Fabrication of disconnected three-dimensional silver nanostructures in a polymer matrix

Kevin Vora,[1,a)] SeungYeon Kang,[1] Shobha Shukla,[1] and Eric Mazur[1,2]
[1]*School of Engineering and Applied Sciences, Harvard University, 9 Oxford Street, Cambridge, Massachusetts 02138, USA*
[2]*Department of Physics, Harvard University, 9 Oxford Street, Cambridge, Massachusetts 02138, USA*

(Received 1 November 2011; accepted 17 January 2012; published online 10 February 2012)

We present a simple, one-step technique for direct-writing of a structured nanocomposite material with disconnected silver nanostructures in a polymer matrix. A nonlinear optical interaction between femtosecond laser pulses and a composite material creates silver structures that are embedded inside a polymer with submicrometer resolution (300 nm). We create complex patterns of silver nanostructures in three dimensions. The key to the process is the chemical composition of the sample that provides both a support matrix and controlled growth. The technique presented in this letter may offer a cost-effective approach for the fabrication of bulk optical devices with engineered dispersion. © *2012 American Institute of Physics*. [doi:10.1063/1.3684277]

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.[1] 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.[2,3] Structures much smaller than the diffraction limited laser spot size are now readily produced in transparent media such as glasses[4] and polymers.[5–8] 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.[1,9–11] One method for creating metal structures in 3D is to supplement the direct laser writing of polymer patterns with a metal deposition step, either by coating 3D polymer structures[12–15] or by filling contiguous volumetric voids.[16] 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[17,18] or coupled metal rod[19,20] 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,[20–24] low resolution 3D structures,[21,23] or freestanding 3D structures.[25–27] 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 $AgNO_3$ solution, with polyvinylpyrrolidone (PVP) as support polymer and water (H_2O) as solvent. Our technique does not require addition of two-photon dyes, seed nanoparticles, or non-commercially available reagents.

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 $AgNO_3$ in H_2O can be used to direct-write silver nanostructures[25] but does not offer a solid matrix for support. In contrast, an alcohol based system using $AgNO_3$, PVP, H_2O, and ethanol[22,23] has a polymer that could act as a support matrix, but the redox interactions between ethanol -OH groups 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.[28,29] By optimizing the concentration of PVP in H_2O, we simultaneously gain control over the

[a)]Author to whom correspondence should be addressed. Electronic mail: kvora@fas.harvard.edu.

localization of Ag^+ reduction processes and obtain a polymer support matrix.

Figure 1 schematically depicts our multiphoton absorption lithography process. A solution of $AgNO_3$, PVP, and H_2O is coated onto a substrate through a drop casting technique, and the sample is baked to create a polymer matrix doped with silver ions. An objective with a numerical aperture (NA) of 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 1.3×10^6 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)[32] shows silver features created along the same vertical axis, further demonstrating disconnected features in the z-direction. When we reduce the laser exposure to 2.8×10^5 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

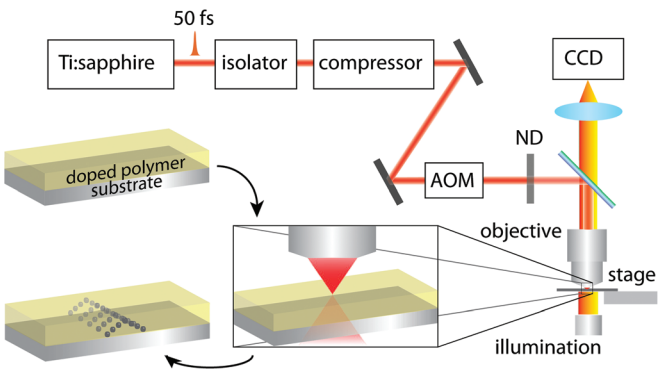

FIG. 1. (Color) Schematic of the fabrication process. A microscope objective (NA 0.8) focuses laser pulses from an 11-MHz ultrafast Ti:sapphire laser system inside a doped polymer sample. The microscope objective also provides *in-situ* imaging. A high-precision and long-travel three-axis translation stage scans the sample in the x-, y- and z-directions while an acousto-optic modulator shutters laser pulses to control exposure. The result is a direct-written dielectric-embedded silver structure in 3D.

