Nanofabrication on 2D and 3D Topography via Positive-Tone Direct-Write Laser Lithography

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Direct laser writing (DLW) lithography using two-photon absorption is a powerful technique mostly used for the fabrication of complex structures in micro- and nanoscale, by photopolymerizing a negative-tone resist. In contrast, herein, it is demonstrated that DLW is also well suited for fabricating nano- to microscale metallic structures using liftoff and a positive-tone photoresist. It is shown first that versatile, fast, and large-area fabrication is possible on flat 2D insulating substrates, and an expression for how the line width varies with the scanning speed is derived, with excellent agreement with the experiments. Even more interestingly, a unique application for the DLW lift-off process is demonstrated, by fabricating submicron scale metallic wiring on uneven substrates with sloping elevation changes as high as 20 μm. Such fabrication is practically impossible with more standard lithographic techniques.

1. Introduction

3D, direct laser writing (DLW) lithography based on two-photon absorption (TPA) is a fairly recent and powerful technique used for 3D writing of nano and microscale structures into photoresists,[1–3] Some of the main application areas demonstrated are photonics,[4,5] micro-optics,[6,7] mechanical metamaterials,[8,9] microfluidics,[10,11] biomimetics,[12,13] and micro and cell biology.[14–16] In most of these applications, the goal of the fabrication is the direct patterning of complex shapes, and as such, negative-tone photoresists, where exposed areas form the final structure, are often preferred and heavily used. Moreover, typically the highest-resolution resists are liquids, allowing only negative-tone operation.

In contrast, in traditional top-down nano- and microfabrication such as planar 2D UV photolithography and electron-beam lithography, positive-tone solid-state resists are very commonly used as a mask in nano- and microscale electrical device fabrication, where the exposed regions can be removed in a development step. This is highly useful where small features are deposited onto or etched into the substrate, as only the small feature areas (lines, dots, etc.) need to be exposed.

In contrast, in the field of direct-write TPA microfabrication, positive-tone solid-state resists have not been so widely used. For 3D structuring, combining positive-tone resists with electrodeposition of metallic structures without electrical contacts and liftoff was demonstrated for photonic[17] and mechanical metamaterials,[18] magnetic microrobots,[19] and magnetic nanostructures[20] with the smallest feature size in the metal around 400–500 nm. In addition, 3D 4 × 4 μm² microchannel structures[21] and micrometer scale molds[22] have also been demonstrated via positive-tone resists and TPA writing. In addition, a recent study[23] also pointed out the relevance of TPA direct writing in fabricating purely 2D, large-area metallic nanostructures (feature sizes above 400 nm) designed for plasmonic applications, using a positive-tone resist and liftoff.

In this article, our focus is twofold: first, we demonstrate the capabilities of the TPA writing for flat surfaces in the fabrication of long and narrow metal wiring and wire meshes using a positive-tone resist and liftoff and discuss its strengths in comparison with more traditional lithographic techniques. Second, and perhaps more importantly, we also demonstrate the fabrication and electrical measurement of submicron conducting wiring on uneven, 3D topography using a positive-tone photore sist and DLW TPA fabrication. Especially, this second application offers unique opportunities, as such fabrication is not available with traditional electron beam, ion beam, or photolithography. Inkjet printing could be used to pattern some materials onto uneven surfaces, but the resolution available with that technique is typically about an order of magnitude inferior, and it is limited by the available metal nanoparticle pastes.

It is also possible, alternatively, to use DLW to write metallic structures using photoreduction, even in 3D.[24,25] Although those techniques are promising, the method presented here has the benefit that it relies on the established photoresists and evaporation techniques, known to produce high-quality pure materials with low roughness, important for advanced devices such as tunnel junctions, for example. In addition, the whole palette of metals is available, whereas the range of materials (Ag, Au, and Cu) produced by the DLW photoreduction technique (often metal–polymer composites) and their quality are limited by the chemistry involved.[24,25]

The article is organized as follows: we first systematically investigate the quantitative characteristics of applying our DLW nanofabrication tool (Photonic Professional by Nanoscribe GmbH) to a positive-tone solid-state resist which has not been
reported before for TPA lithography (AR-P 3120 photoresist by Allresist GmbH). We use both the common immersion objective method, Figure 1a, which can only be used with transparent substrates, and the air-gap objective method, Figure 1b,c, suitable also for opaque substrate materials. Section 2.1 first describes the writing tests on the resist using an immersion objective, whereas in Section 2.2, we compare similar results obtained with an air-gap objective. In Section 3, we demonstrate some examples of a full fabrication process of metallic wiring structures, using liftoff on flat surfaces, down to 330 nm wire width and 650 nm pitch. Finally, in Section 4, we demonstrate the fabrication of metallic wiring on complex, engineered 3D topography.

