Mesoscopic photonic structures in glasses by femtosecond-laser fashioned confinement of semiconductor quantum dots

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Mesoscopic photonic structures in glasses by femtosecond-laser fashioned confinement of semiconductor quantum dots

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Optically tunable mesoscale structures offer unparalleled potential for photonic device applications. Here, we report the creation of composite photonic structures consisting of CdS_xSe_{1-x} quantum dots (QDs) customized within lines, first written in a glass by femtosecond laser pulses. CdS_xSe_{1-x}-doped borosilicate glasses were pulsed with a fs-laser using a 473 kHz repetition rate to create chemically distinct microscopic regions. Upon further heat treatment, these regions served as "micro-crucibles" within which quantum dots were precipitated exclusively. These results open prospects of developing other semiconductor doped glasses for versatile photonic structures useful over broader optical wavelengths. © *2013 AIP Publishing LLC* [http://dx.doi.org/10.1063/1.4802724]

Photon based signal processing and manipulation for applications ranging from sensors to telecommunications relies heavily on integrated optical circuitry written with a high degree of precision. The use of tightly focused femtosecond (fs) laser pulses to fashion deliberate architectures in optical media such as glasses[1–11] is a promising approach for fabrication of a variety of photonic devices with improved functionalities. Examples include telecom-band directional couplers,[12,13] optical gratings,[14–18] 3-D optical storage, and photonic crystals.[19,20] The ability to localize quantum dots (QDs) to specific regions of a photonic medium can allow integration of interfaces between different elements of devices.

Femtosecond laser processing for tailoring defined architectures has evolved as an effective tool for engineering a variety of photonic devices. The many advantages[21] of femtosecond laser processing, over established lithographic techniques for example, include spatial confinement of optical alterations, ability to make complex shapes by sample translation, and integration of multiple photonic devices on a single platform. The broad spectrum of possibilities are based on exploiting the power of non-linear ultrafast light-matter interactions for shaping, carving, or embedding structures-within-structures at nano, micro, and mesoscopic scales. Focusing ultrashort laser pulses down to a few microns in diameter produces a brief, but extremely high electrical field at the focal point, which triggers non-linear interactions *inside* a normally transparent medium, such as glass. This highly localized, intensity dependent energy absorption is ripe for tailoring three-dimensional photonic structures with unprecedented precision and versatility. Thus, mesoscopic structures for specific functionalities, such as waveguides, gratings, and data storage devices, have been made in glasses using low repetition rate fs-lasers (up to 100 kHz) that avoid thermal damage and heat accumulation effects. More recently, fs-laser systems with MHz range repetition rate capabilities with attendant heat accumulation effects have achieved preliminary success in writing near-cylindrical waveguides[22,23] and other photonic features.[24,25]

Deliberately engineered mesoscopic composites, such as metal or semiconductor nanocrystals embedded in a dielectric (see Fig. 1), offer great potential for photonic devices, with many photonic functionalities not readily attainable in traditional bulk materials.[25–28] Some measure of effort has already been directed towards precipitation of metal nanoparticles, and femtosecond laser writing in semiconductor-doped glasses (SDGs) has also been explored in the context of modifying glasses with already precipitated nanocrystals or irradiating homogeneous glasses to create high refractive index structures.[29] SDGs offer a particularly interesting substrate for optical applications due to their ability to precipitate quantum dot quality semiconductor nanocrystals upon heat treatment. The precipitated quantum dots exhibit high nonlinearities and highly tunable, size-dependent optical properties.

