An Integrated Method for Selective Metallization on Glass Surface: Laser Direct Writing Coupled with Supersonic Spray Coating

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Abstract

Surface metallization on glass surface has the potential in optoelectronics, microelectronics, and microfluidic applications. Previously, laser direct writing (LDW) technology combined with subsequent copper plating process has been widely applied to glass metallization. The traditional LDW method, however, has important limitations to metalize the deep internal walls of the laser-irradiated regions, and to achieve narrow electrodes (<5 μm) with uniform thickness. Nonuniform seed material coating on the glass surface and evaporation of as-coated seed material (*e.g.*, silver nitrate, silver nanowire) during the laser irradiation are mainly responsible for poor quality resultant electrodes. In this study, we report a new approach for glass metallization by coupling the femtosecond laser writing with supersonic spray coating. The method includes three steps: (i) femtosecond laser irradiation of the glass surface, (ii) supersonic spray deposition of the atomized seed material (*i.e.*, silver nitrate droplets) onto the irradiated regions, (iii) selective electroless copper plating. The laser irradiation process is independent of as-coated layer uniformity unlike the traditional LDW, which provides more precise laser ablation on the bare glass surface. Moreover, supersonic spray coating, owing to the high-impact velocity of the spray flow, allows seed material droplets to impinge on the deeper internal walls of the irradiated regions, resulting in uniform, precise, and compact electrodes. The results show that the copper electrodes having a linewidth of 708 nm with high electrical conductivity ($7.75 \times 10^6\ \Omega^{-1}.\mathrm{m}^{-1}$) can be achieved by using the proposed approach, which has the potential for lab-on-a-chip applications.

Keywords: Copper electrode, Glass, Laser direct writing, Metallization, Spray flow, Supersonic nozzle

1. Introduction

Laser direct writing (LDW) technology has been widely studied for selective metallization on glass surfaces due to its advantages including design flexibility and mask-free procedure. This technology has potential applications in optoelectronics, micro-electronics, and lab-on-a-chip applications **[1-3]**.

Many procedures have been developed to enhance the quality of metallic patterns, the adhesion force between the substrate and plated patterns, and electric conductivity. Typically, two-step methods (*e.g.,* traditional LDW) have been widely used owing to their strong mechanical adhesion performance over one-step methods such as laser-induced chemical liquid deposition, which also requires a post-annealing process to improve the adhesion performance **[4]**.

The traditional two-step methods begin with seed material deposition on the target surface, and it is followed by laser irradiation and electroless plating. Applying to seed material deposition as the first step in LDW leads to poor quality electrodes (*i.e.*, poor adhesion, poor electrical conductivity). Moreover, it limits to achieve narrower lines (<5 μm) due to as-coated seed material evaporation during the laser irradiation, resulting in a non-uniform seed layer onto the glass surface.

In this study, we introduce a new procedure for the first step (*i.e.*, deposition of seed material) of the typical glass surface metallization to address the issues described above. Traditionally, dip coating is an ordinary way of preparing a thin film of the seed layer (*e.g.*, silver nitrate) on a glass surface before the focused laser irradiation **[5]**. Inherent nonuniformity of the dip-coating process hinders achieving uniform and high-quality micro/mesoscale electrically conductive patterns on the glass surface.

In the proposed approach, as shown in Fig.1, we replace the dip coating with the atomization-based supersonic spray coating and place the spray coating process right after the laser irradiation. Supersonic spraying, owing to its high-impact velocity, can deposit/impinge the silver nitrate ($AgNO_3$) droplets on the deep internal wall of the glass surface, allowing narrower, uniform, and compact electrodes. Moreover, it is a fast, scalable, and cost-effective nanomaterial deposition method **[6]**. The supersonic spraying process is then followed by the subsequent cleaning and electroless plating steps, which are the same as the way used in the traditional LDW.

2. Materials and methods

In this section, first, we describe the materials used in the experiments. Each step (*i.e.,* laser direct writing, spray deposition, plating) is then outlined and discussed.

2.1. Materials

All the chemicals were purchased from Sigma-Aldrich (St.Louis, Mo) and used without further purification. Silver nitrate ($AgNO_3$) solution was prepared at room temperature by dissolving the $AgNO_3$ powders in the deionized (DI) water and diluted with the ethanol to a final concentration of 12.5 mg/mL in 6.25% DI water, and 93.75% ethanol. Electroless copper plating (ECP) bath was prepared based on a published study **[7]**. The 200 mg/L of potassium ferrocyanide and 15 ml/L of formaldehyde were used to make the ECP process more stable.

