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Letters

Selective metallization on glass surface by laser direct writing combined with supersonic particle deposition

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ABSTRACT

Selective metallization on glass surface technique has lot of potential applications in optoelectronics. Particularly, ultra-fine copper lines provide better optical transparency, which may enable to meet the demands of novel optoelectronic devices. In this paper, we propose a new manufacturing procedure to overcome the limitations of the traditional process and to achieve narrower copper lines on the glass surface. We, first, irradiate the glass surface by the femtosecond laser for more precise ablation, and then deposit the silver nitrate particles onto the irradiated region by using a supersonic particle deposition system. Copper lines with a linewidth of 1 μm were achieved by means of this new procedure, which is, to best our knowledge, the narrowest linewidth ever reported so far using laser direct writing and the subsequent electroless copper plating. We also demonstrate a highly transparent heater (i.e., 97% optical transparency) as an application of the proposed manufacturing approach.

1. Introduction

Laser direct writing (LDW) technology and selective metallization on transparent materials have been widely studied over the last decades owing to its potential applications in the automotive industry, sensors, antennas, photovoltaic cells, etc. [1–3] The major advantages of this method include design flexibility, mask-free procedure, and, large-scale application feasibility [4].

The conventional laser selective metallization begins the deposition of seed material onto the targeted substrate and then followed by laser irradiation [5,6]. The conventional method, however, has serious limitations for micro and mesoscale fabrication; which are the nonuniform seed material distribution, limited seed material involved in the plating process, and limited metal seed on the groove formed after laser ablation [7,8]. The coating methods reported so far have a considerable amount of nonuniformity in thickness and material distribution. The nonuniform distribution of seed material negatively affects the quality of the laser machining process especially when the laser fluence is close to the ablation threshold. This phenomenon results in some non-laser-ablated regions, causing failure to achieve conductive narrow copper lines.

In this research, we propose a new procedure to overcome these limitations of the traditional process. Compared to the conventional method, our technique is independent of the interaction between laser and coated material owing to the decoupled spraying process followed by laser irradiation. Therefore, our approach provides more seeds with uniform distribution onto the substrate enabling fabricating deeper grooves with repeated laser scanning without damaging the seed materials.

Another key feature of this research is to employ the supersonic particle deposition system (SPD) in the LDW technology. The SPD of nanomaterials provide better resultant coating properties owing to the high impact velocity [9]. The SPD is also a cost-effective, scalable, and versatile coating technique offering a fast deposition rate [9,10]. As such, we utilize the SPD in the laser-assisted metallization of the borosilicate glass surface. To best of our knowledge, we are the first to employ the SPD after the LDW process. We also show a transparent heater as an application by utilizing the described manufacturing approach. The main objective of this study is to introduce and study the selective electroless metallization of the glass surface using a new manufacturing route that integrates laser direct writing and supersonic particle spraying.

