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Multiphoton polymerization using optical trap assisted nanopatterning

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In this letter, we show the combination of multiphoton polymerization and optical trap assisted nanopatterning (OTAN) for the additive manufacturing of structures with nanometer resolution. User-defined patterns of polymer nanostructures are deposited on a glass substrate by a $3.5\text{ }\mu\text{m}$ polystyrene sphere focusing IR femtosecond laser pulses, showing minimum feature sizes of $\lambda/10$. Feature size depends on the applied laser fluence and the bead surface spacing. A finite element model describes the intensity enhancement in the microbead focus. The results presented suggest that OTAN in combination with multiphoton processing is a viable technique for additive nanomanufacturing with sub-diffraction-limited resolution. © 2013 AIP Publishing LLC.

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The creation of nano-scale features is of critical importance in a wide range of technologies. In order to address this need, laser direct-write techniques which have the ability to add, remove or modify materials have been developed.¹ Classical far-field laser techniques are limited by diffraction. Therefore, in order to generate features smaller than the optical wavelength several advanced laser direct-write techniques based on either optical nonlinear absorption or near-field effects have been developed.^{2,3}

Nanopatterning through multiphoton polymerization^{4,5} has been shown to be an efficient way to generate complex nanostructures. An ultrafast laser is tightly focused to a tiny voxel (volumetric pixel) where the nonlinear absorption takes place with a sharp threshold in the focus of a high numerical aperture objective. By scanning the voxel inside a polymer precursor with advanced scanning optics or spatial light modulators, the addition of nanoscale features can be realized.⁵ The size of the generated structures can be reduced by controlling the exposure⁶ as well as using a shorter wavelength.⁷ Recently enhanced resolution in multiphoton polymerization based on the stimulated emission depletion (STED) approach⁸ has been demonstrated.^{9–11}

Generating nanofeatures with the use of micro-focusing elements takes advantage of the evanescent near-field, allowing light to be focused below the diffraction limit.¹² For example, near-field enhancement induced by an atomic force microscope (AFM) tip,¹³ near-field scanning optical microscope (NSOM) probe,^{14,15} array of polymer microparticles,¹⁶ and plasmonic lenses^{17,18} has been applied to sub-wavelength nanostructuring. Optical trap assisted nanopatterning (OTAN),^{19–21} a particle based laser direct-write technique, not only harnesses the aforementioned benefits, but also adds additional advantages, such as focus shaping by choice of particle size, shape and material, replacing the near-field probe on the spot or working with uneven surfaces.

While nonlinear absorption is readily applied to multiphoton polymerization for additive nanomanufacturing, the utilization of microparticle near-field focusing for focus shaping and increased resolution has been used mainly for material modification or removal so far. In our experiments, we combined OTAN with multiphoton processing (MP) for additive nanomanufacturing. First preliminary results demonstrating proof of concept of the suggested approach have been published in Ref. 22. Figure 1 shows the principle of our nanostructuring approach and our experimental setup. A microbead ($3.5\text{ }\mu\text{m}$ polystyrene, Bangs Labs) submerged in a liquid photopolymer (NOA84, Norland Products) controlled by an optical trap was used to focus ultrashort laser pulses in order to induce multiphoton polymerization. NOA84 was chosen due to its low viscosity of 40–75 cps. Its refractive index of $n_{\text{NOA84}} = 1.46$ is lower than that of polystyrene ($n_{\text{PS}} = 1.58$) allowing for a stable optical trapping.

FIG. 1. Optical trap assisted multi-photon polymerization: principle and experimental setup.

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FIG. 2. Optical trap assisted multi-photon polymerization: polystyrene microbead ($d = 3.5 \mu\text{m}$) in NOA84 trapped by a cw laser ($\lambda = 1064 \text{ nm}$), polymerization is induced by single femtosecond laser pulses ($\tau = 120 \text{ fs}$, $\lambda = 800 \text{ nm}$): (a) trapped bead above the substrate surface during structuring; (b) generated “LPT” pattern on the substrate surface (LPT = Lehrstuhl für Photonische Technologien / Chair of Photonic Technologies); (c) inner glass structures fabricated without a bead by the femtosecond laser focus beneath the substrate surface.

