Planar wave guides as chemical and biological sensors

by

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Introduction

Wave guides are films or fibers made of high refractive index material embedded between/in lower index materials. If the light wave introduced into the high index film or fiber arrives to the boundary at an angle which is greater than the critical angle of total reflection the light wave is confined inside the wave guide. The multiple reflected wave components interfere with each other. The interference is constructive supposing the phase change during travelling across the film plus those due to reflectance from both boundaries of a planar wave guide is integer multiple of 2π . In this case, a stationary guided light mode results that travels along the length of the wave guide with an effective propagation velocity and the amplitude of the electromagnetic field varying along the cross section of the wave guide (Figs. 1.,2.,3.) We define the *effective refractive index of the guided mode N* as the ratio of the speed of light in vacuum and the effective speed in the wave guide. N is different for the different modes and depend not only on the refractive index and thickness of the wave guiding film but also on the surrounding. To excite the guided mode the light should be *coupled into the wave guide* either from the cross section or from the surface with a prism or grating. Detecting the guided modes we get information about the refractive index of the material that covers the wave guide film or both the refractive index and thickness of a deposited thin layer can be determined. In the first case the wave guide is used as *refractometer.* In the second case, it can be used as a *sensor for a specific molecule* if it is coated with a mono molecular chemoresponsive layer that makes this molecule selectively adsorbed on the surface. Both the refractive index and the thickness of the adsorbed layer can be determined and the process of adsorption in situ monitored.

The structure of a planar grating coupler sensor chip

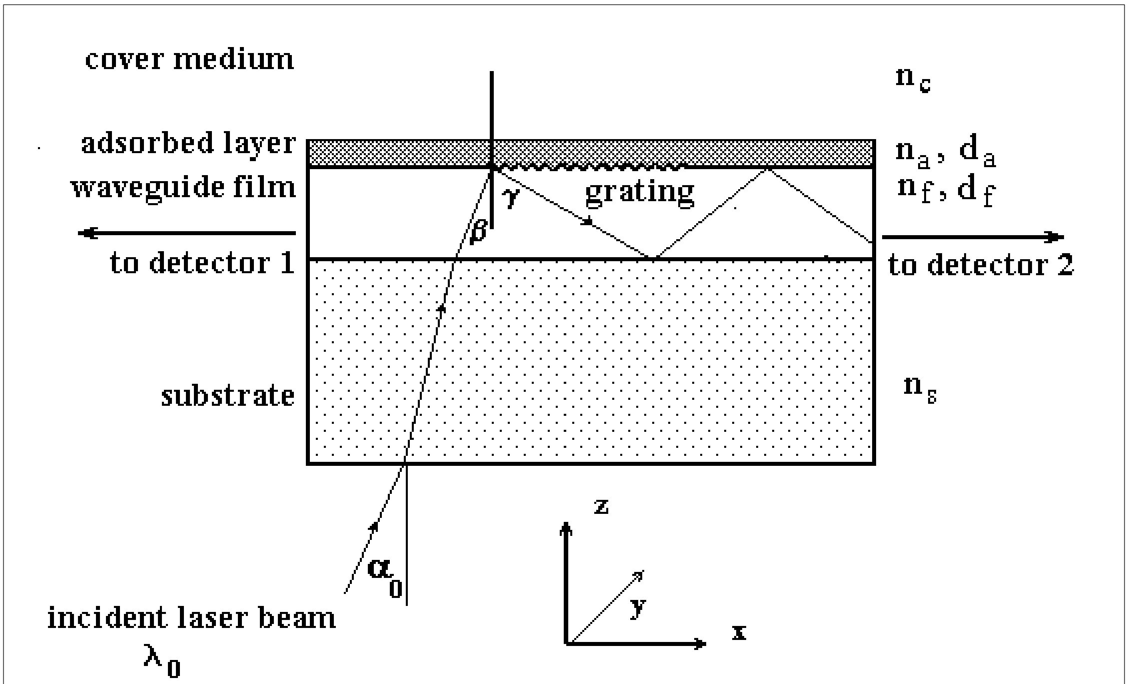

Fig. 1. Principle of the wave guide sensor. At certain angles of incidence a *, modes are excited and detected. Either* n_c or n_f *and* d_f *or* n_a, d_a *can be determined by detecting the angles* a_{TE} *and* α_{TM} *where the transversal electrical TE and the transversal magnetic TM modes, respectively, are excited*.
n_c is refractive index of the covering medium, n_a is refractive index of the adsorbed layer , d_a is its thickness; n_f is refractive index of the wave guide, d_f is its thickness; N is the effective refractive index of the wave guide; l_0 is the vacuum wavelength of the laser light incident upon the sensor chip and exciting the guided mode by the grating, of grating period D; a is the angle of incidence of the laser beam (in air), β is the angle of incidence at the grating, γ is the angle between the diffracted beam and the normal of the wave guide film: this is the direction of propagation of the plane waves which are totally reflected at the boundaries.

