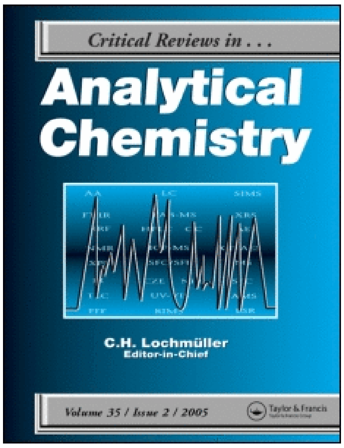

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Slab Waveguides in Chemistry

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Slab Waveguides in Chemistry

Lee Kang and Raymond E. Dessy

ABSTRACT

Technological development in the telecommunications and related areas have made available a wide variety of optical structures such as thin silica rods, hollow cylinders, fiber bundles, and many planar geometries such as thin films or channels resting on flat substrates. These devices have become the basis of various chemical sensor studies. The application of cylindrical fiber optics has been leveraged heavily in developing microscopic detectors in which they serve as light pipes to transport spectrometric information between the source, analyte, and photodetector. Slab waveguides, on the other hand, offer many advantages over their cylindrical counterparts. Slab waveguides consist of planar or rectangular structures with a thickness ranging from 0.1 μm to 1 mm. They can also be molded as multilayers or channels on a substrate. Both thin and thick slab waveguides are useful in chemical sensing. In this article, the concept of waveguiding phenomena in thick and thin waveguides is introduced. Emphasis is placed on both the quantum nature and a phenomenological description of light guiding in thin slab waveguides. Several optical coupling techniques are discussed. The remainder of the article is devoted to specific applications in chemistry.

I. INTRODUCTION

Slab waveguides were originally introduced in microwave engineering. Osterberg and Smith[1] carried out the first rudimentary experiments with optical guided waves using planar waveguides in the early 1960s. The concept brought about great expectations for the use of planar optical waveguides as optical computing components to replace integrated electronic circuits. The spectroscopist began to use thin film waveguides as tools to solve chemical characterization problems when Harrick[2] and Fahrenfort[3] introduced the Attenuated Total Reflection (ATR) technique. Today, slab waveguides are playing an important and ever-increasing role in modern chemistry. This research includes the application of surface-enhanced Raman spectroscopy, monolayer absorption spectrometry, evanescent excitation fluorometry, surface plasmon resonance, spectroelectrochemistry, and various developments of extrinsic and intrinsic chemical sensors.[4-9]

The waveguiding phenomenon is well known to physicists and electro-optical engineers. Chemists, however, are often frustrated by inadequate backgrounds in optics and electromagnetic theory as they explore the use of such waveguides. In order to attain a physical understanding of planar optical waveguides, perhaps it is best to use a physical analogy with which all spectroscopists are familiar. In this article, we first introduce the basic concepts of waveguiding phenomena by using a geometrical optics approach. Then, an analogous model is set up to portray the quantum nature of the light beam in a waveguide channel. Complex mathematics are not introduced. However, several key equations have to be presented in order to elucidate a few important concepts. The purpose of this article is to provide a platform for scientists so that they may develop novel solutions to their own problems.

II. MULTIPLE INTERNAL REFLECTION

Light propagation in a slab waveguide can be understood by first examining the behavior of a light ray at a dielectric interface. In Figure 1A, as the incident beam encounters the interface from the denser medium, n_1, to the rarer medium, n_2, a portion is reflected and a portion refracted. The bending or refracted beam at the interface results from the difference in the speed of light between two materials having different refractive indices. The relationship between angles and refractive indices follows a simple equation called Snell's law. If the incident angle gets bigger, the refracted beam deviates away from the normal until it is parallel to the surface. At this point, the incidence angle is known as the critical angle, θ_c. Beyond the critical angle, the incident beam is totally reflected back into the denser media. This is called total internal reflection. The waveguide phenomenon is, therefore, based on light propagating in a denser medium by multiple internal reflections, as shown in Figure 1B. In waveguides made from slabs of glass with a thickness of a few millimeters, light is considered as a particle beam traveling in straight lines until reflected at the interface. As the guide's dimension grows smaller (into the micrometer region), the wave and quantum nature of light becomes evident. Both thick slab waveguides and thin slab waveguides are useful in chemical sensing.

A. Phase Change by Reflection

When a beam of light is totally reflected at a dielectric interface, a phase change occurs in the reflected wave. This phase shift is dependent upon the angle and polarization of the incidence according to Fresnel's formulas.[10] It turns out to be a very important parameter in discussing the quantum nature of the waveguide and is examined later.

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B. Goos-Hänchen Shift

In addition to the phase shift, the reflected beam is physically displaced from its normal axis. It appears as if the incident beam enters the medium of lower index of refraction through one region of the interface and then emerges from it at a displaced region, as shown in Figure 2. This lateral shift is known as a Goos-Hänchen shift. The shift distance is determined by the polarization of the beam, incident angle, and refractive indices at the dielectric interface.[11] The Goos-Hänchen shift is an important element in bringing the geometric ray and wave theories into agreement.

III. SINGLE-MODE AND MULTIMODE WAVEGUIDES

Thin slab waveguides can be divided into what are called single- and multimode classes. As the names imply, a single-mode waveguide sustains only one mode of propagation, whereas multimode waveguides may contain many hundreds of modes. Single-mode slab waveguides are more difficult to manufacture and of less practical importance in chemistry. Multimode waveguides are used in many applications. These modes are guided electromagnetic waves, each propagating in the waveguide with well-defined phase velocity, cross-sectional energy distribution, and polarization. Each propagating mode is a uniform plane wave that repeats itself along the waveguide. Only a certain discrete number of modes are capable of propagating along the guide. This discrete nature of the propagation is one of the most important characteristics of the waveguides. To describe the mode concept, we examine two different theoretical approaches: ray optics theory and wave theory. Both approaches have their merits, and one finds oneself switching back and forth according to which description is most "convenient" in each situation.

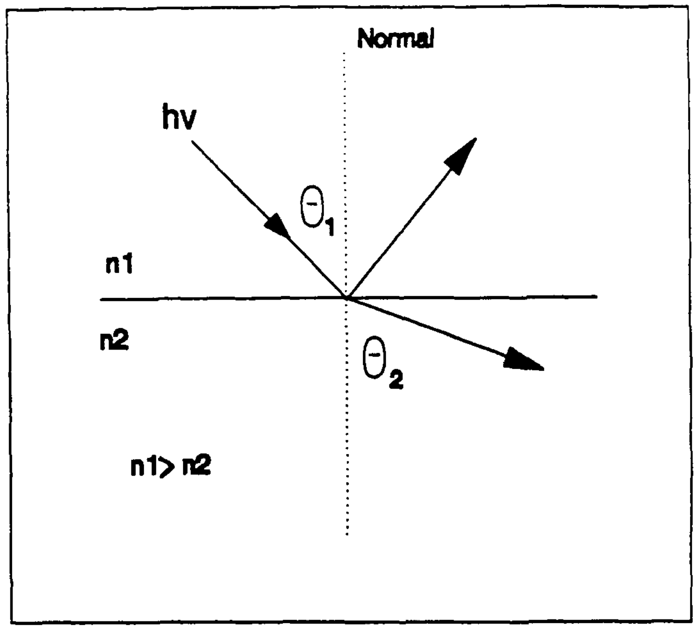
A. Ray Optics Theory

To help describe the modes, it is possible to conceive that each mode is a light ray confined in the waveguide and that it travels in a zigzag fashion through the waveguide, as shown in Figure 3. The light rays travel with the same velocity along their paths. However, the angle of reflection in the zigzag path is different for each mode, resulting in different longitudinal components. This will determine the phase velocity and effective guide index, N, for each propagation mode:

