonated. While, as the pH of the PAH

solution is increased, its amine groups become deprotonated, and the charge density of PAH will decrease. As charge density decreases, less repulsion between neighboring charges allows more polymer chains to be adsorbed on the substrate with loops and tails to induce thicker layers. Furthermore, since PCBS has a higher refractive index than PAH, a higher percentage of PCBS results in a higher composite index of the ISAM film while a higher percentage of PAH results in lower composite index. Therefore, the thickness and refractive index of ISAM films can be precisely controlled by adjusting the pH values of the polyelectrolyte solutions.
(b) Refractive index of PCBS with pH=6, 7, 8.

(c) Thickness of PAH with pH=6, 7.5, 9.
Fig. 5-9. Thickness and refractive index of 20 bilayer PAH/PCBS ISAM films on glass slides measured by ellipsometry. (a) Thickness vs. pH value of PAH. (b) Refractive index vs. pH value of PAH. (c) Thickness vs. pH value of PCBS. (d) Refractive index vs. pH value of PCBS.

5.5.2. Scanning electron microscopy results

Similarly, we did the same investigation of the dependence of the properties of ISAM films on the variation of the pH of the polyanion and polycation solutions by using Scanning Electron Microscopy (SEM). At this time, standard single-mode fibers were used as substrates. Same as in the ellipsometry experiment, PAH at 10 mM concentration was used as polycation, and PCBS at 10 mM concentration was used as polyanion. Several samples were fabricated with PAH and PCBS solutions of different pH levels. The selections of pH of the PAH and the PCBS solutions were the same as those in ellipsometry experiment. All samples were prepared by depositing 15 bilayers of PAH/PCBS on the fibers. Finally, the fibers were well-cleaved by using a standard
commercial fiber cleaver. Fig.5-10a shows a photo of the cross-section of an optical fiber taken by SEM. Fig. 5-10b is a typical scanning-electron micrograph of the surface of a fiber coated with an ISAM film, showing characteristic thicknesses achieved by the ISAM technique.
Fig. 5-10. SEM image of (a) cross-section of an optical fiber (b) ISAM film on an optical fiber.

Fig. 5-11 shows exemplary SEM images of ISAM films on an optical fiber where the ISAM films were synthesized with different pH combinations of PAH and PCBS. Fig. 5-12 shows the values of total thickness $d_{\text{tot}}$ as a function of pH of the polyanion/cation solutions. We notice that the SEM results are qualitatively in good agreement with the ellipsometry results: when the pH of the PCBS solution is fixed, $d_{\text{tot}}$ increases as the pH of the PAH solution increases; in contrast, when the pH of the PAH solution is fixed, both $d_{\text{tot}}$ as the pH of the PCBS solution increases. However, there is an apparent discrepancy between the absolute thickness values measured by SEM and ellipsometry respectively. The thickness values measured by SEM are much larger than the corresponding thickness values measured by ellipsometry. We think the reason for this discrepancy is mainly because the SEM is operating in the vacuum environment with an ultra-low pressure, which inflates the polymer as water is removed and then increases...
the thickness of the ISAM film. Therefore, the results measured by ellipsometry should be more close to the actual thickness values of ISAM films than those measured by SEM.
Fig. 5-11. SEM images of ISAM film on an optical fiber and ISAM films were synthesized with different pH combinations of PAH and PCBS. (a) PAH at pH=7.5 and PCBS at pH=6; (b) PAH at pH=7.5 and PCBS at pH=8; (c) PAH at pH=9 and PCBS at pH=6; (d) PAH at pH=9 and PCBS at pH=8.
Fig. 5-12. Thickness and refractive index of 15 bilayer PAH/PCBS ISAM films on optical fibers measured by SEM. (a) Thickness vs. pH value of PAH. (b) Thickness vs. pH value of PCBS.

5.5.3. ISAM-coated LPG results

Note that the thickness of the films described in the previous section are of the
order of several nm, and their “bulk” refractive indices are significantly higher than that of silica. Normally, this regime would not be very interesting for LPG tuning applications, since LPGs are most responsive to ambient index changes for bulk refractive index values slightly lower than silica. To test the influence of ISAM films on LPGs, different pH values for the PAH and PCBS solutions were utilized in fabricating films. As noted earlier, this film deposition process is agnostic to substrate topology or geometry, and thus obtaining cylindrically symmetric ISAM films on fibers requires no additional set up. The pH of the PAH solutions for this experiment varied from 7.5 to 9, while the pH of PCBS solutions ranged between 6 and 8. The LPGs were UV-induced on TrueWave™ RS fibers with a grating period of 116 µm and a length of 5 cm. This yielded gratings that couple the fundamental mode to the LP_{0,12} cladding mode at a resonant wavelength of 1420 nm. The transmission spectra were measured by an optical spectrum analyzer after deposition of every five PAH/PCBS bilayers.

