Femtosecond laser-induced two-photon polymerization of inorganic–organic hybrid materials for applications in photonics

J. Serbin, A. Egbert, A. Ostendorf, and B. N. Chichkov

Laser Zentrum Hannover e.V., Hollerithallee 8, D-30419 Hannover, Germany

R. Houbertz, G. Domann, J. Schulz, C. Cronauer, L. Fröhlich, and M. Popall

Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, D-97082 Würzburg, Germany

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Investigations of two-photon polymerization of inorganic–organic hybrid materials initiated by femtosecond Ti:sapphire laser pulses are performed. First applications of this technique for the fabrication of three-dimensional microstructures and photonic crystals in inorganic–organic hybrid polymers with a structure size down to 200 nm and a periodicity of 450 nm are discussed. © 2003 Optical Society of America

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It was recently demonstrated that two-photon polymerization (2PP) of photosensitive materials allows one to fabricate complicated three-dimensional (3D) microstructures.[1–12] When they are tightly focused into the volume of a liquid resin (which is transparent in the infrared), femtosecond laser pulses can initiate 2PP and produce structures with submicrometer resolution. Among the structures that have already been fabricated are photonic crystals,[3–5] microrotors driven by laser tweezers,[6] microscopic models, and mechanical devices (a bull,[2] tubes,[7] oscillators,[8] gear wheels,[9,10] chains[11,12]). So far, in all these experiments commercial acrylate- or epoxy-based resins were used.

Very promising materials for photonics are multifunctional inorganic–organic hybrid polymers (such as ORMOCER, used in this work) whose properties can be tuned from those that are characteristic of organic polymers to those that are similar to inorganic glasses. ORMOCERs are produced by solgel synthesis.[13–15] Important advantages of these materials are an adjustable refractive index (in the range 1.47–1.56), high optical transparency with low losses (for both liquid and polymerized materials) at data and telecommunication wavelengths (<0.06 dB/cm at 830 nm, <0.2 dB/cm at 1310 nm, and <0.6 dB/cm at 1550 nm), exceptional thermal and mechanical properties, high chemical resistance, and quite low cost.

In this Letter investigations of 2PP of optically high-quality inorganic–organic hybrid materials (ORMOCERs) are reported. The possibilities of use of this technique for fabrication of low-loss micro-optical devices and three-dimensional photonic structures with a lateral resolution below 200 nm are studied.

The specific applied material is ORMOCER-1.[14,15] This material is designed for UV photolithography and contains the Irgacure 369 initiator, which is sensitive to UV radiation. In the near IR, especially at 780 nm, all ORMOCERs are transparent, which allows one to focus femtosecond Ti:sapphire laser pulses into the volume of the liquid resin. The high photon density in the focal volume triggers two-photon absorption by initiator molecules and results in the generation of radicals that, in turn, initiate the polymerization of the resin. When the laser focus is moved through the resin in three dimensions, polymerization occurs along the trace of the focus; i.e., any computer-generated 3D structure can be fabricated by direct laser recording into the volume of the ORMOCER. The nonirradiated liquid resin can be dissolved in alcohol, leaving the polymerized copy of the computer model.

In our experiments a Ti:sapphire oscillator with a repetition rate of 80 MHz, a pulse duration of 80 fs, and a laser wavelength of 780 nm is used. The number of laser pulses and the irradiation time are controlled by a mechanical shutter with a minimum switching time of 5 ms. Femtosecond laser pulses are focused by a 100× immersion lens microscope objective with a N.A. of 1.4 and filled with a refractive-index-matching oil ($n_{\mathrm{oil}} = 1.515$).

Because of the threshold behavior of the 2PP process, a resolution beyond the diffraction limit can be realized by control of the laser-pulse energy and the number of applied pulses. To predict the size of the polymerized volume (volume pixel or voxel) one needs to define a polymerization threshold. We assume that the resin is polymerized as soon as the particle density of radicals, $\rho = \rho(r, z, t)$, exceeds a certain minimum concentration (threshold value) ρ_{th}. For the same initiator, this value is independent of the particular initiation process that leads to the generation of radicals and should be the same for single- and two-photon absorption. From experiments performed with UV light, the lowest measured density of radicals required for polymerization of ORMOCERs is approximately $\rho_{\mathrm{th}} = 0.25$ wt.%.

