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Formation of Si nanocrystals in glass by femtosecond laser micromachining

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ABSTRACT

We report on the precipitation of Si nanocrystals inside a borosilicate glass by using an 800 nm, 250 kHz femtosecond laser irradiation, which was confirmed with X-ray diffraction, Raman spectra and transmission electron microscopy analyses. Refractive index profile reveals that the refractive index of the Si nanocrystals precipitated region increased up to 8.7% in comparison with that of the unirradiated area, leading to a large diffraction efficiency of the fabricated dot structure. Furthermore, the third-order optical nonlinearity of the Si nanocrystals precipitated glass is greatly enhanced based on the *Z*-scan measurement. These results may find applications for the fabrication diffractive optical devices and optical switches.

1. Introduction

Transparent glass-ceramics, i.e., composite of crystalline and glassy phases have found a wide range of applications [1]. Generally, glass-ceramics are formed through fine controlled heat treatments. In this case, it is difficult to achieve crystallization in spatially selected regions of the glass. However, it is of interest and of importance to develop transparent glass-ceramic, in which functional crystals are induced in a desired part in glass matrix. Such composite materials will have potential applications for fabrication of functional optical components [2]. In recent years, crystallization of glass by femtosecond laser irradiation at a high repetition rate has been recognized as a unique method for the micromachining of glasses [3–5]. The nonlinear nature of femtosecond laser absorption allows for space-selective micromachining inside bulk glass, while the high repetition rate nature generated heat accumulated effect allows crystallization of glass, thus providing complete three dimensional (3D) controls for creating the desired functional crystal-glass composite material [6,7]. Recently, various functional crystals have been precipitated successfully within glasses [3,8–10].

Silicon nanocrystals have been studied extensively in past decades because of their potential applications in nanophotonics and nanoelectronics [11]. However, to our best knowledge, silicon nanocrystal induced by femtosecond laser irradiation remains largely unexplored. At present, K. Miura [12] and N. Uchida [13] have formed Si structures using femtosecond laser in silicate glasses. Thus far, however there are no reports that demonstrated the functionality of silicon structure in glasses. In this study, we use femtosecond laser to achieve crystallization of Si nanocrystals within selective area of borosilicate glass. In addition, we also demonstrate an enhancement of third-order optical nonlinearity and refractive index from the formed silicon nanocrystal structure in glass.

2. Experimental

Glass with composition (in mol%) of $10Na_2O–15B_2O_3–75SiO_2$ (i.e., similar to commercial float borosilicate glass) was doped with 5 mol% Al. Details of the glass fabrication process are available in [10]. A commercial Ti: sapphire regenerative amplifier (RegA 900, Coherent Inc.) was used to generate 800 nm, 150 fs, and 250 kHz laser beam. The laser beam was focused via a microscope objective (50×, NA = 0.8) into the glass sample that was fixed on a computer controlled three dimensions *XYZ* stage. The laser induced crystalline phase inside the glass was identified by X-ray diffraction (XRD) using Cu K_α radiation (Rigaku D/MAX-RA diffractometer). Micro-Raman spectra were also measured by a Raman spectrometer (Renishaw inVia) with a 488 nm laser excitation. Composition of the laser induced crystalline line and unirradiated glass was analyzed using a scanning electron microscope (SEM) (JSM-6360LA) equipped with an energy dispersive X-ray (EDX) microanalysis system. Microstructure of the glass was recorded with a 200 kV JEOL 2010 Transmission electron microscopy (TEM) instrument. The nonlinear optical properties of the laser irradiated and unirradiated glasses were measured using Z-scan experiment setup with 800 nm, 120 fs, 80 MHz laser pulses, which were generated from the oscillator of a commercial Ti: sapphire femtosecond laser.

