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# One-Step Photolithographic Surface Patterning of Nanometer-Thick Gold Surfaces by Using a Commercial DLP Projector and Fabrication of a Micro-Heater

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## ABSTRACT

A one-step photolithographic approach to pattern gold- and copper-coated surfaces is presented. The metal is selectively etched by light triggered local release of cyanide from a potassium ferrocyanide solution. The site-specific dissolution of gold by cyanide is extremely fast and essentially irreversible. An arbitrarily configurable light pattern can be produced with a commercial Digital Light Processing (DLP) projector directly pointed to the surface of the submerged sample. This procedure requires only minimal pre- and post-processing operations and non-toxic chemicals. As an example of application, the rapid fabrication of a small 2-zone differential heater is presented.

## INTRODUCTION

Surface patterning consists in the creation of chemically or physical delimited regions on a surface. Whilst the interest of humans in drawing and writing goes far back in time, the evolution of the microelectronic industry has fueled the development of new methods to micropattern substrates in batch processes.<sup>1</sup>

In any two-dimensional surface patterning technique the desired pattern can be generated from scratch directly onto a surface, i.e. by writing through mechanical or electromagnetically displacement, or it can be first produced on a mask and then replicated onto a different substrate.<sup>2</sup> In the latter case, the mask is used to modulate a flux (either chemical or electromagnetic, such as light), which can modify the surface of the substrate. The process of patterning by modulating a light source through a mask (known as photolithography) has been the driving technology for the development of the semiconductor industry in the past decades.<sup>2</sup>

One relevant industrial application of lithography can be found in the printed circuit board (PCB) industry,<sup>3</sup> which relies on lithography processes based on a polymer mask in contact with a resist-coated substrate. The conventional manufacturing procedure starts by printing the board layout into a photo negative mask, which is then applied onto a copper layer covered with a photo resist. During exposure to UV light, only areas of the photo resist layer not covered by the mask harden while the rest of the material can be washed away, leaving the copper unexposed and, therefore, ready to be chemically etched in a later step. More recently, the development of digital micromirror devices (DMDs) at Texas Instruments has led to a maskless manufacturing procedure called DLP-enabled PCB lithography<sup>4</sup>, in which the pattern is transferred at high speed and high-resolution directly onto the photoresist-coated copper layer. Although this improvement eliminates the need

for the initial photo film, the production process still involves the creation of a photo negative mask and the subsequent copper etching with hazardous chemicals.

It has been known for many years<sup>5</sup> that gold, as well as other metal of interest for the electronic industry (such as copper), can be dissolved in a cyanide solution, although the main drawback of this approach is its toxicity.<sup>6-8</sup> Recently, however, it has been shown that light can be used to trigger cyanide release from a non-toxic solution of potassium ferrocyanide.<sup>9</sup> In our work, we have combined the use of a commercial DLP (Digital Light Processing) projector to selectively illuminate a solution of potassium ferrocyanide and locally trigger the release of cyanide in order to pattern a metal-coated surface (Figure 1). This one-step photolithographic method presents a simplified procedure where the pattern can be directly transferred from the design files onto the substrate, by means of a single-step procedure (Figure 2Figure 2). In analogy with consumer 3D printing devices, our setup allows for the creation of the final product directly from the design file, with minimal preparation work or post-processing steps. Thanks to the use of only inexpensive, non-toxic chemicals, this technology could be broadly adopted also outside of the context of chemical laboratories. As an example, we have demonstrated the production and use of a 2-zone differential heater that can be manufactured in a very short time and that is able to heat up two small samples in parallel at different heating rates.

