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Optical study of planar waveguides based on oxidized porous silicon impregnated with laser dyes

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ABSTRACT

Oxidized porous silicon optical planar waveguides were elaborated and impregnated with rhodamine B and rhodamine 6G. The waveguiding, absorption, and photoluminescence properties of these impregnated waveguides were studied. Successful impregnation of the structure with laser dyes is shown from photoluminescence and reflectivity measurements. Furthermore, the reflectivity spectra prove the homogenous incorporation of both dye molecules inside the pores of the matrices. The refractive indices of waveguide layers were determined before and after dye impregnation to indicate the conservation of guiding conditions. The optical losses in the visible wavelengths are studied as a function of dye concentration. The dye absorption is the main reason for these losses.

1. Introduction

The composite system based on an organic dye that has impregnated a solid matrix has attracted wide interest because of its useful applications, such as light concentrators in solar cells, optical waveguides, lasers, sensors and nonlinear optical components [1–4]. Different methods to trap organic molecules within solid substrates have been developed, including direct soaking of the host material with dye solutions [5–7]. It has been shown that porous silicon (PS) can be impregnated with laser dyes by the latter method [8–10].

When PS is fully oxidized, it becomes porous SiO_2 glass losing its light-emission properties but becomes transparent in the visible. In addition, the porosity variations are conserved in the glass. In this application, it would be more interesting to observe amplification in an optically homogeneous medium, for example, an oxidized PS-based waveguide. The main advantage of PS-based structures is that the optical microcavities are very easy to grow [11], and these structures can show vertical laser action if doped with an amplifying medium. These systems have been studied with organic dyes [12] but lasing has not still been reported.

In this paper, we have studied the optical properties of oxidized PS planar waveguides (OPSW) before and after impregnation with rhodamine B (RhB) and rhodamine 6G (Rh6G) dyes. RhB and Rh6G are known to be very efficient dyes. The propagation losses were studied as a function of wavelength and dye concentration. The different contributions to the losses are discussed.

2. Experimental

Porous silicon WG structures were elaborated using (1 0 0)-oriented Si substrates. The resistivity of the p^+-type wafer was 4–6 mΩ cm. The electrolyte was composed of HF (50%):H_2O: ethanol = 2:1:2 for volume proportions, respectively. Two-layer slab waveguides were grown—a core and a cladding—by applying current densities of 50 and 80 mA/cm^2, respectively. In order to have single-mode waveguides, the core thickness was set above 900 nm, and the cladding thickness was above 5 μm to prevent the radiative mode from the silicon substrate. The samples were firstly oxidized at 300 °C in air for half an hour, followed by full oxidation at 1000 °C in air for 2 h in order to obtain P-silica.

The samples were subsequently impregnated for 75 min in RhB or Rh6G solutions, which had different concentrations of C ($C = 5 \times 10^{-6}$ M, 10^{-5} M, 5×10^{-5} M and 10^{-4} M). Then, the formed structures were rinsed in ethanol in order to remove all residual dye molecules from the top surfaces of the samples.

The reflectance spectra of the non-impregnated and dye-impregnated OPSW were studied by a LAMBDA 900 Perkin Elmer beam spectrometer equipped with a specular reflectance module with a 6° fixed angle. These measurements enabled the optical path length to be determined by evaluating the beat of the

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interference fringes on the basis of the effective medium theory (Bruggeman model) [13,14] .The PL measurements were performed using a triple monochromator and a GaAs photomultiplier. The excitation sources were an argon laser and He–Ne laser (632.8 nm). All the measurements were performed at room temperature.

Optical losses were measured by studying the scattered light from the surface of the waveguide [15,16].

Laser light at 632.8 and 445 nm was single-mode fiber-coupled along the waveguide direction. The collecting optical fiber is placed at the input of waveguide for measurements of the guided PL. The intensity of scattered light was recorded with a digital camera placed above the sample. Transverse scanning along the light propagation direction enabled the 2-D light intensity distribution of the guided modes to be obtained. The longitudinal variation was obtained by integrating the data along each sampling transverse line. The light intensity decreased exponentially with the *z*-propagation distance.

In this study, the attenuation values were the average of several measurements performed on several samples. From the photograph taken of the waveguide, the first 1–2 mm at the input facet were ignored in order to improve the signal-to-noise ratio and also not to take the multiple scattering at the injection point into account. The polarization of the coupled light entering the waveguide was not controlled. In addition, the near-field profiles of guided modes were observed at the output of the waveguides at the excitation wavelengths.