Optics of Planar Wave guides

Consider the wave guiding chip in Fig. 1 laterally infinite and homogeneous. For such geometry, the electromagnetic field is composed from plane waves. We choose the (*xy*) plane of the co-ordinate system parallel to the interfaces in the chip, with the axis *x* pointing along the wave guide. The axis *z* is perpendicular to the interfaces. The propagation vector of the incident monochromatic light, a plane wave of wavelength λ_0 , lays in the plane *(xz).* As the system is homogeneous in the direction *y* **E** and **H** depend only on *x* and *z*. Applying the complex notation , the electromagnetic field intensities can be described as combinations of plane waves of form

$\mathbf{A} = \mathbf{A_0} \exp(\, i\,(\omega t - k_x x - k_z z)\,)$. (1)

A means either the electric field intensity **E** or the magnetic field intensity **H**. k_x and k_z are the components of the propagation vector **k** (or wave vector) and ω is the angular frequency. (It is easy to calculate with complex exponentials of the form (1) and we get the real field intensities as the real part of the resulting complex field.)
The electromagnetic field intensities obey Maxwell's equation. For no external currents and charges

rot $\mathbf{H} = \partial \mathbf{D}/\partial t$ (I)

rot $\mathbf{E} = -\partial \mathbf{B}/\partial t$ (II)

(2)

div$\mathbf{D} = 0$ (III)

div$\mathbf{B} = 0$ (IV).

If all media are isotropic and transparent the relation between **D** and **E** and **B** and **H** are

$\mathbf{D} = \varepsilon \mathbf{E}$, $\mathbf{B} = \mu \mathbf{H}$ (“material equations”) (2a)

where ε is the permittivity and μ is the magnetic permeability of the medium.

The boundary condition require continuity for those components of both **E** and **H** which are parallel to the interface between two different media.

In the layered structure in Fig 1., ε and μ are assumed constant inside a layer that is, our system is piece wisely homogeneous. All components of the electromagnetic field in a homogeneous medium satisfy the wave equation:

$\partial^2 A/\partial x^2 + \partial^2 A/\partial z^2 + \varepsilon\mu\, \partial^2 A/\partial t^2 = 0$, (3)

Inserting the function (1) for A in the wave equation the so called dispersion relation is obtained for the magnitude of propagation vector **k**:

$^3\ \mathbf{k}^{2\,3} = k_x^2 + k_z^2 = \omega^2 \varepsilon \mu = k_0^2\, \varepsilon_{r\mu\, r}$

$\varepsilon_{r,\mu r}$ are the relative permittivity and permeability, respectively, $k_0 = 2\pi/\lambda_0$ and $\lambda_0 = 2\pi c/\omega$ is the wavelength in vacuum. As μ_r is practically unity at the optical frequencies, we can write that

$k_x^2 + k_z^2 = (k_0 n)^2$, (4)

where $n=\sqrt{(\varepsilon_r)}$ is the refractive index of the medium.

There are two independent systems of solution of Maxwell's equations concerning the direction of the field vectors:

The ***Transversal Electric (TE) Mode:*** The electric field **E** is perpendicular to the plane of incidence, and the magnetic field **H** is parallel with it: $E_x = E_z = 0$, $E_y = E$, $H_y = 0$;

the ***Transversal Magnetic (TM) Mode:*** The magnetic field **H** is normal to the plane of incidence and the electric field **E** is parallel to it $H_x = H_z = 0$, $H_y = H$, $E_y = 0$.

We call $E_y = E$ and $H_y = H$ the “transversal field components” .

Once the field is a pure TE or TM mode in any medium of the system it stays the same everywhere. If the incident wave is a mixed mode the TE and TM components travel separately through the system and the resulting field intensity is the sum of both modes.

