Optical gain in dye-impregnated oxidized porous silicon waveguides

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Positive optical gain under pulsed excitation in oxidized porous silicon planar waveguides impregnated with Nile blue (LC 6900) is reported. Amplified spontaneous emission measurements show a dramatic line narrowing when the pump energy is increased, together with a strong superlinear behavior. Variable stripe length measurements were performed to characterize quantitatively the amplification, and an unambiguous transition from losses to gain is observed with a threshold of ∼3 mJ/cm² at 700 nm. A maximum gain coefficient of 8.7 cm⁻¹ (∼40 dB/cm) is reported. Shifting excitation spot measurements confirm the reliability of our results. This system is interesting in view of an optically pumped silicon-based pulsed laser. © 2006 American Institute of Physics. [DOI: 10.1063/1.2219121]

Light emission from silicon-based structures has been investigated very actively during the last years, mainly because an efficient light source would allow monolithic integration of optoelectronic circuits. Porous silicon (PS) has been one of the most studied materials after it was discovered that it showed efficient luminescence at room temperature. Recent reports of optical gain in porous silicon nanocrystals have increased its interest even more. This material can be electrochemically formed on silicon by employing standard wafer processing technology. On the other hand, its porosity can be varied in depth with an arbitrary profile, making possible to fabricate many different photonic devices, such as filters, waveguides, or resonators.

When PS is fully oxidized, it becomes a porous SiO₂ glass loosing the light emission properties but becoming transparent in the visible. In addition, the porosity variations are conserved in the glass. This porous silica glass is a very appealing host for the impregnation of different substances. Indeed organic dyes have been impregnated in this material. In 2002, randomly oriented stimulated emission was observed in this system, although this was only observed when microdroplets that appear during the evaporation of the dye dissolution created a strongly scattering medium inside the structure. From the device point of view, 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 optical microcavities are very easy to grow, and these structures can show vertical laser action if doped with an amplifying medium. These systems have been studied too, not only with organic dyes but also with rare earth ions, but lasing has not still been reported. In this letter, we report positive optical gain in dye-impregnated oxidized porous silicon-based planar waveguides.

Porous silicon samples were fabricated by electrochemical etching of (100)-oriented heavily doped (0.01 Ω cm resistivity) p-type silicon. The electrolyte was made mixing 31% of aqueous HF (48 wt. %) with ethanol. Two-layer slab waveguides were grown (a core and a cladding) by applying current densities of 40 and 80 mA/cm², respectively, to a 1 cm² circular area. In order to have single-mode waveguides, the core thickness was set to 500 nm, and the cladding thickness was 10 μm to isolate the mode from the silicon substrate. The samples were annealed at 900 °C in air for 3 h in order to oxidize the silicon skeleton and convert it into porous silica. The refractive indices of the core and cladding decreased after oxidation from 1.75 and 1.36 down to 1.25 and 1.15, respectively. The waveguide modes were characterized at 633 nm with a prism-coupling setup, where only one guiding mode was observed for each polarization, confirming that the waveguides were single mode. We report a detailed characterization of similar waveguides in Ref. 14. The samples were subsequently impregnated by 1 min long immersion in Nile blue (LC 6900) (Ref. 15) dissolved in an ethanoic solution, at concentrations between 10⁻⁶M and 10⁻⁴M. Finally, the samples were cleaved along one side to be able to measure the emission exiting from a waveguide facet (guided luminescence).

Spectroscopic measurements were performed by pumping with a frequency-doubled Nd:YAG (yttrium aluminum garnet) laser (532 nm) in Q-switching mode, which gave 5 ns pulses with vertical polarization. A lens system focused the pump beam on the waveguide to a horizontal line which was 3 cm long and 300 μm wide. The maximum pump energy employed was 3 mJ (30 mJ/cm²). A metal blade was placed in front of the waveguide in order to vary the illumination length L. The distance between the waveguide and the blade was only 5 mm in order to minimize diffraction effects, and the end-face guided light was collected with a lens (10 cm focal length) to avoid confocal effects. The lens was partially covered with an opaque surface to avoid collecting nonguided signal. The guided luminescence was im-
aged into a monochromator interfaced with a photomultiplier tube (PMT), which allowed single shot luminescence measurements. All the spectra were collected with 1 nm spectral resolution, and all the measurements at fixed wavelength, with 5 nm resolution.

Gain measurements were performed with the variable stripe length (VSL) method, which consists in collecting the guided amplified spontaneous emission ($I_{\text{ASE}}$) while varying $L$. Assuming a one-dimensional amplifier with a net modal gain coefficient $g$, \begin{equation}
I_{\text{ASE}}(L) \propto \frac{1}{g} (e^{gL} - 1),
\end{equation}
where $g$ has to increase from negative to positive values when the pump energy ($E_P$) is increased. In our experiment, one single laser shot was used per each $L$ value.

We also performed “shifting of excitation spot” (SES) measurements to characterize the waveguide losses. This technique consists in scanning a pump spot through the waveguide surface and measuring the guided luminescence versus the distance $\ell$ from the edge. The curve should follow an exponential decay, which would give the total losses, and this value should correspond to $-g$ measured with VSL at very low power. This agreement would confirm the reliability of the VSL measurement. The slit we used for these measurements was 50 $\mu$m wide.

