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One-step direct-laser metal writing of sub-100 nm 3D silver nanostructures in a gelatin matrix

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Abstract

Developing an ability to fabricate high-resolution, 3D metal nanostructures in a stretchable 3D matrix is a critical step to realizing novel optoelectronic devices such as tunable bulk metal-dielectric optical devices and THz metamaterial devices that are not feasible with alternative techniques. We report a new chemistry method to fabricate high-resolution, 3D silver nanostructures using a femtosecond-laser direct metal writing technique. Previously, only fabrication of 3D polymeric structures or single-/few-layer metal structures was possible. Our method takes advantage of unique gelatin properties to overcome such previous limitations as limited freedom in 3D material design and short sample lifetime. We fabricate more than 15 layers of 3D silver nanostructures with a resolution of less than 100 nm in a stable dielectric matrix that is flexible and has high large transparency that is well-matched for potential applications in the optical and THz metamaterial regimes. This is a single-step process that does not require any further processing. This work will be of interest to those interested in fabrication methods that utilize nonlinear light–matter interactions and the realization of future metamaterials.

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1. Introduction

Three-dimensional (3D) nanofabrication is important for realizing various types of photonic crystals and metamaterials [1–3]. Although various 3D designs that require metal and dielectric components have been studied, few methods allow fabrication of these 3D nanostructures. [1–8] Femtosecond-laser writing permits high-resolution fabrication of complex 3D patterns. [1, 9, 10] Direct femtosecond-laser writing is inherently three-dimensional and utilizes the nonlinear interaction between laser pulses and nonlinearly absorbing functional groups of various chemicals to achieve material modification inside bulk media [9–11]. Most developments in direct laser writing, however, have focused on polymer structures. To obtain conducting structures, metals have been incorporated into certain polymer structures through post-patterning techniques, including chemical vapor deposition, atomic layer deposition and electro-less plating [3, 11–15]. The development of direct laser writing of 3D metallic structures has been slow [16–19]. Reported resolutions of direct-laser-written metallic structures are not high enough for applications in optical metamaterials, which consist of only a single layer and have large surface roughness [16–19]. One exception is a recent report of 3D silver patterns grown inside polyvinylpyrrolidone. The silver patterns, however, have a

[1] SeungYeon Kang and Kevin Vora have made equal contributions to the present work.

short shelf life and only a limited number of layers, and the resolution is not high enough for optical metamaterial applications [20, 21]. Here, we present a new method to overcome these limitations and fabricate high-resolution, 3D silver nanostructures using femtosecond-laser direct metal writing.

Nonlinear absorption inside a gelatin matrix doped with silver ions induces growth of silver nanostructures embedded inside the dielectric matrix. Gelatin provides several advantages over previously reported materials for the fabrication of 3D metal nanostructures. Gelatin is an easy to use, inexpensive, non-toxic, biodegradable and water-soluble polymer that has hydrogel-like gelling properties. These properties allow us to make thicker and more durable samples with reduced brittleness and an increased sample lifetime. The numerous electron donor groups in the polymer chain help the fabrication of high-resolution silver structures and limit unnecessary growth, which results in fewer defects in the matrix. We obtained sub-100 nm silver features and fabricated more than 16 layers in a single-step process that does not require any further processing. The doped gelatin matrix is also stretchable up to 10%, enabling flexible devices. Lastly, gelatin has large transparency windows that are well-matched for potential applications in the optical and THz regimes.

2. Experimental methods

To prepare samples, we use a mixture of gelatin, silver nitrate ($AgNO_3$) and deionized water. This mixture was drop-cast onto a glass slide and allowed to dry at room temperature; the end result is a 200 μm thick film of gelatin doped with silver ions. We use a Ti:sapphire laser producing 50 fs pulses (centered at 795 nm) with an 11 MHz repetition for the irradiation process. See the Experimental section below for further details on chemical preparation and laser fabrication.

2.1. Material

We obtained the silver nitrate ($AgNO_3$) and gelatin from Sigma-Aldrich. The gel strength is indicated by 'Bloom', which can be determined by a method that was developed in 1925 by O T Bloom [23]. For this method, a Bloom grade of 75 was chosen to fabricate a flexible substrate. We purchased mercapto propyl trimethoxy silane (MPTS) from Alfa Aesar and used deionized water.

