Silica layers produced by the sol-gel method as dielectric masks in ion exchange processes

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Received November 25, 2012; accepted December 19, 2012; published December 31, 2012

Abstract—This paper presents experimental results produced by the sol-gel method silica layers usage as dielectric masks in ion exchange processes in producing stripe waveguides. Such layers were produced on the glass substrate (soda-lime glass) by the dip-coating method. Their thicknesses gained during single deposit on the substrate were in the range of 78÷150nm. Those layers had the compactness comparable to thermal silica. The $Ag^+ \leftrightarrow Na^+$ ion exchange processes with the use of $AgNO_3/NaNO_3$ solution with the mole fraction of κ_{Ag}=0.0025 were completed. The permeability of the layers for dopant ions (Ag^+) depending on the thickness of the layer and the diffusion time was tested.

The production of gradient structures of integrated optics with the use of the ion exchange method often requires the use of selective diffusion processes of an ion dopant into the glass substrate. In this way, gradient stripe waveguides are produced, as well as all kinds of diffractive structures (such as microlenses). The processes of selective diffusion of admixture ions into glass require the use of respective masking layers to ensure the blocking of admixture access to the masked areas of glass. Such layers should be chemically resistant to the environment of a liquid source of admixture (these are usually strong oxidizers operating at high temperatures). They must also display good adhesion to the glass surface and be able to undergo photochemical processing (shaping coverage topology). Generally, masking layers used in the ion exchange processes can be distinguished into metallic and dielectric. Most commonly used [1-4] metallic layers (Al, Ti, Cr) are applied on the glass surface by the vacuum evaporation technique. By using photolithographic processes a corresponding pattern is formed in the applied layer exposing the glass surface at selected locations. There is also a possibility of oxidation of the metallic layer with an etched pattern. This technique is applied in aluminum layers by electrolytic oxidation, providing a dielectric layer of Al_2O_3. Other dielectric layers that are applied directly by the vacuum evaporation technique or cathode sputtering are: SiO_2, Ta_2O_5. In this paper, we propose the use of silica as a masking layer. Those layers are produced by the sol-gel method. Depending on the manner of their manufacturing process, they may have a different porosity [5]. For applications of such layers as dielectric masks the preference will be the compact layers comparable to thermal silica. The use of such layers as dielectric masks is also possible due to the possibility of chemical etching [6-7] allowing the formation of masking areas topology in ion exchange processes. The following test results are applicable to determine the degree of permeability of the silica layers by using them as masks for ion-exchange processes. The research included thickness of the layers and duration of the processes.

The subject of the research was substrate of soda-lime glass (Menzel Glasser's). Completed technological processes aimed at producing areas partially masking the surface of the glass. The masking layer was silica produced by the sol-gel method [5]. The layers covering glass substrates were applied by immersion. Glass substrates were immersed in the sol as to obtain a partial coverage. The thickness of applied layers was dependent on substrate's ascent rate from sol solution. After applying the sol layer on the glass substrate they were annealed during time t=45' and at temperature T=500°C. The thickness and refractive index of the layers was determined by ellipsometry (SENTECH SE400 ellipsometer) for wavelength λ=632.8nm. The resulting silica layers had a thickness in the range of 78nm≤ d≤150nm. Their refractive index was n=1.462 which shows the compactness of produced silica. In the prepared substrates the diffusion processes of $Ag^+ \leftrightarrow Na^+$ ion exchange were subsequently carried out. The source of admixture was $AgNO_3/NaNO_3$ solution of the mole fraction κ_{Ag}=0.0025. All diffusion processes were carried out at the temperature T_{diff}=350ºC. As a result of the ion exchange process in the unmasked part of glass substrate, a gradient waveguide area is produced. However, in the area of glass coated with a masking silica layer, as a result of its partial permeability, a shallower waveguide area can also be expected to be produced. To study the waveguide properties of these two areas of glass a waveguide method was used based on the goniometric measurements of the synchronous angles of waveguide modes [8]. In this method, the measuring element is a prism coupler. Due to the small thickness of masking silica layers it can be used to stimulate potential waveguide modes under a masking layer. The effective refractive indices determined in this way have uncertainties of ~10^{-4} [8]. All measurements were carried out for the wavelength λ=677nm and TE polarization. An overview of number of waveguide modes

generated in the unmasked and masked areas of glass is shown in Table 1.

Table 1. Number of TE modes (@λ=677nm) in the unmasked and masked areas of glass.

