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14. ABSTRACT We use high-intensity femtosecond laser pulses to induce the photoreduction of metal ions through multiphoton absorption. The non-linear nature of the absorption process allows us to access the bulk of a material, thus propelling the technique to three-dimensions (3D). The non-linear nature of the interaction also allows us to create structures that are smaller than the diffraction limit of the excitation light source. The technique we use directly writes metal structures, which is different from more common femtosecond writing processes that fabricate polymer structures. During the funding period of the grant, we developed a process to direct write silver in 3D inside a polymer matrix, enabling us to create true 3D disconnected metal structures. We achieved a resolution between 200 and 300 nm. This development is a significant step towards creating 3D metallic metamaterials using femtosecond laser fabrication.						
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Final Technical Report FY12: Nanofabrication of three-dimensional metamaterials

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Abstract

We use high-intensity femtosecond laser pulses to induce the photoreduction of metal ions through multiphoton absorption. The non-linear nature of the absorption process allows us to access the bulk of a material, thus propelling the technique to three-dimensions (3D). The non-linear nature of the interaction also allows us to create structures that are smaller than the diffraction limit of the excitation light source. The technique we use directly writes metal structures, which is different from more common femtosecond writing processes that fabricate polymer structures. During the funding period of the grant, we developed a process to direct write silver in 3D inside a polymer matrix, enabling us to create true 3D disconnected metal structures. We achieved a resolution between 200 and 300 nm. This development is a significant step towards creating 3D metallic metamaterials using femtosecond laser fabrication.

Introduction

Creating metal patterns with submicron resolution requires a combination of nanofabrication tools and several material processing steps. For example, steps to create planar metal structures using ultraviolet photolithography and electron-beam lithography can include sample exposure, sample development, metal deposition, and metal liftoff. To create 3D metal structures, the sequence is repeated multiple times. The complexity and difficulty of stacking and aligning multiple layers limits practical implementations of 3D metal structuring using standard nanofabrication tools. Two-photon polymerization is an emerging technique that can be used to directly write 3D polymer patterns. Voids in these patterns can be subsequently filled with metals to create 3D metallic structures. However, the resultant metal structures can only be disconnected over two spatial axes—metal structures are contiguous over the third axis—yielding a 2D array of 3D metal structures. Here, we developed a material system to create 3D arrays of 3D metallic structures.

Ultrafast-laser micromachining allows for three-dimensional fabrication of structures much smaller than the diffraction limited laser spot size in transparent media such as glass. Under a linear regime, the medium does not absorb light at the operating wavelength of the laser. However, using ultrafast pulses, we can obtain material modification through non-linear absorption. The technique can also be used to induce chemical reactions. High intensity femtosecond laser pulses can induce the photoreduction of metal ions through non-linear absorption. We present an ultrafast laser technique for the direct-writing of patterned silver structures of tunable size (hundreds of nanometers to micrometers) in three-dimensions inside a polymer matrix.

Results

By utilizing nonlinear optical interactions between a composite material—comprised of metal precursor, polymer and solvent—and femtosecond pulses, we limit the metal-ion photoreduction process to a focused spot smaller than that of the diffraction-limit. This creates metal nanostructures in a focal volume that is scanned rapidly by means of a computer-controlled translation stage to produce complex patterns. The nonlinear nature of the interaction allows us to access the bulk of a transparent medium and fully extend the process to three-dimensions.

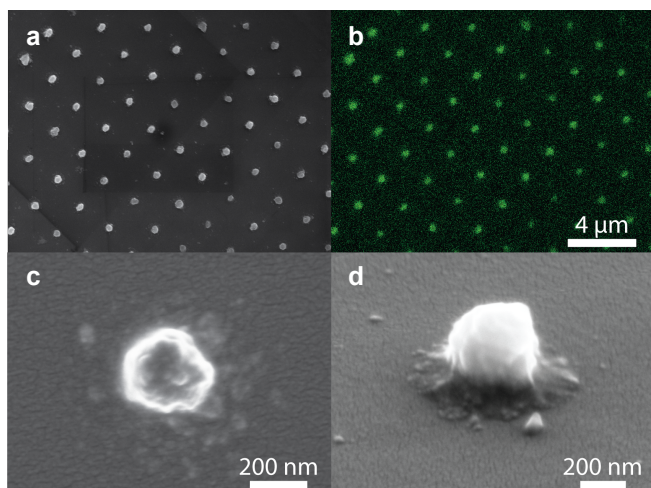


Fig. 1. SEM images of silver nanostructures.

