Three-dimensional silver nanostructure fabrication through multiphoton photoreduction

Kevin Vora*[a], SeungYeon Kang[a], Shobha Shukla[a], Eric Mazur[a,b]
[a]School of Engineering and Applied Sciences, 9 Oxford St, Cambridge, MA, USA 02138;
[b]Department of Physics, 17 Oxford St, Cambridge, MA, USA 02138

ABSTRACT

Metal nanofabrication techniques have become increasingly important for photonic applications with rapid developments in plasmonics, nanophotonics and metamaterials. While two-dimensional (2D) techniques to create high resolution metal patterns are readily available, it is more difficult to fabricate 3D metal structures that are required for new applications in these fields. We present a femtosecond laser technique for 3D direct-writing silver nanostructures embedded inside a polymer. We induce the photoreduction of silver ions through non-linear absorption in a sample doped with a silver salt. Utilizing nonlinear optical interactions between the chemical precursors and femtosecond pulses, we limit silver-ion photoreduction processes to a focused volume smaller than that of the diffraction-limit. The focal volume is scanned rapidly in 3D by means of a computer-controlled translation stage to produce complex patterns. Our technique creates dielectric-supported silver structures, enabling the nanofabrication of silver patterns with disconnected features in 3D. We obtain 300 nm resolution.

Keywords: 3D fabrication, multiphoton, nanofabrication, ultrafast, femtosecond, direct writing, photoreduction, silver

1. INTRODUCTION

Advances in nanofabrication techniques are critical for scientific progress in fields ranging from nanophotonics, to microelectronics, to biosensing. Bottom-up methods can be used to synthesize large quantities of nanostructures, but top-down approaches are usually required to create complex micro- and nano-systems. Electron beam lithography and UV photolithography are two examples of top-down fabrication techniques commonly used to created complex devices with sub-micrometer resolution. Unfortunately, like most top-down approaches, both of these techniques are planar. Many applications require precise nanostructuring in three-dimensions (3D). Building 3D micro-systems using 2D techniques is difficult.

Femtosecond laser direct-writing is an inherently 3D fabrication technique. Non-linear light-matter interactions are used to gain access to the bulk of a transparent material. If the light intensity is high enough, it is possible to obtain material modification inside a focal volume in the bulk. Over the past decade, femtosecond lasers have enabled precise 3D nanofabrication in a variety of materials.[1] Sub-diffraction structures are readily created in transparent media such as glasses[2] and polymers.[3] An underdeveloped direction in femtosecond-laser based patterning is the direct-writing of metals. Until recently, research in direct-writing metal structures had not demonstrated the 3D fabrication of disconnected metal nanostructures.[4-7] We have developed a femtosecond-laser based approach to grow silver nanostructures inside a polymer matrix, allowing us to create 3D disconnected metal patterns.[8]

2. EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic of our sample preparation and fabrication setup. We use a combination of $AgNO_3$, polyvinylpyrrolidone (PVP) and water (H_2O) to prepare our samples.[8] A Ti:sapphire laser centered at 800 nm provides 50 fs laser pulses with a repetition rate of 11 MHz. The acousto-optic modulator allows us to control the exposure of the sample and the microscope objective focuses the laser pulses. The sample is mounted on a high precision three-axis translation stage. Exposing samples to the laser induces the photoreduction of silver ions inside a focal volume. Sample fabrication is a single-step process—the only step required to pattern a sample is laser exposure as there is no post-processing.

*kvora@fas.harvard.edu

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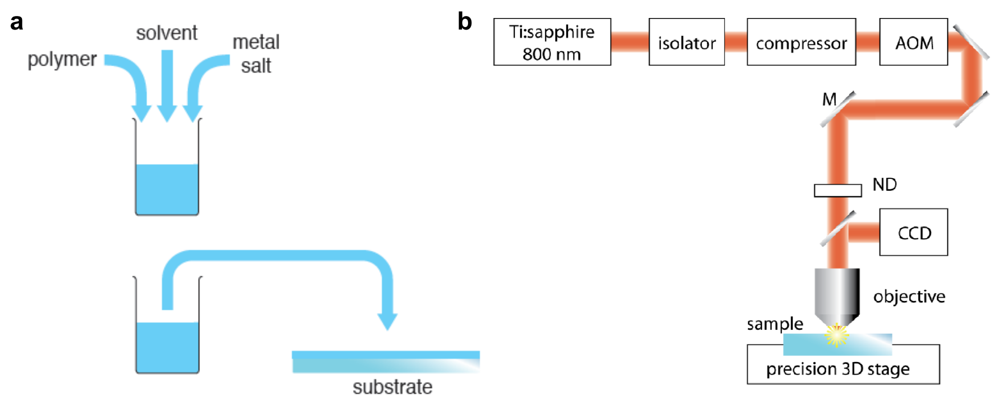

Figure 1. Schematic of (a) sample preparation and (b) fabrication setup used to direct-write silver nanostructures.