2.2. Sample preparation

To fabricate the nanostructures we use a mixture of gelatin, silver nitrate ($AgNO_3$) and deionized water. We prepare a solution by dissolving 0.8 g of gelatin in 4 mL of deionized water in a vial. We mix the two components using a vortex mixer and then heat up the sample vial in a 55 °C water bath to dissolve the gelatin. We repeat this step until all the gelatin has fully dissolved. Next, we add 0.105 g of $AgNO_3$ to the vial and repeat the above mixing step until all the $AgNO_3$ has completely dissolved. We drop-cast the prepared solution onto a 2.5×2.5 mm^2 glass slide. Finally, the sample is air-dried at room temperature overnight. The resulting sample consists of an approximately 200 μm thick gelatin film doped with silver ions on a glass substrate. To create 2D samples for scanning electron microscopy (SEM) analysis, the glass substrate is oxygen-plasma-treated and silanized with MPTS prior to depositing the mixture. The fabricated samples that include patterns bound to the glass substrate are then immersed in water at 55 °C to dissolve the polymer layer, leaving behind only the 2D patterns for further analysis.

2.3. Laser fabrication

We use a Ti:sapphire laser centered at 795 nm with an 11 MHz repetition rate and 50 fs pulse length for the irradiation process. A detailed description of the laser fabrication set-up can be found in [12] and [13]. The laser exposure is limited to individual voxels in which the focal volume has a full-width half-maximum diameter of 1 μm. The numerical aperture (NA) of the objective is 0.8, and the working distance is 3 mm. 3D structures are created by focusing laser pulses inside the bulk of the gelatin matrix; layers are patterned sequentially starting from the layer closest to the substrate and moving up toward the air interface. This single-step process does not require any further processing. To create planar 2D patterns that are suitable for SEM analysis, for example, laser pulses are focused near the substrate such that the grown silver is bound to the glass.

2.4. Structure characterization

SEM and EDS measurements were performed in Zeiss Ultra and SUPRA 55VP microscopes using in-lens and EDAX detectors. The stretchability of a 200 μm thick silver-doped gelatin matrix was determined using an Instron 3342 tensile measurement set-up. Transmittance measurements were made in four different regions on a 200 μm thick unpatterned silver-doped gelatin matrix. The 200–1750 nm wavelength range was probed using a Cary 500i UV–vis-NIR dual-beam spectrophotometer. Transmittance in the 1.8–15 μm wavelength range was measured using a Thermo Fisher continuum Fourier transform infrared (FTIR) microscope connected to a Thermo Fisher FTIR6700 spectrometer. The 15–200 μm wavelength range was measured using a Thermo Fisher FTIR6700 spectrometer. The 200–1500 μm (THz) range was measured using a broadband Hg-arc lamp THz source and a liquid helium-cooled Si bolometer detector.

3. Results and discussion

Transmission optical microscopy images of a fabricated 3D silver pattern are shown in figure 1. Figures 1(a) and (b) show two representative *in situ* images taken from a ten-layer array of dots. Figure 1(c) shows a computer-generated model to illustrate the 3D pattern. The pattern contains alternating layers of silver dots arranged in a square (figure 1(a)) and pseudo-hexagonal arrays (figure 1(b)). The full stack of ten layers can be seen in a video where the microscope focal