The experimental results of the ISAM-coated LPG are shown in Fig. 5-13. Fig.5-13a shows an example of the shift in the LPG resonance as the number of bilayers of the ISAM film (and hence its thickness) is increased. Note that the shift in the resonance is reminiscent of shifts attributed to increasingly higher ambient index values for an LPG in silica fiber, with the ambient index value remaining lower than that of silica. This is further illustrated in Fig.5-13b, which shows the change in resonant wavelength as a function of the film thickness for a variety of pH combinations of PAH and PCBS solutions. A record steep resonant wavelength shift of 1.6 nm/nm is obtained for the case where the pH of PAH is 7.5 and that of PCBS is 6. Note that this is the pH combination that yields the highest ISAM film refractive index.
According to LPG resonant condition equation,

\[ \lambda_{\text{res}} = (n_{\text{core}} - n_{\text{clad}}) \Lambda, \]  

where \( \lambda_{\text{res}} \) is the resonant wavelength, \( n_{\text{core}} \) is the effective index of the fundamental core mode, \( n_{\text{clad}} \) is the effective index of the coupled cladding mode, and \( \Lambda \) is the grating period. Therefore, \( \lambda_{\text{res}} \) of the LPG is normally determined only by the index of the ambient film coating (all other parameters being obviously constant). The data of Fig. 5-13a shows, on the other hand, that \( \lambda_{\text{res}} \) shifts due to changes in index as well as thickness of the ISAM films. Another apparently non-intuitive result arises from the fact that the refractive indices of all the ISAM films studied here were higher than that of silica. A bulk medium of these refractive index values surrounding an LPG will cause diminished coupling which cannot be spectrally tuned. This is because the higher ambient index medium frustrates the total internal reflection (TIR) at the glass-cladding surface, a condition necessary for the existence of well-guided cladding modes. In such cases, a substantially weak resonance is obtained. Moreover, changes in the index of the ambient would not cause spectral shifts. This is because a leaky mode is not guided due to TIR, but exists because of (weak) Fresnel reflections at the glass-ISAM boundary, and such reflections have no spectral phase dependence. However, the changes in ISAM deposition conditions (leading to changes in their indices) clearly produce spectral shifts of strong resonances. This may be resolved by considering the mechanism of coupling in ISAM-coated LPGs.

The evanescent tail of the cladding-mode field normally extends by 100-200 nm into the ambient medium. Since all the ISAM films we investigated are thinner than this
value, the cladding mode interrogates both the ISAM as well as the surrounding air. The effective index $n_{\text{eff}}$ of a guided mode can be approximated by\textsuperscript{74}:

$$n_{\text{eff}}^2 \sim \iint n^2(r) \cdot |E(r)|^2 \cdot dA$$

(5-4)

where $E(r)$ is the mode field distribution, $n(r)$ is the refractive index profile of the fiber, and $\iint dA$ signifies an integration across the cross-sectional area of the fiber. Equation 5-4 shows that the effective index of a mode is approximately proportional to the average refractive index of the region in which light exists, weighted by the local intensity profile.

Since a typical cladding mode samples both the high index ISAM as well as the surrounding (low index) air, the net index of an ambient comprising 10-50-nm thick ISAM films is that of an equivalent bulk medium with index lower than silica. Moreover, this net index value will depend on the film-thickness in addition to the index of the film, with thicker films leading to a larger ISAM contribution to the net index, as is evident from Eq. (5-4).

