Single-shot two-photon exposure of commercial photoresist for the production of three-dimensional structures

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We report the use of an amplified femtosecond laser for single-shot two-photon exposure of the commercial photoresist SU-8. By scanning of the focal volume through the interior of the resist, three-dimensional (3-D) structures are fabricated on a shot-by-shot basis. The 800-nm two-photon exposure and damage thresholds are 3.2 and 8.1 TW/cm^2, respectively. The nonlinear nature of the two-photon process allows the production of features that are smaller than the diffraction limit. Preliminary results suggest that Ti:sapphire oscillators can achieve single-shot two-photon exposure with thresholds as low as 1.6 TW/cm^2 at 700 nm, allowing 3-D structures to be constructed at megahertz repetition rates. © 1998 Optical Society of America

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Because the absorption of light proceeds from the surface of a photoresist down to the substrate, photolithographic techniques are inherently limited to the production of two-dimensional (2-D) structures. Modern applications such as microelectromechanical systems or photonic crystals, however, require the ability to produce fully three-dimensional (3-D) structures. Multilayer techniques can produce limited 3-D structures by stacking of a few conventional 2-D layers, but even simple structures produced in this way come at the expense of difficult layer-to-layer alignment.

Recently several groups have opened the door to the lithographic production of 3-D structures by the use of two-photon absorption (2PA).[1–3] This method uses high-peak-power light whose wavelength is too red to expose the resist in the conventional one-photon way. When it is focused with a high-numerical-aperture objective, however, the peak intensity in a small volume ("voxel") near the focal region has sufficient intensity to expose the resist by 2PA, even though the intensity is insufficient to expose the resist at its surface. By scanning of the focal volume, truly 3-D structures can be fabricated in a single step.[1–3]

In the work published to date, the light sources for 2PA were ~100-fs pulsed oscillators with relatively low peak intensities per pulse owing to their high repetition rates (80–100 MHz).[1,2] Two-photon exposure of photoresist thus far has required multiple laser shots at each voxel. This need for multiple shots limits the ability to produce large structures quickly: The total average power that can be applied to the sample is limited so that problems with heating are avoided, and the beam must dwell long enough at each voxel to ensure a dose that is sufficient for 2PA.[1,2]

In this Letter we report two-photon exposure of a commercial photoresist with a single laser shot. We accurately determine the two-photon exposure and the damage thresholds for the material and demonstrate fabrication of 3-D structures built on a shot-by-shot, voxel-by-voxel basis. The nonlinear nature of 2PA offsets the use of longer-exposure wavelengths by allowing the creation of sub-diffraction-limited features.[4] With optimization of the excitation wavelength for 2PA it is also possible to expose photoresist with a single shot from a Ti:sapphire oscillator. This allows structures to be produced as fast as the repetition rate of the laser, 80–100 million voxels/s. Thus rapid writing of 3-D structures is limited only by the ability to scan from voxel to voxel.

The laser that was used for the majority of the experiments was a regeneratively amplified Ti:sapphire system (Spectra Physics) that produced slightly elliptical (4 mm × 5 mm diameter), 120-fs-duration, 1-mJ pulses of light at 800 nm with a 500-Hz repetition rate. For some experiments pulses at 660 nm were produced by the second harmonic of the signal beam from a dual-pass optical parametric amplifier. An optical filter (Schott RG 630) was used to remove any residual light in the excitation beam that might have caused one-photon exposure. For threshold measurements or structure fabrication, sample films were drawn through the focal volume either by hand or with motors at a rate sufficient to ensure that consecutive shots had the desired degree of overlap.

For these experiments we chose SU-8 (Microlithography Chemical Corp.), a negative resist consisting of a photoinitiator that polymerizes an organic resin. SU-8 has been shown to be particularly suited for production of very thick 2-D structures by one-photon exposure.[5] For threshold measurements, we prepared sample films of 25-μm thickness by spin coating a commercial solution (SU-8 25) onto glass substrates at 3000 rpm. We evaporated the solvent by heating the films to 100 °C for 0.25 h (prebake), and after exposure we developed the film by heating it to 100 °C for 0.5 h (postbake) and soaking it in the developer

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solution for 0.5 h, as is standard for developing one-photon structures from this material. Some 3-D structures washed off the substrate during development owing to the small contact area between the exposed resist and the substrate. We largely alleviated this problem by first spinning a thin film of the resist onto the substrate and developing it thermally by curing at 300 °C from 2–5 min and then overlaying a thick layer of resist for two-photon exposure (i.e., adhesion of developed resist is better to developed resist than to glass).