Inserting solutions of the form (1) for **E** and **H** in Eqs. 2, we get the relations between the components of the electromagnetic field and from that, the following boundary conditions for **E** and **H** are obtained:

TE mode:

$H_x = -i/(\mu\,\omega)\,\partial E/\partial z$, $H_z = i/(\mu\,\omega)\,\partial E/\partial x \rightarrow E$ and $\partial E/\partial z$ are continuous (as $\mu = \mu_0$). (5a)

TM mode:

$E_x = i/(\varepsilon\,\omega)\,\partial H/\partial z$, $E_z = -i/(\varepsilon\,\omega)\,\partial H/\partial x \rightarrow H$ and $1/\varepsilon\,\partial H/\partial z$ are continuous. (5b)

From the continuity of the tangential field components (E_{xy} , H_{xy}), it follows that k_x = const in the whole system,

$k_x = k_0 n_f \sin\gamma = k_0 N$ (Snell’s law). (6)

N is called the effective refractive index of the wave guide. From (4)

$k_z = \pm$û (n^2-N^2). (7)

The + sign corresponds to the travelling wave and the **-** sign to the reflected one. The field is composed from both a travelling wave and a reflected one in each medium:

$A(x,z)=\exp(i(\omega\, t-k_x))\,(A^+ \exp(-ik_z) + A^- \exp(ik_z))$ (8)

We will omit the dependence both on x and on the time t because they are the same in all media of the system. The z component of the propagation vector will be denoted according to the medium, in medium “i” it is

$k_i =$û $(n_i^2-N^2)$. (9)

Select the z=0 plane at the interface between the substrate and wave guide film. Assume that a light wave is excited somehow in the film and its direction of propagation ensures total reflectance at both boundaries that is, $N>n_c$ and $N>n_s$ holds. The multiple reflected waves give rise to a guided mode in the film, but there will be only one single wave travelling away from the wave guide in the infinite substrate and in the cover as well. The *z* dependence of the transversal field components in the different media is summarized in Table 1. :

Table 1. Electromagnetic Field in Different Media

medium	refractive index	z dependence of the field
substrate	n_s	$A_s \exp(ik_s z)$
wave guide film	n_f	$A_f^+ \exp(-ik_f z) + A_f^- \exp(ik_f z)$
adsorbed layer	n_a	$A_a^+ \exp(-ik_a(z-d_f)) + A_a^- \exp(ik_a(z-d_f))$
covering medium	n_c	$A_c \exp(-ik_c(z-d_f-d_a))$

We will apply the boundary conditions (5) separately for both the TE and TM modes. First we omit the adsorbed layer; assume that the covering medium joins directly to the wave guide film. (Table 2.)

Table 2. Three Medium Wave guide: Boundary Conditions

TE mode	TM mode
z=0 : (10a)	z=0 : (10c)
$E_s=E_f^+ + E_f^-$,	$H_s=H_f^+ + H_f^-$,
$i\, k_s E_s = -ik_f (E_f^+ - E_f^-) \rightarrow$	$i/\varepsilon_s k_s H_s = -i/\varepsilon_f k_f (H_f^+ - H_f^-) \rightarrow$
$\boldsymbol{r_{fs}} = E_f^+/E_f^- = (k_f - k_s) / (k_f + k_s)$	$\boldsymbol{r_{fs}} = H_f^+/H_f^- = (k_f/\varepsilon_f - k_s/\varepsilon_s)/(k_f/\varepsilon_f + k_s/\varepsilon_s)$
$z=d_f$: (10b)	$z=d_f$: (10d)
$E_f^+ \exp(-ik_f d_f) + E_f^- \exp(ik_f d_f) = E_c$	$H_f^+ \exp(-ik_f d_f) + H_f^- \exp(ik_f d_f) = H_c$
$-ik_f (E_f^+ \exp(-ik_f d_f) - E_f^- \exp(ik_f d_f))=$	$-i/\varepsilon_f k_s (H_f^+ \exp(-ik_f d_f) - H_f^- \exp(ik_f d_f))=$
$= -ik_c E_c \rightarrow$	$= -i/\varepsilon_c k_c H_c \rightarrow$
$\boldsymbol{r_{fc}} = E_f^- \exp(ik_f d_f) / (E_f^+ \exp(-ik_f d_f))=$	$\boldsymbol{r_{fc}} = E_f^- \exp(ik_f d_f) / (E_f^+ \exp(-ik_f d_f))=$
$=(k_f - k_c) / (k_f + k_c)$	$=(k_f/\varepsilon_f - k_c/\varepsilon_s)/(k_f/\varepsilon_f + k_c/\varepsilon_s)$
$\rightarrow \boldsymbol{r_{fs}}\, \boldsymbol{r_{fc}} \exp(-i2k_f d_f)=1$	$\rightarrow \boldsymbol{r_{fs}}\, \boldsymbol{r_{fc}} \exp(-i2k_f d_f)=1$