2. Resolution and Speed of 2D Patterning Using a Positive-Tone Resist

2.1. Resist Tests on Glass Substrates Using an Immersion Objective

The exposed volume in the positive-tone resist will be removed after the development, leaving openings to the resist, in contrast to negative-tone resists, where the exposed volume is polymerized and thus directly forms the corresponding voxel shape. This gives us a way to measure the lateral resolution of the voxel under scanning electron microscopy (SEM). First, we study the lateral resolution of both stationary spots and continuously scanned lines as a function of the laser output power, the spot exposure time, or the scan speed.

Using the immersion oil method (details in Section 6), we first systematically exposed our sample at single stationary locations, with varying laser power (ranging from 0.2 to 8 mW) and exposure time (ranging from 0.8 ms to 1 s), as shown in Figure 2d. The laser focus was kept at the resist to air interface. The lateral diameters of the exposed spots were measured with an SEM (eLiNE, Raith GmbH, manual fitting) and plotted as a function of exposure time t with different laser output powers, as shown in Figure 2a, and as a function of laser output power P with different exposure times, as shown in Figure 2b. In both figures, theoretical fits to a function $A \sqrt{\ln(BP^2)}$ (with A and B as the fitting parameters) are also shown, with excellent agreement. This non-linear dependence is based on known TPA theory\cite{26,27} and agrees with studies on negative-tone\cite{26,28,29} and positive-tone\cite{30} resists reported by other groups. We stress that we only plot exposures that resulted in well-behaving round spots, as exemplified in Figure 2d. Odd-shaped spots were typically generated when the resist was underexposed and thus more susceptible to external interference such as vibrations and acoustic noise.

Moreover, we found that the voxel diameter dependence on the laser power P and the exposure time t can be combined into a collective exposure parameter $P^t$, where the square of the laser power $P^2$ is multiplied by the exposure time t, as shown in Figure 2c. This dependence is in agreement with the nonlinear absorption rate of the second order photons in the TPA process, as seen before,\cite{27} and indicates that it is this collective exposure parameter (proportional to an effective dose) that needs to be tuned, based on the requirements for the resolution in the AR-P 3120 positive-tone resist lithography. Note that for one-photon absorption, the effective dose would be proportional to $Pt$ instead.

We performed another experiment by continuously exposing the sample with different stage scanning speeds, ranging from 10 to 400 μm s⁻¹ using different laser output powers (ranging from 2 mW to 6 mW). The line width was again measured with the SEM (Figure 3d), and in Figure 3a, we plot the measured width as a function of the stage scanning speed, with different laser output powers. From Figure 3a, we see that the line width has clearly a nonlinear dependence on the scanning speed, as can be seen from the fitting functions. These fits were obtained using a theory for the line width w, derived in the Supporting Information, assuming linear motion of the laser spot with speed v.
where $\omega_0$ is the beam waist at the focal plane, $\sigma_2$ is the effective two-photon cross section, $I_0$ is the time-averaged laser beam photon flux intensity at the beam center (photons/area/s), and $C = \ln[\rho_0/(\rho_0 - \rho_{th})]$ is a resist-dependent material parameter, with $\rho_0$ the initiator density and $\rho_{th}$ the threshold density for radicals to initiate reaction in the resist. In the experiment, the parameter controlling $I_0$ is the output power of the laser $P$, as there is a direct proportionality between the two.\(^{[26,27]}\)

Comparing with the spot exposure experiment, Equation (1) predicts that the exposure parameter controlling the line width in scanning mode is $P^2/\nu$ instead of $P^2$. We can check this by plotting all line-width data as a function of $P^2/\nu$, as shown in Figure 3c. Again, we obtain great agreement between the experiment and the theory, except at the highest $P^2/\nu$ values, where possibly the density of radicals saturates and diffusion rate starts increasing.

