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# Sol-gel derived optical waveguide films for planar sensors with phase modulation

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The paper presents the results of investigation of the technology of optical waveguide films produced with the sol-gel technique. The silica-titania films were deposited on glass substrates by a deep coating method. The influence of withdrawal speed and aging time of sol on the refractive index and film thickness has been tested.

Keywords: sol-gel, silica-titania film, dip coating, planar waveguide, planar sensor.

## 1. Introduction

One of the most extensively developed branches of optoelectronics over the last years has been the branch of planar waveguide sensors. Planar technologies used for their manufacture have a number of advantages. They make it possible to produce planar optics systems of the required properties. The parameters of planar waveguides are optimized for particular sensor structures. Therefore, they have the character of special waveguides. The waveguides for planar sensors are produced using different technologies, such as: ion exchange in glass [1]–[4], semiconductor technologies [5] and sol-gel technology [6], [7]. For amplitude systems, it is the technology of ion exchange that is particularly useful. Planar waveguides for sensors with phase modulation, should be characterized by high value of refractive index [8], [9], and hence the sol-gel technique is particularly useful for their production. The sol-gel technique offers great potential involving the production of optical films of different refractive indices [6], and it particularly involves two-component systems $SiO_2$:$TiO_2$, for which the refractive index, depending on the composition and course of technological processes, may reach the values ranging from 1.2 to 2.3. Therefore, such films, depending on their optical and geometrical parameters, can be applied as waveguide films, protective coat, and when they change their properties due to the influence of external factors, they can be used as sensitive films for amplitude sensors in a one-component system, where silica $SiO_2$ is used as the matrix binding a respective indicator [10]. For planar phase sensors, waveguide films of high refractive indices are produced in a two-component system $SiO_2$:$TiO_2$.

The paper presents the results of investigation of the technology of optical waveguide films produced with the sol-gel technique. The films were deposited on glass substrates by a deep coating method. The influence of withdrawal speed and aging time of sol on the refractive index and film thickness has been tested.

## 2. Sol-gel processing

### 2.1. Chemical basis

The sol-gel technique is a chemical method for obtaining amorphous materials from solutions [6]. Respective organic or non-organic compounds are precursors of these materials. For silica, the most commonly applied organic precursors are tetraethoxysilane, $Si(OC_2H_5)_4$, referred to as TEOS and tetramethoxysilane, $Si(OCH_3)_4$, referred to as TMOS. For titania the most commonly applied organic precursors are titanium(IV)ethoxide, $Ti(OC_2H_5)_4$, referred to as TET or titanium(IV)methoxide, $Ti(OCH_3)_4$. The author used TEOS and TET (Aldrich) as precursors of waveguide films. The remaining output components included ethyl alcohol (EtOH) and water. Hydrochloric acid (HCL) was applied as a catalyst. The following stages can be distinguished in the generation process of respective films with the application of sol-gel technique [6], [7]:

– generation of colloidal system (sol), in which the applied precursor is the dispersed phase, and the dispersion phase is made up by respective alcohol and water;

– hydrolysis, which is either complete or partial, depending on the quantity of solvent and the presence of catalyst:

$$M(OR)_4 + H_2O \rightarrow HO\text{–}M(OR)_3 + ROH \qquad (1)$$

or

$$M(OR)_4 + 4H_2O \rightarrow M(OH)_4 + 4ROH \qquad (2)$$

where: M – metal atom, R – alkyl group, ROH – alcohol;

– generation of manomer. The particles, which earlier were subjected to hydrolysis can now join each other forming the manomer. The reactions usually follow the scheme as presented below:

$$(OR)_3M\text{–}OH + OH\text{–}M(OR)_3 \rightarrow (OR)_3M\text{–}O\text{–}M(OR)_3 + H_2O \qquad (3)$$

or

$$(OR)_3M\text{–}OH + OH\text{–}M(OR)_3 \rightarrow (OH)_3M\text{–}O\text{–}M(OR)_3 + ROH; \qquad (4)$$

– gel is formed in effect of the polymerization of manomer resulting in the formation of large particles, and particles join each other into chains and later into network;

– deposition of gel film on the substrate;

– drying and annealing of deposited films.

The reactions of condensation start before the reactions of hydrolysis are finished. The proportions of the applied output components, kind and amount of the applied catalyst as well as parameters characterizing particular stages of the technological process have the influence on the properties of the films obtained.