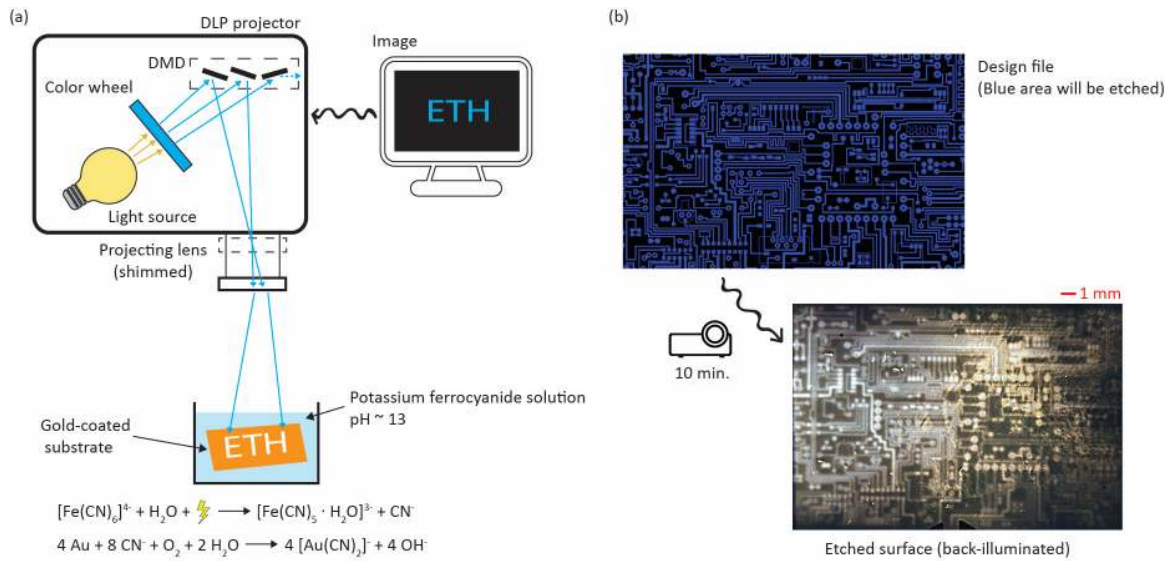


Figure 1: (a) Schematic representation of the setup and (b) example of a design pattern and the resulting etched surface after 10 —minutes of exposure

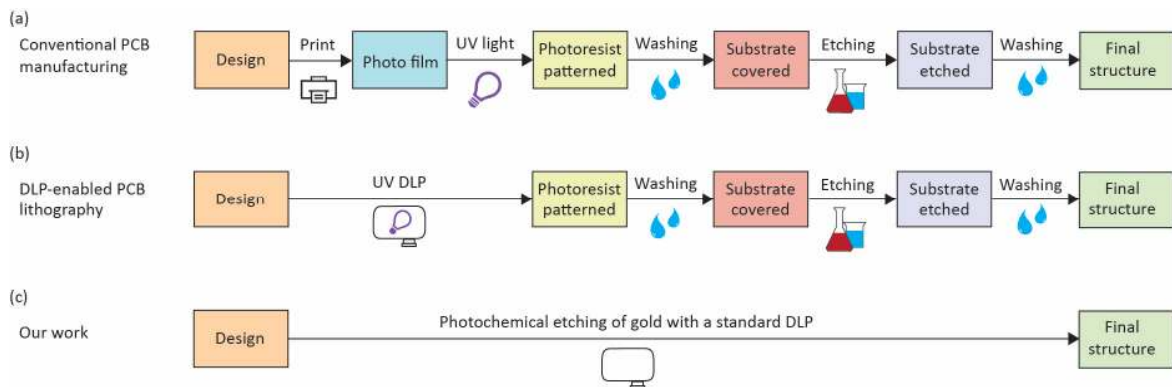


Figure 2: Comparison of established PCB production techniques against our technology. (a) Conventional Printed Circuit Boards (PCB) manufacturing consists of several steps and (b) the introduction of an Ultraviolet Light Digital Light Processing (UV-DLP) projector only partly simplifies it. (c) Our technology allows for a one-step procedure from the design file to the final structure.

## EXPERIMENTAL SECTION

### **Light source and mask**

A DLP projector Acer X152H equipped with a 200 W UHP light source was used for all the experiments. In such a device, a first filter blocks undesired UV radiation, and a second set of filters (assembled in a spinning “color wheel”) further selects only the desired wavelength (Figure 1). The light then travels to the DMD, an array of micro mirrors that creates the desired pattern by selectively reflecting the light towards the target. After being reflected, the rays are magnified and focused by means of a projecting lens. In order to create a compact setup and focus the light on a small target, the distance between the projecting lens and the DMD was increased by 20 mm, as described in an open-source online project.<sup>10</sup> The final distance between the projecting lens and the samples turned out to be approximately 25 mm. The projector, connected to a laptop by means of an HDMI interface, was placed on a vertical stand, pointing vertically down into the reaction chamber containing the sample. The projected patterns have been created with Adobe Illustrator®.