Diffusion time t_{diff}=1h, diffusion temperature T_{diff}=350ºC		
Thickness of silica layer (nm)	Unmasked area	Masked area
78	7	1
95	7	1
100	7	1
110	7	1
123	7	1
150	7	2
Thickness of silica layer d=150nm, diffusion temperature T_{diff}=350ºC		
Diffusion time (h)	Unmasked area	Masked area
0.5	5	1
1.0	7	2
2.0	10	4
4.0	14	9
8.0	20	15

The information obtained from measurements about mode properties of waveguides produced in the unmasked and masked areas of glass was used to quantify the permeability of silica layers for Ag^+ ions. These estimates were carried out by theoretical modeling of ion exchange between the liquid source of admixture with unlimited capacity and the glass, the surface of which was covered with a mask limiting the kinetics of exchange. The ion exchange processes were simulated based on the mathematical model of a two-component ion exchange phenomenon. The dependence of diffusion coefficients of exchanged ions on their normalized concentrations in the glass area was assumed [8]. In the case of multimode waveguides formed in the unmasked areas of glass, the refractive index profiles were reconstructed based on effective indices of the modes on the basis of White-Heidrich waveguide method [9]. For such designated refractive profiles the matching of theoretical refractive profile was performed, which is a solution of the diffusion equation in the planar case [8]:

$$\frac{\partial u}{\partial x}=\frac{D_{0A}e^{Au}}{1-\alpha u}\cdot\frac{\partial^2 u}{\partial x^2}\cdot \cdot\frac{D_{0A}e^{Au}\left[\alpha+(1-u)A\right]-u(1-\alpha)^2 D_{0B}Be^{B(1-u)}}{(1-\alpha u)^2}\cdot\left(\frac{\partial u}{\partial x}\right)^2, \quad (1)$$

where: $\alpha=1-\frac{D_{0A}}{D_{0B}}\cdot\exp\left[u(A+B)-B\right]$.

In the above equation, the function $u(x)$ is the spatial distribution of the normalized concentration of admixture (Ag^+ ions). The transformation of the concentration to the refractive index profile is based on the relationship:

$$n(x)=n_b+\Delta n_s\cdot u(x), \quad (2)$$

where: n_b – refractive index of the glass substrate (without admixture), Δn_s – increase of the refractive index at the glass surface.

Equation (1) was solved with the initial and boundary conditions:

$$u(x,t=0)=0 \quad \text{for} \quad x\geq 0, \qquad \Phi_u=\beta(u_r-u_0) \quad \text{for} \quad x=0, \quad (3)$$

where: β – the proportionality factor, u_r and $u_0=u(0)$ – mean normalized admixture concentration respectively in the phase of the source and at the glass surface, Φ_u – the normalized admixture stream passing through the glass surface from the source phase to the volume of the glass.

Parameters determined in the process of fitting the model solution to measuring points (refractive index profile of the waveguide in the unmasked area of glass) were diffusion coefficients of exchanged ions: D_{0A}, D_{0B}, A and B, and the parameters β and u_r describing the admixture stream through the surface of the glass. The $\beta=\beta_f$ coefficient determined for this area defines the kinetics of the exchange process through the unmasked surface. Its value was still taken as the maximum (100%). For single or multimode waveguides resulting in a masked area of the glass it is not possible to reconstruct their refractive index profile on the basis of the waveguide method used [8]. In this case, on the basis of the parameters set for the unmasked area: D_{0A}, D_{0B}, A, B and u_r, Eq. (1) was being solved with the boundary condition [Eq. (3)], where the value of $\beta=\beta_m<\beta_f$ was reduced such that from the resulting refractive index profile (using modal equation) a calculated effective index of the mode compatible with the measurement can result. The values of such determined coefficients β_m expressed in % of maximum β_f were taken as quantitative information about the permeability of masking layers. Figure 1 shows the rule for determining the permeability of the mask described above. The presented result concerns a masking layer with the thickness d=78nm. The duration of the diffusion process was t_{diff}=1h and was carried out at the temperature T_{diff}=350ºC. The measurement of the effective index of TE_0 mode of the waveguide formed in the masked area of glass gave the value N_0=1.5111±0.0004. The permeability of the mask during this process was β_m=6.5±0.8 %.

The used method allowed to determine the permeability of silica layers according to their thicknesses. For this purpose, the diffusion processes were realized at fixed duration t_{diff}=1h, and temperature T_{diff}=350ºC for glass substrates partially masked with silica layers with different thicknesses (the first part of Table 1). The values of permeability of these layers as a function of their thicknesses are shown in Fig. 2.

It can be seen that the permeabilities of layers with thicknesses of 78÷123nm show almost similar values at

the level of β_m=6÷9%. The value of permeability of approximately β_m=18% for the silica layer with a thickness d=150 nm, which is clearly different from other values, can be explained by the formation of micro-cracks in the layer of such thickness.