Fig. 5-13. Experimental results of ISAM film coatings on an LPG. (a) LPG transmission spectra with 0, 5, 10, 15 and 20 bilayers of PAH/PCBS ISAM film for PAH solution pH of 9 and PCBS solution pH of 8. (b) $\Delta \lambda_{\text{res}}$ of LPG as functions of thickness of ISAM film with different pH combinations of PAH and PCBS [(7.5,6), (7.5,8), (9,6), (9,8)] which offer corresponding refractive index $n$ [1.7107, 1.6912, 1.6887, 1.6715], respectively.
As mentioned before, Fig.5-13b shows the experimental results of the resonant wavelength shifts $\Delta\lambda_{\text{res}}$ of the ISAM thin-film coated LPG, which depicts $\Delta\lambda_{\text{res}}$ of LPGs versus the thickness $d$ of ISAM film with different pH combinations of PAH and PCBS [(7.5,6), (7.5,8), (9,6), (9,8)] which offer corresponding refractive index $n_3$ [1.7107, 1.6912, 1.6887, 1.6715], respectively. In Fig. 5-13b, each $\Delta\lambda_{\text{res}}$-versus-$d$ curve is for a fixed $n_3$ obtained from a fixed pH-combination of PAH and PCBS. We note that experimental results exhibit: (i) for fixed $n_3$, $\Delta\lambda_{\text{res}}$ gradually increases with increased $d$ (e.g. for $n_3=1.7107$ [curve (7.5,6)]) - a wavelength shift of $\sim 12$ nm is obtained when $d$ is increased from the first data point to the second data point by $\sim 8$ nm, but a wavelength shift of $\sim 18$ nm is obtained when $d$ is increased from the second data point to the third data point by the same increment. Other curves show the same behavior.; (ii) for fixed $d$, $\Delta\lambda_{\text{res}}$ increases as $n_3$ increases {e.g. for $d = 25$ nm, a wavelength shift of $\sim 7$ nm is obtained when $n_3$ is increased from 1.67 [curve(9,8)] to 1.69 [curve(7.5,8)] by $\sim 0.2$, but a wavelength shift of a wavelength shift of $\sim 20$ nm is obtained when $n_3$ is increased from 1.69 [curve (7.5,8)] to 1.71 [curve (7.5,6)] by $\sim 0.2$}; (iii) for fixed $d$, the magnitude of $\Delta\lambda_{\text{res}}$ upon fixed increment of $n_3$ is obviously larger at larger $d$ {e.g. a wavelength shift of $\sim 8$ nm is obtained at $d = 10$ nm when $n_3$ is increased from 1.67 [curve(9,8)] to 1.71 [curve (7.5,6)] by $\sim 0.4$, but a wavelength shift of $\sim 20$ nm is obtained at $d = 20$ nm under the same condition}. The result of (i) means the sensitivity to the thickness becomes gradually higher with increased thickness, and the results of (ii) and (iii) mean the sensitivity of the cladding mode to the thickness/index of the ambient thin-film increases as the index/thickness of the ambient thin-film increases, respectively. These results qualitatively agree with the preceding theoretical analysis in Chapter 4.
In practical LPG-based sensor applications, the thin-film will most often serve as the sensing element by incorporating sensing chemical/biological molecules into it. An LPG serves as an optical transducer for signaling the occurrence of a chemical/biological interaction event of interest. Here we could obtain a guideline for building efficient LPG-based sensors for practical use as follows: first we need to consider the precondition of this type of thin-film coated LPG-based sensors. Reference [15] shows that the coupled guided cladding mode would cut off and turn into a leaky cladding mode when the LPG is coated with a thin-film whose refractive index is higher than that of the cladding glass and thickness is larger than a cutoff thickness $d_{\text{cut}}$. In such case, a substantially weak resonance is obtained [67]. This is because a leaky mode is not guided due to total internal reflection, but exists because of (weak) Fresnel reflections at the glass-thin-film boundary. Therefore, in this case, the thin-film coated LPG is not suited for sensing applications. Hence, the precondition of this type of thin-film coated LPG-based sensor is to guarantee the existence of the coupled guided cladding mode, and we can achieve it by coating the LPG with a thin-film of a thickness smaller than $d_{\text{cut}}$. Then, in order to enhance the sensitivity of the LPG, the thickness of the thin-film should approach $d_{\text{cut}}$ as close as possible. In addition, the materials for synthesizing the thin-film should have a high refractive index - i.e. both the ISAM film as well as the sensing molecules should have index greater than silica. Furthermore, this guideline for building efficient sensors is also helpful for building efficient LPG-based modulating devices.
5.6. ISAM-coated LPGs for use as biosensors

5.6.1. Background of Biotin-(Strept)avidin Systems for biosensors

- **Biotin**

  Biotin is one of B vitamins and is soluble in water.\(^{75}\) Because of the high affinity between biotin and the biotin-scavenging proteins avidin and streptavidin, biotin is useful in molecular biology as a chemical tag on antibodies or nucleic acid probes. These biotin-binding proteins (avidin and streptavidin) can be coupled to fluorescent dyes, colloidal gold, or enzymes, which can be detected by using chromogenic reactions. Hence, they allow detection of biotin-labeled antibodies or probes.

- **Biotin-(Strept)avidin system**

  Avidin is an egg-white derived glycoprotein, and the affinity between avidin and biotin is extraordinarily high (affinity constant > \(10^{15} \text{ M}^{-1}\)).\(^ {76}\) Streptavidin has similar properties to avidin but streptavidin has a lower affinity for biotin than avidin. The very strong interaction of biotin and (strept)avidin is due to the shape-specificity of the biotin-binding pocket on (strept)avidin, which allows the formation of multiple hydrogen bonds and van der Waals interactions.\(^ {77}\) Such binding is stable over a wide range of pH values and temperatures. One major difference between avidin and streptavidin is that avidin carries a positive charge at neutral pH whereas streptavidin is nearly neutral. The main advantage of the usage of biotin lies in the fact that many biotin molecules can be

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\(^{75}\) [http://www.informatics.jax.org/mgihome/other/glossary.shtml](http://www.informatics.jax.org/mgihome/other/glossary.shtml)

\(^{76}\) [http://www.vectorlabs.com/](http://www.vectorlabs.com/)

coupled to a protein, then the biotinylated protein is able to bind more than one molecule of (strept)avidin. The biological activity of the biotinylated protein can be preserved if the biotinylation is performed under gentle conditions. Therefore, the sensitivity of the related biosensor system will be increased. The biotin-(strept)avidin system can be built by covalently linking (strept)avidin with different ligands such as enzymes, fluorochromes, or EM markers. The biotin-(strept)avidin system can be used to investigate a broad variety of biological processes and structures. The biotin-(strept)avidin system has been proven to be particularly useful in the detection of glycoconjugates, antigens, or nucleic acids by adopting biotinylated lectins, antibodies, or nucleic acid probes respectively.