### 2.2. Film formation by dip coating methods

In sol-gel technique the films are produced with the application of three methods: spin coating method, dip coating method and meniscus coating method [7]. In the presented studies the dip coating method was applied, in which substrate withdrawal speed from the sol is the basic parameter having the influence on the thickness of the film obtained. When the sol shows the properties of Newtonian liquid and its viscosity $\eta$ and substrate withdrawal speed $v$ are high enough to reduce the curvature radius of meniscus, then the dependence of the thickness $d$ of the sol film can be defined by means of the following expression [6], [7]:

$$d = c_1\left(\frac{\eta v}{\rho g}\right)^{1/2} \tag{5}$$

where $c_1 \approx 0.8$, $\rho$ is the concentration of sol and $g$ is the acceleration due to gravity. When the movement of substrate does not result in the reduction of meniscus curvature, the dependence of thickness $d$ of the film being obtained versus the speed $v$ of the substrate is expressed by the expression of Landau and Levich [6], [7]:

$$d = \frac{0.94(\eta v)^{2/3}}{\sigma_{L,V}^{1/6}(\rho g)^{1/2}} \tag{6}$$

where $\sigma_{L,V}$ is the liquid-vapor surface tension.

When deriving the above relations the evaporation of solvents was not considered. The sol films deposited on the substrate are then subjected to drying and heating. In the above processes the films are getting concentrated whereby their thickness is considerably lower. This effect can be allowed for by complementing the above expression with a contraction factor [11]. Taking into consideration expressions (4) and (5), the dependence of the final film thickness on the speed of substrate withdrawal from the sol can be written in the following form:

$$d = A\xi v^{\alpha} \tag{7}$$

where $\xi = 1$ (cm/min)$^{-\alpha}$ is a scaling factor. For a given technological process the factor of proportionality $A$ and exponent $\alpha$ can be derived empirically. Frequently, the relation $d(v)$ is presented in the literature in the logarithmic scale and hence the exponent $\alpha$ is referred to as a slope. With Eqs. (5) and (6) taken into consideration, we can expect that its value is within the range from 0.50 to 0.66.

### 2.3. Film fabrication

The following precursors were applied: TEOS for silica and TET for titania. Ethyl alcohol (EtOH) was applied as the homogenizing agent, and hydrochloric acid was used as catalyst. The hydrolysis processes of TEOS and TET were carried out in two stages. First, the hydrolysis of each precursor was carried out separately. Then the solutions were mixed in an appropriate proportion and the process was continued. The molar ratio TEOS : TET of the sols used in the investigations was 1 : 1. The molar ratio (TEOS + TET) : EtOH : $H_2O$ was 1 : 6 : 1.8. For the final solutions the measured pH = 3. The produced sols were kept (subjected to aging) in tightly closed vessels at a temperature of 18°C. The films were deposited on glass substrates by means of controlled dip coating from the sol. Microscope slides (Menzel–Glaser) of the dimensions 76×26×1 mm were applied as substrates. Substrate glass was subjected to cleaning procedure which involved the following: mechanical washing in water with detergent, rinsing in deionized water, soaking in the solution of ammonia water, rinsing in deionized water, rinsing in acetone and drying. The sol from which the substrates were dip coated was in a beaker and the whole was shielded by a glass cylinder. The application of such a procedure ensured that accidental movement of air could be avoided, and, in consequence, the films obtained were of homogeneous character. The films were then annealed at 300°C for 1.5 hours.

## 3. Measuring method

The thickness and refractive indices of silica-titania films were measured in the ellipsometric way. The ellipsometric method consists in changing the polarization state, which happens due to the light beam being reflected from the sample under investigation [12]. The basic ellipsometric equation has the following form:

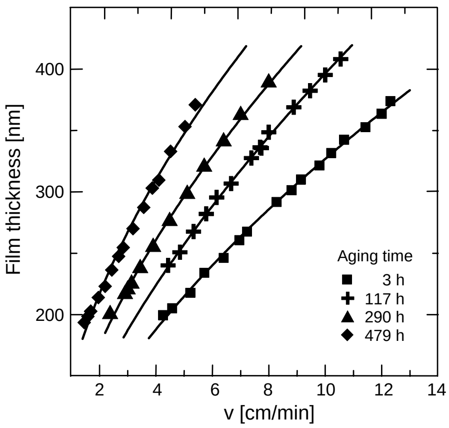
$$\rho = \frac{R_p}{R_s} = \tan\Psi \exp(i\Delta) \tag{8}$$

