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Undistorted 3D microstructures in SU8 formed through two-photon polymerization

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This paper presents the wavelength dependence of two-photon polymerization in SU-8 between 720-780 nm. The study is performed by microstructuring SU-8 through a single-shot exposure of SU-8 to 140 fs tunable laser pulses with 80 MHz repetition rate, or by laser direct writing. Two-photon absorption is closely related to one-photon absorption in pristine SU-8. By careful design of the neighboring micro-structures, or by varying wet-processing parameters during development, undistorted and unbended 3D micro-structures have been fabricated through direct laser writing. [doi:10.1063/1.3646148]

I. INTRODUCTION

Three-dimensional (3D) microstructuring of materials is essential for the fabrication of devices for applications including photonic crystals,[1] tissue-engineering scaffolds,[2–4] microfluidics,[5] gradient-index metamaterials for cloaking devices,[6] and bio-inspired photonic structures.[7] There are several approaches to the fabrication of 3D structures. One method for 3D microstructuring is that of the conventional semiconductor layer-by-layer process through photolithography and thin-film deposition.[8] Conventional one-photon based holographic lithography has been used for micro-patterning 3D structures by exposing photosensitive materials to a multi-beam laser interference pattern.[1] This method facilitates the patterning of large-volume, in one step, but it is less flexible in the fabrication of engineered structures as compared with 3D laser direct writing.[9–14]

3D laser direct writing based on two-photon or multi-photon absorption offers a direct and dynamic route to the fabrication of 3D microstructures.[9–14] Short-pulse lasers in the near-infrared have typically been used for the 3D micro/nano-patterning of a negative or positive-tone photoresist, driven by two-photon absorption. When high-intensity light shines on a material, the probability of two-photon absorption is proportional to the square of the optical field intensity, and thus it is greatest at the center of a Gaussian laser beam. When tightly focused into the volume of a photosensitive resin, the polymerization process can be initiated by the non-linear absorption of near infrared femtosecond laser pulses within the focal volume. By moving the laser focus three-dimensionally through the resin, any desired pattern can be realized by the two-photon polymerization that takes place in the focus volume.[11]

Commercial SU-8 (Microchem) photoresist has been used for the laser direct writing of 3D microstructures with high aspect ratios.[9,10,13] SU-8 is an epoxy based negative tone resist. The cured SU-8 films have excellent chemical and thermal stability (glass-transition temperature, $T_g \sim 200$ °C and degradation temperature, $T_d \sim 380$ °C).[10] 3D structures have been fabricated in SU-8 through holographic lithography.[1] Teh *et al.* have reported two-photon polymerization in SU8 by an ultrafast mode-locked laser oscillator of 80 MHZ, 800 nm with 70 fs pulses.[9,10] Simple 3D structures with high

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aspect ratio have been fabricated in SU-8.[9,10] A variety of structural distortions, such as bending, were common in these structures. Arbitrary 3D microstructures have also been demonstrated in SU-8 through two-photon polymerization using amplified Ti: Sapphire laser systems with 1-kHz repetition rates, and 800-nm central wavelengths by the means of two-photon lithography.[12,13] A massive wall was fabricated around the 3D structures to prevent bending and to reduce distortions in the structures.[13] Often super-critical CO_2 drying was employed to avoid the distortions in 3D structures, after the samples were developed in SU-8 developer and were rinsed with iso-propanol.[12]

In this paper, we first studied the laser wavelength dependent two-photon polymerization of SU-8 at wavelengths between 720-780 nm. The studies were performed through a single-shot exposure of SU-8 to 140 fs tunable laser pulses with an 80 MHz repetition rate, and by scanning the laser pulses in SU8 photoresist. Un-distorted 3D micro-structures were fabricated by changing the design of the neighboring micro-structures or changing the wet-processing parameters during development.