3. RESULTS

The silver nanostructures that are created inside the focal volume are held in place by the background polymer matrix. Thus, it is possible to create silver nanostructures that are disconnected in 3D—structures that need not be self-supporting. By utilizing nonlinear optical interactions between the chemical mixture and femtosecond pulses, we limit metal-ion reduction processes to a focused spot much smaller than that of the diffraction-limit. We have obtained structures as small as 300 nm.[8] Figure 2(a) shows a scanning electron microscopy (SEM) image of a fabricated sample. The overlaying polymer layer was removed prior to SEM imaging, leaving behind structures adhered to the surface of the substrate. The image is produced using a back-scattered electron detector that shows a strong contrast between fabricated silver structures and the glass substrate; silver structures are shown by a bright signal. Energy dispersive x-ray spectroscopy (EDS) confirms that we are creating silver particles (Figure 2(b)). The Si signal comes from the substrate.

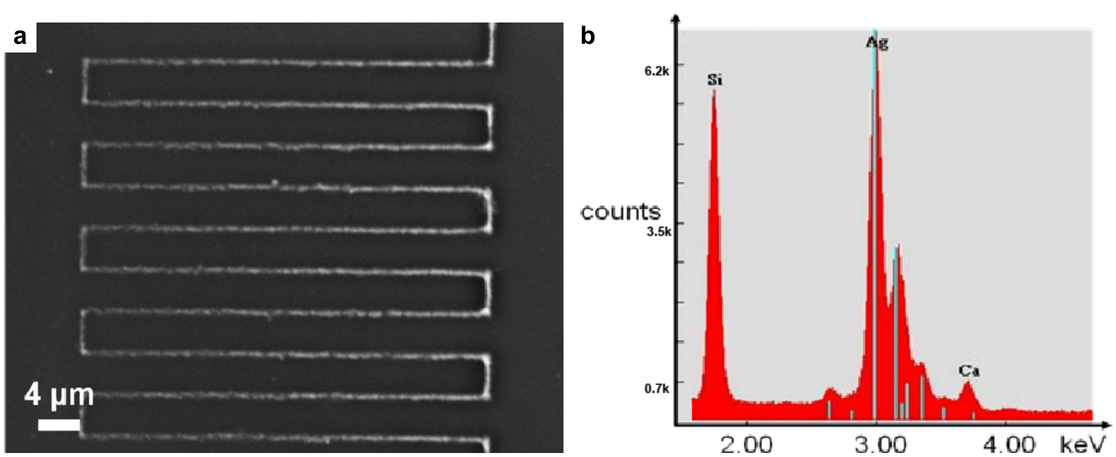

Figure 2. (a) SEM image of femtosecond laser assisted silver grown on a glass substrate. The overlaying polymer matrix is removed to image silver structures adhered to the substrate interface. (b) EDS data showing a strong silver signal from fabricated features.

The SEM cannot be directly used to image the bulk of our 3D samples. Thus, we examine silver structures embedded inside the polymer using optical microscopy. Figures 3 and 4 show in-situ brightfield optical microscopy images of 3D silver patterns inside a polymer matrix. By varying the distance between sample and imaging microscope objective, different *z*-planes come in and out of focus. Thus, each panel of Figures 3 and 4 shows different silver features at varying depths inside the polymer. Figure 3 shows rows of silver dots fabricated in a tent pattern, where the apex of the tent is at the center of the each image. Figure 4 shows 6 pairs of lines arranged as concentric squares; each pair of lines is at a different depth inside the polymer matrix.

