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Laser-induced selective activation of polyimide for robust electroless plating

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Abstract

The fabrication of conductive copper patterns on polyimide substrates has garnered growing research interest due to its potential applications. This paper presents a novel approach to electroless metallization on polyimide substrates, utilizing a laser-induced selective activation (LISA) process. By using a nanosecond pulsed laser, the polyimide surface is modified to form a special layer with microporous structures. This modification enhances the stability of electroless plated metallic structures on the polyimide surface, resulting in superior mechanical stability under repeated bending and harsh environments.

Keywords: laser-induced selective activation, microporous structure, electroless plating, polyimide flexible electronics

1. Introduction

Flexible conductive circuits with unique deformability are increasingly in demand for wearable electronic devices [1], medical implants [2], and electromagnetic interference materials [3, 4]. Photolithography has been the primary method for industrial etching of substrate surfaces [5], but it is time-consuming, expensive, and requires rigorous operating conditions. Laser direct structuring (LDS) has emerged as a commercially available technology over the past decade, allowing for the selective deposition of metal patterns by utilizing specialty plastic materials doped with laser sensitizers [6]. However, this process is limited to plastics that contain metal compounds, leading to increased costs and the possibility of heavy metal contamination [7].

Researchers are exploring laser-induced selective activation (LISA) to directly deposit metal onto polymeric materials [8,9]. LISA involves adsorbing catalytic particles onto a microporous interlayer created by liquid-assisted laser modification, which can bind metallic ions and particles for electroless deposition. While common thermoplastics can form porous structures in LISA [10], it is challenging to treat high-performance polymers like polyimide(PI) directly [11]. Thus, a simple and precisely controlled laser-induced surface modification technique is urgently needed to leverage the unique properties of high-performance polymer-based flexible circuits.

This paper presents a facile patterned metallization process based on LISA for the fabrication of microscale metallic structures on PI substrates. In contrast to previous techniques, this approach enables low-cost, high-performance PI-based flexible circuit fabrication while also enhance the mechanical anchoring of the polymer-metal layer interface for improved robustness.

2. Materials and Methods

2.1. Materials Preparation

PI films purchased from Runhai Electronics were used, and an activation solution was prepared by dissolving 16.9 g/L silver nitrates in DI water to replace the previously used Pd/Sn as the electroless copp plating (ECP) catalyst[8]. An ECP bath was then prepared, and 12g/L copper sulfate pentahydrate, 15g/L sodium hydroxide, and 15ml/L formaldehyde aqueous solution(37 wt%) were added stepwise until a homogeneous solution was formed.

2.2. Set-Up of the Laser Processing System

The laser processing system used in this study (Figure 1) was equipped with a customized NIR pulsed fiber laser (WF-LD20, Woofee Laser Tech) with a 1064 nm wavelength and 100 ns pulse duration. The laser beam was focused on the substrate surface through a digital galvanometer (F10, Feeltek Laser Tech).

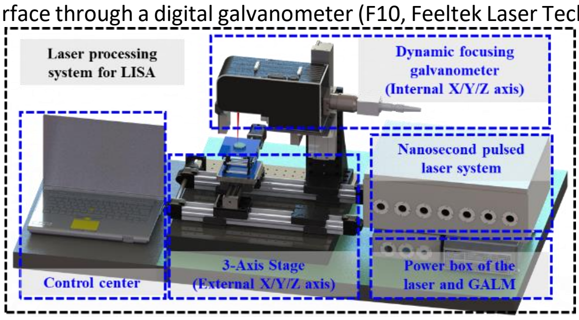

Figure 1. The set-up of the customized laser processing system

2.3. Manufacturing of Metallic PI Films

PI films were cleaned in an ultrasonic bath with ethanol and DI water, then immersed in the DI water and selectively scanned with NIR laser to generate porous structures on their surfaces. The laser-modified PI films were immersed in the activation bath, heat-dried, and then immersed in the ECP bath at 40 °C for 60 min, where copper ions were reduced by formaldehyde and deposited on the activated areas of PI substrate (Figure 2).