- **Advantages of Biotin-(Strept)avidin system**

  The biotin-(strept)avidin system has several advantages over the method of the direct coupling of the marker to a lectin, an antibody, or a nucleic acid probe as follows:

  1. The biotin-(strept)avidin system can improve the sensitivity of biosensor systems because of the potential for amplifications due to multiple site binding between biotin and (strept)avidin;
  2. (Strept)avidin conjugates are very stable, and high fluorochrome to protein ratios can be obtained in the preparation of (strept)avidin;
  3. Because it can be utilized with a wide variety of biotinylated lectins, antibodies, or probes, only a single labeled conjugate, namely (strept)avidin, need be kept for use;
  4. Biotin-(strept)avidin system reagents are able to overcome the problem of background fluorescence which sometimes occurs in the use of heavily fluorescein-labeled or rhodamine-labeled antibody;
(5) The extraordinarily high affinity between (strept)avidin and biotin guarantees that the user can obtain a rapidly-formed and stable complex between the (strept)avidin conjugate and the biotin-labeled protein;

(6) Biotin-(strept)avidin system can simultaneously localize more than one antigen in the same tissue section even with two or three primary antibodies from the same species. More than one antigen can be localized in the same tissue section by utilizing either separate enzyme systems, two different substrates for the same enzyme, or assorted fluorochrome conjugates.

5.6.2. Experimental procedure of ISAM-coated LPGs as biosensors

5.6.2.1. Buffer solutions

In our biosensor experiments, the buffer solutions we often used are Phosphate Buffered Saline (PBS) solution and Sodium Phosphate buffer. PBS (Product #: P4244) at pH=7.2 was purchased from Sigma-Aldrich Corp. For preparation of the Sodium Phosphate buffer, the powder of Na$_2$HPO$_4$ (Product #: S0876) and NaH$_2$PO$_4$ (Product #: S0751) were purchased from Sigma-Aldrich Corp. Then, the Sodium Phosphate buffer at pH=7.2 was prepared as follows $^{78}$:

1. Prepare 100mL 1M Na$_2$HPO$_4$, and 100mL 1M NaH$_2$PO$_4$ with DI water, respectively.

2. Prepare 68.4mL 1M Na$_2$HPO$_4$ + 31.6mL 1M NaH$_2$PO$_4$ + 900mL DI water in 1000mL beaker.

3. Adjust pH to pH=7.2 by adding NaOH solution.

$^{78}$ http://home.planet.nl/~skok/techniques/laboratory/buffers.html
According to calculation of step 1 – 3 described above, another method for preparation of the Sodium Phosphate buffer is to dissolve Na$_2$HPO$_4$ (MW=141.96) (9.71g) and NaH$_2$PO$_4$ (MW=119.98) (3.791g) in 1000mL DI water.

5.6.2.2. Experimental procedure

For preparation of the biosensor experiment, biotin-N-hydroxysuccinimide Ester (Product #: H1759), streptavidin (Product #: S4762), and anti-streptavidin from rabbit (Product #: S6390) were purchased from Sigma-Aldrich Corp. All of these chemicals were stored in the freezer immediately after their arrival. In the following, the detailed experimental procedure of ISAM-coated LPG as biosensors is presented:

1. Before depositing PAH/PCBS ISAM films onto the grating, the spectrum of the LPG at room temperature is taken.
2. Deposit PAH/PCBS ISAM films onto the LPG, the outmost layer is PAH. In our preliminary experiments, we deposited 1.5 bilayers PAH/PCBS at pH combination of (7,7).
3. Dissolve the biotin (immediately taken out from the freezer) in the Sodium Phosphate buffer to the concentration of 10 mg in 10 mL (suggested by Dr. K. Vancott 10 mg/mL). Dissolve biotin for 15 minutes with stirring.
4. Immediately immerse LPG into the biotin solution and incubate it for 45 minutes (suggested 30~60 minutes).
5. Immerse the LPG in the Sodium Phosphate buffer/PBS buffer for 3 minutes, then rinse it with the Sodium Phosphate buffer/PBS buffer, the spectrum of the LPG at room temperature is taken.
6. Dissolve streptavidin (immediately taken out from the freezer) in the Sodium Phosphate buffer to the concentration of 1mg in 10mL for 15 minutes with stirring.

7. Immediately immerse the LPG into the streptavidin solution and incubate it for 45 minutes.

8. Immerse the LPG in the Sodium Phosphate buffer/PBS buffer for 3 minutes, then rinse it with the Sodium Phosphate buffer/PBS buffer, the spectrum of the LPG at room temperature is taken.

9. Dilute Anti-StreptAvidin (Anti-SA) by 100x (99mL the Sodium Phosphate buffer + 1mL Anti-SA) for 15 minutes with stirring, then further dilute it by 10x (9mL the Sodium Phosphate buffer + 1mL 100x Anti-SA) for 15 minutes with stirring.

10. Immediately immerse LPG into the Anti-SA solution and incubate it for 45 minutes.

11. Immerse LPG in the Sodium Phosphate buffer/PBS buffer for 3 minutes, then rinse it with the Sodium Phosphate buffer/PBS buffer, the spectrum of the LPG at room temperature is taken.

Note: The spectrum of the LPG at room temperature could be taken in any ambient circumstance (e.g. the LPG is immersed in air, PBS buffer, or the Sodium Phosphate buffer), the experimental procedure is the same as depicted above.

