The burgeoning field of metamaterials has seen many ground-breaking theoretical advances in recent years, but experimental advances for infrared and optical devices have been hampered by the difficulty in patterning metals in three dimensions (3D) at the submicrometer scale. Multiphoton absorption lithography, or femtosecond laser direct-writing, has emerged as a pre-eminent technique that addresses true 3D fabrication at the micro- and nano-scales. Structures much smaller than the diffraction limited laser spot size are now readily produced in transparent media such as glasses and polymers. What makes sub-wavelength structuring possible is the nonlinear optical interaction between the femtosecond laser pulses and material of interest. The excitation wavelength of the fabrication laser is chosen such that photons are not linearly absorbed in the target medium. Yet, when the laser emission is compressed to ultrashort pulses and tightly focused with a lens, multiple photons can converge in time and space to collectively bridge the target’s energy gap and create an electronic transition. This multiphoton absorption can lead to material change that is confined to femtoliter or even attoliter volumes within the tightly focused region.

Femtosecond direct laser writing is mostly limited to the patterning of dielectric media, such as glasses and polymers. Only limited advances have been made in the direct-writing of metals, which are critical for applications of metamaterials such as negative refraction. One method for creating metal structures in 3D is to supplement the direct laser writing with a chemical deposition step, either by coating 3D polymer structures or by filling contiguous volumetric voids. However, this approach precludes the creation of arbitrary 3D metal nanostructures that are disconnected, such as a volumetric array of metal dots. Three-dimensional arrays composed of fully disconnected metal features would enable the creation of bulk optical and infrared metamaterials comprising coupled metal dot or coupled metal rod resonators.

In this letter, we present a silver growth technique for direct-writing disconnected silver nanostructures in 3D. We leverage nonlinear optical light-matter interactions and an accompanying photoreduction reaction to fabricate 3D silver structures at the nanoscale. Previous work on direct metal writing has largely been applied to generate two-dimensional (2D) structures, low resolution 3D structures, or freestanding 3D structures. We demonstrate the writing of disconnected silver structures in 3D with 300-nm resolution and writing speeds up to 100 µm/s. The silver is grown inside a polymer support matrix, enabling us to move beyond freestanding structures to create arbitrary 3D disconnected silver patterns with submicrometer resolution. The critical difference with previous work arises from the combination of chemical reagents we use. The chemical mixture from which our samples are fabricated consists of a 0.16M AgNO₃ solution, with polyvinylpyrrolidone (PVP) as support polymer and water (H₂O) as solvent.

Most work on high-resolution 3D femtosecond laser direct-writing involves reagent combinations that either include an alcohol solvent or omit the polymer. For example, a solution of AgNO₃ in H₂O can be used to direct-write silver nanostructures but does not offer a solid matrix for support. In contrast, an alcohol based system using AgNO₃, PVP, H₂O, and ethanol has a polymer that could act as a support matrix, but the redox interactions between ethanol and Ag⁺ ions begin immediately upon reagent mixing causing nanoparticle growth throughout the sample. Thus, the ethanol mediated growth technique, as it is, cannot be used to provide a polymer support matrix for 3D laser writing. By omitting the alcohol solvent, however, we found that the reduction reactions decrease significantly. We retained PVP as support matrix because it helps control silver nanoparticle synthesis. By optimizing the concentration of PVP in H₂O, we simultaneously gain control over the
located nanostructure fabrication, our process is approximately bulk 3D nanolithography. In addition to enabling 3D disconnection, a longer working distance (3 mm), which is useful for focal volume, the primary advantage of the lower-NA objective (NA 0.8) focuses the pulses from a Ti:sapphire laser (795-nm center wavelength, 11-MHz repetition rate, 50-fs pulse duration) into the sample. The exposure is controlled by an acousto-optic modulator, and a high-precision translation stage selects the region that is exposed. At the focus, nonlinear light-matter interactions induce metal-ion photoreduction processes in a volume smaller than the diffraction-limited focal spot, initiating silver nanoparticle growth.

By varying the laser parameters, we can adjust the size of the resulting silver structures. At an exposure of $1.3 \times 10^6$ pulses per voxel with 0.15 nJ per pulse, we create structures clearly resolved by optical imaging. Figure 2 shows a 3D rendering of stacks of sequential 2D bright-field optical images taken of an array of silver voxels; adjacent rows of voxels are in different vertical planes. The images highlight a key attribute of our fabrication process: we can direct-write silver structures that are disconnected in 3D inside a polymer. Supplementary Figure S1 (and associated video) shows silver features created along the same vertical axis, further demonstrating disconnected features in the z-direction. When we reduce the laser exposure to $2.8 \times 10^5$ pulses per voxel with 0.2 nJ per pulse, the silver features are reduced to submicrometer scales (less than 300 nm, Figure 3). At the operating wavelength of 795 nm, the theoretical transverse resolution of our overfilled microscope objective is approximately 600 nm—about twice the size of the fabricated nanostructure in Figure 3(c). Unlike most multiphoton absorption lithography techniques that use oil immersion objectives to achieve high resolution, our results were obtained with an NA of 0.8. Although higher-NA objectives have a smaller focal volume, the primary advantage of the lower-NA objective is a longer working distance (3 mm), which is useful for bulk 3D nanolithography. In addition to enabling 3D disconnected nanostructure fabrication, our process is approximately two orders of magnitude faster than other 3D direct-write techniques with similar resolution using an 11-MHz laser, we achieve write speeds of 100 μm/s.

