Ion-Exchange Processes in Active Glasses: Spectroscopic and Structural Characterization

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INTRODUCTION

The major force behind the recent advances in photonic components and devices has been the fast progress in optical fiber communication systems; as optical networks are spreading towards the final customers, the need of compact, low-cost and rugged integrated optical devices becomes more and more evident.

Fabrication technologies, therefore, must be capable of high yield, with assured reproducibility within specified tolerances, and of intrinsic low operation cost. Among the various technological routes explored in the last decades, ion exchange is one that well fulfills the imposed requirements [1]. Even the limitations due to the intrinsic passive nature of glassy materials have been overcome by using proper processing (e.g. phase separation) or introducing suitable dopants into the glass matrix; in this way, electro-optical and nonlinear-optical phenomena, as well as lasing and optical amplification were already demonstrated.
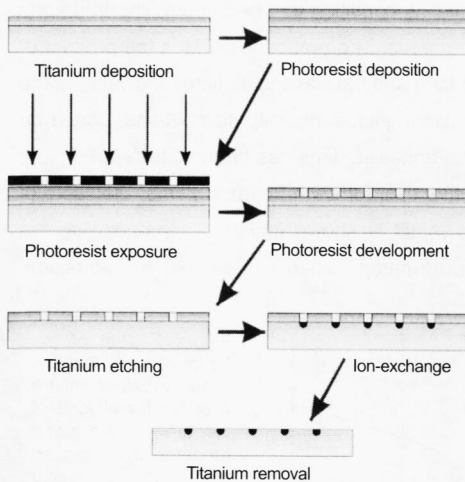
It is well known that ion exchange, as a technique to color glasses, dates back to the first millennium. Real technological advances, however, were related to the use of ion-exchange to produce chemical surface tempering of glass and may be dated to 90 years ago, in 1913, when a fundamental paper by Schulze was published [2];

a few years later, in 1918, Schott researchers observed that ion exchange also produced an increase of the refractive index in the diffused layers. It was in the early 1970's that the pioneering works of Izawa and Nakagome [3] and of Giallorenzi *et al.* [4] demonstrated how to take advantage in integrated optics of such a local modification of the refractive index. Since then, scientific and technological advances and industrial applications have been largely demonstrated [5-7].

The recent fast-growing request of higher bandwidth and speed in fiber telecom systems has increased the need of high-performance components, like integrated optical (IO) amplifiers based on Er^{3+} ions, which operate in the 1.5 μm band. Oxide glasses are well-known hosts for rare-earth ions: the first thin-film waveguide glass amplifier and laser were demonstrated in 1972 [8] and in 1974 [9], respectively, both in Nd:glasses. The interest for Er^{3+}-doped glasses arose quite later, in the late 1980s, when the main operational wavelength for optical fiber systems had shifted towards the 1.5 μm band. Many remarkable results in the fabrication of Er^{3+}-doped waveguide amplifiers (EDWAs) have been already achieved using various technological routes [10]: deposition techniques (e.g. RF-sputtering, sol-gel, PECVD) are competing with diffusion techniques (like ion-exchange in bulk doped glasses), and no one so far has clearly emerged as the winner. Ion-exchange, however, is a very convenient technology, and well suited to this goal.

ION-EXCHANGE PROCESS TO FABRICATE ACTIVE WAVEGUIDES

To achieve a high optical gain in an EDWA it is necessary to combine proper spectroscopic properties of the glass with a low-loss waveguide. Thus, it is very important to optimize both the doping level and the waveguide fabrication process. Generally, at low Er^{3+} concentration, the lifetime of the metastable level is longer and quantum efficiency is higher, but obviously the total intensity of stimulated emission is lower, while at higher concentrations fluorescence quenching may occur, due to ion clustering or ion-to-ion interaction. Propagation losses, on the other hand, would affect, among other factors, the pump threshold, i.e. the power at which the material becomes transparent. Ion-exchange proved to be a quite flexible process, able to respond to designers' requirements; as an example, let us refer to some of our experimental results [11,12]. We produced by melt a set of different glass rods, all having the same matrix (71 SiO_2 - 14 Na_2O - 10 CaO - 2 Al_2O_3 - 1 P_2O_5 - 1 K_2O wt%)

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Titanium deposition

Photoresist deposition

Photoresist exposure

Photoresist development

Titanium etching

Ion-exchange

Titanium removal

Figure 1: Diagram of the main steps in the photolithographic process followed to produce a channel waveguide by ion-exchange.

but different concentrations of Er_2O_3 and Yb_2O_3. The rods were subsequently cut into plates and polished. Channel waveguides were fabricated in these samples by the process steps indicated in Fig.1. After the cleaning process, a 200 nm thick titanium layer was deposited on a 3.5 cm long substrate; then, by ordinary photo-lithographic techniques straight openings in the Ti layer, 2-10 μm wide, were produced. Monomode guides were obtained by means of ion-exchange in a 99.5% $NaNO_3$/0.5% $AgNO_3$ salt melt at 325°C for ≈ 15 minutes.