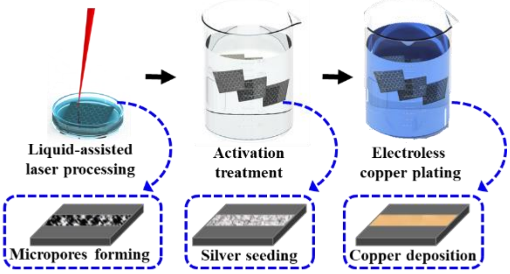

Figure 2. The fabrication process of laser-induced selective activation and metallization on PI films

3. Results and Discussion

The mechanism of selective metallization of PI was investigated in detail. Previous studies have shown that the LISA process is commonly used on other types of polymers in water [8-10], indicating the significance of the laser process at the interface between water and PI for effective surface modification. Surface morphology of PI after laser irradiation in air and water was compared (Figure 3), and the mechanism of laser modification at the interface was speculated. Laser irradiation in air resulted in the formation of macropores with a diameter of 30 μm, while laser irradiation in water formed microporous structures. During the ECP process, copper grew irregularly along the macropore structure formed in air, resulting in uneven copper deposition due to reduced adsorption of activation solution. On the other hand, microporous structures formed in water resulted in a uniform copper deposition and better adhesion of the polymer-metal layer interface. These findings highlight the crucial role of the laser process at the water-PI interface in modifying the surface of the polymer for effective selective metallization.

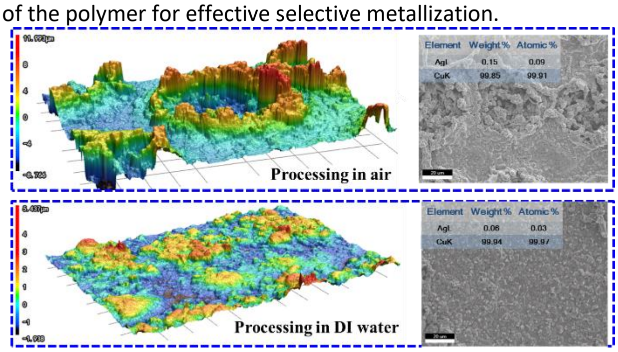

Figure 3. Morphology of a laser-modified PI surface in air and in water.

The formation of microporous structures in water is attributed to nucleate boiling at the interface between water and the PI surface. The rapid temperature rise of the polymer surface can lead to local area transfer to the glassy or molten state, resulting in deformation and the formation of a local microcrack as a nucleation center for nucleate boiling. As water changes from liquid to gas phase, the resulting bubble grows and separates, and the surrounding low-temperature liquid quickly flows in to fill the cavity and solidify the molten surface, forming a porous morphology.

The mechanical stability of electroless plated metallic layer on PI surfaces was evaluated, as demonstrated by their superior performance under repeated bending tests. The resistance variations of the metallized coating were investigated for 500 cycles of bending load, as depicted in Figure 4. The resistance changes observed under compression stress and expansion stress were relatively similar, with an overall range of 2-15 mΩ. These resistance changes satisfy the requirements for conventional applications.

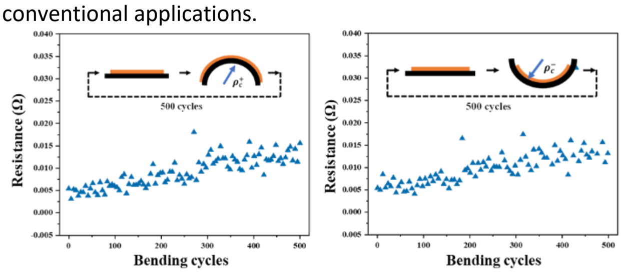

Figure 4. Schematic diagram of the cyclic bending test performed on two types of bending states, along with the corresponding variations in resistance observed in the samples.

Figure 5 illustrates the application of a surface mounted device (SMD) circuit in a typical lighting array based on LISA technology. The circuit design involves creating a trace layout for a series circuit of SMD light-emitting diode(LED) and SMD resistor, followed by preparing a metallized circuit on the polyimide surface using LISA technology. Next, the current-limiting resistor and the LED were fixed on the pad area. Upon connecting the power supply, the LED lighted up successfully.

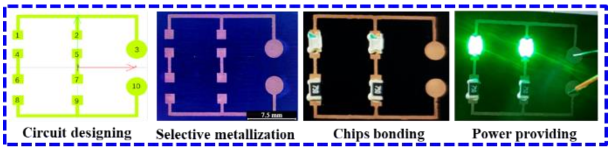

Figure 5. Demonstration of application of a flexible circuit in a typical lighting array based on LISA technology.

4. Conclusion

In summary, based on LISA technology, we have developed a facile electroless metallization process of microscale metallic structures on PI substrates for flexible electronic applications. This process utilizes the laser modification of PI surfaces and the selective adsorption of catalytic silver ions on porous modified surfaces, enabling the electroless metallization on the PI substrates and showing great application potential.

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