Glass transition-assisted microstructuring in polystyrene

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We report on the use of a *shape transition* process to resize patterns prerecorded inside polystyrene film. The shape transition, which is shrinkage in two dimensions and expansion in the third (the volume is conserved), was brought about by annealing polystyrene above the glass transition temperature. This caused approximately twofold lateral shrinkage and fourfold axial stretching of the film, inside which micrometer-sized patterns had been recorded by femtosecond pulses. The transformation of these patterns corresponded to the macroscopic shape transformation of the film. The shape transition was also used to transform a diffraction grating. This allowed the transformation to be confirmed by the corresponding change in diffraction efficiency. The applicability of the shape transition process to nanofabrication is discussed. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1641182]

Interest has increased lately in nano-/microfabrication which exploits the self-organization behavior of materials to form three-dimensional patterns.[1,2] In some shaping and forming processes, such as sheet forming, a plastic material is, usually, thermally quenched and made into a thin sheet by means of pressure. If the melt is cooled slowly under ambient pressure, the resulting glassy structure of the plastic is much different from the one obtained by fast thermal quenching.[3] The relaxation of quenched material strained into a form of thin film could be exploited for nano-/microfabrication tasks. Here, we report how thermal annealing of sheet-formed polystyrene above the glass transition temperature, T_g, could be used to resize structures recorded inside the material by femtosecond pulses. We call such resizing a *shape transition*, which is shrinkage in two dimensions and expansion in the third, with overall conservation of the volume. Shape transition is a thermally activated process of relaxing stress in plastic that has been compressed and thermally quenched.

For the recording material, we used polystyrene films available commercially from Ukita Ltd. and Acrysunday Co., Ltd., both of Japan. The polystyrene from both manufacturers had the same optical transmission, threshold of femtosecond recording, and glass transition temperature. Polystyrene is available in A4 sheets of 0.2–0.4 mm thickness for stationary use and modeling. Its most common use is illustrated in Fig. 1. A miniature of a color picture drawn on a 0.2-mm-thick polystyrene film (Acrysunday) was made by annealing the sample at 130 °C for 2 min. The glass transition temperature of polystyrene is 100 °C.[3] The shape transition brought about by annealing above T_g caused the sample to shrink laterally by about 2.1-fold [Fig. 1(b)] and to stretch axially by 4.4-fold [Fig. 1(d)]. The corresponding change in volume resulting from the shape transition can be expressed as $V_{\text{after}}/V_{\text{before}} \equiv 1/x \cdot 1/y \cdot z/1 \simeq 99.8\%$, where x, y, and z are the dimensions after the shape transition expressed via fractions of the corresponding dimensions before the transition. Polystyrene films 0.4-mm-thick had a 12% smaller modification of dimensions after annealing, and the extent of modification was marginally dependent on the annealing temperature and duration. This phenomenon, the shape transition, was used to resize patterns recorded inside polystyrene by femtosecond pulses. The size of the voxel (the volume element) recorded by femtosecond pulse can be smaller than the cross section of the focal spot,[4,5] which is determined by diffraction laws and aberrations. Hence, it is possible to trace the shape transition-induced changes of patterns formed of voxels on a submicrometer scale.

The laser setup of fs fabrication was based on an oscillator (Tsunami) with a regenerative amplifier (Spitfire, both from Spectra Physics) operating at 800 nm wavelength and a microscope (Olympus IX70). A PZT stage (Polytec PI) was employed to scan the sample according to preprogrammed fabrication patterns. The pulse energy stability was about 3%. The laser radiation was focused inside the sample by a microscope objective lens of $100^{\times}$ magnification that was set at a numerical aperture (NA) of 1.35 (UplanAPO$100^{\times}$). Direct contact between the sample and the objective lens was achieved with the use of immersion oil. This minimized the aberrations, since the refractive indices of the immersion oil and polystyrene were approximately the same, $n \simeq 1.52$. The actual diameter of a focal spot depends on the truncation ratio of the incident beam at the entrance of the objective lens and the beam's quality factor, and can be evaluated precisely.[4]