5.6.3. Experimentation of ISAM-coated LPGs as biosensors

5.6.3.1. Preliminary experimental results
Based on our prior experimental work, we demonstrated an ISAM-coated LPG worked as a biosensor to detect ligand/target binding event, where the ligand/target were oppositely-charged polyelectrolytes. In LPG-based biosensor applications, the ligand/target binding event will induce the refractive index variation or the thickness variation or both of the ambient medium surrounding the glass cladding of the LPG, which gives rise to the transmission spectrum variation of the LPG. We used the very strong affinity biotin-streptavidin interaction and the streptavidin-anti-streptavidin interaction as our biosensor model system. The biotin-streptavidin system is currently the most widely used technique for studying a wide variety of biological structures and processes and for clinical diagnostics.\(^{76}\) The biotin and streptavidin system serves as the antigen-antibody system in this biosensor demonstration. The streptavidin is immobilized on the fiber grating through the biotinylated PAH, which is deposited on the grating by the ISAM procedure. The buffer solutions used are the sodium phosphate buffer and Phosphate Buffered Saline solution (PBS). Powder of Na\(_2\)HPO\(_4\), NaH\(_2\)PO\(_4\) and the PBS solution, biotin-N-hydroxysuccinimide ester, streptavidin and anti-streptavidin from rabbit were purchased from SigmaAldrich Corp. The sodium phosphate buffer (0.1M, pH=7.2) was prepared according to reference.\(^{78}\) The experimental details are described in section 5.6.2. The LPG we used was UV-induced on TrueWave RS\(^{\text{TM}}\) fibers with a grating period of 112 \(\mu\)m and a length of 5 cm, which is provided by OFS.\(^{79}\) This yielded gratings that couple the fundamental mode to the LP\(_{0,14}\) cladding mode. It was a Turn-Around-Point (TAP) LPG\(^{23,24}\). We need to point out that in all of following biosensor experiments, we used the same LPG (ID: SG-C) for all experiments.

\(^{79}\) http://www.ofsoptics.com/
The experimental procedure is described as following: (1) Measure the bare LPG spectrum in the PBS solution at room temperature before depositing PAH/PCBS-based ISAM films on it. (2) Deposit (1-bilayer PAH/PCBS followed by 1-monolayer PAH) ISAM films on the LPG. (3) Rinse the LPG with the PBS solution and immerse the LPG in the PBS solution for three minutes, then measure the LPG spectrum. (4) The ISAM-coated LPG was immediately immersed into the biotin solution of 1mg/mL. The biotin will biotinylate the primary amines of PAH side-groups. (5) Repeat step [3]. (6) The LPG was immersed into the streptavidin solution of 0.1mg/mL. (7) Repeat step [3]. (8) The LPG was immersed into the anti-streptavidin solution. (9) Repeat step [3].

We deposited a 1.5-bilayer ISAM film (1-bilayer PAH/PCBS followed by 1-monolayer PAH), biotin, streptavidin, and anti-streptavidin onto the LPG in sequence. LPG spectra were taken after each deposition. Fig.5-14a and Fig.5-14b show the right peak of the LPG spectra measured when the LPG was immersed in PBS and when the LPG is exposed to air, respectively. There is a clearly measurable resonant wavelength shift after each deposition step. Each adsorption caused either a change of the thickness of the surrounding thin-film and/or a change of its refractive index, which resulted in the resonance shift of the grating. Compared to Fig.5-14a, Fig.5-14b shows a larger LPG spectrum shift after each step, which means the sensitivity of the LPG was higher when LPG was operating in air than in the PBS solution. The reason for this is a special feature of the TAP-LPG — if the operating range is closer to the TAP (approximately at the middle point between the two attenuation peaks) of the grating, the sensitivity will be larger. Seen from the insets of Fig.5-14, we noticed that the operating range of doing LPG measurements in the air is much closer to the TAP than that in the PBS solution.
Therefore, the sensitivity is higher with measurements in air than that in the PBS solution. Therefore, in order to increase the sensitivity of the grating operating in the PBS solution or other aqueous environments, we can design the grating to move the attenuation peak to be closer to the TAP. In addition, we also can design a grating with a higher order coupled cladding mode to obtain higher sensitivity.\textsuperscript{67}
Fig. 5-14. ISAM-coated LPGs as Biosensors. (a) LPG spectrum shift after each immersion step [bare LPG → ISAM → biotin → streptavidin → anti-streptavidin (AntiSA)], measured in PBS buffer. (b) LPG spectrum shift after each immersion step [bare LPG → ISAM → biotin → streptavidin → anti-streptavidin (AntiSA)], measured in air.

5.6.3.2. Specificity study

Additionally, we did a control experiment to verify the specificity of the system, which confirmed that the observed LPG spectral variations are due to the specific binding of the biotin to the streptavidin. We use the non-relevant protein bovine serum albumin (BSA) to test the nonspecific binding. After immersing LPG in the biotin solution, we immersed the grating in the BSA solution. As shown in Fig. 5-15, there was no obvious resonant wavelength shift after immersing the grating in the BSA solution. It suggested that there was no non-specific binding occurring on the grating surface.
Fig.5-15. Control experiment to verify the specificity — LPG spectrum shift after each immersion step [bare LPG $\rightarrow$ ISAM $\rightarrow$ biotin $\rightarrow$ bovine serum albumin (BSA)], measured in PBS buffer.

