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Formation of voids in a doped polymethylmethacrylate polymer

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We report on the formation of submicrometer voids within a doped polymethylmethacrylate (PMMA) polymer under multiphoton absorption excited by an infrared laser beam. An ultrashort pulsed laser beam of pulse width 80 fs at a repetition rate of 82 MHz and a wavelength of 800 nm is focused into a PMMA-based photorefractive polymer consisting of 2,5-dimethyl-4-(*p*-nitrophenylazo)anisole, 2,4,7-trinitro-9-fluorenone, and *N*-ethylcarbazole. The large change in refractive index associated with a void allows confocal reflection microscopy to be used as a detection method. Voids can be arranged in a multilayered structure for read-only high-density optical data storage. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1467615]

Formation of voids under multiphoton excitation has been an active topic because of their potential applications in microfabrication and high-density optical storage.[1–7] A void can be induced by an ultrashort pulsed laser beam through a microexplosion mechanism in a transparent medium (a medium having no absorption at the illumination wavelength).[2] The resulting structure is a central volume of less dense material (typically a void), surrounded by a region of higher density material.[1,2] It has been reported that voids can be generated in dielectric materials (silica, quartz, and sapphire)[1,2,6,7] and polymer material[3] using a single-shot regeneratively amplified ultrashort pulsed laser. As the single-shot excitation method limits the maximum processing speed,[4] a high repetition-rate laser oscillator has been successfully used to produce optical breakdown in glass.[4] A recent publication by Yamasaki *et al.*[3] demonstrates the formation of voids in an undoped polymethylmethacrylate (PMMA) film using single-shot ultrashort pulses of a wavelength of 400 nm. It has been shown that the voids in the PMMA polymer can be readout under two-photon excitation.[3] A polymer material has a low threshold of optical damage and provides a possibility of doping with absorbing dyes, which would allow the use of a long excitation wavelength to reduce the scattering effect and the manipulation of the refractive index of polymer.

In this letter, we report on the generation of voids in a doped PMMA polymer using a high repetition-rate ultrashort pulsed laser operating in the infrared region. It is discovered that a high concentration of dopant compounds results in a more stable fabrication condition. In addition, the large change in refractive index associated with a void allows reflection confocal microscopy[8] to be used as a detection method and can be used for read-only high-density optical data storage.

The doped PMMA material used in this letter consists of the nonlinear chromophore 2,5-dimethyl-4-(*p*-nitrophenylazo)anisole (DMNPAA), the photosensitive compound 2,4,7-trinitro-9-fluorenone (TNF), the plasticizer *N*-ethylcarbazole (ECZ); all doped into the polymer PMMA. This polymer material exhibits a photorefractive property and has been used for rewritable/erasable three-dimensional bit data storage with an appropriate concentration of the doped compounds.[9,10] To understand the effect of the nonlinear chromophore (DMNPAA) on the formation of voids, we fabricated three types of the polymer material with a concentration of the dopants (DMNPAA:PMMA:ECZ:TNF) of 0:100:0:0, 10:73:16:1, and 30:53:16:1, respectively. In fact, the first type of the polymer was an undoped PMMA material which is the polymer used in Ref. 3. It has been demonstrated that the doped PMMA material has an absorption band cut off approximately at wavelength 600 nm.[9] Therefore, it is a transparent material under infrared beam illumination. However, it can be excited under multiphoton excitation at wavelength 800 nm.[9,10]

The optical setup for fabricating voids was the same as that used previously for three-dimensional bits data storage.[9] In order to create the high peak power for multiphoton excitation an ultrashort pulsed laser (Spectra Physics, Tsunami) with a 10 W pump laser was used. The pulse width and repetition rate of the laser were 80 fs and 82 MHz, respectively. The void was produced by focusing the beam at wavelength 800 nm with power 35 mW through an objective with numerical aperture 0.8 and a magnification factor of 100. A He–Ne laser was coupled to the Olympus FluoView300 microscope for reading in a transmission mode and in a confocal reflection mode. The objective used for reading was an Olympus PlanApo oil-immersion objective with numerical aperture 1.4 and a magnification factor of 60. An average power less than 2 mW was used to produce the images.