The UV–visible absorption spectrum of an unexposed, undeveloped SU-8 film is shown in Fig. 1. Clearly, neither the resin nor the initiator has any one-photon absorption at 800 nm, so exposure at this wavelength must be due to a two- or higher-order photon process. As discussed below, the damage and exposure thresholds for SU-8 at 800 nm differ by only a factor of 2.5. This limited range makes studying the intensity dependence to determine the precise order of the exposure process difficult. Thus, although we refer to the absorption events leading to exposure as two-photon, there remains the possibility that initiation results from higher-photon processes.

Figure 2 shows optical micrographs of the developed resist following exposure to ~120-fs, 800-nm pulses of four different energies, focused to a near-diffraction-limited elliptical spot (FWHM) of ~130 μm × 160 μm with a 1-m focal-length lens. The top left-hand panel shows the result of exposing the resist to a single pulse with 300 μJ of energy. At this energy most of the center of the exposed region is simply burned away. At lower intensities near the edge of the spot, however, there is a region where the resist has been developed but not damaged. Outside this region the resist remains unexposed; the exposed region is made visible by the dark shadow projected from the exposed to the unexposed regions. The overall size of the developed spot is ~210 μm × 150 μm. The top right-hand panel shows the result of using a 180-μJ pulse. Clearly this energy is just above the damage threshold at the center of the beam, whereas the rest of the spot is uniformly exposed. The bottom left-hand panel shows the slightly smaller and uniform spot produced just below the damage threshold by use of incident energy of 120 μJ. Finally, the bottom right-hand panel shows what happens just as the two-photon exposure threshold of 60 μJ is reached. The developed spot (~70 μm × 50 μm) is smaller than the diffraction-limited beam, indicating that only the center of the beam profile was intense enough to expose the resist. This nonlinearity of the resist response can thus be used to our advantage: With careful control of the light intensity, it is possible to produce features in the resist that are smaller than the diffraction limit.[4]

Using a series of micrographs like those shown in Fig. 2, we determined that the threshold for two-photon exposure is 3.2 TW/cm^2 and that for optical damage is 8.1 TW/cm^2. Thus there is a factor-of-2.5 window for two-photon exposure of SU-8 without damage. With the full energy available from amplified Ti:sapphire lasers, single-slot exposure through masks should be possible for areas of the order of 1 mm^2, allowing rapid production of large-scale devices. Moreover, at these thresholds, the single-shot two-photon exposure threshold is within reach of currently available high-power Ti:sapphire oscillators. Preliminary results obtained with only 100-mW average power at 700 nm from an 80-MHz oscillator with 60-fs pulses focused to a 1-μm spot show single-shot two-photon exposure with a 1.6-TW/cm^2 threshold. Thus, the rate at which structures can be written is limited only by the ability to scan from voxel to voxel, all the way up to the 80-MHz repetition rate of the oscillator; this is a significant improvement over previous efforts in which the beam was required to dwell at each location for 10^4–10^6 shots.[1–3]

Since SU-8 is not optimized for two-photon work, there is significant room for improving the window between exposure and damage by specific tailoring of the initiator and the resist. The preliminary data with the oscillator discussed above also suggest that the threshold can be lowered by use of a more suitable wavelength. To verify this we examined the resist after it was exposed to femtosecond pulses at 660 nm. As is evident from Fig. 1, the one-photon absorption of SU-8 is significantly greater at 330 than at 400 nm, providing more states for two-photon excitation at 660 than at 800 nm. We find that the two-photon exposure threshold at 660 nm is ~5 times lower than that at 800 nm and roughly half that at 700 nm, whereas the threshold for optical damage is not significantly changed. Thus, with proper choice of excitation

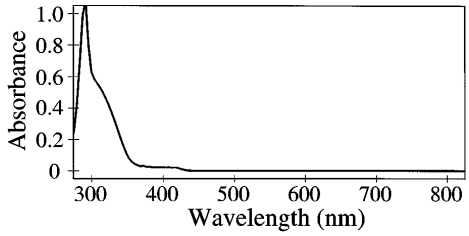

Fig. 1. Optical absorption spectrum of an unexposed SU-8 film.