5.6.3.3. Optical-intensity based biosensors

Finally, in order to demonstrate that ISAM coated LPGs could serve as optical-intensity based biosensors, we etched the LPG with the hydrofluoric (HF) acid and the operating point of the LPG was set at the TAP of the LPG. The benefits of this optical-intensity based TAP LPG biosensor scheme is as follows: (1) we can make an inexpensive biosensor system with inexpensive optical components. Inexpensive optical sources (e.g. LEDs) could be used rather than tunable lasers that are often employed in the real-time measurement systems. Also, powermeters could be used as detectors rather than an expensive optical spectrum analyzer. (2) the sensitivity of the LPG would be dramatically increased if the operating range is set at the TAP of the LPG. Fig. 5-16a shows the experimental results of HF etching the LPG to TAP. Fig. 5-16b shows the
experimental results of the demonstration of an optical-intensity based biosensor by utilizing the biotin-streptavidin system with the same condition and procedure described above. We note that the sensitivity was clearly improved, and an optical-intensity based biosensor system could be achieved by tracking the optical intensity variation at the wavelength of 1386nm. The dynamic range of this scheme is much larger than the resonant wavelength shift based optical intensity based measurement scheme. Its dynamic range depends on the strength of the LPG, and stronger LPGs (e.g. 30 dB LPGs) would lead to larger dynamic range.
Fig. 5-16. (a) HF etching LPG to the Turn-Around-Point (TAP) of the LPG. (b) Demonstration of an optical-intensity based biosensor by utilizing the biotin-streptavidin system [bare LPG $\rightarrow$ ISAM $\rightarrow$ biotin $\rightarrow$ streptavidin], measured in air.

5.6.3.4. Sensitivity versus concentration of streptavidin

By taking advantage of the optical intensity-based TAP LPG, we did the study of the sensitivity versus the concentration of the streptavidin used in the biotin-streptavidin system. The experimental procedure is the same as that in previous experiments. We obtained 0.0125mg/ml, 0.025mg/ml, 0.05mg/ml, and 0.075mg/ml streptavidin by diluting 0.1mg/ml streptavidin. Before doing the study of the sensitivity versus the concentration, we etched the TAP LPG (used in Fig. 5-16b) by three seconds more to gain a larger dynamic range as shown in Fig. 5-17a. Fig. 5-17b shows a biosensor test to verify the operation condition of the new-etched TAP LPG using the biotin before the sensitivity study. Finally, Fig. 5-17c shows the experimental results of the sensitivity versus the concentration of the streptavidin (SA). We note that the optical intensity variation for
0.0125mg/ml streptavidin is about 1.6 dB. It suggests that this biosensor system could detect the streptavidin with lower concentrations. In addition, Fig. 5-17c illustrates that the dynamic range for the optical intensity-based sensor operation is from 0mg/ml to 0.075mg/ml in this system. Due to the unique characteristic of TAP LPGs, the single broad peak splits into two separate peaks after the concentration of the streptavidin is larger than 0.075mg/ml. We could etch the TAP LPG more to gain a larger dynamic range as shown in Fig. 5-16a.
Fig. 5-17. (a) HF etching LPG by three seconds; (b) Biosensor test before the sensitivity study; (c) study of the sensitivity versus the concentration of the streptavidin (SA) by utilizing an optical-intensity based biosensor and the biotin-streptavidin system [bare LPG → ISAM → biotin → streptavidin], measured in air.
Chapter 6. Conclusion

6.1. Conclusion

Biosensors have the potential to revolutionize the way genomics, proteomics, diagnostics, and environmental monitoring is performed. Biosensors possess huge application markets, which are mainly involved into five applications areas. Medical applications overshadow the other seemingly important applications areas. The increasing rate of obesity and the alarming rise in the rate of diabetes in the industrialized world is driving a need for more biosensors to monitor diabetic patients' glucose levels. The pharmaceutical research industry is driving the need for new rapid assay biosensors to speed the progress of drug discovery. Biosensors also help monitor food safety and detect environmental pollution. Finally, as mentioned before, the war on terrorism is driving the need for new rapid detection biosensors against biowarfare agents for military and civil defense applications.

In general, biosensor platforms use specific biomolecular recognition between an affinity ligand or enzyme and the target biomolecule (protein, toxin, cell, etc.). The ligand/target binding event is transduced into a measurable signal by a variety of methods: e.g., enzymatic reaction, refractive index change at the sensor surface, change in electrical or acoustic properties, or incorporation of fluorescently or radioactively labeled reagents. In all biosensor applications, the most important features are specificity,
sensitivity, and the time required to attain a positive or negative signal. Also, if a sensor platform is to be used in the field, it must be portable, simple to operate, and rugged. Ideally, the ligand/target binding event should be transduced to a measurable signal without requiring the use of a complex protocol or fluorescently- or radioactively-labeled reagents. A biosensor platform that combines the features of sensitivity, specificity, portability, and simplicity is needed to respond to the many challenges in national security, environmental monitoring, and life sciences research.