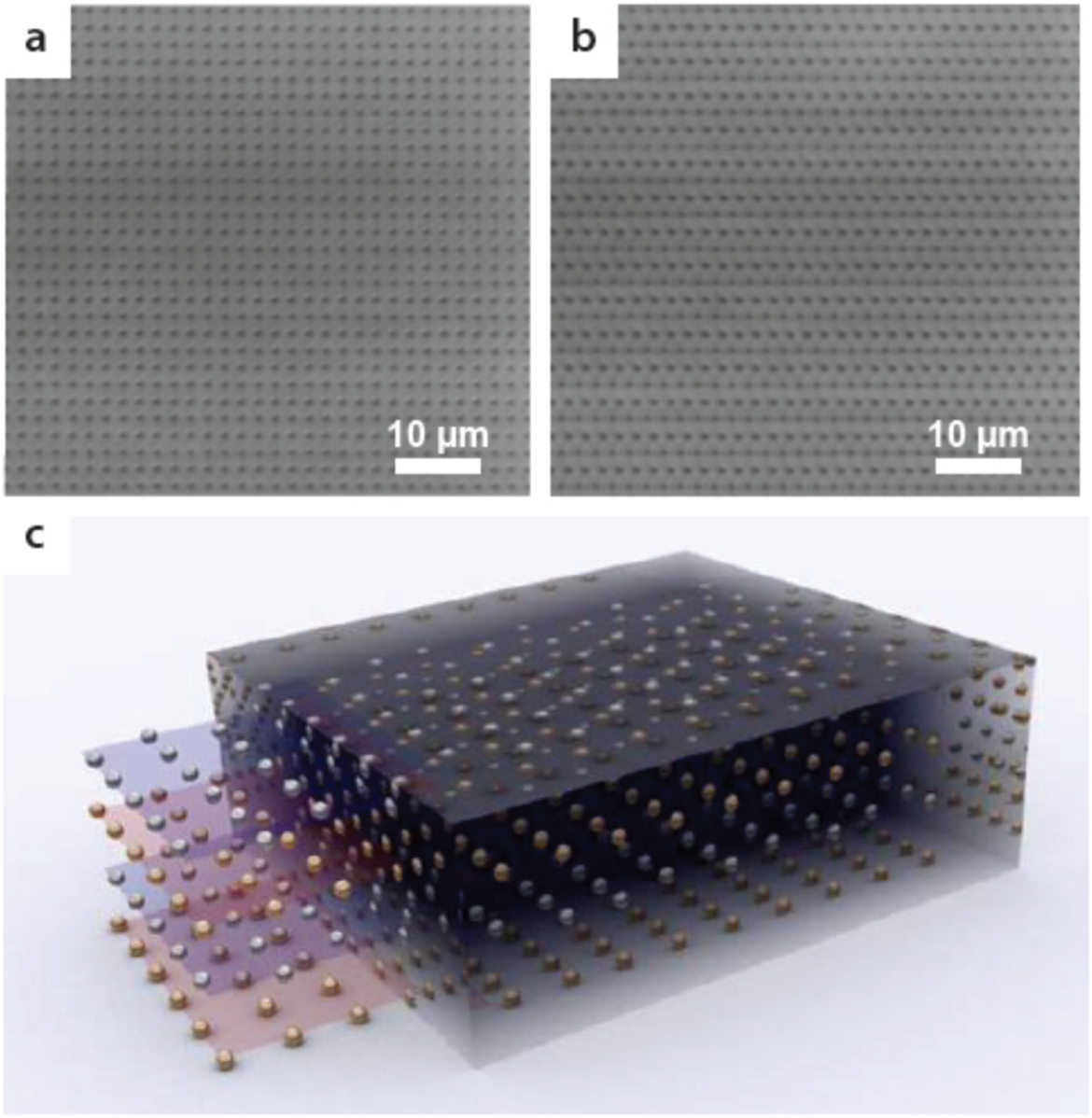

Figure 1. *In situ* optical images of interleaved (a) square and (b) pseudo-hexagonal arrays of silver dots that alternate over the *z*-direction as part of a ten-layered 3D pattern inside gelatin. The pitch between the dots is 2 μm in the *x*-direction, 2 μm in the *y*-direction and 4 μm in the *z*-direction. (c) A computer-generated image provides a schematic illustration of the 3D pattern.

plane traverses the pattern along the *z*-axis (supplemental information figure S1). The 3D pattern is fabricated by irradiating the layers sequentially. Because the background matrix is solid and provides mechanical support, it is possible to create silver structures that are disconnected in the *z*-direction, as shown in figure 1.

Figure 2 shows a SEM image of an array of silver dots with sub-100 nm size, which is smaller than any other previously reported direct metal writing results [16–22]. We observed silver structures with diameters as small as 80 nm. Unlike previous reports showing silver nanoparticle aggregates with high roughness, there are no readily visible domain separations in the nanostructures reported here [16–22]. The dots are fabricated with an exposure of 79 000 pulses with 0.1 nJ per pulse at a stage translation speed of 10 μm s^{-1}.

Figure 3 shows a SEM image of a 100 nm fabricated dot (figure 3(a)) and its corresponding energy dispersion spectroscopy (EDS) map (figure 3(b)) of a silver-element signal. We also show the EDS spectra from the nanodot (figure 3(c)) and a directly adjacent area (figure 3(d)). The spectra show a strong silver signal from the dot compared to the neighboring area. The signals next to the silver peak are from the indium-tin-oxide layer on the substrate (under the silver dot). The EDS data indicate that fabricated dots are composed of silver. Furthermore, the SEM image shows a smoother structure compared to previous reports [16–22]. The silver signal from the spectrum is also significantly stronger than any previously reported for the silver direct laser writing method [16–21].