### **Substrate fabrication**

Two types of metal-coated substrates were tested: glass-based and Teflon-based. Glass-based substrates were obtained by depositing Cr/Au (2 nm/40 nm) or Cr/Cu (2 nm/40 nm) by physical vapor deposition (PVD) on a standard, untreated laboratory glass slide (Thermo Scientific, Menzel Gläser, approximate size: 1x25x25 mm). A cross section of the coated substrates was imaged with a Focused Ion Beam system (FIB-SEM) and the thickness measured in different spots resulted in the range 30-80 nm (Figure S1 in the supporting information). Teflon-based electrodes were obtained by depositing Au (40 nm) by PVD on small Teflon plates (1.5x25x25 mm). Gold sputtering was also tested as a mean to fabricate Teflon-based electrodes, but the resulting gold-layer showed a very weak adhesion to the Teflon surface and therefore this approach was

discarded. The main difference between the two types of substrates tested was the presence on the glass plates of a 2 nm chromium layer, which was deposited to improve the adhesion of gold.

### **Solution preparation and exposure**

The samples were submerged in a potassium ferrocyanide solution (8 mL, 0.5 M,  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ,  $\geq 98.5\%$ , Sigma-Aldrich) with the addition of a buffer solution (2 mL) with pH 13 (0.1 M KCl,  $\geq 99.5\%$  Sigma-Aldrich and 0.02 M NaOH,  $\geq 97.0\%$  Fisher Chemical).<sup>9</sup>

### **Characterization**

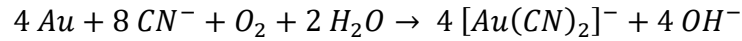
Resistance measures have been carried out using the 4-wire sensing method with a commercial voltmeter (Mastech, MS8239C), as this technique produces more accurate and consistent results especially for low resistances.<sup>11</sup> A MCH-K305D power supply was used to apply a voltage across the electrodes for the application example.



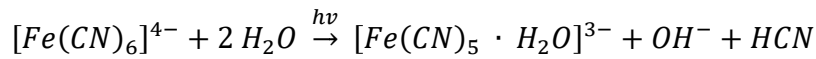
## RESULTS AND DISCUSSION

### Chemistry and working principle

The dissolution of gold in a cyanide solution is described by the Elsner equation:<sup>5</sup>



In order to overcome the issues related to the toxicity of this process, our system takes advantage of the release of cyanide from potassium ferrocyanide upon illumination<sup>9</sup> in agreement with the following reaction:<sup>5</sup>



As a result, almost no free cyanide is present in the solution, making the handling of the device relatively safe (as discussed in the section about toxicity).

The light source of our system is the original mercury lamp contained in the Digital Light Processing (DLP) projector. Similarly to what shown in other contexts,<sup>12,13</sup> we exploit the projector and in particular the Digital-Micromirror-Device (DMD) to selectively reflect the light only onto specific areas of the metal-coated substrate. Upon illumination, the potassium ferrocyanide solution releases cyanide, which then reaches the metal surface by diffusion and subsequently reacts with the metal coating. As the process does not require additional elements between the light source and the target, it can be classified as maskless photolithography process.

### Experimental characterization

In a first set of experiments, we have qualitatively investigated the influence of the wavelength on the outcome of the photolithographic process. After a setting up the system (as schematically shown in Figure 1a) and performing a qualitative calibration based on the sharpness of the project image on a dummy target, we have projected the same image on four gold-coated glass substrates, each time with a different color (white, red, green, blue) and for the same amount of time (20 minutes). The results (Figure 3) indicate that the sharpest etching can be obtained from the purely

blue design image, while green and red pattern exhibit a much lower etching effect. This is also in agreement with literature data of the decomposition of potassium ferrocyanide,<sup>5</sup> which suggest the use of a wavelength below 500 nm, as also confirmed by the absorbance spectra of the solution (Figure S2 in the supporting information).

As the light projected onto the surface is partly converted to heat, convective flows might be generated within the liquid solution, and this would accelerate the movement of cyanide ions and ultimately decrease the resolution of the system (as cyanide would also travel to regions of the surface not exposed to light). To minimize heat generation, only pure blue images were projected in the rest of the study.

### **Gold and copper etching rate**

A second set of experiments was performed in order to evaluate the etching rate as a function of the light exposure. Due to the projector's working principle (Figure 1), the density of the light shining on the substrate can be controlled only by binary action on the individual DMD mirrors. Therefore, different light densities are obtained by varying the fraction of time (in fast cycles) in which the mirrors are reflecting the light away from the target, rather than by actively modulating the intensity of the light source. For this reason, the overall exposure time of the substrate to the desired pattern was chosen as independent variable in the evaluation of the etching rate.