Under the conditions used for fabrication, the three types of the doped PMMA polymer were excited with different exposure times. Figure 1 shows the transmission images [Figs. 1(a), 1(c), and 1(e)] and the confocal reflection images [Figs. 1(b), 1(d), and 1(f)] of the areas after excitation. Unlike the situation of Ref. 3, no void could be created in the undoped PMMA polymer [Figs. 1(a) and 1(b)] because there is no effective absorption at wavelength 800 nm even under multiphoton excitation. When the concentration of DMNPAA is increased, voids could be created but are not uniform for low concentrations [Figs. 1(c) and 1(d)]. Only in

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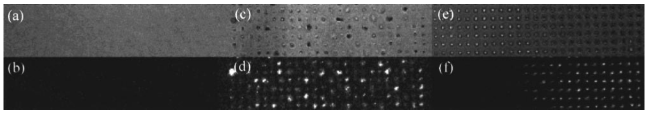

FIG. 1. Transmission and confocal reflection images of bits (or voids) (the bit spacing is 5 μm) recorded in the three types of the doped PMMA polymer containing different concentrations of the dopants DMNPAA:PMMA:ECZ:TNF. The concentration is 0:100:0:0 in (a) and (b); 10:73:16:1 in (c) and (d), and 30:53:16:1 in (e) and (f).

the highly doped PMMA polymer were uniform voids fabricated successfully. In Figs. 1(e) and 1(f), the bits (or voids) in each column were recorded with the same exposure time and the exposure time was varied from 10 ms (left-hand side) to 55 ms (right-hand side). As a result, the bits (or voids) on the right-hand side of the confocal image [Fig. 1(f)] show bright spots, while on the left-hand side no reflected signal is produced below a threshold of the exposure time.

The threshold of the exposure time in the third type of the doped PMMA polymer is further demonstrated in Fig. 2 that shows the dependence of the diameter of the bits (or voids) and the reflection confocal intensity on the exposure time. The linear region of the bit–diameter curve in Fig. 2 represents the condition for melting,[9,10] while the saturated region indicates that bits (or voids) are produced by microexplosion processes. The reflection–intensity curve in Fig. 2 demonstrates that there is a threshold of the exposure time below which no confocal reflection signal is produced. This threshold therefore indicates where the energy deposited in the focal region is enough to create microexplosion via multiphoton absorption. The energy corresponding to this threshold is 1.22 mJ of the employed laser.

The bits (or voids) recorded below and above the threshold are examined in detail using transmission microscopy and confocal reflection microscopy, as shown in Figs. 2(a)–2(h). At the shorter exposure time of 30 ms, i.e., below the threshold, the bit is formed as a result of melting of the polymer. The change in refractive index associated with a melted bit is not large enough to produce a reflection signal. Therefore, an image of a melted bit obtained by reflection confocal microscopy shows nothing [see Figs. 2(c) and 2(d)]. However, when the recording exposure time is increased past a threshold, multiphoton ionization of the doped polymer leads to microexplosion in the material and results in the formation of a void. A void can be imaged using confocal reflection microscopy [see Figs. 2(g) and 2(h)] as the change in refractive index between the void and the surrounding medium is significantly larger than that for a melted bit.[8,11,12] The axial confocal reflection scan of the void [see Fig. 2(h)] clearly shows both the top and bottom surfaces of the void. In this case, both of the surfaces suffer from severe spherical aberration caused by the mismatch in refractive indices and exhibit strong side lobes associated with confocal axial scans.[13,14]