II. WAVELENGTH DEPENDENT TWO-PHOTON POLYMERIZATION BASED ON SINGLE-SHOT EXPOSURE

A commercial tunable Ti: Sapphire femtosecond laser (Chameleon, Coherent Inc.) was used with a repetition rate of 80 MHz and pulse width of 140 fs. The wavelength can be tuned between 720 and 950 nm. For a single-shot exposure, the laser beam was expanded by a negative spherical lens, collimated by a positive spherical lens to a size of 6 mm, and focused by a cylindrical lens with a focal length of 100 mm, as shown in Fig. 1(a). The SU-8 sample was placed outside of the focal point to provide flexible processing windows without burning of the sample. The SU-8 was spin-coated on microscopic glass slides at speed of 4000 rpm for two minutes. The sample was pre-baked on a hot-plate for 1 minute at 65 °C and for 5 minutes at 95 °C before exposure to the laser beam. After the exposure, the SU-8 sample was baked at 95 °C for five minutes, developed in propylene glycol methyl ether acetate (PGMEA) for several minutes, rinsed by isopropyl alcohol (IPA) for 10 seconds, and left to dry in ambient air. The laser power was 2200, 2480, 2660 and 2960 mW for 720, 730, 740, and 750 nm wavelength respectively, as read from the control panel of the laser system. Because the laser pulses were not tightly-focused inside the SU-8, a long exposure time was necessary to observe the two-photon polymerization. Fig. 1(b) shows optical micrographs of developed SU-8 structures following exposure to laser pulses for 40 seconds. The SU-8 structure had an elliptical shape, similar to the shape of the laser beam inside the sample. Fig. 1(c) shows the line width (square points) of two-photon polymerized SU-8 samples after exposure to laser pulses with different wavelengths for 40 seconds. The line width increases when the wavelength shifts from 750 to 720 nm. Because different powers were used at different wavelengths, the line widths were further normalized to the same laser energy dose and plotted as triangle points in the same figure. After normalization, the line-widths appear to be more sensitive to the wavelength of exposure, more so than before normalization. The larger the line-width, the higher the two-photon absorption should be. The two-photon absorption at 720 nm is higher than that at 750 nm. This can be explained by the absorption spectrum of pristine SU-8 as shown in Fig. 1(c). The trend of the wavelength dependence of the line-width looks similar to the one-photon absorption spectrum and the one-photon absorption at 360 nm is stronger than that at 375 nm.

For pure two-photon absorption, the line-width d can be related to the energy threshold E_{th} of two-photon polymerization by $d = w_0\sqrt{\ln(E/E_{th})}$, where w_0 is the Gaussian beam waist.[14] The beam waist is almost the same for these wavelengths. The line-width obtained at 720 nm is larger than that at 750 nm. This can be explained by a smaller energy threshold E_{th} at 720 nm due to a strongertwo-photon absorption as compared with that at 750 nm.

III. TWO-PHOTON POLYMERIZATION BASED ON SCANNING PROCESS

For scanning two-photon polymerization, the laser pulses were expanded, and then focused into the resist using a 0.55 NA aspheric lens as shown in Fig. 2(a). Neutral density filters were used to attenuate the laser power to 100 mW as measured before the aspheric lens. A 3D motion

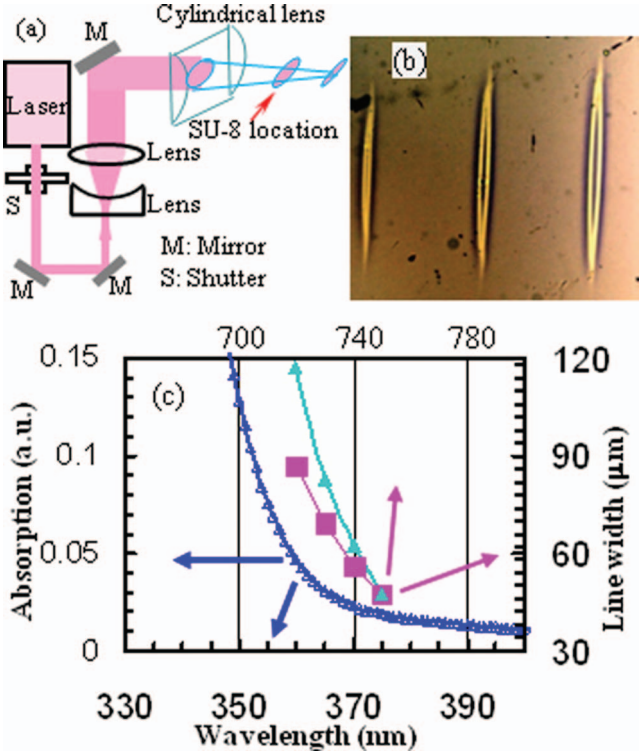

FIG. 1. (Color online) (a) Schematic of optics setup for voxel recording and (b) optical micrograph of the voxel; (c) Voxel line-width dependence on wavelength imposed on absorption spectra of pristine SU-8.