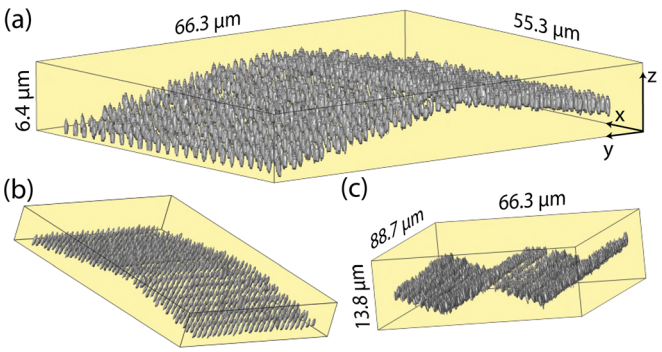

FIG. 2. (Color online) 3D rendering of stacks of sequential *in-situ* bright-field optical microscopy images of fabricated structures. For clarity, the z-scale is stretched by a factor of 1.6 relative to the x- and y-scales. (a,b) An array of silver dots fabricated in a tent structure at an exposure of 1.3×10^6 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.

two orders of magnitude faster than other 3D direct-write techniques with similar resolution[27]—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[32]). 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

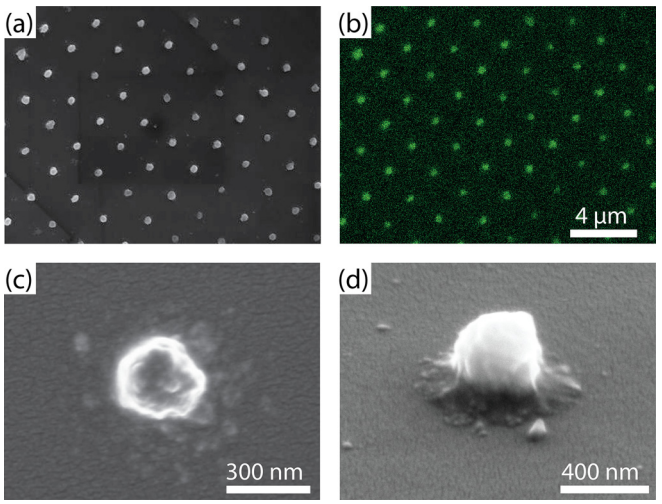

FIG. 3. (Color online) High-resolution SEM images of a patterned sample. (a) An image of a 2D array of dots and (b) its corresponding EDS silver elemental map confirm that silver structures are grown in areas irradiated by the laser. Close-up views of individual dots shown (c) head on and (d) at a 61°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

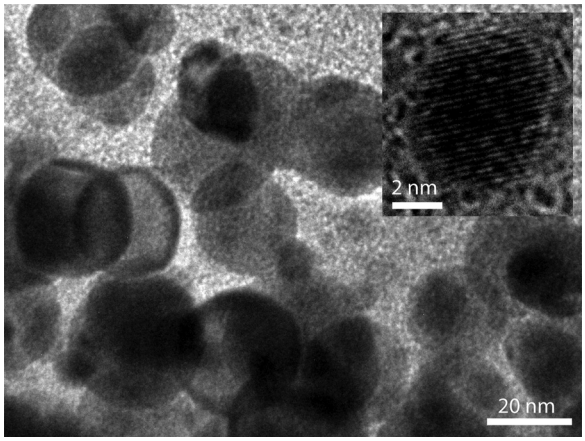

FIG. 4. TEM image of fabricated silver structures. The silver does not grow as a single crystal in each irradiated voxel. Instead, the silver structures are composed of agglomerations of smaller silver nanoparticles. The inset shows a close-up view of a silver nanoparticle.

the fabrication process. Ultraviolet and visible micro-absorption and scattering spectroscopy (supplementary Figure S3 (Ref. 32)) show a characteristic silver surface plasmon peak centered around 425 nm. The broad extinction spectrum confirms polydispersity in the constituent silver nanoparticle size.

The key to our fabrication process is the chemical composition of the sample. Conventional methods to synthesize silver nanoparticles and nanostructures through polyol processes[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_2O, 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.[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.[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.

We acknowledge Paul J. L. Webster for the 3D rendering of the optical data with Amira. Dr. Paul Peng and Professor James M. Fraser provided feedback on the manuscript throughout its development. The research described in this paper was supported by the Air Force Office of Scientific Research under Grants FA9550-09-1-0546 and FA9550-10-1-0402.