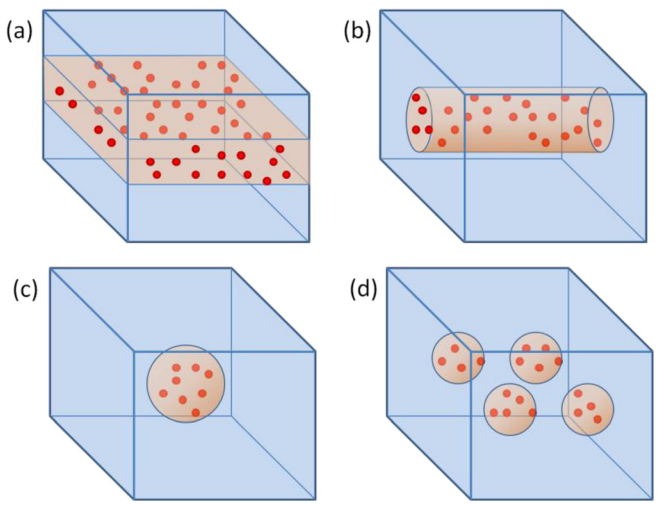

FIG. 1. Examples of mesoscale composite structures: (a) a 2D planar structure, (b) a 1D line, such as a waveguide, (c) a zero-dimensional structure and (d) array of such structures.

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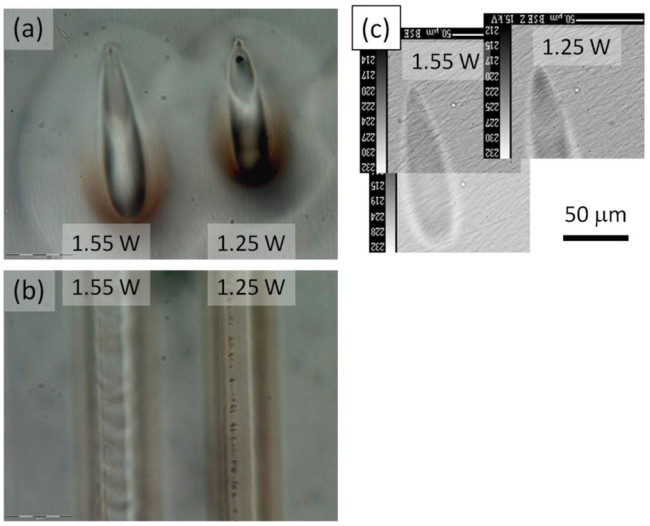

FIG. 2. Lines written with 1.55 W and 1.25 W average power. Transmitted light micrographs of the lines' cross sections (a) and side view (b); and BSE image (c) of the cross sections. For (a) and (c), the modifying laser beam is directed from the bottom of the page. For (b), it is directed into the page.

The semiconductor-doped glass used in this experiment was prepared from a commercially available OG570 long pass filter glass from Schott, Inc. OG570 is a borosilicate glass and owes its orange coloration to nanocrystals of CdS_xSe_{1-x}, where x is approximately 0.7. The OG570 glass was melted at 1450 °C for 30 min to dissolve the dopant semiconductor, then cast into a graphite mold to remove residual thermal stress, annealed at its glass transition temperature, 510 °C, for 10 min after which the material was allowed to cool with the furnace. The resultant glass, at this point designated OG570-Q, was clear with no evidence of semiconductor crystals.

We began by using the fs-laser to write lines in OG570-Q to form structures similar to the 1-D line shown in Figure 1(b). The laser used was a 1030 nm fiber laser with 750 fs pulse width, 473 kHz pulse repetition rate, and available average power of 1.55 W. The lines were written transversely at 1 mm/s scan speed with the beam focused using an aspherical objective with W.D. = 6 mm, N.A. = 0.50, and a focal spot of 2.5 μm. After fs-laser processing, the samples were cross-sectioned and polished, to expose the modified regions, and elemental distribution was analyzed using backscattered electron (BSE) and wave dispersive x-ray spectroscopy (WDS) tools of CAMECA SX-100 electron microprobe. Figure 2 shows two lines written at powers 1.25 W and 1.55 W. The cross section profile of the lines written (Fig. 2(a)) shows the inner, strongly modified region, elongated in the direction of the laser, and the larger, less pronounced modified region around it. The latter is typically observed in high-repetition rate photomodification and attributed to viscoelastic effects. BSE imaging of the cross section (Fig. 2(c)) shows a pattern corresponding to the inner modified region. As BSE contrast highlights fluctuation in elemental composition, with signal proportional to the atomic number, Figure 2(c) suggests that ultrafast laser irradiation of the SDG has introduced elemental segregation across the modification, with heavier elements concentrated towards the periphery of the strongly modified region.

