Small mode-size waveguides in quantum-dot-doped glasses by Ag-film ion exchange

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We present a silver-sodium ion-exchange process for fabricating small mode-size waveguides in glass doped with PbS semiconductor quantum dots. We show that the process does not alter the optical properties of the quantum dots by comparing the waveguide and bulk luminescence spectra. We also show that the optical mode is highly confined. This field confinement produces high optical intensities, which are essential for nonlinear optical applications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2202736]

Recently, we presented a technique for fabricating lowloss waveguides in a glass doped with PbS quantum dots (QDs).¹ We discussed the use of a molten salt of KNO₃ in order to produce K⁺-Na⁺ ion-exchanged waveguides. K⁺-Na⁺ ion-exchanged waveguides are weakly guided with a large mode size due to low index contrast. AgNO₃ molten salt cannot be used to produce ion-exchanged waveguides in this glass due to the reduction of silver in the form of nanoparticles.¹ In this Communication, we demonstrate an alternate method of fabricating waveguides in a QD-doped glass using a Ag-film ion-exchange process.^{2,3} The principal advantage of this Ag-film process over the previous process is a fivefold decrease in mode area (resulting in a fivefold increase in optical intensity), which is due to a higher index change ($\Delta n_{\text{max}} \approx 0.045$). This maximization of intensity is of crucial importance for nonlinear integrated-optical circuits (IOCs). This higher index change also allows for the waveguides to be buried, which minimizes surface interaction, coupling loss, and birefringence.⁴

For about a decade, high quality QD-doped glasses have been produced using the proper thermal treatment of a glass containing the semiconductor's chemical constituents.⁵ The three-dimensional quantum confinement of the QDs allows us to tailor the optical absorption.⁶

Producing waveguides in QD-doped glasses is advantageous because the field confinement and increased interaction length enhance the nonlinear optical effects. Fabricating integrated optical devices using QD-doped glasses is far less expensive than grown structures, e.g., through molecular beam epitaxy (MBE). This makes QD-doped glass an attractive candidate for photonic devices.

The PbS QDs in our glasses provide strong carrier confinement since they have radii (2-5 nm) that are much smaller than the bulk exciton Bohr radius (18 nm). The small bulk band gap energy of PbS (0.4 eV at 300 K) allows tuning of the optical resonances throughout the near infrared. The room-temperature absorption spectra of several PbS QD-doped glasses are shown in Fig. 1. The QD radii R quoted in Fig. 1 are calculated using a hyperbolic band (HB) model:^{7,8}

$$(\hbar\omega_{1s})^2 = \left(\frac{hc}{\lambda_{1s}}\right)^2 = E_g^2 + \frac{2\hbar^2 E_g}{m^*} \left(\frac{\pi}{R}\right)^2,\tag{1}$$

where we used the room-temperature (T=300 K) band gap energy of $E_g=0.41$ eV and effective mass of $m^*=0.12m_e$ for PbS.⁸

Strongly confined QDs exhibit strong optical nonlinearities,⁹ which include bleaching and optical gain. Both of these effects have been measured in these PbS QD-doped glasses.^{10–12} These measurements were performed in bulk glasses, whereas most applications are for integrated optics. Initially, we demonstrate the production of QD-doped waveguides.

IOCs produced using ion exchange are commercially available using molten salts and a field-assisted burial



FIG. 1. Room-temperature absorption spectra of PbS QD-doped glasses. Waveguide samples are represented using solid lines. The mean QD radius R for each sample is listed.

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FIG. 2. Ag-film ion-exchange process. After surface polishing and cleaning, the glass is (a) coated with photoresist, which is patterned and cured, (b) coated with silver on both sides, (c) a dc field is applied for ion exchange, and (d) the silver is stripped off and the glass is annealed. For our ion exchange, we used a field of 250 V/mm at 105 °C for 2.5 h, followed by a 2.5 h annealing at 200 °C.

process.¹³ These waveguides have extremely low loss and the process can be optimized to eliminate birefringence and polarization dependent loss (PDL).⁴ Previously, a K⁺–Na⁺ ion-exchange process has been used to produce waveguides in other semiconductor-doped glasses.^{14,15} Recently, we reported the fabrication of very low loss waveguides in PbS QD-doped glass using a similar technique.¹ Using Ag-film ion exchange, we demonstrate a process to produce waveguides in PbS QD-doped glass.

In the ion-exchange process, the physical mechanism is the thermal diffusion of ions (can be field assisted), which produces an index change by altering the local glass density and mean polarizability.^{13,16} In molten salt ion exchange, the molten salt supplies replacement ions for sodium ions in the glass. In the case of Ag-film ion exchange, a thin film of silver supplies the replacement ions with the aid of an applied electric field. This electric field keeps the ions moving in the glass, which prevents silver reduction and nanocrystal formation. Ag-film ion exchange has been used to produce waveguides in undoped glass^{2,17} and in Er-doped glass;¹⁸ however, until now, semiconductor-doped waveguides have never been reported using *any* type of Ag⁺–Na⁺ ion exchange.