The reflection coefficient can be defined at each boundary of a layer as the transversal field (E for the TE mode and H for the TM mode) intensity of the wave reflected from the boundary divided by field intensity in the wave which is incident upon the boundary. The wave, which travels in the wave guide film towards the substrate (in -z direction), is incident at the interface with the substrate at z=0 and the reflected wave travels towards +z from here. At the interface with the covering medium ($z=d_f$), however, the +z direction belongs to the incident wave and the -z direction means the reflected one. The continuity requirements (10) at each interface result in the same condition for the existence of a guided wave in the film, for both the TE and the TM mode:

$\boldsymbol{r_{fs}}\, \boldsymbol{r_{fc}} \exp(-i2k_f d_f)=1$, (11a)

The absolute value of the product $\boldsymbol{r_{fs}}\ \boldsymbol{r_{fc}}$ must be unity, which means that if one reflection coefficient is smaller than one the other must be larger than one. The magnitude of the reflected wave can not be larger than that of the incident wave, therefore both reflection coefficients have unit absolute value. That is $\boldsymbol{r}_{fs}=\exp(i\psi_{fs})$, $\boldsymbol{r}_{fc}=\exp(i\psi_{fc})$ and the guiding condition is

$\psi_{fs}+\psi_{fc}-2k_f d_f = 0$ ñ $2\pi m$. (11b)

That means guided mode can exist only if the phase changes due to the reflectance at both boundaries ψ_{fs} and ψ_{fc} and the phase shift $-2k_f d_f$ during travelling through the layer add up resulting in integer multiple of 2π .
For total reflection, both $n_c < N$ and $n_s < N$ should hold. That means that both k_c and k_s are imaginary $k_s=-i| k_s|$, $k_c=-i| k_c|$. The waves can not travel either in the substrate or in the cover: although the field penetrates into those media its intensity exponentially decreases with the distance from the interface. The phase of the reflectance coefficients can be derived from Table 2.

For the TE mode

$\boldsymbol{r}_{fs}=(k_f - i | k_s |) / (k_f + i | k_s|)$, $\boldsymbol{r}_{fc}=(k_f - i | k_c |) / (k_f + i | k_c|)$,

$\psi_{fs}= 2\mathrm{arctg}(| k_s| /k_f)$, $\psi_{fc}=2\mathrm{arctg}(| k_c| /k_f)$, (12a)

and for the TM mode:

$\boldsymbol{r}_{fs}= (k_f /\varepsilon_f -i | k_s | /\varepsilon_s) / (k_f /\varepsilon_f + i | k_s | /\varepsilon_s)$, $\boldsymbol{r}_{fc}= (k_f /\varepsilon_f -i | k_c | /\varepsilon_c) / (k_f /\varepsilon_f + i | k_c | /\varepsilon_c)$,

$\psi_{fs}= 2\mathrm{arctg}(| k_s| / k_f\, \varepsilon_f /\varepsilon_s)$, $\psi_{fc}=2\mathrm{arctg}(| k_c| / k_f\, \varepsilon_f /\varepsilon_c)$. (12b)

Four Medium Wave guide

If there is an adsorbed layer between the wave guide film and the cover the guiding condition is analogous to (12)

$\boldsymbol{r}_{fs}\ \boldsymbol{r}_{fac} \exp(-i2k_f d_f)=1$, $\psi_{fs}+\psi_{fac}-2k_f d_f= 0$ (13)

where $\boldsymbol{r_{fac}}$ means the reflection coefficient at the film-adlayer interface. As total reflection must happen either at the film-adlayer or at the adlayer-substrate interface, ³ $\boldsymbol{r}_{fac}$³ =1, but the phase change during reflectance is influenced by the adsorbed layer.