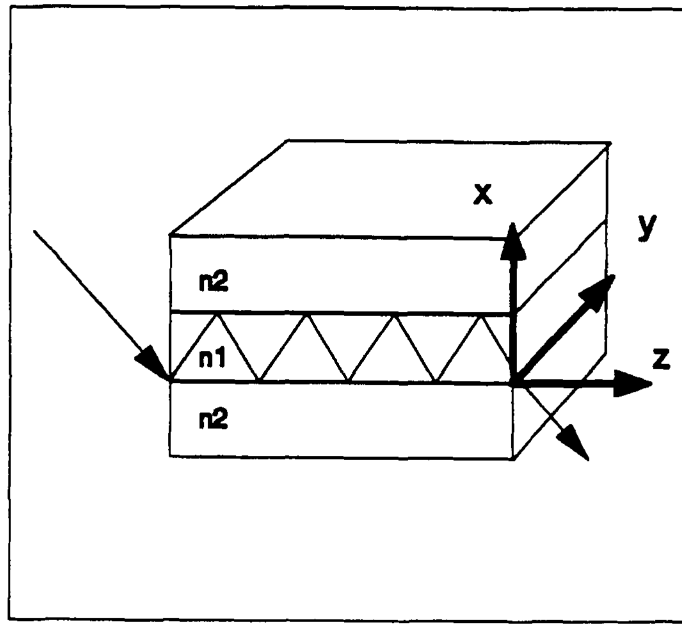
$$N = \frac{c}{v_p} \tag{1}$$

where c is the velocity of light in free space, and v_p is the phase velocity of the individual mode.

Although this simple ray picture appears to allow rays at any angle less than the critical angle to propagate in a waveguide, the discrete nature of propagation can be understood by examining the phase conditions required for the standing wave. The total phase shift that results when the wave gets reflected twice at the boundary must be equal to an integer multiple of 2π rad to allow constructive interference. If this phase condition is not satisfied, the wave would interfere destructively with itself and die out. As a result of this phase requirement, only certain incidence angles or paths are permitted, and the



A.



B.

FIGURE 1. (A) Ray picture at the dielectric interface. Snell's law: $n_1 \sin \theta_1 = n_2 \sin \theta_2$. Critical angle: $\theta_c = \sin^{-1}(n_2/n_1)$. (B) Waveguiding phenomenon. (This coordinate system is used throughout the article.)

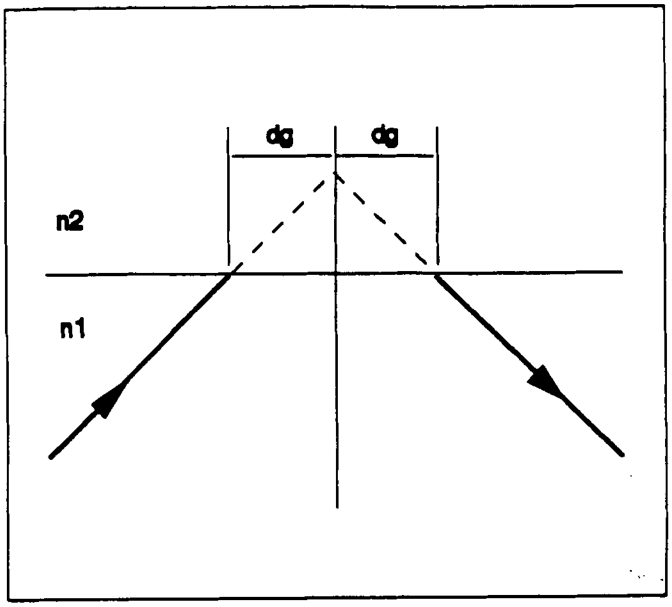


FIGURE 2. Goos-Hänchen shift: lateral displacement, d_g, of the reflected beam.

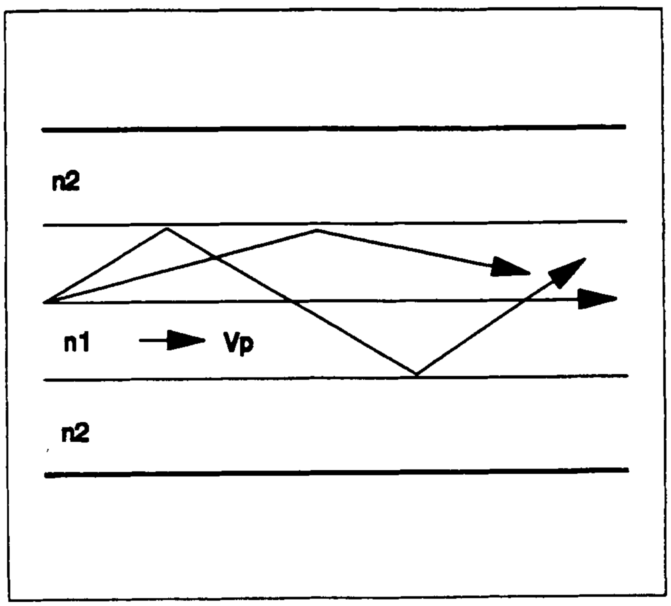


FIGURE 3. Ray tracing diagram: modes described by ray optics theory.

propagation of light through the guide becomes quantized. This formulation, based on the geometrical optics approach, is called ray-optic theory. The ray-optics model provides physical insight into the waveguiding phenomena. It is very useful in explaining the behavior of the guide, the conditions of propagation, and the existence of modes. However, there are a number of limitations and discrepancies that exist between it and an exact mathematical model, which invokes wave theory. An important case is the analysis of single-mode waveguides. It must be dealt with by using electromagnetic theory and Maxwell's equations.[12] Another limitation of the ray-optic approach is that it fails to explain the evanescent loss, which is also an important waveguiding phenomenon.

B. Wave Theory

To have a complete picture of the field distribution across the guide, electromagnetic theory and Maxwell's equations must be used. Although the overall analysis of modes in wave theory is well established, the lengthy mathematical description of the guided modes is rather complex and formidable. The reason is that the Maxwell's equations involve six-component hybrid electromagnetic fields, E_x, E_y, E_z, H_x, H_y, and H_z, having very involved mathematical expressions. Hence, the general derivation of the equations is not presented here. The interested reader should refer to *Light Transmission Optics*, by Marcuse.[13]

The derivations for planar waveguide using Maxwell's equations leads to a second order wave equation for the electric field, shown in Equation 2:

$$\frac{d^2E_y}{dx^2} + (n^2k^2 - \beta^2)E_y = 0 \qquad (2)$$

where β is the propagation constant in the waveguide, k is the propagation constant in free space, and n is the refractive index of the medium.

The differential equation for the magnetic field can be derived based on the same formulation. The propagation constant, β, determines the phase velocity and the effective guide index of each guided mode, as defined by

$$\beta = N \times k \qquad (3)$$

The equation must be solved to satisfy the boundary conditions at the dielectric interface and the orthogonality of electric and magnetic fields in the waveguide. Since the y dimension is large (as depicted in Figure 1B), the mathematical expressions for the modes are only governed by the wave equation in the x direction. This makes the mode analysis in planar waveguides a great deal simpler than that in cylindrical waveguides. The mathematical details of the solutions are omitted here, since it is more illustrative to examine the electric field distributions for the several lower-order guided modes in a symmetrical slab waveguide, as shown in Figure 4A. Viewing these field distribution diagrams, readers may perceive a connection with the wave function of the particle-in-a-box model in quantum chemistry. In the particle-in-a-box model, solving the Schrödinger wave equation according to imposed boundary conditions will lead to the probability density diagrams shown in Figure 4B. The boundary conditions are that the potential

