Ultrafast Laser Processing of Hybrid Micro- and Nano-structures in Silicate Glasses

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ABSTRACT

This study describes the fabrication of hybrid micro- and nanostructures of semiconductor nanocrystals arranged in microscopic lines inside of a borosilicate glass doped with CdS_xSe_{1-x}. This was performed using a two step process of (1) ultrafast laser modification and (2) heat treatment. The glass was photomodified using focused sub-picosecond infra-red pulses with 1 MHz repetition rate to create linear domains with local compositional variations. Heat treating the sample at temperatures near glass transition preferentially precipitated semiconductor in the modified regions, as evidenced by confocal fluorescence microscopy. The optical properties of the precipitated nanocrystals varied with heat treatment duration.

INTRODUCTION

Ultrafast laser processing of glasses has potential for applications in a host of photonic devices [1]. Short pulses, in the femtosecond to picosecond range, when focused inside a normally transparent glass produce extremely high electromagnetic fields at the focal point, which leads to non-linear effects and absorption of laser energy. The rapid absorption and dissipation of energy leads to structural changes [2], which can be induced with a great degree of control in three dimensions. This micron scale modification lies at the heart of a lot of currently investigated photonic devices, such as basic waveguides [3,4] interferometers [5], couples and splitters [6], etc..

Recently there has been interest and notable advances in using active glasses, i.e. glasses that can exhibit signal gain [7], and that can be used either for signal amplification along the waveguide, or, with proper cavity construction, compact waveguide lasers [8]. The focus of active glass waveguides so far has been on glasses doped with ions, such as Er and Yr. One shortcoming of such systems, is that in rare earth ions optical transitions, dictating gain bandwidth, are narrow and do not easily yield themselves to tuning.

Previously, quantum dots (QDs) have been considered as good candidates for gain media due to being easily invertible, thus having low lasing threshold, and, perhaps more importantly, having optical properties tunable with particle size [9]. In this light, quantum dot doped glasses make intriguing candidates for the aforementioned photonic applications, as the particle size in these glasses, and therefore their optical properties, can be easily controlled by adjusting simple processing conditions that govern their nucleation and growth, such as heat treatment temperature and duration [10, 11].

To explore this possibility we aim to create linear domains of quantum dots, defined by ultrafast laser exposure. We use a two step process: an ultrafast laser modification followed by heat treatment.

EXPERIMENT

A commercially available colloidal filter glass was used as a starting material. In this case, OG570 filter glass from Schott Inc was used. This glass is doped with CdS_xSe_{1-x}, which is already precipitated, and is responsible for the filter's color. To dissolve the semiconductor crystals, the OG570 glass was melted at l450 °C for ½ hour, then cast in to a graphite mold, and annealed at 510 °C, its glass transition temperature, to remove internal stresses. This approach is similar to what was used in a number of earlier studies on precipitation dynamics of semiconductor in glass [12] The result was a clear glass, hereafter referred to as OG570-Q, which was then cut and polished into workable samples.

The ultrafast laser modification of the glass was performed at using a Uranus series fiber laser from PolarOnyx Inc.. The laser wavelength was 1030 nm, with pulse width <1 ps, and repetition rate of 1 MHz. After brief preliminary experimentation it was found that pulse energies of 300 nJ and above produced the desired scale of modification, and 300 nJ was the pulse energy used in this experiment. The laser beam was focused with a 50X objective, with N.A. = 0.55. The sample was translated transversely with respect to the beam focus at a rate of 100 μm/s to produce a line consisting of a series of overlapping modified regions.

To expose the linear modification for analysis, the irradiated sample was cut into cross sections and polished. The cross sections were analyzed using scanning electron microscopy (SEM) and wavelength dispersive spectroscopy (WDS). Then the samples were subjected to heat treatment at 500 °C to precipitate the quantum dots. The progress was monitored using confocal fluorescence microscopy in a setup detailed in ref. 4, using a diode 473 nm excitation laser and a 20X focusing objective with N.A. = 0.4. The fluorescence spectra were acquired from a raster of points in a 50 micron by 50 micron area at 1 micron steps. The analysis of the fluorescence spectra consisted of the mapping of integrated spectral intensities for all the points to produce an image of the analyzed area, as well as a closer analysis of the individual spectra.

