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Square-shape distribution of ZnO crystals in glass by using a spatial light modulator

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ABSTRACT

We report on square-shape distribution of ZnO crystals in glass by simultaneous femtosecond laser irradiation at multiple spots with the application of a spatial light modulator. Raman spectra and Raman mapping were used to characterize the formation of ZnO crystals and distribution of ZnO crystals, respectively. The shapes of the laser-modified region and the distribution of ZnO crystals were compared between the cases of one spot irradiation and multiple spot irradiation. The elemental distributions of the laser-modified region were investigated by an Electron Probe Microanalyzer.

1. Introduction

Femtosecond (fs) laser possesses the unique characteristics of ultrashort pulse and ultrahigh peak intensity, which makes it a powerful tool for micromachining in transparent materials [1,2]. During the interaction of the femtosecond laser and transparent materials, many novel and attractive phenomena have been found [3–6]. High repetition rate femtosecond laser can induce crystallization in glasses, which have potential applications in fabrication of functional optical components due to their ability to rapidly and precisely deposit energy through nonlinear excitation and absorption. When glass is irradiated by a high repetition rate femtosecond laser, an increasing amount of energy will continuously accumulate in the modified region [7,8]. If the local temperature in the modified region reaches a certain temperature range for nucleation and crystal growth, localized crystallization will occur. Until now, a series of functional crystals such as β-BaB_2O_4 [9], $Ba_2TiSi_2O_8$ [10], $LaBGeO_5$ [11,12], $LiNbO_3$ [13] and ZnO [14] have been space-selectively precipitated in glass using femtosecond laser irradiation.

However, the shape of the crystal distribution is always ring-shape [14–17] in the case of one spot irradiation as shown in Fig. 1(a), because the accumulated heat in the modified region is radially symmetric about the beam axis [7,8,18]. Sakakura et al. have achieved the shape control of elemental distributions inside a glass by simultaneous femtosecond laser irradiation at multiple spots [19]. A spatial light modulator can modulate the femtosecond laser pulses through phase hologram, which makes it a powerful tool to achieve simultaneous multiple spot irradiation. Herein, square-shape distribution of ZnO crystals in glass was investigated by simultaneous femtosecond laser irradiation at multiple spots. The shape of the crystal distribution can be expected by using a spatial light modulator as shown in Fig. 1(b). This strategy might provide a new way for femtosecond laser induced crystallization.

2. Experimental

A glass sample with the composition of $45SiO_2$-$15Al_2O_3$-$25ZnO$-$15K_2O$ (mol%) was prepared by conventional melt-quenching technique. Details of the glass preparation methods are available in ref. [14]. Schematic illustration of the femtosecond laser irradiation system was shown in Fig. 2. High repetition rate (250 kHz, pulse width ~50 fs; Coherent Inc., Mira-RegA) and low repetition rate (1 kHz, pulse width ~120 fs; Coherent Inc., Mira-Legend) amplified femtosecond lasers which generated laser pulses with a central wavelength of 800 nm were employed. A spatial light modulator (LCOS-SLM, Hamamatsu) was applied to achieve the simultaneous femtosecond laser irradiation at multiple spots. 1 kHz laser pulses were polarization-dependent and only the spatial phase distributions of 1 kHz laser pulses were modulated by the SLM. Therefore, 250 kHz laser pulses without modulated were focused at a single spot inside a glass sample, while modulated 1 kHz laser pulses were focused at multiple spots inside a glass sample. The

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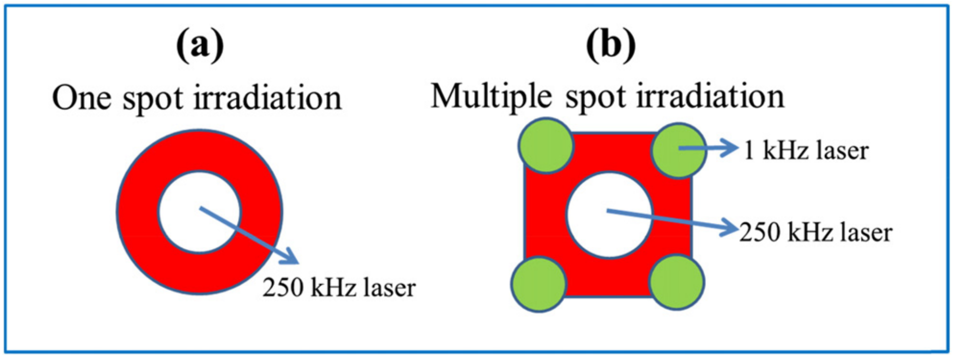

Fig. 1. Schematic illustration of the shape of the crystal distribution by one spot irradiation (a) and multiple spot irradiation (b), the red color means the precipitated crystals in the modified region.

focal positions of 1 kHz pulses were controlled by selecting a phase modulation pattern (phase hologram) on the SLM. The phase hologram was calculated by the Optimal Rotation Angle method [20]. The distribution of ZnO crystals in glass was analyzed by a Raman spectrometer (Nanofinder 30) with a laser excitation source of 532 nm. An Electron Probe Microanalyzer (EPMA; JXA-8100, JEOL) was used to investigate the elemental distributions.