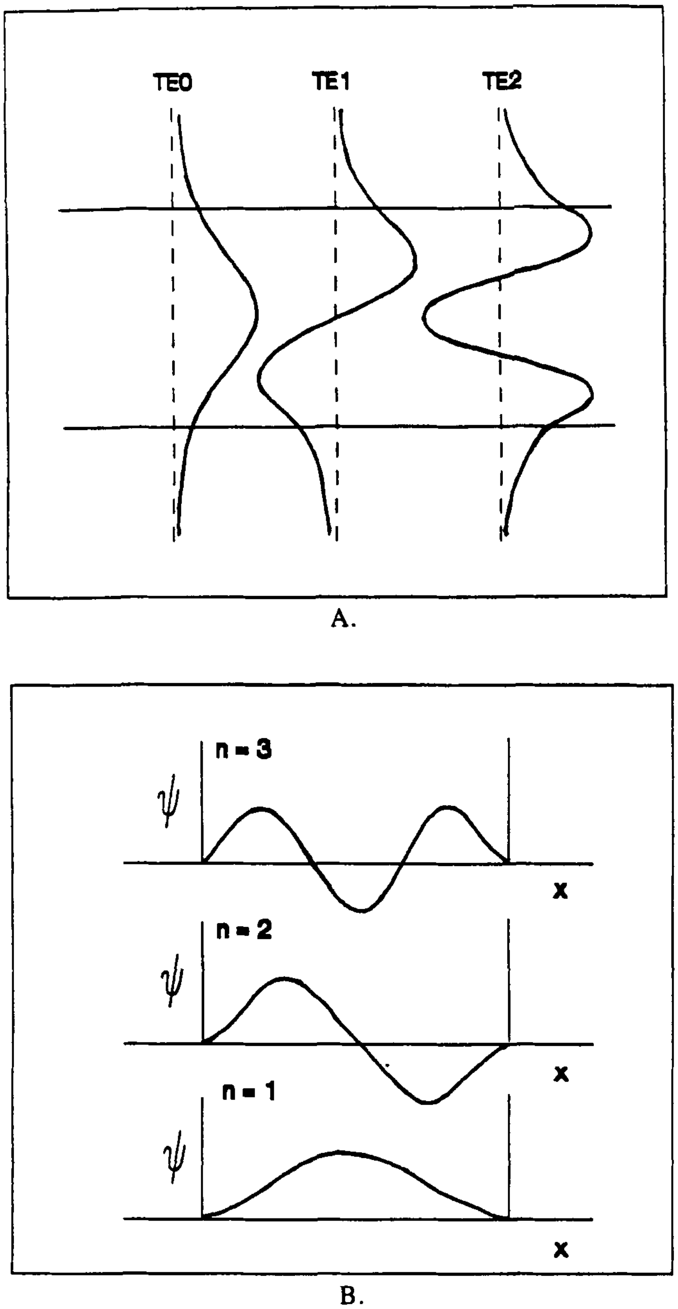


FIGURE 4. (A) Field distributions of three lowest modes. (B) Field distributions of three lowest energy states in the particle-in-a-box model.

energy of the particle be zero within the box, and infinite outside the box. If the potential energy outside the box has a value other than infinity, the probability function will no longer be zero at the wall, rather it will protrude through the wall with a tailing area. This is the so called tunneling effect. The field diagram of each mode in a waveguide analysis shows great resemblance, both mathematically and conceptually, to the density function of the particle-in-a-box model. In this analogy, the walls of the box are replaced by the real dielectric discontinuities at the material interfaces. The tunneling effect in the waveguide system leads to what is called the evanescent field. The area of the tailing is determined by the refractive index difference at the interface in likeness to the potential energy difference in the particle-in-a-box model.

Another important feature in both analyses is the discrete nature of the solutions. The calculated energy for each state of distribution in the particle-in-a-box model is quantized. In mode analyses, the solution of Maxwell's equation allows only certain discrete values of the propagation constant, β. In essence, the square of effective guide index, N^2, corresponds to the energy level and n^2 to the potential energy well. (Readers may see the relations between Equation 2 and the Schrödinger wave equation.)

C. Guided Modes

According to the wave theory, there is only a limited number of guided modes that can exist when β is in the range:

$$kn_2 < \beta < kn_1 \tag{4}$$

The guided modes can be further divided into two types of propagation according to their transverse properties. They are TE_V modes if they contain the field components E_y, H_z, and H_x ($E_z = E_x = H_y = 0$); they are TM_ν modes if they contain the field components H_y, E_z, and E_x ($H_z = H_x = E_y = 0$), as illustrated in Figure 5. The discrete quantum numbers, ν, specify the orders of the modes and determine the roots of the wave functions due to oscillatory properties. These terms for the modes are technical designations associated with complex computational expressions (hence, they will not be developed further). In the actual system, there are degeneracies and mode mixing that make the physical visualization of each individual mode very difficult. Therefore, it is advisable to investigate the entire optical pattern at the far field of the waveguide end

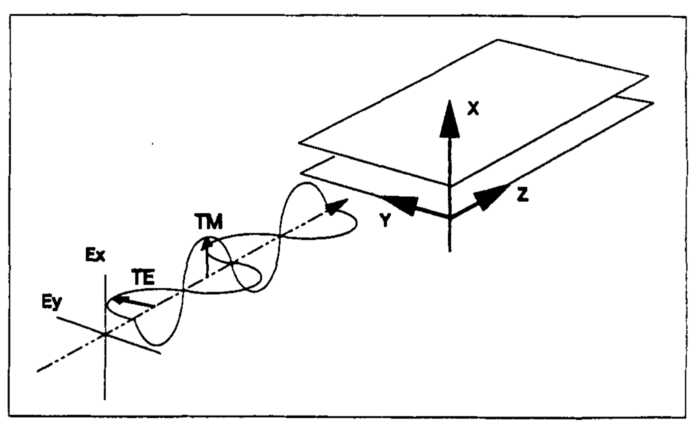


FIGURE 5. Polarization of modes: TE and TM modes.

because the total optical pattern is subject to the guided mode characteristics in the waveguide channel.

D. Radiation Modes and Leaky Modes

For the thin slab dielectric waveguide, there are two other categories of modes present in the system: radiation modes and leaky modes. These modes are not trapped in the waveguide, but are still the solutions of the same boundary-value equations. A simple diagram of these possible modes in a planar waveguide is shown in Figure 6. Radiation modes basically result from optical energy outside the waveguide acceptance angle being refracted out of the guided region. Leaky modes are only partially confined to the waveguide region, and are attenuated by continuous radiation of their power out of the dielectric interface as they propagate along the waveguide.

E. Evanescent Fields

The power radiating out of the waveguide results from the tunneling effect mentioned earlier. This energy tailing is, as mentioned, called the evanescent field, as described in Figure 7. The evanescent field penetrates into the surroundings and decays exponentially with distance from the interface.[14] The evanescent penetration depth, d_p, is defined as the distance required for the electric field amplitude to fall to 1/e of its original surface value, and can be calculated by Equation 5:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2\theta - \left(\frac{n_2}{n_1}\right)^2}} \qquad (5)$$

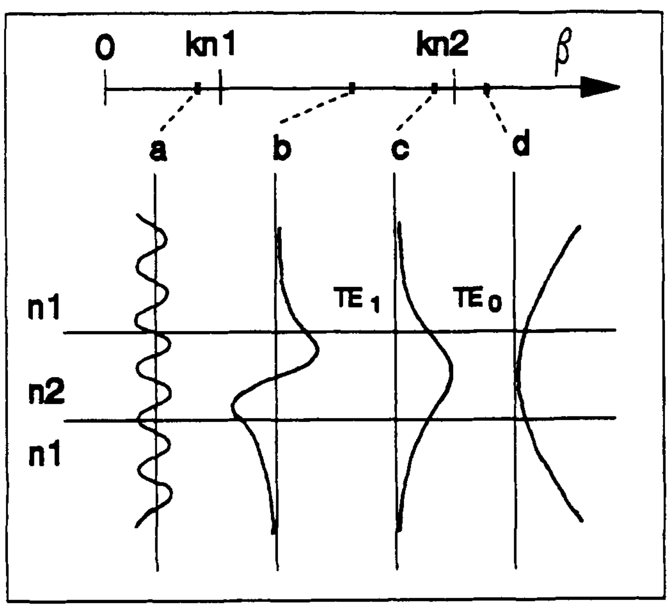


FIGURE 6. Field distributions of several possible modes in a planar waveguide system: (a) is leaky modes, (b) and (c) are guided modes, and (d) is radiation modes.