DISCUSSION

Figure 1 shows a series of six lines, spaced 10 microns apart, "written" in the OG570-Q sample. Figure 1a shows the view of modifications from the top. It is apparent that each line consists of overlapping spherical modifications, with the overlap direction corresponding to the back-and-forth translation direction of the sample. It's important to note that at 1 MHz pulse repetition rate and 100 μm/s translation speed the laser pulse would hit the sample 10^4 times for each micron traveled, so the spheres that we see in figure 1a are certainly not the result of individual pulses.

The sample cross section that is shown in figure 1b shows very apparent modifications. The slightly zigzagging pattern of the locations of the lines is due to a small hysteresis of the air-bearing translation stage as the sample was moved back and forth to write the lines.

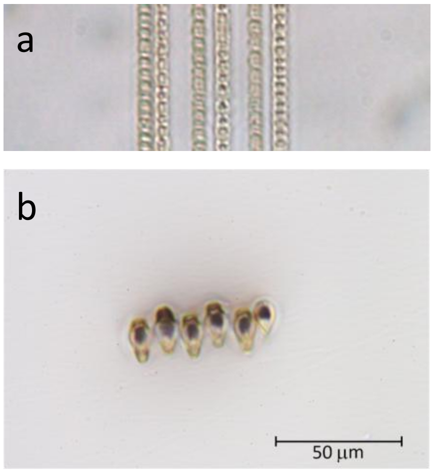

Figure 1. Ultrafast laser-induced linear modifications in OG570-Q glass; view of lines from the top (a) and of their cross section (b). The direction of the modifying laser is into the page in image (a), and from the top in plane with the page in (b).

Elemental redistribution

SEM backscattered electron (BSE) image is shown in figure 2. The contrast in BSE imaging is due to different elastic scattering cross sections of different elements, with heavier elements scattering more and showing a brighter signal. From this it is apparent that photomodification of OG570-Q has resulted in desegregation of the elements, a result observed previously [13].

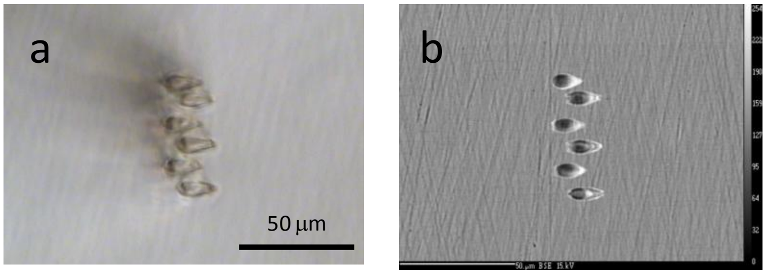

Figure 2. Optical (a) and SEM backscattered electron image (b) of the modified lines' cross-sections.

Wavelength dispersive spectroscopy gives a closer look at the distribution of major cations around the modified region (figure 3). From literature [ref. thermophoresis] it is expected for network modifiers to migrate to the outside of the modified region, while the more strongly bonded network formers generally stay towards the center in what is known as the Ludwig-Soret effect. This is indeed what we see here, with silicon, part of the silica network, showing a higher concentration in the center of modification (fig. 3c), and sodium, potassium and zinc, cations of network modifying oxides, migrating to the periphery of the modified regions (fig 3d-f).