Pulse energy was directly measured at the point of irradiation by an energy meter (Laserstar OPHIR) using a solid immersion lens (SIL) according to procedures reported

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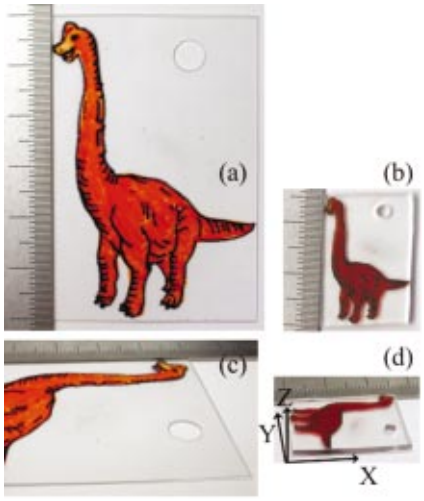

FIG. 1. (Color) Downsizing of a picture drawn on polystyrene (Acrysunday Co., Ltd.) by shape transition, induced by heating the material above the glass transition temperature. Pictures (a), (c) before and (b), (d) after heat treatment at 130 °C for 2 min are shown on the same scale in (a), (b) and (c), (d). The smallest division on the ruler was 0.5 mm.

recently.[6] In order to calculate the recording irradiance at the focus, the pulse duration at the focus was measured by the Grenouille technique[7] (Swamp Optics), and the pulse duration the [full width at half maximum (FWHM)] was retrieved by the frequency-resolved optical gating (FROG) algorithm (Femtosecond Technologies). The pulse duration at the focus was 225 ± 20 fs at a FROG error of less than 2% (more details can be found in Ref. 8).

The spatial dimensions of the pulse focus, a ''light pen'' used for recording, were close to those evaluated by scalar Debye theory[9] and were (axial×lateral)$\simeq(0.87\times0.29)$ μm^2 (at FWHM) calculated for aberration-free focus inside a medium with refractive index $n=1.5$. Here, the apodization function was chosen to obey the sine condition, which is standard for an aplanatic objective lens.[9] The light intensity at the focus can be calculated from the point spread function (PSF), which defines the electric field amplitude at the focus. For focus of a high numerical aperture lens, the PSF can be found from Debye theory and is given by

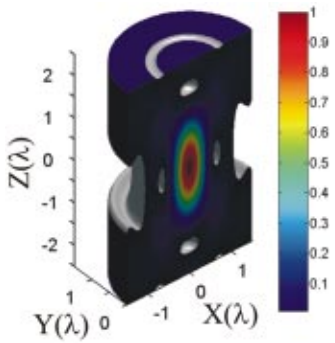

FIG. 2. (Color) Normalized light intensity distribution $I=|E(v,u)|^2$ [Eq. (1)] in the focus of an aplanatic objective lens with NA=1.35. The dimensions are given in units of λ. The intensity threshold of the isosurface (shown in gray) was set at 1%.

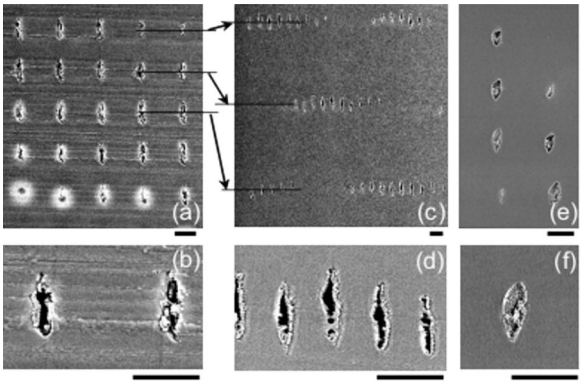

FIG. 3. SEM side-view images of the 0.2-mm-thick polystyrene film (Acrysunday Co., Ltd.) (a), (b) after recording, (c), (d) with subsequent annealing, and (e), (f) after recording into the annealed material. The recording irradiance was about 1.25×LIDT. Annealing was carried out at 135 °C for 100 s. The scale bars are equal to 1 μm.

