Letter to the Editor

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Photosensitive Material Enabling Direct Fabrication of Filigree 3D Silver Microstructures via Laser-Induced Photoreduction

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Dear Editor

Laser-induced photoreduction (LPR) as a direct fabrication technique that promises to be one of the most versatile routes for fabricating highly conductive 3D metallic microstructures on-chip (e.g., metamaterials, electro-mechanical systems, and high-frequency components like antennas). This technology has the potential to directly fabricate circuits on elastic and bendable substrates as well as antennas on complementary metal-oxide-semiconductor (CMOS) chips or on substrates with considerable topography. However, the fabrication of three-dimensional (3D) structures of high quality remains challenging. Here, a novel photosensitive material is used for the additive fabrication of filigree 3D conductive silver microstructures of almost arbitrary geometry via LPR. The material is based on silver perchlorate and gelatine solution. Structures fabricated with this material have a resistivity on the order of 10^{-6} Ω m, a material density of approximately 95%, and consist of almost 100 wt% silver. As a first functional component, a chiral metamaterial is presented.

Owing to the high demand for metallic microstructures, several techniques have been developed for fabricating-

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metallic microstructures¹⁻⁴. three-dimensional (3D) Usually, these structures are fabricated via indirect methods. First, a template is manufactured using subtractive micromachining or additive microfabrication. Thereafter, the metallic structure is electrochemically grown inside the template, and the template is removed subsequently². Although this method produces structures of outstanding quality, it has two crucial disadvantages: limited freedom of design and difficulty with on-chip fabrication. Considering this, it would be useful to have a direct method for fabricating arbitrary microstructures on arbitrary substrates, such as circuits on elastic and bendable substrates and antennas on CMOS chips or substrates. Further, this technique would be able to produce microstructures with substantial topography. Most existing direct methods that enable the fabrication of 3D metallic microstructures either require a conductive substrate (e.g., electro-hydrodynamic printing) or have been slow thus far (e.g., electron beam-induced deposition)⁴. Direct laser writing (DLW) via multiphoton absorption can quickly fabricate almost arbitrary and highly accurate microstructures without the aforementioned drawbacks. DLW uses a laser beam to selectively harden a photoresist via polymerisation⁵⁻⁷. LPR, similar to DLW, exploits multiphoton absorption but employs photo-reducing agents that reduce the metal precursors. The fundamental building block of the microstructure is formed via consequent nucleation, growth, and agglomeration (Fig. 1)⁸⁻¹⁸. Some research groups have exploited this mechanism to fabricate

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planar silver⁹⁻¹¹ and gold^{12,13} as well as 3D silver¹⁴⁻¹⁶ and gold-composite microstructures¹⁷. However, the full potential of this technology could not be exploited till now owing to the difficult-to-control chemical reactions involved with this method. While the quality of planar structures is similar to those of their polymeric counterparts, 3D metallic microstructures exhibited rather rough surfaces, had limited geometric complexity, and/or were formed from metal-polymer composite materials, which resulted in low conductivity¹⁸. This is undesirable for high-frequency applications, because roughness leads to large scattering losses and large ohmic losses (in the case of composite materials). Therefore, for a novel photosensitive material, we focus on using liquid gelatine as a host matrix. It simultaneously functions as a reducing agent, viscous solvent for the silver precursor, and stabilising agent. Compared to a polymer matrix, it has the advantage of enabling and dispersing a large active substance load. Further, it is almost completely displaceable by the evolving silver structure and completely dissolvable under mild conditions. Overall, this material promises high purity and density and thus, high conductivity of the resulting microstructure, while preserving on-chip compatibility.

The strength of LPR is its versatility, in that it can fabricate almost every geometric shape. We demonstrate its versatility by fabricating numerous sample structures, with different geometries, using the novel material. The results are depicted in Fig. 2: filigree helices, beams with right angles, but also structures with closed surfaces such as hollow pyramids, and an array of miniature horn antenna structures are observed. Overhanging structures are more challenging to fabricate compared to those fabricated along the downward writing direction (against the direction of laser beam propagation) because the radiation pressure drives evolving particles away from the structure rather than towards it. However, the right-angled beam in Fig. 2b clearly demonstrates that such demanding structures are possible to fabricate by virtue of the high viscosity of gelatine. Naturally, upward writing directions are not possible with this approach because the pre-written structure parts block or attenuate the incoming laser radiation. However, similar to DLW, where structures are fabricated via a layer-by-layer top-down approach, fabricating structures in a top-down writing direction does not substantially limit the structural variety.