We use again the boundary conditions to derive the expression for $\boldsymbol{r}_{fac}$**:**

At $z=d_f$:

$E_f^+\exp(-ik_f d_f)+E_f^-\exp(k_f d_f)=E_a^+ +E_a^-$

$-ik_f(E_f^+\exp(-ik_f d_f)-E_f^-\exp(k_f d_f))=-ik_a(E_a^+-E_a^-)$,

and at $z=d_f+d_a$:

$E_a^+\exp(-ik_a d_a)+E_a^-\exp(k_a d_a)=E_c$

$-ik_a(E_a^+\exp(-ik_a(d_f+d_a))-E_a^-\exp(k_a(d_f+d_a))= -ik_c E_c$,

hence

$\boldsymbol{r}_{fac}=(\boldsymbol{r}_{fa}+\boldsymbol{r}_{ac} \exp(-2ik_a(d_f+d_a)))/(1+ \boldsymbol{r}_{fa}\ \boldsymbol{r}_{ac} \exp(-2ik_a(d_f+d_a)))$, (14) where $\boldsymbol{r}_{fa}$ (TE) = $(k_f-k_a)/(k_f+k_a)$, $\boldsymbol{r}_{fa}$ (TM) = $(k_f/\varepsilon_f-k_a/\varepsilon_a)/(k_f/\varepsilon_f+k_a/\varepsilon_a)$ (14a)

are the "surface" reflection coefficient of the interface film-adlayer and

$\boldsymbol{r}_{ac}$(TE) = $(k_a-k_c)/(k_a+k_c)$, $\boldsymbol{r}_{ac}$ (TM) = $(k_a/\varepsilon_a-k_c/\varepsilon_c)/(k_a/\varepsilon_a+k_c/\varepsilon_c)$ (14b)

are those for the interface adlayer-cover.

The adsorbed layer is usually very thin compared to the wavelength that is , $2k_a d_a \ll 1$. We expand r_{fac} with respect to $2k_a d_a$ and stop at the linear term arriving at the approximate expression

$$r_{fac} = r_{fc} \exp\left(-2ik_a d_a \frac{r_{ac}(1-r_{fa}^2)}{(r_{fa}+r_{ac})(1+r_{fa}r_{ac})}\right) = r_{fc}\exp(-2ik_a d_a^{'})$$

(15)

d_a' is the effective thickness of the adsorbed layer. Inserting formulae (14a) and (14b) for the reflection coefficients in (15) we get the effective thickness for both modes

d_a'(TE) = $k_f/k_a\,(k_a^2-k_c^2)/(k_f^2-k_c^2) = k_f/k_a\,(n_a^2-n_c^2)/(n_f^2-n_c^2)\,d_a$ (16a)

d_a'(TM) = $(k_f/k_a)(n_a^2/n_f^2)\,((k_a/n_a^2)^2-(k_c/n_c^2)^2)\,/\,((k_f/n_f^2)^2-(k_c/n_c^2)^2)$ =

= $k_f/k_a\,(n_a^2-n_c^2)/(n_f^2-n_c^2)\,(1-N^2(n_c^2+n_a^2))/(1-N^2(n_c^2+n_f^2))d_a$ (16b)

From (14),

$\Psi_{fac}=\Psi_{fc}-2k_a d_a$'

with that and using (12) the guiding condition follows:

$\Psi_{fs}+\Psi_{fc}-2k_f d_f-2ik_a d_a$'= 0 ñ 2π m (m integer).

Using expressions (16) for d_a':

$\Psi_{fs}+\Psi_{fc}-2k_f\,(d_f-d_a\,(n_a^2-n_c^2)/(n_f^2-n_c^2)\,[\,(1-N^2(n_c^2+n_a^2))/(1-N^2(n_c^2+n_f^2))\,]^{\rho}) = 0$ ñ 2π m (17)

where
ψ_{fs}= 2arctg($|k_s|/k_f\,(n_f/n_s)^{2\rho}$), ψ_{fc}=2arctg($|k_c|/k_f\,(n_f/n_c)^{2\rho}$)

and ρ =0 in the case of TE mode and ρ =1 at TM mode. The components of the propagation vectors are:

$k_f=\sqrt{}\,(n_f^2-N^2)$, ³ k_s ³ $=\sqrt{}\,(N^2-n_a^2)$, ³ k_c ³ $=\sqrt{}\,(N^2-n_c^2)$.