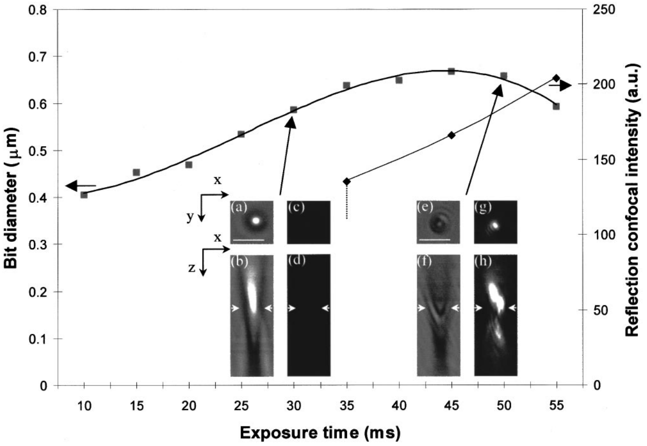

FIG. 2. Dependence of the bit/void diameter and the confocal reflection intensity on the exposure time in the third type of the doped PMMA polymer. (a) and (b) are transverse and axial transmission images of a melted bit, while (c) and (d) are its corresponding transverse and axial confocal reflection images. (e) and (f) are transverse and axial transmission images of a void, while (g) and (h) are its corresponding transverse and axial confocal reflection images. The white arrows indicate the position of the transverse image shown in (a), (c), (e), and (g). The dotted vertical line represents the threshold. The scale bar is 1 μm for *x, y*, and *z* directions.

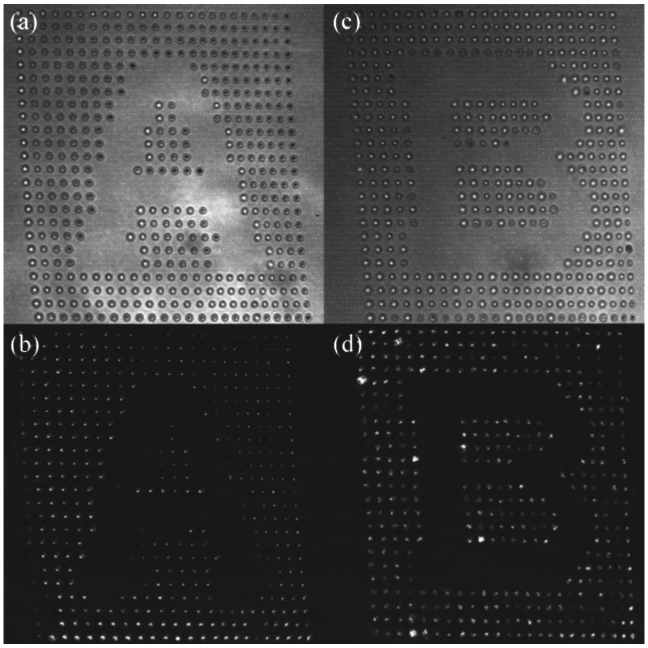

FIG. 3. Multilayered arrays of voids in the third type of the doped PMMA polymer. The first layer including the letter A is recorded near the surface and the second layer including the letter B is recorded with a separation of 15 μm in the depth direction. (a) and (c) are images in transmission microscopy while (b) and (d) are images in confocal reflection microscopy.

An application of voids is in three-dimensional bit optical data storage.[1,3] To demonstrate the feasibility of using the voids in the doped PMMA polymer for three-dimensional bit data storage, we illustrate in Fig. 3 two layers of voids recorded in the third type of the doped PMMA polymer. Figures 3(a) and 3(b) are the transmission and confocal reflection images, respectively, of the first layer of information. Figures 3(c) and 3(d) are the transmission and confocal reflection images of the second layer. The spacing between bits is 6.5 μm and between layers is 15 μm. With the ability to read the voids using confocal reflection microscopy, the layer separation could be reduced considerably without risking cross talk between layers.

In contrast to the previous work on void formation,[3] the highly doped polymer used in these experiments exhibits strong absorption in the ultraviolet to visible region of the spectrum but negligible beyond the wavelength at approximately 600 nm.[9] Therefore, it may be suggested that the mechanism for the generation of voids in the doped polymer is the ionization caused by multiphoton absorption under infrared beam illumination. The efficiency of a high repetition rate pulse train for PMMA has not been considered; however, previous research[4] has illustrated that there is little difference between the efficiencies of single-shot and multishot, multiphoton excitation. Further spectroscopic work should be conducted to determine the number of absorbed photons responsible for the ionization process or other void formation mechanism such as a phase-explosion-like process.

In conclusion, we have demonstrated the formation of voids in a doped PMMA polymer using multiphoton absorption under infrared beam illumination. It has also been shown that a high repetition-rate ultrashort pulsed laser is capable of producing microexplosions in the doped polymer. The utilization of a high repetition-rate pulsed laser for infrared excitation may prove advantageous for fast fabrication of three-dimensional microstructures within a bulk medium. The ability to create voids allows for three-dimensional read-only bit optical data storage and the utilization of reflection confocal microscopy for reading out the recorded information.

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