$$E(v,u)=\frac{2\pi i}{\lambda}\exp(-ikz)\int_0^{\alpha}P(\theta)J_0\left(\frac{v\sin(\theta)}{\sin(\alpha)}\right)\times\exp\left(\frac{iu\sin^2(\theta/2)}{2\sin^2(\alpha/2)}\right)\sin(\theta)d\theta, \quad (1)$$

where $v=kr\sin(\alpha)$ and $u=4kz\sin^2(\alpha/2)$ are the lateral and axial optical coordinates, respectively, $k=2\pi/\lambda$ is the wave number defined by wavelength λ at the focus, J_0 is the zero-order Bessel function of first kind, and α is the half-cone angle of focus. The numerical aperture in material with refractive index n is $\mathrm{NA}=n\sin(\alpha)$, and $P(\theta)=\sqrt{\cos(\theta)}$ is the apodization function that satisfies the sine condition (aplanar focusing). The result of the calculation by Eq. (1) is plotted in Fig. 2, showing that the axial focal length was approximately 2.95 times larger than the lateral one at FWHM under our experimental conditions; i.e., the aspect ratio was $f_a\simeq3$.

The dimensions of the void that had been optically recorded in polystyrene by a single laser pulse were measured by a field emission scanning electron microscope (SEM) (JEOL JSM-6700FT). A Pt film with thickness of a few nanometers was evaporated for SEM observation after the sample was sliced by a biomicrotome (Ultracut UTC), which allowed the soft material to be cut without distortion of the internal features. The cutting procedures were ruled out as a

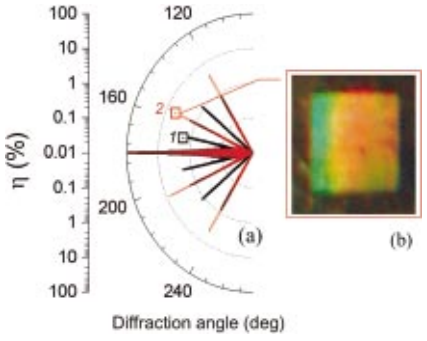

FIG. 4. (Color) (a) Diffraction efficiency, η, vs the diffraction angle, θ [see Eq. (2)] for wavelength λ=532 nm. Theoretical and experimental data are plotted for the gratings: (1) as recorded and (2) after the shape transition. The experimental efficiency was calculated as $\eta=(I_1/I_1+I_0)$, where I_1 and I_0 are intensities diffracted into zeroth and first order, respectively. (b) Image of the 2×2 mm^2 structure taken under white light reflection.

cause of any artifacts in the SEM images. As a reference, the sample after annealing was also irradiated to observe the typical morphology and size of the voxel recorded by a femtosecond pulse. These results are summarized in Fig. 3, where the cross sections along the recording beam propagation are examined. Voids were formed at the focus. These voids should be surrounded by densified cladding of displaced material as we observed inside polymethylmethacrylate.[5] The mechanism of void formation by a single femtosecond pulse is as follows:[10] at dielectric breakdown, when a highly conductive (metallic) state of material is formed at the pulse front, the ensuing pulse energy is absorbed within the skin depth. The absorbed energy surpasses the binding energy and a formed high-pressure gaseous plasma eventually creates voids.