Such a process, however, had to be optimised, first of all to achieve a good matching between the guided optical fields in the amplifier structure and the input/output fibres. Since the modal field of an ion-exchanged monomode channel waveguide has a different shape and is usually smaller than the field of a standard telecom fibre, a better geometrical and index matching may be obtained by a thermal annealing post-process. Its effect, however, is also to enlarge the waveguide cross-section and therefore to diminish the achievable pump power density inside the waveguide, decreasing the pumping efficiency and thus increasing the threshold above which net gain can be obtained. Moreover, higher-order modes could start to get supported by the guiding structure, generating beats which would further decrease device efficiency. Thus, there is a limit above which there is no advantage in further annealing the waveguide. On the other hand, a second requirement concerns the optimisation of the pump and signal fields overlap, since in this way the pumping efficiency is maximum. We therefore carried out a numerical simulation based on the actual ion-exchange parameters, introducing a

figure of merit (FOM) to find the annealing condition that best meets the trade-offs between the above mentioned requirements. The proposed FOM is the product of the coupling efficiency between input fibre and the waveguide times the value of the overlap integral between pump and signal guided intensity distributions. Based on the 15 minutes ion-exchange time, the annealing time has been considered to vary from 0 up to 120 minutes, by 2-minute steps; for each annealing time, the value of the FOM has been calculated. The result is shown in Fig. 2 together with the corresponding growth of the area of the pump guided mode intensity distribution.
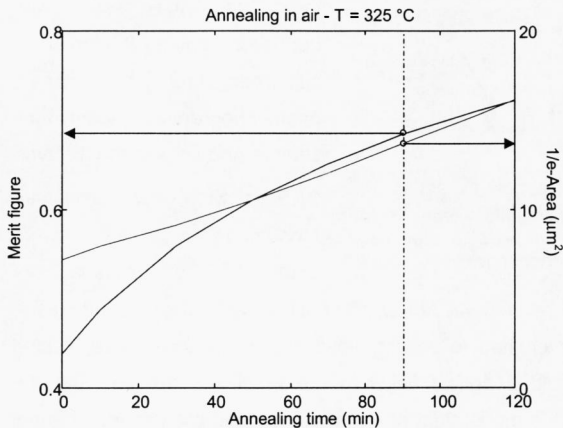

Figure 2. Plot of the figure of merit, that can assume values in the 0 to 1 interval, and of the area of the pump fundamental guided mode vs. annealing time for a channel guide 7 µm wide. The mode area was calculated at 1/e of the maximum intensity.

The figure of merit would continue to increase for annealing times longer than 120 minutes, but, as the modal field area continues to increase as well, we assumed that a value of FOM of the order of 0.7 could be a reasonable compromise. The corresponding modal field area is about 14 µm^2, that compares well with the values reported in literature for well-performing integrated optical amplifiers [13,14]. In a device fabricated according to this model the insertion loss measured at 1.3 µm wavelength was about 28 dB prior to= and 10 dB after-annealing, so confirming the effectiveness of the thermal post-process. In order to increase pumping efficiency, however, a set of narrower waveguides was produced; in this case, a 60 minutes annealing process was optimal. In 3.5 cm long and 4 µm wide channel waveguides, at an input signal intensity of =-33 dBm, transparency at 1536 nm was reached by using 100 mW pump power; a maximum net gain of 5 dB was measured with

250 mW pump power.

SPECTROSCOPIC CHARACTERIZATION

Waveguide spectroscopy is a powerful characterization technique: Raman spectroscopy provides important structural information [15] and can be used for studying the acoustic vibrations of nanoclusters included in the guide [16]. Luminescence spectroscopy allows to study the intrinsic defects of the glass or the spectroscopic properties of optical activators such as transition metal or rare earth ions added to the glass [17]. In particular, in graded-index waveguides, by comparison of spectra (Raman, luminescence) taken by exciting different modes, it is possible to characterize the guide at different depths. In fact, luminescence from silver ions and Raman scattering from the optical vibrations of the glass and from the acoustic vibrations of silver nanoclusters depend on the silver concentration. The method has been successfully applied to silver ion-exchanged waveguides obtained in the (undoped) glass described above [18]. As an example, it was possible to deduce a mean silver particle size of about 1.3 nm, with a large size dispersion. Such an analysis may also be important in view of assessing a phenomenon, which has been the subject of a few papers and that still is open to discussion, namely the photoluminescence enhancement effects that silver might have on rare earth ions in oxide glasses [19-22]. In an early paper, Malta et $al.$ [19] reported a decrease in fluorescence from Eu^{3+} ions in the presence of small Ag particles in melt glasses, and proposed that the fluorescence can increase or decrease depending on the size of Ag particles and the lifetime of the upper level of Eu^{3+}. Recently, in the case of silver particles in Eu^{3+}-doped silica glasses, prepared by the sol-gel method, a doubling of fluorescence intensity was reported in the presence of silver particles of 4.3 nm size, and attributed to local field enhancement around Eu^{3+} ions, owing to the surface plasmon resonance of these particles [20].