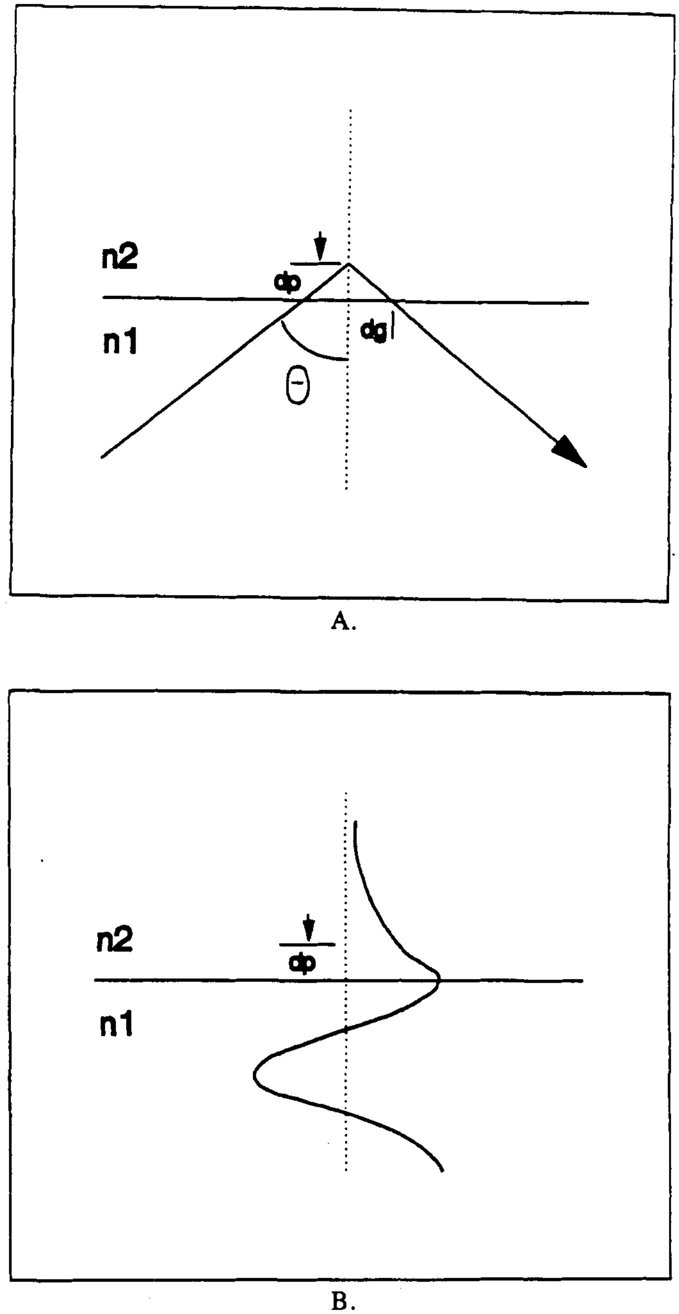


FIGURE 7. (A) Evanescent fields described by ray optics theory. $d_p = d_g/\tan\theta$. (B) Evanescent fields described by wave theory. $d_p \approx (1/2)\,\lambda$ according to Equation 4 for a typical system: $n_1 = 1.5$, $n_2 = 1.3$, and $\theta = \theta_c + 10^0$.

From the expression, the apparent depth of penetration ranges from a fraction of the wavelength up to several wavelengths, depending on (1) the propagation wavelength, λ, (2) the angle of incidence, θ, and (3) the refractive index of both the guide and surroundings. It can be shown that d_p gets larger as θ approaches the critical angle, and becomes infinite when θ equals the critical angle. This means the light is no longer totally guided in the medium.

F. V-Number

According to Equation 4, the permissible range for each guided mode must satisfy the cutoff condition deduced from the wave function. A mode is referred to as being cut off when it is no longer confined in the waveguide. The cutoffs for the various guided modes can be obtained by solving fairly complex differential equations and hence are not shown here. However, to make the results of such complex numerical evaluation more broadly applicable, an important parameter, the V-number, connected with the cutoff condition, is introduced. It is defined as

$$V = \frac{2\pi}{\lambda} h\sqrt{n_1^2 - n_2^2} \qquad (6)$$

where h is the thickness of the guide.

The V-number is a dimensionless number that determines how many guided modes a waveguide can support.[15] From the expression, the number of modes permitted depends on the propagation wavelength, thickness of the waveguiding layer, and refractive indices of the materials. Thus, the modes can be cut off by deliberately varying the electro-optic characteristics (i.e., refractive index) in the waveguide. These fundamentals account for the operation of most electro-optic modulators and switches in planar optical integrated circuits. It also paves the way for the development of intrinsic chemical sensors.

IV. SYMMETRIC, ASYMMETRIC, MULTILAYER, AND CHANNEL WAVEGUIDES

The following is a look at a basic three-layer slab waveguide system with refractive indices n_1, n_2, and n_3, as shown in Figure 8. It is called a symmetric waveguide when the waveguiding layer with refractive index n_1 is bounded on both surfaces by identical layers with refractive index n_2 less than n_1 ($n_2 = n_3$). Another type of slab waveguide is the asymmetric waveguide, in which $n_1 > n_2 > n_3$. It can be made by depositing a thin film on a substrate of somewhat smaller refractive index, while the top surface of the waveguiding layer is either left open to the air or coated with a metal layer. In an asymmetric waveguide, the field distribution of the mode will be unbalanced with respect to the longitudinal axis. They can have cutoffs for all the modes, unlike symmetric waveguides for which the lowest order mode cannot be cut off.[16] The asymmetric waveguides are particularly useful in chemical analyses and sensor design. The multilayer and channel waveguides are primarily used in optical integrated circuits and semiconductor lasers. However, Miller and Bohn[17] have shown the application of multilayer waveguides in quantitative Raman spectroscopy with internal standards.

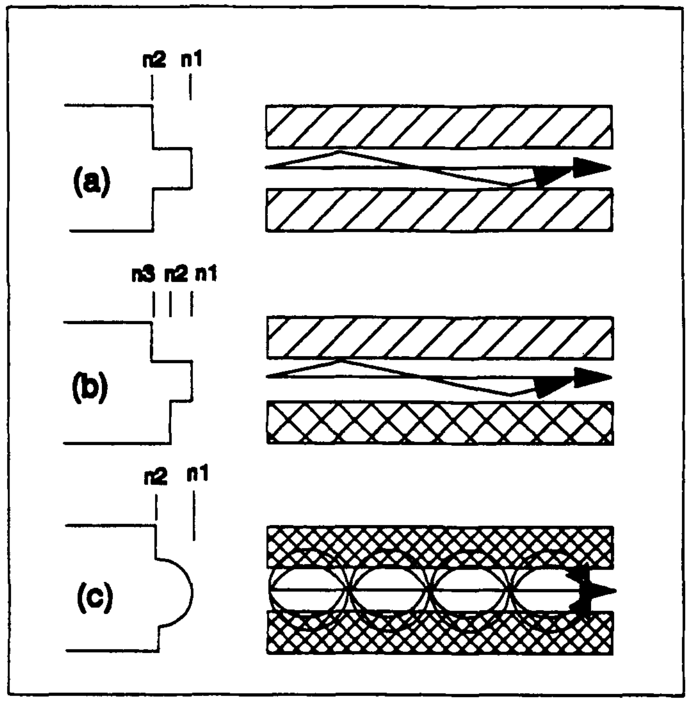


FIGURE 8. Three-layer systems of planar slab waveguides. Index profile: (a) symmetric/step, (b) asymmetric/step, and (c) graded index.

V. STEP AND GRADED-INDEX WAVEGUIDES

Slab waveguides may be fabricated using many different technologies, such as polymer spin-coating, dipping, plasma polymerization, ion exchange, ion migration, proton bombardment, and epitaxial layer growth, etc.[18-23] Variations in the material composition give rise to the commonly used waveguide types shown in Figure 8. In cases where the refractive index of the waveguiding region is uniform throughout and undergoes an abrupt change (or step) at the boundary, they are called step-index waveguides, as shown in Figure 8a and b. In other cases, the refractive index is made to vary as a function of the distance from the center axis of the waveguide. They are graded-index waveguides as shown in Figure 8c.

