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Research Article

3D Photonic Nanostructures via Diffusion-Assisted Direct fs Laser Writing

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We present our research into the fabrication of fully three-dimensional metallic nanostructures using diffusion-assisted direct laser writing, a technique which employs quencher diffusion to fabricate structures with resolution beyond the diffraction limit. We have made dielectric 3D nanostructures by multiphoton polymerization using a metal-binding organic-inorganic hybrid material, and we covered them with silver using selective electroless plating. We have used this method to make spirals and woodpiles with 600 nm intralayer periodicity. The resulting photonic nanostructures have a smooth metallic surface and exhibit well-defined diffraction spectra, indicating good fabrication quality and internal periodicity. In addition, we have made dielectric woodpile structures decorated with gold nanoparticles. Our results show that diffusion-assisted direct laser writing and selective electroless plating can be combined to form a viable route for the fabrication of 3D dielectric and metallic photonic nanostructures.

1. Introduction

Direct fs laser writing is a technique that allows the construction of three-dimensional micro-and nanostructures [1]. It is based on the phenomenon of multiphoton absorption and subsequent polymerization; the beam of an ultrafast laser is tightly focused into the volume of a photosensitive material, initiating multiphoton polymerization within the focused beam voxel. By moving the beam three-dimensionally, arbitrary 3D, high-resolution structures can be written. By simply immersing the sample in an appropriate solvent, the unscanned, unpolymerized area can be removed, allowing the 3D structure to reveal. A variety of applications have been proposed including microfluidics [2], micro-optics [3, 4], scaffolds for biomolecules and cells [5–7], and photonics and metamaterials [8–10].

There has been a lot of research efforts to improve the resolution of DLW technology, which for a long time has been in the range of 100 nm. The method which most successfully and substantially has increased the resolution not only of single lines but also of 3D structures is DLW inspired by stimulated-emission-depletion (STED) fluorescence microscopy [11, 12]. In STED-DLW, two laser beams are used; one is used to generate the radicals, and the second beam to deactivate them. Several schemes have been proposed including single-photon (rather than multiphoton) excitation [13], a one-color scheme [14] and multiphoton two-color scheme [15, 16]. Structures with

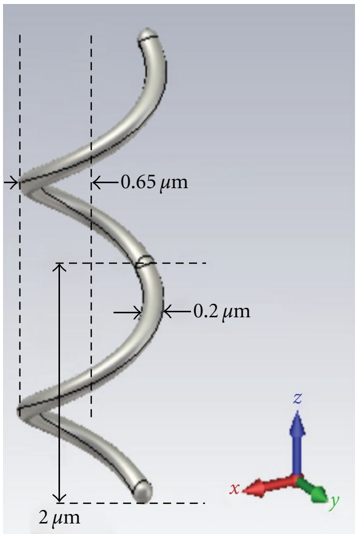


Figure 1: The design of the 3D spirals.

very high resolution and very small intralayer distances have been fabricated using this approach. However, the implementation of DLW-STED is complicated, requiring very fine beam control and specialized photoinitiators which not only have high two-photon cross-section, but also high fluorescence quantum efficiency [15, 17]. Consequently, only geometrically simple structures have been fabricated to-date.