Based on Equation (1), we see that for a fixed target line width $w$, if one wants to increase the writing speed, the power does not need to be increased linearly, as would be the case for one-photon absorption, but only as a square root. Figure 3b shows this fact for our experimental conditions, where we plot the quadratic scanning speed increase with the increased laser output power, for three different line widths, based on the fits of Figure 3a. The possibility to increase the scanning speed quadratically with the laser output power enables ultrafast DLW for a large-scale 2D fabrication. As we see from Figure 3b, one could use writing speeds of $\approx 6\text{ mm s}^{-1}$ for a 400 nm line for this resist with a realistic output power of 10 mW. Unfortunately, in this study, we were limited by the accuracy of our motorized stage and could...
not test the ultrafast DLW mode at speeds above a millimeter per second. Setups using galvo mirrors (commercially available) can reach up to 20 mm s\(^{-1}\) scanning speeds,\(^{[31]}\) and fast TPA writing with such a setup and a different resist (AZ MiR 701) was demonstrated before.\(^{[23]}\) Moreover, the nonlinear relation between the scan speed and the line width can also be utilized as a velocity-dependent “shutter mechanism” for DLW without using physical shutters, as reported before for the negative SU-8 resist.\(^{[29]}\)

Note that smaller diameters and line widths of the order of 100 nm have been reported in the literature for DLW writing into a positive-tone resist,\(^{[30]}\) using a much thinner resist layer of \(\approx 150\) nm. The thin resist allows one to shift the focus plane in such a way to use only the tip of the voxel, to gain in resolution. However, this type of tuning was not considered in this article, as the resist profile generated in such a manner\(^{[30]}\) is not suitable for liftoff and transfer of the pattern to metallic structures.

2.2. Resist Tests on Glass Substrates Using an Air-Gap Objective

DLW can be also performed with an air-gap objective, which provides a more versatile alternative to an immersion oil objective, as it is not in contact with the substrate. This makes it possible, e.g., to expose features on the front side of opaque substrates, and particularly on an already existing larger surface topography, an option we will focus on in Section 4. However, for comparison with the results obtained earlier with the immersion oil objective, we first study the characteristics of exposing the same AR-P 3120 positive-tone resist through glass substrates with the air-gap objective (numerical aperture, \(NA = 0.75\), magnification \(63 \times\), Zeiss GmbH), as shown in Figure 1b. An obvious drawback of such an air gap objective is its lower resolution. However, if 1–2 \(\mu m\) scale features are wanted, the writing speed can be faster compared with the immersion oil method.

Figure 3. Line tests with the immersion oil method. a) Measured line width as a function of the stage scan speed, with different laser output powers. The solid points are the measured data, and the lines are two-parameter fits to the theory of Equation (1). b) Simulation of the stage scan speed as a function of laser output power for different desired line widths, based on the measured data. c) Measured line width as a function of the collective exposure parameter \(P^2/v\). The solid points are the measured data; the solid line is a two-parameter fit based on the theory of Equation (1) \(w = A\sqrt{\ln(BP^2/v)}\), with \(A = 370\) nm, \(B = 133.4\) m W\(^{-2}\) s\(^{-1}\). d) SEM image of a grid of line exposures with varying exposure parameters. The inset is a zoomed-in SEM image of an exposed line after development.
As in Section 2.1, the resolution of the air-gap method was studied by measuring the diameter of single spots exposed by varying the laser power $P$ and the exposure time $t$ (Figure 4a) and by measuring the line widths by varying the laser power $P$ and the stage scanning speed $v$ (Figure 4b), with the laser focused at the surface of a 500 nm thick resist. The smallest spots and lines have dimensions $\approx 400$ nm, but they do not go completely through the resist. The optimal points have a larger 600–800 nm diameter. As before for the immersion oil method, the theories for the spot diameter \cite{26,27,30} and the line width, Equation (1), fit very well to most of the data, when plotted as a function of the correct combined effective dose parameters ($P^2 t$ for spots $P^2 / v$ for lines), as evident in Figure 4c,d. Only at the highest effective dose ranges do the diameters and widths increase beyond what is expected from the theory. This effect, which is an abrupt change in the case of stationary spots, was observed to be caused by the collapse of the overhanging edges, as the exposed resist profile has an undercut at high doses. From Figure 4b, we also see that we managed to use high speeds of $2 \text{ mm s}^{-1}$ to write lines of width below 500 nm.