Figure 4 shows a transmission spectrum of the doped but unpatterned gelatin matrix spanning a range of 0.2 μm to

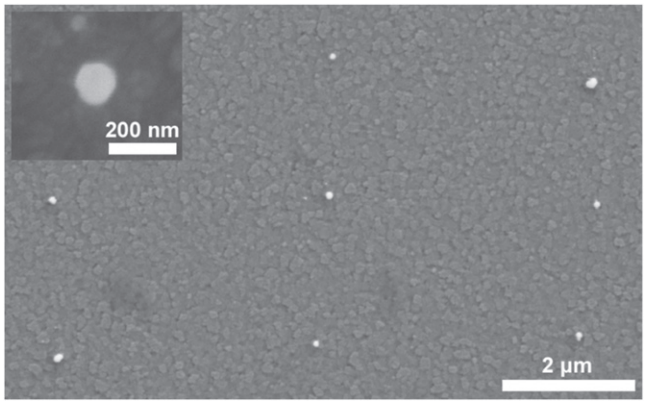

Figure 2. SEM image of an array of fabricated silver nanostructures. There is some variability in the size, with the smallest structures being sub-100 nm in diameter. The inset shows a close-up view of a single silver nanostructure.

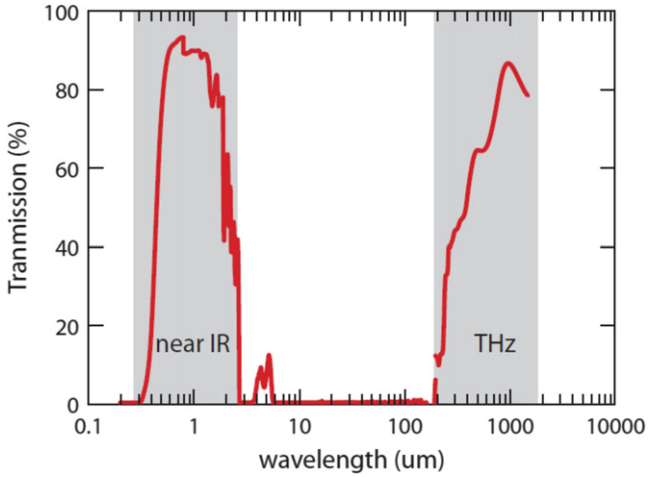

Figure 4. Transmission spectrum for an unpatterned silver-ion-doped gelatin sample. The spectrum, obtained through measurements on multiple instruments, spans the ultraviolet to terahertz wavelength range of the electromagnetic spectrum (0.2–1500 μm). The spectrum shows two transmission windows (grey shading). The first window is in the visible to near-IR range, and the second window is in the terahertz range. These windows show the spectral regions in which this material can be used for device applications.

1500 μm. There are two transparency windows in the optical and THz regimes that permit creating electromagnetic metamaterial devices in these regions with minimal loss.

The critical difference between the method described here and previously reported femtosecond-laser writing methods is the choice of gelatin as the background matrix