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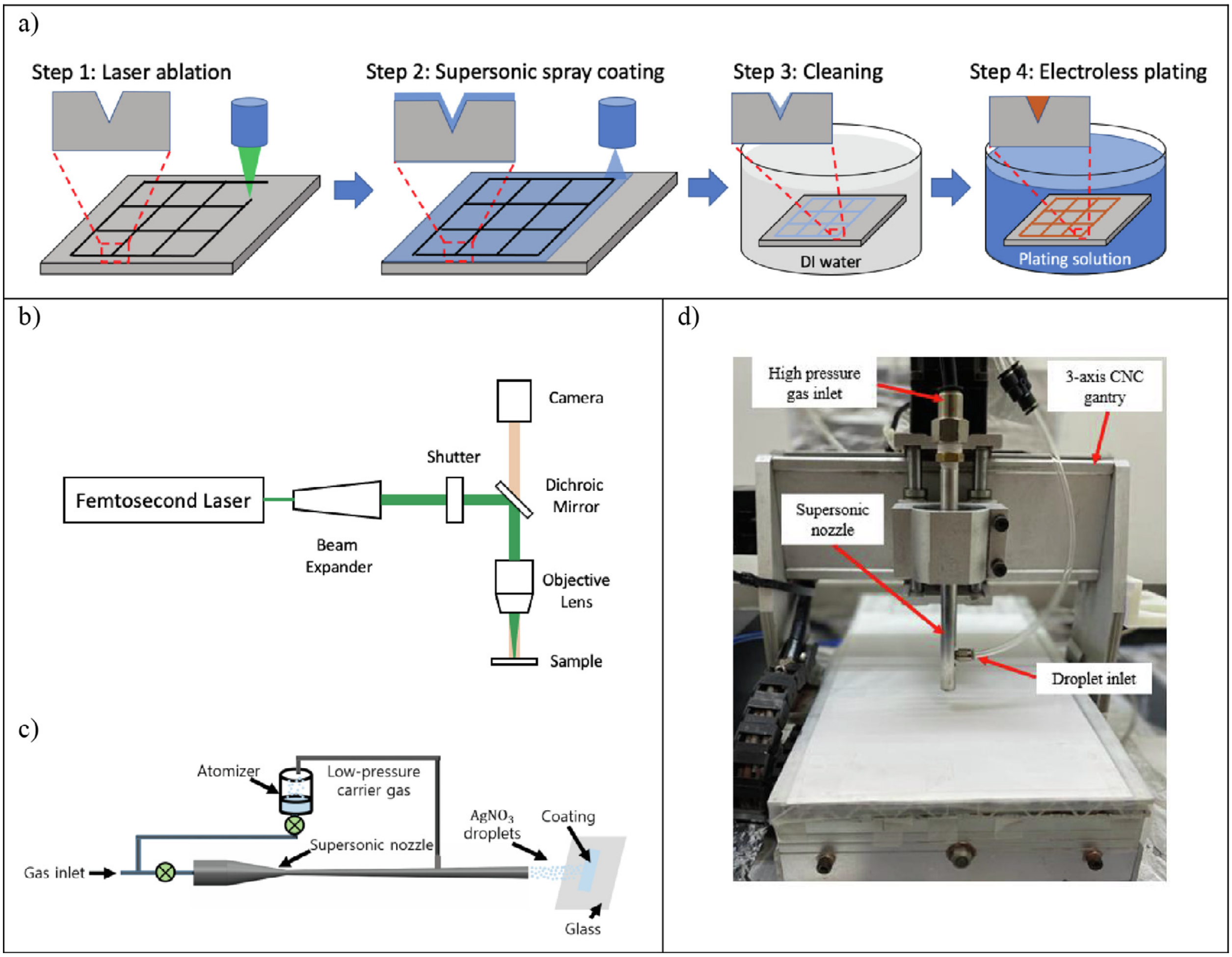

Fig. 1. Schematic of (a) the fabrication procedure, (b) the laser setup, (c) the supersonic spray deposition system; (d) experimental setup of the spray deposition system.

2. Experimental details

Fig. 1a shows the fabrication procedure of the described new approach for glass surface metallization. It includes LDW of the glass with the femtosecond laser, the SPD of silver nitrate ($AgNO_3$) onto the glass surface, and selective electroless copper plating (ECP) of the laser-ablated region, respectively. The details of each step are discussed in the following sections.

2.1. Femtosecond laser direct writing

A glass slide having a thickness of 1 mm was used as the substrate. The LDW process was conducted using a femtosecond laser system (04-1000, CARBIDE) at the second harmonic (515 nm) laser wavelength. Fig. 1b shows theschematic of the laser machining system. Laser parameters were chosen to minimize redeposition of debris, thermally affected zone, and linewidth of groove but to provide uniform result even with slight aligning errors. Pulses with a pulse duration of 229 fs, 60 kHz repetition rate, and laser power of 5.2 mW resulted in 1 μm linewidth groove (See Fig. 2a) on the surface.