Another interesting aspect is the length of a voxel at different working parameters. This was studied by moving the laser focus vertically so that the length of a voxel can be determined from the end points where the very “tail” of a voxel still exposes the resist. The plot of the voxel length as a function of $P^2 t$ is shown in Figure 5. The results indicate that voxels are rather tall ($=2 \mu$m) even with the lowest doses. However, an elongated voxel is a benefit for 2D patterning: a thicker resist can be exposed with

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure4}
\caption{Point and line tests with the air-gap method. a) Diameter of single spots exposed with the air-gap objective, as a function of the exposure time $t$ and the laser power $P$ (points). The lines are the best fits to functions $A \sqrt{\ln(B P^2 t)}$. b) Width of the exposed lines as a function of the stage scanning speed with different laser output powers. The lines are two-parameter fits to Equation (1). c) Diameter of the exposed spots as a function of the combined exposure parameter $P^2 t$. The points are the SEM measured data; the solid line is a two-parameter fit to $A \sqrt{\ln(B P^2 t)}$ with $A = 590 \text{ nm}$, $B = 4.78 \times 10^8 \text{ m W}^{-2} \text{ s}^{-1}$. d) Measured line widths as a function of the combined exposure parameter $P^2 / v$. The points are the measured data; the solid line is a two-parameter fit based on the theory of Equation (1), $w = A \sqrt{\ln(B P^2 / v)}$, with $A = 560 \text{ nm}$, $B = 26.9 \times 10^8 \text{ m W}^{-2} \text{ s}^{-1}$. The discrepancy between the theory and experiment at high effective doses is due to the collapse of the undercut profile of the resist, and those points were excluded from the fits.}
\end{figure}
a single pass line, with an aspect ratio of roughly 5:1. To expose resists thicker than $\approx 1\,\mu\text{m}$, several passes at different vertical focal points can easily be used. Also, we point out that the undercut profile can likely be tuned by choosing an appropriate ratio between the resist thickness and the voxel length and by the placement of the focal plane. Undercut control is of course quite critical for successful lift-off processing, one of the major ways of using positive-tone resists.

3. Large-Scale Fabrication of Submicron Metallic Wiring on Flat Glass Substrates

With the aforementioned exposure knowledge, we have designed and fabricated metallized prototype samples, using the immersion oil DLW technique. It is quite important to demonstrate a complete fabrication sequence for devices, not just resist exposure tests, including metal evaporation and liftoff. We are aware of only one previous report\cite{23} that studied TPA DLW writing with positive-tone resist in such a manner. One of the possible applications with this technique is the fabrication of submicron centimeter-long conducting wires and wire grids on transparent substrates, for electro-optical experiments. Such samples would be much harder, if not impossible, to fabricate with more standard techniques such as electron-beam lithography, due to difficulties with charging and stitching of the write fields.

The sample, shown schematically in Figure 6a, contains several sets of 2 cm long, continuous, and electrically conducting silver lines on a transparent glass substrate, with design line widths 450, 600, and 800 nm. For the narrowest line sets, we thus have an ultrahigh aspect ratio of width to length over 1:40 000. The sample also contains two $3\times 3\,\text{mm}^2$ square mesh structures, which consist of hundreds of either 450 or 600 nm wide,
3 mm long crossing silver lines (Figure 6b). This sample thus demonstrates the advantages of TPA DLW for high-resolution, stitching-free, charging-free, fast-scanning-speed, large-scale, and versatile nanofabrication.