The density of radicals, ρ, produced by femtosecond laser pulses can be calculated by solution of a simple rate equation:

$$\partial\rho/\partial t = (\rho_0 - \rho)\sigma_2 N^2, \tag{1}$$

where $\sigma_2 = \sigma_2{}^a\eta$ is the effective two-photon cross section for the generation of radicals [cm^4 s], which is defined by the product of the ordinary two-photon absorption cross section, $\sigma_2{}^a$, and the efficiency of the

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initiation process, $\eta < 1$ (Ref. 16); $N = N(r, z, t)$ is the photon flux, and ρ_0 is the primary initiator particle density. We approximate the light distribution in the main maximum at the focal plane ($z = 0$) by a Gaussian distribution $N(r, t) = N_0(t)\exp(-2r^2/r_0^2)$, instead of using more-complicated exact expressions in terms of Lommel functions.[17] Moreover, the photon flux, $N_0(t) = N_0$, is considered to be constant during the laser pulse, since reaching the polymerization threshold requires many laser pulses. Neglecting the losses of radicals between the laser pulses, we can obtain the following estimate for the pixel diameter, defined as a region where $\rho(r, z) \geq \rho_{\text{th}}$ is fulfilled:

$$d(N_0, t) = r_0[\ln(\sigma_2 {N_0}^2 n\tau_L/C]^{1/2},$$
$$C = \ln[\rho_0/(\rho_0 - \rho_{\text{th}})], \tag{2}$$

where $n = \nu t$ is the number of pulses, ν is the laser-pulse repetition rate, t is the total processing–irradiation time, and τ_L is the laser-pulse duration.

To estimate the maximum voxel length along the beam axis at $r = 0$, we use the same expression for the axial light distribution, $N(z) = N_0/(1 + z^2/{z_R}^2)$, as for a Gaussian laser pulse. In this approximation, the pixel length is determined by

$$l(N_0, t) = 2z_R[(\sigma_2 {N_0}^2 n\tau_L/C)^{1/2} - 1]^{1/2}, \tag{3}$$

where z_R is the Rayleigh length. To compare Eqs. (2) and (3) with the experimental data, we replaced N_0 with

$$N_0 = \frac{2}{\pi {r_0}^2 \tau_L} \frac{P\mathcal{T}}{\nu\hbar\omega_L}, \tag{4}$$

where P is the average laser power and $\mathcal{T}$ is the fraction of light transmitted through the objective.

In Fig. 1, the measured data for the voxel diameter and its length are shown. Measurements are performed with a scanning electron microscope (SEM). By fitting these data by use of Eqs. (2)–(4), we can find the unknown parameters $r_0 = 320$ nm, $z_R = 0.725$ μm, and $\sigma_2/C = 2.76 \times 10^{-54}$ cm^4 s. The corresponding fits are shown in Fig. 1 by the solid curves. The numerical values of parameters r_0 and $2z_R$ are close to the resolution limits of the objective.[18] The lateral resolution of our objective is given by $r = 0.61\lambda/\text{N.A.} = 340$ nm; the axial resolution, by $z = 2\lambda n_{\text{oil}}/\text{N.A.}^2 = 1.2$ μm.

The curves for both the voxel length and the voxel diameter cross the x axis at $tP^2 = 1.7 \times 10^{-5}$ W^2 s. For an average power of 30 mW, an irradiation time of 19 ms at an 80-MHz repetition rate is needed to polymerize the resin in the center of the laser focus; i.e., 1.5×10^6 pulses have to be applied. The laser energy used in this case is 0.57 mJ. Since the laser beam was expanded before the objective lens, so that $\mathcal{T} = 15\%$, only $E_L = 86$ μJ is focused into the sample. The accumulated threshold fluence for polymerization ($E_L/\pi {r_0}^2$) is therefore 27 kJ/cm^2. For this threshold value, the theoretical voxel size should be infinitely small, but in fact the minimum voxel size is always limited by the pointing stability and power fluctuations of the laser. The resin that we used contained 2.4 wt. % of photoinitiator molecules ($\rho_0 = 2.4\%$). Taking into account that the threshold density of radicals required for polymerization of ORMOCERs is equal to 0.25 wt. %, from the ratio σ_2/C we can find the effective two-photon cross section for the generation of radicals, $\sigma_2 = 3 \times 10^{-55}$ cm^4 s. This value is relatively small, which is explained by the fact that we use conventional UV-absorbing initiators (Irgacure 369) with a single-photon absorption maximum at 328 nm. Much higher two-photon sensitivity can be obtained with specially designed initiators based on π-conjugated compounds with a two-photon absorption cross section $\sigma_2{}^a$ in the range 10^{-50} to 10^{-47} cm^4 s.[3]

To realize real 3D microstructuring with femtosecond lasers we scanned the laser beam with an x–y galvo scanner and moved the sample in the z direction with a translation stage. In Fig. 2, SEM images of a micrometer-scale Venus statue that was fabricated by 2PP are shown. To accelerate the fabrication process, which was approximately 5 min long, we irradiated only the shell with femtosecond laser pulses. After that the liquid resin was washed out, and the statue was irradiated with UV light for final polymerization of the inner body.[2,12]

