Dual Regime Spray Deposition Based Laser Direct Writing of Metal Patterns on Polymer Substrates

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Abstract

In recent years, metallization of polymers has been intensely studied due to its superior properties of both plastics and metals. Laser direct structuring (LDS) is one of the most widely used technologies to obtain metal patterns on polymer substrates. In LDS technology, different methods including injection-molding, drop casting, dip coating, and spin coating are utilized for surface preparation of polymer materials prior to laser activation process. In this study, an atomization based dual regime spray coating system is offered to prepare LDS materials. Furthermore, its advantages and limitations are discussed. The results show that the dual regime spray coating system can be potentially used to obtain uniform thin film coating with relatively less material consumption on polymer materials for laser direct writing.

Keywords: Electroless plating, laser-assisted metallization, nanowires, polymer materials, spray coating

1. Introduction

Over the last decades, metallization of polymers has been intensely studied due to its potential applications in automation, robotics, sensors, conducting wires, PV cells, and anti-electrostatic coating [1, 2]. Additionally, increasing demand for small size, lightweight, and high-speed portable and wearable electronics devices has created a significant need for a new technology, which enables an efficient fabrication process for metallization of polymers and overcomes the environmental problems [1,3,4]. Hereby, the laser direct structuring (LDS) technology has drawn a significant attention due to its wide applications including flexible electronics, light-emitting displays (LEDs), medical equipment, automotive, microelectronics, bioelectronics etc. [5-7].

A prominent technique, LDS technology utilizes the laser that have ultrashort pulse width extremely high peak intensity such as femtosecond laser. This property provides unique advantages in material processing, which cannot be achieved by traditional methods. The major advantages of the LDS technology comparing with other methods include design flexibility, short fabrication cycle, and accuracy, ease of integration, mask-free processing, and large-scale manufacturing [6]. This technology also allows the fabrication of ultra-fine structures, which have less than 100 µm widths and gaps [8].

In the last decades, many different LDS techniques have been developed to meet the demand for metal patterns on polymer materials. The main difference among these techniques is the way of preparation of the polymer for laser activation process. One of the polymer preparing methods for LDS is the injection-molding technique [9-11]. In this method, the LDS additives (generally metal oxide or organic metal complex) are placed inside the polymer matrix using injection-molding. However, only the metal seeds that are close enough to polymer surface are activated by laser irradiation. In other words, the rest of these seeds are not used in that process. Furthermore, injection-molding has its own drawbacks such as it is not a flexible process, it is not efficient for material consumption, it is limited to thin walled parts, it has high tooling and equipment cost, and long lead time. Another method used to prepare LDS material is drop casting [12-14]. Although drop casting is a very simple method and it has low waste of material, this method has significant drawbacks such as thickness control, poor uniformity, limitations in large area coating etc. Dip coating is another method used to obtain thin film on polymer materials [15, 16]. Even though dip coating is easy, fast, cost-effective and suitable for large surfaces, it also has some significant shortcomings such as large amount of coating liquid, low deposition rate, difficulty of controlling the coating thickness [17]. One of the other methods to produce LDS polymers is spin-coating [18-23]. Although thin films can be obtained quickly, simply, and uniformly by spin-coating method, this technique has also some important limitations, which are waste of the solution, limitation for only 2D surfaces, and unsuitability for mass production.

In this study, an atomization based dual regime spray coating system is developed as an innovative method for surface preparation of the LDS materials. In the described design, silver nanowires (AgNW) solution is firstly atomized by the droplet generator and the droplets are then carried to the substrate through the central high-speed air flow. Therefore, the proposed system attempts to overcome the limitations of currently used techniques. The experimental results show that the designed spray deposition system could be successfully used for preparation of LDS materials.

2. Design

In spraying process, impingement regime has a significant effect on quality of the deposition. In general, there are four impingement regimes identified in the droplet-substrate interaction phenomenon [24]. As shown in Fig. 1, the first regime is the stick regime, which occurs when an impinging droplet adheres to the substrate in nearly a spherical form. This often

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happens when the impact energy is extremely low. The second is the rebounding regime where the impinging droplet bounces off the substrate. The third regime, spreading, is where wetting occurs. Finally, the fourth regime is where splashing or further atomization occurs, and the droplet breaks into many secondary droplets.