The details of the elemental segregation as elucidated by WDS are shown in Figure 3. What we can see is that the single-valent cations, such as sodium and potassium (Figs. 3(b) and 3(c)) were concentrated towards the "northern" tip of the modification, away from the modifying laser; zinc (Figure 3(d)) was distributed on the periphery of the modification; silicon, (Fig. 3(e)) meanwhile, congregated at the "southern" half of the modification, closer towards the modifying beam. The concentration of the semiconductor (<1 wt. %) was too low to be reliably mapped using this method. Such redistribution of glass elements is a consequence of heat transfer and mass transfer coupling that occurs at extremely high temperature gradients that accompany high repetition rate laser processing and is known as the Ludwig-Soret effect. The L.-S. effect results in separation of ions based on their respective mobilities and would suggest migration of faster network modifiers, such as sodium, potassium, and zinc to the periphery of the modification, while the network formers, such as silicon, would remain near the center. Our observation differs from this expectation. And while the elongated shape of the elemental redistribution can be explained by an inherent anisotropy of transverse fs-laser writing geometry, the distinctly different migration pattern for single-valent (Na, K) and di-valent (Zn) ions is more difficult to explain. The exact nature of the process driving this irregular distribution is not entirely clear and remains to be fully elucidated, but we theorize that it may be a result of a feedback loop of (1) the composition dependent light absorption and (2) the energy distribution dependent diffusion.

The cadmium sulfo-selenide quantum dots were precipitated by heating the cross sectioned sample at temperatures of 500 °C, 550 °C, and 600 °C, and the progress of semiconductor precipitation was monitored using fluorescence spectroscopy, with set up described elsewhere.[4] Fluorescence analysis of the fs-laser induced modification cross section was performed by

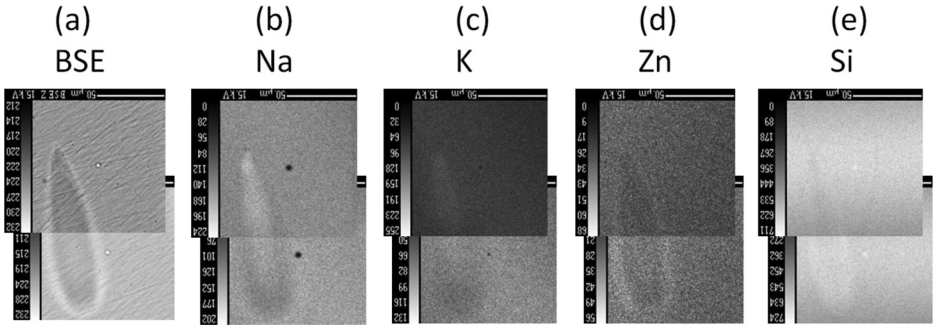

FIG. 3. Backscattered electron image (a) and wavelength dispersive x-ray spectroscopy elemental distribution maps (b)–(e) of the 1.55 W line's cross section.

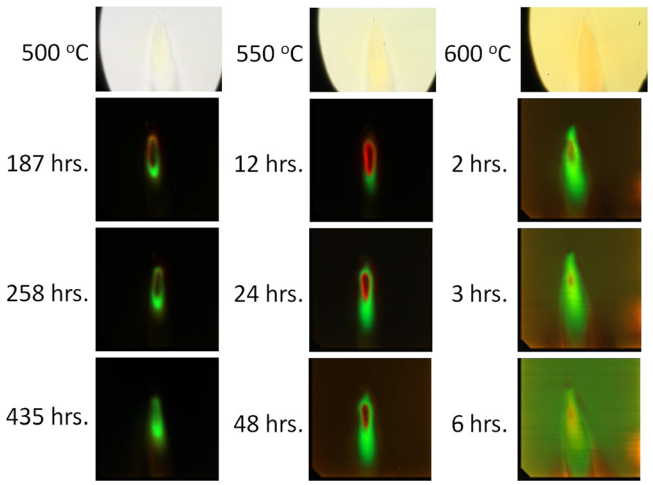

FIG. 4. Evolution of fluorescence with time in a 1.55 W line for various durations at different temperatures. The top images are transmitted light micrographs of the line at the final stage of heat treatment at that temperature.