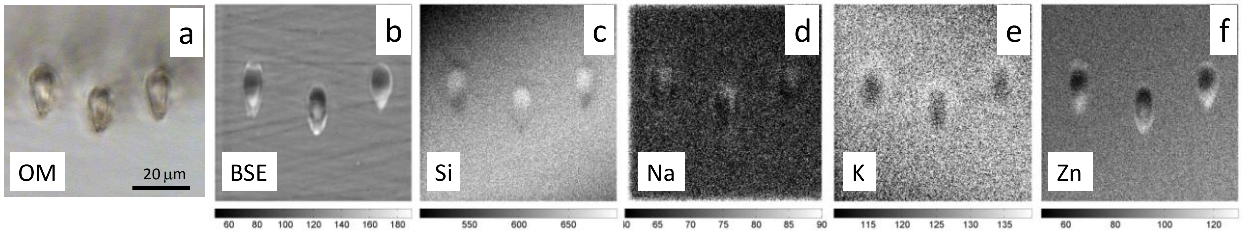

Figure 3. Optical micrograph (a) and backscattered electron image (b) of an area analyzed with wavelength dispersive spectroscopy. Silicon is more highly concentrated towards the center of the modification (c), sodium and potassium (d,e) are distributed towards the periphery with slightly higher concentrations towards the top of the modification in the direction opposite to the modifying beam (from the top); zinc, likewise, moved to periphery, but with higher amount moving in the direction of the modifying beam, towards the bottom of the image.

However, it is interesting to note that zinc and potassium display very different distributions. The signal of sodium in WDS is very low due to its tendency to diffuse under the probe's electron beam [14], but it appears to follow generally the same pattern as potassium. This indicates that there may be fundamental differences in diffusion mechanics between the cations, with cation valence possibly playing a role.

From figure 3 it can be seen that as a result of photomodification the cross section of the line forms roughly three chemically distinct regions: K-rich, Si-rich, and Zn-rich in the direction of the modifying beam.

Fluorescence

Figure 4 shows evolution of fluorescence (fig 4b-g) of the modified area (fig 4a) as the sample is treated at 500 ^{o}C. Initially there is little fluorescence of the modifications themselves, and a degree of fluorescence in the area immediately surrounding them (fig 4b). However, as the sample undergoes heat treatment, the fluorescence of the surrounding area disappears, while the modifications develop brighter and brighter fluorescence in areas that correspond to increased potassium and zinc concentrations. The rapidly disappearing fluorescence in the area surrounding the modifications is likely due to defects in the glass, which are commonly produced in ultrafast laser modification, and are generally unstable at high temperatures [15].

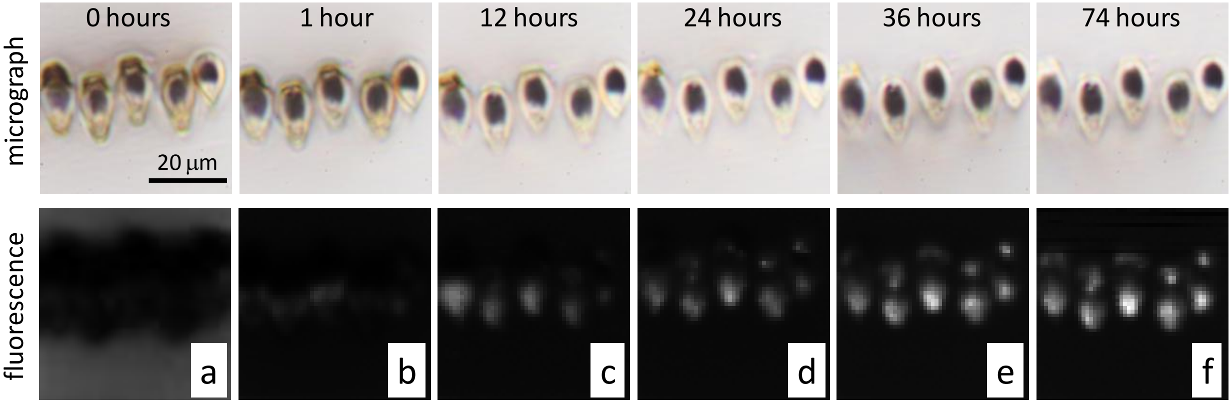

Figure 4. Changes in total intensity of fluorescence as a result of heat treatment at 500 ^{o}C; untreated (a), 1 hour (b), 12 hours (c), 24 hours (d), 36 hours (e) and 74 hours (f).

Fluorescence spectra from a sample point in the K-rich zone are shown in Figure 5. Here we can see that after 12 hours of heat treatment a distinct peak emerges at 590 nm (fig. 5c). With subsequent exposure to the elevated temperature, the peak grows in intensity and shifts right toward the redder wavelengths (fig 5d-f). This is typical of quantum dot growth, as characteristic optical transitions shift from blue to red with increasing particle size. For comparison, the fluorescence spectra of the area immediately surrounding the modification is shown in Figure 6, where we see little change after the first hour (fig 6b-f), indicating that either nothing happens, of that the precipitating semiconductor is too small to be resonant with the 473 nm excitation beam.