A modal analysis of an optical waveguide based on solving Maxwell's equations can only be carried out exactly for a step-index waveguide. In the graded-index waveguide, approximation methods are needed. The WKB method, named after Wenzel, Kramers, and Brillouin, is the most widely used analysis of modes in a graded-index waveguide.[24] The method involves selection of a trial value for the propagation constant, β, for each mode and iterative solutions. The derivation is therefore beyond the scope of this article. In a graded-index waveguide, the ray trace of each mode will be a trajectory due to the index gradient of the material. Hence, the periodicity of the bounces for each mode in the guide can be maintained constant, as shown in Figure 8c. The advantage of the graded-index waveguide is that it can reduce the intermodal dispersion which is a primary concern in optical communication.[25] Since the refractive index distributions determine the integrity of the guided wave, it is important to calibrate the profile of refractive indices. Several refractive index numerical analyses, such as the weighted index method and the effective index method, are commonly used.[26,27]

VI. COUPLING TECHNIQUES

Coupling the optical energy into or out of a waveguide can be difficult. The application of lasers greatly aids the coupling efficiency. A number of techniques have been devised for the conversion of a light beam into a guided wave. Each method has particular advantages and disadvantages; no single method is clearly superior. The choice of a specific coupling technique is determined by the desired application and the facilities available. Thus, a knowledge of coupler characteristics is necessary for the designer. The various beam couplers for planar guides can be classified into two principal categories: (1) transverse couplers, in which the beam is focused on an exposed cross-section of the guide, and (2) longitudinal couplers, in which the beam is incident obliquely onto the guide. The former category is also called the direct focusing technique, whereas the latter involves the use of an auxiliary optical component, such as a prism or grating.

A. Direct Focusing

The simplest method of coupling a laser beam to a slab waveguide is the direct focusing or end-firing approach. This may be accomplished by means of a focusing lens. A typical coupler of the transverse variety is shown in Figure 9A. The conversion of beam energy to a given waveguide mode is achieved by matching the beam-field to the waveguide mode field. This is particularly useful for coupling laser beams to the fundamental waveguide mode because of the similarity between the gaussian beam profile and the TE_0 mode shape. In principle, the coupling efficiency could be nearly 100%. However, in practice, the match between laser beam, lens, and guiding film (on the order of microns) requires sensitive micromanipulation and critical alignment. If any mismatch occurs, energy will be lost into unwanted scatterings. Also, the imperfection of the waveguide end will also reduce the coupling efficiency. End-firing techniques are often used because of their convenience and conceptual easiness, yet, the difficulty of maintaining alignment limits their application.

B. Prism Coupling

In cases where the waveguide's end face is not exposed or not clear-cut, a longitudinal coupling technique has to be used. The operation of a prism coupler is illustrated in Figure 9B. In this scheme, a laser beam is introduced at the prism base at a specific angle. The coupling mechanism involves applying pressure on top of the prism against the waveguide surface. The coupling strength can be controlled by adjusting the air gap between the prism and waveguide. If the air spacing is small enough so that the evanescent tails of the prism modes overlap the tails of the waveguide mode, there is coherent coupling of energy from the prism mode to the waveguide mode. The principle of the operation is based on optical tunneling.[28]

An important requirement for the prism is that the refractive index must be greater than that of the waveguide. This is because the incident angle at the prism interface must satisfy both the total reflection condition and the phase-matching condition. Strontium titanate, Rutile, and dense flint glass are common materials for the prism. In addition, the incident beam must be highly collimated because of the critical angular dependence of the coupling efficiency for a given mode. The incidence must also exactly intersect the right-angle corner of the prism, otherwise, maximum coupling efficiency will not be achieved.[29]

If the waveguide allows more than one mode to propagate (i.e., multimode waveguide), light can be coupled in at specific angles corresponding to each mode. Because of this characteristic, it is possible to launch a desired mode somewhat preferentially. To couple the guided wave out of the slab waveguide by reciprocity, a decoupling prism is used. The various modes constituting the light beam will emerge from the prism at different angles. When these beams are intercepted by a screen, each one of them appears as a bright line, thus producing a set of what is called "m-line" mode profiles, where m corresponds to particular mode numbers. These m-lines are subject to the physical properties of the planar waveguide. Therefore, the prism coupler setup can be used as an analytical tool to investigate the refractive index, the thickness of the film, and the chemical properties at the interface.[30,31]

C. Grating Coupling

The grating coupler, like the prism coupler, functions to produce a phase matching between a particular waveguide mode and an optical beam which is incident at an oblique angle to the surface of the waveguide. The prism and air-gap configuration is replaced by a grating layer, as shown in Figure 9C. The coupling operation takes advantage of the Bragg effect caused by the slant fringed pattern. The coupling efficiency depends strongly on the blaze angle, spacing, and thickness of the grating bars.[32] Grating couplers can be more mode-selective than a prism due to the fixed blaze angle. It can also be used as an output coupler. Perhaps the greatest disadvantage of the grating coupler is that it is fairly difficult to fabricate. A sophisticated holographic process with photomasking and etching techniques is mandatory. Once fabricated, however, it is an integral part of the waveguide structure. The coupling effi-