2.2. Supersonic spray deposition

The $AgNO_3$ solution (i.e., active nanomaterial solution) was prepared at room temperature by dissolving the $AgNO_3$ in the deionized (DI) water and then diluting it with ethanol to obtain a final concentration of 12.5 mg/mL in 6.25% water, and 93.75% ethanol. All chemicals were purchased from Sigma-Aldrich (St.Louis, Mo) and were used as received without further purification. The deposition of $AgNO_3$ onto the laser-ablated glass surface was then carried out using a supersonic spray system as schematically shown in Fig. 1c. The spray deposition system mainly consists of a convergent-divergent nozzle, an atomizer, the high-pressure driving gas flow inlet, and the low-pressure carrier gas flow inlet sections. In the deposition process, the $AgNO_3$ solution is first atomized into the microscale fine droplets. The atomized droplets are then transported to the divergent section of the nozzle by the low-pressure carrier gas flow. Finally, the high-pressure gas flow expands in the nozzle and accelerates the droplets to supersonic velocities onto the glass surface, which allows to deposit/impinge the droplets into the laser-irradiated grooves. The image of the experimental setup, the dimensions of the nozzle, and the operating parameters used in the experiments are presented in Fig. 1d and Table 1, respectively.

2.3. Electroless copper plating (ECP)

Following the supersonic spraying, the glass samples were cleaned in the ultrasonic bath for 5 min to remove the residuals and then dried with airflow. The electroless copper plating (ECP) bath was prepared at room temperature using the recipe given in Ref. [11] by only changing the amount of potassium ferrocyanide (200 mg/L) and formaldehyde (15 ml/L) to make the process more