The sample is fabricated on a 170 μm thick glass substrate using a 500 nm thick layer of AR-P 3120 photore sist, spin coated, and developed as described in Section 6. The line width was controlled by a combination of the laser power and scanning speed used, with 2, 2.5, and 4 mW laser power, and 300, 180, and 50 μm s⁻¹ stage scanning speed used during the exposure for the 450, 600, and 800 nm line widths, respectively. Note that the scanning was performed with a motorized stage instead of the piezoelectric scanner, to allow for scanning lengths beyond the scan range of the piezostage, limited to 300 μm. After development, the exposed glass surfaces were cleaned by a 40 mTorr, 40 W, 50 sccm oxygen-plasma cleaning process in a reactive-ion etcher, followed by an ultrahigh vacuum (1 × 10⁻⁸ mbar) e-beam evaporation of a 200 nm-thick silver film. After the evaporation, liftoff was done with a hot AR 300-76 remover (Allresist GmbH) with a 2 s sonication.

Figure 6b shows a representative SEM image of a part of the 450 nm silver mesh, and Figure 6c presents an example of a higher-magnification SEM image of a long 450 nm silver line. As contact pads were also fabricated, we were also able to perform resistivity measurements on the structures, demonstrating the continuity of lines across such long lengths.

We also fabricated samples to find the resolution limits for this technique. For these samples, the same AR-P 3120 resist was used, but the thickness was lowered to 450 nm and the piezoelectric scanner was used for more accurate control of the scanning speed. Instead of silver, we used titanium for the metallization to improve adhesion. To find the highest possible pitch, we fabricated a sample with varying pitch, laser power, and focal height. The scanning speed was kept at 20 μm s⁻¹ based on the dose tests. With a 3 mW laser power and the laser focus at 400 nm below the resist surface, we achieved 450 nm lines with a 200 nm distance between them (Figure 6d). Similarly, we found the narrowest possible line, but now instead of the pitch, we also varied the scanning speed. The narrowest line was 330 nm wide (Figure 6e), drawn with a 2.5 mW laser power and a 50 μm s⁻¹ scanning speed.

4. Wire Fabrication on 3D Topography

Next, we demonstrate an even more promising application of 2D TPA DLW lithography: fabrication of metallic wiring on uneven surface topography. This application is very useful, as such a fabrication is extremely challenging with more standard photo- or e-beam lithographic techniques that operate on a flat focal plane. The uneven writing surface is not a problem with TPA DLW because the required height changes for the focal plane can easily be included in the wire design, as the sample stage can be moved in all coordinate directions. The technique also allows trivially the use of nonconducting substrate materials, in contrast to e-beam lithography. For this application, the air-gap objective is the only choice as the exposure needs to be done from the side of the 3D topographic structures and not through the substrate, schematically shown in Figure 1c. This is because of limitations of the working distance for through-substrate writing. Also, if the laser had to travel through multiple interfaces and the 3D structures, the laser intensity and resolution would be reduced. Writing through the substrate would also limit the usable substrate materials.

Wire fabrication on 3D topography was tested by first fabricating tall structures using the same DLW system. In this case, the structures were fairly simple cuboidal structures of height 20 μm, shown in Figure 7a,b, with ramps on the sides so that wiring from the substrate surface can be routed onto the cuboid. The cuboid structures were fabricated using the DiLL (Dip in Laser Lithography) method, in which an objective (NA = 1.3, 100 ×) is dipped in a liquid negative-tone photore sist (IP-Dip, Nanoscribe GmbH) for the exposure and photopolymerization. Transparent sapphire substrates were used to reduce reflections at the interface between the resist and the substrate.

After their fabrication, the cuboid structures need to be coated with the positive-tone AR-P resist for the wire fabrication (details in Section 6). Straightforward spin coating cannot be used due to the large 20 μm height of the structures; instead, direct spray coating could be used. However, this method was not available to us, so we had to make modifications to the cuboid structure itself, to still allow for spin coating. First, walls had to be added to the outer rim of the cuboid, to create a sort of a bowl for the resist to stay in during spin coating (Figure 7b). Second, the structures...
were made much wider (≈60 × 60 μm²); otherwise the proximity of the walls to the metal wiring would make the lift-off process unnecessarily hard. The walls are sloped on the inside to reduce their horizontal surface area. This smaller surface area reduced the amount of resist that adheres to the walls in the lift-off process.