Our team has shown recently that it is possible to increase the writing resolution of multiphoton polymerization by employing diffusion-assisted DLW (DA-DLW), a scheme based on quencher diffusion, in a chemical equivalent of STED [18]. This is based on the combination of a mobile quenching molecule with a slow laser scanning speed, allowing the diffusion of the quencher in the scanned area, the depletion of the generated radicals, and the regeneration of the consumed quencher. The material used as quencher is 2-(dimethylamino) ethyl methacrylate (DMAEMA), an organic monomer which is also part of the polymer structure. Due to its amine moieties, this is the same monomer we have employed in the past as a metal ligand, to enable the selective metallization of 3D photonic crystals [19]. In general, metallic nanostructures are very interesting due to their potential electromagnetic functionalities, which are not observed in bulk materials [20–23]. Metallic periodic nanostructures can significantly modify the properties of light with wavelength close to their periodicity, resulting in potential applications in scientific and technical areas such as filters, optical switches, sensing, imaging, energy harvesting and photovoltaics, cavities, and efficient laser design [24]. Several fabrication techniques have been employed for the fabrication of such structures, including colloidal lithography, [25] focused ion beam drilling [26], photopolymerization and photoreduction [27], and others [28]. Our approach was to fabricate 3D dielectric nanostructures containing the metal binding material DMAEMA and subsequently selectively metallize them with silver using electroless plating (EP). EP is a fairly simple process that does not require any specialized equipment, and the metal deposition can be done without using any electrical potential [29, 30]. In general, it is characterized by the selective reduction of metal ions at the surface of a catalytic substrate immersed into an aqueous solution of metal ions, with continued deposition on the substrate through the catalytic action of the deposit itself. Using DLW and selective EP, we successfully fabricated 3D metallic photonic crystals with bandgaps at optical wavelengths [31].

In this paper, we combine these two methodologies to fabricate 3D metallic and structures with complex geometries and subdiffraction limit resolution. We fabricate woodpile and spiral photonic crystals, and we show that they have well-defined diffraction patterns, indicating the quality of their fabrication and their internal periodicity. In addition, we have fabricated 3D structures decorated with gold nanoparticles. Such structures can be useful in applications such as biosensing.

2. Design

In this paper, we present three kinds of nanostructures.

(i) Silver-coated woodpile structures with a period of 600 nm: these type of structures were investigated theoretically and experimentally in [31], and they were found to have bandgaps at optical wavelengths.

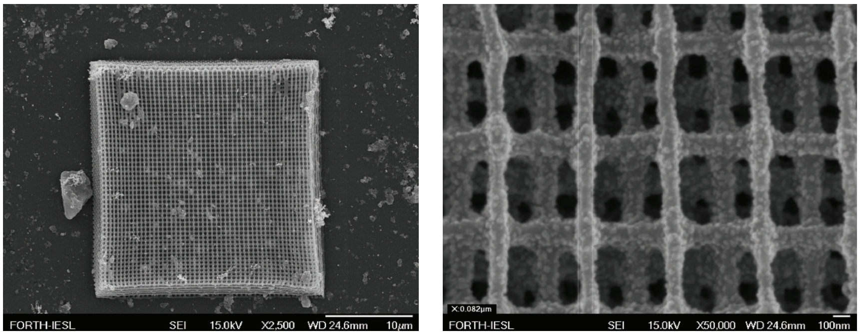
(ii) Dielectric woodpile structures, also with period 600 nm, decorated with gold nanoparticles: these can be useful in applications such as biosensing, where thiol chemistry can be employed for biomolecule immobilization [32].

(iii) Spiral photonic structures: these were modeled on the structures presented in [33] by Ganzel and colleagues from KIT, Germany (Figure 1). In the KIT study, voids were fabricated into a positive photoresist using DLW, which were subsequently filled with gold using electroplating. Their structures were used as broadband polarizers. In our study, we have copied the spiral design and used a metal-binding negative photopolymer to recreate these spiral structures. As these spirals have high aspect ratio and it is difficult for them to remain free standing during the sample development process, support structures were added to the design, as it will be shown in the Results section.