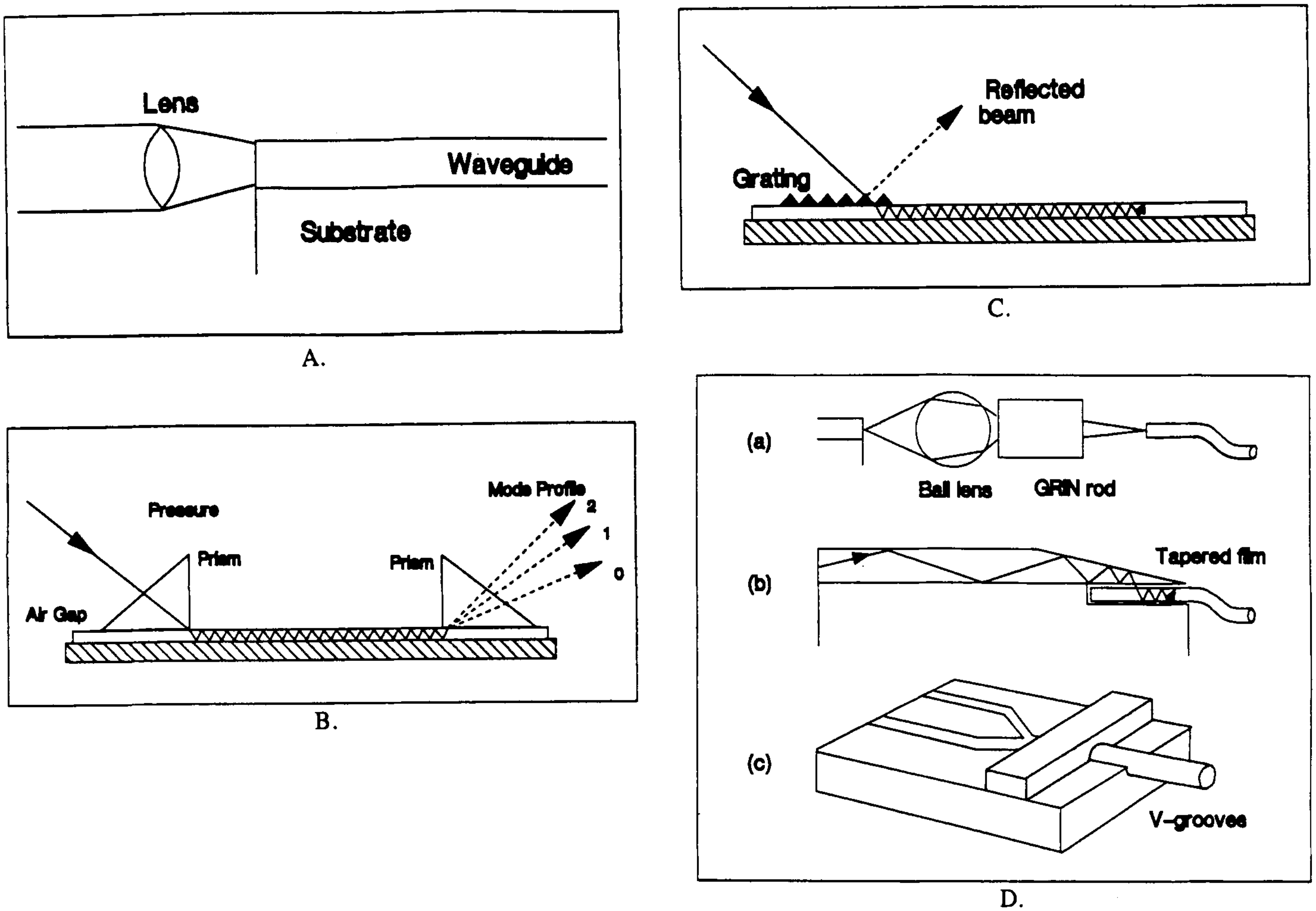


FIGURE 9. (A) Direct focusing techniques. (B) Prism coupling techniques. (C) Grating coupling techniques. (D) Typical waveguide-fiber optic couplers.

ciency remains constant and is not altered by vibration or ambient conditions. Hence, the grating coupler is promising for integrated optics applications.

D. Optical Fiber Coupling

The usefulness of an optical fiber is its ability to carry information over a long distance. Slab waveguides and fiber optics can cooperate and together offer signal processing powers and remote control capabilities. The difficulty lies primarily in the fact that the fiber core is relatively small and therefore it is difficult to connect it to a slab waveguide in such a manner that the coupling efficiency is high enough. Recent studies have shown that some optical components and mechanical connectors, such as ball lens and GRIN (GRaded INdex) rod (shown in Figure 9D), can be used to facilitate end-on alignment of the fiber and waveguide.[33] Tapered film fiber couplers provide a more rigid coupling scheme.[34] Embossed V-grooves techniques have been applied to the problem of aligning a channel waveguide with a single-mode fiber.[35,36] These methods apply mechanical pressure and refractive index matching fluid to clamp the fiber onto slab waveguides, as shown in Figure 9D. These research areas have ample room to grow.

VII. APPLICATIONS TO CHEMISTRY

Thick and thin slab waveguides have been used to replace and improve conventional optical components for chemical analyses in a number of ways. Spectroscopists can gather spectral information about surface molecules. Chemists have already looked at several surface reactions, such as adsorption, wetting, chemical bonding, and energy transfer at the planar interface. Sensors developers have tried to make transducers with small dimensions based on various optical characteristics.

There are several fundamental advantages in performing spectroscopic measurements in slab waveguides: (1) high power throughput, (2) small physical dimension, (3) unique detection scheme, and (4) a typical streak-like geometry. High power throughput results from the small aperture of the thin film. The optical power emerges into a decreased cross-sectional area propagating as a guided wave that can increase its irradiance by approximately 1000-fold.[37] Also, emitted energy from samples on the surface will be largely trapped and concentrated into a narrow edge of the element due to the angular emission distribution.[38] Therefore, experiments that depend on the irradiance of the excitation or emission can be aided greatly. Small physical dimension is a fundamental characteristic of the guided wave. Since the optical interaction region is in the thin film or at the interface with the guided beam, the bulk of the sample can be ignored. This can reduce the sample size to a great extent and provide the requisite optical sensitivity at monolayer levels.[39] Unique detection schemes can be developed because of the different spatial energy distributions of various modes. The energy profiles of various modes with their evanescent tails characterized by different electric-field amplitude distributions can provide the experimenter with a spatially tunable energy source.[40,41] Analytes with strong absorbance or imbedded in complex scattering matrices, which cannot be analyzed by conventional transmission spectroscopic techniques, can be accommodated by this technique.[42] Also, the orientation of the organic molecules in a Langmuir-Blodgett film can be probed by selectively launching orthogonal TE or TM modes. Thus, geometrical information of a thin film, such as symmetry and birefringence, can be obtained by this scheme.[43,44] In addition, the natural structure of the guided wave is that of a long streak of radiation. This structure can be easily imaged into the entrance slit of a spectrometer. The optical sensitivity may be enhanced by elongating the waveguiding distance. Finally, one should recall that one of the strongest reasons for investigating the use of slab waveguides is that the energy distribution is a great deal simpler, physically and theoretically, than that in cylindrical fiber optics. Also, slab waveguides are rigid and hence less susceptible to the pressure fluctuations than their cylindrical counterparts.

A. Absorption Studies

Midwinter has demonstrated that the thin film slab waveguide can be 1000-fold more sensitive than an ATR device and comparable to conventional transmission techniques.[45] Polky and Harris[46] concluded that both direct bulk absorption and absorption by adsorbed molecules from the evanescent portion of the beam were responsible for the power attenuation. The evanescence absorption by bilirubin in whole blood has been measured.[47] Spectra of some organic monolayers have been obtained by using guided wave techniques.[48,49]

B. Raman Studies

Levy et al.[50] first examined the Raman spectra of very thin polymer films by casting them on a substrate and using them as planar waveguides. Surface-enhanced Raman effects on thin film waveguides were recently reported.[51,52] Coherent anti-Stoke Raman scattering (CARS) is one of many different Raman processes developed by Stegeman, Hetherington, and coworkers.[53,54] The principle is based on a nonlinear conversion of two surface beams into a coherent, laser-like Raman beam of high intensity in the anti-Stoke region. The emission is often many orders of magnitude greater than normal Raman spectrometry. Since this wavemixing process is executed with the evanescent field outside the waveguide, the surface Raman effect can provide spectral information of surface-active materials with exceptional sensitivity. Several waveguide CARS experiments have produced the spectra of monolayer adsorbates on ZnO waveguide surfaces.[55,56]

C. Fluorescence Studies

Fluorescence excitation by evanescent waves, introduced by Hirschfeld,[57] opens up another domain for waveguide studies. Recent work has been done by Lok et al.,[58] and Andrade et al.[59,60] The fluorescence emission can be picked up at right angles or it may be trapped inside the waveguide and collected at the end face. The in-bound fluorescence intensity is reportedly enhanced by one order of magnitude in comparison with that emitted at right angles.[61] The pre- and postfiltering effects, which are nuisances in fluorometric measurements, can be minimized because the excitation and emission energy no longer travels through the solution bulk. This may correct for the nonlinearity of fluorescence measurements at high concentrations.[62]

D. Surface Plasmon Studies

Optical surface plasmon resonance (SPR) was first demonstrated by Kretschmann and Raether[63] and Otto.[64] The phenomenon was observed by an ATR technique with a thin metal film deposited, as shown in Figure 10B, the so called Kretschmann configuration. The surface plasmon can be described as a collective oscillation in the free electron plasma at a metal boundary.[65] These oscillations can be produced by the electric field of an incident beam with parallel (TM) polarization. At the metal-air interface, the evanescent field will be amplified when compared to that without a metal film. This is one reason for the high sensitivity of SPR. The other is that the angular position of the resonance is very sensitive to variations in the refractive index of the medium just outside the metal film, such as adsorbates at the metal surface. This is a new optical technique in the field of chemical sensing.[66-68] It is proposed that the sensitivity can be enhanced by using multiple internal reflection (MIR) attachments.[69]

E. Spectroelectrochemistry Studies

Thin layer electrochemical techniques were developed by Kuwana and Heineman.[70] They involve introducing the optical beam through the back side of a transparent electrode at an angle greater than the critical angle so that the beam is totally reflected, as shown in Figure 10C. Spectral changes near the