Before doing the lithography for the wiring, most 3D structures were conformally coated with a 50 nm layer of aluminum oxide using atomic layer deposition (ALD). This was done to make the structures mechanically stronger for the liftoff, although successful liftoff was also shown to be possible for non-coated, pure IP-Dip polymer structures. After the ALD coating, the structures were spin coated with four nominally 800 nm thick layers (1500 RPM and time 90 s) of the AR-P 3120 resist to get good coverage also on top of the structures. Then, the samples were exposed with DLW for the wiring with a line pattern that follows the ramp and platform topography of the underlying cuboid structure in 3D space, with alignment performed with the integrated optical microscope before the exposure. A writing speed 20 μm s⁻¹ was used, and the width of the lines was determined by changing the laser power between 10 and 20 mW, producing a smallest line width ≈800 nm. With faster speeds or lower power values, the resist was not fully exposed. At the base of the cuboid, several passes with varying focal points in z-direction were used to fully expose the somewhat thicker resist that accumulated in those regions.

After the development, the samples were coated with a 70 nm gold layer, with a thinner ≈20 nm titanium adhesion layer underneath, by electron beam evaporation in ultrahigh vacuum. The evaporation had to be done from multiple angles from the sides of the ramps, to get good film coverage also on the ramps (Section 6), as they contained small ≈100 nm vertical steps, as can be seen in Figure 7a. A finished sample with gold wiring routed from the substrate surface onto the cuboid platform using the ramps is shown in Figure 7c. As the figure shows, we have successfully demonstrated metal wire fabrication on 20 μm tall 3D structures, with the wiring climbing the structure from the substrate surface, using DLW and liftoff with a positive-tone resist. The continuity of the wiring was also demonstrated with electrical measurements, with the observed room-temperature resistance values typically around 35–40 kΩ. For one sample, we also characterized the temperature dependence of the resistivity, showing a standard metallic behavior and an RRR of ≈2.8.

5. Conclusions

Our results clearly demonstrate the capabilities of DLW using TPA also for 2D lithography with liftoff, with metallic lines down to 450 nm width fabricated on very large areas, up to 2 cm. On smaller areas, 650 nm pitch and 330 nm line width were also demonstrated. As 2D lithography and liftoff are very common and established techniques in general, we should critically evaluate the strengths and weaknesses of using the TPA DLW technique for this purpose. The fact that the writing is maskless gives it versatility and suitability for research problems and prototyping, as opposed to standard photolithography that uses masks. DLW, in contrast, can be done in 2D with one-photon absorption, if UV lasers are used. A typical writing speed with the highest resolution (nominally around 300 nm) of such a laser lithography tool is of the order of millimeter per second; in other words, the resolution and speed are similar to what was demonstrated here. The main difference between one-photon absorption and TPA comes with how the line width scales with intensity, Equation (1). It means that if the intensity of the laser can be increased, the writing speed increase is quadratic in two-photon absorption as opposed to linear in one-photon absorption, favoring TPA eventually.

Even though the liftoff worked for the processing described here, one can also envision simple improvements that would enhance the undercut profile and thus help the liftoff. One could implement the well-known technique where two layers of different resists are used, with the more sensitive layer underneath. In addition, the TPA DLW technique uniquely allows for writing just one layer of resist at two different heights with different exposure parameters, which can be used to tune the undercut profile.

Even more promising, however, is the possibility we demonstrated here that 2D lithography is performed on uneven, nonflat topography. This seems to be the strong point of doing 2D lithography with an inherently 3D lithography system. We showed the feasibility of fabricating submicron scale metallic wires on a 3D structure with an elevation change as high as 20 μm, on a complex structure, using a positive-tone resist and liftoff. Such fabrication is extremely challenging, if not impossible, with more standard techniques that have to rely on the flatness of the substrate.

6. Experimental Section

Two-Photon Lithography Tool: The DLW nanofabrication tool used (Nanoscribe Photonic Professional) is based on a 80 MHz repetition rate pulsed fiber laser with a near-infrared wavelength (780 nm), with maximum laser power of 90 mW. A three-axis piezoelectrical stage is used for accurate motion of the substrate of distances below 300 μm, and a motorized stage is used for larger area movements.