Furthermore, the polystyrene particles generally supplied in aqueous solution need to be diluted in the photopolymer. This is possible with the chosen material configuration, as NOA84 can dissolve small amounts of water. Our applied optical tweezers system was based on a modified Thorlabs optical trapping kit using standard optic components. We used a Nikon oil immersion objective ($100\times/1.2$) and a Spectra Physics IR cw laser (wavelength $\lambda = 1064 \text{ nm}$) with an effective power of 0.05 W after the objective for manipulation of the microparticle. The choice of a Gaussian beam optical trap allowed to control the bead in three dimensions. As absorption of NOA84 starts at wavelengths below $\lambda = 450 \text{ nm}$, a femtosecond laser (pulse duration $\tau = 120 \text{ fs}$) in single pulse operation mode at a wavelength of $\lambda = 800 \text{ nm}$ was chosen.

The microparticle was trapped above the glass substrate. We then focused the femtosecond laser inside the glass substrate so that it was out of focus at the particle plane. The particle was therefore illuminated with a quasi homogeneous intensity distribution. Polymer voxels were created on the glass substrate at fluences between 50 and 200 J/m^2 . In the following we call this structuring approach OTAN-MP.

Figure 2 shows the OTAN-MP structuring procedure. The microbead was positioned by the optical trap at a distance of approximately one bead diameter above the substrate and irradiated with single femtosecond laser pulses inducing two-photon polymerization (2PP) in the particle focus. Even if each femtosecond laser pulse induced a shock wave leading to a small lift of the bead, the bead did not escape from the trap during structuring and could be moved on to the next position. By this, we fabricated an “LPT” pattern consisting of single voxels (see Figure 2(a)). In order to demonstrate that the microbead focus is responsible for feature generation, we drew a rectangle around the generated pattern at identical processing conditions, but without a bead. By focusing the CCD camera on the glass substrate plane, it became obvious that voxels had been generated only in presence of the bead (see Figure 2(b)). Without the bead, a rectangle of inner glass structures was fabricated beneath the surface by the focus of the pulsed laser (see Figure 2(c)). When using a bead, the focus was shifted above the substrate, leading to multiphoton polymerization inside the photopolymer. In this case, the remaining intensity of the laser pulse was not sufficient any more to generate inner

FIG. 3. Features generated by OTAN-MP with $3.5 \mu\text{m}$ polystyrene microbeads in NOA84: (a) line of voxels ($\bar{d} = 390 \pm 40 \text{ nm}$); (b) line of voxels ($\bar{d} = 83 \pm 11 \text{ nm}$); (c) single voxel ($d = 80 \text{ nm}$); (d) partly detached voxel.

glass structures. The images shown in Figure 2 demonstrate that it is possible to manipulate polystyrene microbeads in a low viscous photopolymer with an optical trap. By irradiation with ultrashort laser pulses, multiphoton polymerization in the microbead focus can be induced leading to the generation of 3D voxels on the substrate surface. During the direct-write structuring procedure, the bead neither gets lost nor damaged.

Figure 3 shows scanning electron microscope images of structures that have been fabricated by OTAN-MP. The line of voxels shown in Figure 3(a) was generated by irradiation of an optically trapped $3.5\text{ }\mu\text{m}$ polystyrene microbead with femtosecond laser pulses. The average voxel size is $\bar{d} = 390 \pm 40\text{ nm}$. Figures 3(b) and 3(c) show further examples of voxels we fabricated in our experiments. At a processing wavelength of $\lambda = 800\text{ nm}$, our smallest generated voxels had a size of 80 nm . These results demonstrate that by proper choice of processing parameters voxel sizes of $\lambda/10$ can be fabricated. Based on the assumption of a hemispherical voxel shape, the voxel volume range can be estimated. It is on the scale of 10^{-4} to $10^{-3}\text{ }\mu\text{m}^3$.

The experiments showed that the most relevant processing parameters are the distance between particle and surface and the femtosecond laser fluence. Therefore, we performed a more detailed analysis of these parameters.