stage (Newport) was controlled to move the photoresist under the beam. SU-8 film was prepared by spin-coating at 2000 rpm for 2 minutes followed by a pre-bake at 65 °C for 20 minutes to produce a thicker film of about 40 microns. Laser directly written multi-layer structures were fabricated at various scan speeds and then developed in PGMEA for several minutes and then rinsed with IPA. The top layer structure was suspended from the substrate and was used for the true measurement of structural parameters. Fig. 2(b) shows the written two-layer structures. The cross-section of the top single line has a high aspect ratio, approximately 4. The solvent evaporation process can drive two top line-structures together due to the capillary force between the big surface areas of the line-structures, as shown in Fig. 2(b).[12] This happens when the bottom structures in the neighboring layer have a large distance and thus provide less support for the top structures. Further studies were prepared as above but with a final rinse of water immediately after the IPA. Water has a large contact angle on the resist and can reduce the capillary force among the rods and thus keep the micro-structures undistorted.[12]

The line-width was measured as a function of scanning speed at wavelengths of 730, 750, and 780 nm. At the short wavelength of 730 nm, the line-width is not sensitive to the scanning speed in the range of 1.1 and 2.0 mm/s. Due to a high two-photon absorption and low energy threshold for two-photon polymerization, the laser dose received at these scanning speeds far exceeds the energy threshold E_t.[14] Thus, the line-width is not sensitive to the scanning speed. Using a laser pulse at 780 nm, the two-photon absorption in SU-8 is weaker than at 730 nm. Thus the line widths obtained at780 nm show sensitivity to the scanning speed.

IV. 3D MICRO-STRUCTURE FABRICATION BASED ON TWO-PHOTON POLYMERIZATION

3D microstructures can be formed through two-photon polymerization if the neighboring structures provide support for each other. Fig 3(a) shows an SEM image of the direct laser written 3D micro-structures in SU8 using 740 nm pulses at exposure powers of 144 mW as measured before the

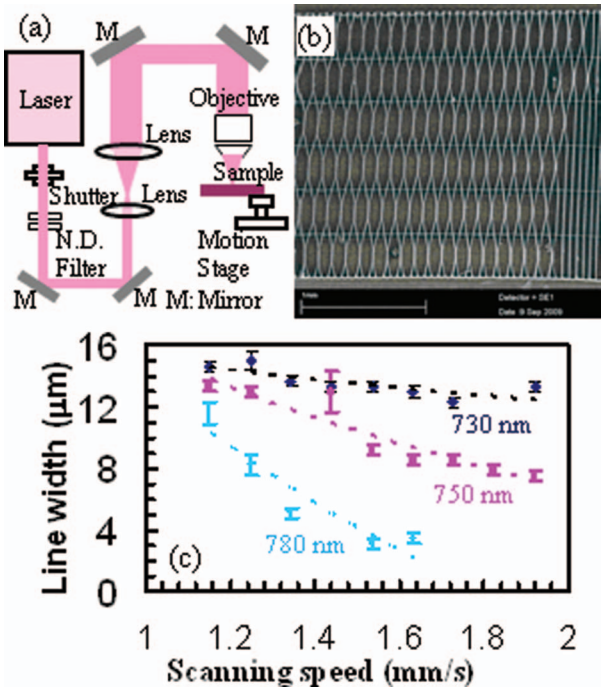

FIG. 2. (Color online) (a) Schematic of optics setup for laser direct writing; (b) SEM of laser directly written structures in SU-8; (c) Scanning speed dependence of written line-width for various wavelengths.

aspheric lens with a scanning speed of 1 mm/s. After scanning the first layer, the second layer was directly written by laser pulses with a 4 μm displacement in z-direction relative to the first layer. The sample was developed in PGMEA overnight and rinsed with IPA. As illustrated in Fig. 3(a`), the rod-like structures in the first layer are in contact with the rods in the fifth layer. These structures are stable as seen from the SEM.