The motivation of this work is to address all these recent increasing needs for biosensors. For example, one of the most difficult problems facing people (e.g. military and law enforcement personnel) is to develop biosensors capable of rapid detection and confirmation of the release of biological agents in acts of bioterrorism. Simple conventional colorimetric assays yield rapid results, but they lack the sensitivity needed for detection of microbes and toxins that will be in environmental samples. Highly sensitive immunoassays, cellular response assays, and “lab on a chip” formats have been developed, but they generally require multiple or specialized reagents for detection, and some formats can be time-consuming.

Optical biosensors are most popular for biological analysis and are today’s largest group of transducers because of their unique characteristics. In this work, we studied a new optical biosensor platform with the potential for exceptional sensitivity, low cost, and rapid results. This biosensor platform is based on ISAMs adsorbed on LPGs. This general idea is as follows. The ISAM films contain probe biological molecules — an affinity ligand in it. A LPG is an optical fiber-based device that can be extremely sensitive to the environment surrounding the fiber. Adsorption of a species to the fiber
alters the environment around the fiber, and thus generates a signal (i.e. changes of transmission spectra of LPGs). Thus, if a target biological molecule binds to an affinity ligand on the fiber, a signal is generated, without the need for additional reagents.

Chapter 2 introduces the principle of LPGs. An UV-induced LPG is an optical fiber with a periodic refractive index change inside the fiber core. They couple light between copropagating modes of an optical fiber. LPGs that couple the fundamental mode of a single-mode fiber (SMF) to one of its cladding modes are ultra-sensitive to the refractive index of the material surrounding the fiber, and this high sensitivity and high resolution have led to extensive investigations of LPGs for use as chemical and biological sensors. Chapter 2 describes the fundamental theory of optical fibers, the coupled-mode theory for analyzing LPGs, and the fundamental LPG theory. Then, some simulated results illustrate the optical properties of LPGs. Finally, we focus on a type of important LPGs — Turn-Around-Point (TAP) LPGs. In contrast to conventional LPGs, TAP LPGs have several unique features including stronger strengths, broader spectral bandwidths, and wavelength-independence. Especially, the sensitivity of TAP LPGs are much higher than that of conventional LPGs. The sensing mechanism of conventional LPGs is based on sensing the resonant wavelength shift of the LPG, while the sensing mechanism of TAP LPGs can be achieved by two ways — (1) monitoring the variation of the optical intensity of the TAP LPG, and (2) monitoring the resonant wavelength shift of the TAP LPG. Thus, by using the optical-intensity-based measurement technique of TAP LPGs, we can potentially make an inexpensive biosensor system with inexpensive optical components. Inexpensive optical sources (e.g. LEDs) could be used rather than tunable
lasers that are often employed in the real-time measurement system. Also, powermeters could be used as detectors rather than expensive optical spectrum analyzer.

Chapter 3 introduces the principle of ISAMs. It describes the ISAM process for building nm-thick thin films, which involves the immersion of a charged substrate into oppositely charged aqueous poly-electrolytic solutions of polyanions and polycations in alternating sequence at room temperature and ambient conditions. This results in a multilayered thin-film to grow on the substrate with molecular-level control. The resulting macroscopic properties of the thin-film are determined by the properties of individual molecules as well as the dipping sequence or the architecture of the composite thin-film. The ISAM technique possesses many advantages over other traditional thin film techniques such as: (1) ISAM procedure is simple, rapid, environmentally friendly, and inexpensive; (2) Diversity of ISAM film materials (e.g. various polyelectrolytes incorporated with clay platelets, proteins, virus particles, etc.); (3) Diversity of substrate materials with various nature, sizes, topology (e.g. metals, glass, silica, mica, etc.); (4) Thickness of ISAM films can be precisely controlled at the nm level; (5) Refractive index of ISAM films can be controlled by using different film materials or altering pH of polycation and/or polyanion solutions; (6) Flexibility of film structure, which depends on dipping sequences (e.g. ABAB, ABCBAB); (7) Good reliability, thermal stability, and film quality. The methods for characterizing ISAM films can be classified into ex situ characterization methods and in situ characterization methods. Reported ex situ methods include UV/Vis spectroscopy, X-ray/neutron-ray reflectometry, nuclear magnetic resonance (NMR), while reported in situ methods include zeta potential, quartz crystal microbalance, surface plasmon spectroscopy, optical waveguide lightmode spectroscopy
(OWLS), optical reflectometry in stagnation point flow cells, scanning angle reflectometry (SAR), ellipsometry, in situ atomic force microscopy (AFM), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), surface forces measurements, and second harmonic generation (SHG).

Chapter 4 describes the theoretical approach for simulating thin-film-coated LPG spectra, belongs to which the case of ISAM-coated LPGs. It provides the detailed theoretical background for building the computer model of thin-film-coated LPGs including how to calculate the parameters of the fundamental core mode, the parameters of cladding modes, and how to utilize these parameters to simulate the LPG spectra. Based on the simulated results, it is shown that LPGs can be highly sensitive to the presence of nm-thick thin films on the cladding surface and that TAP LPGs are even more sensitive than conventional LPGs. The results shows that (i) the sensitivity to the thickness of the thin-film adsorbed on LPGs becomes gradually higher with increased thickness; (ii) the sensitivity to the refractive index of the thin-film adsorbed on LPGs becomes gradually higher with increased refractive index; (iii) the sensitivity of the cladding mode to the thickness/index of the ambient thin-film increases as the order of the cladding mode increases, respectively.