3. Results and discussion

In order to evaluate the effect of the presence of the dye and to characterize the optical properties of the waveguides, reflectivity measurements were performed before and after dye infiltration (Fig. 1). From these measurements, it is possible to extract the refractive index and thickness of both guiding and cladding layers [14]. The reflectance spectrum of the impregnated monolayer was adjusted from a model relative to single-layers. It can be assumed that the dye profile can be considered homogeneous according to the depth of each PS layer of the waveguide [17]. These results are reported in Table 1. It can be seen that, after oxidation, the refractive index of each layer decreased and had a lower value than the one of silica, which indicated that the oxidized layers remained porous. Moreover, the increase in layer thickness can be explained by the transformation of silicon into silica, which led to volume expansion [18]. After impregnation of layers in laser dye solutions with concentrations equal to 10^{-4} M, the refractive index of both cladding and guiding layers was slowly increased. This reveals the effect of the dye molecules on the optical properties and proves that dye had infiltrated into the porous layers. After impregnation, the guiding conditions were always conserved. In fact, the refractive index of the guiding layer was higher than that of the cladding layer.

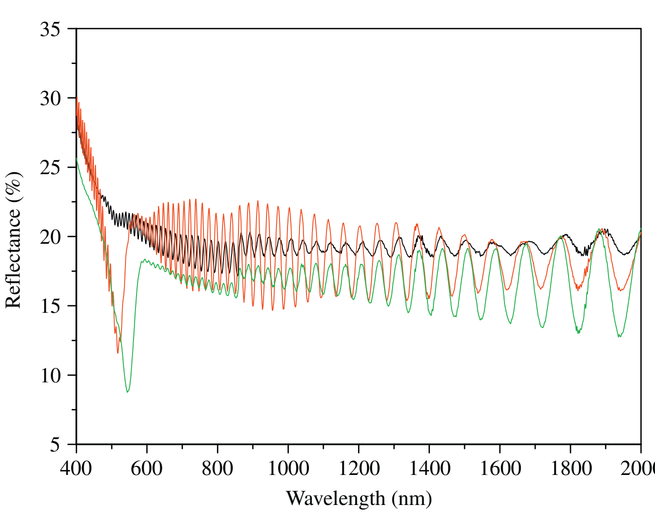

Fig. 1. Reflectivity spectra of OPSW (black line), OPSW/RhB (green line) and OPSW/Rh6G (red line). (For the interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1
Refractive indices of the oxidised porous silicon single layer before and after impregnation with RhB and Rh6G (a) at 445 nm and (b) at 633 nm..

	Refractive index of cladding layer	Refractive index of guiding layer
At 445 nm		
Porous silicon	1.78	2.2
Oxidized porous silicon	1.32	1.37
Oxidized porous silicon/RhB	1.34	1.39
Oxidized porous silicon/Rh6G	1.34	1.39
At 663 nm		
Porous silicon	1.69	2.03
Oxidized porous silicon	1.32	1.37
Oxidized porous silicon/RhB	1.33	1.39
Oxidized porous silicon/Rh6G	1.33	1.39

Fig. 1 shows the reflectivity spectra before and after impregnation of the OPSW. The absence of the interference fringes in the visible is principally due to the absorption of dye molecules in this range. This is also a proof of dye incorporation inside the pores of the matrix. We note the presence of two absorption bands centered at 520 and 540 nm. They correspond, respectively, to the absorption bands of RhB and Rh6G in the porous silica matrix. Theses bands are slightly shifted compared to those of the rhodamines containing ethanol solution (540 nm for RhB and 530 nm for Rh6G). Such a shift is probably due to the dry state of dyes in a porous silica matrix.

Fig. 2 shows the photoluminescence (PL) intensity of OPSW impregnated with RhB (10^{-4} M) and Rh6G (10^{-4} M) solutions at 514.5 and 488 nm exciting wavelengths. The efficient PL of both samples is proof of the incorporation and dispersion of the dye molecules inside the porous matrix. Indeed, dye luminescence depends on its concentration since the coupling between the molecules changes with the distance D according to the interaction type and can be written as D^{-n}, where n is related to the interaction ($n \geqslant 6$). That is to say that the luminescence signal of the dye decreases with the aggregation of the molecules and dye molecules need dispersion to luminesce [19]. The PL of OPSW/RhB is red shifted and is more efficient than that of OPSWG/Rh6G. This result can be explained by the effect of absorption, which is higher and red shifted when RhB rather than Rh6G is used (Fig. 1).