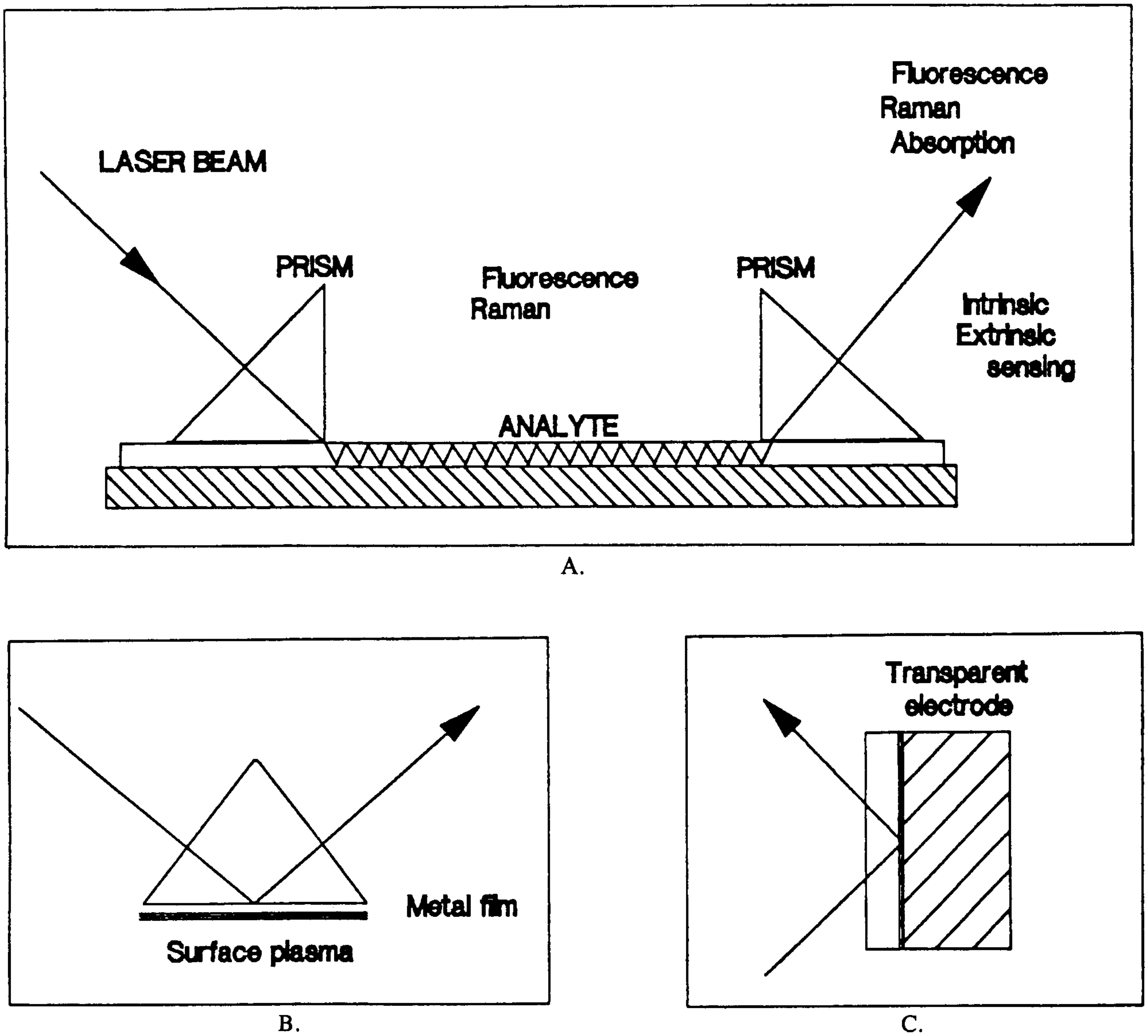


FIGURE 10. (A) Detection schemes of slab waveguides. (B) Kretschmann devices. (C) Spectroelectrochemistry applications.

electrode are observable due to the small penetration of the evanescent field into the solution. Thus, spectral measurements and the electrogeneration process can be simultaneously monitored. The technique is useful in probing electrochemical phenomena at the electrical double layer when the solution undergoes electrolysis. Sensitivity can be enhanced by multiple reflections.[71]

F. Extrinsic Chemical Sensor Studies

Another important application of slab waveguides is the incorporation of chemically specific agents onto the waveguide surface as chemical sensors. This leads to the opportunity for studies directed at biosensing technologies, such as affinity sensors, catalytic biosensors, and metabolic and enzymatic sensors.[72-74]

Tiefenthaler and Lukosz[75] have used a very thin film glass waveguide to develop a gas sensor. Bohn[76] later extended the theory to cover perturbation of the guided beam in a planar guide by a surface adlayer. Andrade et al.[77] have shown the potential use of a fluoroimmunoassay technique that can fluorescently identify labeled antigens complexed with surface immobilized antibodies on slab waveguides.

G. Intrinsic Chemical Sensor Studies

Chemical sensors can be built based on intrinsic changes in the elasto-optic parameters of the waveguides. These intrinsic changes may be brought about by environmental alterations, such as temperature and pressure. Many temperature, pressure, and magnetic sensors based on various transduction mechanisms such as interferometric splitting[78-80] and mode conversion,[81] have been proposed using slab waveguides.

VIII. FUTURE PROSPECTS

One of the major driving forces in modern technology is to seek miniaturization of form and function, and the slab waveguide has unique properties that serve this trend. Monolithic integrated optic systems are ready to leave the laboratory and enter commercial applications. These opto-electronic devices complement their fiber optic equivalent and can offer miniaturization and integration of the source, with modulation and detection elements on the same substrate.[82] The technique offers a new realm for the development of microsensors and microinstrumentation based on slab waveguides.[83] There are few technological or material problems impeding the development of waveguide microsensors. Instead, the largest stumbling block is the lack of explicitly defined application areas in which planar microsensors can perform in a clearly superior way. This requires the practicing analytical chemist to consider them as alternatives to more classical techniques and fiber optics. The field of slab waveguides will continue to grow as the need for robust, versatile, and integrated sensors increases.

