Video Article

A Method to Fabricate Disconnected Silver Nanostructures in 3D

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Abstract

The standard nanofabrication toolkit includes techniques primarily aimed at creating 2D patterns in dielectric media. Creating metal patterns on a submicron scale 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. Femtosecond-laser direct-writing has emerged as a pre-eminent technique for 3D nanofabrication.[1,2] Femtosecond lasers are frequently used to create 3D patterns in polymers and glasses.[3-7] However, 3D metal direct-writing remains a challenge. Here, we describe a method to fabricate silver nanostructures embedded inside a polymer matrix using a femtosecond laser centered at 800 nm. The method enables the fabrication of patterns not feasible using other techniques, such as 3D arrays of disconnected silver voxels.[8] Disconnected 3D metal patterns are useful for metamaterials where unit cells are not in contact with each other,[9] such as coupled metal dot[10,11]or coupled metal rod[12,13] resonators. Potential applications include negative index metamaterials, invisibility cloaks, and perfect lenses.

In femtosecond-laser direct-writing, the laser wavelength is chosen such that photons are not linearly absorbed in the target medium. When the laser pulse duration is compressed to the femtosecond time scale and the radiation is tightly focused inside the target, the extremely high intensity induces nonlinear absorption. Multiple photons are absorbed simultaneously to cause electronic transitions that lead to material modification within the focused region. Using this approach, one can form structures in the bulk of a material rather than on its surface.

Most work on 3D direct metal writing has focused on creating self-supported metal structures.[14-16] The method described here yields sub-micrometer silver structures that do not need to be self-supported because they are embedded inside a matrix. A doped polymer matrix is prepared using a mixture of silver nitrate ($AgNO_3$), polyvinylpyrrolidone (PVP) and water (H_2O). Samples are then patterned by irradiation with an 11-MHz femtosecond laser producing 50-fs pulses. During irradiation, photoreduction of silver ions is induced through nonlinear absorption, creating an aggregate of silver nanoparticles in the focal region. Using this approach we create silver patterns embedded in a doped PVP matrix. Adding 3D translation of the sample extends the patterning to three dimensions.

Video Link

The video component of this article can be found at http://www.jove.com/video/4399/

Protocol

1. Preparing Metal-ion Doped Polymer Film

1. Measure 8 ml of water in a beaker.
2. Add 206 mg of PVP to water. Mix using magnetic stirrer or vortex mixer until the solution is clear.
3. Add 210 mg of $AgNO_3$ to solution. Mix using magnetic stirrer or vortex mixer until solution is clear.
4. Coat glass slide with solution through drop casting.
5. Place glass slide in an oven set at 100 °C. Bake sample for 30 min.
6. Remove sample from oven and let cool for 30 min.

2. Fabrication of Disconnected Silver Structures

1. Align setup depicted in **Figure 1** on optical table with vibration isolators.
2. Adjust compressor to obtain 50-fsec pulses after microscope objective.

3. Adjust neutral density filters to obtain 3-nJ pulses after the objective.
4. Ensure laser spot size is larger than back aperture of microscope objective.
5. Set acousto-optic modulator to produce 10-μsec exposure windows during which the sample is irradiated.
6. Block laser beam before it reaches the microscope and place sample onto 3-axis translation stage. The beam path of the femtosecond laser pulses should pass through the imaging microscope objective and into the sample.
7. Turn on microscope illumination source to observe the sample *in-situ* using CCD camera.
8. Translate *z*-axis of stage to find interface between glass substrate and polymer film. Then, refocus microscope to the desired depth inside polymer for patterning bottom-most layer. *Z*-translation during patterning must be in the direction away from the glass-polymer interface to avoid scattering with fabricated structures.
9. Unblock laser-beam and set motion-controller software to translate sample in *x*-, *y*- and *z*- directions with speed of 100 μm/sec. Irradiate single voxels for 10 μsec and separate neighboring voxels by at least several micrometers for clear *in-situ* imaging. Setting acousto-optic modulator repetition rate to 25 Hz will produce 4-μm spacing. Laser exposed areas will contain silver structures.