The image projected consisted of a single blue rectangular region that was intended to create two fully separate areas on the surface of the substrate. After exposure, the samples were washed and dried in air, and the resistance was measured across the patterned region using the 4-wire sensing method (Figure 4). Gold-coated glass substrates showed an initial low etching rate, with no significant increase in the resistance for exposure time up to 10 minutes. Between 10 and 30 minutes, however, the etching rate increased and a clearer separation between the two areas could

be noticed also by eye, especially when applying a back-illumination to the substrate. Experiments carried out for more than 30 minutes did not show any further significant increase in the resistance, which settled on approximately 15 Ohm, probably due to the presence of a residual thin layer of metal that could not be completely etched. Copper-coated glass substrates were analyzed in the same experimental conditions and the results showed not only a shorter time before significant etching started, but also much higher etching rates. However, experiments carried out with exposure times higher than 20 minutes produced samples with similar resistances, which reached a final value of approximately 160 Ohm. The presence of a 2 nm Chromium layer that was introduced in order to improve the adhesion between the metal (gold or copper) and the substrate (glass) could explain why the dissolution reaction was not able to completely remove the material from the region of interest. Moreover, the surface reaction between gold and cyanide could be further slowed down by the formation of a polymeric layer of  $\text{AuCN}_{\text{ads}}$  or an adsorbed layer of  $\text{AuOH}_{\text{ads}}$  on the surface,<sup>14,15</sup> which would protect the underneath metal from further etching. Gold-coated Teflon substrates showed a high etching rate for exposure times below 10 minutes. Longer exposure times led to a complete consumption of the gold on the region of interest, and therefore the resistance increased significantly and it reached values comparable to those of plain Teflon plates (non-coated). Although passivation of the gold surface might still have been present, the different nature of the substrate and the absence of an additional chromium layer facilitated the complete consumption of the gold and, therefore, a complete etching could be achieved in a relatively short time. A negative control was also performed for both glass- and Teflon-substrates in the same experimental conditions by projecting a black image onto the samples for 50 minutes. Although some residual light generated inside the projector was still going through the lens and it

could reach the samples, no significant increase in the resistance was observed in any of the control experiments.

### **Image and etching resolution**

In order to investigate the resolution of our system we have performed a set of experiments with the “1951 USAF resolution test chart” (developed by the U.S. Air Force, Figure 5). The elements of the target, which are progressively smaller and smaller, consist of black bars of precisely defined width and spacing. The bars are numbered and organized into groups identified with a pair of numbers (group number and sub-group number). The measure of the resolution is calculated based on the smallest features that can be distinguished,<sup>16</sup> considering the appropriate rescaling factor due to the different size of the target used,<sup>17</sup> and it is measured in line pairs per millimeters (lp/mm). In a first set of experiments, the working distance between the DLP projector and the surface of the sample was progressively varied in order to better approach the theoretical focal length of the setup. The position of the sample was varied in 5 steps of 1 mm around the value previously determined by eye and the final distance was chosen by calculating the highest score with the “1951 USAF resolution test chart” (Figure S3 in the supporting information).

We have then varied the height of the liquid solution above the surface of the sample in order to evaluate the impact on the resolution of the system. We have performed the experiments on gold-coated glass substrates and we have fixed the exposure time to 20 minutes, as this was already enough to produce a clear image on the surface of the sample. For this amount of time, the characteristic diffusion length of hydrogen cyanide can be calculated as follows:

$$L_d = \sqrt{4 * D * t} = \sqrt{4 * 1.21 * 10^{-3} * (20 * 60)} = 2.4 \text{ mm}$$

Where D is the diffusion coefficient of hydrogen cyanide in water at ambient temperature (25°C), calculated with the Stokes-Einstein equation (Table S1 in the additional information). As

the characteristic diffusion length represents the average length a molecule moves in any direction in this amount of time, we performed experiments with a liquid level below and above this value. As shown in Figure 5, as the height of liquid solution is increased a loss in resolution is observable, which could be explained by the stronger effect of cyanide production and diffusion. Indeed, assuming a simplified 2-dimensional model of the system, where cyanide is produced only along the z-axis (at an arbitrary, constant x-coordinate) and completely consumed along the x-axis, a higher liquid solution leads to more generation of cyanide, which produces more etching on the substrate's surface. This effect is more visible when the height of the liquid solution is varied around the characteristic diffusion length, as shown in a simplified simulation performed with Comsol Multiphysics® (details in the additional information). Other factors that might have an influence on the resolution of the system are the light diffraction (which also depends on the liquid height), convective flows within the liquid solution and the reflection of the residual light that travels through the sample, hits the bottom plate and is partly reflected back into the reacting solution.