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REFERENCES

1. **Osterberg, H. and Smith, L. W.**, *J. Opt. Soc. Am.*, 54, 1073, 1964.
2. **Harrick, N. J.**, *Phys. Rev. Lett.*, 4, 224, 1960.
3. **Fahrenfort, J.**, *Spectrochim. Acta*, 17, 698, 1961.
4. **Angel, S. M. and Myrick, M. L.**, *Anal. Chem.*, 61, 1648, 1989.
5. **Stephens, D. A. and Bohn, P. W.**, *Anal. Chem.*, 61, 386, 1989.
6. **Ives, J. T., Reichert, W. M., Suci, P. A., and Andrade, J. D.**, *J. Opt. Soc. Am.*, 2, 53, 1985.
7. **Matsubara, K., Kawata, S., and Minami, S.**, *Appl. Opt.*, 27, 1160, 1988.
8. **Richmond, G. L.**, *Surf. Sci.*, 147, 115, 1984.
9. **Dessy, R. E.**, *Anal. Chem.*, 61, 1079A, 1989.
10. **Hecht, E. and Zajac, A.**, *Optics*, Addison-Wesley, Reading, MA, 1979, 71.
11. **Tamir, T.**, *Topics in Applied Physics: Integrated Optics*, Springer-Verlag, Berlin, 1982, 25.
12. **Haavind, R.**, *High Technol.*, November/December, 35, 1982.
13. **Marcuse, D.**, *Light Transmission Optics*, Academic Press, New York, 1974.
14. **Harrick, N. J.**, *Internal Reflection Spectroscopy*, John Wiley & Sons, New York, 1979.
15. **Ramaswamy, V. and Kogelnik, H.**, *Appl. Opt.*, 13, 1857, 1974.
16. **Kapany, S. and Burke, B.**, *Optical Waveguides*, Academic Press, New York, 1972.
17. **Miller, D. R. and Bohn, P. W.**, *Appl. Spectrosc.*, 41, 249, 1987.
18. **Hunsperger, R. G.**, *Integrated Optics: Theory and Technology*, Springer-Verlag, Berlin, 1982, 47.
19. **Giuliani, J. F., Kim, K. H., and Butler, J. E.**, *Appl. Phys. Lett.*, 48, 1311, 1986.
20. **Findakly, T.**, *Opt. Eng.*, 24, 244, 1985.
21. **Zhenguang, H., Srivastava, R., and Ramaswamy, R. V.**, *J. Lightwave Technol.*, 7, 1590, 1989.
22. **Booth, B. L.**, *J. Lightwave Technol.*, 7, 1445, 1989.
23. **Leppihalme, M. and Viljanen, J.**, *J. Appl. Phys.*, 51, 3563, 1980.
24. **Owyang, G. H.**, *Foundations of Optical Waveguides*, Elsevier, New York, 1981, 192.
25. **Keiser, G.**, *Optical Fiber Communications*, McGraw-Hill, New York, 1983, 21.
26. **Raine, K. W., Baines, J. G. N., and Putland, D. E.**, *J. Lightwave Technol.*, 7, 1162, 1989.
27. **Robertson, M. J., Kendall, P. C., Ritchie, S., McIlroy, P. W. A., and Adams, M. J.**, *J. Lightwave Technol.*, 7, 2105, 1989.
28. **Tien, P. K. and Ulrich, R.**, *J. Opt. Soc. Am.*, 60, 1325, 1970.
29. **Tamir, T.**, *Optik*, 37, 204, 1973.
30. **Tien, P.**, *Rev. Mod. Phys.*, 49, 361, 1977.
31. **Bohn, P. W.**, *Spectroscopy*, 3, 38, 1987.
32. **Tamir, T. and Peng, S. T.**, *Appl. Phys.*, 14, 235, 1977.
33. **Kitano, I., Toyama, M., and Nishi, H.**, *Appl. Opt.*, 22, 396, 1983.
34. **Seligson, J.**, *Appl. Opt.*, 26, 2609, 1987.
35. **Hillerich, B., Rode, M., and Gottsmann, H.**, *J. Lightwave Technol.*, 7, 1654, 1989.
36. **Sheem, S. K. and Giallorenzi, T. G.**, *Opt. Lett.*, 3, 73, 1978.
37. **Stephens, D. A. and Bohn, P. W.**, *Anal. Chem.*, 59, 2563, 1987.
38. **Lee, E., Benner, R. E., Fenn, J. B., and Chang, R. K.**, *Appl. Opt.*, 18, 862, 1979.
39. **Swalen, J. D.**, *J. Phys. Chem.*, 83, 1348, 1979.
40. **Miller, D. R., Han, O. H., and Bohn, P. W.**, *Appl. Spectrosc.*, 41, 245, 1987.
41. **Harris, J. H. and Shuberg, R.**, *IEEE Trans. Microwave Theory Tech.*, MTT-19, 269, 1971.
42. **Chabay, I.**, *Anal. Chem.*, 52, 1071A, 1982.
43. **Swalen, J. D., Rieckhoff, K. E., and Tacke, M.**, *Opt. Commun.*, 24, 146, 1987.
44. **Naselli, C., Rabolt, J. F., and Swalen, J. D.**, *J. Chem. Phys.*, 82, 2136, 1985.
45. **Midwinter, J. E.**, *IEEE J. Quant. Electr.*, QE-7, 339, 1971.
46. **Polky, J. N. and Harris, J. H.**, *J. Opt. Soc. Am.*, 62, 1081, 1972.
47. **Mitchell, G. L.**, *IEEE J. Quant. Electr.*, QE-13, 173, 1977.
48. **Swalen, J. D., Schlotter, N. E., Santo, R., and Rabolt, J. F.**, *J. Adhesion*, 13, 189, 1981.
49. **Stephens, D. A. and Bohn, P. W.**, *Anal. Chem.*, 61, 386, 1989.
50. **Levy, Y., Imbert, C., Cipriani, J., Racine, S., and Dupeyrat, R.**, *Opt. Commun.*, 11, 66, 1974.
51. **Rabolt, J. F., Santo, R., and Swalen, J. D.**, *Appl. Spectrosc.*, 34, 517, 1980.

52. Iwamoto, R., Ohta, K., Miya, M., and Mima, S., *Appl. Spectrosc.*, 35, 584, 1981.
53. Stegeman, G. I., Fortenberry, R., Karaguleff, C., Moshrefzadeh, R., Hetherington, W. M., III, Van Wyck, N. E., and Sipe, J. E., *Opt. Lett.*, 8, 295, 1983.
54. Hetherington, W. M., III, Van Wyck, N. E., Koenig, E. W., Stegeman, G. I., and Fortenberry, R. M., *Opt. Lett.*, 9, 88, 1984.
55. Ho, Z. Z., Wijekoon, W. M. K. P., Koenig, E. W., and Hetherington, W. M., III, *J. Phys. Chem.*, 91, 760, 1987.
56. Wijekoon, W. M. K. P., Ho, Z. Z., and Hetherington, W. M., III, *J. Chem. Phys.*, 86, 4384, 1987.
57. Hirschfeld, T. E., *Can. Spectrosc.*, 10, 128, 1965.
58. Lok, B. K., Cheng, Y. L., and Robertson, C. R., *J. Coll. Interface Sci.*, 91, 104, 1983.
59. Andrade, J. D., Van Wegenen, R. A., Grepanis, D. E., Newby, K., and Lin, J. N., *IEEE Trans. Electron. Devices*, ED-32, 1175, 1985.
60. Ives, J. T., Reichert, W. M., Suci, P. A., and Andrade, J. D., *J. Opt. Soc. Am.*, 2, 53, 1985.
61. Lee, E., Benner, R. E., Fenn, J. B., and Chang, R. K., *Appl. Opt.*, 18, 862, 1979.
62. Angel, S. M., *Spectroscopy*, 2, 38, 1987.
63. Kretschmann, E. and Raether, H., *Z. Naturforsch.*, 23a, 2135, 1968.
64. Otto, A., *Z. Physik*, 216, 389, 1968.
65. Raether, H., *Surface Plasma Oscillations and Their Applications: Physics of Thin Films*, Vol. 9, Academic Press, New York, 1977, 145.
66. Kooyman, R. P. H., Kolkman, H., Van Gent, J., and Greve, J., *Anal. Chim. Acta*, 213, 35, 1988.
67. Lloyd, J. P., Pearson, C., and Petty, M. C., *Thin Solid Films*, 160, 431, 1988.
68. Matsubara, K., Kawata, S., and Minami, S., *Appl. Opt.*, 27, 1160, 1988.
69. Bender, W. J. H., Ph.D. proposal, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, 1989.
70. Kuwana, T. and Heineman, W. R., *Acc. Chem. Res.*, 9, 241, 1976.
71. Heineman, W. R., *Anal. Chem.*, 50, 390A, 1978.
72. Moon, B., *Sensor Rev.*, 8(3), 121, 1988.
73. Krull, U. J., *Can. Chem. News*, March, 13, 1988.
74. Scheller, F., Tan, P. M., and Moritz, W., *Analyst*, 114, 653, 1989.
75. Tiefenthaler, K. and Lukosz, W., *Opt. Lett.*, 10, 137, 1984.
76. Bohn, P. W., *Anal. Chem.*, 57, 1203, 1985.
77. Andrade, J. D., Herron, J., Lin, J. N., Yen, H., and Kopeckova, P., *Biomaterials*, 9, 76, 1988.
78. Johnson, L. M., Leonberger, F. J., and Pratt, G. W., *Appl. Phys. Lett.*, 41, 134, 1982.
79. Izutsu, M., Enokihara, A., and Sueta, T., *Technical Digest, 2nd Eur. Conf. on Integrated Optics*, SPIE, Firenze, Italy, 1983, 144.
80. Izutsu, M., Enokihara, A., and Sueta, T., *Electron. Lett.*, 18, 867, 1982.
81. Shah, M., Crow, J. D., and Wang, S., *Appl. Phys. Lett.*, 20, 66, 1972.
82. Valette, S., *Electron. Lett.*, 19, 883, 1983.
83. Murray, R. W., Dessy, R. E., Heineman, W. R., Janata, J., and Seitz, W. R., *Chemical Sensors and Microinstrumentation*, ACS Symp. Ser. 403, American Chemical Society, Washington, D.C., 1989.