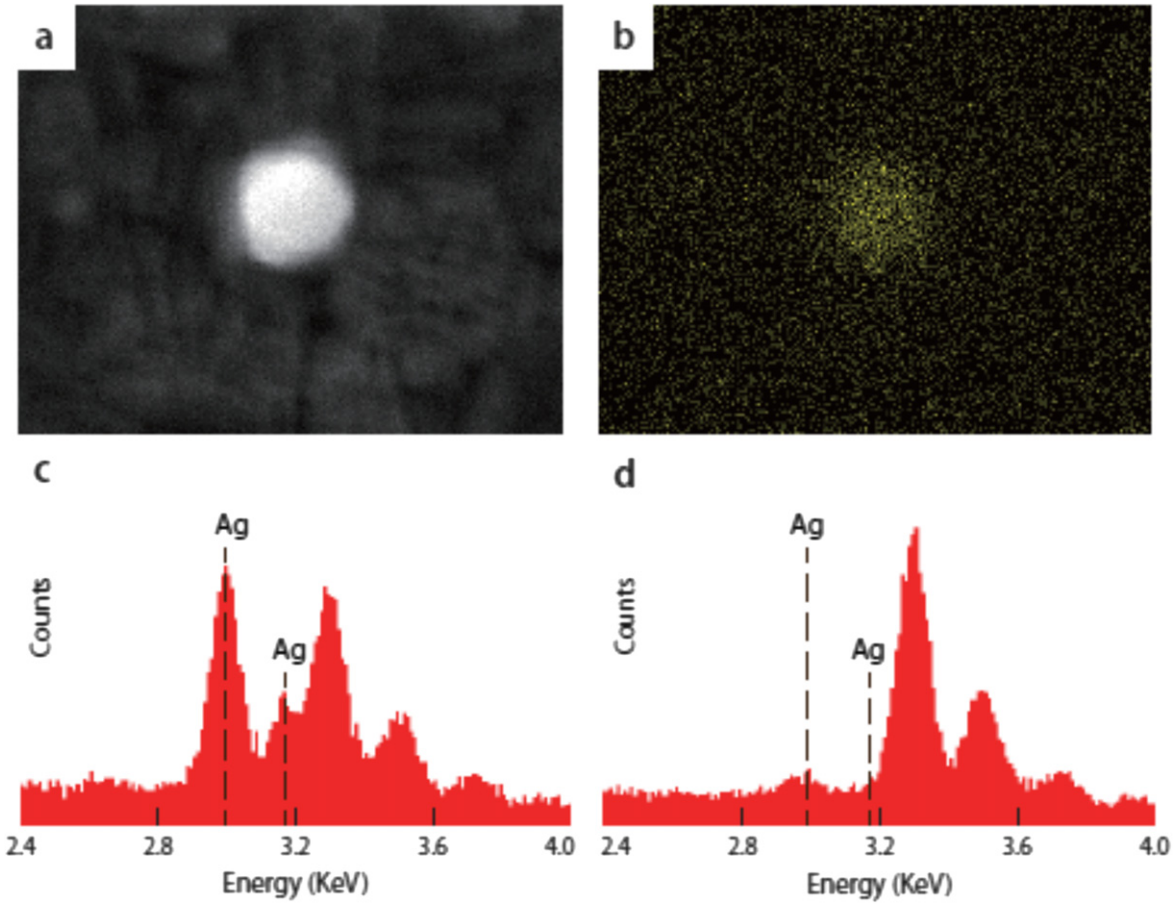

Figure 3. (a) A SEM image and its corresponding (b) EDS map of elemental silver for a 100 nm fabricated structure. The EDS map shows a strong silver signal from the nanodot. The EDS spectra taken from (c) the nanodot (d) and its neighboring area indicate that the silver signal stems from the fabricated nanostructure. The peaks next to the silver signal are from a layer of indium tin oxide on the glass substrate to avoid charging problems during SEM analysis.

[16–22]. This matrix both promotes silver crystal growth and mechanically supports the silver nanostructures. Gelatin is comprised of long strands of high molecular weight, water-soluble protein derived from collagen, which leads to large amounts of –C=O, –COOH and $–NH_2$ polar groups. We hypothesize that nonlinear optical interactions between the carbonyl group and the femtosecond laser pulses induce a metal-ion photoreduction process, and the extra lone pairs in the polar groups (such as –COOH and $–NH_2$) restrain silver particle growth through strong affinity toward Ag+ ions. Compared to other polymers, gelatin has a large number of lone pair groups that restrain silver growth during femtosecond laser irradiation, which allows us to fabricate sub-100 nm-sized 3D silver nanostructures in a matrix with few defects.

Furthermore, gelatin goes through a gelation process during the air-drying procedure where abundant oxygen and hydrogen in the long strands of protein form weak hydrogen bonds to create a tangled network. Water can remain captured between these hydrophilic strands, which allows gelatin to have hydro-gel-like (or elastomer-like) behaviors. This increased viscosity allows us to make samples that are thick (over 200 μm) and stretchable (measurements with a tensile testing device show approximately 10% stretchability). By carefully choosing the gel strength and optimizing its concentration, we obtain gelatin films that are durable (reduced brittleness and increased sample lifetime), stretchable and at the same time suitable for 3D silver growth during femtosecond laser irradiation.

4. Conclusion

In conclusion, the method we describe takes advantage of unique gelatin properties to yield high-resolution 3D silver nanostructures in a stable dielectric matrix with a resolution of less than 100 nm. The doped-gelatin matrix enables bulk 3D metal nanofabrication over volumes of up to tens of cubic millimeters. Compared to other 3D fabrication techniques that yield metal nanostructures [16–22], the method presented in this letter can easily produce many disconnected layers of metal patterns; we readily produce over 15 layers of structures using a single-step writing process. The stretchability of the matrix also open the door for creating tunable optical devices. The method may enable the realization of bulk metal-dielectric optical and THz metamaterial devices that are not feasible with alternative techniques.

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Supporting information

Supporting Information is available online or from the author.

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