Representative Results

The acousto-optic modulator and neutral density filters (**Figure 1**) allow one to control the amount of energy deposited into the sample. Using an exposure of 110 pulses per voxel and 3 nJ per pulse, with the stage translating at 100 μm/sec, the resulting silver structures are readily visible through the *in-situ* optical microscope. Lower laser exposure levels (by reducing pulse energy and/or pulse number) lead to smaller silver features; we have observed features as small as 300 nm.[8] It is possible to create silver structures using a broad range of pulse energies from less than one nanojoule to several nanojoules. **Figure 3** shows 3D renderings of optical images taken of a fabricated sample. The pattern, consisting of an array of dots on top of another array, is shown from two angles. The data can also be visualized through videos; sequential optical microscopy images are animated in the video article. The thickness of the polymer matrix is controlled by the amount of solution used during the drop casting process. One milliliter of solution on a 2.5 cm x 2.5 cm glass slide approximately yields a 15-μm thick film.

High-resolution images of fabricated silver structures can be obtained through SEM imaging. **Figure 4** shows SEM images of a sample consisting of a 2D array of dots that are fabricated directly on the glass substrate. We readily obtain silver features that are sub-micrometer in size.

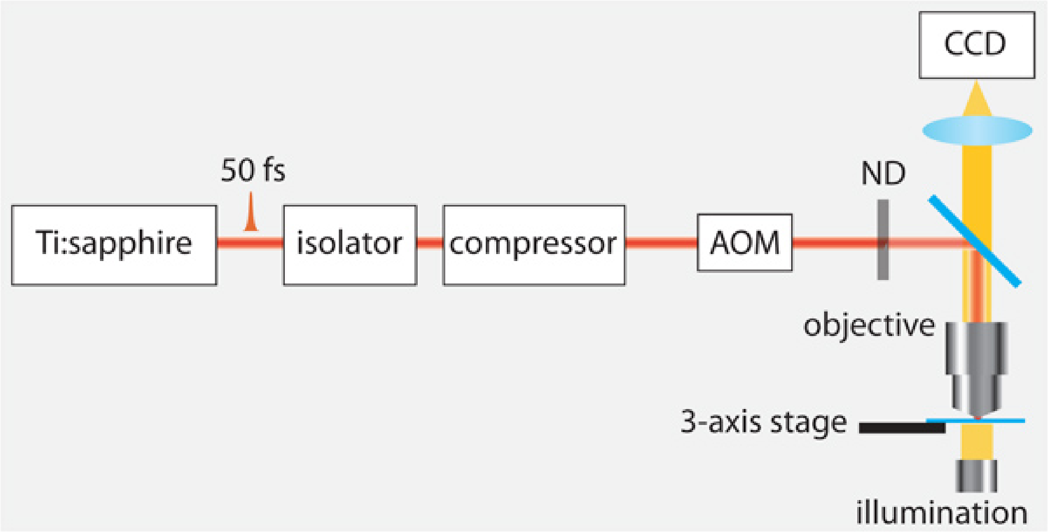

Figure 1. Laser fabrication setup. The primary components of our fabrication setup include a femtosecond laser, a Faraday isolator, a compressor, an acousto-optic modulator (AOM), a neutral-density (ND) filter, a microscope with camera, a high precision 3-axis translation stage, and an optical table mounted on vibration isolators. The laser produces 50-fs laser pulses centered at 800 nm with a repetition rate of 11 MHz. The compressor pre-compensates for the dispersion in the optical beam path to obtain 50-fs pulses at the sample. The AOM and ND filter function as a shutter and an attenuator to control the laser exposure of the sample. We use a 0.8-NA microscope objective to simultaneously focus the laser beam and image the sample during fabrication. The sample position is controlled by a high-precision 3-axis translation stage. The entire setup is mounted on an optical table with vibration isolation.

