# An additive method for photopatterning of metals on flexible substrates

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**Abstract.** Here we present an additive and cost effective process for plastic electronic manufacturing. Metal tracks are fabricated on polyimide substrates via simple chemical processes combined with direct laser writing or photomask exposure. Laser write speed up to 0.5 $m.s^{-1}$ and metal track linewidth as low as 5 µm were achieved. Further, this process was easily extended to 3D manufacturing; a helical silver track was written onto a cylindrical substrate. Selective electroless plating was also demonstrated on the photopatterned microstructures which showed promising conductivity close to that of bulk silver metal.

**Keywords:** polyimide, laser, direct writing, 3D manufacturing, ion-exchange, silver, electroless plating, fine linewidth, flexible circuits, plastic electronics.

## 1. Introduction

Rapid, cost effective prototyping and manufacturing is gaining increasing attention amongst academic researchers and industries. This is driven by the future demands of customisable and low volume production of high technology devices. To meet these demands, some drastically different fabrication methodologies have emerged recently with the aim of replacing traditional techniques which are either time-consuming or lacking adaptability.

In the field of plastic electronic technology at present, various routes on a roadmap to a standard manufacturing process are being developed. One such route, presented in this paper, is an additive method for photopatterning of metals on polyimide flexible substrate that comprises a multitude of benefits. These include eliminating the use of evaporation or any vapour phase chemical precursors and therefore no vacuum chambers are needed. The reliance on photoresist processing or expensive stencil masks for printing and proprietary conductive paste or ink is also unnecessary.

The present method developed by our group utilised a photoreactive coating which upon illumination of light with suitable wavelength, assisted the photochemical reduction of silver ions on a polyimide substrate [1]. The silver ions were first incorporated into a thin depth of the substrate surface by potassium hydroxide (KOH) modification and then a simple ion-exchange process using a silver nitrate ($AgNO_3$) solution. After exposure to light, the silver ion source in the exposed area was reduced to metallic silver particles. The exposure can be carried out by laser direct-writing or via a photomask exposure system. Since the metalisation is a photochemical reduction process instead of a thermally driven mechanism, it has an advantage of allowing low energy fluence source to be used. Therefore ultra-fine resolution feature can be realised whilst the effects of excessive laser energy diffusion and thermal degradation to the substrates can be minimised.

After washing out the unreacted silver ions and an annealing step, the patterned silver particles serve as an active seed layer for subsequent electroless plating in order to produce a thicker layer with better conductivity.

The morphology of the laser written tracks and the effects of write speed are presented along with a demonstration of 3-dimensional fabrication. Also discussed are conductivity results of electrolessly plated microstructures, which were patterned with a photomask exposure system.

## 2. Experimental Setup

### 2.1 Substrate preparation

Kapton HN (50 µm) from DuPont was used as a substrate. After cleaning rinse steps of acetone, isopropyl alcohol and deionised water, this was treated in 1 M KOH at 50°C for 5 minutes to cleave the imide rings within the polymer matrix and allow potassium ions to bond electrostatically with the carboxylic acid ions. It was then immersed in 0.1 M $AgNO_3$ solution at room temperature

for 15 minutes, exchanging the potassium ions with silver ions. Samples were then spray-coated with 100 $g.l^{-1}$ methoxypolyethylene-glycol (MPEG) in absolute ethanol. This coating served as a reducing agent during the photopatterning step.

### 2.2 Direct laser writing exposure

The first photopatterning method was laser direct writing using a HeCd laser of wavelength 325 nm with Gaussian $TEM_{00}$ beam profile. The maximum available power at the writing plane was ~3 mW. Different focussing lenses were used to provide spot sizes ranging from a few microns up to approximately 35 µm. Various write speeds up to 0.5 $m.s^{-1}$ were employed.

### 2.3 Photomask exposure

Samples were also patterned using a Tamarack mask aligner UV-exposure system using a roughly collimated light source, emitting in the range 250 - 450 nm, for various times at an intensity of ~50 $mW.cm^{-2}$. A chrome on glass photomask was used, with the exposed areas forming the silver seed-layer regions.

