Dual-beam, 3D photolithography provides exceptional resolution

Linjie Li, Rafael Gattass, and John Fourkas

An ultrafast laser is used to initiate multiphoton absorption polymerization, while a second, spatially shaped, continuous wave laser selectively deactivates polymerization to enhance the resolution.

Despite the remarkable progress in micro- and nanoscale fabrication that has occurred over recent decades, lithographic feature sizes are still generally restricted by the diffraction limit of the optical system. The resolution in conventional photolithography is generally constrained to approximately one quarter of the wavelength ($\lambda$) of the light used. Higher-resolution alternatives to photolithography (such as electron-beam lithography) usually require expensive equipment and cannot be performed under ambient (e.g., atmospheric pressure) conditions. Multiphoton absorption polymerization (MAP) offers another option for high-resolution fabrication. Using nonlinear optical and chemical effects, MAP systems employing 800nm laser excitation can generate features with transverse dimensions as small as 80nm. Shorter-exposure wavelengths or polymeric shrinkage can provide even smaller transverse dimensions. MAP has the additional capability of fabricating arbitrary 3D structures, which is essential to many applications. However, for 3D fabrication, the resolution in the axial direction remains about three to five times lower than in the transverse direction due to the shape of the laser focal volume.

In MAP, a femtosecond laser beam is focused into a photosensitive resist through a microscope objective. A single photon from the excitation laser does not have enough energy to excite a photoactivator molecule. However, the simultaneous absorption of two photons by a photoinitiator can induce polymerization. Because two-photon absorption is a nonlinear process, polymerization occurs only when there are enough photons in a given volume. The photon density is highest in the focal region, restricting fabrication to a volume element (voxel) at the laser focus. 3D microstructures can be fabricated by scanning the laser focal point with respect to the resist. Unexposed areas of the resist are washed away, leaving the final structure on the substrate.

Inspired by stimulated emission depletion (STED) fluorescence microscopy, we have developed a fabrication technique that can overcome the diffraction limit. In STED, fluorescent

Continued on next page
molecules are excited from the ground state to the first excited electronic state by an ultrafast laser pulse. A second laser pulse is used to de-excite the molecules through stimulated emission. By spatial phase shaping of the de-excitation beam, fluorescence can be confined to a small region of the excitation-beam focal volume, allowing for high-resolution imaging.

We have developed a lithographic technique called resolution augmentation through photo-induced deactivation (RAPID). In analogy to STED, RAPID relies on a laser to photo-induce deactivation of the polymerization process. However, the mechanism behind RAPID is not stimulated emission. In this technique, the excitation pulse drives the photoinitiator molecules to a long-lived intermediate state that initiates polymerization on a relatively slow time scale. A second laser can be used to quench this intermediate to the ground state, preventing polymerization. The molecule that we use for this purpose is malachite green carbinol base (MG-C). MG-C has the added benefit that the lifetime of the intermediate state is long enough that a continuous wave (CW) laser beam can be used for de-excitation. This feature simplifies RAPID by removing the need to establish timing between excitation and deactivation pulses.

Figure 1(a) illustrates the experimental setup used for RAPID lithography. An 800nm pulsed laser (excitation beam) initiates polymerization, and a second CW laser (deactivation beam) inhibits polymerization. Resolution augmentation depends on the spatial phase mask used. We employed a phase mask for which deactivation occurs at the peripheral area of the excitation-beam focal region, leaving a smaller focal point for fabrication, as indicated in Figure 1(b).

Figure 2 demonstrates that RAPID can reduce the voxel size dramatically. Figure 2(a) shows an scanning electron microscope (SEM) image of a voxel fabricated with conventional MAP, while Figure 2(b) shows a voxel fabricated with RAPID. In Figure 2(c) we present the scaling of the voxel height with respect to the deactivation power for a fixed excitation power. By using RAPID lithography, the resolution along the laser axis was improved from about 600nm ($\lambda/1.33$) to 40nm ($\lambda/20$). The aspect ratio of the voxels was correspondingly reduced from 3 to 0.5. Figure 2(d) and (e) shows the axial compression of ridges around the towers, demonstrating that enhancement of resolution can also be attained in 3D structures.

In this first demonstration of RAPID lithography we have achieved $\lambda/20$ axial resolution. Similar enhancement is expected in the transverse dimension by employing a different phase mask. We believe that ultimately the smallest feature size that can be attained with RAPID will be limited by the intrinsic properties of the photoresist rather than by diffraction. With the appropriate materials, a resolution as low as 10nm may be feasible while still using an 800nm light source.

**Author Information**

Linjie Li and Rafael Gattass  
Department of Chemistry and Biochemistry  
University of Maryland  
College Park, MD

Linjie Li received his BS from the University of Science and Technology of China and his MS from the University of Maryland. He is currently a PhD student with John Fourkas. His research focuses on micro- and nanofabrication, photonic devices, and multiphoton absorption microscopy.

Rafael Gattass obtained his PhD in applied physics in 2006 from Harvard University and is currently a postdoctoral associate at the University of Maryland, College Park. His main research interests include nonlinear optical effects and their applications in nanophotonics.

Continued on next page
John Fourkas received his BS and MS from Caltech and his PhD from Stanford University. He is the Millard Alexander Professor of Chemistry at the University of Maryland and a fellow of the American Physical Society, the Optical Society of America, and the American Association for the Advancement of Science.

References