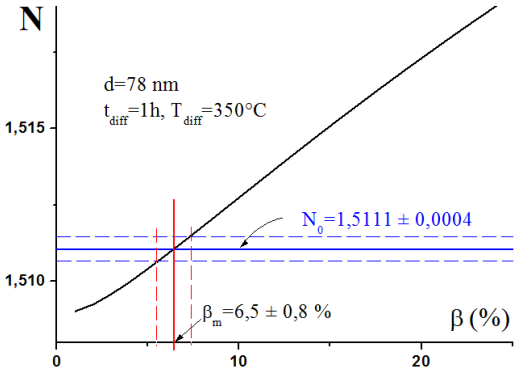

Fig. 1. The rule for determining the permeability coefficient of the masking layer.

Despite the pre-heating, the difference of thermal expansion between silica and the glass substrate is a source of major tension in the layer, resulting in the final formation of micro-cracks.

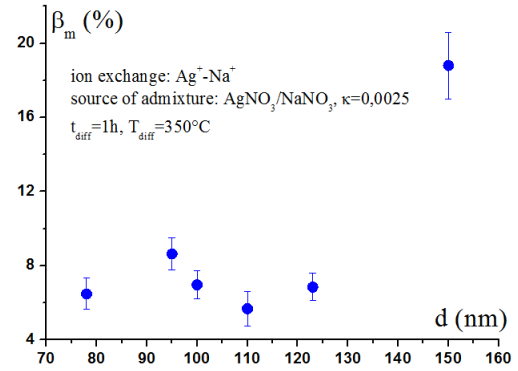

Fig. 2. The permeability of the silica layer as a function of their thicknesses.

Thus, the thick layers may have a much higher permeability than the thin layers. This is confirmed by the amount of waveguide modes resulting in the masked area of the glass (Table 1). Figure 3 shows the results of permeability calculations of the layers of equal thickness d=150nm, depending on the duration of the diffusion process. Those were accordingly: 0.5, 1, 2, 4 and 8h. The temperature of each process was equal T_{diff}=350ºC. In these cases, the waveguides resulting in a masked area of the glass are multimode (second part of Table 1). The single mode exception is a waveguide produced in a process with a duration of t_{diff}=0.5h. Due to the multimodeness of resulting waveguides the permeability coefficients were calculated for each individual mode. As a final representative value of a given layer, a weighted average was assumed. The weights were the uncertainties of determining the permeability for each modes order (see Fig. 3). The calculation results obtained in this way show an increasing trend of the permeability of the layers with the duration of the diffusion. This is probably caused by the rising amount of micro-cracks of the masking layer during the process. The maximum permeability values reach here the level of β_m≈40%.

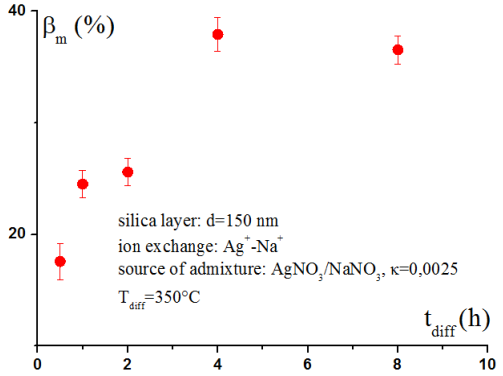

Fig. 3. The permeability of the silica layers as a function of the diffusion time.

It can be concluded that the compact silica layers formed on glass substrates by the sol-gel method can be used as masks for the ion-exchange processes. The obtained results show good masking properties of the silica layers with the thicknesses below 100nm. Such a method for producing dielectric masks is far less expensive and less time consuming in comparison with the vacuum methods.

This work was funded by the National Science Centre on the basis of decision number DEC-2011/01/B/ST7/-06525.

References

[1] E. Okuda, I. Tanaka, T. Yamasaki, Appl. Opt. **23**, 1745 (1984).
[2] S.I. Najafi, Appl. Opt. **27**, 3728 (1988).
[3] J.G. Gallagher, R.M. De la Rue, Electr. Lett. **12**, 397 (1976).
[4] P. Simova, J. Savatinova, T. Tsonev, Appl. Phys. **22**, 237 (1980).
[5] P. Karasiński, Opt. Applicata, **35**, 117 (2005).
[6] P. Karasiński, R. Rogoziński, Opt. Comm. **245**, 237 (2005).
[7] P. Karasiński, C. Tyszkiewicz, R. Rogoziński, J. Jaglarz, J. Mazur, Thin Solid Films **519**, 5544 (2011).
[8] R. Rogoziński (2012). *Ion Exchange in Glass – The Changes of Glass Refraction, Ion Exchange Technologies*, Ayben Kilislioğlu (Ed.), ISBN InTech; http://www.intechopen.com/books/ion-exchange-technologies/ion-exchange-in-glass-the-changes-of-glass-refraction.
[9] J.M. White, P.F. Heidrich, Appl. Opt. **15**, 151 (1976).