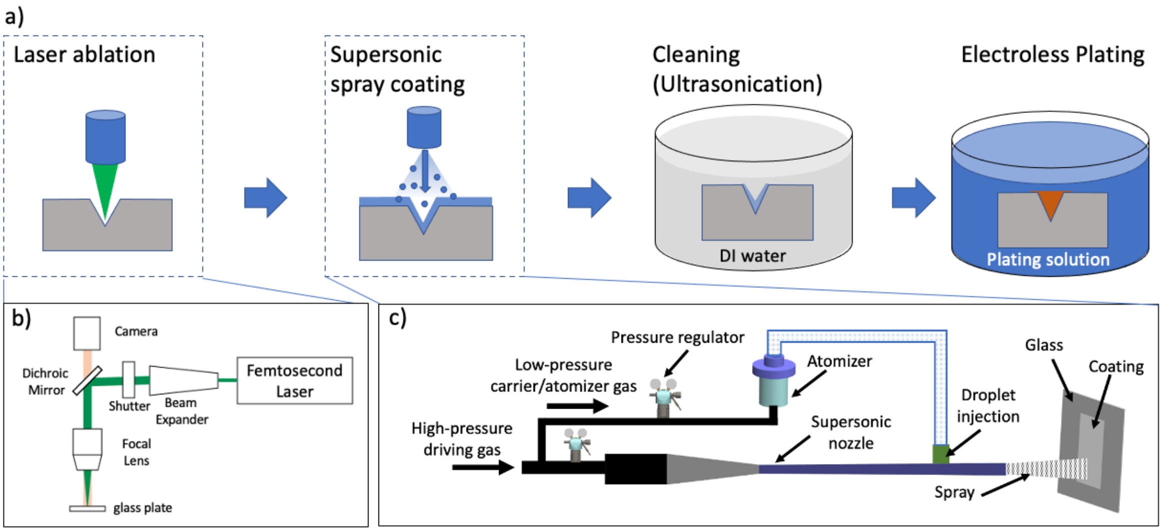

Fig.1 (a) Schematic of the suggested fabrication procedure, **(b)** laser setup, **(c)** supersonic spray coating setup.

2.2. Laser direct writing

A femtosecond laser system (04-1000, CARBIDE) with 515 nm center wavelength and 229 fs of pulse duration was used. Owing to its ultra-fast and ultra-short pulse, femtosecond laser ablation enables fabricating narrow and deep grooves with rough surfaces on glass plates. The laser pulses with 4W of maximum power and 60 kHz repetition rate were enlarged up to five times and guided to the focal lens using silver-coated metallic mirrors. Fig. 1b shows the schematic of the laser setup.

2.3. Supersonic spray coating

In this section, first, the supersonic nozzle used in the experiments is described. The flow behavior of continuous phase (*i.e.*, high-pressure driving gas) was investigated via computational fluid dynamics (CFD). The experimental setup of the spray is introduced.

2.3.1. Nozzle configuration and flow domain

A convergent-divergent nozzle (*i.e.*, de Laval nozzle) was designed to accelerate the droplets to supersonic velocity onto the glass substrate. Fig.2a schematically shows the nozzle geometry with its dimensions. Fig.2b presents the flow domain used in the numerical simulations.

The flow domain was extended from the nozzle exit section (*i.e.*, 100 mm axially, 30 mm radially) to apply the outlet boundary condition and analyse the flow profile at the nozzle outlet. The domain was discretized using the structured elements with the cell number of 122500 to ensure the grid-independent result. A two-dimensional axisymmetric model was applied to reduce computational cost. Pressure and temperature inlet were used as the inlet boundary conditions and were set to 0.7 MPa (gauge) and 298 K, respectively. An adiabatic wall with no-slip boundary conditions was applied at all sides of the nozzle and the substrate. The pressure outlet boundary condition (P_0=1 atm) was applied at the nozzle exit.

2.3.2. Governing equations

The Eulerian approach was used to simulate the continuous gas phase. Air was chosen as the driving gas and the ideal gas law was used to consider the compressibility effects. The governing equations of a two-dimensional steady compressible flow can be written as follows:

Continuity equation

$$\frac{\partial(\rho u_i)}{\partial x} = 0 \quad (1)$$

Momentum equation

$$\frac{\partial(\rho u_i u_j)}{\partial x} = -\frac{\partial P}{\partial x} + \frac{\partial(\tau_{ij})}{\partial x} \quad (2)$$

Energy equation

$$\frac{\partial(\rho e u_i)}{\partial x_i} = -\frac{\partial P u_i}{\partial x_i} + \frac{\partial(u_j \tau_{ij} - q_i)}{\partial x_i} \quad (3)$$

Equation of state

$$P = \rho R T \quad (4)$$

where ρ, u, e, P, T, τ, q, R are the gas density, gas velocity, internal energy, pressure, temperature, viscous shear stress, heat flux, and ideal gas constant, respectively. The realizable k-ε turbulence model was used to model the turbulence flow. The details of the realizable k-ε turbulence model can be found elsewhere **[8]**.