Immersion Objective Method: In the immersion objective method, a transparent glass substrate with 170 μm thickness was mounted on the piezoelectrical stage with the resist side facing up, and an inverted microscope objective with 100× magnification and 1.4 NA was dipped into the immersion oil on the backside of the substrate as shown in Figure 1a. Instead of using the conventional liquid negative-tone resist, a spin coated, solid, positive-tone UV photore sist AR-P 3120 consisting of novolac resin and naphthoquinone diazide was used. The thickness of the resist was controlled by the spin speed and a short pre-exposure baking immediately followed after the spin. In our case, a 500 nm-thick resist was spun with 5000 RPM for 60 s, followed by a bake for 1 min at 100. After the laser exposure, the sample was first developed in a 1:1 mixture of AR 300-47 and deionized water for 1 min, then rinsed for 2 min in pure deionized water, and finally blow-dried with nitrogen gas.

Air-Gap Objective Method, Writing through Glass: In the air-gap objective method, an objective (Zeiss GmbH) with NA = 0.75 and magnification 63× was used, not in contact with the substrate. A transparent glass substrate with 170 μm thickness was mounted on the piezoelectrical stage with the resist side facing up. The same spin-coated, solid, positive-tone UV photore sist AR-P 3120 was used (500 nm thickness), spun with 5000 RPM for 60 s, followed by a bake for 1 min at 100, and developed in a 1:1 mixture of AR 300-47 and deionized water for 1 min, then rinsed for 2 min in pure deionized water, and blow-dried with nitrogen gas.

Air-Gap Objective Method, Wire Deposition on the 3D Topography: The 3D structures were spin coated with four 800 nm thick layers (1500 RPM
Table 1. Angles with respect to surface normal and thicknesses d used in the multiple angle evaporation sequence.

| Angle ['] | d Ti [nm] | d Au [nm] |
|-----------|-----------|-----------|
| ±75       | 1         | 3         |
| ±60       | 2         | 5         |
| ±45       | 3         | 10        |
| ±30       | 3         | 10        |
| ±15       | 4         | 15        |
| 0         | 6         | 30        |

and time 90 s) of the AR-P 3120 resist, which was baked at 100 °C for 30 s between layers and for 1 min after the last layer. After the exposure and development (1:1 solution of AR 300-47 and deionized water for 1 min), the samples were coated with a ≈0.7 nm gold layer, with a thinner ≈20 nm titanium adhesion layer underneath, by electron beam evaporation in ultrahigh vacuum. The evaporation was done from six different angles from both sides of the structure, first Ti, then Au, in a sequence shown in Table 1. The liftoff was done with heated and sprayed AR 300-76 remover.

**Electrical Characterization of the Samples:** The metalized wire samples of Section 3 were electrically characterized by measuring their resistance with a Keithley 2450 SourceMeter at room temperature. The resistance of the wiring on the 3D topography in Section 4 was measured with a multimeter, and in the case of the temperature dependence, with a Stanford SR830 lock-in amplifier at a frequency of ≈15 Hz.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

direct laser writing, liftoff, nanofabrication, positive-tone resist, two-photon absorption