3. Fabrication

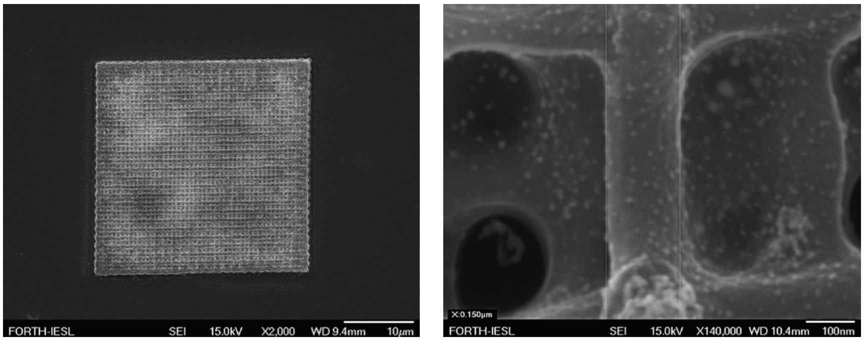
The materials investigation, synthesis, and metallization protocols employed have been described in detail previously in [18, 19, 31]. The silver-coated structures were fabricated using 30% DMAEMA [19], while the gold-nanoparticle-covered ones 10% DMAEMA [18]. The gold nanoparticles were prepared following the metallization process described in [19], omitting the last plating step.

For the fabrication of the 3D nanostructures, a Ti: Sapphire femtosecond laser (800 nm, 75 MHz, <20 fs) was



(a) (b)

Figure 2: Woodpile photonic crystals: (a) the whole structure, (b) detail.



(a) (b)

Figure 3: Woodpiles decorated with gold nanoparticles (a) the whole structure, (b) detail.

focused into the photopolymerisable composite using a high numerical aperture focusing microscope objective lens (100x, N.A. = 1.4, Zeiss, Plan Apochromat). Sample movement was achieved using piezoelectric and linear stages, for accurate and step movement, respectively (PI). The whole DLW setup, which is described in detail in [34], was computer controlled using the 3DPoli software. Here, the average laser power used for the fabrication of the high-resolution woodpile structures was 1.85 mW, measured before the objective, while the average transmission to the sample was 20%. For the spiral structures, the average power was increased to 5.5 mW, scanning the beam at 10 μ/s and 20 μ/s to write the spirals and the supports, respectively. To avoid contact with the lens immersion oil, all structures were fabricated upside down with the glass substrate in contact with the oil. They were built in a layer-by-layer fashion starting from the top with the last layer adhering to the substrate. This way, the laser beam did not cross an already polymerized layer, causing second polymerization or beam distortion.

4. Diffraction Spectra

To check the quality of the structures, we used the diffraction pattern in the transmitted waves produced by the structure when illuminated using a white light beam. In general, diffraction patterns reveal structural characteristics as well as sample quality [35]. For this, a home-built setup was employed, built according to [36, 37]. Light from a Ti:Sapphire laser (800 nm, 180 fs, 1 mJ/pulse, 1 KHz repetition rate) was focused using an $f = 3$ cm lens into a 3 cm long cell filled with distilled water, in order to produce white light continuum, providing a useful broad spectral range of 450 nm to 1000 nm wavelength. The light was collimated and then focused on the sample. The sample was mounted to have accurate 3D and rotational control. The half-opening angle of the incident light was reduced to 5°, assured by iris diaphragms.

5. Results and Discussion

Figure 2(a) shows a scanning electron microscopy (SEM) image of a woodpile structure with 600 nm period fabricated and metallized using the procedure described earlier. Figure 2(b) shows a detail of such a structure. It can be seen that the resolution achieved is in the order of 100 nm.

Figure 3 shows SEM images of woodpile structures decorated with gold nanoparticles. Figure 3(a) shows the whole structure, while Figure 3(b) shows a detail of such a structure, where the nanoparticles are clearly visible. The density of these nanoparticles can increase or decrease by increasing or decreasing the percentage of DMAEMA, respectively [19]. The size of the nanoparticles can be modified by altering the growing conditions [19].