[1]C. M. Soukoulis and M. Wegener, Nat. Photonics **5**(9), 523 (2011).
[2]G. von Freymann, A. Ledermann, M. Thiel, I. Staude, S. Essig, K. Busch, and M. Wegener, Adv. Funct. Mater. **20**(7), 1038 (2010).
[3]C. N. LaFratta, J. T. Fourkas, T. Baldacchini, and R. A. Farrer, Angew. Chem., Int. Ed. **46**(33), 6238 (2007).
[4]R. R. Gattass and E. Mazur, Nat. Photonics **2**(4), 219 (2008).
[5]L. Li, R. R. Gattass, E. Gershgoren, H. Hwang, and J. T. Fourkas, Science **324**(5929), 910 (2009).
[6]W. Haske, V. W. Chen, J. M. Hales, W. Dong, S. Barlow, S. R. Marder, and J. W. Perry, Opt. Express **15**(6), 3426 (2007).
[7]J. F. Xing, X. Z. Dong, W. Q. Chen, X. M. Duan, N. Takeyasu, T. Tanaka, and S. Kawata, Appl. Phys. Lett. **90**(13), 131106 (2007).
[8]D. Tan, Y. Li, F. Qi, H. Yang, Q. Gong, X. Dong, and X. Duan, Appl. Phys. Lett. **90**(7), 071106 (2007).
[9]R. A. Shelby, D. R. Smith, and S. Schultz, Science **292**(5514), 77 (2001).
[10]V. M. Shalaev, Nat. Photonics **1**(1), 41 (2007).
[11]D. R. Smith, J. B. Pendry, and M. C. K. Wiltshire, Science **305**(5685), 788 (2004).
[12]F. Formanek, N. Takeyasu, T. Tanaka, K. Chiyoda, A. Ishikawa, and S. Kawata, Opt. Express **14**(2), 800 (2006).
[13]N. Takeyasu, T. Tanaka, and S. Kawata, Appl. Phys. A: Mater. Sci. Process. **90**(2), 205 (2008).
[14]M. S. Rill, C. Plet, M. Thiel, I. Staude, G. von Freymann, S. Linden, and M. Wegener, Nature Mater. **7**(7), 543 (2008).
[15]K. Kaneko, K. Yamamoto, S. Kawata, H. Xia, J.-F. Song, and H.-B. Sun, Opt. Lett. **33**(17), 1999 (2008).
[16]J. K. Gansel, M. Thiel, M. S. Rill, M. Decker, K. Bade, V. Saile, G. von Freymann, S. Linden, and M. Wegener, Science **325**(5947), 1513 (2009).
[17]A. N. Grigorenko, A. K. Geim, H. F. Gleeson, Y. Zhang, A. A. Firsov, I. Y. Khrushchev, and J. Petrovic, Nat. Photonics **438**(7066), 335 (2005).
[18]A. N. Grigorenko, Opt. Lett. **31**(16), 2483 (2006).
[19]V. M. Shalaev, W. Cai, U. K. Chettiar, H.-K. Yuan, A. K. Sarychev, V. P. Drachev, and A. V. Kildishev, Opt. Lett. **30**(24), 3356 (2005).
[20]A. Ishikawa, T. Tanaka, and S. Kawata, Appl. Phys. Lett. **91**(11), 113118 (2007).
[21]F. Stellacci, C. A. Bauer, T. Meyer-Friedrichsen, W. Wenseleers, V. Alain, S. M. Kuebler, S. J. K. Pond, Y. Zhang, S. R. Marder, and J. W. Perry, Adv. Mater. **14**(3), 194 (2002).
[22]T. Baldacchini, A.-C. Pons, J. Pons, C. LaFratta, J. Fourkas, Y. Sun, and M. Naughton, Opt. Express **13**(4), 1275 (2005).
[23]S. Maruo and T. Saeki, Opt. Express **16**(2), 1174 (2008).
[24]Y.-Y. Cao, X.-Z. Dong, N. Takeyasu, T. Tanaka, Z.-S. Zhao, X.-M. Duan, and S. Kawata, Appl. Phys. A: Mater. Sci. Process. **96**(2), 453 (2009).
[25]T. Tanaka, A. Ishikawa, and S. Kawata, Appl. Phys. Lett. **88**(8), 081107 (2006).
[26]A. Ishikawa, T. Tanaka, and S. Kawata, Appl. Phys. Lett. **89**(11), 113102 (2006).
[27]Y.-Y. Cao, N. Takeyasu, T. Tanaka, X.-M. Duan, and S. Kawata, Small **5**(10), 1144 (2009).
[28]Y. Sun and Y. Xia, Science **298**(5601), 2176 (2002).
[29]B. Wiley, Y. G. Sun, B. Mayers, and Y. N. Xia, Chem.-Eur. J. **11**(2), 454 (2005).
[30]H. H. Huang, X. P. Ni, G. L. Loy, C. H. Chew, K. L. Tan, F. C. Loh, J. F. Deng, and G. Q. Xu, Langmuir **12**(4), 909 (1996).
[31]D. Ö. Güney, T. Koschny, and C. M. Soukoulis, Opt. Express **18**(12), 12348 (2010).
[32]See supplementary material at http://dx.doi.org/10.1063/1.3684277 for methods, videos, and supplementary figures.