We first measured the guided luminescence spectra for different pump powers illuminating the whole sample length ($L \approx 8$ mm). No change in the band shape was observed between the low and high pump power spectra for the waveguides impregnated with $10^{-4}M$ and $10^{-5}M$ concentrations. However, the waveguide impregnated with a $10^{-5}M$ solution showed a strong line narrowing at high pump power (Fig. 1). The integrated intensities $I_{\text{ASE}}(\lambda)$ of two significant spectral windows, centered at $\lambda = 650$ and 700 nm, are reported in the inset of Fig. 1. For pump energy densities $E_P$ up to 2.30 mJ/cm$^2$, both regions grow linearly with $E_P$. Above a threshold $E_P = 2.80$ mJ/cm$^2$ a strong superlinear behavior of $I_{\text{ASE}}(\lambda = 700 \text{ nm})$ is observed. At this $E_P$ also the spectral shape of the luminescence changes with a band at 700 nm emerging from the wide emission background. For ten times higher powers, another band appears which is centered at 680 nm. These superlinear emission bands were transverse electric (TE) polarized, whereas the transverse magnetic (TM) component of $I_{\text{ASE}}$ showed a linear behavior.

Figure 2 reports the SES measurements for three wavelengths: 680, 700, and 720 nm. For distances shorter than the first half millimeter, nonguided signal emitted from the cladding (which is 20 times thicker than the core) is also being collected. For longer distances, where only guided luminescence is present, the SES data show an exponential attenuation. From the result of the fit we obtain loss values of $\alpha = 30, 10.2$, and $7.7 \text{ cm}^{-1}$ at $\lambda = 680, 700$, and 720 nm, respectively. The increase of the losses when the wavelength decreases is due to the absorption band of Nile blue, which is peaked at 633 nm.

Figure 3 shows the VSL curves at 700 nm for different $E_P$ values. For low $E_P$ a sublinear behavior of $I_{\text{ASE}}(L)$ is observed, while, when $E_P$ increases, $I_{\text{ASE}}(L)$ becomes a positive exponential, demonstrating unambiguously positive optical gain. A fit with Eq. (1) yields the gain coefficient values. Note that, at maximum power, the gain is constant along the first half centimeter, reaching a total signal amplification of almost 20 dB, and beyond that length the gain starts to saturate.
The transparency energy density values are 700 nm and 680 nm should be 2400 cm\(^{-1}\) per mol/liter concentration; in our case. Indeed we observed that after 1000 pump pulses higher.

Figure 4 reports the gain coefficients versus pump energy density (fluence) for three representative wavelengths: 680, 700, and 720 nm. At 700 and 680 nm, g increases from a negative value (losses) to a positive value (amplification). The transparency energy density values are \(-3 \text{ mJ/cm}^2\) at 700 nm and \(-10 \text{ mJ/cm}^2\) at 680 nm. At higher powers, g saturates in both cases. At 720 nm no gain was observed \((g < 0)\), although almost transparency was achieved at the highest pump power. A reliability check of the data extracted from VSL measurements is to compare g at very low power with \(-\alpha\) measured by the SES technique: for all the three wavelengths they are the same within the error bars.

From the datasheets of the dye,\(^\text{15}\) the absorption at 680 nm should be 2400 cm\(^{-1}\) per mol/liter concentration; thus with the measured absorption value of 30 cm\(^{-1}\), we can estimate the average concentration of dye molecules in the waveguide, which is \(\sim 8 \times 10^{18} \text{ cm}^{-3}\). This concentration is roughly two orders of magnitude higher than the concentration of the solution we used, which means that the dye molecules get adsorbed to the internal walls of the porous matrix during the immersion. It is worth mentioning that this number is obtained assuming that the dye is homogeneously distributed along the core and bottom cladding of the waveguide. However, we have recently found experimental evidence that in this kind of sample, the main contribution of the emission comes from the first 200 nm of the core,\(^\text{19}\) so in that case the concentration would be around three times higher.

Laser dyes usually undergo bleaching after a certain number of pulses, especially when they are not circulated, as in our case. Indeed we observed that after 1000 pump pulses the amplified signal starts to decrease appreciably. After 10\(^4\) pump pulses, the waveguide still showed amplification, but with approximately four times higher pump threshold. When the sample is rinsed and impregnated again, the original behavior is recovered.

In conclusion, optical gain has been observed in dye-impregnated oxidized porous silicon planar waveguides in a pulsed regime. This material system can be tailored to make a laser or an amplifier in the visible since different dye molecules can be infiltrated in the porous silica glass host to change the gain spectral region. More work is needed to electrically excite the system and to make the molecule stable enough not to bleach to allow cw operation. However, this study shows the feasibility of a laser in a porous silica glass host when active molecules are impregnated in it. A factor of further interest is the way the porous silica is produced, which is based on standard silicon processing, such as electrochemical etching and thermal oxidation.

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