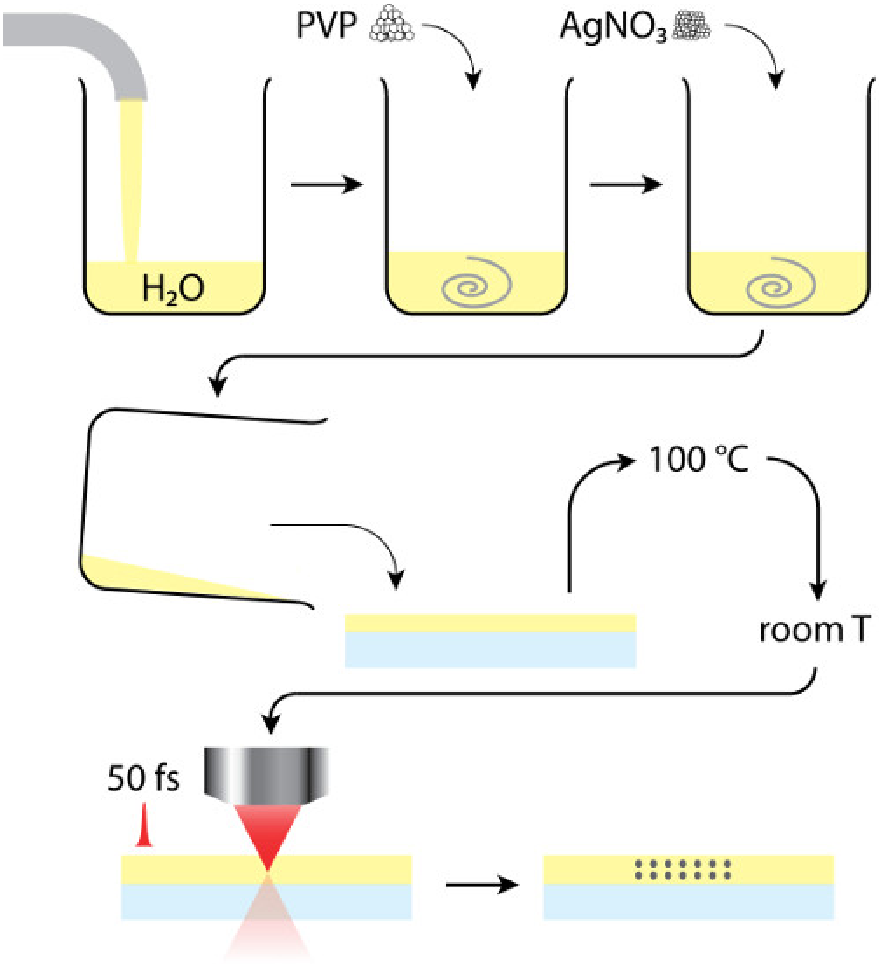

Figure 2. Overall schematic of the experiment. A sample is prepared by coating a glass slide with a mixture of PVP, $AgNO_3$, and H_2O. Once the sample is prepared, patterning is a single-step process.