Coupling the laser light into the wave guide

In order to excite the guided mode, light wave with appropriate propagation vector should be introduced into the wave guide. Appropriate direction of propagation means that the x component of the wave vector is $k_x=k_0N$. The coupling may be accomplished directly through the edge, but this is difficult as the wave guide layer is very thin. It is better to use coupling devices as prism or grating. We will discuss the grating method (Fig. 2.)

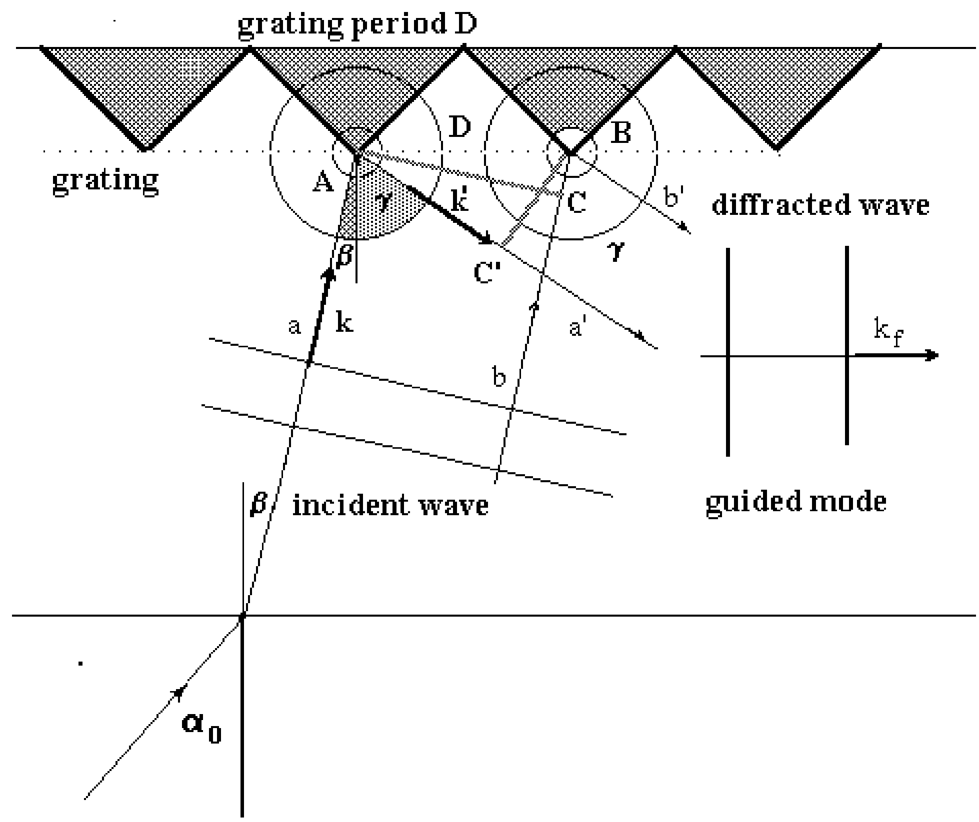

Fig. 2. Exciting the guided mode by a grating coupler

Fig. 2 shows the wave guide film equipped with a grating of period *D.* The light beam entering into the film makes an angle β with the normal of the layer. The propagation vector is **k**, with horizontal component $k_x= k_0n_f\sin(\beta)$.The electromagnetic field is constant all over a plane which is normal to **k** and it has the same value on every parallel planes with the phase difference of 2π m with respect to the original plane. These planes are called wave fronts**.** They are $\lambda = \lambda_0/n_f$ distance apart where λ is the wavelength in the film.

The incident light beam arrives to and is diffracted by the grating. According to Huyghens' principle, all points of the wave front (at the grating) are sources of elementary spherical waves and of these elementary waves new wave fronts form by interference. We can imagine that light rays are emitted from each period of the grating and the rays which emerge from the different periods of the grating and travel into the same direction interfere with each other and make a new, diffracted wave. The diffracted light wave is most intense in those direction where the phase difference between the rays which emerge from neighboring periods of the grating is integer multiple of 2π (or we can say that the optical path difference between them is integer multiple of the wavelength λ_0). The rays ***a*** and ***b*** reach the grating at points **A** and **B**, respectively, but their common wave front **(AC)** arrives to **B** a bit later than to **A.** Diffracted wavelets emerge in every direction both from **A** and **B.** We choose those rays a' and b' which make the angle **γ** with the normal. These two rays interfere with each other and form a new wave with **(BC')** as the first new wave front. Between the last common wave front and the first new one the optical path difference between the individual rays ***a*** and ***b*** is n_f [**(AC') - (BC)**] . The interference is constructive if this difference is integer multiple of 2π that is