A doped polymer matrix is prepared using a mixture of silver nitrate (AgNO_3), polyvinylpyrrolidone (PVP) and water (H_2O). A laser centered around 800 nm, producing 50-fs pulses with a repetition rate of 11 MHz, is used to induce the multiphoton photoreduction of silver ions inside the composite material. We create an aggregate of silver nanoparticles in the focal volume of the microscope. Figure 1 shows patterned silver nanostructures imaged with an SEM. Figure 1a and 1b show an SEM image and its corresponding EDS elemental map, indicating the presence of elemental silver. We fabricate silver dot and line arrays in two- and three-dimensions embedded inside the doped polymer matrix, as

illustrated in Figure 2.

There are two important facets to our recent results. First, we can pattern silver features below 300 nm in diameter. Second, we are able to create structures that are disconnected—silver structures do not need to be supported in the z -direction by other silver structures as other techniques require. The latter property allows us to create multiple layers of metallic patterns on top of each other. Figure 3 shows optical images of pairs of patterned lines arranged as concentric squares, with each pair being at a different depth. The sample is progressively moved further from the microscope objective as it steps from Figure 3a to 3d.

We are in the process of determining parameters such as roughness, conductivity and sample lifetime. Precise characterization is non-trivial for these samples because of their 3D nature. A combination of atomic force microscopy, simulations, and optical spectroscopy are being used.

We expect significant increase in resolution through improvements in the optical setup. For example, focusing the laser beam further using a higher numerical aperture (NA) microscope objective should yield a feature resolution between 100 and 200 nm. (We currently use an NA of 0.8, whereas an NA of 1.4 is common in femtosecond laser fabrication work.) We have also begun exploring alternate material systems to obtain thicker samples, reduced defects, and higher resolution.

Impacts

We developed a method to pattern disconnected silver nanostructures inside a polymer matrix in 3D, creating structured nanocomposite materials. This is an essential step towards creating bulk

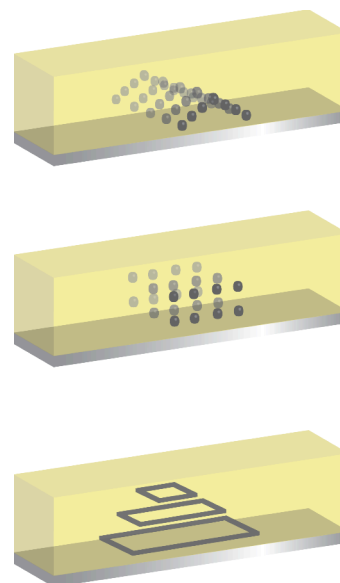


Fig. 2. Schematic of fabricated 3D patterns.

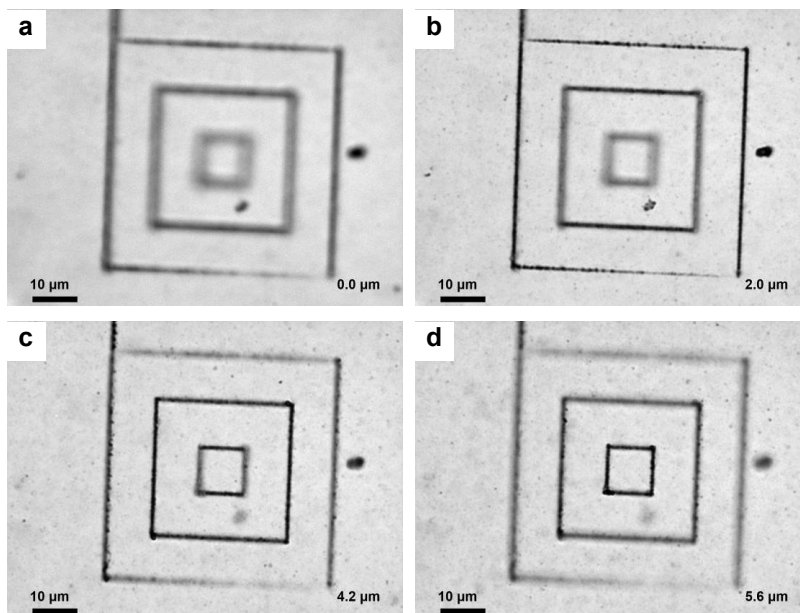


Fig. 3. Optical microscopy images of a 3D silver structure. Each image is taken at a different depth by varying the distance between the sample and the microscope objective, bringing different z-planes into sharp focus. The silver structures are embedded in a polymer matrix.