To determine the constituent elements in the direct written features, we used high-resolution energy dispersion x-ray spectroscopy (EDS) and scanning electron microscopy (SEM). Figure 3 shows SEM images of an array of dots fabricated on a glass substrate (see supplementary material). Figures 3(a) and 3(b) show the fabricated array and its corresponding high-resolution EDS silver elemental map, confirming that the fabricated dots contain silver. The presence of silver is corroborated by a strong silver signal in the EDS spectrum (supplementary Figure S2 (Ref. 32)) of a patterned feature. Further characterization through transmission electron microscopy (TEM) (Figure 4) indicates that the silver does not grow as a single crystal in each irradiated voxel; rather, structures are composed of agglomerations of smaller silver nanoparticles. The inset of Figure 4 is a higher magnification image of a single silver nanoparticle created during fabrication.

FIG. 2. (Color online) 3D rendering of stacks of sequential in-situ bright-field optical microscopy images of fabricated structures. For clarity, the z-scale is stretched by a factor of 1.6 relative to the x- and y-scales. (a,b) An array of silver dots fabricated in a tent structure at an exposure of $1.3 \times 10^6$ pulses with 0.15 nJ per voxel. Neighboring rows of dots are in different z-planes. The stage was translated at 10 μm/s during fabrication. (c) Portion of an array of tent structures fabricated using the same parameters.

FIG. 3. (Color online) High-resolution SEM images of a patterned sample. (a) An image of a 2D array of dots and (b) its corresponding EDS silver elemental map confirm that silver structures are grown in areas irradiated by the laser. Close-up views of individual dots shown (c) head on and (d) at a 61° tilt angle. SEM imaging requires a washing step to avoid sample contamination from additional silver growth driven by the electron beam.

FIG. 1. (Color) Schematic of the fabrication process. A microscope objective (NA 0.8) focuses laser pulses from an 11-MHz ultrafast Ti:sapphire laser system inside a doped polymer sample. The microscope objective also provides in-situ imaging. A high-precision and long-travel three-axis translation stage scans the sample in the x-, y- and z-directions while an acousto-optic modulator shuts laser pulses to control exposure. The result is a direct-written dielectric-embedded silver structure in 3D.
FIG. 4. TEM image of fabricated silver structures. The silver does not grow as a single crystal in each irradiated voxel. Instead, the silver structures are composed of agglomerations of smaller silver nanoparticles. The inset shows a close-up view of a silver nanoparticle.

The key to our fabrication process is the chemical composition of the sample. Conventional methods to synthesize silver nanoparticles and nanostructures through polyol processes\textsuperscript{28,29} are subject to redox reactions unfavorable for polymer-embedded 3D silver nanofabrication. In the process we present here, PVP is dissolved in H\textsubscript{2}O, minimizing reduction reactions outside the laser-irradiated volume. PVP plays an important role in controlling the size and shape of silver nanoparticles: the strong affinity of N and O atoms in the amide groups of PVP to surfaces of transition-metal clusters restrains their growth.\textsuperscript{28–30} By combining PVP and water, we obtain both a support matrix and controlled growth; nonlinear light matter interactions then permit the direct writing of silver nanostructures in the bulk of the sample. Transmission measurements show the polymer matrix has several transparency windows in the near-infrared portion of the electromagnetic spectrum; these regions of transparency may be useful for device fabrication.

Methods for patterning metals at the micro- and nanoscales are used extensively in broad ranging applications—from microelectronics, to optics, and biosensors—highlighting the importance of metal lithography. We demonstrate high-resolution 3D disconnected silver nanostructure fabrication in a dielectric matrix through multiphoton absorption of ultrashort laser pulses. The approach presented in this letter may permit the creation of metamaterials and other photonic devices previously limited by current fabrication techniques.\textsuperscript{31} The process only requires readily available chemical reagents, a simple experimental setup, and a single fabrication step. By using a higher-NA objective and modifying the chemistry, we expect it will be possible to further increase the resolution and fabrication speed and to extend the method to other metals, such as gold.

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