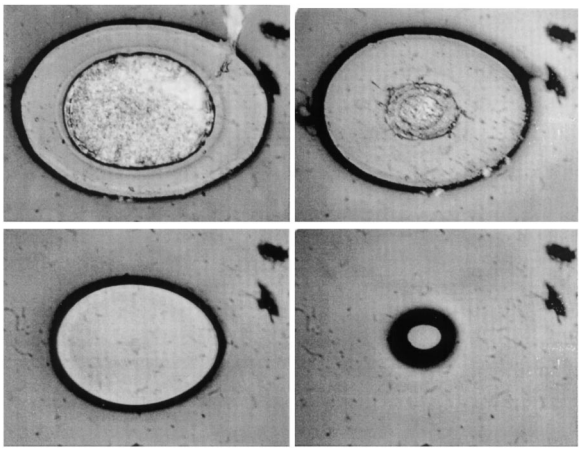

Fig. 2. ~250 μm × 200 μm optical micrographs of developed SU-8 following exposure to ~120-fs, 800-nm pulses with energy of 300 μJ (top left), 180 μJ (top right), 120 μJ (bottom left), and 60 μJ (bottom right).

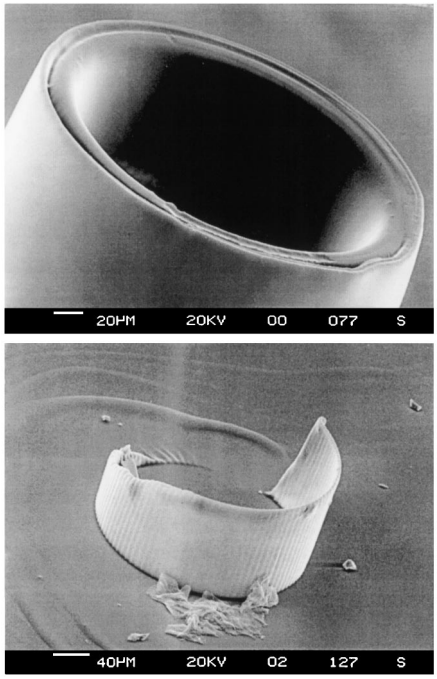

Fig. 3. 3-D structures in developed SU-8 produced by consecutive laser shots with two-photon exposure (see text). The scale bars in the top and bottom panels are 20 and 40 μm, respectively.

wavelength and specially designed initiators, dramatic improvements in the ability to two-photon expose photoresist[3] in a single shot can be expected.

Finally, Fig. 3 presents what are to our knowledge the first 3-D structures fabricated by two-photon lithography with a series of single laser shots. We produced the cylinder in the scanning electron micrograph shown in the top panel by rotating the sample while translating it slowly along the substrate normal (z axis). Here, we focused single laser shots with a 25-mm lens overlap to expose a circular pattern in the resist, which grew into a cylinder as the height of the exposed circle was changed by the z axis translation. The thickness of the cylinder walls is $\sim$20 μm, limited by wobble in the chopper wheel that we used to rotate the sample. The height of the cylinder is $\sim$300 μm, and since the voxels are well overlapped in the z direction, the height is limited only by the thickness of the resist.

The bottom panel of Fig. 3 shows a spiral produced by fast z-axis translation with simultaneous sample rotation. With the 25-mm focal-length lens, an individual voxel is $\sim$4 μm in diameter and roughly 80 μm tall. The fluted appearance is the result of construction from single-voxel columns that were only slightly overlapped to produce the desired 3-D spiral. The short columns at the left are produced when most of the focal volume is in the substrate below the resist. As the sample translates in the z direction, the voxel moves into the resist layer until the spiral stops growing because the focal volume has moved above the substrate so that the exposed resist is not anchored and washes away during development.

In summary, we have demonstrated single-shot two-photon exposure of commercial photoresist. The ability to selectively expose regions in the interior of photoresist allows one to produce 3-D structures. Even an off-the-shelf resist has a factor of at least 2.5 between the exposure and the damage thresholds, offering great promise for the development of future resists that are optimized for two-photon work. The nonlinear nature of the absorption opens the potential for producing features that are smaller than the diffraction limit, a potential boon if the two-photon exposure mechanism can be extended into the UV. The above-measured thresholds are such that either large-area exposures from amplified femtosecond lasers or single-voxel exposures from high-power oscillators will permit rapid fabrication of large-scale 3-D devices. Overall, the ability to lithographically produce 3-D structures with single laser shots opens a whole new direction for applications such as 3-D circuits, microelectromechanical systems, and photonic crystals.

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