3. Results and discussion

Fig. 3(a) shows a transmission optical microscope image of modified region inside glass with only 250 kHz femtosecond laser irradiation. The pulse energy was about 1.6 μJ, and the exposure time was 120 s. After one spot irradiation, the shape of the modified region was circular, which was a common phenomenon in the field of the interaction between the femtosecond laser and glasses and can be explained by the multiphoton absorption process of the laser with Gaussian distribution. The shape of the modified region turns to square shape after multiple spot irradiation as shown in Fig. 3(b), the pulse energy was about 2.0 μJ, and the exposure time was 120 s. This phenomenon is the same as that observed in ref. [19].

Raman spectra and Raman mapping were used to compare the structural change in the two modifications. The Raman spectrum of a glass sample heat-treated at 750 °C for 2 h (blue curves in Fig. 4(a) and (b)), in which precipitation of ZnO crystals was confirmed by X-ray diffraction (XRD) [21], is added in Fig. 4 for comparison. The Raman spectrum of the heat-treated glass sample exhibits sharp band at 437 cm^{-1}, which can be assigned to the E_2 (high) mode for wurtzite ZnO crystals. In both the circular and square-shape modifications, Fig. 4(a) and (b) shows that no Raman bands of ZnO crystals can be found in the unmodified region but a Raman band due to ZnO crystals at 437 cm^{-1} [22] was observed in the modified region. Therefore, precipitation of ZnO crystals inside the glass was confirmed by both one spot irradiation and multiple spot irradiation. Raman mapping was used to make a detailed investigation in the definite spatial distribution of the precipitated ZnO crystals with the two experimental conditions. The variation of the most intense characteristic Raman intensity at 437 cm^{-1} relative to the baseline represents the distribution of ZnO crystals. Fig. 4(c) shows the Raman mapping results in the case of one spot irradiation. The distribution of the ring-shape crystallization was the same as the results of ref. [14], which is consistent with the previous publications [14–17] that a nearly ring-shaped distribution was observed in the case of one spot irradiation. However, when the multiple

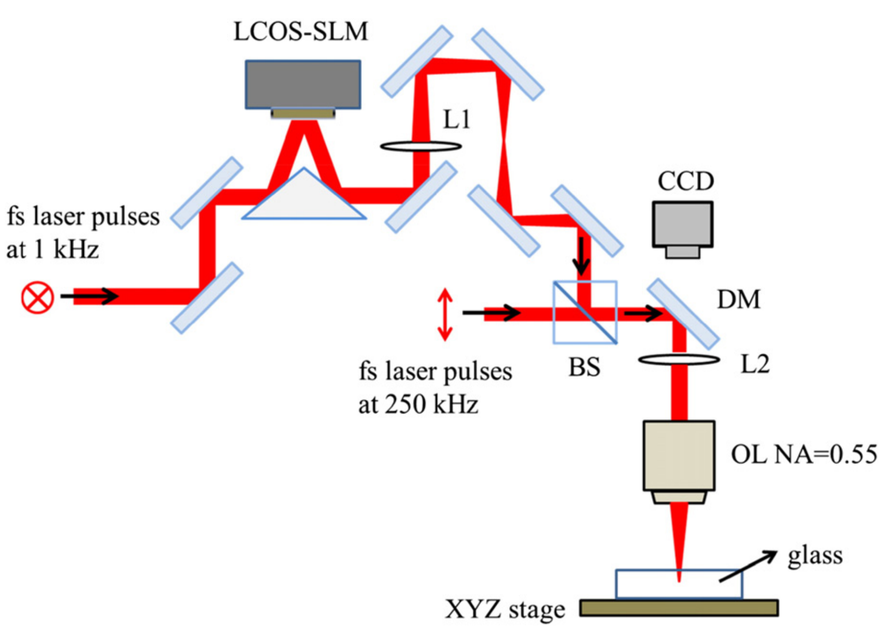

Fig. 2. Parallel laser irradiation system with two fs laser sources and a spatial light modulator. BS: a polarization beam splitter; DM: dichroic mirror, which reflects light around 800 nm; OL is an objective lens; L1, L2: lenses of focal lengths of 220 mm and 90 mm, respectively.