Overall, the best resolution obtained across all experiments was higher than 7.5 lp/mm, which corresponds to a single-line thickness of approximately 70  $\mu\text{m}$ . The theoretical minimum feature size, calculated with the resolution of the DLP projector (1920x1080 pixel) and the size of the image projected (roughly 45x25 mm), is approximately 23  $\mu\text{m}$ .

### **Fabrication of a 2-zone differential heater**

The one-step photolithographic system that we have developed has the ability to replicate a pattern on a metal-coated substrate by selectively etching part of the metal and therefore creating regions with different coating thickness. As many metals (including gold and copper) are commonly used as electrical conductors, and as the quantity of metal in the conductor affects

directly its electrical resistance, which is directly related to its heat dissipation, we have investigated the use of our system for the creation of small electrical heaters. We took advantage of the design freedom of our setup to fabricate a 2-zone differential heater by shining two areas of a gold-coated glass slide with two different light intensities in order to generate different thicknesses in the gold layer and therefore different resistances (Figure 6). Both regions are connected to the same electrodes and therefore can be exposed to the same voltage, which generates a higher current flow through the lower-resistance region and a lower current flow in the other area. As the passage of an electric current through a conductor produces heating according to Joule's first law, we have used our heater to heat up two small droplets of water at different rates (differential heating):

$$P = R I^2$$

$$I = \frac{V}{R}$$

$$P = \frac{V^2}{R}$$

As stated by the Joule's heating equation combined with Ohm's law, once a fixed voltage (V) is applied to a conductor the heat produced decreases with the resistance of the conductor itself, as a higher resistance limits the flow of electrons (electrical current). The resistance in the two heating regions of our conductors depends on the thickness ( $t$ ) of the gold layer (having a length  $L$ , height  $t$  and base  $b$ ) in agreement with Pouillet's law:

$$R = \rho * \frac{L}{A} = \rho * \frac{L}{b * t}$$

$$R_{b,L,\rho \text{ const.}} \sim \frac{1}{t}$$

As previously discussed, the thickness of coating layer can be controlled by varying the amount of light that is shined on the surface. As our 2-zone heater is produced in a single step process, we have selectively controlled the etching rate by shining one heating region with blue light (that

would produce more etching) and the other heating region with a black pattern (therefore minimizing the etching). By exposing our sample to the desired pattern for 15 minutes, we have successfully reproduced the heater's structure on the gold-coated surface. In order to validate our system we have applied two drops (3  $\mu\text{L}$  each) of blue-dyed water (Solvent Blue 35, Sigma-Aldrich) on each of the two heating spots and we have sampled the temperature of the drops with a IR camera (Flir i7) after applying a voltage of approximately 2 V across the pads. As expected, the results (Figure 6) show a faster increase in temperature in the upper pad, which corresponds to the pad with lower resistance.

### **Toxicity**

As cyanide, known for its acute toxicity, is an intermediate product of our process, we have evaluated the toxicity of the chemicals (reactants and products) used in our system. Potassium ferrocyanide is considered nontoxic with a LD50 (median lethal dose) comparable to that of kitchen salt (LD50 in rats: 3613 mg kg<sup>-118</sup>). The chemicals used in the pH-regulating buffer (KCl and NaOH) have also very high LD50s, therefore the concentrations used in our setup do not pose a toxic hazard. As soon as the light induced chemical reaction starts, hydrogen cyanide is produced in the liquid solution: in order to evaluate the potential hazard generated we have evaluated the worst-case scenario with a complete conversion of the reactants and no further consumption of the hydrogen cyanide by the metal surface. Given the acute oral lethal dose of hydrogen cyanide for humans (1.52 mg kg<sub>body weight</sub><sup>-119</sup>), the maximum volume of potassium ferrocyanide solution should therefore be limited to approximately 3 mL (assuming a 30-kg reference child). Although in some of the experiments we have used a larger initial amount of potassium ferrocyanide, we have also successfully performed several runs with lower quantities (as low as 0.716 mL of total reaction volume) and we were always able to successfully reproduce the desired pattern on the metal-coated

substrates. In these conditions, the maximum amount of cyanide that could be produced (approximately 8 mg) would be lower than the maximum amount accepted in 1 kg of Cassava flour (10 mg, assuming a safe limit of 10 ppm as given by the WHO for this popular root vegetable).<sup>10</sup> Additionally, the high pH required for the formation of  $\text{CN}^-$  from potassium ferrocyanide prevents the formation of gaseous HCN. For these reasons we believe that our technology could be considered safe to use with appropriate sample, waste and chemical handling routines in place.