We determined the resolution, feature size, contour accuracy, and surface roughness of the structures presented in Fig. 2. The smallest reproducible helix pitch is of 2 μ m, and thus, the resist supports an axial resolution of 500 lines/mm. From the close-up of the helix (Fig. 2d) that toppled during washing, we found that the lateral and axial feature sizes were nearly equal (approximately 760 nm). The spherical voxel possibly stemmed from the deteriorating effect of the evolving structure on the focal field. We measured the deviation of the diameter from the mean diameter of the helix as a measure for contour accuracy and found it to be in the order of \pm 100 nm with a mean roughness of approximately \pm 30 nm.

As shown in Fig. 2c, e, closed structures with thinwalled silver surfaces may also be fabricated. However, since these structures were fabricated using a layer-bylayer writing approach and the laser-structure interaction played an important role in direct metal writing, these surfaces had some particularities to them. A wave-like topography with periodicity and an average pitch of approximately 670 nm was observed. This can be attributed to the same mechanism that is responsible for the formation of laser-induced periodic surface structures¹⁶. The incident light interfered with scattered or diffracted



light close to the surface of the structure. This additional topography reduced the contour accuracy compared to that of structures fabricated from a single line. Further, it led to a peak-to-valley deviation of the flat surface of approximately \pm 150 nm.

As mentioned, gelatine enables the diffusion of the dissolved silver precursor and is displaced by growing silver seeds. Therefore, we expected structures with a high silver content and material density. Fig. 3a shows an electron diffraction X-ray (EDX) count map and a corresponding scanning electron microscopy (SEM) analysis, which verified that silver is present only in the exposed parts. Furthermore, Fig. 3b shows an EDX spectrograph acquired from the top of a freshly fabricated silver block (inset). An acceleration voltage of 10 kV was used for the measurement, and this corresponds to an approximate probing depth of 300 nm. Only silver and iridium (which appeared since we sputtered a 10 nm thick layer of it on top of the entire sample to avoid charging during SEM) was detected. This proves that the structures consist of almost 100 wt% silver close to their surface. EDX measurements of the internal parts (revealed by focused ion beam milling, not shown) of such blocks revealed approximately 99 wt% silver with some trace impurities (calcium, lead, and sulfur).

From the milled cross-section, we also determined the material density and phase of the internal microstructure of the fabricated structures (Fig. 3c). The cross-section had an average material density of 95% with an average pore diameter of 27 nm. The silver structures were mostly composed of the amorphous phase, except in the vicinity of large voids. The larger voids developed due to microexplosions occurring sporadically during writing up to 2 μ m away from the substrate. Further away from the substrate, the writing process reached a thermodynamic equilibrium that manifests in very stable writing conditions. Under those conditions, the amorphous phase was favoured. Note that the fabrication power window is

exceedingly small (typically, a few tens of microwatts) because of the strong laser-matter interaction. Thus, a small deviation from the optimal writing parameters decreases the material density and surface roughness of the fabricated structures.

Since these structures exhibited high purity and material density, we also expected them to show a high conductivity. Indeed, without annealing, the resistance of 3D wires (90 µm in length and 1 µm in diameter) was measured to be on the order of 1.9 k Ω , which is almost three orders of magnitude lower than the resistance of similar-sized gold-polymer composite bridges¹⁷. Further, the specific resistivity, calculated using a simple wire model, was on the order of $3.3 \times 10^{-5} \Omega m$ (bulk silver: $1.6 \times$ $10^{-8} \Omega$ m). It is well known that annealing further reduces the resistivity. However, the high temperatures (several hundred degrees Celsius) involved usually oppose on-chip compatibility of the material. Since gelatine melts at moderate temperatures, we tested whether heating it at 50 °C has an influence on its resistivity. Indeed, there was an exponential drop of resistivity over the heating time, and it approached $6.7 \times 10^{-6} \Omega m$ after three hours. This value compared favourably with that of directly written conductive polymers that, furthermore, only supported 2D structures¹⁹. Thus, the material enables the fabrication of conductive functional components. To prove this, we fabricated arrays of helices in the C₄ geometry (Fig. 4) with a diameter and pitch of 3 µm. Within the unit cell, each of the helices had a phase shift of $\pi/2$ with respect to its direct neighbour to avoid linear birefringence. The polarised Fourier transform infrared (FTIR) measurements on a leftand right-handed set of helices demonstrated that only little linear birefringence was observed (grey curves) (Fig. 4a). Concurrently, these structures also had a strong chiroptical response. While right-circularly polarised light was well transmitted over a broad spectrum, the transmittance of left-circularly polarised light was strongly suppressed (blue and red curves, respectively). The chiroptical responses