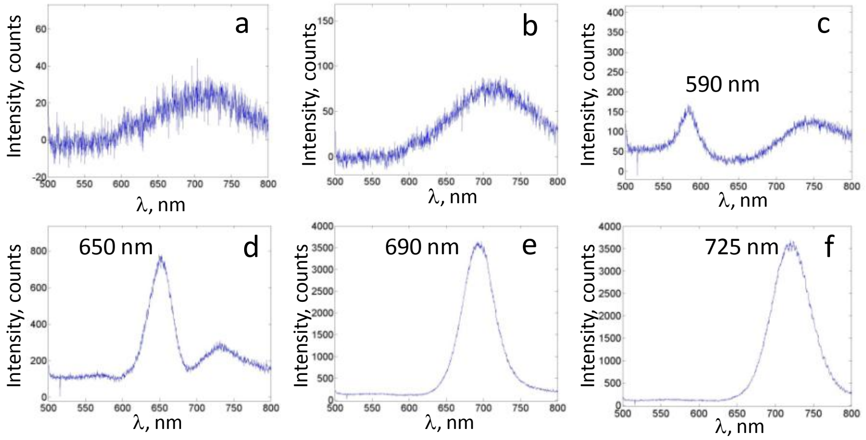

Figure 5. Evolution of fluorescence at a sample point in a potassium rich region of the modifications at zero (a), 1 hour (b), 12 hours (c), 24 hours (d), 36 hours (e) and 74 hours (f).

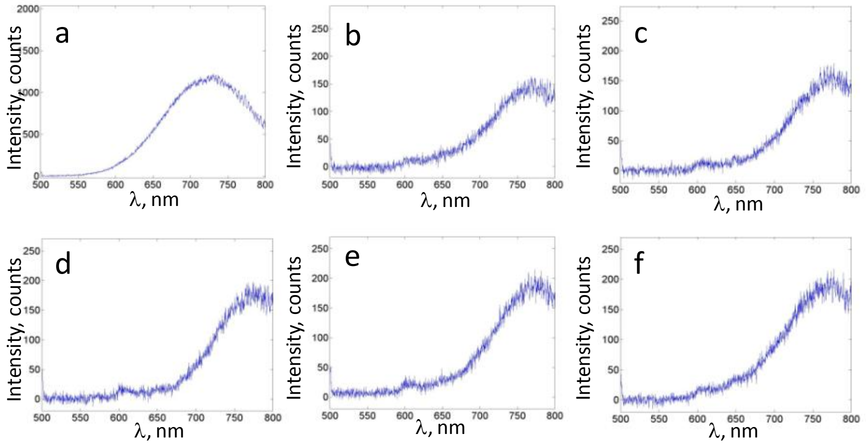

Figure 6. Evolution of fluorescence at a sample point in a region immediately surrounding the modifications at zero (a), 1 hour (b), 12 hours (c), 24 hours (d), 36 hours (e) and 74 hours (f).

Mechanism

The presence of network modifiers, such as potassium or zinc, serves to break up the borosilicate glass network, generally depressing the melting and glass transition temperatures. From this we can surmise that the glass transition in K-rich and Zn-rich regions occurs at a lower temperature than in the bulk, and for any given temperature, the network mobility is considerably higher in these regions than in the rest of the glass. As a consequence, at a particular range of temperatures, it should be possible to obtain a reasonably fast semiconductor nucleation and growth in the irradiated areas, while keeping precipitation extremely slow in the surrounding bulk. Of course, this ignores the changes to the solubility limit of the semiconductor components due to local compositional changes as well as possible phase separation of new compositions. These factors need to be taken into account if developing a more comprehensive model.

CONCLUSIONS

Using a high repetition rate ultrafast laser, a glass doped with dissolved CdS_xSe_{1-x} was modified to produce linear domains a few microns across. WDS study of cross sections indicated elemental desegregation with three distinct regions across those lines: K-rich, Si-rich and Zn-rich. Of these, the potassium and zinc rich areas displayed changes in fluorescence with heat treatment characteristic of growing quantum dots.

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