### **Comparison with other manufacturing techniques**

As shown in our results, our system is able to pattern metal-coated surfaces with good resolution and within minutes. By using a commercial DLP projector, we eliminate the need for a photomask and a dedicated light source (e.g. UV). The main drawback of this system is the fact that potassium ferrocyanide has a high absorbance only in the UV part of the spectrum<sup>5</sup> (Figure S2 in the additional information). As the amount of UV light that exits the DLP projector is very low (due to the presence of the UV-blocking filter and to the UV absorbance of the internal components) the reaction still requires several minutes to produce appreciable results.

In comparison with other manufacturing techniques than can be used to pattern a metallic surface (Table 1), our technology requires only a small initial investment and very few easily available and non-toxic chemicals. The process can be carried out in a few minutes and it does not involve long pre- or post-processing steps. We have demonstrated that submillimetre features can easily be achieved and we believe that there is potential for further improvements. As our setup is designed to work with a small substrate (around 25x25 mm) coated with only a very thin layer of metal ( $\sim 40$  nm), the cost of the raw materials results considerably low (e.g. 0.03 \$ for the gold applied on a substrate).



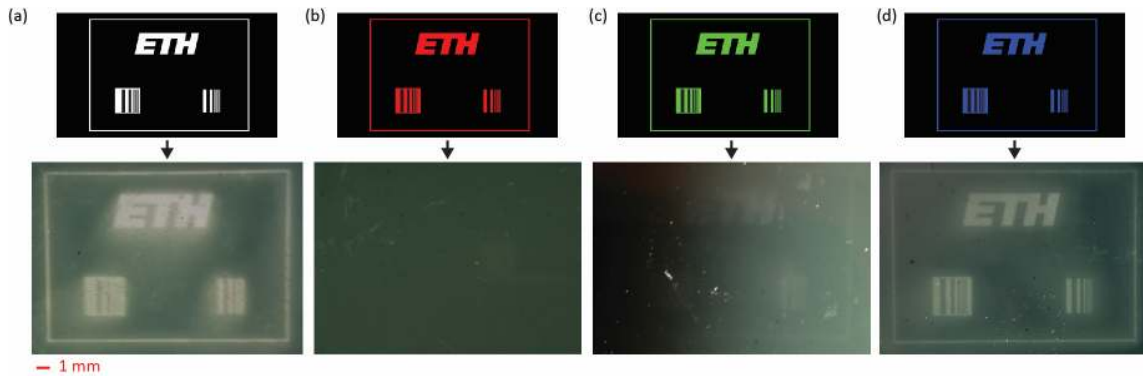


Figure 3: Gold-coated glass substrates (back-illuminated) etched at the same conditions with light at different wavelengths. (a) The etching is clearly visible when the pattern is projected with white light. (b, c) Red and green light sources do not produce any appreciable etching, while blue light gives the best results (d).

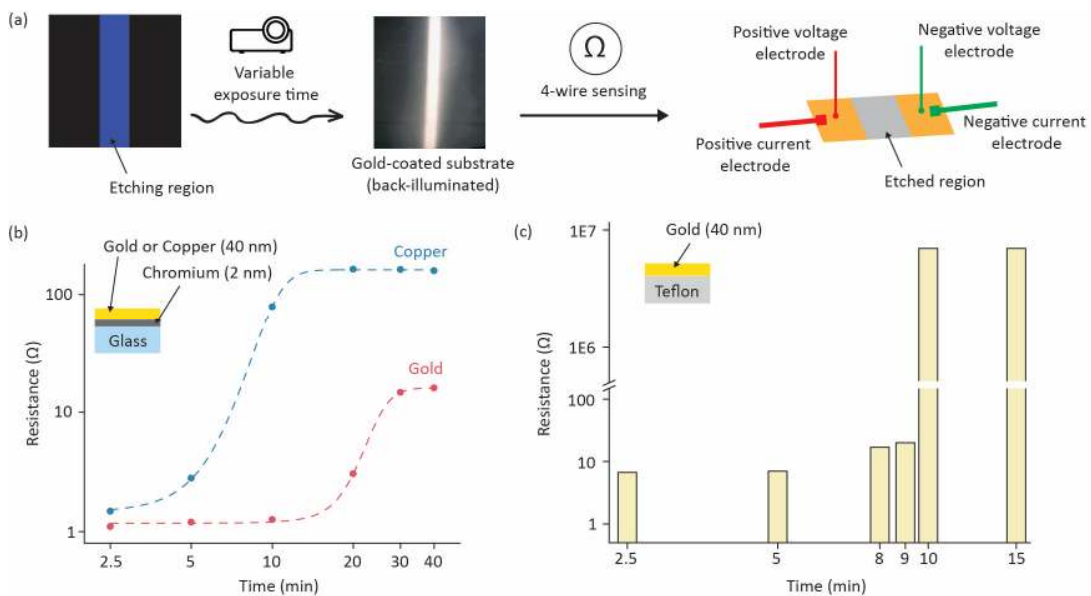


Figure 4: (a) Procedure to determine the etching rate of different substrates by measuring the resistance across a rectangular area etched with different exposure times. (b) Gold- and copper-coated glass slides exhibit an initially low etching rate, which then increases (faster in the case of