### 2.4 Post-Exposure Treatment

After exposure the samples were submerged in 1% w/w sulphuric acid solution for 15 minutes to remove the unreduced silver ions from the substrate before annealing in an oven at 300 $^{o}C$ for various times. This step induced both the reimidisation of the previously cleaved imide ring and the agglomeration of silver nanoparticles.

### 2.5 Electroless Plating

The plating was carried out using two baths. The first was a formaldehyde EDTA based copper bath Circuposit 4750 sourced from Rohm & Haas. This bath was operated at a temperature of 53$^{o}C$ and a pH near 13. The second was a cyanide based silver bath ESM series (ESM 100 and ESM 500) from Polymer Kompositer AB, Sweden. This particular product was chosen as the less alkaline pH was more favourable for polyimide substrates. For plating, the bath was heated to 67$^{o}C$, and the pH was adjusted to values in the range of approximately 7 to 9.

### 2.6 Characterisation

Characterisation of the samples was carried out using optical microscopy using a Leica DM LM microscope, a Zygo white light interferometer, field emission gun scanning electron microscope (FEGSEM), scanning electron microscope (SEM) and a four-point probe station.

## 3. Laser Direct-Writing Results

### 3.1 Morphology

In the present direct-write approach, silver particles can be formed in situ during laser writing from the metal ion source in the substrate. The beam profile of the laser light can directly change the geometry of the written lines. Fine linewidth from less than 15 µm down (Figure 1) down to about 10 µm (Figure 2) have been demonstrated.

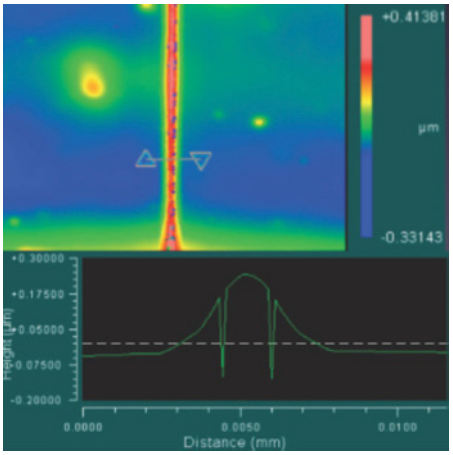



**Fig. 1** Zygo white light interferometry profile of a silver track directly metalised by CW UV laser scanning.

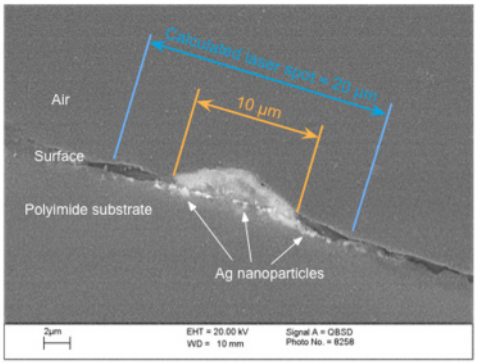
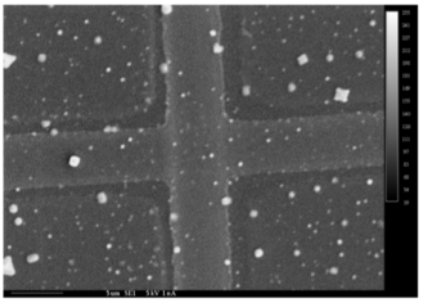



**Fig. 2** FEGSEM image of cross-section of laser written track.

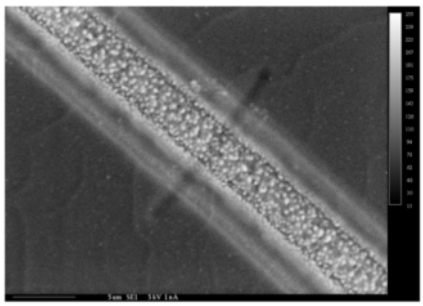
The white light interferometry profile above showed that silver aggregates were grown above the surface of the substrate from the $Ag^{+}$ ion source embedded within the substrate. This is believed to be the result of the extremely rapid nucleation of silver particles from the UV photoreduction of the $Ag^{+}$ ions. The height profile of the silver deposit mirrors the Gaussian shape of the laser intensity profile. A cross-section of a track was imaged by FEGSEM as shown in Figure 2. It can be seen that a thin layer of silver nanoparticles was formed just underneath the surface of the substrate. At the centre of the laser spot where the incident energy was most intense,

a much larger amount of silver aggregates were protruding from the surface of the substrate.