Fig. 3 a SEM images and EDX silver-count map of a 3D sample structure. b Electron diffraction X-ray spectrograph of a freshly fabricated 3D sample structure verifying the high silver purity of the structure. Besides silver, only the peaks of iridium are visible. The iridium peaks are due to post-fabrication sputtering of a 10 nm iridium layer that reduces charging effects during SEM. The inset shows the region where the spectrum was acquired. c SEM image of a focused-ion-beam-milled cross-section of a 3D sample structure showing a high material density and small average pore size.



clearly showed the expected mirror symmetry, thereby demonstrating the high structural quality of the written arrays. Fig. 4b shows a rendering of the unit cell in C_4 symmetry. A light microscope image of a fabricated array is depicted in Fig. 4c.

In summary, we have presented a novel photosensitive material that enables the fabrication of filigree (highly conductive 3D silver microstructures) via laser-induced photoreduction. This technique allows the fabrication of almost arbitrary 3D geometries, including right angles. These structures have feature sizes below 1 μ m and a resistivity of approximately 10⁻⁵ Ω m without annealing. Structures consisting of approximately 100 wt% silver have a material density of approximately 95% and are mostly amorphous. This novel photosensitive material paves the way for the direct on-chip fabrication of 3D

functional electrical or optical components. As a first application example, we demonstrate the chiroptical response of arrays of helices.

Materials and Methods

Preparation of photosensitive material: A solution was prepared by heating 0.5 g of gelatine (Roth Gold) in 10 ml of distilled water at 40 °C for 3 h without stirring. The gelatine solution was transparent at a writing wavelength of 780 nm, and it was used as a stock solution. To this solution 0.4 M AgClO₄ (Sigma Aldrich) was added and stirred at 40 °C for 1 h (500 rpm) using a magnetic stirrer. The photosensitive material was kept at room temperature (294 K) and remained in a liquid state.

Fabrication process: Glass plates (BK7, Schott) with a thickness and diameter of $170 \mu m$ and 30 mm, respectively,

were cleaned in an acetone ultrasonic bath for 10 min. This was followed by a 10 min ultrasonic bath in isopropanol and subsequent rinsing using distilled water. Two stripes of scotch tape were glued on the plate as spacers (100 μ m height). The photosensitive material was drop-casted on the plate between the spacers. A second glass plate (18 mm square, BK7, Zeiss), cleaned in the same way, was placed on top of the spacers.

A home-built spatial-light-modulator-based DLW setup was used²⁰. The setup was built around an 80 MHz pulsed femtosecond Ti:Sa laser (Chameleon Ultra VIS, Coherent) operated at a wavelength of 780 nm and an inverted microscope (Axio Observer, Zeiss). То ensure compatibility of the presented photosensitive material with commercially available DLW systems, we did not change the wavelength. The power of the laser was controlled using an acousto-optical modulator (3080-125, Crystal Technology), and the aberration correction was enabled by a spatial-light-modulator (X10468-02, Hamamatsu). The laser was focused into the resist using a high-numericalaperture objective lens (NA = 1.4, 63x, Leica). The filigree structures were fabricated by slowly moving the sample with piezo-electrical stages at speeds of approximately 1 µm/s, while compact structures required speeds up to 20 µm/s. Typically, a few milliwatts of laser power were required for the fabrication.

Post-process: To remove unexposed parts, a small drop of the photosensitive material was casted on the sample. Subsequently, the sample was rinsed with distilled water and gently blow-dried using nitrogen gas.

Resistivity measurements: Two silver electrodes, separated by approximately 90 μ m, were prepared via sputtering and cutting using a razor blade. We verified that the electrodes were not electrically connected using a linear four-point measurement setup. Subsequently, the novel silver resist was used to fabricate a 10 μ m-high silver bridge across the gap. The bridge had a diameter of approximately 1 μ m. After washing and blow drying, the four-point measurement setup was used to determine the resistance of the 3D structure from the fitted slope of *I-V* curves. To determine the resistivity, the above geometric dimensions and a simple wire model were used:

$$\rho = \frac{R \cdot A}{L}$$

where R is the measured resistance, L is the length of the wire, and A is its cross-sectional area.

FTIR measurements: FTIR measurements of the helices were conducted using a Bruker Vertex 80 FTIR spectrometer coupled to a Bruker Hyperion 2000 microscope. To generate circular-polarised light, a combination of an

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Author contributions

E. H. W. developed the materials, fabricated the structures, and characterised the samples. J. K. performed the FTIR measurements. E. H. W and G. v. F. designed the experiments. All authors discussed the results and wrote the paper.

Conflict of interest

The authors declare no conflict of interests.

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