acquiring spectra from a 2D raster of points with a 1.428 μm step size with the sampled area 100 μm by 100 μm. The sample was excited with a 100 mW, 473 nm diode laser. To obtain a qualitative assessment of spatial distribution of fluorescence and to visualize the 4D data set presented by a 2D raster of point spectra, each spectrum was represented as a pixel with its red-green-blue (RGB) coordinates determined by taking an inner product of the spectrum and the three color matching function (red, green, and blue). This produced a 2D fluorescence map of the analyzed area, where the pixel color then was roughly representative of the spectral shape, and its brightness was indicative of overall spectral intensity. Therefore, obtained fluorescence maps of the photomodified OG570-Q cross sections for different times at several temperatures (Fig. 4) show significant fluorescence evolution in the sodium and potassium rich region, towards the "north" of the modification. For temperature of 500 °C there was little observable fluorescence in the bulk surrounding the modification, suggesting that the growth of quantum dots occurred in the single-valent network modifier region exclusively. For heat treatment at 550 °C and 600 °C, some fluorescence was observed emerging in the bulk over the course of the heat treatment, suggesting that both bulk and the modification precipitated the semiconductor. However, it is still clear that the photo-written lines show preferential evolution of fluorescence.

Figure 5 presents a closer look at the spectra representative of the fluorescence maps in Figure 4. The spectra show key time points during the QD growth, with heat treatment at 550 °C (Fig. 5(a)) capturing the earlier stages of the semiconductor precipitation and heat treatment at 600 °C (Fig. 5(b)) capturing more advances stages of QD growth. Figure 5(a) shows that the red fluorescence that emerged initially is due to a broad peak around 710 nm developing in the early hours of the heat treatment (compare signal intensities between 1 and 12 h in the figure). With continued heat treatment, this peak diminished, and a partial peak appears at the blue end of the spectrum (Fig. 5(a) 24 h). Eventually, this partial peak shifts to longer wavelength, forming a full peak, as can be seen in Figure 5(b), and the peak position gradually red-