A very recent study of silica-titania waveguides doped with Er^{3+} and Ag^+ ions, prepared by sol-gel technique, however, did not detect any clear influence of the presence of Ag particles on the measured lifetimes of the metastable level of Er^{3+}, despite the presence of metallic Ag nanoparticles, evidenced by visible absorption spectroscopy, XRD and TEM, with estimated sizes in the range of 2–12 nm [21]. Very significant results, on the contrary, were reported for a borosilicate glass doped

with erbium by ion implantation and with silver by ion exchange [22]. A broad excitation band of the photoluminescence of Er^{3+} in the visible and near-ultraviolet was observed, with luminescence enhancements up to a factor of 70 at a pump wavelength of 488 nm. The authors suggested that absorption of light occurred at a silver ion/atom pair or similar defect, followed by energy transfer to Er^{3+}, and excluded that silver nanocrystals were part of the dominant excitation mechanism.

CONCLUSIONS

Ion exchange technology constitutes one of the most convenient processes for the fabrication of integrated optical devices and especially of Er^{3+}-doped glass amplifiers, both in research laboratories and at industrial level. Even if deeper investigations are still necessary in order to fully understand some energy-transfer mechanisms, it appears that silver ion-exchange may also be exploited to greatly enhance photoluminescence properties of Er^{3+} ions.

REFERENCES

[1] G. C. Righini, S. Pelli, Proc. SPIE vol. **4453**, 93-99 (2001).
[2] G. Schulze, Angew. Physik, **40**, 335-367 (1913).
[3] T. Izawa and H. Nakagome, Appl .Phys. Lett., **21**, 584-586 (1972).
[4] T.G. Giallorenzi, E.J. West, R. Kirk, R. Ginther, R.A. Andrews, Appl. Opt. **12**, 1240 (1973)
[5] T. Findakly, Opt. Engin., **24** 244-250 (1985).
[6] R.V. Ramaswamy and R. Srivastava, J. Lightwave Techn., **LT-6**, 984-1002 (1988).
[7] S. I. Najafi, Ed., *Introduction to Glass Integrated Optics* (Artech House, 1992).
[8] H. Yajima, S. Kawase, Y. Sekimoto, Appl. Phys. Lett., **21**, 407-409 (1972).
[9] M. Saruwatari, T. Izawa, Appl. Phys. Lett., **24**, 603-605 (1974).
[10] G.C. Righini, S. Pelli, M. Ferrari, M. Brenci, Proc. MOC'01 (Osaka, 2001), 346-349.
[11] G.C. Righini, S. Pelli, M. Brenci, M. Ferrari, C. Duverger, M. Montagna, R. Dall'Igna, J. Non-Cryst. Solids, **284**, 223 (2001).
[12] G. C. Righini, M. Brenci, M.A. Forastiere S. Pelli G. Ricci, G. Nunzi Conti, N. Peyghambarian, M. Ferrari, M. Montagna, Phil. Magaz. B, **82**, 6, 721-734 (2002).
[13] P. Camy, J.E. Roman, F.W. Willems, M. Hempstead, J.C. Van Der Plaats, C. Prel, A. Beguin, A.M.J. Koonen, J.S. Wilkinson, C. Lerminiaux, , Electr. Lett., **32**, 321 (1996).
[14] D. Barbier, P. Bruno, C. Cassagnettes, M. Trouillon, R.L. Hyde, A. Kevorkian, J.M.P. Delavaux, *OFC'98 Tech. Digest*, 45 (1998).
[15] C. Armellini, L. Del Longo, M. Ferrari, M. Montagna, G. Pucker, and P. Sagoo, J. Sol-Gel Science Technol. **13**, 599 (1998).
[16] M. Montagna, M. Ferrari, F. Rossi, F. Tonelli, and C. Tosello, Phys. Rev. B **58**, R547 (1998).
[17] A. Polman, J. Appl. Phys. **82**, 1 (1997).
[18] M. Ferrari, M. Montagna, S. Ronchin, F. Rossi, G.C. Righini, Appl. Phys. Lett. **75**, 1529-1531 (1999).
[19] O.L. Malta, P.A. Santa-Cruz, G.F. de Sá, F. Auzel, J. Luminesc. **33**, 261-272 (1985).
[20] T. Hayakawa, S. Tamil Selvan, M. Nogami, Appl. Phys. Lett. **74**, 1513-1515 (1999).
[21] R. Almeida, A.C. Marques, M. Ferrari, J. Sol-Gel Sci.Techn. **26**, 891–896 (2003).
[22] C. Strohhofer, A. Polman, Appl. Phys. Lett. **81**, 1414-1416 (2002).