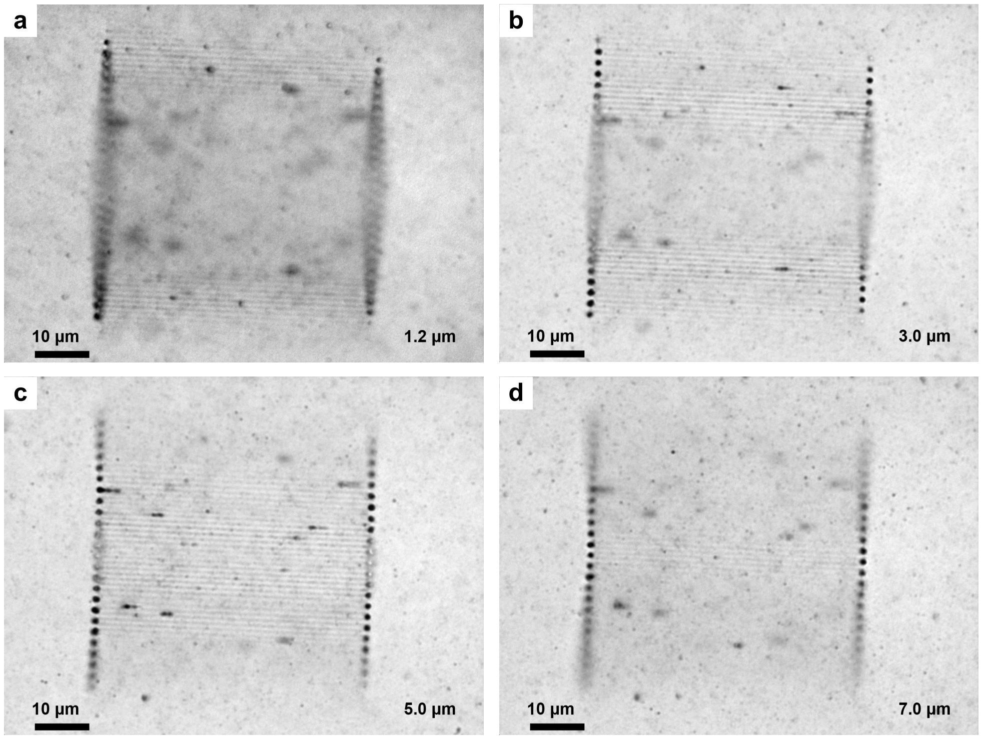

Figure 3. Optical microscopy images of rows of silver dots fabricated in a tent structure. Each image is taken at a different depth by varying the distance between the sample and the microscope objective, bringing different features into sharp focus. The silver structures are embedded in a polymer matrix. The vertical scale indicates the distance scanned in the *z*-direction.

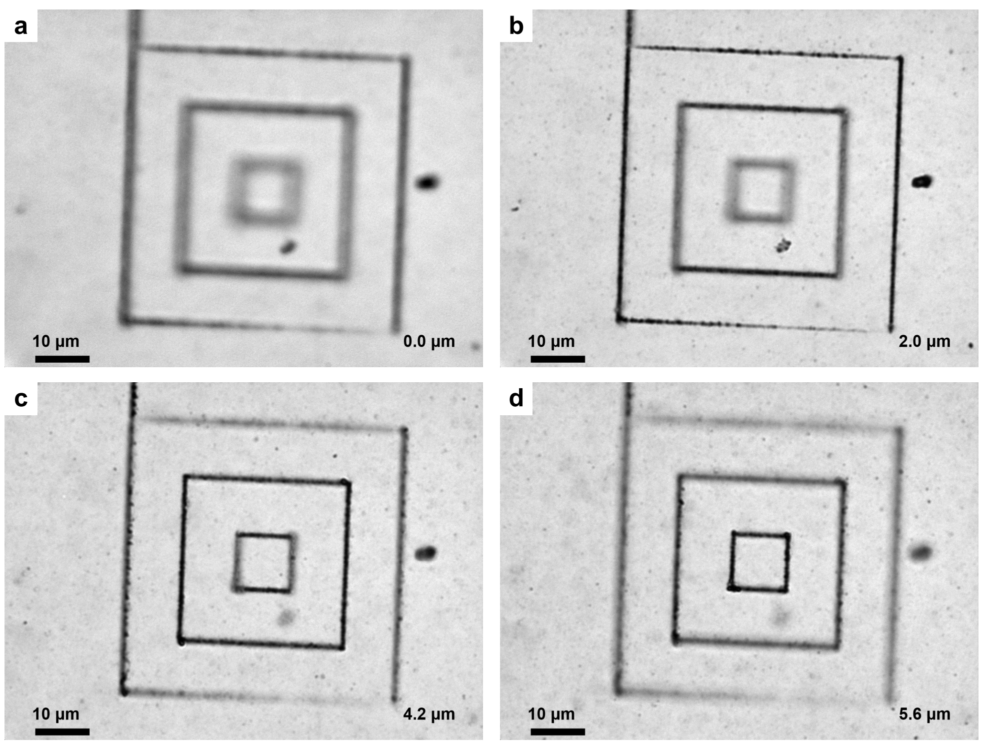

Figure 4. Optical microscopy images of 6 pairs of lines fabricated in different *z*-planes. Each image is taken at a different depth by varying the distance between the sample and the microscope objective, bringing different features into sharp focus. The silver structures are embedded in a polymer matrix. The vertical scale indicates the distance scanned in the *z*-direction.

4. DISCUSSION

We have developed a method to create silver nanostructures that are embedded inside a support matrix.[8] Femtosecond laser pulses allow us to access the bulk of a transparent chemical mixture containing silver ions and induce photoreduction reactions. Thus, it is possible to create disconnected 3D silver patterns. Such structures may have applications in metamaterials or photonic crystals, where structured 3D nanocomposite materials are required. Further research in the area may lead to different material combinations suitable for 3D metal nanofabrication.

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