with $R_p$ and $R_s$ indicating the reflection coefficients, respectively, for the light polarized in parallel (subscript *p*) and perpendicularly (subscript *s*) to the incidence plane. The angles $\Psi$ and $\Delta$ are referred to as ellipsometric angles and they generally depend on film parameters, substrate and the surrounding medium. From the measurements of ellipsometric angles, film parameters are determined. The experiments were carried out for the wavelength of $\lambda = 632.8$ nm with the application of a monochromatic ellipsometer Sentech SE400 (Germany). During the measurements the relative humidity in the room was about 40%.

## 4. Experimental results

It was demonstrated in Sec. 2.2. that the thickness of the films produced depends on the dip speed $v$ and viscosity $\eta$ of the sol. As a result of condensation processes, which are taking place in the sol during the aging, its viscosity changes. This means that with the same parameters of film coating, in time, films of different thickness will be obtained from the same sol. Within the scope of investigations the results of which are presented here, the influence of aging time of the sol on the thickness of the films produced was determined. The influence of aging time of the sol on the slope $\alpha$ and proportionality factor $A$ was determined (see Eq. (7)).

The dependence of the thickness of the films versus the withdrawal speed for selected aging times of the sol is illustrated in Fig. 1. There are experimental points marked in the picture, which were approximated with the relation (7). The film thickness increases with the dip speed $v$. All films, for which the results are presented, were characterized by good optical properties, they were homogeneous and crack-free. It can be seen from the relations presented that with an increase of aging time of the sol, the same dip speeds $v$ correspond with greater thickness of the films. The case for the withdrawal speed $v$ = 5 cm/min was illustrated in Fig. 2. Particular points marked on the diagram were determined from the approximation curves of the relation $d(v)$, the latter being linear. The reactions of hydrolysis and condensation taking place during the aging process of the sol change its properties. The viscosity of the sol increases and the structure of its particles changes. Hence the change of approximation parameters $\alpha$ and $A$ which describe the relation $d(v)$. The dependence of the parameters $\alpha$ and $A$ versus aging time of the sol is presented in Fig. 3. We can observe a monotonic increase of the factor $A$ together with the increase of aging time of the sol. This principally results from an increase of the sol viscosity. At the same time, the results obtained indicate a non-monotonic dependence of the exponent $\alpha$ versus aging time of the sol. At first, the increase of $\alpha$ is observed and then, for a few days, its value is maintained on almost the same level, and after about one week it begins to decrease tending towards the value 0.5. This bespeaks the change in the structure of sol particles.



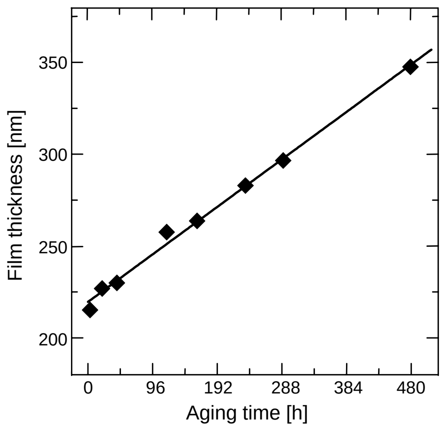




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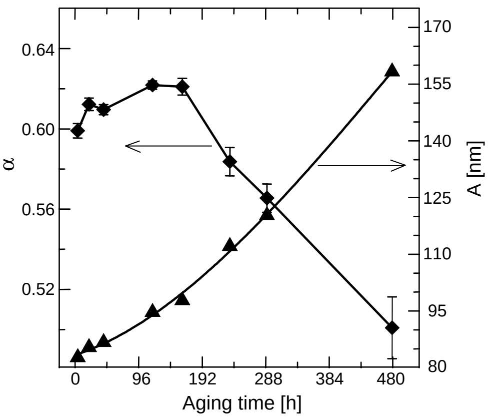
Fig. 1. Film thickness as a function of withdrawal speed for selected aging times of the sol.

Fig. 2. Film thickness as a function of aging time of the sol. Withdrawal speed $v$ = 5.0 cm/min.