copper surfaces) and finally it settles on a constant value. (c) Gold-coated Teflon substrates show an increase in the etching rate and after approximately 10 minutes of light exposure a complete consumption of gold is achieved, leading to a full separation between the two regions of interest.

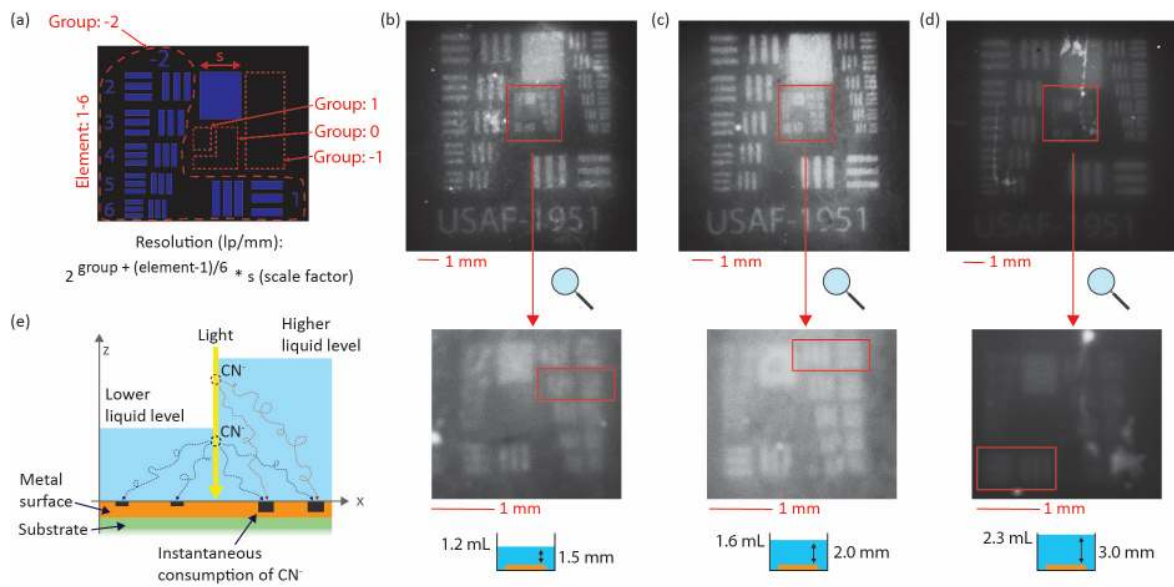


Figure 5: Study on the influence of the height of the liquid level above the gold-coated substrates. (a) Schematic of the “1951 USAF resolution test chart” that was used as a reference pattern. (b, c, d) The effect of three different liquid levels was compared by imaging the etched samples (back-illuminated) and identifying the smallest distinguishable set of lines. (e) Schematic representation of the diffusion transport for two different liquid levels.