The SEM images (Figure 3) below showed laser direct-written tracks with ultra fine linewidth of ~5 µm demonstrated. The high magnification image (Figure 3b) clearly showed that the centre of the track consisted of a rough nanoparticle morphology with a particle size distribution between 100 – 700 nm. The shoulders of the Gaussian beam profile with a much weaker intensity caused a significantly slower rate of photoreduction of silver ions on both edges of the track, and hence a lower density of metallic silver present.



a



b

**Fig. 3** SEM images of: (a) laser direct-written tracks with linewidth ~5 µm; (b) high magnification image.

### 3.2 Effects of Write Speed

The effects of varying the laser write speed, and therefore the energy fluence, on the profile of the tracks were investigated (Figure 4). It was found that at higher write speeds such as 10,000 $\mu m.s^{-1}$, a uniform, reflective silver track with straight track edges was formed. At slower write speeds, it can be observed that the silver at the centre of the track became discontinuous islands or disappeared completely. This phenomenon could be attributed to the excessive laser energy at such slow write speeds causing degradation of the polymer substrate underneath the silver. The silver nanoparticle sufrace morphology at the track centre serves as a catalyst to initiate electroless plating. Figure 5 shows a microcoil plated with the electroless copper bath.

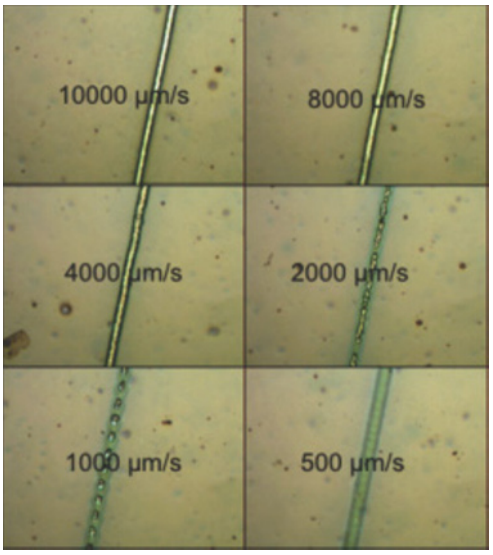



**Fig. 4** Microscope images of tracks produced by different laser writing speeds

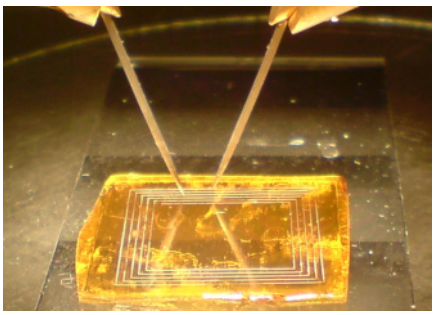


**Fig. 5** An electroless Cu plated micro-coil fabricated by laser direct-writing.

### 3.3 3-Dimensional Direct-Writing

The direct-writing method presented here uses a dry photoreactive coating and was carried out simply in an air atmosphere. Since no evaporation or lamination steps are required in the entire fabrication process, it allows the flexibility for the photopatterning to be carried out on contoured or 3-dimensional (3D) surfaces. A long helical metal track on a cylindrical polyimide substrate was fabricated by laser direct-writing whose setup is shown in Figure 6. A fine linewidth track of 15 µm was directly written on a 1 cm diameter polyimide cylinder, with a helix spacing of about 0.1 cm. A continuous coil of 20 turns was demonstrated, shown in Figure 7. This 3D patterning technology is envisaged to enable the manufacturing of advanced 3D interconnection for packaging. The process lends itself to low cost manufacturing of planarised or 2.5D structures such as spiral inductors or interdigital elements used in components such as capacitors or inter-digital electrodes.