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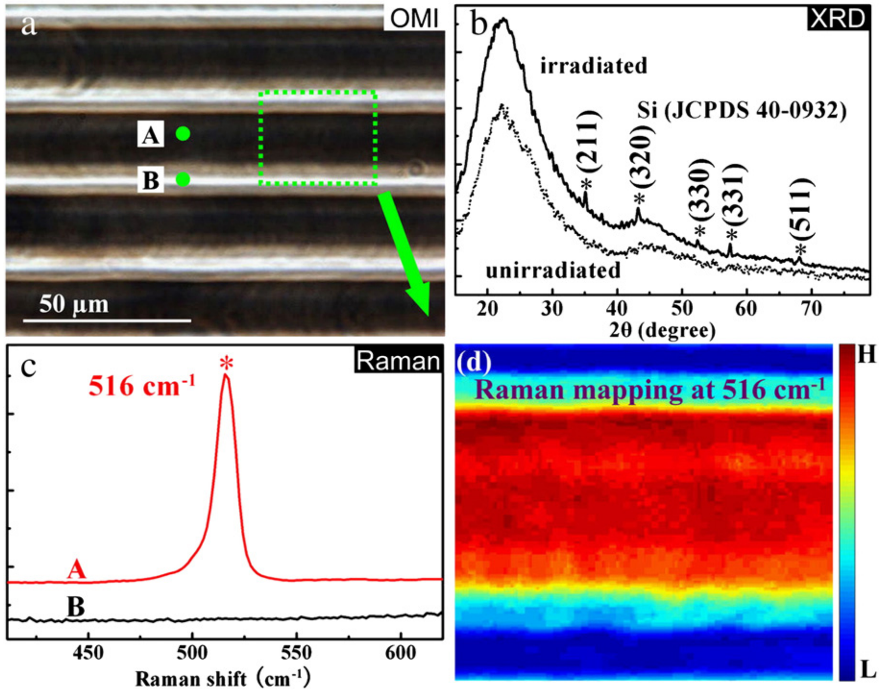

Fig. 1. (a) Optical microscope image (OMI) of the laser induced grating structure. (b) XRD patterns of laser irradiated and unirradiated glasses. (c) Micro-Raman spectra from two positions as shown in (a). (d) Raman mapping picture of the selected area as shown in (a), which is characteristic Raman peak (516 cm^{-1}) of Si nanocrystal.

3. Results and discussion

Fig. 1(a) shows optical microscope image (OMI) of the laser induced parallel grating structure with the size of 3 mm × 3 mm which is 100 μm beneath the surface of the glass sample. The writing speed is 40 μm/s and the pulse energy is 1.0 μJ. It is noticed that the laser irradiated area shows a black color while the laser unirradiated area is colorless. In order to analyze the nature of structural modification after the femtosecond laser irradiation, XRD and micro-Raman spectroscopic measurements were performed. Fig. 1(b) shows the XRD patterns of the laser irradiated and unirradiated glasses. The broad XRD peaks of the unirradiated glass indicate its amorphous nature, while five sharp and weak peaks appeared

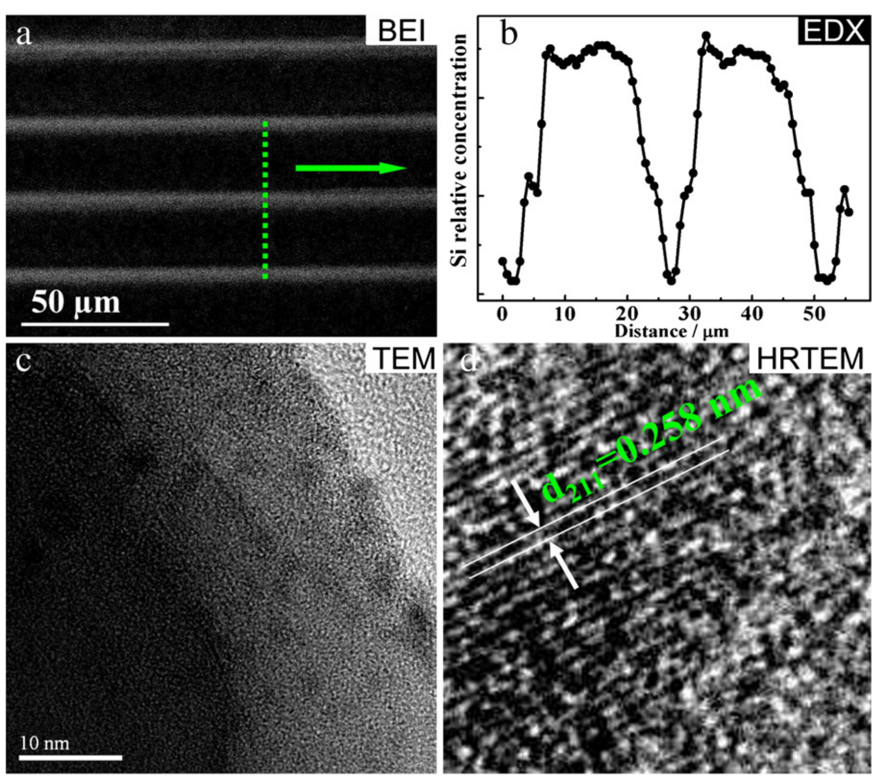

Fig. 2. (a) Backscattering electron image (BEI) of the laser induced grating structure. (b) EDX line (dot line as shown in (a)) scanning spectrum showing the relative concentration changes of Si element. (c) TEM and (d) HRTEM images of the laser modified glass.