$$n_f D (\sin(\gamma) - \sin(\beta)) = m \lambda_0. \quad (18)$$

In order to obtain the guided mode from the diffracted beam, $k_0 n_f \sin(\gamma)=k_0 N$ should hold for the x component of its wave vector, so we arrive to the incoupling condition

$$N-n_f \sin(\beta)=m \lambda_0/D.$$

The light wave arrives from air through the substrate into the wave guide film. In air, the angle of incidence is α_0. That is the angle we can measure. According to Snell's law $n_0\sin(\alpha_0)=n_f\sin(\beta)$, that means a guided wave exist and maximum signal is detected if

$$n_0\sin(\alpha_0)=N - m \lambda_0/D. \quad (19)$$

The effective refractive index of the guided mode can be determined by (19). Inserting N into eqs. (10) we get the z dependence of the transversal field components. The x dependence is sin(Nx), along the length of the wave guide. Fig. 3 shows the TE_0 mode electric field in an SiO_2-TiO_2 wave guide on glass substrate and with air as cover medium, if a He-Ne laser is used (λ_0=632,8 nm) and the grating constant is 1/2400 mm.

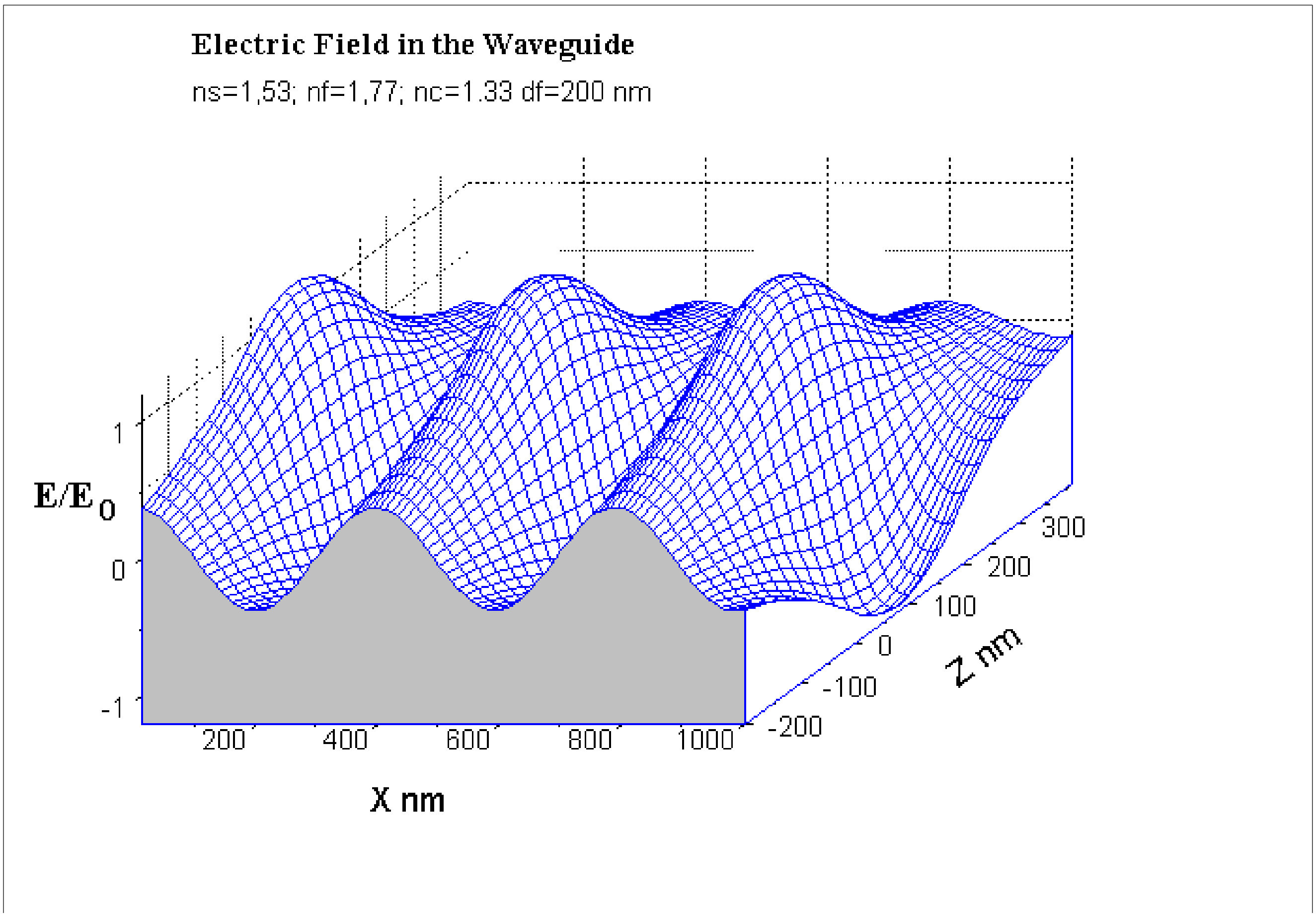

Fig. 3. Distribution of the electric field in a wave guide: the wave propagates along the long axis of the wave guide, the amplitude of the wave changes in the direction normal to the propagation.
(TE_0 mode in a 200 nm thick SiO_2- TiO_2 wave guide illuminated with a He-Ne laser.The chips are pruduced by the Hungarian company Microvacuum Ltd*.)*

Experimental Setup

An apparatus working with SiO_2- TiO_2 sensor chip is set up at Microvacuum Ltd.. The chip is placed onto a rotating plate, together with detectors for positive and negative angles at the respective end faces of the wave guide (Fig. 4). A stepper motor rotates the chip and the signal of the appropriate detector is monitored. As the guiding condition is different for both the TE and TM modes we get maximum signal at two different angles with both detectors, according to (19). The positive and negative angles should be mirror images of each other with respect to the normal of the chip which is not measured directly. The arithmetic mean of the positive and negative angles both for TE and TM modes (α_{TE} and α_{TM}) are calculated and used for further calculations.

Applications of the wave guide sensor