2.3.3. Numerical Simulation

Numerical simulations were performed utilizing ANSYS-FLUENT V19.1 software to predict the turbulent gas flow field. The governing equations were solved using a steady-state pressure-based solver. Fig.3a and Fig.3b show the contour plots of gas velocity and Mach number inside and outside of the nozzle, respectively. As can be seen, the spray flow is correctly-expanded (*i.e.*, the shear layer expands freely from the nozzle). A maximum Mach number of 2.1 was achieved using the described nozzle design and boundary conditions. Moreover, the impact velocity of the spray flow is 530 m/s at the exit of the nozzle. Fig.3c also shows the gas velocity and Mach number profile along the nozzle axis. The gas flow expands in the divergent section of the nozzle, reaching supersonic velocities.

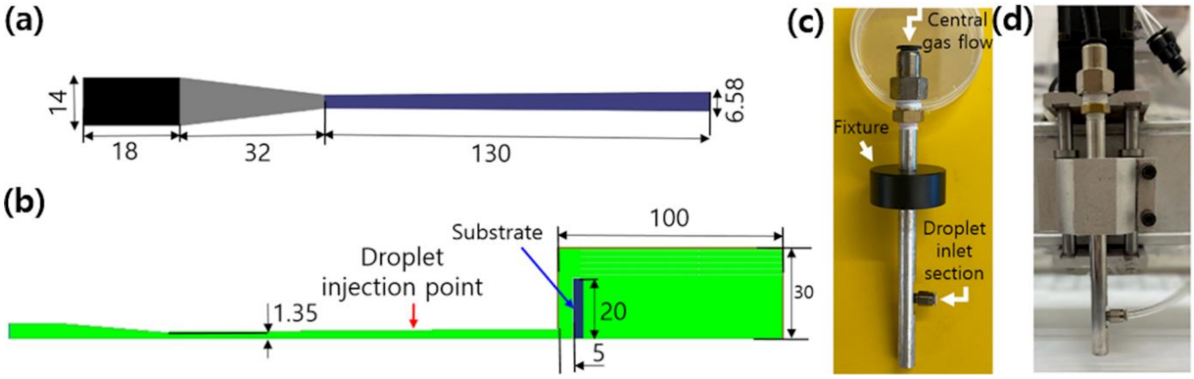

Fig.2 (a) Configuration of the nozzle, **(b)** Computational domain, **(c)** The manufactured nozzle, **(d)** Experimental setup with the nozzle mounted on a 3-axis CNC router (All dimensions are in mm).

Table 1
Spray parameters used in the experiments.

Parameter	Value
Driving gas inlet pressure (kPa)	700
Driving gas inlet temperature (K)	298
Atomization pressure (kPa)	35
Nozzle stand-off distance (mm)	5
Nozzle transverse speed (mm/min)	1000

2.3.4. Spray experimental setup

The nozzle was manufactured by wire electrical discharge machining to be used in the coating experiments. Fig.2c and Fig.2d show the nozzle including its important sections. Moreover, Fig.1c illustrates the spray setup.

In the spray experiments, first, the $AgNO_3$ solution was atomized into microscale droplets using a pneumatic jet nebulizer. The droplets are then carried to the divergent section of the nozzle through a low-pressure carrier gas flow**.** The high-speed central gas flow accelerates the droplets onto the glass surface, resulting in a uniform coating on the laser-irradiated regions. As such, the droplets can impinge to even deep internal walls of the laser machined glass surfaces owing to the high-impact velocity of the droplets. Hence, the precise electrodes with high electrical conductivity and adhesion strength can be obtained after the plating process.

The spray process parameters used in the coating experiments are listed in Table 1. The nozzle was mounted on a 3-axis CNC gantry to precisely control the coating process. Through this setup, advanced control on the spray deposition process can be applied by tuning the atomization process (*i.e.*, droplets size, droplets flow rate), central gas flow (*i.e.*, gas pressure, gas temperature), and spray kinematics (*i.e.*, nozzle speed, nozzle stand-off distance).

2.4. Plating

The as-sprayed glass samples were cleaned in the ultrasonic bath for 5 minutes to remove the residuals. The electroless copper plating (ECP) process was conducted at room temperature for 30 minutes by placing the glass samples vertically in the ECP bath. The plated samples were then rinsed in the ultrasonic bath for 5 minutes.