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[1] H.-B. Sun, S. Matsuo, H. Misawa, *Appl. Phys. Lett.* 1999, 74, 786.
[2] S. Kawata, H.-B. Sun, T. Tanaka, T. Takada, *Nature* 2001, 412, 697.
[3] M. Deubel, G. von Freymann, M. Wegener, S. Pereira, K. Busch, C. M. Soukoulis, *Nat. Mater.* 2004, 3, 444.
[4] T. Ergin, N. Stenger, P. Brenner, J. B. Pendry, M. Wegener, *Science* 2010, 328, 337.
[5] J. B. Reeves, R. K. Jayne, T. J. Stark, L. K. Barrett, A. E. White, D. J. Bishop, *Nano Lett.* 2018, 18, 2802.
[6] S. Thiele, K. Arzenbacher, T. Gissibl, H. Giessen, A. M. Herkommer, *Sci. Adv.* 2017, 3, e1602655.
[7] E. Johlin, S. A. Mann, S. Kasture, A. F. Koenderink, E. C. Garnett, *Nat. Commun.* 2018, 9, 4742.
[8] T. Bückmann, M. Thiel, M. Kadic, R. Schittny, M. Wegener, *Nat. Commun.* 2014, 5, 4130.
[9] L. R. Meza, A. J. Zelhofer, N. Clarke, A. J. Mateos, D. M. Kóchmann, J. R. Greer, *Proc. Natl. Acad. Sci.* 2015, 112, 11502.
[10] M. H. Olsen, G. M. Hjortø, M. Hansen, Ø. Met, I. M. Svane, N. B. Larsen, *Lab Chip* 2013, 13, 4800.
[11] Y. Lin, C. Gao, D. Gritsenko, R. Zhou, J. Xu, *Microfluid. Nanofluid.* 2018, 22, 97.
[12] M. Röhrig, M. Thiel, M. Worgull, H. Hölscher, *Small* 2012, 8, 3009.
[13] X. Liu, H. Gu, M. Wang, X. Du, B. Gao, A. Elbaz, L. Sun, J. Liao, P. Xiao, Z. Gu. *Adv. Mater.* 2018, 30, 1800103.
[14] F. Klein, T. Striebel, J. Fischer, Z. Jiang, C. M. Franz, G. von Freymann, M. Wegener, M. Bastmeyer, *Adv. Mater.* 2010, 22, 868.
[15] D. Nishiguchi, I. S. Aranson, A. Snezhko, A. Sokolov, *Nat. Commun.* 2018, 9, 4486.
[16] A. Marino, C. Filippeschi, V. Mattoli, B. Mazzolai, G. Ciofani, *Nanoscale* 2015, 7, 2841.
[17] J. K. Gansel, M. Thiel, M. S. Rill, M. Decke, K. Bade, V. Saile, G. von Freymann, S. Linden, M. Wegener, *Science* 2009, 325, 1513.
[18] X. W. Gu, J. R. Greer, *Extreme Mech. Lett.* 2015, 2, 7.
[19] M. A. Zeeshan, R. Grisch, E. Pellicer, K. M. Sivaraman, K. E. Peyer, J. Sort, B. Öz kale, M. S. Sakar, B. J. Nelson, S. Pané, *Small* 2014, 10, 1284.
[20] G. Williams, M. Hunt, B. Boehm, A. May, M. Taverne, D. Ho, S. Giblin, D. Read, J. Rarity, R. Allenspach, S. Ladak, *Nano Res.* 2018, 11, 845.
[21] W. Zhou, S. M. Kuebler, K. L. Braun, T. Yu, J. K. Cammack, C. K. Ober, J. W. Perry, S. R. Marder, *Science* 2002, 296, 1106.
[22] I. Bernardeschi, O. Tricinici, V. Mattoli, C. Filippeschi, B. Mazzolai, L. Beccai, *ACS Appl. Mater. Interfaces* 2016, 8, 25019.
[23] A. Braun, S. A. Maier, *ACS Sens.* 2016, 1, 1155.
[24] E. H. Waller, G. von Freymann, *Nanophotonics* 2018, 7, 1259.
[25] L. Hirt, A. Reiser, R. Spolenak, T. Zambelli, *Adv. Mater.* 2017, 29, 1604211.
[26] J. Serbin, A. Egbert, A. Ostendorf, B. N. Chichkov, R. Houbertz, G. Domann, J. Schulz, C. Cronauer, L. Fröhlich, M. Popall, *Opt. Lett.* 2003, 28, 301.
[27] Y. Zhou, Y. Hou, J. Lin, *AIP Adv.* 2015, 5, 030701.
[28] T. Tanaka, H.-B. Sun, S. Kawata, *Appl. Phys. Lett.* 2002, 80, 312.
[29] W. H. Teh, U. Dürig, U. Drechsler, C. G. Smith, H.-J. Güntherodt, *J. Appl. Phys.* 2005, 97, 054907.
[30] H.-Z. Cao, M.-L. Zheng, X.-Z. Dong, F. Jin, Z.-S. Zhao, X.-M. Duan, *Appl. Phys. Lett.* 2013, 102, 201108.
[31] T. Bückmann, R. Schittny, M. Thiel, M. Kadic, G. W. Milton, M. Wegener, *New J. Phys.* 2014, 16, 033032.
[32] K. A. Cooper, C. Harbel, B. Whitney, K. Weiermann, K. J. Krammer, Y. Zhao, H. Gentile, *Conformal Photoresist Coatings for High Aspect Ratio Features,* SUSS MicroTec Waterbury Center, Williston, VT 2007.
[33] S. M. George, *Chem. Rev.* 2010, 110, 111.