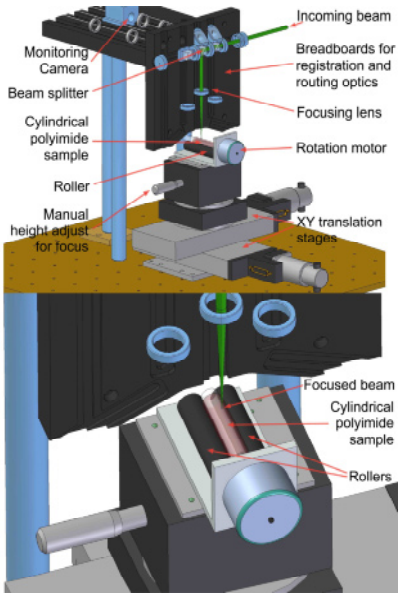



**Fig. 6** Schematic diagram of the 3D laser writing set up.

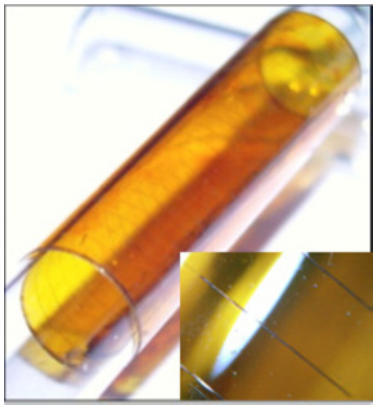


**Fig. 7** Long silver helix track fabricated by a laser on glass pipette coated with a polyimide film. Inset showed magnified image of the track with a linewidth ~15 µm.

### 3.4 Photomask Exposure and Plating Results

Electroless plating was applied to grow a conductive silver layer on microstructres as shown in Figure 8. Samples were immersed in the bath for approximately 6 minutes, until the plated layer was visibly distinguishable to the naked eye. Plating heights of ~2 µm were produced. Using the resistance measured by a probe station the resistivity, $\rho$, was found by:

$$\rho = R\frac{A}{l} \quad (1)$$

where $A$ and $l$ are the cross-sectional area and length of the measured section respectively and $R$ is the measured resistance. A value of $7.6 \times 10^{-7}$ Ω.m was measured between the points shown in Figure 8. This value is an order of magnitude higher than that of bulk silver ($1.59 \times 10^{-8}$ Ω.m). However, the parameters of the bath can be optimised to improve the plated silver quality. The ESM bath was found to produce more consistent plating in terms of selectivity and under/over-plating compared to the Circuposit Cu bath in the present process.

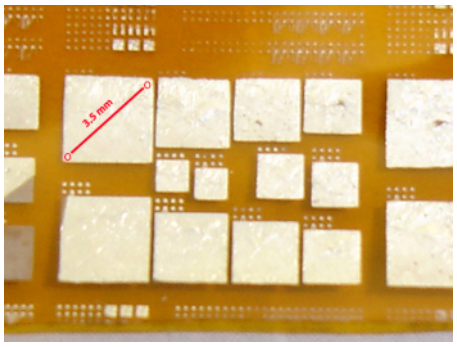



**Fig. 8** Image showing the microstructures plated with electroless Ag. Red line indicates points of resistivity measurement.

## 4. Conclusion

The present process is easy to use, requires low cost raw materials, does not require sophisticated equipments and due to its additive nature is low on waste materials. Feature sizes as small as ~5 µm have been demonstrated.

Further advantages are that process can be easily adapted for 3-D manufacturing, reduced processing steps leading to quicker turnover times, and the amount of proprietary products (photoresist material, developer solution, conductive paste or ink) required is minimized.

The less alkaline ESM bath was found to produce more consistent results due to the pH sensitivity of polyimide [2]. The bath was also more configurable, therefore more suitable during process development as well as showing promising conductivity and selectivity during initial tests.

## Acknowledgement

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## References

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