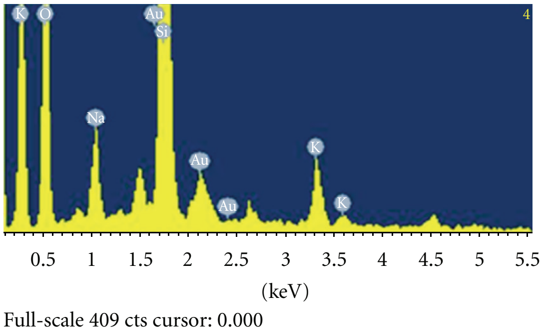
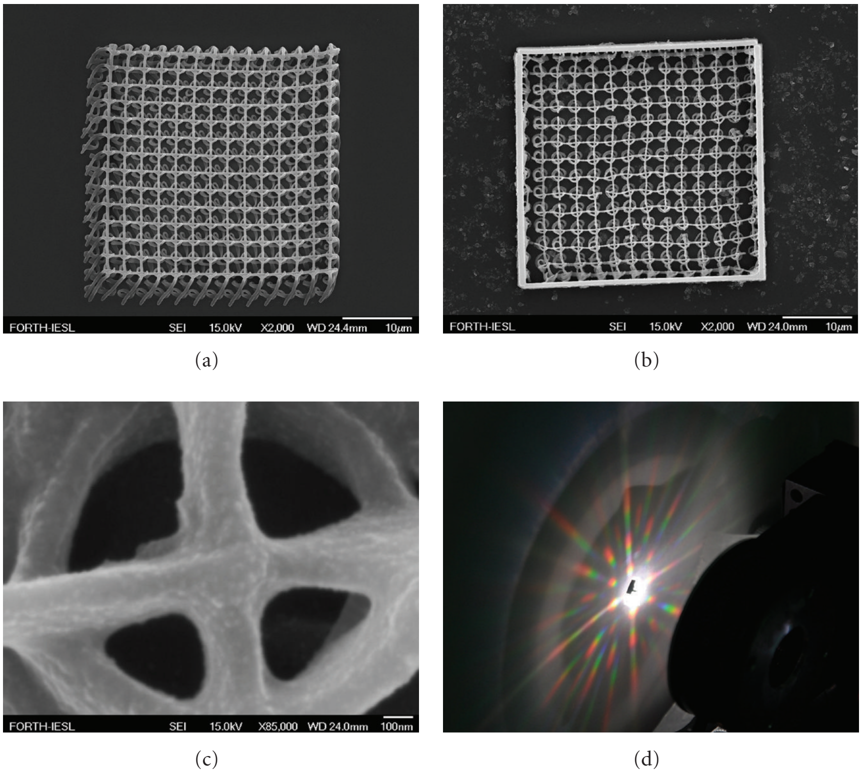


Figure 4: EDX spectrogram of the woodpile structures. The gold (Au) peaks are clearly visible.



(a)

(b)

(c)

(d)

Figure 5: Spiral photonic crystal structures. (a) An array of dielectric spirals. (b) An array of metalized spirals. (c) Detail of a spiral with lateral resolution is in the order of 100 nm. (d) The diffraction pattern generated when the structure is illuminated with white light.

Figure 4 shows the energy-dispersive X-ray (EDX) spectrogram of the woodpile structures, where the gold (Au) peaks are clearly visible.

Figure 5 shows a series of dielectric and silver-coated spiral structures fabricated as described earlier. Figures 3(a) and 3(b) show 14 × 14 arrays of spirals before silver coating, respectively. Support lines between the spirals are clearly visible. It is also clear that even thought there is some debris on the glass substrate, the silver metallization is selective. Figure 3(c) shows a close SEM image of a spiral; the resolution achieved is in the order of 100 nm. In addition, the silver coating is fairly uniform, with no visible large silver grains. Figure 3(d) shows the diffraction pattern produced when the spirals were illuminated with white light. As it can be seen, the pattern is regular, symmetric, and having well-defined colours, indicating the periodicity of the structures. This periodicity is not disturbed by the support structures.

6. Conclusions

To conclude, we have employed DA-DLW and EP of a metal-binding hybrid material to make helical spirals and woodpile structures with 600 nm intralayer periodicity. The fabricated nanostructures have a smooth surface and exhibit well-defined diffraction spectra, indicating their good fabrication quality and internal periodicity. We have shown that this methodology combination can be employed as a viable route for the fabrication of 3D dielectric, nanoparticle-coated, and metallic photonic nanostructures.

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