The lateral shrinkage and axial expansion of the polystyrene sample were confirmed to follow precisely those observed macroscopically [in Figs. 1(a)–1(c), the transition marked by arrows], i.e., the same ratio of resizing was observed on an outer perimeter of the sample. The dimensions of the voids recorded at the intensities close to the light-induced damage threshold (LIDT) $1.25\times I_{\mathrm{LIDT}}$ in polystyrene were approximately 0.25 μm in diameter and 1 μm in length. The LIDT in terms of pulse energy was 8.5 nJ, the fluence was 4.5 J/cm^2, and the irradiance was 20 TW/cm^2 (FWHM). The shape transition was found to not significantly change the cross section of the voids [Figs. 3(b) and 3(d)], whereas the intravoid distances followed macroscopic scaling precisely (Fig. 1). Since the shape transition conserved the volume, and the optical transmission was found to be unchanged (within an error of margin of less than 10%), we can assume that the refractive index and absorption coefficient of the material were also unaffected.[11] This is because the mass density remained constant. It is instructive to compare the dimensions of voids recorded in untreated versus annealed polystyrene. Recording in the annealed polystyrene [Figs. 3(e) and 3(f)] resulted in voxels with an internal void of 0.92×0.36 μm^2 cross section (the corresponding aspect ratio was $f_a=2.6$) at 10 μm depth, when the pulse energy was approximately $1.25\times I_{\mathrm{LIDT}}$. These dimensions of the recorded voxels are comparatively close to the focal size derived from Debye theory (Fig. 2). On the other hand, the aspect ratio of the void recorded in the polystyrene was $f_a=4$ [Fig. 3(b)] and it rose to 4.7 [Fig. 3(d)] after annealing. These values are considerably larger than the expected aspect ratio of the focal spot.

The larger f_a values of voids recorded in polystyrene before annealing can be explained by local heating during dielectric breakdown, which caused the shape transition to take place in localized fashion. It is worth noting that the recording power per pulse at LIDT was just 38 kW, much lower than the critical power of self-focusing, which is about 1–2 MW for glassy materials. This is the reason why this laser recording can be considered *direct laser writing*.[12] That is, photomodification of the material is expected to closely follow the proportions of the light intensity distribution at the focus. A slightly larger aspect ratio of voids compared to the ideal focal spot can also be caused in part by aberrations.[13]

The shape transition process was applied to resize a diffraction grating recorded in polystyrene by scanned femtosecond pulses. The intensity of diffraction into zeroth and first order was measured. Figure 4 shows the experimental and calculated diffraction efficiencies. The diffraction efficiency was calculated as that of a multislit according to[14]

$$\frac{I}{I_i}=\left(\frac{\sin\beta}{\beta}\right)^2\left(\frac{\sin(N\gamma)}{N\sin\gamma}\right)^2, \tag{2}$$

where I_i and I are the intensity of incident and transmitted light, respectively, N is the number of slits, and the phase parameters $\beta=\frac{1}{2}kb\sin\theta$ and $\gamma=\frac{1}{2}kh\sin\theta$ are determined by the opening length b, the period h, the wave vector $k=2\pi/\lambda$, the wavelength λ, and the diffraction angle θ. Since the Eq. (2) describes the angular dependence of the diffraction efficiency for a transmission grating, the theoretical simulation should be considered quantitative. Shrinkage of a 2.5 μm period grating with an approximately 0.3 μm void at the core upon the shape transition was confirmed qualitatively by measuring the diffraction efficiency (Fig. 4), where theoretical curves were calculated for a 10-slit grating by Eq. (2). As one can see, a twofold decrease of the grating period did indeed increase the diffraction efficiency, and the diffraction angle became twofold larger as expected. This experiment confirms the principle and demonstrates that the shape transition could be useful for photonic applications.

Femtosecond laser fabrication is capable of recording voids and channels in polymethylmethacrylate with cross-sectional dimensions of about 0.4 μm, as we reported earlier.[5] Thus, one can expect that nanostructuring of polymers with feature size of about 100 nm is within reach for femtosecond microfabrication.

In conclusion, we have demonstrated the possibility of resizing a recorded pattern in polystyrene by annealing it above the glass transition temperature. The dimensions of voids recorded in polystyrene were found to be almost unchanged after the shape transition.

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