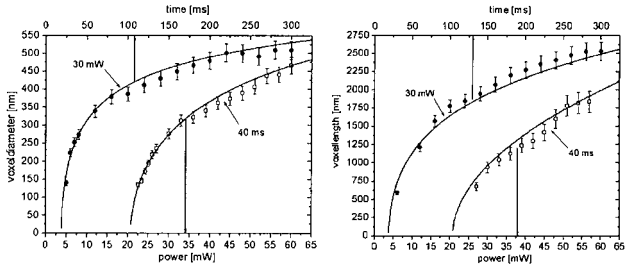

Fig. 1. Predicted and measured data for (left) the diameter and (right) the length of the polymerized volume as a function of the average laser power (for constant irradiation time $t = 40$ ms) and as a function of the irradiation time (for constant laser power $P = 30$ mW).

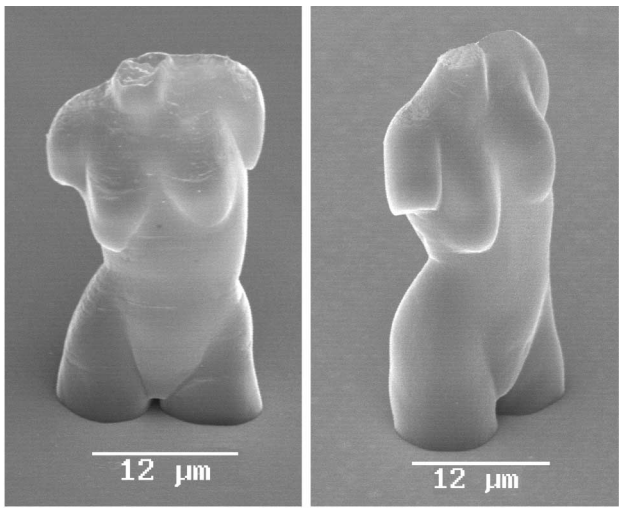

Fig. 2. SEM micrometer-scale image of Venus fabricated by 2PP. Only the shell was irradiated by femtosecond laser pulses; the inside region was cured with a UV lamp after the liquid resin was washed away.

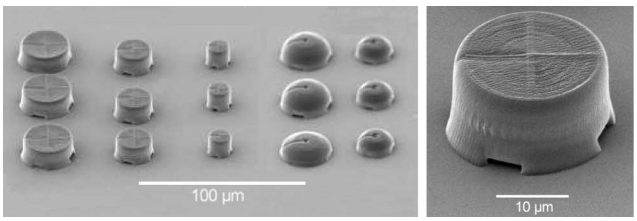

Fig. 3. Examples of application of the 2PP technique to fabrication of microcapsules.

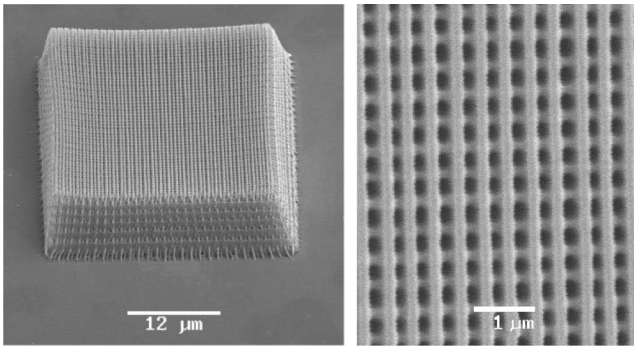

Fig. 4. SEM image of a photonic crystal structure fabricated by 2PP.

Another example of 3D microstructuring is presented in Fig. 3. The SEM images show small microcapsules that have been fabricated in ORMOCER by use of femtosecond laser pulses. This material is biocompatible and can be used for medical and biological applications.

Since the optical losses of ORMOCERs are lower than 0.6 dB/cm at data and telecommunication wavelengths, the 2PP microstructuring technique is very attractive for fabrication of micro-optical components and devices. In Fig. 4, an example of a photonic crystal structure fabricated in ORMOCER by use of the 2PP technique is shown. The photonic crystal was built up from individual rods with a diameter of 200 nm and a spacing between the rods of 250 nm. The total fabrication time was 10 min.

In conclusion, femtosecond laser-induced microstructuring of polymer-forming hybrid materials, which have exceptionally good optical and mechanical properties, has been performed for what is believed to be the first time. The minimum achievable structure sizes and the resolution limits of the two-photon polymerization technique were investigated. First applications of the 2PP technique for the fabrication of micromodels and photonic crystals in hybrid polymers were demonstrated. It is expected that 2PP of ORMOCERs will be used for low-cost fabrication of artificial microstructured and nanostructured components for different applications in optics, medicine, and biology.

B. N. Chichkov's e-mail address is ch@lzh.de.

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