Chapter 5 describes the experimental results of studies of the index sensitivity of TAP LPGs, studies of the index sensitivity of ISAMs coated LPGs, and ISAMs adsorbed on LPGs for use as biosensors. We found that TAP LPGs can serve as ultra-sensitive LPGs whose attenuation can be changed by 25 dB (~99.7%) over a 48-nm spectral band, with ambient-index changes of only $2.7 \times 10^{-4}$. The TAP LPGs device schematic allows arbitrarily high index sensitivities to be achieved, which makes it an attractive platform
for realizing sensors and modulators that respond to small index changes. In addition, we found through simulations that the resonant wavelength shift of LPGs could result from either the variation of the thickness of the film and/or the variation of its refractive index. Furthermore, it illustrates that the sensitivity of LPG-based sensors could be enhanced by using a film (e.g. ISAM film) of nm-thickness and refractive index greater than silica. We demonstrated experimentally that ISAM films of nm-thicknesses deposited on LPGs induce dramatic shifts in the resonant wavelength (e.g. 40 nm resonance shifts for film thicknesses of only 25 nm). The refractive index and the thickness of the ISAM film was precisely controlled by altering the relative fraction of the anionic and cationic materials combined with layer-by-layer deposition. This coating technique potentially provides an attractive method for precisely tuning the resonant wavelength of LPG after its fabrication. Additionally, the ISAM-film coating can be easily removed by acid-stripping with 95% H$_2$SO$_4$:5% HNO$_3$. This offers a reversible process for tuning the resonance of LPG. Finally, we demonstrated that ISAM-coated LPGs can function effectively as biosensors. Biotin, streptavidin and anti-streptavidin were deposited onto the ISAM-coated LPG in sequence, each inducing a measurable resonant wavelength shift of the LPG. These demonstrations, combined with the fact that ISAMs can incorporate a variety of chemical and biological sensing compounds, provides for a thermally-stable, reusable, and robust platform for building efficient optical sensors.

6.2. Future work

The title of this thesis “Ionic self-assembled multilayers adsorbed on long period fiber gratings for use as biosensors” describes the ultimate goal of our research. There is
till a great deal of work that is needed to be done before we could achieve this goal. In this section, some of the planned future work is listed as follows:

6.2.1. Sensitivity improvement of TAP-LPGs

There are several viable approaches for dramatically increasing the sensitivity of the LPG response and such studies are in progress.

- Set the operating wavelength of the LPG at TAP of LPG because the sensitivity of the grating is proportional to the inverse of the slope of the phase-matching curve.\(^{24}\)

- Deposit ISAM films with larger thickness and larger index onto the LPG because the sensitivity of the grating will be increased as the thickness and the index of the film increase.\(^{80}\)

- Use a buffer solution with larger refractive index (closer to 1.45) in the sensor system because the sensitivity of the grating will be increased dramatically when the ambient index is close to the index of the glass cladding.\(^{23}\)

- Design new TAP-LPGs with larger sensitivity through designing new fibers and new LPGs whose sensitivity is much higher.

6.2.2. Study of ISAM-LPG biosensors

- Sensitivity study by using different concentrations of analyte (e.g. different concentrations of streptavidin)
- Optical response vs. time (dynamical process study of binding kinetics)
- Reliability and repeatability — tests of multiple ISAM-LPG biosensors because different LPGs may give rise to different response.
- Several different classes of affinity ligands, including peptides, enzymes, and antibodies to evaluate flexibility of the sensor, e.g.
  a. Antibodies against anthracis toxin protein for detecting infectious disease agents in biological fluids.
  b. Protein interactions within flavonoid multienzyme complex to test utility of sensor for defining protein interaction interfaces in vitro.

6.2.3. Develop ISAM-LPG biosensor system for practical use

Finally, the ISAM-LPG biosensor system could be developed for practical use including designing the flowcell, the instrument box, the opto-electronic circuits, the computer-software (user-interface) and related components.
References


[64] Handbook of Variable Angle Spectroscopic Ellipsometer (VASE©) ellipsometer by J.A. Woollam Co.

[65] Lecture notes of the class “Optical Waveguides” instructed by Dr. A. Safaai-Jazi of Electrical Engineering Department at Virginia Tech.


Appendix A

The Sellmeier’s equation is expressed as

\[ n_i = \left[ 1 + \sum_{j=1}^{3} A_{ij} \frac{\lambda^2}{\lambda_j^2 - \lambda_{ij}^2} \right]^{1/2}, i = 1, 2 \]

where \( A_{ij} \) and \( \lambda_{ij} \) are material constants.

The material with refractive index \( n_1 \) is germanium-doped glass (7.0 m/o \( GeO_2 \), 93.0 m/o \( SiO_2 \)) and the material with refractive index \( n_2 \) is pure fused silica (100 m/o \( SiO_2 \)). The Sellmeier coefficients for these two materials are:

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<th>( A_{11} )</th>
<th>( A_{12} )</th>
<th>( A_{13} )</th>
<th>( \lambda_{11} )</th>
<th>( \lambda_{12} )</th>
<th>( \lambda_{13} )</th>
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