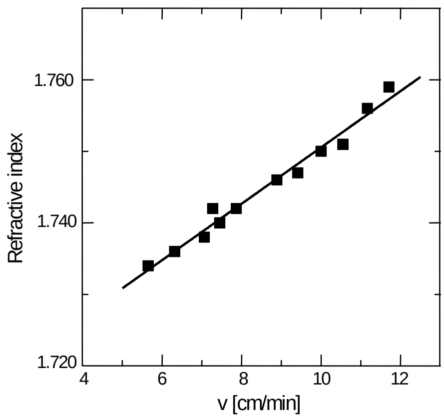




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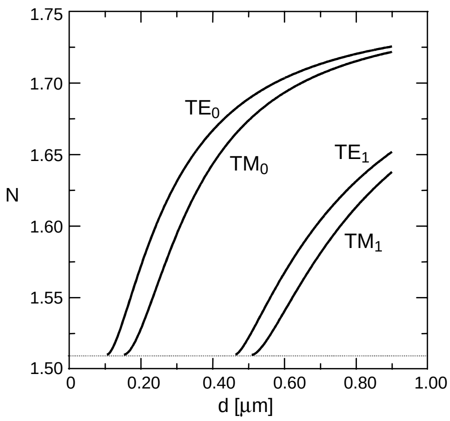
Fig. 3. Approximation parameters *vs.* aging time of the sol.

Fig. 4. Refractive index *vs.* withdrawal speed.

However, in order to define the character of these changes, the films must be subjected to structural tests. Such tests have not been carried out so far. For higher dip speeds, we obtain thicker films which must be dried for a longer time. Hence, sol particles have more time to settle in the structure, and, in effect, the films obtained are more compact and dense, and their refractive indices have higher values than those for thinner films. The dependence of refractive index on the dip speed subjected to aging for 21 h is presented in Fig. 4. It can be seen that with the increase of the dip speed *v*, the refractive index of the sol increases as well. With the change of dip speed from 5.65 to 11.71 cm/min the refractive index increases from 1.734 to 1.759.

## 5. Modal properties

The waveguide films produced may contribute to the development of sensor systems with phase detection. The technology involving the production of strip waveguides was described in detail in work [13]. Planar waveguides can be applied in sensors working in the systems of difference interferometer [8]. The simplest system of such an interferometer is built from a substrate on which a waveguide film has been coated. If both fundamental modes ($TE_0$ and $TM_0$) are excited in such a structure, then by placing an appropriately oriented polarizer behind the structure, we can obtain a signal, which is the result of the interference of both modes. In this way we can monitor the changes involving the coating conditions of waveguide film. Using the matrix method 4×4 of waveguide analysis [14], [15] we carried out the analysis of the modal properties of the waveguides. We also determined the sensitivities offered by these waveguides when they are applied in planar systems of phase sensors. The calculations were carried out assuming the following: refractive index of the waveguide layer $n_1 = 1.750$, refractive index of the substrate $n_b = 1510$, wavelength $\lambda = 632.8$ nm.



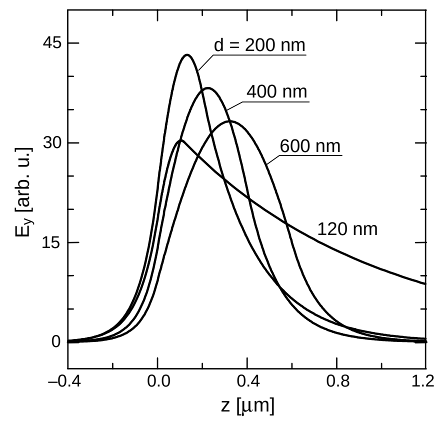




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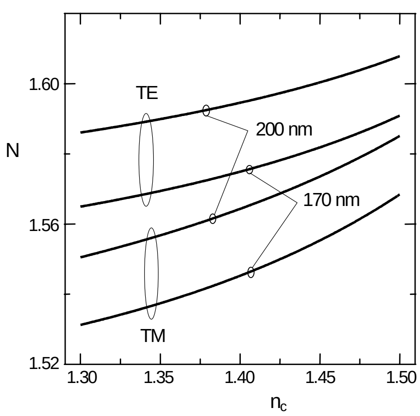
Fig. 5. Modal characteristics of homogenous waveguide. Refractive indices: waveguide $n_1$ = 1.75, substrate $n_b$ = 1.51, cover $n_c$ = 1.00; wavelength $\lambda$ = 632.8 nm.