metal/dielectric metamaterials for IR and optical frequencies. We filed for a patent entitled “Micro-and Nano-Fabrication of Connected and Disconnected Metallic Structures in Three-Dimensions Using Ultrafast Laser” with application number 61/434,997 on January 21, 2012. We also published the work and presented at several conferences, as listed below. We are in the process of designing devices to demonstrate the capabilities of the technique we have developed.

Publications

Kevin Vora, SeungYeon Kang, Eric Mazur, “A method to fabricate disconnected silver nanostructures in 3D,” (accepted) *Journal of Visualized Experiments*, 2012.

Kevin Vora, SeungYeon Kang, Shobha Shukla, Eric Mazur, “Fabrication of disconnected three-dimensional silver nanostructures in a polymer matrix,” *Applied Physics Letters* **100**(6), February 6 2012.

Kevin Vora, SeungYeon Kang, Shobha Shukla, Eric Mazur, “Three-dimensional silver nanostructure fabrication through multiphoton photoreduction,” *Proc. SPIE 8247, Frontiers in Ultrafast Optics: Biomedical, Scientific, and Industrial Applications XII*, 824710 (February 9 2012), doi:10.1117/12.906839.

Conference presentations (not including DoD program review meetings)

Kevin Vora, SeungYeon Kang, Eric Mazur, “Fabrication of Structured Nanocomposite Materials for Three-Dimensional Metamaterial Applications,” (accepted) oral presentation, MRS Fall Meeting, Boston, MA (November 28 2012).

SeungYeon Kang, Kevin Vora, Shoba Shukla and Eric Mazur, “Nanofabrication of 3D Metal Structures in a Polymer Matrix by Direct Laser Writing,” oral presentation, US Korea Conference 2012, CA (August 9 2012).

Kevin Vora, SeungYeon Kang, Shobha Shukla, Eric Mazur, “Toward 3D metamaterials with femtosecond laser writing of silver,” poster presentation, Plasmonics—Gordon Research Conference, Waterville, ME (June 14 2012).

SeungYeon Kang, Kevin Vora, Shobha Shukla, Eric Mazur, "Direct laser writing of three dimensional metal nanostructures using a femtosecond laser and various chemistries," oral presentation, APS March Meeting 2012, Boston, MA (February 28 2012), J18.00004.

Kevin Vora, SeungYeon Kang, Shobha Shukla, Eric Mazur, "Three-dimensional silver nanostructure fabrication through multiphoton photoreduction," oral presentation, SPIE Photonics West, San Francisco, CA (January 24 2012), 8243-35 and 8247-35.

SeungYeon Kang, Kevin Vora, Shobha Shukla, Eric Mazur, "Controlling the nanofabrication of metal structures in direct laser writing using various chemistries," poster presentation, SPIE Photonics West, San Francisco, CA (January 24 2012), 8249-55.

Kevin Vora, SeungYeon Kang, Shobha Shukla, Eric Mazur, "3D Laser Writing of Silver Nanostructures for Photonic Applications," oral presentation, MRS Fall Meeting, Boston, MA (November 29 2011), G1.4.

Kevin Vora, SeungYeon Kang, Shobha Shukla, Eric Mazur, "2D and 3D Writing of Silver Nanostructures Through Multiphoton Photoreduction," oral presentation, OSA Frontiers in Optics, San Jose, CA (October 18 2011), FTuAA2.

Kevin Vora, SeungYeon. Kang, Michael Moebius, Eric Mazur, "Femtosecond laser nanofabrication of metal structures through multiphoton photoreduction," oral presentation, SPIE Photonics West 2011, San Francisco, CA (January 25 2011), 7927-14.

SeungYeon Kang, Kevin Vora, Shobha Shukla, Eric Mazur, "Femtosecond laser nanofabrication of metal structures through multiphoton photon reduction," poster presentation, Keio-Harvard Workshop 2010 Horizons of Nanophotonics and Nanoelectronics, Cambridge, MA (December 20 2010).