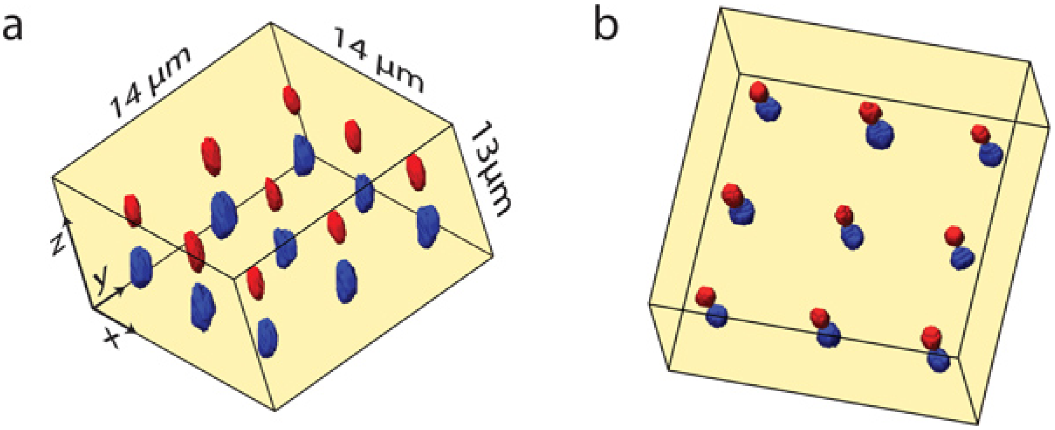

Figure 3. 3D rendered images of a silver dot array inside a matrix. (a) 2-layer array of 18 silver dots created inside a matrix. For clarity, the two layers of dots are represented in different colors. The rendering was created by stacking sequential optical microscopy images. (b) A different view of the 3D array.

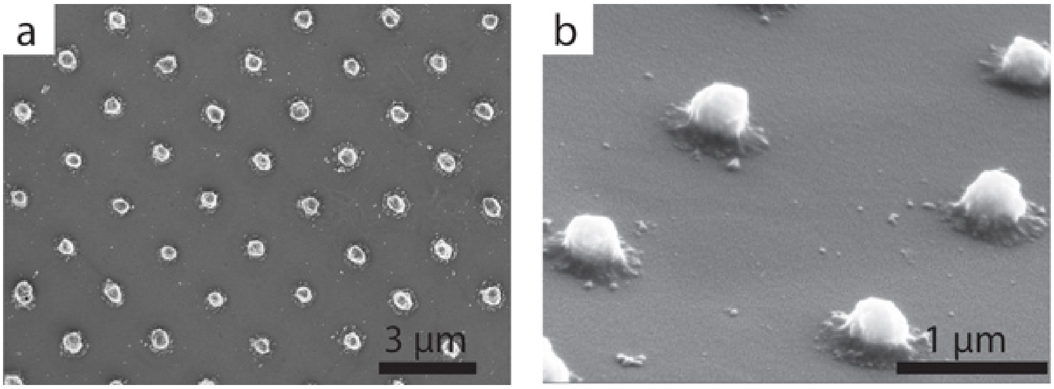

Figure 4. High-resolution SEM images of a patterned sample. Silver dots are created at the glass/polymer interface to allow SEM imaging. The polymer matrix is removed after fabrication to avoid additional silver growth driven by the electron beam.[8] (a) Image of a 2D array of silver dots on a glass substrate. A) Close up view of silver dots from a 61° tilt angle.

Discussion

The key to the process is obtaining a doped dielectric matrix that allows high resolution fabrication, but does not degrade soon after preparation. A simple mixture of PVP, $AgNO_3$ and H_2O allows the creation of high-resolution silver nanostructures that are embedded inside a support matrix. Varying the PVP to $AgNO_3$ ratio will change the laser energy needed for fabrication, and potentially other properties such as feature resolution. A low ratio leads to faster degradation of the dielectric matrix, and a high ratio leads to very low amounts of silver in fabricated features.

The minimum laser spot size-which depends on wavelength, laser beam mode parameter, and microscope objective numerical aperture (NA)-is 900 nm for our system. The nonlinear nature of the light-matter interactions can lead to silver features that are smaller than this spot size. We have demonstrated 300-nm silver features using our optical setup.[8] The objective used in this experiment has an NA of 0.8 and a working distance of 3 mm, allowing the potential to pattern thick 3D samples. Stronger focusing-an NA of 1.4 is typical for femtosecond laser patterning techniques-would lead to a much smaller laser spot size with the tradeoff of a shorter working distance.

The resolution of the technique could be increased with stronger focusing optics and, potentially, by modifying the chemistry. In the opposite direction, larger features can be readily created by increasing laser energy and irradiation time. Specific shapes, such as short lines, can be obtained by scanning the laser continuously over a distance. Future applications of the technique may include negative index metamaterials, invisibility cloaks, and perfect lenses for the optical and infrared wavelength regimes.[9] These applications will strongly depend on the optical properties of the silver nanostructures.

Disclosures

No conflicts of interest declared.

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