The dependence of PL intensity on the excitation wavelength is attributed to dye absorption (inset of Fig. 2). In fact, when the dye absorption increases, the PL intensity also increases. We note that absorption spectra of rhodamine in solution and in the porous silica matrix are quite similar [20]. Particular attention should be paid to the PL band. The emission is either stokes or anti-stokes, the spectral position of the PL band depends slightly on the excitation wavelength beam (inset of Fig. 2). This means that the PL mechanism is governed by an interaction process between dye

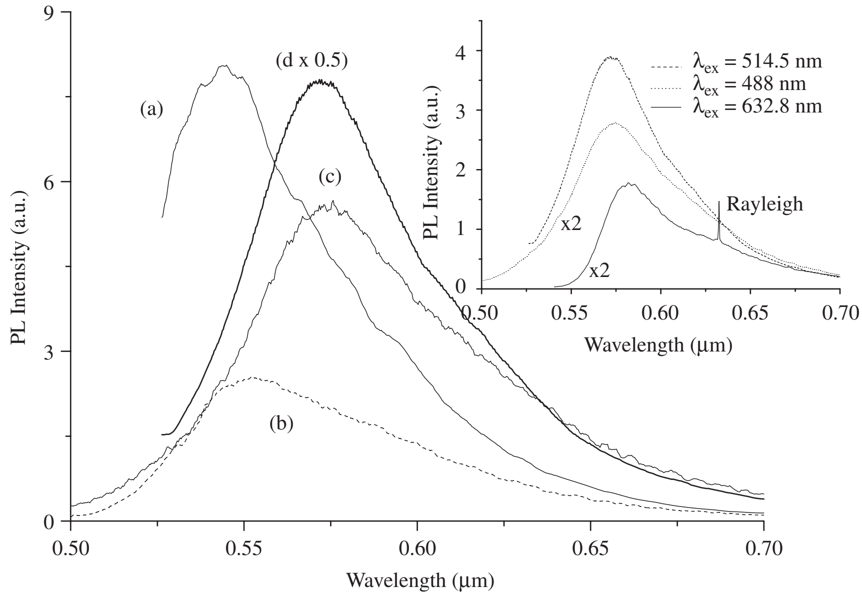

Fig. 2. PL intensity of OPSW/Rh6G for the excitation wavelengths 514.5 nm (a) and 488 nm (b) and OPSW/RhB for the excitation wavelengths 488 nm (c) and 514.5 nm (d). *Inset*: comparison of the PL spectra of OPSW/RhB for the excitation wavelengths 488, 514.5 and 633 nm.

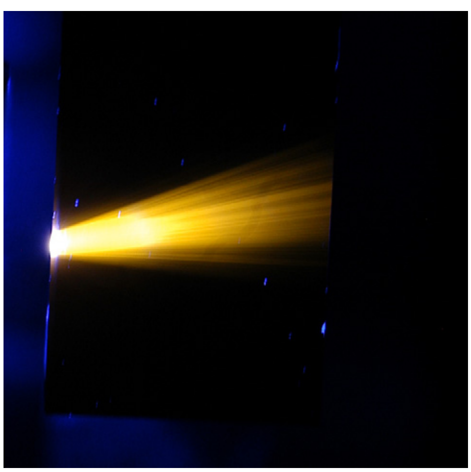

Fig. 3. Top view of the propagated light in the impregnated OPSW at 445 nm.

molecules and chemical compounds on the internal surface of porous silica [21]. In fact, RhB and Rh6G are both cationic laser dyes. They interact preferentially with anionic sites like oxygen, which is the principal constituent of the porous silica matrix [22]. We have shown in our previous work [8] that the PL intensity of porous silicon–laser dye composites depends strongly on the oxidation degree of the porous silicon layer.

Single-mode waveguides were manufactured and impregnated in the dye solutions with different concentrations. The light propagation in OPSW at both 632.8 and 445 nm was performed by observing the near-field profiles of guided modes at the output of the waveguides. Fig. 3 represents a typical top view of light propagation in an OPSW for an excitation wavelength equal to 445 nm. This figure proves the participation of dye molecules in propagated light. In fact, this light is red shifted compared to the incident light.

The optical losses were obtained from these waveguides by measuring scattered light from the surface of the waveguide. For example, the two-dimensional light intensity of the scattered light intensity at 445 nm as a function of the propagation distance for the OPSW impregnated with RhB is reported in Fig. 4. The intensity *I* decreased exponentially and a fit was performed to deduce propagation losses. The optical loss results for OPSW before and after dye impregnation, at 445 and 633 nm wavelengths, are illustrated in Fig. 5.

Before impregnation, the optical loss value increases from 1.6 dB/cm, at 633 nm to 3.2 dB/cm at 445 nm. The decrease in losses with the wavelength is due principally to the volume scattering of porous silica [16]. However, such values of losses are relatively higher than those reported in the literature [16,23]. This is probably due to the fact that some Si crystallites were not completely oxidized since the oxidation process is performed in air and not in pure oxygen.