3. Results and discussions

The electrode obtained with a narrow linewidth, which is one of the advantages of the proposed new method, is shown in Fig.4a. The linewidth was measured by a Phenom Desktop SEM. We achieved

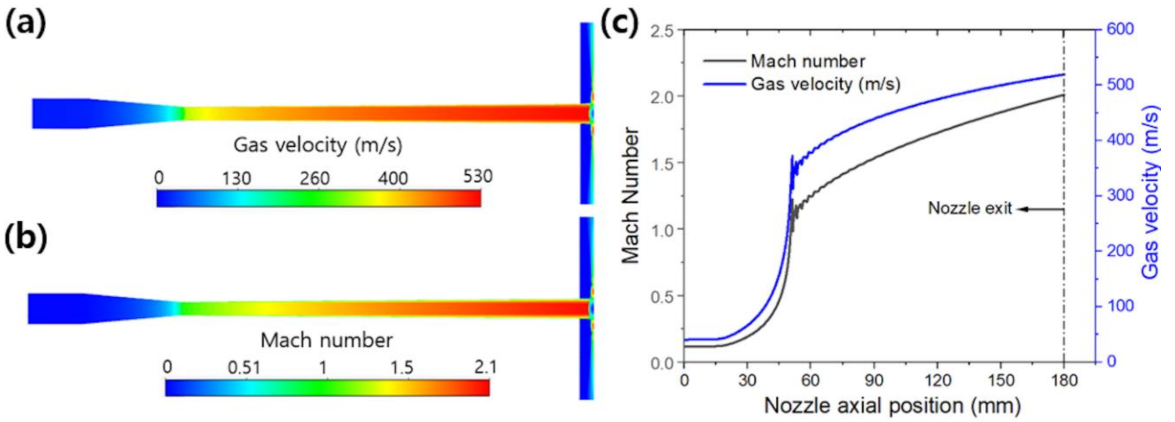

Fig.3 (a) Contour of gas velocity, **(b)** Contour of Mach number inside and outside of the nozzle, **(c)** Gas velocity and Mach number profile along the nozzle axis.

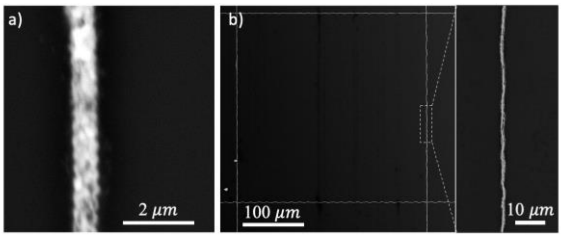

Fig.4 SEM images of plated copper lines: **(a)** narrowest linewidth of 708 nm, **(b)** copper grid with 1 µm linewidth and 300 µm spacing.

the copper electrode having a linewidth of 708 nm, which is the narrowest result ever reported so far to best of our knowledge by using the laser direct writing method. To obtain this result, 4.6 mW of laser power and a focal lens with high NA (Zeiss EC Plan-NEOFLUAR, 0.75 NA) were used. Focusing laser beam directly on the bare glass surface was one the of major factors for this precise laser machining.

To apply these narrow copper lines in real applications, a uniform plating result must be guaranteed. Uniform distribution of seed using supersonic spray helps to accomplish uniform copper plating minimizing over or under the plated copper layer.

We fabricated a 10 mm x 30 mm grid pattern on a glass plate with 1 µm linewidth and 300 µm spacing to show the uniformity of our new method. Fig.4b demonstrates the grid pattern we fabricated and its uniformity visually. All four corners are electrically conductive to each other, meaning that the continuous copper lines are well-plated from end to end.

Moreover, the optical transparency of the fabricated electrode layer was investigated by using a basic equation given below **[9]**;

$$Optical\ Transparency = \left(\frac{\ell}{w+\ell}\right)^2 \qquad (5)$$

where w is linewidth and ℓ is space between lines. At 625 nm, the measured optical transparency of this grid is 97% and it matches well with the theoretical value. Transparent and conductive characteristics of the fabricated electrode layer could be used in many applications including transparent antenna, windshield heaters, and touch sensors.

Interfacial mechanical adhesion was also tested and verified by an ultrasonication in DI water, Scotch tape test, and sandpaper. The results show that the proposed procedure offers strong mechanical adhesion performance. Porous structure on glass plates induced by laser pulses leads to high adhesion force between substrates and plated copper patterns by anchoring effect **[2]**.

4. Conclusion

An integrated manufacturing approach (*i.e.*, LDW coupled with supersonic spray coating) for surface metallization on glass surfaces was introduced. Femtosecond laser irradiation of bare-glass surface allowed to obtain precise micro/mesoscale patterns on the substrate surface. The subsequent supersonic spraying process enabled to impinge atomized $AgNO_3$ seed droplets on even deep internal walls of the laser-irradiated glass owing to its high-impact velocity. Moreover, a numerical study was conducted to investigate the supersonic spray flow inside and outside of the nozzle. Through the described manufacturing method, narrower (*i.e.*, linewidth of 708 nm), uniform, and high electrically conductive ($7.75 \times 10^6\ \Omega^{-1}\mathrm{m}^{-1}$) copper electrodes were achieved on the glass surface. The proposed integrated approach has the potential for optoelectronics, microelectronics, and lab-on-a-chip applications.

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