Figure 4 shows arrays of voxels that have been generated at laser fluences of 70 and 90 J/m^2 . From the left to the right, the distance between the bead and the substrate was decreased in steps of 160 nm . The initial position z_0 is defined as the upper distance at which at a fluence of 90 J/m^2

no voxel generation on the substrate could be observed. The diagram shows an analysis of the voxel sizes determined from the SEM images. At both fluences, we could fabricate features at a wide range of bead surface spacings. The depth of field for feature generation on the surface is approximately $1\text{ }\mu\text{m}$. Smallest feature sizes were obtained at a large bead surface spacing. Due to the shape of the voxel in the SEM image, we assume that in this case the generated voxel partly detached from the surface due to the small contact area and the pressure wave induced by the occurring gas bubble. The aspect of microbead dynamics caused by bubble formation in OTAN has been extensively discussed in Ref. 23. Figure 3(d) shows an image of such a partly detached voxel. With decreasing distance, the generated voxel completely sticks to the surface and feature size grows. If the bead gets too close to the surface, no voxels can be generated any more. As it is a threshold process, both voxel size and depth of field decrease with decreasing laser fluence.

For a better understanding of the obtained results, we performed finite element simulations of the microbead focus. The simulation model is based on the RF-module of COMSOL Multiphysics and calculates a stationary solution of the electromagnetic wave equation. In our simulation model, we assumed symmetry in the x-z- and y-z-plane. The particle was irradiated by an x-polarized electromagnetic wave propagating in -z-direction. Boundary conditions were defined as “perfect magnetic conductor”²⁴ for x-z- and “perfect electric conductor”²⁴ for y-z-boundaries. The top and bottom boundaries were described as “scattering boundary conditions.”²⁴ Figure 5(a) shows the intensity, respectively, energy flux

FIG. 4. Arrays of voxels generated by OTAN-MP with $3.5\text{ }\mu\text{m}$ polystyrene microbeads in NOA84, from left to right the distance between bead and substrate was reduced in steps of 160 nm : (a) 90 J/m^2 , (b) 70 J/m^2 , (c) size analysis.

FIG. 5. Finite element simulation of intensity enhancement beneath polystyrene microbead ($d = 3.5 \mu\text{m}$) in NOA84 irradiated with a wavelength of $\lambda = 800 \text{ nm}$. The simulation shows one quarter of the bead, as symmetry in x - z - and y - z -plane was assumed: (a) intensity distribution S/S_0 , (b) squared intensity distribution $(S/S_0)^2$.

distribution described by the time-averaged poynting vector²⁵ beneath a polystyrene microbead in NOA84 irradiated with a collimated laser beam at a wavelength of $\lambda = 800 \text{ nm}$. Due to the low difference in refractive index between bead ($n_{PS} = 1.58$) and photopolymer ($n_{NOA84} = 1.46$), the bead acts like a spherical lens with extreme spherical aberrations. The focus with a depth of field of several micrometers has a size of 560 nm (FWHM) and is located $2.7 \mu\text{m}$ beneath the bead. As two-photon polymerization probability depends quadratically on the photon flux,²⁶ for an analysis of feature size the squared intensity must be regarded (see Figure 5(b)). The full width at half maximum of the squared intensity distribution is 235 nm .

Both focal spot size and position are in good correspondence with our experimental findings. The focal shift allows a structure generation without damaging the bead. Besides, the generated voxel does not attach to the surface of the bead. Furthermore, the focal shift explains that voxel generation stops when the bead gets too close to the substrate (compare Figure 4) as in this case the focus is located completely in the glass substrate. Even if the focal spot created using our OTAN-MP system is diffraction limited, the multi-photon absorption threshold effects allow us to fabricate sub-100-nm voxels. The high depth of field of the microbead focus has its origin in spherical aberrations of the bead and makes the technique relatively robust.

In this contribution, we demonstrated that an optically manipulated particle can be applied to focus an ultrafast laser in order to induce multiphoton polymerization. NOA84 photopolymer in combination with polystyrene microbeads was identified to be a suitable material system for this additive nanomanufacturing approach. $3.5 \mu\text{m}$ polystyrene microbeads can be three-dimensionally positioned inside the photopolymer by an optical trap and femtosecond pulses can be used in order to induce multiphoton polymerization in the particle focus. Feature sizes of $\lambda/10$ are feasible. The presented technique is a promising approach to utilize the

focus of transparent dielectric particles in order to reduce resolution to a sub-100-nm scale in laser based additive nanomanufacturing.