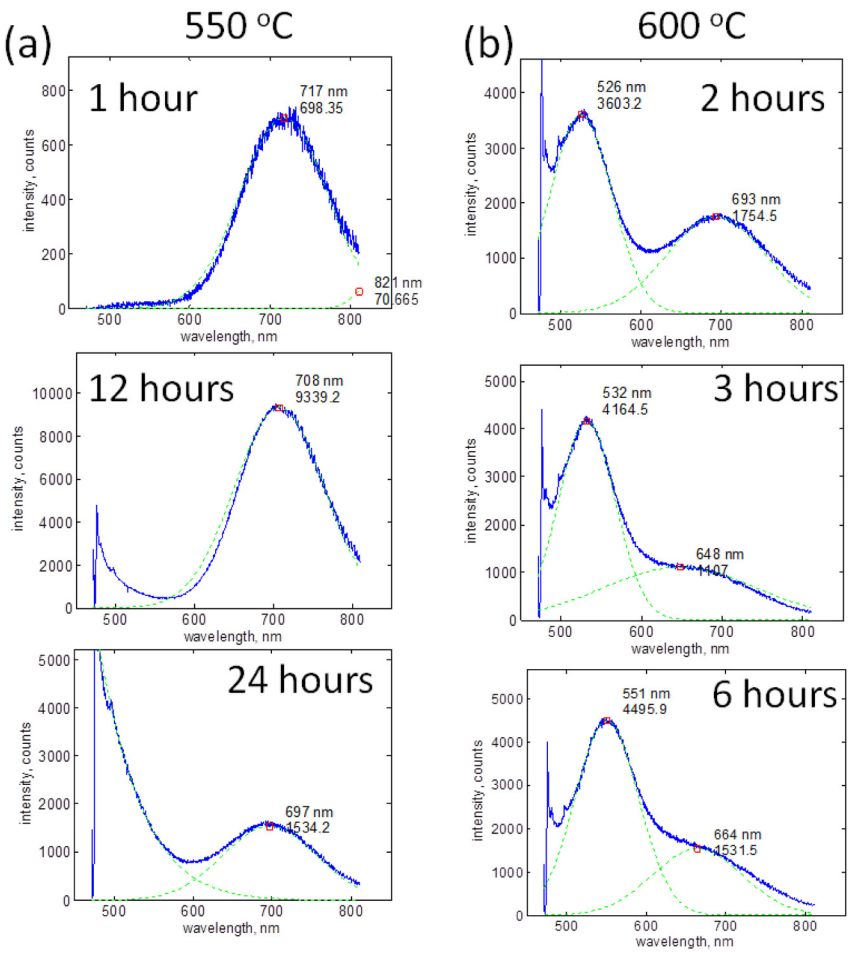

FIG. 5. Representative spectra of the 1.55 W photo-written line in samples heat treated at 550 °C (a) and 600 °C (b) for various durations.

shifts with continued exposure to elevated temperature (compare 2, 3, and 6 h in the figure).

The nature of the 710 nm peak that occurs in the early stages of the heat treatment can be attributed to formation of Se^{-2}. The peak shape and location are consistent with earlier observations of the selenium-containing glasses.[30] This peak is generally not observed in such intensity during cadmium sulfo-selenide growth in bulk OG570-Q, but in this case, a local change in composition might have pushed the semiconductor solubility even farther beyond the solubility limit, and this additional instability is partly relieved by rapid formation of diselenide ions. Subsequently, diselenide gets consumed by the growing quantum dots, which explains the reduction of the 710 nm peak with continued heat treatment.

The emergence of a blue partial peak (Fig. 5(a)) is a consequence of growing CdS_xSe_{1-x} quantum dots becoming resonant with the pump laser, whereby electrons can now be excited across the shrinking bandgap and then recombine. At this point, only the larger dots fluoresce, producing only a portion of a peak. At later stages of QD growth (Fig. 5(b)), this peak can be observed nearly in full, as all quantum dots are resonant. At this stage, a shift of the peak position to longer wavelength with growing quantum dot size can be readily observed. The second, broader peak around 700 nm observed in some of the spectra is attributed to fluorescence of the surface trap states and not direct electron-hole recombination.

The localization of the fluorescence evolution to the modified region rich in single-valent ion (Fig. 4) is a result of three composition dependent factors that contribute the semiconductor precipitation: (1) semiconductor concentration, (2) its solubility, and (3) network mobility. Without further analysis, it is impossible to separate the first two factors. The emergence of an intense 710 nm selenium cluster peak in this case suggests that these two factors combine in driving towards less stable semiconductor solution and, thus, favor precipitation. The exact extent of this contribution, however, is not easy to determine and may vary with glass composition. Although consideration that the semiconductor generally tends to behave as a network modifier, it is suggested that the observed contribution of these two factors may be quite consistent.

The third contributing factor, a composition-dependent increase in network mobility, is very straightforward contribution to assess qualitatively. An increase of the network modifying cations, such as sodium, potassium, or zinc, serves to break up the glass network, resulting in higher network mobility, or, conversely, lower glass transition temperature. By fabricating in the SGDs microscopic regions rich in network modifiers, we effectively create "micro-crucibles," which would exhibit faster semiconductor precipitation dynamics at any given temperature than the surrounding bulk. Furthermore, with careful choice of temperature that places the bulk below its glass transition while the "micro-crucible" is above, it should be possible to suppress QD growth in the bulk altogether and achieve exclusive spatial selectivity for semiconductor precipitation. In fact, it appears that this is what is occurring at 500 °C ($T_g = 510$ °C), where there is no observable QD growth in the bulk even after 435 h.

In summary, we have shown that unique mesoscopic photonic structures can be created in glasses by using the intense focusing capability of fs-lasers based on first writing lines at will in certain regions of the glass. The fs-laser writing is shown to cause elemental segregation that allows selective growth of quantum dots in localized regions. The fs-laser can thus become a powerful tool to direct which segment of the integrated photonic circuitry is designed to form quantum dots. This selectivity will permit making of a vast variety of highly tunable photonic devices with the capacity to guide photons in three dimensions.

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