The Ag-film ion-exchange process (see Fig. 2) starts with production of the ion-exchange mask. The glass sample was surface polished, cleaned, and coated with photoresist. The developed photoresist serves as the ion-exchange mask, which can contain any two-dimensional (2D) pattern to form any IOC. The photoresist is patterned, developed, and cured. The photoresist is coated with a thin (100–150 nm) film of silver (on both faces). The ion exchange is performed by applying a dc electric field (typically a few 100 V/mm, producing a few microamperes), which drives silver ions into the glass. After ion exchange, the residual silver was removed and the sample was cut and polished for device characterization.

The losses were analyzed by using the fiber-waveguideobjective method.¹ In addition, near-field images of the modes were measured and used to calculate the ideal coupling efficiencies of these modes using¹⁹

$$\eta = \left| \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sqrt{I_1(x,y)} \sqrt{I_2(x,y)} dx dy \right|^2,$$
(2)

where the intensities, I_1 and I_2 , are properly normalized. The coupling loss is given by $\Gamma = 1 - \eta$. Table I summarizes losses

TABLE I. Average propagation, guide, coupling, and ideal coupling losses in QD-doped waveguides having the absorption spectrum shown in Fig. 1 with QD radius of R=3.2 nm. All measurements were performed at 1550 nm.

Mask (µm)	Prop. loss (dB/cm)	Guide loss ^a (dB/cm)	Coup. loss (dB)	Ideal coup. loss ^b (dB)
2	$3.5 \pm 0.8^{\circ}$	2.2	$2.4 \pm 0.3^{\circ}$	1.3 ± 0.3^{c}
3	3.7 ± 0.5	2.4	1.9 ± 0.2	1.2 ± 0.3
4	4.3 ± 0.6	3.0	1.5 ± 0.1	1.2 ± 0.3

^aEstimated QD absorption (1.3 dB/cm) was removed.

^bOverlap integral between the waveguide and SMF-28 mode profiles [see Eq. (2)].

 c Standard deviation of measurements (six waveguides per mask width). The single-waveguide measurement error is 0.2 dB/cm.

of several QD-doped waveguides. Figure 3 shows a typical mode profile of these channel (surface) waveguides as compared with that of single-mode fiber (SMF-28). Notice that these waveguide modes are very small. These mode profiles should be contrasted with the large mode profiles of our earlier K^+ -Na⁺ ion-exchanged waveguides. The small mode size provides increased intensity and stronger field interaction with the QDs in the waveguide, which is a major advantage for nonlinear optical applications.

These waveguides not only provide optical confinement, they are semihomogeneously doped with PbS QDs. The linear absorption through the thickness of the glass remained unchanged throughout the ion-exchange process. Scattering processes (surface, Rayleigh, and Mie) in the waveguides overshadow the linear QD absorption of $\alpha \approx 0.3 \text{ cm}^{-1}$ =1.3 dB/cm. Within experimental error, guides in the host glass (without QDs) had the same losses, so the nonuniformity of the glass and surface interaction were determined to be the predominate sources of the waveguide losses. So, instead of a direct measure of QD absorption in the waveguides, we collect photoluminescence (PL) emitted by the semiconductor QDs within the waveguides. The spectral location and shape of this PL is characteristic of the size and shape of the PbS QDs; therefore, any change in QD chemistry, size, or shape as a result of the waveguide fabrication process would be observed in the PL spectrum.

Figure 4 shows PL from a sample before ion exchange and collected from an ion-exchanged waveguide. Notice that there are no noticeable differences between these spectra,



FIG. 3. Measured near-field mode profiles from (left) a QD-doped waveguide and (right) SMF-28 (loss γ =1.1 dB). The waveguide mode has a 7.5 μ m e^{-1} width and a 5.8 μ m e^{-1} height. The mode (1550 nm light) was collected using a 0.6 numerical aperture (NA) objective and imaged onto a NIR camera.

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FIG. 4. Typical luminescence collected from a PbS QD-doped waveguide (solid) along with luminescence from this glass before (dotted) and after (dashed) ion exchange. The QD absorption (open circles) is shown for comparison (see the R=3.2 nm sample in Fig. 1). The pump wavelength was 1064 nm, which coincides with the absorption of the first excited state of the QDs.

which demonstrates that the optical properties of the quantum dots remain unchanged through the ion-exchange process. Additionally, in waveguide measurements, the maximum PL signal was found when the input and output optics were aligned to the waveguide, which shows that the waveguides are doped with QDs. We would like to emphasize that waveguide PL was measured using two different collection schemes with the same results. In both setups, we coupled the pump light into the waveguide using a microscope objective. In one setup, we collected the light leaving the exit facet of the waveguide, and in the other setup, we used a multimode fiber to collect light from the top of the waveguide.

In conclusion, we fabricated Ag-film ion-exchanged waveguides in a QD-doped glass. These waveguides have a small mode size producing a fivefold increase in optical intensity as compared with previous results. This is essential for many nonlinear optical applications. For these applications, this increase in intensity allows us to tolerate higher waveguide losses. Furthermore, losses <0.2 dB/cm can be achieved with small mode-size Ag-film ion-exchanged surface waveguides when commercial glass substrates with high

uniformity and very smooth surface are used.²⁰ Additionally, we confirmed that the waveguides are doped with QDs by measuring their PL spectra. This method shows great promise for nonlinear integrated-optical circuits in QD-doped glass.

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