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¹C. B. Arnold, P. Serra, and A. Pique, *MRS Bull.* **32**, 23–31 (2007).

²M. Ali, M. Shakoor, and P. Molian, *J. Laser Appl.* **20**, 169–184 (2008).

³L. Li, M. Hong, M. Schmidt, M. Zhong, M. Ajay, B. H. in't Veld, and V. Kovalenko, *CIRP Ann.* **60**, 735–755 (2011).

⁴S. Kawata, H.-B. Sun, T. Tanaka, and K. Takada, *Nature* **412**, 697–698 (2001).

⁵C. LaFratta, J. Fourkas, T. Baldacchini, and R. Farrer, *Angew. Chem. Int. Ed.* **46**, 6238–6258 (2007).

⁶X.-Z. Dong, Z.-S. Zhao, and X.-M. Duan, *Appl. Phys. Lett.* **92**, 091113-3 (2008).

⁷W. Haske, V. Chen, J. Hales, W. Dong, S. Barlow, S. Marder, and J. Perry, *Opt. Express* **15**, 3426–3436 (2007).

⁸S. Hell and J. Wichmann, *Opt. Lett.* **19**, 780–783 (1994).

⁹J. Fischer, G. Freymann, and M. Wegener, *Adv. Mater.* **22**, 3578–3582 (2010).

¹⁰L. Li, R. Gattass, E. Gershgoren, H. Hwang, and J. Fourkas, *Science* **324**, 910–912 (2009).

¹¹T. F. Scott, B. A. Kowalski, A. C. Sullivan, C. N. Bowman, and R. R. McLeod, *Science* **324**, 913–917 (2009).

¹²Z. Wang, N. Joseph, L. Li, and B. Lukyanov, *J. Mech. Eng. Sci.* **224**, 1113–1127 (2010).

- ¹³A. Chimmalgi, C. P. Grigoropoulos, and K. Komvopoulos, *J. Appl. Phys.* **97**, 104319 (2005).
- ¹⁴D. J. Hwang, A. Chimmalgi, and C. P. Grigoropoulos, *J. Appl. Phys.* **99**, 044905 (2006).
- ¹⁵S. M. Huang, M. H. Hong, B. S. Luk'yanchuk, Y. W. Zheng, W. D. Song, Y. F. Lu, and T. C. Chong, *J. Appl. Phys.* **92**, 2495–2500 (2002).
- ¹⁶K. Piglmayer, R. Denk, and D. Bauerle, *Appl. Phys. Lett.* **80**, 4693–4695 (2002).
- ¹⁷W. Srituravanich, L. Pan, Y. Wang, C. Sun, D. B. Bogy, and X. Zhang, *Nat. Nanotechnol.* **3**, 733–737 (2008).
- ¹⁸W. Srituravanich, N. Fang, C. Sun, Q. Luo, and X. Zhang, *Nano Lett.* **4**, 1085–1088 (2004).
- ¹⁹E. McLeod and C. B. Arnold, *Nat. Nanotechnol.* **3**, 413–417 (2008).
- ²⁰Y.-C. Tsai, K.-H. Leitz, R. Fardel, A. Otto, M. Schmidt, and C. B. Arnold, *IOP Nanotechnol.* **23**, 165304 (2012).
- ²¹U. Quentin, K.-H. Leitz, L. Deichmann, I. Alexeev, and M. Schmidt, *J. Laser Appl.* **24**, 042003 (2012).
- ²²Y.-C. Tsai, K.-H. Leitz, R. Fardel, M. Schmidt, and C. B. Arnold, *Phys. Procedia* **39**, 669–673 (2012).
- ²³R. Fardel, Y. C. Tsai, and C. B. Arnold, *Appl. Phys. A* **112**, 23–28 (2013).
- ²⁴*COMSOL Multiphysics RF Module User's Guide-Version 4.2* (COMSOL, 2011).
- ²⁵S. G. Lipson, H. S. Lipson, and D. S. Tannhauser, *Optik*, 3rd ed. (Springer, Berlin, 1997).
- ²⁶J. Serbin, A. Egbert, B. Chichkov, R. Houbertz, G. Domann, J. Schulz, C. Cronauer, L. Frhlich, and M. Popall, *Opt. Lett.* **28**, 301–303 (2003).