The parameters that influence the impingement dynamics of the atomization process are the diameter ($d_0$) and velocity ($w_0$) of the incident droplet, the liquid dynamic viscosity ($\mu$), density ($\rho$), surface tension ($\sigma$). [25]. The conditions of the receiving surface such as the film thickness ($h$) for wet surfaces also play a major role in controlling the outcome of a droplet-surface collision. The regime transition criteria is determined based on the Reynolds number, the Weber number, Ohnesorge number, and the film thickness number of the incident droplet [25]. The Reynolds number, the Weber number, Ohnesorge number, and the film thickness number are defined as:

$$Re = \frac{\rho w_0 d_0}{\mu}, \quad We = \frac{\rho w_0^2 d_0}{\sigma}, \quad Oh = \frac{\mu}{\sqrt{d_0 \sigma \rho}} h_{nd} = \frac{h}{d_0}$$

where $\rho$ is the liquid density, $w_0$ is the droplet normal to the impact surface, $d_0$ is the droplet diameter, $\mu$ is the liquid dynamic viscosity, $h$ is the film thickness, and $h_{nd}$ is the non-dimensional film thickness number. The criteria of impingement regimes for dry walls are given in the Table 1. In the equation given for the spread regime criterion, $v$ is kinematic viscosity, and $f$ is the frequency of impinging drops. $f$ is also known as the splashing threshold for the multi-drop impact with a thin liquid film [28].

Table 1

<table>
<thead>
<tr>
<th>Regime</th>
<th>Criterion</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Stick</td>
<td>$We &lt; 5$</td>
<td>[26].</td>
</tr>
<tr>
<td>Rebound</td>
<td>$5 &lt; We &lt; 10$</td>
<td>[26,27].</td>
</tr>
<tr>
<td>Spread</td>
<td>$10 &lt; We &lt; 18^2 d_0 \left( \frac{\rho}{\sigma} \right)^{1/2} v^{1/4} f^{3/4}$</td>
<td>[28].</td>
</tr>
<tr>
<td>Splash</td>
<td>$18^2 d_0 \left( \frac{\rho}{\sigma} \right)^{1/2} v^{1/4} f^{3/4} &lt; We$</td>
<td>[28,29].</td>
</tr>
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</table>

Establishing a rebound regime within the deposition system before the droplets leave the nozzle is important for a coating system consists of a spray generation unit and nozzle. Accordingly, it helps to prevent the condensation of liquid on tube and nozzle walls and building up of material on the internal surfaces [30]. Therefore, the Weber number should be selected as $5 < We < 10$ to satisfy the rebound regime for the travelling droplets to the nozzle. On the other hand, droplets should spread on the substrate to provide optimum distribution and adhesion of deposited material [30]. Therefore, a non-dimensionless number, $K_m$, was employed by Mundo et al. [29] to provide a guideline for the splashing regime. To prevent splashing, the criterion should satisfy $K_m < K_{mfc}$ where $K_{mfc} = 57.7$ and the formula for the $K_m$ is defined as:

$$K_m = \left( \frac{Oh^{2/5} We^{6/5}}{\rho} \right)^{5/8}$$

Therefore, a dual-regime nozzle design is a very good candidate to ensure the rebound condition on the internal surfaces as well as preventing splashing on the substrate. Given that, it can be achieved an efficient deposition on the substrate with minimal material waste using the dual-regime spray deposition system. Furthermore, decoupling of the atomizer and the nozzle provides better control of spray velocity and deposition [30]. Hence, the system given in the Fig 2, was employed to overcome the limitations of currently available techniques, which are used for surface preparation of LDS materials.

Fig 2. Schematic of the dual regime spray system.

In this system, the AgNW solution was atomized by the pneumatic atomizer. Then, the low velocity carrier gas takes the droplets to the deposition nozzle through a T-connection. At the nozzle exit, the particles are accelerated and focused through the high-speed velocity air applied in the center of the nozzle. Furthermore, a flow-conditioning unit (FCU) was added to the system in order to prevent condensation and provide uniform droplet size and symmetry of particle stream. Larger particles collide with the wall of the FCU due to the cyclone effect, they condense, and drained out of the FCU [30]. The 3D CAD model of the nozzle and the fabricated nozzle are shown in Fig 3.

Fig 3. The nozzle mounted on a CNC router (left), 3D section model of the nozzle (right).
3. Experimental section

3.1. Materials

The Kapton polyimide-poly(4,4'-diphenylene pyromellitime, PI) film, whose thickness is 0.001", temperature range is -450°F to 750°F, and tensile stress is 16,500 psi, was supplied by the du Pont Co. Inc., USA as a polymer substrate. AgNW were home-made synthesized using the polyl method [31].

3.2. Atomization based dual regime spray coating

The AgNW were deposited on the Kapton polyimide film using the described spray deposition system. The spray system was mounted in a 3 axis CNC router to control the motion of the nozzle. The atomization pressure, and high-speed air pressure were set to 3 psi, and 31 psi, respectively. The nozzle stand-off distance and nozzle gun feed rate were fixed to 5 mm, and 50 mm/min respectively. The atomization flow rate of the AgNW solution was measured as 0.00272 mL/s and the coating time per piece of PI film was 7 minutes. Therefore, the total AgNW solution consumption rate per PI samples was calculated to be 1.1424 mL, which corresponds to relatively less amount of AgNW solution.