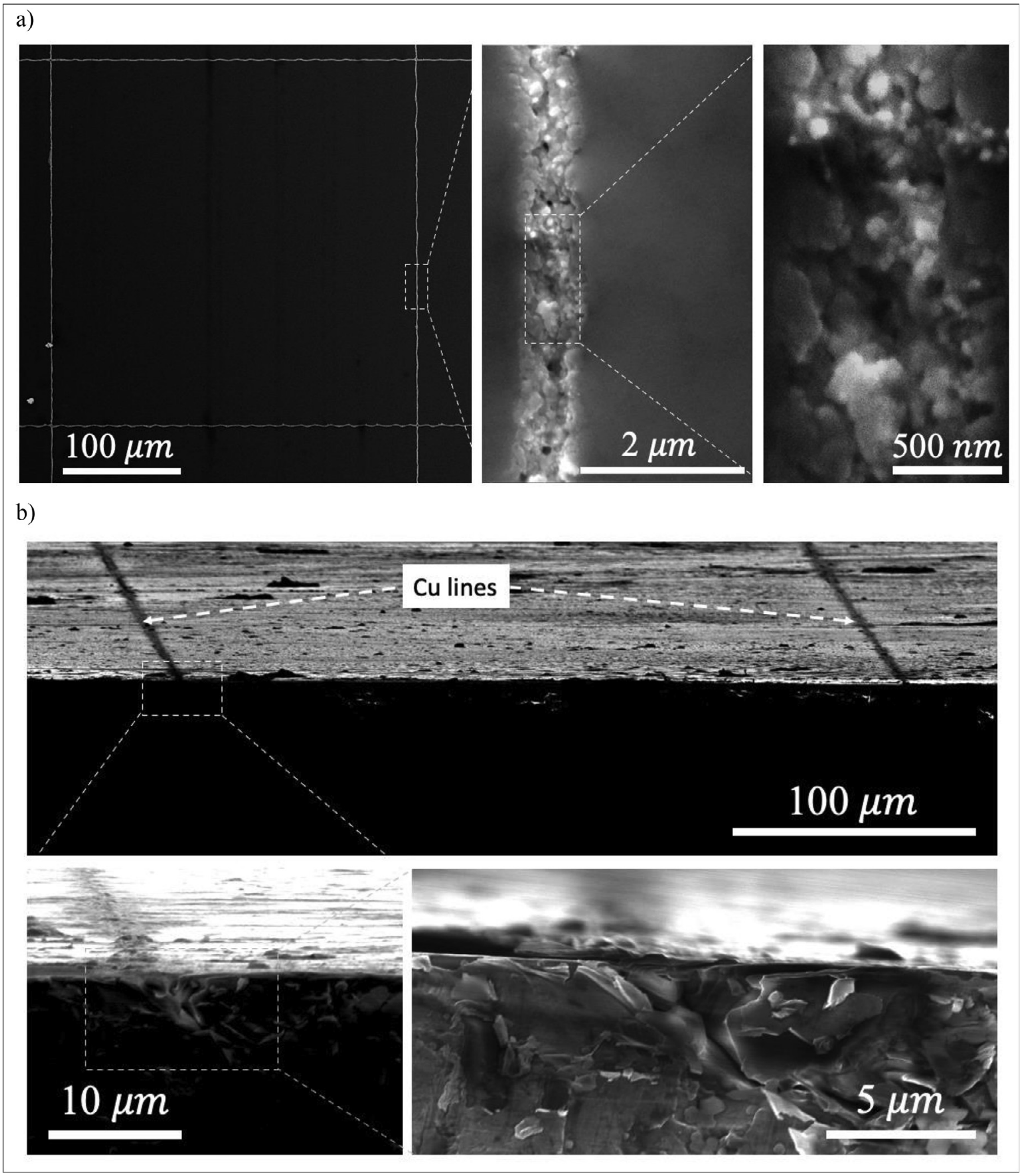

Fig. 2. SEM images of the copper grid: a) surface view, b) cross-sectional view.

Table 1
Nozzle dimensions and supersonic particle deposition process parameters.

Nozzle dimensions	Value	Process parameter	Value
Nozzle inlet diameter (mm)	7	Droplet injection diameter (mm)	2.4
Nozzle throat diameter (mm)	4.5	Driving gas inlet gauge pressure (kPa)	700
Nozzle outlet diameter (mm)	6.5	Carrier/atomizer gas inlet gauge pressure (kPa)	35
Convergent length (mm)	50	Nozzle stand-off distance (mm)	5
Divergent length (mm)	130	Nozzle transverse speed (mm/min)	1000

stable. The samples were vertically located and evenly spaced in the ECP bath, and plated for 30 min and then cleaned in the ultrasonic bath for 5 min, respectively.

2.4. Characterization

The morphology and cross-section of fabricated copper layers were observed by the SEM (Phenom Desktop SEM). A red LED (Thorlabs, M625F2) working at 625 nm wavelength and a power meter (Newport 1918-C and 918D-UV-OD3) were used to measure the transmittance of the grid, and the four-point probe (Jandel, RM3-AR) was used to measure the sheet resistance. The mechanical

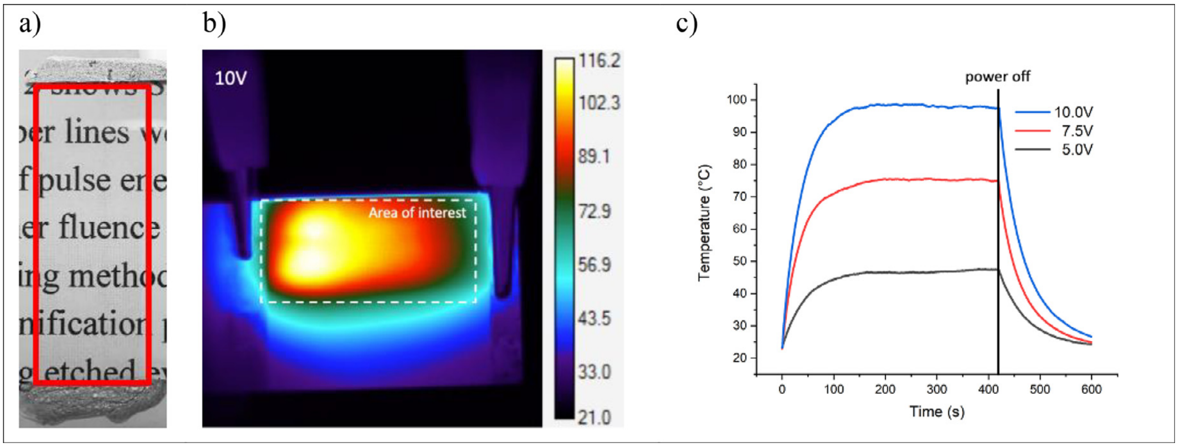

Fig. 3. a) Optically transparent heater, b) A thermal camera image. (The average temperature inside the area of interest is 97.6°C), c) The temperature profile of the heater for different voltages.