The wave guide chip serves both as a refractometer to identify the cover layer or the wave guide itself or it can be used for adsorbed layers: to determine their thickness and refractive index or monitoring adsorption kinetics. If the incident radiation is polarized at 45^0 angle with respect to the plane of incidence both TE and TM modes are excited, at the angles α_{TE} and α_{TM} , respectively. From those angles, the effective refractive indices N_{TE} and N_{TM} are obtained with eqs. 19. and these effective refractive indices serve for further evaluations.

For a three-medium wave guide, the thickness d_f is eliminated from eqs. (12) in order to calculate the refractive index either of the wave guiding film or the cover medium. The unknown refractive index (n_c or n_f) is obtained as the result of an iterative procedure. Knowing all indices, we get the thickness d_f from any of the original equations. Once the characteristic values of the wave guide film n_f ,d_f are known, we fill the sample holder and determine the refractive index of the sample n_c from the new measurement results.

To investigate a layer on the wave guide, the refractive index and the thickness of the wave guide film have to be known. Now d_a is eliminated from eqs. 16 and n_a the refractive index of the adsorbed (or deposited) layer is obtained by iteration. The thickness d_a of the adsorbed layer comes directly from any of the eqs. (16).

The process of adsorption also can be followed. In this case we can make the meter scan only around the expected angles and to repeat the measurement till the results α_{TE} and α_{TM} become steady.

The method has some restrictions. Eqs. 16 apply only in the case when the adsorbed layer is laterally homogeneous and isotropic. The last condition certainly does not hold for oriented adsorption of long polymeric molecules.

We estimate the amount of adsorbed material on unit area of the chip, assuming that the refractive index is a linear function of the concentration of the adsorbent.

$$n_a = n_c + c_a \, dn/dc$$

c_a is the concentration of the adsorbent on the surface of the chip and n_c is the refractive index of the solvent or that of the homogeneous solution far away from the surface. The concentration dependence of the refractive index is obtained prior to the experiment by measuring the refractive index in standard solutions.

The quantity of adsorbed material per unit area is

$$M = \int_{d_f}^{d_a+d_f} c_a dz \approx \overline{c_a} d_a$$

As the adlayer is usually very thin, the concentration is replaced by the average value, and that is obtained from n_a, arriving to an expression for the adsorbed mass as:

$$M = \frac{n_a - n_c}{dn / dc} d_a$$