After impregnation with laser dyes, the optical losses increase with the dye concentration irrespective of the wavelength. Moreover, the optical losses increase when dye absorption increases. Furthermore, for the same dye concentration, the optical loss relative to the OPSW/RhB is higher than the optical loss of the OPSW/Rh6G because absorption, in the visible range, of RhB is more important than that of Rh6G. For all liquid medium, the quantum yield of Rh6G is higher than that of RhB. Moreover, the effect of absorption is clearly observed in PL measurement. So, despite the more important quantum yield of Rh6G, its PL intensity is weak compared to that of RhB. Consequently, in addition to the quantum yield, the main difference between the optical losses value is due to the absorption effect. In fact, the quantum yield of Rh6G is more important than that of RhB in the same solution. So this is verified by the losses value for both laser dyes.

All these results prove that dye absorption is the principal origin of losses in OPSW/dye structures. Losses due to volume scattering can also be considered but they are of the second order. In another study [24], comparable values for losses have been reported, at different wavelengths, for OPSW impregnated with organic dye (nile blue). The increase of losses is also attributed to dye absorption.

The particular enhancement of the optical losses for OPSW/Rh6G with a concentration 10^{-4} M, observed at the 445 nm wavelength (Fig. 5), can be explained by the important absorption due to dye molecules at this wavelength and also by a possible formation of dye aggregates.

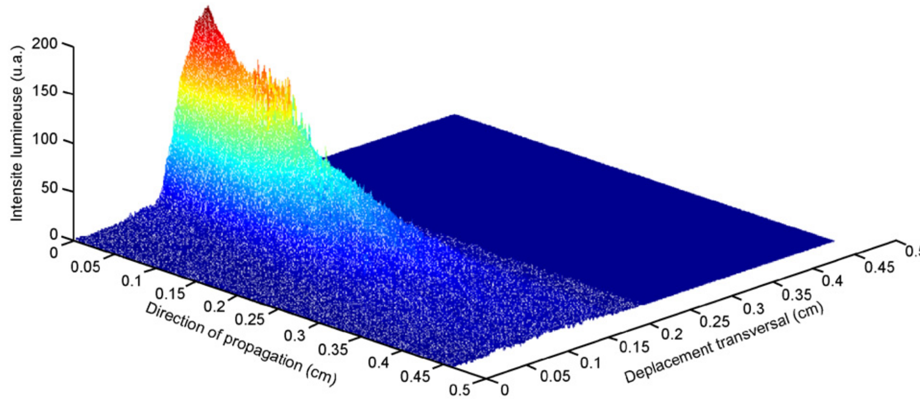

Fig. 4. Two-dimensional light intensity of the scattered light intensity at 445 nm as a function of the propagation distance for the OPSW impregnated with RhB.

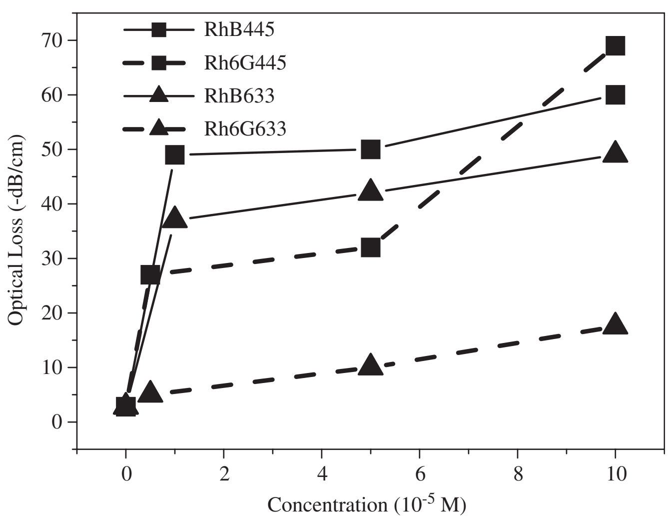

Fig. 5. Optical losses at 445 and 633 nm of OPSW/RhB and OPSW/Rh6G versus dye concentrations.

4. Conclusion

Optical properties of oxidized porous silicon waveguides impregnated with laser dyes were studied. Successful incorporation and dispersion of RhB and Rh6G in OPSW were obtained by simple immersion. The refractive index variation and efficient PL intensity evidenced the effect of the laser dyes incorporation on waveguide optical parameters. The optical parameters of the waveguide before and after dye impregnation were determined from the reflectance spectra. The PL of the impregnated OPSW was mainly due to dye absorption and interaction between dye molecules and oxygen sites. The waveguiding properties were studied in the visible range for the impregnated OPSW as a function of dye concentration. The optical losses were attributed principally to dye absorption.

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