Fig. 6. Distributions of electric field of the mode $TE_0$ for selected thickness of waveguide film. Parameters: $n_1$ = 1.75, $n_b$ = 1.51, $n_c$ = 1.0.

Figure 5 presents modal characteristics of the waveguide. The range of single-mode operation, when both fundamental modes $TE_0$ and $TM_0$ are supported, corresponds with the thickness of waveguide film from 153 to 463 nm. It can be seen from the above that all the waveguides produced were single-mode ones. The distribution of electric field of the mode $TE_0$ for the selected thickness of waveguide film is presented in Fig. 6. For the film thickness $d$ = 120 nm the mode is close to cut-off.

The influence of refractive index of the cover $n_c$ on effective refractive indices of the fundamental modes for the waveguide films of respective thicknesses $d$ = 170 nm



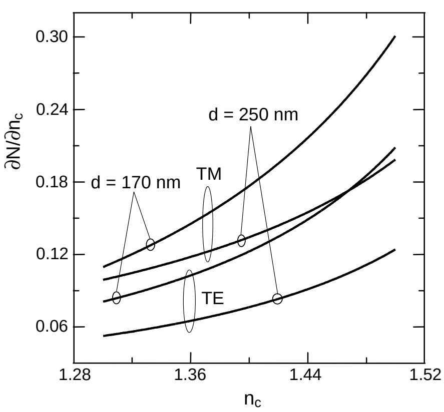




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Fig. 7. Effective index as a function of refractive index of the cover.

Fig. 8. Sensitivity as a function of refractive index of the cover.

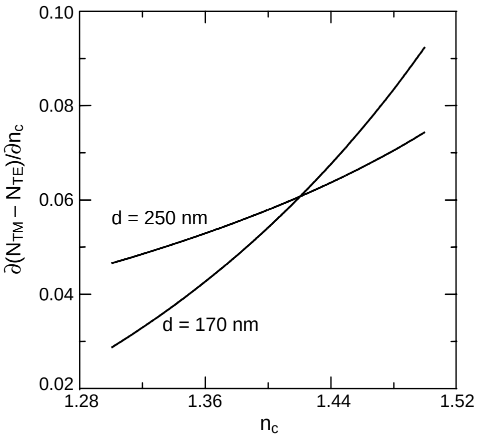


Fig. 9. Sensitivity for difference interference *vs.* refractive index of the cover.

and $d$ = 200 nm is presented in Fig. 7. The increase of refractive index of the cover in each case results in the increase of effective refractive indices. The dependence of the optical sensitivities [9]:

$$S_{nc} = \frac{\partial N_{\mathrm{eff}}}{\partial n_c} \tag{9}$$

on the refractive index of the cover $n_c$ is presented in Fig. 8. The relations correspond with the fundamental modes $TE_0$ and $TM_0$. It can be seen that higher sensitivities correspond with the thinner waveguide film and with polarization TM. Decreasing the refractive index of the substrate and optimizing for a particular case the thickness of waveguide film, we can obtain higher values of sensitivity [8], [9]. The dependence of sensitivity on the refractive index of the cover, for the case of difference interference of modes $TE_0$ and $TM_0$, is presented in Fig. 9. It can be seen that for lower values of refractive index of the cover $n_c$, higher sensitivities correspond with the thicker waveguide film, whereas for lower values of refractive index of the cover the situation is reverse. The influence of the parameters of waveguide film on sensitivity, for difference interference, was described in detail in work [8].

## 6. Conclusions

The paper presents the results of investigation of waveguide films $SiO_2:TiO_2$ produced with the application of sol-gel technique. We presented the influence of the withdrawal speed of substrate on the thickness and refractive index of the films obtained. It was demonstrated that with an increase of the dip speed the refractive index of the films increases, too. During the aging of sol, as a result of hydrolysis and condensation, the sol changes its viscosity and the structure of its particles. In effect, it brings about the change of slope index $\alpha$ and proportionality factor $A$. It was demonstrated that the dependence of slope index $\alpha$ on aging time of the sol is non-monotonic. And the dependence of proportionality factor $A$ versus aging time of sol is an increasing function.

The analysis of modal properties presented in the work shows that the produced waveguide films applied for the construction of sensors for refractive index changes will yield high levels of sensitivity. The production technology of waveguide film presented in the work, with the application of sol-gel technique is being developed in view of its application for the production of planar sensor systems with phase detection.

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