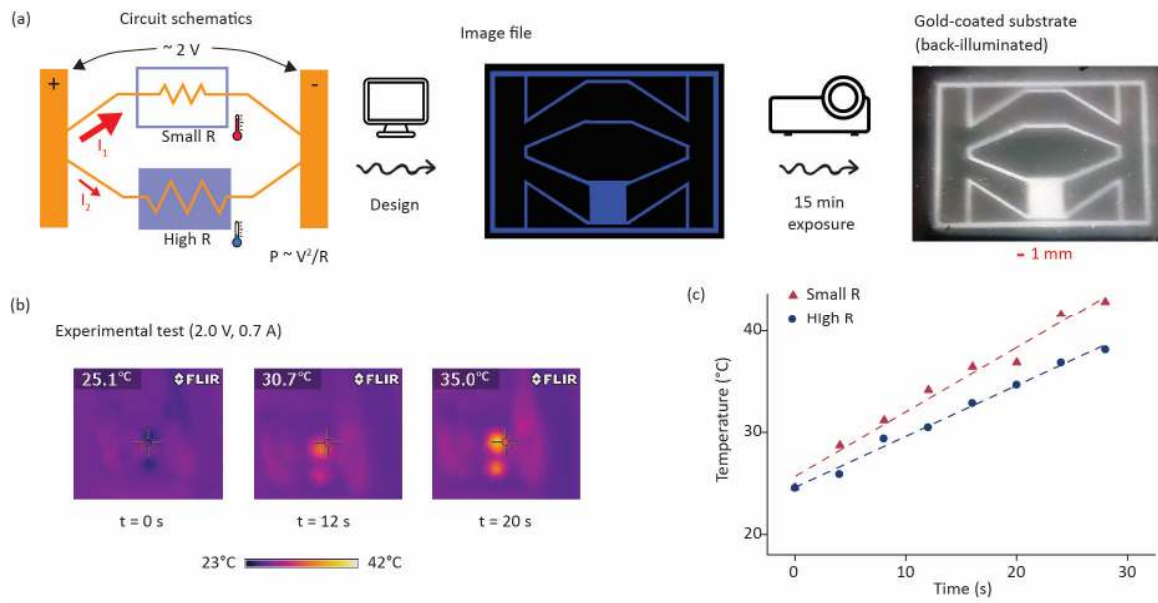


Figure 6: (a) Schematics of the fabrication procedure of a 2-zone differential heater by etching two areas of a sample with different intensities (by means of different colors in the design file) leading to regions with different metal thickness and electrical resistance. (b, c) With this heater, two samples can be heated up simultaneously at different rates.

Table 1: Comparison of different surface patterning techniques

	<b>Traditional photo etching (photolithography)</b>	<b>DLP-enabled PCB lithography</b>	<b>Inkjet printing</b>	<b>One-step DLP-based photolithography</b>
<b>Speed</b>	~ minutes (in an industrial setup) Several steps involved	Similar to photo etching	~ minutes	~ minutes
<b>Investment cost</b>	1000+ k\$ <sup>20</sup> (for industrial applications)  < 1 k\$ (for low-resolution or hobbyist applications)	Similar to photo etching (higher cost for low-resolution applications due to the UV-DLP)	< 1 k\$ <sup>21</sup>	< 1 k\$
<b>Equipment</b>	Industrial setup: Clean room, Mask aligners, Steppers, Direct writing tools, Wafer inspection tools, chemical etching facilities	DLP Sub-system and chemical etching facilities (as in photoetching)	Commercial inkjet printer, dedicated chemicals	Commercial DLP projector (with minor modifications), chemicals (simple and inexpensive)
<b>Sample preparation / post-processing</b>	Photoresist application, exposure, development, chemical etching	Similar to photo etching	Preparation of the paper (with a layer of activated carbon/carbon nanotubes) and the ink (ionic liquid/ultraviolet-cured triacrylate polymer-based solid-state electrolyte)	Preparation of the chemical solution (a few steps), exposure, final washing (in plain water)
<b>Feature size</b>	<0.1 $\mu\text{m}^2$	~10 $\mu\text{m}^4$	20-50 $\mu\text{m}^2$	<100 $\mu\text{m}$
<b>Challenges</b>	Several steps involved,	Similar to photo etching, Resolution (for	Substrate structure and ink chemistry <sup>23-25</sup>	Resolution, reproducibility

	chemical hazards, waste disposal <sup>22</sup>	high-end applications) <sup>22</sup>		
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## CONCLUSIONS

We have developed a one-step photolithographic process to transfer a pattern from a digital file to a gold-coated surface that requires only an inexpensive setup and a non-toxic potassium ferrocyanide solution. After investigating the effect of several working parameters, we have analyzed the etching rate on both glass- and Teflon-substrates and for both gold- and copper-coatings. We have demonstrated the potential for applications by realizing a simple 2-zone differential heater that is able to heat up two drops of fluid at different speed. Our setup is relatively simple to build and it does not require extensive training to be utilized.

## SUPPORTING INFORMATION

- “Supporting Information - One-step photolithographic surface patterning”: Additional figures and tables further describing the etching process and its characteristic and details about the diffusion simulation.

This information is available free of charge via the Internet at <http://pubs.acs.org/>.

## AUTHOR INFORMATION

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### **Author Contributions**

M.G. and W.S. conceived of the presented idea. M.G, W.S. and R.G. developed the theory, designed and performed the experiments, analyzed the data and contributed to the final manuscript.

## CONFLICTS OF INTEREST

The authors declare no competing financial interest.

## ACKNOWLEDGEMENTS

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