3.3. Laser selective activation

The surface selective activation was performed via the ultrafast laser machining system (04-1000, CARBIDE, Light Conversion, Lithuania), which can provide 1030nm center wavelength, 229fs to 10ps pulses, 4W maximum power, and 1 MHz repetition rate. In the experiments, 10ps laser beam with a repetition rate of 10 kHz and the pulse energy of 1.1 μJ was focused onto polymer film by a 20X microscope objective lens (Mitutoyo, 042 NA). The fluence of the focused beam is 14.7 J/cm². The sample was moved in x-y direction by Hybrid Hexapod from ALIO with the scanning speed of 4 mm/s. The schematic representation of the laser selective activation process is given in Fig.4. After selective laser activation, the samples were cleaned with DI water in an ultrasonic bath for 5 minutes at ambient temperature to remove the residual AgNW.

![Fig.4: The schematic diagram of laser activation process.](image)

3.4. Electroless copper plating

In this study, a homemade electroless copper plating bath was used, which contains 18 g/L of copper sulphate pentahydrate(CuSO4.5H2O) as a source of Cu²⁺ ions, 48 g/L of ethylene diamine tetra-acetic acid(EDTA) as the chelating agent, 57.3 mg/L of potassium ferrocyanide(K₃Fe(CN)₆) as the stabilizing agent, 45g/L of sodium hydroxide(NaOH), 18mL/L of hydrochloric acid (1N HCl) and 10mL/L of formaldehyde (HCHO) as the reducing agent in deionized water [32]. In the process of electroless plating, the substrate as immersed in the solution at room temperature until the pink colour of Cu is fully visible over the area of sintered region.

![Fig.5: Schematic illustration of the fabrication process.](image)

4. Results and discussions

4.1. Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) were conducted by the scanning electron microscope (Quanta FEG 650) at 10 kV, 15 kV, and 25 kV to investigate the morphology of the deposited AgNW and the fabricated copper patterns. As it can be seen in Fig 6.(a), the AgNW was successfully deposited onto the surface of the PI film using the given deposition system. Following the selective laser activation and electroless plating steps, the copper pattern, whose width is 226.90 μm, was achieved on the polymer as shown in Fig.6 (d) below.

![Fig.6: (a) SEM image of the deposited AgNW (b) SEM image of surface morphology after femtosecond laser activation (c) SEM image of the fabricated copper pattern (d) Fabricated copper pattern on PI film.](image)

4.2. Electrical performance measurement

The electrical properties of the obtained copper layers were analysed by the Jandel 4-point probe system (U.S.A) model no RM3-AR with a constant current of 10 mA at room temperature to remove any contact resistance error from the measurements. The average sheet resistance was determined from five consecutive regions along the fabricated copper patterns. From these tests, the mean sheet resistance of the fabricated copper pattern was measured as around 6 mΩ/sq. In addition, the sheet resistivity formula given below was used to calculate the resistivity value of the fabricated copper pattern where Rs is the sheet resistance, ρ is the resistivity, t is the...
sheet thickness.

\[ R_s = \frac{\rho}{t} \]

The sheet thickness was obtained from SEM image analysis shown in Fig 7. Thus, the resistivity of the fabricated copper pattern was calculated as 1.98×10⁻⁶ Ωm, which is close enough to the bulk resistivity of copper.

Fig 7. SEM image of fabricated copper pattern on PI film.

4.3. Adhesion test

The performance of mechanical adhesion between the copper layer and the polymer substrate was evaluated using Scotch tape test (ASTM D3359-02). A pressure sensitive tape was removed rapidly at angle nearly 90°. The results show an excellent adhesion having the scale 4 and 5 respect to ASTM D3359-02 standard.

5. Conclusions

In this paper, an atomization based dual regime spray coating system was presented as a new method for surface preparation of the LDS materials. AgNW was successfully deposited on PI film with relatively small amount of the AgNW solution. To show the success of the coating method for the LDS application, copper patterns were successfully deposited on the PI film samples followed by selective laser activation and electroless plating processes. Therefore, the surface of the polymer was successfully modified electrically conductive, having the sheet resistance of 6 mΩsq. The main advantages of this system are: greatly reduced material consumption, spray deposition control, elimination of masking, increased process flexibility, and suitability for multi-automation and mass production. Furthermore, the described deposition head could be easily integrated with a multi-axis robotic arm for spraying curvature parts. However, a parametric study is required to investigate the effects of the laser activation and electroless plating on the process and these parameters are needed to be optimized. The authors are planning to perform additional studies to investigate and optimize these parameters more carefully. Overall, this work may find application in a field of area where the material consumptions, deposition control, masking, and/or flexibility are an issue and metallic conductivity is required on the polymer substrates. It is noteworthy to mention that the given spray deposition system could be easily integrated into conventional LDS technology.

References