adhesion was also tested using a repeated adhesive Scotch tape test, sandpaper, and polishing with sandpapers and a metal scraper. For a transparent heater, a DC generator (AV Prime) was used for power supply, and an infrared thermal imaging camera (FLIR A325sc) was utilized for temperature changes and distributions recording.

3. Results and discussion

Fig. 2 shows SEM images of selectively plated copper lines on the glass surface. Uniform copper lines having a linewidth of 1.0 μm with an aspect ratio of 1.5 were successfully achieved on the glass surface. To obtain these narrow linewidth, 5.2 mW of laser power and 40× (Zeiss EC Plan-NEOFLUAR, 0.75 NA) focal lens was used. To best of our knowledge, it is the narrowest copper linewidth ever achieved by using the LDW method and subsequent electroless copper plating.

A grid pattern was chosen to show the uniform and continuous copper fabrication using the proposed method. The size of the grid is 10 mm ×30 mm with 300 μm spacing as shown in Fig. 2a. The 300 μm spacing was determined to provide high optical transmittance. The metal grid transmitted 97% of the perpendicularly incident light. When the underlying glass substrate was considered, it lowered to 89%, but still highly transparent and imperceptible with bare eyes [12]. In addition to high transparency, the fabricated copper grid structure also has a low sheet resistance of 0.125 Ω/sq. Moreover, the electrical resistivity was calculated as $1.29 \times 10^{-7}\Omega \cdot m$, which is one order higher than the bulk resistivity of copper (i.e., $1.68{\times}10^{-8}\Omega \cdot m$). The obtained electrical conductivity is higher than the commercial ITO and FTO coated glass and copper ink-jet printed glass [13].

A comprehensive optoelectronic performance analysis of the fabricated grid was also conducted by using the figure of merit (FoM), which is the ratio of electrical conductance to optical conductance [14].

$$FoM = \frac{\sigma_{dc}}{\sigma_{opt}} = \frac{188.5}{R_s \times \left(\frac{1}{\sqrt{T}} - 1\right)} \tag{1}$$

where R_s is the sheet resistance and T is optical transmittance. Our copper grid achieved a FoM of $2.4{\times}10^4$, which is among the highest reported values for the electroless plated copper grid on the glass [15].

Besides, the mechanical adhesion performance of the fabricated copper grid was qualitatively evaluated by Scotch tape test, sand paper, and even polishing with sandpaper and metal scraper. Those tests helped to remove the over-plated copper, but barely damaged copper lines embedded into the grooves. This strong adhesion is likely attributed to the anchoring effect between metal seed and rough surface after laser ablation.

A transparent heater, as shown in Fig. 3a, was designed as a practical application of the described manufacturing approach. The silver paste was applied on both ends of the grid to serve as electrodes. The input voltages of 5, 7.5, and 10 V were applied respectively to the electrodes. Fig. 3b and c show the thermal image and temperature changes over time. It takes approximately 150 s to reach the highest temperature and 150 s to completely cool down. The fabricated transparent heater has a potential to be employed on a car windshield or a motorcycle visor, and it could accelerate defogging or defrosting process with a input voltage under 12 V, which is the standard voltage for cars and motocycles.

4. Conclusion

We introduced a new manufacturing approach for selective metallization on glass surface by combining laser direct writing technology with supersonic particle spraying. Through the described method, copper lines with a linewidth of 1.0 μm and a high FoM of $2.4{\times}10^4$ were achieved. These ultra-fine copper grids allowed to achieve a highly transparent heater (i.e., 97% optical transparency) as an application of the proposed method. Both are state-of-the-art results and still have room for improvements by optimizing laser parameters and fabricating grooves with a higher aspect ratio.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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