If the structures in the successive layers are displaced in z-direction by a distance longer than 4 μm, the fabricated micro-structures appear to be that of a wood-pile arrangement. Fig. 3(b) is an SEM of the micro-structures in SU8 exposed with 740 nm pulses at a power of 127 mW before the aspheric lens, and scanned at a speed of 2.4 mm/s. For the fabrication of this structure, the location of the neighboring layers in z-direction was displaced by 6 μm. The sample was developed in PGMEA for 3 hours and rinsed by IPA. A woodpile-type arrangement is clearly demonstrated beneath the top layer. The top layer shows a very wide feature. The formation of this wide feature can be explained with the help from the drawing in Fig. 3(b`). The rods inside the wood-pile structure are well-supported by neighboring rods and are thus stable. However, the rods of the top layer lack a support from above. Due to the capillary force between the large areas of the rod surfaces, two rods fall toward each other and form a single rod as seen from SEM in Fig. 3(b). In this case, the 3D micro-structures are distorted. Undistorted 3D micro-structures were obtained when the developed structures were left in the developer overnight (approximately 15 hours). Figs. 3(c, c`) show the SEM and illustration of the 3D micro-structures fabricated in SU-8 using 740 nm pulses at a power of 120 mW which is measured before the aspheric lens. The structures were fabricated with the neighboring layers displaced in z-direction by 6 μm. The sample was developed in propylene glycol methyl ether acetate and rinsed by IPA. The extended development time has the effect of removing more of the low cross-link density region around the rods. The denser remaining region is more resistant to the capillary forces from rinsing and evaporation, whereas a residue of low-crosslink density would have more self adhesion as in the previous SEM.

In summary, we have studied two-photon polymerization in SU-8 using an ultrafast laser oscillator. The wavelength dependence of two-photon polymerization has been characterized between the range of 720-780 nm through a single-shot exposure of SU-8 to 140 fs tunable laser pulses with

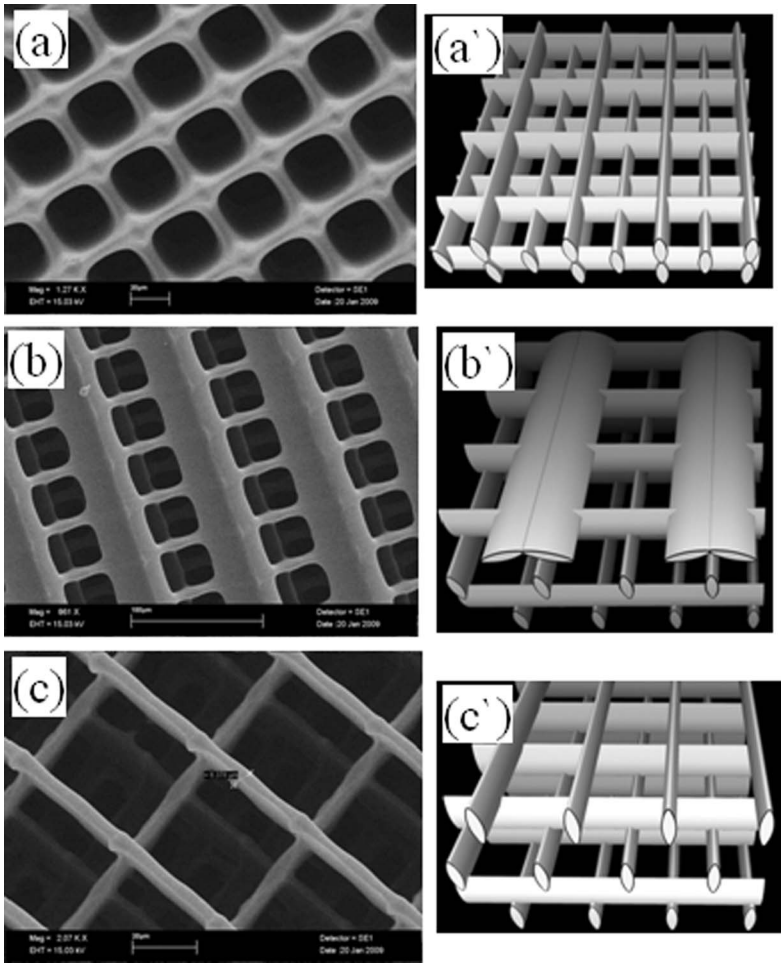

FIG. 3. (Color online) SEM images of 3D microstructures in SU8 with neighboring layers displaced in z-direction by 4μm (a) 6 μm (b) and 6 μm (c) and their corresponding illustrations (a`, b`, c`), respectively.

80 MHz repetition rate, and by scanning the laser pulses in SU8 photoresist. The results obtained by two-photon absorption are closely related to that obtained by one-photon absorption. Laser direct writing has been used to fabricate 3D micro-structures in SU-8. Undistorted and un-bended 3D micro-structures have been fabricated by changing the design of the neighboring micro-structures or changing the wet-processing during development of the micro-structures.

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